THE HAMMETT ACIDITY FUNCTION
FOR SOME SUPERACID MEDIA

THE HAMMETT ACIDITY FUNCTION
FOR SOME SUPERACID MEDIA

By

TERENCE E. PEEL, B.Sc.

A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Doctor of Philosophy

McMASTER UNIVERSITY
September 1971

DOCTOR OF PHILOSOPHY (1971)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: The Hammett Acidity Function for some Superacid Media

AUTHOR: Terence Edward Peel, B.Sc. (Sir George Williams University)

SUPERVISOR: Dr. R. J. Gillespie

NUMBER OF PAGES: xii, 209

SCOPE AND CONTENTS:

The Hammett acidity function, H_o, has been extended from dilute solutions of water in sulfuric acid to the highly acidic HSO_3F-$SbF_5 \cdot 3SO_3$ system, a range of more than eight H_o units. The protonation behaviour of eleven aromatic nitro indicators was studied by means of a spectrophotometric technique. These indicators were found to behave in a similar fashion to the previously studied aniline indicators which have been used to define the H_o function from infinitely dilute solutions of acids in water to concentrated sulfuric acid solutions. The superacid systems studied were H_2O-H_2SO_4-SO_3, H_2SO_4-$HSO_3C\ell$, H_2SO_4-HSO_3F, H_2SO_4-$HB(HSO_4)_4$, KSO_3F-HSO_3F, HSO_3F-SO_3, HSO_3F-AsF_5, HSO_3F-SbF_5, and HSO_3F-$SbF_5 \cdot 3SO_3$ of which the latter is the most acidic solvent system known.

ACKNOWLEDGMENTS

The author would like to express his sincere gratitude for the advice and encouragement given throughout this work by his research director, Professor R. J. Gillespie. He would also like to thank the members of the Department of Chemistry for their kind assistance and companionship.

The encouragement of my family and particularly my wife, Carol, is greatly appreciated. Thanks are also due to Carol for assistance in preparing the figures which appear in this thesis.

Finally the author wishes to thank the National Research Council of Canada for their financial assistance.

TABLE OF CONTENTS

Page

CHAPTER I: INTRODUCTION 1

- A. MEASUREMENTS OF ACIDITY 1
- B. ACIDITY FUNCTION MEASUREMENTS 6
- C. PURPOSE OF PRESENT WORK 19

CHAPTER II: EXPERIMENTAL PROCEDURES 20

- A. PREPARATION AND PURIFICATION OF MATERIALS 20
- B. MANIPULATION OF MATERIALS 24
- C. UV AND VISIBLE ABSORPTION SPECTRA 25
- D. NUCLEAR MAGNETIC RESONANCE SPECTRA 26

CHAPTER III: THE SULFURIC ACID SOLVENT SYSTEM 28

- A. HISTORICAL INTRODUCTION 28
- B. ACIDITY STUDIES IN SULFURIC ACID SOLUTIONS 31
  1. The H_2O-H_2SO_4-SO_3 System near 100% H_2SO_4 33
  2. The H_2SO_4-SO_3 System 39
  3. The H_2SO_4-HSO_3F System 45
  4. The H_2SO_4-$HSO_3C\ell$ System 48
  5. The H_2SO_4-$HB(HSO_4)_4$ System 50
- C. DISCUSSION 50

CHAPTER IV: THE FLUOROSULFURIC ACID SOLVENT SYSTEM 96

- A. HISTORICAL INTRODUCTION 96
- B. ACIDITY STUDIES IN FLUOROSULFURIC ACID SOLUTIONS 103
  1. The H_2SO_4-HSO_3F-SO_3 System 104
  2. The KSO_3F-HSO_3F System 106
  3. The HSO_3F-AsF_5 System 107
  4. The HSO_3F-SbF_5 System 108
  5. The HSO_3F-SbF_5-xSO_3 System 120
  6. The HSO_3F-SbF_5-$3SO_3$ System 123
- C. DISCUSSION 126

TABLE OF CONTENTS (cont.)

Page

CHAPTER V: DISCUSSION 189

A. AROMATIC NITRO INDICATORS 189

B. H_o FUNCTION IN SUPERACID MEDIA 192

C. USE OF N.M.R. IN THE DETERMINATION OF ACIDITY 196

APPENDIX I: ERROR LIMITS 202

REFERENCES 203

LIST OF TABLES

Table		Page
I	Ionization ratios of 2,4,6-trinitroaniline in H_2O-H_2SO_4	54
II	Ionization ratios of p-nitrotoluene in H_2O-H_2SO_4-SO_3	55
III	Ionization ratios of m-nitrotoluene in H_2O-H_2SO_4-SO_3	56
IV	Extinction coefficients of nitrobenzene in H_2O-H_2SO_4-SO_3	57
V	Ionization ratios of nitrobenzene in H_2O-H_2SO_4-SO_3	59
VI	Extinction coefficients of p-fluoronitrobenzene in H_2SO_4-SO_3	60
VII	Extinction coefficients of p-chloronitrobenzene in H_2O-H_2SO_4-SO_3	62
VIII	Ionization ratios of p-fluoronitrobenzene in H_2SO_4-SO_3	64
IX	Ionization ratios of p-chloronitrobenzene in H_2SO_4-SO_3	64
X	$-H_o$ values near 100% H_2SO_4	67
XI	Ionization ratios of p-fluoronitrobenzene in H_2SO_4-SO_3	69
XII	Ionization ratios of p-chloronitrobenzene in H_2SO_4-SO_3	70
XIII	Extinction coefficients of m-chloronitrobenzene in H_2SO_4-SO_3	71
XIV	Ionization ratios of m-chloronitrobenzene in H_2SO_4-SO_3	73
XV	Extinction coefficients of 2,4-dinitrotoluene in H_2SO_4-SO_3	74
XVI	Ionization ratios of 2,4-dinitrotoluene in H_2SO_4-SO_3	76
XVII	Extinction coefficients of 2,4-dinitrofluorobenzene in H_2SO_4-SO_3	77

LIST OF TABLES (cont.)

Table		Page
XVIII	Ionization ratios of 2,4-dinitrofluorobenzene in H_2SO_4-SO_3	82
XIX	H_2SO_4-SO_3 system $-H_o$ values	84
XX	Ionization ratios of p-chloronitrobenzene in H_2SO_4-HSO_3F	86
XXI	Ionization ratios of m-chloronitrobenzene in H_2SO_4-HSO_3F	87
XXII	Ionization ratios of 2,4-dinitrotoluene in H_2SO_4-HSO_3F	88
XXIII	Ionization ratios of 2,4-dinitrofluorobenzene in H_2SO_4-HSO_3F	89
XXIV	$-H_o$ values for the H_2SO_4-HSO_3F system	91
XXV	Ionization ratios for the system H_2SO_4-$HSO_3C\ell$	92
XXVI	H_o values for the system H_2SO_4-$HSO_3C\ell$	93
XXVII	Ionization ratios for the H_2SO_4-$HB(HSO_4)_4$ system	94
XXVIII	$-H_o$ values for the H_2SO_4-$HB(HSO_4)_4$ system	95
XXIX	Evaluation of overlap of nitro indicators in the H_2O-H_2SO_4-SO_3 system	95
XXX	Evaluation of overlap of nitro indicators in the H_2SO_4-HSO_3F system	95
XXXI	Extinction coefficients of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene in H_2SO_4-HSO_3F-SO_3	129
XXXII	Ionization ratios of 2,4-dinitrofluorobenzene in H_2SO_4-HSO_3F-SO_3	131
XXXIII	Ionization ratios of 2,4,6-trinitrotoluene in H_2SO_4-HSO_3F-SO_3	132
XXXIV	H_o values for the H_2SO_4-HSO_3F-SO_3 system	134
XXXV	Extinction coefficients and ionization ratios in the KSO_3F-HSO_3F system	136

LIST OF TABLES (cont.)

Table		Page
XXXVI	H_0 values for the KSO_3F-HSO_3F system	138
XXXVII	Extinction coefficients of 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene in the HSO_3F-AsF_5 system	139
XXXVIII	Ionization ratios of 2,4,6-trinitrotoluene in the HSO_3F-AsF_5 system	141
XXXIX	Ionization ratios of 1,3,5-trinitrobenzene in the HSO_3F-AsF_5 system	142
XL	H_0 values for the HSO_3F-AsF_5 system	143
XLI	Extinction coefficients of 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system	145
XLII	Ionization ratios of 2,4,6-trinitrotoluene in dilute solutions of SbF_5 in HSO_3F	147
XLIII	Extinction coefficients of 1,3,5-trinitrobenzene in the HSO_3F-SbF_5 system	148
XLIV	Ionization ratios of 1,3,5-trinitrobenzene in dilute solutions of SbF_5 in HSO_3F	150
XLV	Extinction coefficients of 2,4,6-trinitrochlorobenzene in the HSO_3F-SbF_5 system	151
XLVI	Ionization ratios of 2,4,6-trinitrochlorobenzene in the HSO_3F-SbF_5 system	153
XLVII	Extinction coefficients of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system	154
XLVIII	Representative absorption spectra of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system	155
XLIX	Adjusted extinction coefficients of protonated 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system	159
L	Ionization ratios of protonated 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system	161
LI	Representative absorption spectra of 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system	162

LIST OF TABLES (cont.)

Table Page

LII Adjusted extinction coefficients of protonated 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system 166

LIII Ionization ratios of protonated 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system 168

LIV H_o values for the HSO_3F-SbF_5 system 171

LV Extinction coefficients of 2,4-dinitrofluorobenzene and 1,3,5-trinitrobenzene as a function of the SbF_5:SO_3 molar ratio 173

LVI Observed and adjusted extinction coefficients of 2,4-dinitrofluorobenzene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 175

LVII Representative absorption spectra of 2,4-dinitrofluorobenzene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 177

LVIII Ionization ratios of protonated 2,4-dinitrofluorobenzene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 181

LIX Observed and adjusted extinction coefficients of 2,4,6-trinitrotoluene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 182

LX Representative absorption spectra of 2,4,6-trinitrotoluene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 183

LXI Ionization ratios of protonated 2,4,6-trinitrotoluene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 186

LXII H_o values for the HSO_3F-$SbF_5 \cdot 3SO_3$ system 187

LXIII Evaluation of overlap of the nitro indicators in the HSO_3F system 188

LXIV ξ_B, ξ_{BH^+}, and pK_{BH^+} values for the aromatic nitro indicators 200

LIST OF FIGURES

Figure		Page
1	The aqueous H_0 functions of some common inorganic acids	8
2	Extinction coefficients of nitrobenzene in H_2O-H_2SO_4-SO_3	58
3	Extinction coefficients of p-fluoronitrobenzene in H_2SO_4-SO_3	61
4	Extinction coefficients of p-chloronitrobenzene in H_2SO_4-SO_3	63
5	Ionization ratios near 100% H_2SO_4	65
6	Ionization ratios near 100% H_2SO_4	66
7	H_0 values near 100% H_2SO_4	68
8	Extinction coefficients of m-chloronitrobenzene in H_2SO_4-SO_3	72
9	Extinction coefficients of 2,4-dinitrotoluene in H_2SO_4-SO_3	75
10	Representative absorption spectra of 2,4-dinitrofluorobenzene in H_2SO_4-SO_3	80
11	Extinction coefficients of 2,4-dinitrofluorobenzene in H_2SO_4-SO_3	81
12	Ionization ratios in H_2SO_4-SO_3	83
13	H_0 values for the H_2SO_4 systems	85
14	Ionization ratios in H_2SO_4-HSO_3F	90
15	Extinction coefficients of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene in the H_2SO_4-HSO_3F-SO_3 system	130
16	Ionization ratios of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene in the H_2SO_4-HSO_3F-SO_3 system	133
17	H_0 values near 100% HSO_3F	135
18	Ionization ratios in the KSO_3F-HSO_3F system	137
19	Extinction coefficients of 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene in the HSO_3F-AsF_5 system	140

LIST OF FIGURES (cont.)

Figure		Page
20	Extinction coefficients of 2,4-dinitrofluorobenzene in dilute HSO_3F-SbF_5 solutions	144
21	Extinction coefficients of 2,4,6-trinitrotoluene in dilute HSO_3F-SbF_5 solutions	146
22	Extinction coefficients of 1,3,5-trinitrobenzene in dilute HSO_3F-SbF_5 solutions	149
23	Extinction coefficients of 2,4,6-trinitrochlorobenzene in the HSO_3F-SbF_5 system	152
24	Representative absorption spectra of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system	157
25	Curve analysis of the absorption spectra of 2,4-dinitrofluorobenzene in a 0.8118 mole % SbF_5 solution	158
26	Curve analysis of the absorption spectra of 2,4-dinitrofluorobenzene in a 5.2537 mole % SbF_5 solution	158
27	Adjusted extinction coefficients of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system	160
28	Representative absorption spectra of 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system	164
29	Curve analysis of the absorption spectra of 2,4,6-trinitrotoluene in a 6.8577 mole % SbF_5 solution	165
30	Curve analysis of the absorption spectra of 2,4,6-trinitrotoluene in a 10.0810 mole % SbF_5 solution	165
31	Adjusted extinction coefficients of 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system	167
32	Ionization ratios in dilute HSO_3F-SbF_5	169
33	Ionization ratios up to 10 mole % SbF_5 in HSO_3F	170
34	H_o values for the HSO_3F systems	172
35	Extinction coefficients of 2,4-dinitrofluorobenzene and 1,3,5-trinitrobenzene in the $HSO_3F-SbF_5-xSO_3$ system	174

LIST OF FIGURES (cont.)

Figure Page

36 Extinction coefficients of 2,4-dinitrofluorobenzene, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 176

37 Representative absorption spectra of 2,4-dinitrofluorobenzene in the HSO_3F-$SbF_5 \cdot 3SO_5$ system 179

38 Adjusted extinction coefficients of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 180

39 Representative absorption spectra of 2,4,6-trinitrotoluene in the HSO_3F-$SbF_5 \cdot 3SO_3$ system 185

40 Relationship between log K_b and pK_{BH^+} in H_2SO_4 and HSO_3F 201

CHAPTER I

INTRODUCTION

A. MEASUREMENTS OF ACIDITY

Acid-base reactions are probably the most widely studied type of chemical reaction. In recent years the terms acid and base have been given much wider implication as compared to the early definition of Arrhenius which was valid only for solutions in which water acted as the solvent. For the purpose of this work acids and bases are defined in the way suggested by Lowry and Bronsted: an acid is a substance which has the tendency to lose a proton.

$$HA \rightleftharpoons A + H^+ \qquad (I\text{-}1)$$

This does not, however, imply that an acid is in equilibrium with a significant amount of free protons, which cannot exist in measurable amount in any solvent, but only that an acid will donate a proton to a suitable base.

$$B + H^+ \rightleftharpoons BH^+ \qquad (I\text{-}2)$$

The reactions most commonly studied have been those in water as a solvent. The determination of the position of the equilibrium

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (I\text{-}3)$$

in dilute solution, in order to determine the strength of an acid, has been carried out by a number of well known classical methods. As a result of such measurements it has been found, for example, that acetic acid is weak, oxalic acid is somewhat stronger, and a number of common mineral acids, such as $HC\ell$, HI, HNO_3, H_2SO_4, and $HC\ell O_4$, are strong acids and completely ionized in dilute aqueous solution.

The acidity of these dilute solutions of strong acids is levelled to that of H_3O^+, the strongest acid possible in the aqueous solvent system. The acidity of such solutions is thus measured by the concentration of the H_3O^+ ion or, more correctly, by the activity of the solvated hydrogen ion, a_{H^+}. In dilute aqueous solutions $pH = -\log[H_3O^+]$ is most commonly used to describe the acidity.

As the concentration of water in solutions of strong acids is decreased and eventually eliminated the difference in acidity of these strong acids becomes apparent. The concept of pH as a measure of acidity for these highly concentrated solutions of strong acids is no longer valid. The concentration of the solvated H_3O^+ ion decreases with decreasing water concentration; however, the acidity of the system, that is its ability to donate a proton to a base, increases with increasing acid concentration. In order to provide a quantitative measure of acidity of such acid-water mixtures Hammett and Deyrup[1] proposed the acidity function Ho defined as

$$Ho = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \qquad (I\text{-}4)$$

where $[BH^+]/[B]$ is the molar ratio of the amount of protonated to unprotonated forms of a suitable base B whose conjugate acid has a dissociation constant, K_{BH^+}, referred to ideal dilute solutions in water.

The Hammett acidity function, Ho, is thus formally related to the activity of the hydrogen ion, a_{H^+}, by the relation

$$Ho = -\log a_{H^+} \frac{f_B}{f_{BH^+}} \qquad \text{(I-5)}$$

where the f's are the activity coefficients of the neutral base B and the protonated form, BH^+. If each individual activity coefficient is taken by convention to approach unity at infinite dilution in water so that a_{H^+} under this condition becomes equal to $[H^+]$ then the Ho function becomes equal to pH in ideal dilute aqueous solutions. In practice the Ho function denotes the ability of a solution to transfer a proton to an uncharged basic molecule.

This method of evaluation of acidity has three major requirements. The uncharged bases, or indicators, must behave in identical ways to changes in acidity of a solution under study. This means that the ionization ratio curves, obtained by plotting $\log[BH^+]/[B]$ versus acid composition, for indicators undergoing protonation must be parallel to each other. This does not, however, mean the individual ionization ratio curves must be straight lines. This requirement, as shall be shown later, is satisfied for indicators of the same basic structural type. The second requirement for good indicator behaviour is that the protonation behaviour, as measured by the ionization constant of the indicator, be independent of the acid system. It has been found that the pK_{BH^+} for most indicators is essentially independent of the acid system used to evaluate it. The third requirement is that the concentration of the basic indicator used in determining the acidity of a solution be small enough that it does not alter the acidity of the solution under study.

The experimental determination of Ho values may be conveniently separated into two parts: the determination of the ionization ratio of an indicator and the evaluation of the ionization constant of the conjugate acid of the indicator. As it is necessary to use very small amounts of the basic indicators, in order that the acidity will not be changed, the most common method used to determine the ionization ratios has been the absorption of light by the indicator in solution as measured by a colorimeter or more recently by a spectrophotometer. Upon the protonation of an indicator its absorption spectrum must thus undergo a characteristic change. In the case of the aniline indicators[1,2,3] both techniques have been used; however, the more accurate spectroscopic technique is now used most commonly. Ionization ratios may be calculated from (I-6) assuming Beer's law is obeyed.

$$\frac{[BH^+]}{[B]} = \frac{\xi_B - \xi}{\xi - \xi_{BH^+}} \tag{I-6}$$

ξ is the measured extinction coefficient of the solution in question and ξ_B and ξ_{BH^+} are the extinction coefficients, at the same wavelength, for the neutral and fully protonated forms of the indicator respectively. The wavelength generally used is that of the maximum absorption of either B or BH^+.

For highly basic indicators whose ionization ratios may be measured in dilute aqueous solution it is possible to determine directly the pK_{BH^+} which is defined as

$$pK_{BH^+} = \log \frac{[BH^+]}{[B][H^+]} + \log \frac{f_{BH^+}}{f_B - f_{H^+}} \tag{I-7}$$

where the activity coefficients are referred to a value of unity for an infinitely dilute solution in water. The indicator concentration is always small thus

$$pK_{BH^+} = \lim_{C_A \to 0} \left(\log \frac{[BH^+]}{[B]} - \log [H^+]\right) \qquad \text{(I-8)}$$

where C_A is the molar acid concentration. For a strong acid, $[H^+]$ is calculable by the relation $C_A = [H^+] + [BH^+]$, hence one may directly determine the ionization constant for highly basic indicators. In practice it has been found[4] that the right hand side of relation (I-8) varies linearly with acid concentration up to at least two molar.

For weaker bases a direct determination of pK_{BH^+} is not feasible and a stepwise comparison must be used. For two different indicators B and C, studied at the same acid concentration, the difference in their ionization constants is given by

$$pK_{CH^+} - pK_{BH^+} = \log \frac{[CH^+]}{[C]} - \log \frac{[BH^+]}{[B]} - \log \left(\frac{f_C\, f_{BH^+}}{f_{CH^+}\, f_B}\right) \qquad \text{(I-9)}$$

If the bases B and C are of similar structures then the last term on the right can be neglected for aqueous solutions and for solutions of high dielectric constant. The validity of neglecting this term for closely related indicators will be shown in later sections. Given that B and C have ionization constants close enough that both indicators' ionization ratios may be measured with reasonable accuracy in the same medium, the difference in their pK values is given by

$$pK_{CH^+} - pK_{BH^+} = \log \frac{[CH^+]}{[C]} - \log \frac{[BH^+]}{[B]} \qquad \text{(I-10)}$$

Once the ionization constant of a reference material has been determined directly in dilute aqueous solutions the ionization constants of weaker bases may be found by the overlap technique. Thus the ionization constants of extremely weak bases can be determined and referred to infinitely dilute solutions in water even though the indicator may be protonated only in very highly acidic non-aqueous solutions. A much more complete treatment of the techniques used to determine ionization ratios and constants is given in the review by Paul and Long[5] and in Chapter Nine (2nd ed.) of "Physical Organic Chemistry" by L. P. Hammett[6]. These two reference works and the references they contain more than adequately describe the details of this method of measurement of acidity.

B. ACIDITY FUNCTION MEASUREMENTS

Hammett and Deyrup[1] originally used a series of substituted aniline indicators to define Ho functions for aqueous solutions of the strong acids $HC\ell O_4$ and H_2SO_4. Their study showed that the anilines did follow the two major requirements for good indicator behaviour; that is, the indicator's ionization ratio curves were parallel with changes in acid concentration, and that the ionization constants were essentially independent of the acid system used. Their Ho function was based[3] upon the relatively strongly basic indicator, p-nitroaniline, whose ionization ratio could be directly determined in dilute solutions of the acids in water.

Since Hammett and Deyrup's original use of the aniline indicators many workers have studied a large number of aqueous and non-aqueous acid systems. The early work has been summarized by Paul and Long[5] who give detailed references to the original workers. This review, besides demonstrating the validity and limitations of the Ho function, lists so-called "best" values for the ionization constants of the many Hammett indicators used. Using the best pK_{BH^+} values and the experimental ionization ratios found by the many different workers, Paul and Long recalculated and tabulated Ho values for aqueous solutions of HNO_3, $HC\ell$, $HC\ell O_4$, H_2SO_4, H_3PO_4, HF, and HBr. Values of the Ho function for other aqueous acid systems such as CF_3COOH, $CC\ell_3COOH$, $KHSO_4$, $CHC\ell_2COOH$, HCOOH, CH_3COOH, $CH_2C\ell COOH$ and CH_3SO_3H are discussed as well as some non-aqueous systems.

Since this review article a number of the acid systems have been reinvestigated making use of other indicators, modern spectrophotometers instead of colorimeters, and in a limited number of cases temperature control apparatus. The Ho function of the strongest aqueous acid, $HC\ell O_4$, has been[7,8] extended up to 72% and some of the earlier work was reinvestigated. Bascombe and Bell[9] reinvestigated the Ho functions, at 25°C, for aqueous solutions of $HC\ell O_4$, $HC\ell$, H_2SO_4, CH_3COOH, HCOOH, $C\ell CH_2COOH$, $C\ell_2CHCOOH$, $C\ell_3CCOOH$, HIO_3, H_3PO_4, CH_3SO_3H and p-toluenesulfonic acid making use of a set of aniline indicators. The H_2O-HNO_3 system has been reinvestigated[10] and Ho values for the H_2O-HF system may be found in references 11 and 12. The most extensively studied system has been the H_2O-H_2SO_4 system which will be discussed more fully later. Figure 1 shows[13] the Ho functions for aqueous solutions of the mineral acid $HC\ell O_4$, $HC\ell$, H_2SO_4, HF, HNO_3 and H_3PO_4.

Figure 1 indicates that the strong acids $HC\ell O_4$, H_2SO_4 and $HC\ell$ all have identical Ho values up to a mole fraction of approximately 0.1. Thereafter the three curves begin to diverge with $HC\ell O_4$ being

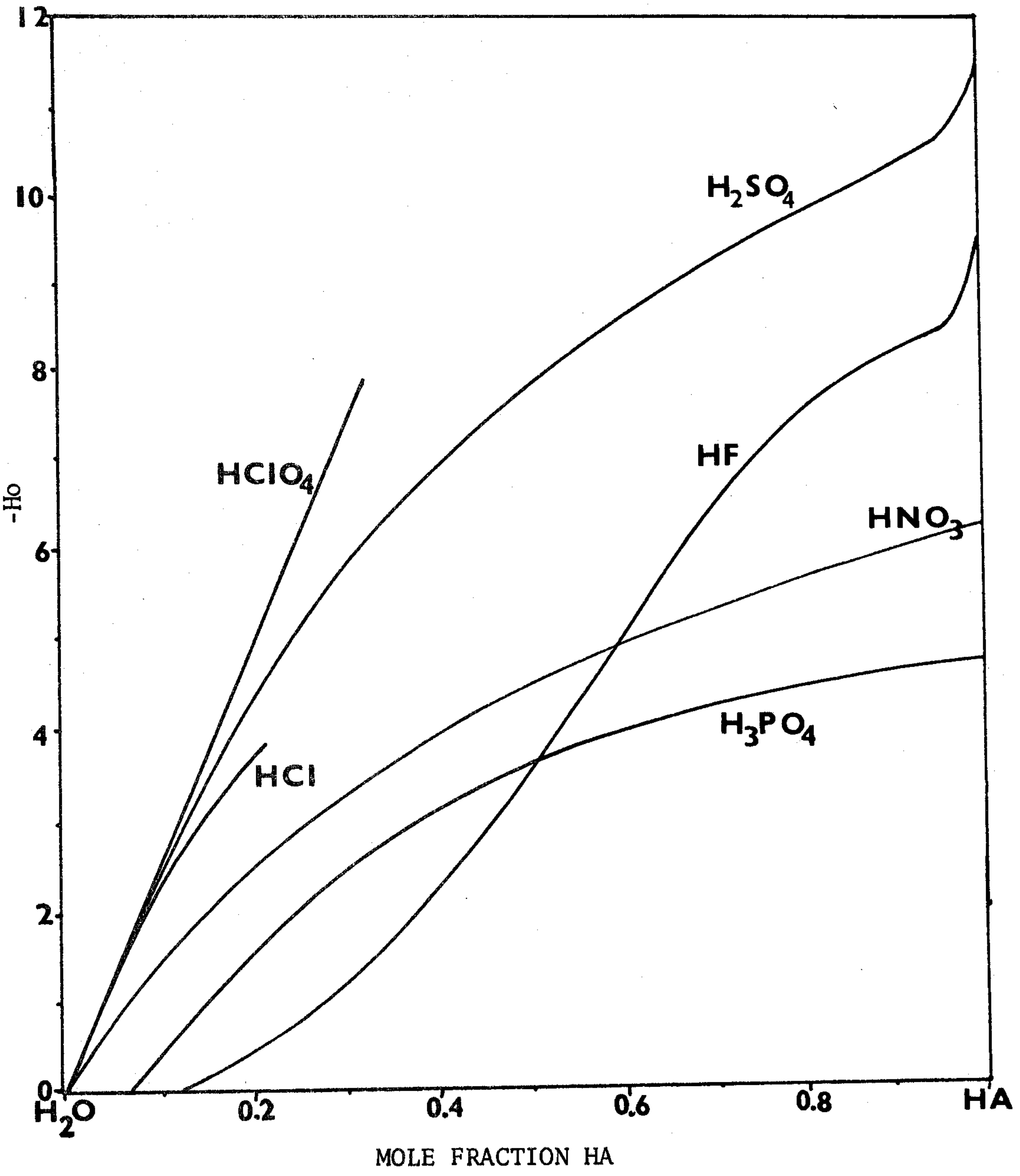

Figure 1. The Aqueous Ho Functions of Some Common Inorganic Acids

the strongest and $HC\ell$ the weakest acid of the three. This presumably reflects the different extents of ionization of these acids. Ho measurements of the system H_2O-$HC\ell O_4$ indicate that $HC\ell O_4$ is the strongest acid in aqueous solutions. These measurements have not been extended to higher acid concentrations because of the inherent instability of concentrated solutions of perchloric acid especially in the presence of organic materials such as the indicators. One hundred percent sulfuric acid had the highest measured acidity of all acids studied. HNO_3, which behaves as a strong acid in dilute solution, is only 50% ionized at a mole fraction of 0.2 and is not detectably ionized at mole fractions above 0.5[14]. Phosphoric acid is a weak acid in dilute solutions and its acidity in more concentrated solutions is less than that of HNO_3. The Ho values for the H_2O-HF system are initially low indicating that HF is a weak acid in dilute aqueous solutions. As the acid concentration is increased its acidity rapidly rises to a value approaching that of H_2SO_4. The increased degree of association of the HF molecules and the formation of the polymeric anions HF_2^- and $H_2F_3^-$ account for this rapid rise in acidity[15].

Other types of indicators have been used in the same way as the substituted anilines, to define similar acidity functions; however, these functions are not identical to the Ho function. Most acidity function measurements have been made with the aniline indicators; however, there is no reason to assume that the Ho scale is better than any other similarly determined acidity scale. As a result of the large amount of information available on the Ho function for various acid mixtures this scale is often used as a reference system for comparisons with other acidity functions; however, this is an arbitrary choice.

The Ho''' acidity function[16], based upon the ionization of a group of 15 N,N-dialkylnitroanilines and N-alkylnitrodiphenylamines, changes much more rapidly with increasing acid concentration than does the Ho function. The behaviour of this set of indicators is as good as the anilines and measurements have been extended up to 96 wt % H_2SO_4.

The H_I acidity function, as developed by Hinman and Lang[17], is based upon the protonation behaviour of a series of alkylated indoles. There is good overlap between successive indicators and the difference between the ionization ratios of any pair of indicators is satisfactorily independent of the H_2SO_4 concentration. The H_I scale has been studied over the water-sulfuric acid concentration range of 0-70 wt % H_2SO_4. The behaviour of the H_I acidity function is very similar to that of the Ho''' scale.

Katritzky first reported[18] in 1963 that the basicity of amides did not follow the Ho function. The H_A function for the H_2O-H_2SO_4 system was proposed by Yates et. al.[19] and later extended[20]. It is based upon the protonation behaviour of a group of amides, whose acidity function changes more slowly with increasing acid composition than does the Ho function. The H_A acidity function is not limited to the use of amide indicators as a number of pyridine N-oxides have been found[21] to have the same protonation behaviour. These have been used to extend H_A measurements up to 93 wt % H_2SO_4. The protonation behaviour of aromatic and α,β unsaturated ketones, aldehydes and carboxylic acids have been suggested[22] to be consistent with the H_A

function; however, Greig and Johnson[23] reported that the ease of up-take of protons by some aromatic carbonyls is significantly greater than that of a base following the H_A function. The protonation of unconjugated carbonyl groups has been shown[22] to follow the Ho function.

The second oldest measure of acidity in concentrated strong acid solutions is the H_R function proposed by Deno et. al.[24] in 1955. It is based upon an overlapping series of arylcarbinols which undergo the reaction

$$(C_6H_5)_3COH + H^+ \rightleftharpoons (C_6H_5)_3C^+ + H_2O \qquad \text{(I-11)}$$

The H_R function was defined as

$$H_R = pK_{R^+} - \log \frac{[R^+]}{[ROH]} \qquad \text{(I-12)}$$

which can be rewritten in the form

$$H_R = -\log a_{H^+} \frac{f_{ROH}}{f_{R^+}} + \log a_W \qquad \text{(I-13)}$$

where R is an arylcarbinol and a_W is the activity of water. If one defines a function H_R'

$$H_R' = pK_{R^+} - \log \frac{[R^+]}{[ROH]} - \log a_W \qquad \text{(I-14)}$$

then

$$H_R' = -\log a_{H^+} \frac{f_{ROH}}{f_{R^+}} \qquad \text{(I-15)}$$

which is of similar form to the Ho acidity function or any other acidity function previously mentioned. Thus the H_R' acidity function may be reasonably compared with the other acidity functions. It was found that the arylcarbinol based function H_R' increased more rapidly with increasing acid concentration than all other acidity function;

however, a diarylolefine based H_R' function was found[25] to be consistent with the Ho function.

Acidity function data for acid systems other than H_2O-H_2SO_4 include Ho''' values for aqueous solution of $HC\ell$, H_3PO_4 and toluenesulfonic acid[26]; H_I values for the H_2O-$HC\ell O_4$ system[17]; H_A values for $HC\ell$ solutions[27]; and H_R or H_R' values for $HC\ell O_4$, HNO_3[28], and $HC\ell$, H_3PO_4 and toluenesulfonic acid[26] solutions. The Do function for the D_2O-D_2SO_4 system has been studied[29] using the series of aniline indicators used for Ho measurements. Numerous other acidity function measurements have been carried out in multi-component systems such as (96% H_2SO_4- 4% H_2O)-CH_3COOH[30]. Other acidity function measurements have been made using charged indicators[31] and various other bases such as sulfoxides, which have been found[32] to follow the H_A acidity function.

Bunnett and Olsen[33] have developed a linear free energy relation to evaluate various acid-base equilibria in moderately concentrated acid solutions,

$$\log \frac{[SH^+]}{[S]} - \log [H^+] = (\phi-1)(Ho + \log[H^+]) + pK_{SH^+} \qquad \text{(I-16)}$$

where S is an indicator whose ionization ratio may be measured in various acid mixtures and ϕ is the response of the protonation equilibrium of that indicator to changes in acid concentration. Each particular class of indicators has a narrow range of ϕ values and all bases whose ϕ values are within this range may be said to behave according to the acidity function generated by that particular class of indicators. Ionization constants may be evaluated by extrapolation of this relationship to zero acid concentration. It is of interest to note that the ionization constants of the amide indicators used to make up the H_A function are in error by approximately 0.3 units according to this method. The H_A function was assumed to be the same as the Ho function below 16.1% H_2SO_4 as no strongly basic amide indicators were available to study this region; this assumption appears to be in error.

The differences in the behaviour of the various acidity functions has been the subject of many recent publications. It is generally felt[6] that differences in the degree of solvation of the various indicators is the most important factor although the molecular size[26] of the indicators may be of some importance. The ϕ values as determined by Bunnett and Olsen[33] may be taken as a convenient measure of this solvation effect[6].

It is readily apparent that an acidity function is not a unique measure of the acidity of concentrated solutions of strong acids. The availability of quantitative information does, however, allow for a much better understanding of acidity and some of the properties of concentrated solutions of strong acids. The use of the acidity function concept has allowed for the determination of the basicity of a large number of weak bases such as phosphine oxides and sulfides[34], benzophenanes[35], azobenzines[36], and many others including all the indicators used to determine the various acidity functions.

Acidity function measurements have aided in the understanding of reaction mechanisms as determined from kinetic studies. The review by Long and Paul[37] indicates some of the many uses of acidity functions in relation to chemical kinetics. The rate of a protonation reaction may, in some cases, be taken as a measure of acidity. This subject has been reviewed by Bunnett and Olsen[33] who used their linear free energy relationship, as previously outlined, to determine ϕ values for some 160 protonation reactions.

Acidity function measurements have made significant contributions to the understanding of the properties of concentrated solutions of acids in addition to the evaluation of their relative strengths. The protonation behaviour of water at high acid concentrations has been of particular interest[38,39,40]. Various attempts have been made to calculate values for the acidity function from the composition of an acid medium particularly in the case of the H_2SO_4-H_2O system at high sulfuric acid concentrations. Brand[41] showed that the relationship

$$Ho = -8.36 + \log \frac{\chi_{HSO_4^-}}{\chi_{H_2SO_4}}$$

where χ's are mole fractions applies in the region of 90 to 99.5% H_2SO_4 assuming that water is completely protonated throughout this region. Deno and Taft[42] accounted for Ho values up to 17% H_2O in H_2SO_4 on the basis of an equilibrium constant of 50 for the protonation of water. Wyatt[39] was able to account for Ho values up to 19.5% H_2O in H_2SO_4 in terms of the formation of various hydrated species such as $H_3O(H_2O)_3^+$, $H_3O(H_2O)_2^+$, etc.

Recent reviews of the acidity function concept and various acidity function measurements include those of Rochester[134], Arnett[43], Deno[44] and Edwards[45]. The problems of media effects in the determination of ionization ratios by absorption spectroscopy are discussed in some detail in the first two references.

The Ho function for the H_2O-H_2SO_4 system has been extensively reinvestigated in recent years and forms the basis for the acidity function measurements to be presented here. Jorgenson and Hartter[46] carried out a critical re-evaluation of the Hammett acidity function at moderate and high acid concentrations of sulfuric acid. Their study was based upon the re-evaluation[47,9] of the pK_{BH^+} values for a number of aniline indicators which had been used to define the acidity of the system up to 60 wt % H_2SO_4. The resulting Ho function is based solely upon a set of seventeen primary aniline indicators thus reliably extending the acidity measurements up to 99.4 wt % H_2SO_4 which has an Ho value of -11.12. The least basic indicator used was 2,4,6-trinitroaniline which was found to have a pK_{BH^+} of -10.10 as determined by the overlap method and based on the direct evaluation of the pK_{BH^+} for p-nitroaniline in dilute aqueous acid.

The temperature variation of the Ho acidity function has been recently reported by Johnson et. al.[48] making use of the same set of primary aniline indicators that Jorgenson and Hartter used. In their work the pK_{BH^+} values for all of the indicators were re-evaluated for each of the five temperatures used. Their results at 25°C, the lowest temperature investigated, are in good agreement with the room temperature results of Jorgenson and Hartter[46]. Values of -Ho were found to decrease with increasing temperature according to

$$Ho(T) = K/T + L$$

where T is the absolute temperature and K and L are constants at a given acid composition. At 99% H_2SO_4 an increase of temperature from

25° to 90°C results in an Ho change of 1.68 while at 50% H_2SO_4 a similar temperature change results in an Ho difference of 0.44. Strict temperature control is thus not required to obtain a meaningful room temperature acidity function.

Johnson et. al.[48] made a quantitative evaluation of the overlap of the aniline indicators by plotting the logarithms of the ionization ratios of two adjacent indicators in various acid strengths against each other. The resulting straight line should have a unit slope if the two overlapping indicators behave identically with changes in acid concentration. The product of all such slopes indicates how the last indicator behaves with respect to the first. The slope product found for the twelve indicators used was 1.04 indicating that the primary aniline indicators form a good self-consistent set of acidity indicators.

Shortly after Johnson et. al. published their temperature study for the Ho function of the H_2O-H_2SO_4 system, Tickle et. al.[49] reported an independent temperature study of the same system. Their results are in general agreement; however, their Ho values are somewhat lower at high acid concentrations than those of Johnson et. al. Tickle et. al. made use of a set of ten indicators over the range of 0-98 wt % H_2SO_4. The limited number of indicators necessitated, in some cases, the use of log $[BH^+]/[B]$ values outside of the limits of ±1.0 as recommended by Johnson et. al. The use of small values for log $[B]/[BH^+]$ (hereafter referred to as log I values where $I = [B]/[BH^+]$) gives the greatest certainty as log I values near zero (50% ionization) are the most accurate. Above a value of -log I of 1.0 the indicator is more than 99% ionized.

Tickle et. al. suggest that their results for 25°C are not consistent with Jorgenson and Hartter's[46] values because of a difference in the ionization constant for 2,5-dichloro-4-nitroaniline. Jorgenson and Hartter made use of Paul and Long's[5] best values for their reference ionization constants, but Tickle et. al. feel that the values determined solely in the sulfuric acid system should have been used. It should be noted that one of the requirements for good indicator behaviour[1] is that the ionization constant for an indicator should be independent of the acid system used in its evaluation. It may be argued that this requirement may not be fully satisfied because of specific indicator-solvent interactions that may be different from one acid system to another. The close similarity of independently evaluated pK_{BH^+} values from different acid systems, as listed by Paul and Long[5], indicates that any such difference must be minimal and that an average or "best" value for a pK_{BH^+} is a meaningful quantity.

Brand[41] in his investigation of the sulfonation of a number of aromatic nitro compounds, determined their protonation ionization constants by the use of the overlap technique basing his values on the original acidity measurements of Hammett and Deyrup[1]. Aromatic nitro compounds were first shown to act as bases in highly acidic media by the early cryoscopic measurements of Hantzsch[50] in 1908. More recently[51,52] their ionization behaviour has been reinvestigated and ionization constants in sulfuric acid have been determined from their cryoscopic and conductimetric behaviour. The n.m.r. spectra of a number of protonated nitro compounds, which have been measured[53-56] at low temperatures, show that the nitro group is protonated on an oxygen atom. Brand extended the Ho scale into the oleum region by the use of these aromatic nitro indicators[41,57]. He showed[57] that an absorption in the ultra-violet region could be assigned to a transition involving only the unprotonated nitro group and that upon increasing the acidity this peak decreased in intensity and a new peak at longer wavelengths appeared. This new peak was assigned to a transition involving the protonated nitro group. Using the changes in intensity of this new peak it was possible to calculate ionization ratios and thus extend the Ho scale.

Brand's work was reinvestigated by Gillespie and Robinson[58] who found that some of the extinction coefficients for the fully ionized indicators were in error. They were able to extend the Ho scale[59] through 100% H_2SO_4 (Ho = -12.08) to a value of -13.50 for a 106.0 wt % H_2SO_4 solution. This unusual acid concentration scale involving percentages greater than 100 was used to allow a continuous measure of acid concentration from aqueous sulfuric acid solutions to oleum solutions. The use of this scale is not encouraged but it will be used near 100% H_2SO_4 in this work. A 106 wt % H_2SO_4 solution corresponds to 44.5 mole % $H_2S_2O_7$ or 30.8 mole % SO_3 in H_2SO_4.

The theses of Barr[60] and Birchall[61] extended these Ho measurements into the acid systems H_2SO_4-$HB(HSO_4)_4$, H_2SO_4-HSO_3F and $HSO_3C\ell$, and HSO_3F-SbF_5. A detailed study of their measurements along with those of Gillespie and Robinson[58] and Gillespie and Janzen[78] indicated that a number of serious discrepancies were present and that a detailed and extensive reinvestigation of all acidity function measurements of higher acidity than those found by Jorgenson and Hartter[46] was required.

C. PURPOSE OF PRESENT WORK

The purpose of this work was to reinvestigate the behaviour of a number of aromatic nitro compounds in solutions of high acidity, by the use of absorption spectroscopy, in order to obtain a quantitative understanding of the acidity of various highly acidic media and to develop an acidity function for use in superacid media. Superacids, which for the purpose of this thesis, are defined as acid solutions more acidic than 100% H_2SO_4 and thus include the system H_2SO_4-SO_3, H_2SO_4-HSO_3F, HSO_3F-AsF_5, HSO_3F-SbF_5, and HSO_3F-SbF_5-SO_3 amongst others. The superacid systems, their uses, and some of their properties will be introduced later.

Some of these superacid media such as HSO_3F-SbF_5 have recently become widely used, for example, for the study of the protonation of a wide variety of weak bases and for the preparation and study of simple carbonium ions such as $C(CH_3)_3^+$. It has been clear from this work that these media have very high acidities, considerably greater than 100% H_2SO_4, but no quantitative conclusions concerning their acidity could be obtained from this work. It was thus of importance to attempt to make a quantitative evaluation of the acidity of such media and this was the primary objective of the work reported in this thesis.

CHAPTER II

EXPERIMENTAL PROCEDURES

A. PREPARATION AND PURIFICATION OF MATERIALS

i) Dry Air or Nitrogen

Compressed air or dry nitrogen (Canadian Liquid Air) was passed through a drying train consisting of a Dreschel bottle containing sulfuric acid, two 12" drying towers containing granular silica gel and molecular sieves, and a three-foot tube packed with phosphorous pentoxide supported on glass wool. High purity, extra dry nitrogen (Canadian Liquid Air) was used directly.

ii) Sulfuric Acid

100% sulfuric acid was prepared by mixing C.P. Reagent grade sulfuric acid (C.I.L.) and Reagent grade fuming sulfuric acid (30% free SO_3) (C.I.L.) until the product had a conductivity of 1.0439×10^{-2} $ohm^{-1}cm^{-1}$ at 25.00°C[62]. The conductivity cell used was constructed as described by Gillespie et. al.[62] and was standardized according to the method of Jones and Bradshaw[63].

iii) Sulfuric Acid-Sulfur Trioxide Solutions

Stock solutions of various concentrations of SO_3 in H_2SO_4 were prepared by weight by distillation of a quantity of SO_3 onto a weighed amount of 100% H_2SO_4. The stock solution was then diluted, in a dry box, by varying amounts of 100% H_2SO_4 to produce the required concentrations of SO_3 in H_2SO_4. The sulfur trioxide used in distillations was Sulfan (Allied Chemicals Corporation), stabilized SO_3.

iv) Fluorosulfuric Acid

Technical grade fluorosulfuric acid (Allied Chemicals Corporation) was purified by fractional distillation through a two-foot reflux column packed with small glass rings. Distillation was carried out in an all glass still with the fraction boiling between 162.5-163.5°C being collected for use. The still was rigorously dried by flaming out and passing a steady stream of dry air or nitrogen through it overnight. Passage of dry air through a granular silica gel packed guard tube was continued during the distillation.

The resulting acid was found to contain a 5×10^{-2} molal excess of SO_3 by cryoscopic titration using a freshly prepared HF-HSO_3F solution to titrate the acid[63]. This excess sulfur trioxide presumably arises from the dissociation reaction of HSO_3F (II-1) that takes place in both the gas and liquid phases[65].

$$HSO_3F \rightleftharpoons SO_3 + HF \qquad \text{(II-1)}$$

During distillation the small quantity of HF produced by this reaction presumably reacts with the glass still thus leaving an excess of SO_3 in the distillate[64]. Calculated additions of a 20% w/w solution of hydrogen fluoride in fluorosulfuric acid were made to adjust the freshly distilled acid to 100% HSO_3F by using an all teflon syringe fitted with a platinum needle (Hamilton Syringe Co. Inc.) and closed with a cap made from 1 mm Kel-F tubing. The freezing point of the resulting acid was periodically checked and good agreement was found with the literature[64] value of -89.000°C.

v) Sulfuric-Fluorosulfuric Acid Mixtures

Mixtures of H_2SO_4 and HSO_3F over the complete composition range of 0-100% HSO_3F were made by weighed additions of 100% HSO_3F to 100% H_2SO_4. Mixtures were generally prepared in small quantities and used immediately. Very dilute solutions of H_2SO_4 in HSO_3F were prepared by mixing small weighed quantities of a dilute solution of H_2SO_4 in HSO_3F (∿10 mole %) with 100% HSO_3F. All operations were carried out in a dry box.

vi) Fluorosulfuric Acid-Sulfur Trioxide Mixtures

Solutions of SO_3 in HSO_3F were prepared by weight, by mixing a stock solution of SO_3 in HSO_3F (∿30 mole %) with 100% HSO_3F. The stock solution was prepared by distillation of a weighed quantity of SO_3 onto a weighed amount of HSO_3F. Where possible procedures were carried out in a dry box.

vii) Fluorosulfuric Acid-Arsenic Pentafluoride Solutions

Solutions of AsF_5 in HSO_3F were prepared, by weight, by distillation in a grease-free pyrex and teflon vacuum line. AsF_5 (Ozark Mahoning Inc.) was found to be free of impurities as shown by its gas phase infrared spectrum and was condensed directly onto frozen 100% HSO_3F. Approximate vapour pressure measurements were made by allowing a flask of HSO_3F-AsF_5 solution to come to equilibrium pressure in a closed previously evacuated, vacuum line. The resulting AsF_5-HSO_3F vapour pressure (22°C) was determined by means of a simple U-tube mercury manometer.

viii) Antimony Pentafluoride

SbF_5 (Ozark Mahoning Company or Allied Chemicals Corp.) was doubly distilled in a pyrex glass still, as described by Barr[60], in an atmosphere of dry nitrogen. The fraction boiling between 142° and 143°C was collected and subsequently distilled under vacuum at room temperature in a grease-free pyrex and teflon vacuum line.

ix) Fluorosulphuric Acid-Antimony Pentafluoride Solutions

Stock solutions of SbF_5 up to 50 mole % in HSO_3F were prepared, by weight in a grease-free pyrex and teflon vacuum line, by distillation of SbF_5 onto frozen 100% HSO_3F. The stock solutions were then diluted in the dry box by mixing various amounts of 100% HSO_3F to obtain the desired concentration of SbF_5.

x) Fluorosulfuric Acid-Antimony Pentafluoride-Sulfur Trioxide Solutions

To obtain solutions of various molar ratios of SbF_5 to SO_3 in HSO_3F the stock solutions, HSO_3F-SbF_5 and HSO_3F-SO_3 as prepared above, were mixed in weighed amounts in a dry box. The resulting solution of the required SbF_5:SO_3 molar ratio was then diluted with 100% HSO_3F, by weight, to obtain the desired concentration of the SbF_5-SO_3 mixture. Solutions were prepared as needed and used immediately.

xi) Hydrogen Fluoride

Anhydrous hydrogen fluoride (Harshaw Chemical Co.) was distilled in a Kel-F and Monel vacuum line.

xii) Aromatic Nitro Compounds

The nitro indicators p-nitrotoluene (m.p. 51.0°; lit.[66] 51.7°C), m-chloronitrobenzene (m.p. 43.5°; lit.[66] 44°C), 2,4-dinitrotoluene (m.p. 69.7°; lit.[66] 70-1°C), 2,4,6-trinitrotoluene (m.p. 80.9°; lit.[66] 82°C), 1,3,5-trinitrobenzene (m.p. 121.9°; lit.[66] 121-2°C), 2,4,6-trinitrochlorobenzene (m.p. 81.9°; lit.[66] 83°C), obtained from Eastman Organic Chemicals and p-chloronitrobenzene (m.p. 83°; lit.[66] 83°C), obtained from Eastern Chemical Corporation, were recrystallized from anhydrous or slightly aqueous methanol. The indicators were air-dried and stored over standard desicants for one week before being sealed in air tight containers.

The indicators nitrobenzene (m.p. 5.7°; lit.[66] 5.7°C) and p-fluoronitrobenzene (m.p. 26.9°; lit.[66] 26°C), obtained from Eastman Organic Chemicals, were dried by standing over $CaC\ell_2$, fractionally distilled under a stream of dry nitrogen at a pressure of 2.4 mm of Hg, fractionally frozen at appropriate temperatures, and stored in dark containers.

m-Nitrotoluene (m.p. 15.3°; lit.[66] 15°C), obtained from Eastman Organic Chemicals, was triply distilled at atmospheric pressure in a dry, dark, simple distillation apparatus. Fractional freezing of the third middle fraction produced a very pale yellow solid. The material was stored as a liquid at room temperature, under dry nitrogen, in a black container.

2,4-Dinitrofluorobenzene (m.p. 25.4°; lit.[66] 25.8°C), obtained from Eastman Organic Chemicals, was purified by repeated fractional freezing. The final product was pale yellow and was stored in a dry dark container.

B. MANIPULATION OF MATERIALS

Rigorous precautions were taken to exclude moisture in this work. Glassware was stored in an oven at 110°C until needed and all manual operations where dryness was important were performed in a dry box.

The dry box (S. Blickman Inc.) had an evacuable port into which the hot glassware was placed immediately prior to use. Evacuation of the port was continued for a minimum period of fifteen minutes before being refilled with extra dry nitrogen. The atmosphere of the dry box was circulated through an external circuit in which any moisture or acid vapour was removed in liquid nitrogen traps. Desicant trays of phosphorous pentoxide and molecular seives were present in the dry box at all times. The dry box was equipped with a Mettler H.6 balance which was later replaced with a Cenco H.5 balance. Both balances were accurate to ±0.0001 gm.

Acid solutions were prepared and transferred by the use of glass-teflon gas tight syringes (2.5 and 5 ml capacity) fitted with platinum needles (Hamilton Syringe Co. Inc.), ground glass syringes (1 ml capacity), and by pouring through small funnels.

C. UV AND VISIBLE ABSORPTION SPECTRA

Solutions for study by absorption spectroscopy were prepared by one of two methods. The first method involved preparing the solutions entirely in the dry box by weighed additions of approximately 0.02 gm of the indicator into a weighed 10 gm sample of the acid mixture under study. An aliquot of approximately 0.02 gm was then diluted to 10 ml, in a volumetric flask, using the same acid mixture. This procedure produced indicator concentrations in the range of 10^{-4} molar but wasted large volumes of acid mixtures.

As an alternative method, and the one most often used, a 0.02 gm sample of the indicator was weighed into 10 gm of acetone outside the dry box. A 0.02 gm aliquot of the resulting solution was weighed into a 10 ml volumetric flask after which the solvent was evaporated and the flask flushed with extra dry nitrogen. The resulting 10^{-4} gm sample of the indicator was then brought into the dry box by means of an air tight box previously flushed with extra dry nitrogen. The 10 ml volumetric flask was then filled to the mark with the acid solution under study. The resulting indicator concentration was approximately 10^{-4} molar. The results obtained by this method for the solid indicators were consistent with the more difficult and somewhat wasteful original method. Solutions of the two liquid indicators were prepared by the first method.

Solutions of the indicators were well mixed by shaking and then transferred into 1.0 cm, Suprasil, U.V. cells (Hellma Ltd.) fitted with standard taper 7.5 ground glass tops and teflon stoppers. A reference sample of the exact composition of the acid mixture under study was transferred into a matching 10 mm U.V. cell. Spectra were recorded as soon as possible making use of a Cary 14 Recording Spectrophotometer (Applied Physics Corporation). Extinction coefficients (ξ) were calculated from the observed absorbance (A) values according to

$$\xi = \frac{A}{c\ell}$$

where c is the concentration of the indicator in molar units and ℓ is the path length of the cell used (1 cm). Absorption spectra were recorded at a room temperature of 22 ± 1°C.

D. NUCLEAR MAGNETIC RESONANCE SPECTRA

^{1}H n.m.r. spectra were recorded with a T-60 (Varian Corp.) or H.A. 100 (Varian Corp.) spectrometer in 5 mm O.D. "Pyrex" n.m.r. tubes. Samples were prepared in the dry box and then later sealed off under vacuum. The resonance of the reference material, tetramethylsilane, was determined by exchange of sample tubes in the probe of the spectrometer. In some cases a coaxial arrangement of the sample and reference was used with the reference material in the outer portion of the coaxial tube. Spectra of very dilute samples were recorded with the aid of a time-averaging computer (Varian Corp. model C-1024) coupled to the H.A. 100 spectrometer.

^{19}F n.m.r. spectra were recorded with a D.P. 60 (Varian Corp.) spectrometer operating at 56.4 MHz and equipped with a variable temperature control unit. Samples were contained in vacuum sealed 5 mm O.D. "Pyrex" n.m.r. tubes. Chemical shifts are reported with reference to fluorotrichloromethane whose resonance was determined by the exchange of sample tubes in the probe of the spectrometer.

CHAPTER III

THE SULFURIC ACID SOLVENT SYSTEM

A. HISTORICAL INTRODUCTION

Sulfuric acid has been the subject of many investigations over the past sixty years and as a result it is now one of the best known non-aqueous protonic solvents. There have been a number of reviews of the properties of sulfuric acid as a solvent[59,67-70] outlining the reactions which have been studied and the physical techniques used. During these investigations many new species have been identified, e.g. the nitronium ion NO_2^+, iodine cations such as I_3^+, acyl ions such as $(CH_3)_3C_6H_2CO^+$, and various carbonium ions.

The nature of 100% sulfuric acid, that is sulfuric acid having the exact composition H_2SO_4, has been studied in some detail and its constitution is well understood. The self-ionization or autoprotolysis of the solvent is probably the most important reaction (1) as it gives

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad \text{(III-1)}$$

rise to the characteristic ions of the solvent, $H_3SO_4^+$ and HSO_4^- ($K_{ap} = 2.7 \times 10^{-4}$)[71]. These are of particular importance as they are produced by the reaction of an acid or a base, respectively, with the solvent. This process is analogous to the reaction of acids and bases in water which gives rise to the characteristic H_3O^+ and OH^- ions.

There are a number of other important reactions involving the components of sulfuric acid. It is slightly self-dissociated according to (2) and thus water and sulfur trioxide are important solutes.

$$H_2SO_4 \rightleftharpoons H_2O + SO_3 \qquad \text{(III-2)}$$

It has been found that water is a strong base in sulfuric acid, extensively but not completely protonated ($K_{H_2O} = 1$)[71].

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad \text{(III-3)}$$

In dilute solutions sulfur trioxide is essentially completely converted to disulfuric acid, $H_2S_2O_7$.

$$SO_3 + H_2SO_4 \rightleftharpoons H_2S_2O_7 \qquad \text{(III-4)}$$

Disulfuric acid is a weak acid ($K_{H_2S_2O_7} = 1.4 \times 10^{-2}$)[71] ionizing according to (5).

$$H_2SO_4 + H_2S_2O_7 \rightleftharpoons HS_2O_7^- + H_3SO_4^+ \qquad \text{(III-5)}$$

Since the ions $H_3SO_4^+$ and HSO_4^- are in equilibrium (1) it follows that H_3O^+ and $HS_2O_7^-$ must also be in equilibrium. This reaction is referred to as the ionic self-dissociation reaction ($K_{id} = 5.1 \times 10^{-5}$)[71].

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \qquad \text{(III-6)}$$

It is a relatively simple matter to recognize compounds which are basic to sulfuric acid, that is a substance that produces the characteristic HSO_4^- ion. Any reaction that involves the protonation of a solute automatically produces a basic solution, such as:

$$(CH_3)_2CO + H_2SO_4 \rightleftharpoons (CH_3)_2CO^+H + HSO_4^- \qquad \text{(III-7)}$$

$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3CO_2H_2^+ + HSO_4^- \qquad \text{(III-8)}$$

$$H_3PO_4 + H_2SO_4 \rightleftharpoons H_4PO_4^+ + HSO_4^- \qquad \text{(III-9)}$$

Metal sulfates such as $KHSO_4$ or Na_2SO_4 act as strong bases in sulfuric acid:

$$MHSO_4 \rightarrow M^+ + HSO_4^- \qquad \text{(III-10)}$$

$$M_2SO_4 + H_2SO_4 \rightarrow 2M^+ + 2HSO_4^- \qquad \text{(III-11)}$$

Solvolysis reactions of common inorganic salts also produce basic solutions:

$$NH_4C\ell O_4 + H_2SO_4 \rightleftharpoons NH_4^+ + HC\ell O_4 + HSO_4^- \qquad \text{(III-12)}$$

$$KNO_3 + H_2SO_4 \rightleftharpoons K^+ + HNO_3 + HSO_4^- \qquad \text{(III-13)}$$

$$HNO_3 + H_2SO_4 \rightleftharpoons H_3O^+ + NO_2^+ + 2HSO_4^-$$

It is more difficult to find acids of the sulfuric acid solvent system. Simple protonic acids act either as bases or non-electrolytes except for fluorosulfuric acid HSO_3F, chlorosulfuric acid $HSO_3C\ell$, and perchloric acid. Perchloric acid is so weak an acid, however, that the extent of its dissociation is too weak to be measured. HSO_3F and $HSO_3C\ell$ both act as very weak acids according to (14) having dissociation con-

$$HSO_3X + H_2SO_4 \rightleftharpoons H_3SO_4^+ + SO_3X^- \qquad X = F,\ C\ell \qquad \text{(III-14)}$$

stants[72] of 2.3×10^{-3} and 9×10^{-4} respectively.

As was previously noted sulfur trioxide acts as a weak acid through the formation of $H_2S_2O_7$ in dilute solutions. At higher concentrations of SO_3 higher polysulfuric acids are formed. The species $H_2S_3O_{10}$ and $H_2S_4O_{13}$ have been identified[73,74] and the presence of $H_2S_5O_{16}$ has been postulated. The formation of these higher polysulfuric acids is, however, incomplete as free SO_3 is present in solutions of the required compositions for these species. As the size of the polyacid increases its acidity is expected to increase with the largest effect being noted at the beginning of the series.

In an effort to find a strong acid of the sulfuric acid system the early measurements of Hantzsch[75] on boric acid as a solute were reinvestigated[76]. It was found that the boron tri(hydrogensulfate), $B(HSO_4)_3$, initially formed reacts further with the hydrogen sulfate anion to form the boron tetra(hydrogensulfate) anion, $B(HSO_4)_4^-$ (15). This clearly indicates that the species $HB(HSO_4)_4$ is a strong acid of the sulfuric acid solvent system. A K_a of 2×10^{-1} has been found[72].

$$H_3BO_3 + 6H_2SO_4 \rightleftharpoons B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^- \qquad \text{(III-15)}$$
$$B(HSO_4)_3 + HSO_4^- \rightleftharpoons B(HSO_4)_4^-$$

If the reaction with boric acid is carried out in a dilute oleum solution instead of 100% sulfuric acid it is possible to eliminate the water produced according to Equation 15 thus allowing the acidic character of the reaction to become apparent (16).

$$H_3BO_3 + 3H_2S_2O_7 \rightleftharpoons H_3SO_4^+ + B(HSO_4)_4^- + H_2SO_4 \qquad \text{(III-16)}$$

Solutions of other complex acids such as $H_2Pb(HSO_4)_6$ and $H_2Sn(HSO_4)_6$ have been prepared[77] but these do not appear to be as strong as $HB(HSO_4)_4$.

B. ACIDITY STUDIES IN SULFURIC ACID SOLUTIONS

In order to develop an acidity function in the super acid region by means of a set of indicators it is necessary to have a reference point on which the ionization constants of the new set of indicators may be based. As the nitro indicators are so weakly basic it is impossible to measure the ionization ratios of even one indicator in dilute aqueous acid. Thus the standard state of infinitely dilute solution in water is not directly obtainable. It has been found that ionization ratios of the most basic nitro indicator used in this study can be measured in concentrated sulfuric acid solutions. It will be shown that the behaviour of p-nitrotoluene, the most basic nitro indicator used, and 2,4,6-trinitroaniline, the least basic aniline indicator studied[46]. is very similar in the region of 95-100% sulfuric acid.

The reference point for this work was thus chosen to be the pK_{BH^+} of 2,4,6-trinitroaniline, -10.10, which was determined by Jorgenson and Hartter[46] in their room temperature study of the Ho function for concentrated solutions of sulfuric acid in water. Ionization constants increase with increasing temperature near 100% sulfuric acid[48,49] and thus the higher value of -10.03 at 25°C for the pK_{BH^+} of 2,4,6-trinitroaniline as found by Johnson et. al.[48] is in good agreement with Jorgenson and Hartter's value of -10.10. Tickle et. al.[49] found values of -9.87 at 25° and -9.97 at 15°C which are in marked disagreement as discussed previously. The value of -10.10 was chosen as the results reported here were carried out at room temperature. Since this work makes use of one consistent set of aromatic nitro indicators the relative acidities so measured are still valid regardless of any changes in the pK_{BH^+} of the reference indicator. If the pK_{BH^+} value of -10.10 for 2,4,6-trinitroaniline should be revised then this will correspondingly alter the magnitude of the Ho values reported in this work but not their relative values.

B.1. THE H_2O-H_2SO_4-SO_3 SYSTEM NEAR 100% H_2SO_4

The behaviour of 2,4,6-trinitroaniline in concentrated sulfuric acid solutions was reinvestigated by Gillespie and Robinson[58] and their results were found to be in excellent agreement with those of Jorgenson and Hartter[46]. The ionization ratios determined over the acid composition range 90.79-99.31 wt. % H_2SO_4 are shown in Table I and Figure 5. These results form the basis of the extension of the Ho scale into the super acid region.

The most basic nitro indicator used, p-nitrotoluene, was first studied as an acidity function indicator by Brand[41] who later revised his original measurements[57]. The basis for his work was the Ho values for concentrated aqueous sulfuric acid as determined by Hammett and Deyrup[1,2] and later revised by Hammett and Paul[3]. Since these early works the Ho scale has been extensively reinvestigated and up-dated. Gillespie and Robinson[58] studied the ionization of p-nitrotoluene over the acid composition range 96.81-100.76 wt. % H_2SO_4. Their ionization ratios are reported in Table II and Figures 5 and 6. A close examination of their measured ξ values in comparison with those of Brand et. al.[57] shows that they are in close general agreement but that the results of Gillespie and Robinson were slightly higher. A check of the ξ value found at 100% H_2SO_4 was made and excellent agreement was found with Gillespie and Robinson's value. Their results are thus accepted and used to extend the Ho scale. As noted by Brand[41,57] p-nitrotoluene is sulfonated at high SO_3 concentrations and thus ξ values were corrected to zero time by means of a first order rate plot.

Ionization ratios for m-nitrotoluene over the range of 99-101 wt. % H_2SO_4 were determined by Gillespie and Robinson[58] and are shown in Table III and Figures 5 and 6. As in the case of p-nitrotoluene a check of their ξ value at 100% H_2SO_4 was made and excellent agreement was obtained. Their measurements are accepted and used up to 101 wt. % H_2SO_4 for the evaluation of the acidity function near 100% H_2SO_4. As in the case of p-nitrotoluene it was noted that sulfonation of the indicator takes place in oleum solutions and thus all ξ values were corrected to zero time. Brand et. al.[57] reported a pK_{BH^+} based upon an out-of-date Ho scale[1,2]but unfortunately a detailed tabulation of ξ values or ionization ratios was not included in the published paper making a comparison of results impossible.

Extinction coefficients of nitrobenzene in various acid mixtures are shown in Table IV and Figure 2. Most of the results reported are those of Gillespie and Robinson[58] except for three measurements at high SO_3 concentrations and a check of their value for 100% H_2SO_4. In calculating the ionization ratios listed in Table V and plotted in Figure 6, average ξ values were taken at regular intervals from Figure 2. The ξ_{BH^+} value of 15,150 was determined from the plot of ξ vs wt. % H_2SO_4 where it levels off at 104.5% H_2SO_4. As reported by Brand[41,57] it was found that nitrobenzene is sulfonated at high SO_3 concentrations and thus, when necessary, extinction coefficients were corrected to zero time. Brand[41] tabulated ξ values and calculated ionization ratios using measurements at 3650 Å only. A small solvent effect causes the position of maximum absorption (λ_{max}) to shift slightly with acid composition and thus Brand later repeated his measurements[57] using ξ values at the λ_{max} to determine the ionization ratios. Unfortunately ξ values or ionization ratios were not reported for his later measurements and thus a comparison of our results with his is not possible.

At very high SO_3 concentrations Brand[41] noted that even when nitrobenzene is fully protonated the extinction coefficient of the indicator continues to rise with increasing SO_3 concentration. He attributed this effect to the possible formation of species such as $ArNO_2 \cdot SO_3H^+$ in addition to the simple protonated species $ArNO_2H^+$. Measurements of ξ values in HSO_3F-SbF_5, where the acidity is much greater than required to fully protonate the indicator, also showed higher values for ξ_{BH^+} than were found in the H_2SO_4-SO_3 system. As no SO_3 is available for the formation of a complex species such as $ArNO_2 \cdot SO_3H^+$ the increase in extinction coefficients may possibly be attributed to hydrogen bonding effects. Hydrogen bonding may be used to explain the rise in ξ values found at very high SO_3 concentrations in the H_2SO_4-SO_3 system.

Extinction coefficients for p-fluoronitrobenzene and p-chloronitrobenzene are given in Tables VI and VII and plotted versus mole % SO_3 in 100% H_2SO_4 in Figures 3 and 4 respectively. It was found that the results of Gillespie and Janzen[78], at low SO_3 concentrations, were consistent with this work as were those of Gillespie and Robinson[58]. ξ_B values were determined in 85 to 95% H_2SO_4 and were found to be 600 and 400 for p-fluoronitrobenzene and p-chloronitrobenzene respectively. ξ_{BH^+} values of 16,500 and 21,800, respectively, were determined from plots of ξ versus mole % SO_3 in 100% H_2SO_4 (Figures 3 and 4) at the point where the curves become independent of acid concentration. Tables VIII and IX list the ionization ratios of the two indicators over the region 100-101 wt. % H_2SO_4. Measurements at higher SO_3 concentrations will be discussed in a later section.

It should be noted that in keeping with the decreasing basicity of the indicators p-nitrotoluene, m-nitrotoluene, nitrobenzene, and p-chloronitrobenzene, as determined by cryoscopic and conductimetric techniques[80], the SO_3 concentration required to fully protonate the indicators increases in the same order. The use of the level portion of the curve of ξ versus wt. % H_2SO_4 as the ξ_{BH^+} for nitrobenzene is thus further justified.

The ionization ratios of 2,4,6-trinitroaniline and the five nitro indicators are plotted versus wt. % H_2SO_4 in Figures 5 and 6. Although the resulting curves are not straight lines, and indeed would not be expected to be so, it is evident that where two or more indicators are used over the same acid composition range they behave in a very similar, if not identical, fashion· giving rise to essentially "parallel" curves. As shall be shown later the degree of parallelism of these six indicators is as good as that of the thirteen aniline indicators used to describe the Ho function up to 99.5% H_2SO_4. The nitro indicators thus give rise to a valid extension of the Ho function into the super acid region and are themselves a consistent set of indicators.

Ionization constants for the five nitro indicators were calculated from Figures 5 and 6 using the average difference between adjacent log I curves in the range $-1 < I < 1$ to obtain the difference in the pK_{BH^+} values of the two indicators in question. The values so determined differ from those of Brand et. al.[57] as his values were based upon an outdated Ho scale. The difference between the pK_{BH^+} values of Brand and those reported here is not constant but ranges from 0.88 to 1.14 with an average of 1.02. On the basis of the difference in the two reference values at 96.65% H_2SO_4 a ΔpK_{BH^+} of 1.16 would be expected. By the application of this correction factor Brand's results become somewhat more compatible with those reported here, but a discrepancy is still present. From the difference between the expected correction factor of 1.16 and the average difference between the two sets of pK_{BH^+} values, 1.02, the importance of using a consistent set of overlapping indicators to define an Ho scale may be seen. The acidity scale of Hammett and Paul [3], used by Brand to overlap with his measurements of the ionization ratios of p-nitrotoluene, was not composed of a consistent set of indicators and thus the acidity scale was not a true Ho scale but some other "composite" acidity function. This "composite" acidity function behaves in a slightly different manner to changes in acid concentration than does the Ho scale based solely on primary aniline indicators. Other differences between the results reported here and those of Brand are due to the choice of ξ_B and ξ_{BH^+} values for the various indicators.

The Ho values listed in Table X were calculated from the log I curves of Figures 5 and 6 and the corresponding pK_{BH^+} value for each indicator. A simple average of the individual (pK_{BH^+} + log I) values for each indicator at the various acid compositions was taken as the Ho value for that composition. The -Ho function versus wt. % H_2SO_4 is shown in Figure 7. The Ho value for 100% H_2SO_4 was found to be -11.93.

It may be seen from Figure 7 that the -Ho function gradually increases with % H_2SO_4 until the region of 100%. Here a more rapid increase in acidity takes place as the concentration of the strong base, water, decreases. The acidity function curve goes through an inflection point at 100% H_2SO_4 followed by a decrease in slope as the SO_3 concentration increases. In an aqueous system a similarly shaped sigmoid curve would be generated by plotting pH versus acid concentration for the titration of a solution of a strong base. The rate of increase near the pure solvent, water or sulfuric acid, is dependent upon the magnitude of the autoprotolysis constant of the solvent. Water, with a much smaller self-ionization constant than sulfuric acid, has a sharper increase in acidity as the concentration of a strong base decreases. The autoprotolysis reaction gives rise to a buffering effect upon the acidity dependent upon the size of the autoprotolysis constant.

The acidity of an aqueous solution, as measured by pH, is directly related to the concentration of the H_3O^+ ion in solution, the most acidic species possible in aqueous solutions. In the region of 100% H_2SO_4 the most acidic species possible in solution is the $H_3SO_4^+$ ion. An acidity function in this region would be expected to be related to the concentration of this species. Figure 7 shows a calculated Ho function from the relation

$$Ho = -\log(H_3SO_4^+) - 13.80 \qquad \text{(III-17)}$$

where the $H_3SO_4^+$ concentration is expressed in molal units. The constant of -13.80 was determined by setting the calculated Ho equal to the experimental one at 100% H_2SO_4.

The observed Ho curve is somewhat higher than calculated for the aqueous solutions and somewhat less in oleum solutions. $H_3SO_4^+$ concentrations were obtained, at various concentrations of H_2O or SO_3, from a table given by Gillespie et. al.[81] who assumed for purposes of the table that water acts as a strong base and is completely protonated. This assumption may not be valid[82] and thus the $H_3SO_4^+$ concentrations for aqueous solutions may be somewhat larger than listed. Correction for this error would tend to decrease the difference between the calculated and experimental curves with larger corrections being noted the higher the water concentration. The remaining difference between the two curves is presumably due to activity coefficient behaviour of the protonated and unprotonated forms of the indicator as well as a solvation effect. Cryoscopic measurements[83] indicate that the electrolyte $H_3O^+HSO_4^-$ is "salting-out" the nonelectrolyte B, the unprotonated form of the indicator, and that "salting-in" takes place in oleum solutions. It seems reasonable that the salt effects upon the protonated form of the indicator would be small and balanced by similar effects on the activity coefficient of $H_3SO_4^+$. The relationship

$$Ho = -\log[(H_3SO_4^+)\cdot f_B] + \text{constant}$$

would more closely represent the experimental Ho function than the simple linear relationship used to calculate Ho's as shown in Figure 7.

B.2. THE H_2SO_4-SO_3 SYSTEM

Acidity studies in the sulfuric acid-sulfuric trioxide system have been carried out up to 75 mole % SO_3 in 100% H_2SO_4. The term mole % SO_3 in H_2SO_4 indicates the concentration of sulfur trioxide over and above that required to produce 100% sulfuric acid; thus 50 mole % SO_3 corresponds to an acid composition equivalent to disulfuric acid, $H_2S_2O_7$.

The extinction coefficients and ionization ratios of nitrobenzene in oleum solutions have been previously tabulated (Tables IV and V). The ionization ratios are shown in Figure 12. Tables XI and XII give the ionization ratios of p-fluoronitrobenzene and p-chloronitrobenzene at regular acid concentrations as calculated from the ξ versus mole % SO_3 curves of Figures 3 and 4. The ξ_B and ξ_{BH^+} values used were those found in the H_2O-H_2SO_4-SO_3 system.

It was found that the ξ values for p-fluoronitrobenzene and p-chloronitrobenzene in concentrated oleum solutions, as well as those of m-chloronitrobenzene, 2,4-dinitrotoluene and 2,4-dinitrofluorobenzene to be discussed shortly, were not consistent with those of Gillespie and Robinson[58]. The reason for this inconsistency is not apparent and may only be explained by some unknown experimental error in the work of Gillespie and Robinson. It was found that on using their uncorrected ξ values to calculate and plot ionization ratios versus mole % SO_3 the resulting curves were not parallel and in the case of two of the indicators they crossed each other. Their results have not been used in this acid region.

Extinction coefficients for the indicators m-chloronitrobenzene and 2,4-dinitrotoluene are given in Tables XIII and XV and are plotted versus mole % SO_3 in Figures 8 and 9 respectively. The ξ_B values for the two indicators were found to be 440 and 1,700 in concentrated sulfuric acid solutions between 95 and 100% H_2SO_4. The curve of ξ versus mole % SO_3 for m-chloronitrobenzene (Figure 8) appears to level out at a value of 12,850 at 65 mole % SO_3. This value is accepted as the ξ_{BH^+} for this indicator in the H_2SO_4-SO_3 system. A similar curve for 2,4-dinitrotoluene (Figure 9) appears to level off at 75 mole % SO_3 with a value of 13,900 but, as measurements could not be carried out above this SO_3 concentration due to the solidification of the acid, this could not be confirmed. Studies of the behaviour of this indicator in the more acidic H_2SO_4-HSO_3F and HSO_3F-SbF_5 systems indicate that the ξ_{BH^+} value for this indicator is indeed 13,900; this will be shown in a later section. The ionization ratios for these two indicators are given at regularly-spaced SO_3 concentrations in Tables XIV and XVI and are plotted in Figure 12.

Brand et. al.[57] reported ξ values for 2,4-dinitrotoluene in various oleum solutions. His ξ_B value of 1,700 in 99% H_2SO_4 is in full agreement with the result reported here. Brand did not carry his measurements to high enough SO_3 concentrations to determine the extinction coefficient of the fully protonated indicator but instead used a least squares method to estimate its value. His estimate of 13,900 is in complete agreement with the ξ_{BH^+} value found in these studies. Unfortunately the ξ values tabulated by Brand at various SO_3 concentrations are all somewhat lower than those found in this work. The method by which Brand found an ξ_{BH^+} value for 2,4-dinitrotoluene, consistent with our value of 13,900, must thus be regarded with some reservations.

Complete absorption spectra for solutions of 2,4-dinitrofluorobenzene in the ultraviolet-visible region of the spectrum, are shown in Table XVII for various concentrations of SO_3 in H_2SO_4. A representative number of these spectra are plotted in Figure 10; they form a family of curves that is typical for the protonation of any one of the indicators studied.

As the concentration of sulfur trioxide in sulfuric acid solutions is increased an absorption due to the solvent moves from less than 210 nm. to more than 270 nm. This intense solvent peak generally hides the absorption maxima due to the unprotonated form of the indicator and only the tail of this peak is seen at high SO_3 concentrations. As the concentration of SO_3 is increased a new peak in the absorption spectra of the indicator appears; this is assigned to the protonated form of the indicator. In all cases it is shifted to longer wavelengths from the peak due to the unprotonated form of the indicator. As the intensity of this new peak increases that of the unprotonated form of the indicator decreases. In the case of mononitro indicators the peak due to the unprotonated form completely disappears when the indicator is fully protonated. For dinitro indicators this lower wavelength absorption only partially disappears with the result that the spectrum of a monoprotonated dinitro indicator consists of a peak due to a protonated nitro group and one due to that of an unprotonated nitro group. It will be shown that it is possible to diprotonate a polynitro indicator with the complete disappearance of the portion of the spectra assigned to an unprotonated nitro group.

As indicated by Brand et. al.[57] the low wavelength absorption in the region of 200-270 nm. in the spectra of an aromatic nitro compound is assigned to an electronic transition localized upon an unprotonated nitro group, $Ar\text{-}NO_2$. The peak at higher wavelengths, 300-350 nm., is assigned to a similar transition localized upon a protonated nitro group $Ar\text{-}NO_2H^+$. It is not possible to differentiate between the species $Ar\text{-}NO_2H^+$, $Ar\text{-}NO_2{\cdot}SO_3$ or $Ar\text{-}NO_2{\cdot}SO_3H^+$ by ultraviolet-visible absorption spectroscopy. Brand[41] assigned the increase in the extinction coefficient of the long wavelength peak of nitrobenzene at high SO_3 concentrations to the formation of $Ar\text{-}NO_2SO_3H^+$. As previously indicated it appears that the increase in ξ values may be due to hydrogen bonding rather than complex formation.

A slight solvent shift to longer wavelengths of the peak due to the protonated form was observed for all indicators as the SO_3 concentration was increased. This solvent effect, which was generally less than 10 nm., explains the lack of the expected isobestic point. As the solvent shift was small all ξ values for the various indicators were taken at the observed λ_{max}.

Table XVII and Figure 11 show the ξ values for 2,4-dinitrofluorobenzene in oleum solutions. An ξ_B value of 920 was observed in the region of 100% H_2SO_4. The acidity of concentrated solutions of SO_3 in H_2SO_4 does not appear to be sufficient to fully protonate 2,4-dinitrofluorobenzene and thus an ξ_{BH^+} value of 12,100, as found in the HSO_3F-SbF_5 system to be discussed later, was used. Ionization ratios are listed in Table XVIII at regularly-spaced SO_3 concentrations and are shown in Figure 12.

Ionization ratios of the six indicators studied in the H_2SO_4-SO_3 system are plotted versus mole % SO_3 in Figure 12. From the shape of the resulting curves it is apparent that the indicators behave in a generally similar fashion over the entire concentration range studied. The behaviour of 2,4-dinitrofluorobenzene is rather poor in that the slope of its ionization ratio curve increases more rapidly than that of 2,4-dinitrotoluene over the range of 45-55 mole % SO_3. Throughout the ranges 20-45% and above 55 mole % SO_3 the curves are parallel but have unequal separations. It is not surprising that in this very highly oxidizing medium the behaviour of the indicators is less than ideal.

Evaluation of ionization constants was done as previously shown in the determination of pK_{BH^+} values for the first five nitro indicators. The difference between the log I curves of p-fluoronitrobenzene and m-chloronitrobenzene over the range 7.5-27.5 mole % SO_3 was used to evaluate the pK_{BH^+} of m-chloronitrobenzene which was found to be -13.20. From similar studies in the H_2SO_4-HSO_3F system, to be discussed in a later section, a value of -13.13 was found. The average, -13.16, was used as the pK_{BH^+} for m-chloronitrobenzene. In the same way values of -13.74 and -13.76 were found, in the two acid systems, for the pK_{BH^+} of 2,4-dinitrotoluene with the average, -13.75, being used; overlap with m-chloronitrobenzene over the region 20-42.5 mole % SO_3 was used to determine the pK_{BH^+} value in the oleum system. Due to the poor behaviour of the log I curves of 2,4-dinitrotoluene and 2,4-dinitrofluorobenzene above 45 mole % SO_3 it was arbitrarily decided to use the Δ log I of the region between 52.5-65.0 mole % SO_3 in calculating the pK_{BH^+} for 2,4-dinitrofluorobenzene. The value of -14.03 was used only between 52.5 and 75 mole % SO_3, all other measurements using 2,4-dinitrofluorobenzene in the oleum system were disregarded. The discrepancy between 2,4-dinitrotoluene and 2,4-dinitrofluorobenzene means that all acidity values above 40 mole % SO_3 are open to some question.

When the correction factor of 1.16, relating this study to that of Brand et. al.[57] as discussed in the last section, is applied to Brand's pK_{BH^+} values for m-chloronitrobenzene and 2,4-dinitrotoluene there is still a difference between his results and those reported here. The major difference is again due to the reference system used by Brand and, to a smaller extent, the differences in experimental ξ values, where tabulated. Brand did not study 2,4-dinitrofluorobenzene in oleum solutions.

Table XIX lists (pK_{BH^+} + log I) values for the six indicators studied in the H_2SO_4-SO_3 system. The average -Ho values are tabulated and are plotted in Figure 13 from 0-75 mole % SO_3 in H_2SO_4. Sulfur trioxide acts as a medium strong acid in sulfuric acid giving a relatively rapid initial increase in -Ho at low SO_3 concentrations. This is consistent with the formation of disulfuric acid which is a medium strong acid in sulfuric acid. The rate of increase in acidity becomes nearly constant between 10 and 60 mole % SO_3 indicating that the acidity of the solvent is directly related to the SO_3 concentration and thus presumably to the degree of polymerization of the H_2SO_4-SO_3 system. As the average size of the acid increases it becomes easier to remove the acidic protons of the acid thus increasing the acidity. This is due to the increased delocalization of the negative charge on the larger anion which exerts less of an attraction for the positively-charged proton as compared to a smaller anion. Above 60 mole % SO_3 the acidity apparently levels off as the concentration of unreacted SO_3 increases more rapidly than the formation of higher polysulfuric acids. Measurements could not be carried out at concentrations higher than 75 mole % SO_3 as the solutions slowly crystallized at room temperature. It is expected that the protonic acidity would eventually decrease as the concentration of protons in the acid decreased.

B.3. THE H_2SO_4-HSO_3F SYSTEM

Barr[60] and Birchall[61] have made a limited number of measurements of the acidity of the H_2SO_4-HSO_3F system by the use of aromatic nitro indicators. In order to confirm their measurements and to firmly establish the Ho scale in this acid system the indicators p-chloronitrobenzene, m-chloronitrobenzene, 2,4-dinitrotoluene and 2,4-dinitrofluorobenzene were reinvestigated over the complete acid composition range.

Tables XX-XXIV list the ξ values and ionization ratios found for the four respective indicators at various acid mixtures. Five ξ values for p-chloronitrobenzene and four for m-chloronitrobenzene are the results of Barr[60]. It was found that Barr's measurements were consistent with this work up to approximately 55 mole % HSO_3F. Above this concentration his ξ values became somewhat lower than those found in this work. Barr's ξ values for 2,4-dinitrotoluene were not consistent with this work as his spectrometer was only capable of recording spectra above 330 nm. Since the absorption maxima of 2,4-dinitrotoluene lies between 325 and 335 nm. Barr's spectra were somewhat incomplete. The reason for the inconsistency in ξ values above 55 mole % HSO_3F for p-chloronitrobenzene and m-chloronitrobenzene must lie in experimental methods and available materials. Barr's measurements indicated that the acidity function for this system became essentially independent of the acid composition over the range 55-80 mole % HSO_3F. This is contrary to the expectation that the acidity should be dependent upon the acid composition.

Birchall's[61] single ξ value for 2,4-dinitrotoluene in H_2SO_4-HSO_3F is in agreement with this work as are three of his four ξ values for 2,4-dinitrofluorobenzene. The remaining measurement was at an acid composition giving rise to an acidity too low to more than barely protonate the indicator.

ξ_B values were those found in the H_2O-H_2SO_4-SO_3 system. ξ_{BH^+} values were determined from plots of ξ versus mole % HSO_3F or mole % SbF_5 in HSO_3F and are 24,350, 14,380, 13,900 and 12,100 for the indicators p-chloronitrobenzene, m-chloronitrobenzene, 2,4-dinitrotoluene and 2,4-dinitrofluorobenzene, respectively. The values for 2,4-dinitrotoluene and 2,4-dinitrofluorobenzene were those used in the H_2SO_4-SO_3 system. The ξ_{BH^+} values for p-chloronitrobenzene and m-chloronitrobenzene are somewhat greater in the H_2SO_4-HSO_3F system than in the H_2SO_4-SO_3 system. There is no apparent reason for this difference although it is known that the extinction coefficients of some materials depends upon the solvent used even though no reaction takes place between the solute and solvent. The ξ_{BH^+} values found in the HSO_3F systems were used to calculate the ionization ratios of p-chloronitrobenzene and m-chloronitrobenzene in the H_2SO_4-HSO_3F system.

Figure 14 shows the log I versus mole % HSO_3F curves for the four indicators studied. The degree of parallelism will be quantitatively discussed in a later section although it is readily apparent that the indicators behave in very similar fashions throughout the complete acid composition range. Using the pK_{BH^+} of p-chloronitrobenzene, -12.70, as a reference the ionization constants of the three remaining indicators were determined by the overlap technique. pK_{BH^+} values of -13.13, -13.76, and -14.52 were found for m-chloronitrobenzene, 2,4-dinitrotoluene and 2,4-dinitrofluorobenzene, respectively. An average value of the ionization constants for m-chloronitrobenzene and 2,4-dinitrotoluene, as found in the H_2SO_4-SO_3 and H_2SO_4-HSO_3F systems, was taken as the actual pK_{BH^+}; i.e., -13.16 for m-chloronitrobenzene and -13.75 for 2,4-dinitrotoluene. The close agreement between the independently evaluated ionization constants as found in the two different acid systems provides a further justification of the validity of acidity function measurements in the super acid region. The ionization constant for 2,4-dinitrofluorobenzene differs greatly from the tentative value discussed for use in the H_2SO_4-SO_3 system. The new value of -14.52 is accepted as the pK_{BH^+} for 2,4-dinitrofluorobenzene.

The log I versus mole % HSO_3F curves of Figure 14 were used to calculate (pK_{BH^+} + log I) values for the four indicators at regularly spaced acid concentrations between 5 and 99 mole % HSO_3F. The results are shown in Table XXIV along with average -Ho values. A curve of -Ho versus mole % HSO_3F in H_2SO_4 is shown in Figure 13. The Ho value of -15.07 for 100% HSO_3F will be discussed in a later section.

The acidity function curve for the H_2SO_4-HSO_3F system increases with increasing concentrations of the stronger protonic acid, HSO_3F. Fluorosulfuric acid is a weak acid in sulfuric acid and thus the slow increase in -Ho at low acid concentrations is consistent with this finding. The acidity function increases linearly between 15 and 80 mole % HSO_3F as would be expected for a mixture of two acids of unequal strength. In the region of 100% HSO_3F, where H_2SO_4 is acting as a weak base, the acidity rises sharply just as it does in the H_2O-H_2SO_4 system near 100% H_2SO_4. This will be discussed later in conjunction with the HSO_3F solvent system.

B.4. THE H_2SO_4-$HSO_3C\ell$ SYSTEM

The acidity function for the sulfuric-chlorosulfuric acid system has been previously measured by Palm[79] making use of two nitro indicators, p-chloronitrobenzene and 2,4-dinitrotoluene over the complete composition range. The pK_{BH^+}, ξ_B, and ξ_{BH^+} values used in his study were those of Brand et. al.[57] and thus the resulting -Ho values cannot be in agreement with this work. Barr[60] reinvestigated this system making use of the indicators m-nitrotoluene, nitrobenzene, p-chloronitrobenzene and 2,4-dinitrotoluene. Barr's ξ values for p-chloronitrobenzene and 2,4-dinitrotoluene were consistent with those of Palm.

No new measurements of extinction coefficients have been made during this study although the acidity function has been recalculated making use of the ξ_B, ξ_{BH^+}, and pK_{BH^+} values found in this work. ξ_B values were those found in the H_2O-H_2SO_4-SO_3 systems as were the ξ_{BH^+} values for m-nitrotoluene, nitrobenzene, and 2,4-dinitrotoluene. The ξ_{BH^+} values for p-chloronitrobenzene and m-chloronitrobenzene were chosen to be the average of the values found in the H_2SO_4-SO_3 and H_2SO_4-HSO_3F systems. Neither of these indicators is completely protonated in 100% $HSO_3C\ell$ although p-chloronitrobenzene is very nearly so. The pK_{BH^+} values used are those discussed in the previous sections and listed in Table LXIV. Table XXV shows the extinction coefficients used at the various acid mixtures along with the newly calculated log I and -Ho values. Table XXVI gives the average -Ho values, where one acid composition has been studied by more than one indicator, and other -Ho values, as found by single indicators, which are plotted in Figure 13 versus mole % $HSO_3C\ell$.

The behaviour of the acidity function for the H_2SO_4-$HSO_3C\ell$ system is very similar to that for the H_2SO_4-HSO_3F system. Chlorosulfuric acid is slightly stronger than sulfuric acid and thus the acidity function increases with increasing $HSO_3C\ell$ concentration. The acidity function in the region of 100% $HSO_3C\ell$ may be somewhat in error due to the difficulty in preparing pure $HSO_3C\ell$. It has been found[84] that the acid decomposes when distilled, even at reduced pressures. The pure acid may have a higher -Ho value than that observed for the impure acid. The marked increase in slope of the -Ho function in the region of 100% $HSO_3C\ell$ indicates that the autoprotolysis reaction of the solvent is important in determining the -Ho of the pure acid.

B.5. THE H_2SO_4-$HB(HSO_4)_4$ SYSTEM

The acidity function for the system H_2SO_4-$HB(HSO_4)_4$ was studied by Barr[60] and has been recalculated making use of the ξ_B, ξ_{BH^+} and pK_{BH^+} values reported in this work. The ξ_B, ξ_{BH^+} and pK_{BH^+} values used are those of the previous section for the indicators m-nitrotoluene, nitrobenzene, p-chloronitrobenzene and 2,4-dinitrotoluene. Table XXVII shows the extinction coefficients used at the various acid mixtures along with the recalculated log I and -Ho values. Average -Ho values are shown in Table XXVIII and plotted versus mole % $HB(HSO_4)_4$ in Figure 13.

As expected for a strong acid in sulfuric acid the acidity of the system rises rapidly at low $HB(HSO_4)_4$ concentrations. Above 10 mole % the acidity levels off, presumably because of the formation of polymeric species in solution. As the concentration of $HB(HSO_4)_4$ is increased above 32 mole % a complex polymeric boron sulfate[76] precipitates from solutions thus limiting the investigation of this system.

C. DISCUSSION

The validity of an acidity function generated by a set of indicators is determined by a number of factors, one of which is the way in which each indicator in the set behaves with respect to the other members of the set. If all the indicators' ionization ratios change at the same rate with changing acid composition then the individual indicators form a self-consistent set and may be used to define an acidity scale for the system in question. If this condition is not satisfied then the function generated by such an inconsistent set of indicators does not represent an acidity function for the system.

Johnson et. al.[48] have indicated a method to test the degree of parallelism of any two indicators in something more than a qualitative fashion. If the log I values for any two overlapping indicators, i and i-1, are plotted against each other at various acid compositions then the resulting curve should be a straight line of slope, $a_{i,i-1}$. If the two indicators are members of a consistent set then the slope will be unity. The product of n $a_{i,i-1}$ values, where n is the number of different indicators, indicates how the nth indicator behaves with respect to the acidity function generated by the first indicator.

Johnson et. al.[48] found $a_{i,i-1}$ values ranging from 0.85 to 1.15, with an average of 1.01, for the twelve aniline indicators used to define the Ho function of the H_2SO_4-H_2O system from infinitely dilute aqueous solutions to nearly 100% H_2SO_4. The product of the twelve $a_{i,i-1}$ values was found to be 1.04. The aniline indicators were thus shown to be a self-consistent set of indicators and the Ho function generated by these indicators to be a valid description of the acidity of the H_2SO_4-H_2O system.

The acidity function generated by the nitro indicators may be called an Ho function, rather than some other acidity function Hx, if the nitro and aniline indicators are both members of the same self-consistent set of indicators. The degree of parallelism, as measured by the $a_{i,i-1}$ value of 1.03 for the indicators 2,4,6-trinitroaniline and p-nitrotoluene, shows that these two indicators behave in very similar fashions and may be classed as members of one set of indicators.

The individual $a_{i,i-1}$ values for seven of the eight indicators used in the H_2O-H_2SO_4-SO_3 systems as well as their products are listed in Table XXIX. A value for 2,4-dinitrofluorobenzene was not included due to the irregular overlap between it and 2,4-dinitrotoluene as previously discussed. Table XXX shows the values found in the H_2SO_4-HSO_3F system. For all systems the individual $a_{i,i-1}$ values range for 0.91 to 1.14 with an average of 1.00. The product for seven indicators in the H_2O-H_2SO_4-SO_3 systems is 1.08 and that for the H_2SO_4-HSO_3F system, based upon the product up to p-chloronitrobenzene in the H_2O-H_2SO_4-SO_3 systems, is 0.95.

The excellent overlap of the eight indicators and the consistency of the pK_{BH^+} values from one acid system to another indicate that a valid acidity scale can be based upon aromatic nitro indicators. The good overlap between 2,4,6-trinitroaniline and p-nitrotoluene in the region of 100% H_2SO_4 indicates that the aromatic nitro and aniline indicators belong to the same self-consistent set of indicators. There is thus reasonable justification for calling the acidity function in the super acid region an Ho function.

The Ho curves for the various acids in sulfuric acid are shown in Figure 13. The rate of increase in -Ho as a function of acid concentration in the region of 100% H_2SO_4 increases in the order $HSO_3C\ell$ < HSO_3F < SO_3, i.e., $H_2S_2O_7$ < $HB(HSO_4)_4$ which is consistent with the strengths of the various acids as measured by their K_a values[71,72]. The Ho function clearly differentiates between the acidity produced by the two weak acids, HSO_3Cl and HSO_3F. The difference in their K_a values of 9×10^{-4} and 2.3×10^{-3} is small but their respective Ho functions are well separated.

The -Ho curves of HSO_3Cl and HSO_3F behave in a very similar fashion as would be expected from their similar structures and physical properties. As might be expected from the difference in electronegativity of fluorine and chlorine the acidity is slightly greater in solutions of HSO_3F in H_2SO_4 than in the H_2SO_4-HSO_3Cl system. The acidity of SO_3 in H_2SO_4 is much greater than that of HSO_3F in H_2SO_4 as expected from the large K_a value[71] of 1.4×10^{-2} for $H_2S_2O_7$ initially formed by SO_3 in H_2SO_4. As the concentration of SO_3 increases the various polysulfuric acids formed cause a steady increase in -Ho up to approximately 70 mole % SO_3 where the acidity begins to level off. The presence of free SO_3 in highly concentrated oleum solutions would lead to the expectation that an acidity function would level off in this region. The Ho curve for $HB(HSO_4)_4$ has the steepest slope consistent with the largest K_a value[72] of 2×10^{-1}. The rapid fall-off in slope is due to the formation[76] of a complex boron sulfate which precipitates from solution above the concentration of 32 mole % $HB(HSO_4)_4$.

TABLE I

IONIZATION RATIOS OF 2,4,6-TRINITROANILINE IN H_2O-H_2SO_4

ξ_B = 8,500[46] ξ_{BH^+} = 200[46] pK_{BH^+} = -10.10[46]

wt. % H_2SO_4	ξ[58]	log I
90.79	7,410	0.82
91.14	7,290	0.77
92.38	6,730	0.64
92.72	6,620	0.59
94.25	5,700	0.29
96.25	4,690	0.07
96.81	3,950	-0.08
97.93	2,880	-0.32
98.18	2,600	-0.39
98.39	2,290	-0.47
98.66	2,030	-0.55
99.31	1,210	-0.86

TABLE II

IONIZATION RATIOS OF p-NITROTOLUENE IN H_2O-H_2SO_4-SO_3

ξ_B = 2,100 ξ_{BH^+} = 19,200 pK_{BH^+} = -11.35

wt. % H_2SO_4	ξ^{58}	log I
96.81	3,250	1.14
97.76	3,470	1.06
98.20	4,270	0.84
98.60	4,760	0.73
98.79	4,960	0.70
98.95	5,700	0.57
99.19	6,790	0.42
99.38	7,760	0.31
99.45	7,580	0.33
99.60	9,220	0.15
99.75	10,200	-0.04
99.95	15,000	-0.48
100.00	16,220	-0.67
100.03	16,620	-0.75
100.38	17,800	-1.05
100.76	18,300	-1.25

TABLE III

IONIZATION RATIOS OF m-NITROTOLUENE IN H_2O-H_2SO_4-SO_3

$\xi_B = 1{,}200$ $\xi_{BH^+} = 16{,}100$ $pK_{BH^+} = -11.99$

wt. % H_2SO_4	ξ^{58}	log I
99.0	2,400	1.05
99.2	2,500	1.02
99.4	2,700	0.95
99.6	3,100	0.84
99.8	4,500	0.55
99.9	5,900	0.34
100.0	9,000	-0.04
100.1	10,400	-0.17
100.2	11,200	-0.31
100.4	12,500	-0.43
100.6	13,400	-0.57
100.8	14,000	-0.68
101.0	14,200	-0.72

TABLE IV

EXTINCTION COEFFICIENTS[58] OF NITROBENZENE IN H_2O-H_2SO_4-SO_3

% H_2SO_4	ξ	% H_2SO_4	ξ
99.80	2,540	100.55	11,000
99.84	2,520	100.61	11,560
99.90	4,020	100.68	11,350
99.94	4,140	100.88	12,580
99.94	6,040	101.40	13,300
100.00	7,040	102.26	13,220
100.00	7,400*	102.71	14,100
100.16	9,700	103.29	13,490*
100.24	8,380	104.00	15,150
100.32	9,540	104.08	14,070*
100.38	10,200	104.86	15,110*
100.50	10,880		

*This work.

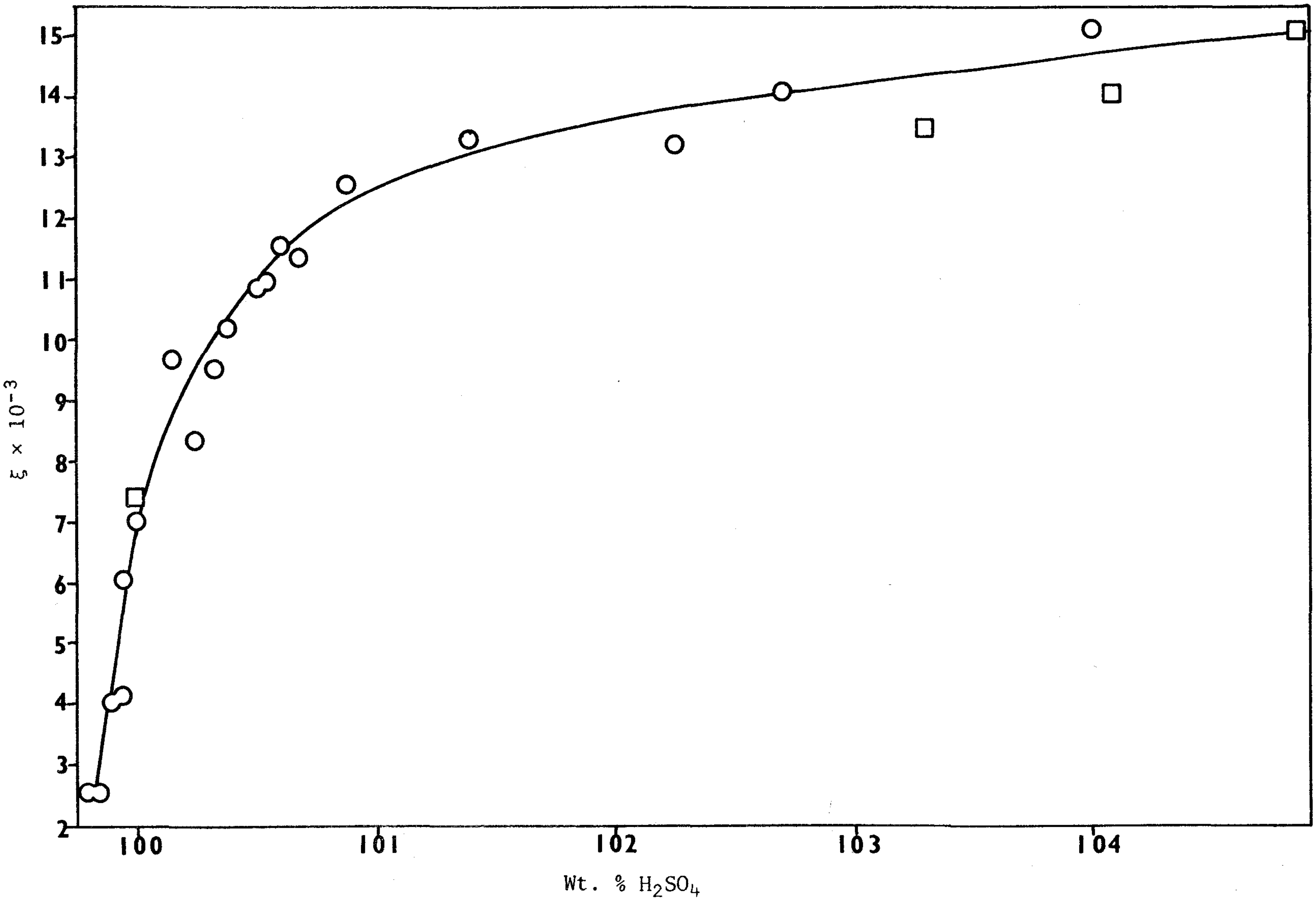

Figure 2. Extinction Coefficients of Nitrobenzene in H_2O-H_2SO_4-SO_3

TABLE V

IONIZATION RATIOS OF NITROBENZENE IN H_2O-H_2SO_4-SO_3

$\xi_B^{58} = 900$ $\xi_{BH^+} = 15{,}150$ $pK_{BH^+} = -12.14$

% H_2SO_4	mole % SO_3	ξ	log I
99.80	-	2,540	0.88
99.84	-	2,520	0.89
99.90	-	4,020	0.55
99.94	-	4,140	0.53
99.94	-	6,040	0.25
100.00	0.00	6,900	0.14
100.10	0.54	8,150	-0.02
100.20	1.09	9,130	-0.14
100.30	1.65	9,860	-0.23
100.40	2.17	10,470	-0.31
100.60	3.24	11,440	-0.45
100.80	4.32	12,070	-0.56
101.00	5.39	12,490	-0.64
101.50	8.04	13,110	-0.78
102.00	10.67	13,540	-0.89
103.00	15.85	14,140	-1.12

TABLE VI

EXTINCTION COEFFICIENTS OF p-FLUORONITROBENZENE IN H_2SO_4-SO_3

mole % SO_3	λ_{max} (nm)	ξ	mole % SO_3	λ_{max} (nm)	ξ
0.0	350 (s)	2,995	29.5673	361	15,681
0.0	353	3,375[78]	30.5703	360	15,023
0.0	353	3,540[78]	32.3077	361	17,329
1.1333	356	7,340[78]	35.5509	360	15,647
1.9239	355	8,020[78]	36.6968	361	15,692
2.9401	356	9,340[78]	41.8496	362	15,425
4.5852	358	11,322	41.9551	360	15,766
7.9892	358	12,766	48.4857	362	16,496
9.2805	358	14,993	48.7383	363	16,033
11.0794	358	13,611	51.7599	363	17,143
11.8282	359	14,013	53.0349	363	16,240
14.6077	359	13,749	57.9315	363	15,730
18.1442	358	16,087	59.8708	364	18,326[†]
20.3750	359	15,092	63.8338	364	17,037[†]
20.4021	360	15,815	68.9078	364	18,129[†]
23.1502	359	14,995	71.1968	365	16,213[†]
24.0238	361	16,004	71.1968	365	17,358[†]
24.0238	360	15,899	74.1176	364	16,458[†]
27.5686	360	16,090			

[†] Calculated ξ at zero time.

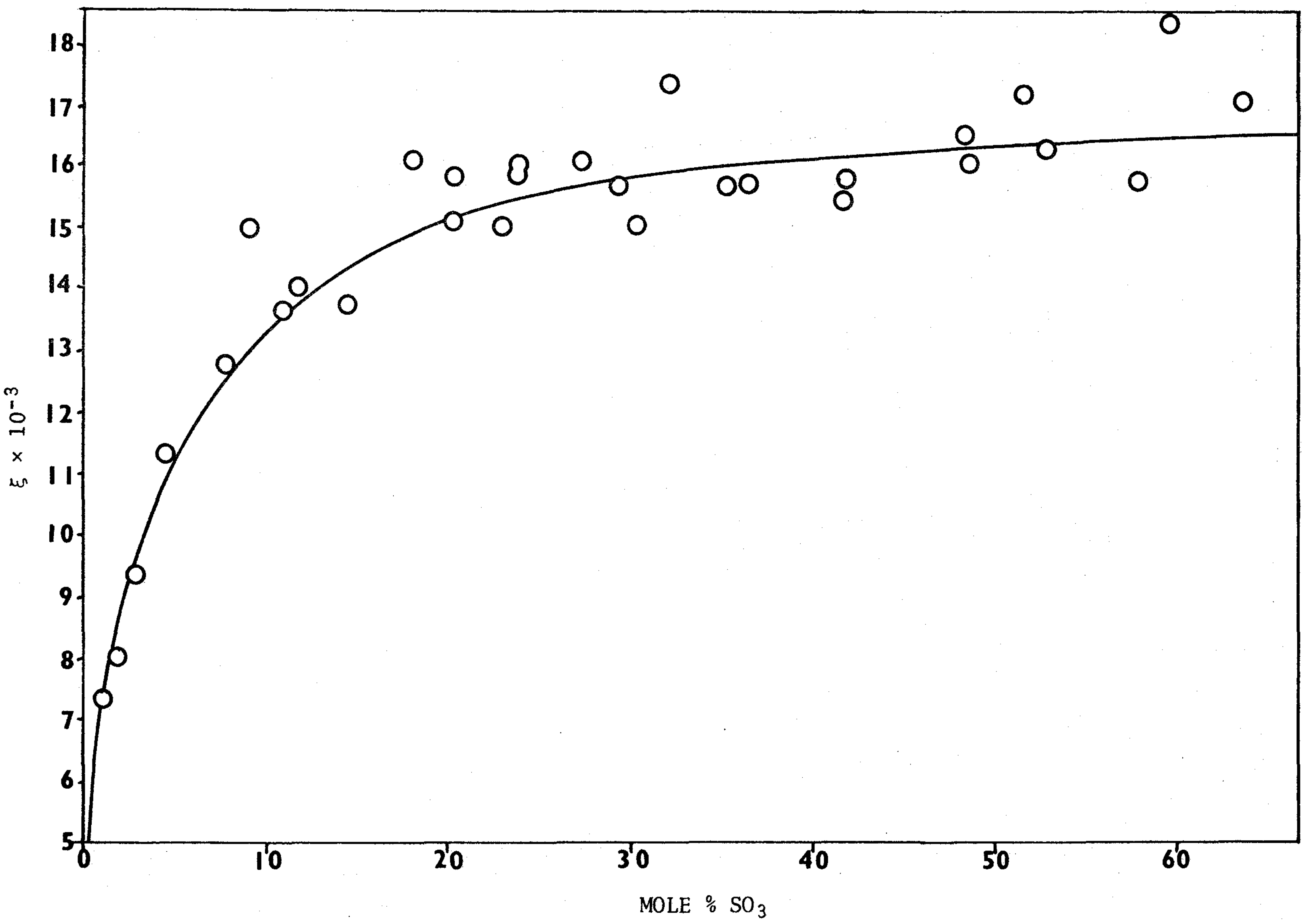

Figure 3. Extinction Coefficients of p-Fluoronitrobenzene in H_2SO_4-SO_3

TABLE VII

EXTINCTION COEFFICIENTS OF p-CHLORONITROBENZENE IN H_2O-H_2SO_4-SO_3

mole % SO_3	λ_{max} (nm)	ξ	mole % SO_3	λ_{max} (nm)	ξ
0.0		3,600[78]	26.1772	382	19,221
1.0863		7,000[78]	26.1772	383	19,576
2.6288		9,200[78]	26.4399	385	18,107
3.2462		10,400[78]	27.8607	384	19,620
4.3197		11,300[78]	27.8607	383	20,148
5.3890		11,700[78]	28.4509	384	19,586
6.0342	381	12,418	30.5445	383	19,401
9.1328	382	15,034	33.0841	385	19,530
10.0778	382	14,764	33.6004	385	20,059
13.6007	381	16,109	34.8322	385	19,998
17.2995	382	18,015	35.9076	384	20.306
17.3211	383	16,598	38.1852	384	19,565
19.0188	382	18,184	38.6897	384	20,643
21.3523	383	19,307	39.5457	385	20,873
21.3523	383	16,534	42.1880	386	20,546
23.1502	383	18,938	43.7431	386	21,848
23.1502	383	18,692	50.0000	388	19,008
23.1612	383	17,128	50.0000	387	17,936
25.2272	384	17,540	51.0006	387	20,955
25.2272	383	18,942	63.8338	389	21,747
			74.1176	392	21,769

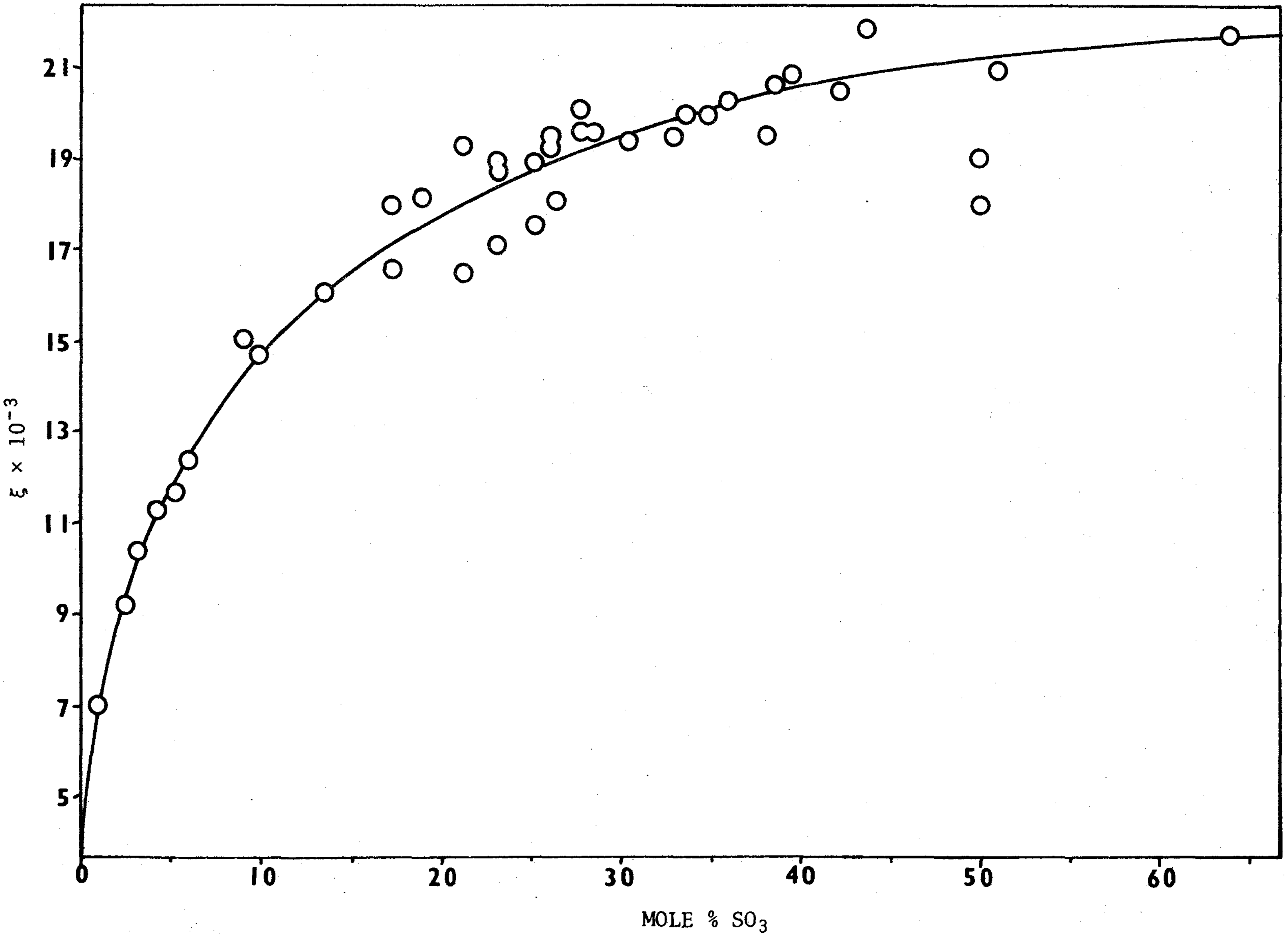

Figure 4. Extinction Coefficients of p-Chloronitrobenzene in H_2SO_4-SO_3

TABLE VIII

IONIZATION RATIOS OF p-FLUORONITROBENZENE IN H_2SO_4-SO_3

$\xi_B = 600$ $\xi_{BH^+} = 16,500$ $pK_{BH^+} = -12.44$

% H_2SO_4	ξ	log I
100.0	3,500	0.65
100.2	6,800	0.19
100.4	8,630	-0.01
100.6	9,900	-0.15
100.8	10,930	-0.27
101.0	11,460	-0.33

TABLE IX

IONIZATION RATIOS OF p-CHLORONITROBENZENE IN H_2SO_4-SO_3

$\xi_B = 400$ $\xi_{BH^+} = 21,800$ $pK_{BH^+} = -12.70$

% H_2SO_4	ξ	log I
100.0	3,600	0.76
100.2	7,000	0.39
100.4	9,200	0.16
100.6	10,400	0.05
100.8	11,300	-0.02
101.0	11,700	-0.05

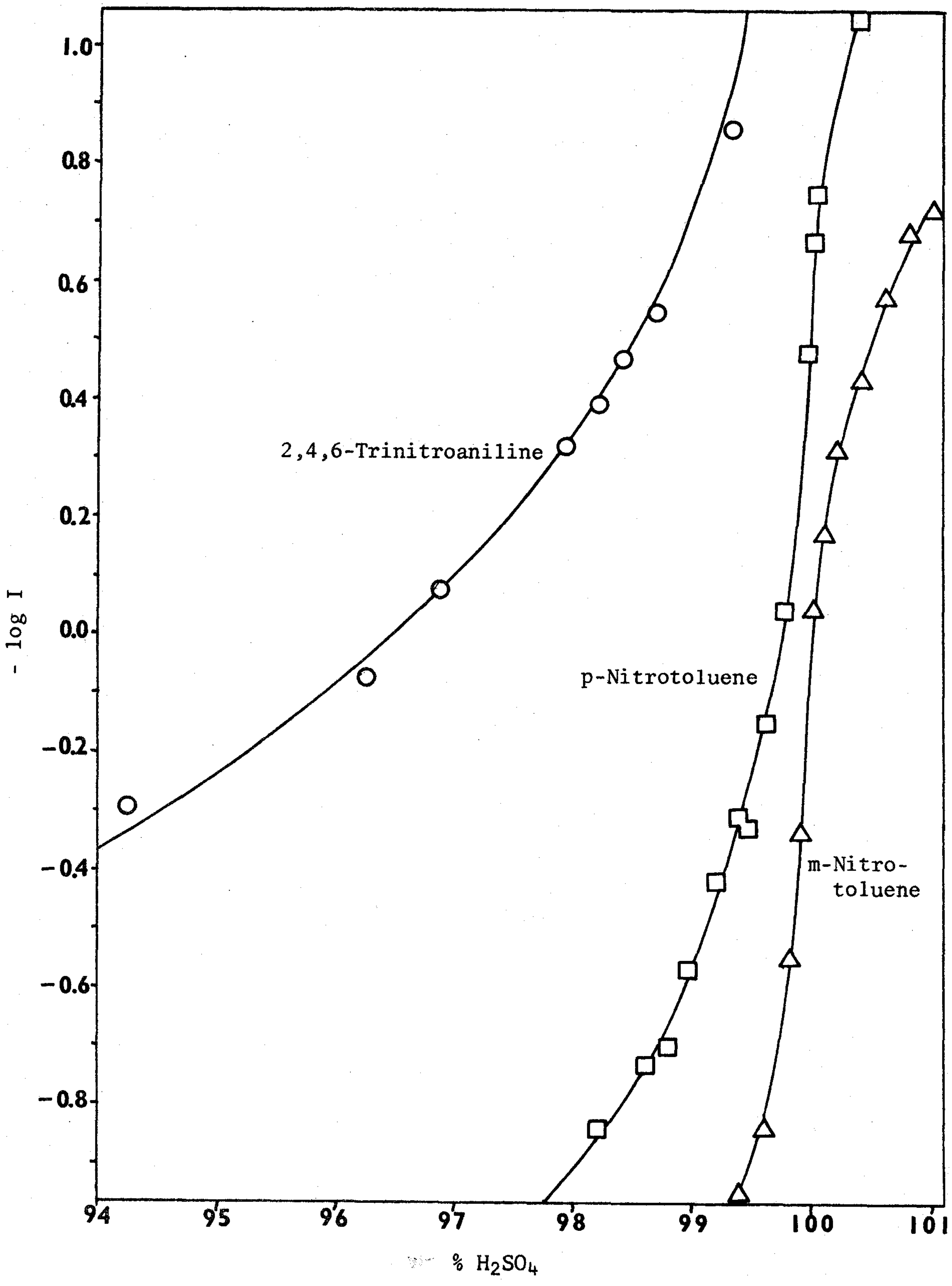

Figure 5. Ionization Ratios Near 100% H_2SO_4

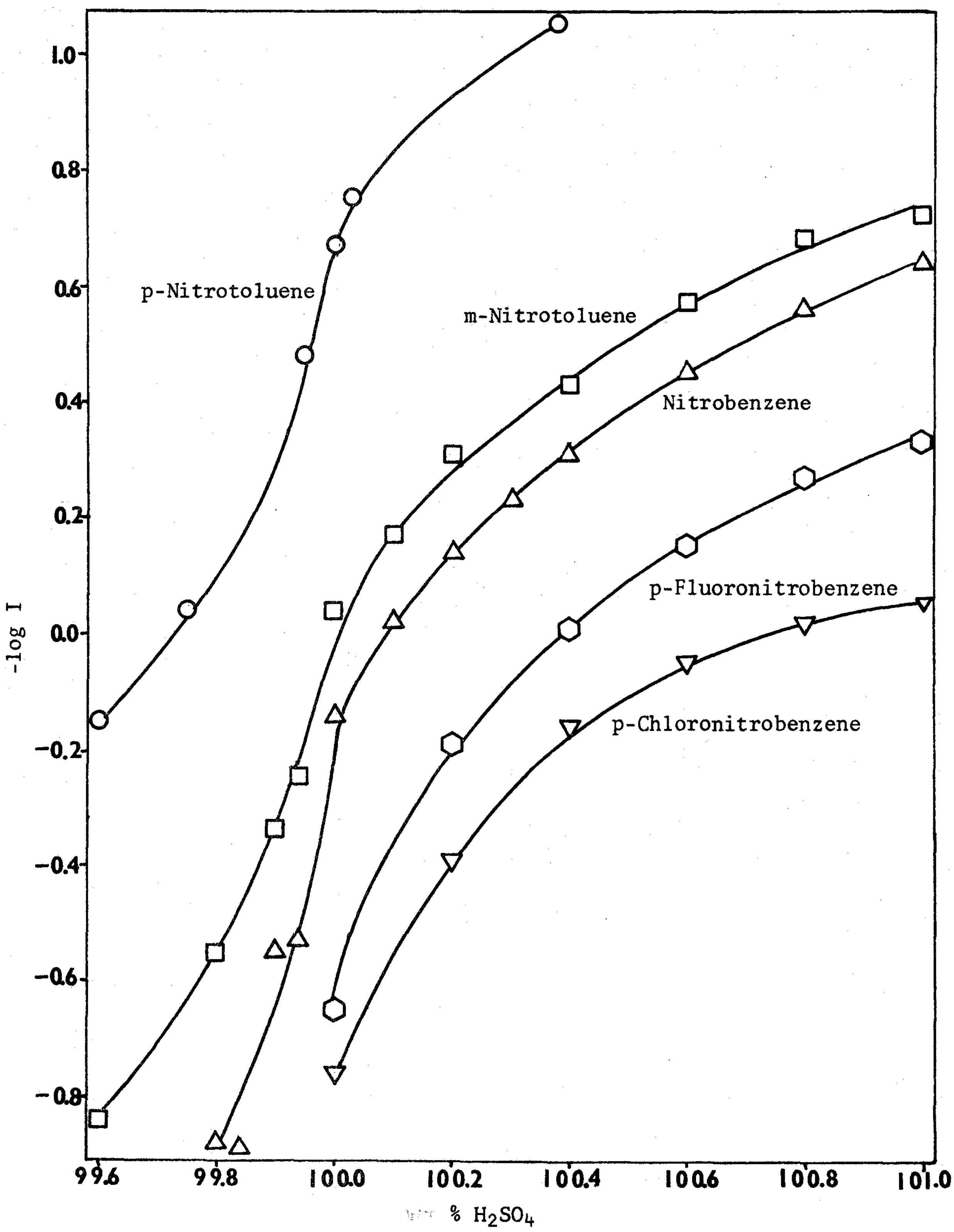

Figure 6. Ionization Ratios Near 100% H_2SO_4

TABLE X

-Ho VALUES NEAR 100% H_2SO_4

% H_2SO_4	2,4,6-TRINITRO-ANILINE	p-NITROTOLUENE	m-NITROTOLUENE	NITROBENZENE	p-FLUORONITRO-BENZENE	p-CHLORONITRO-BENZENE	AVERAGE
95.0	9.86						9.86
95.5	9.94						9.94
96.0	10.02						10.02
96.5	10.10						10.10
97.0	10.20	10.23					10.22
97.5	10.31	10.33					10.32
98.0	10.44	10.44					10.44
98.2	10.50	10.49					10.50
98.4	10.57	10.55					10.56
98.6	10.64	10.61					10.62
98.8	10.73	10.69					10.71
99.0	10.83	10.78	10.91				10.84
99.2	10.94	10.90	10.96				10.93
99.4	11.06	11.04	11.04				11.05
99.6		11.15	11.15				11.15
99.8		11.45	11.44	11.30			11.40
99.9		11.67	11.66	11.59			11.64
100.0		12.02	11.96	11.95	11.80	11.93	11.93
100.1		12.19	12.18	12.16	12.07	12.14	12.15
100.2		12.28	12.27	12.28	12.23	12.30	12.27
100.4			12.43	12.46	12.45	12.53	12.47
100.6			12.56	12.59	12.60	12.65	12.60
100.8			12.66	12.70	12.70	12.72	12.70
101.0			12.73	12.78	12.79	12.76	12.77

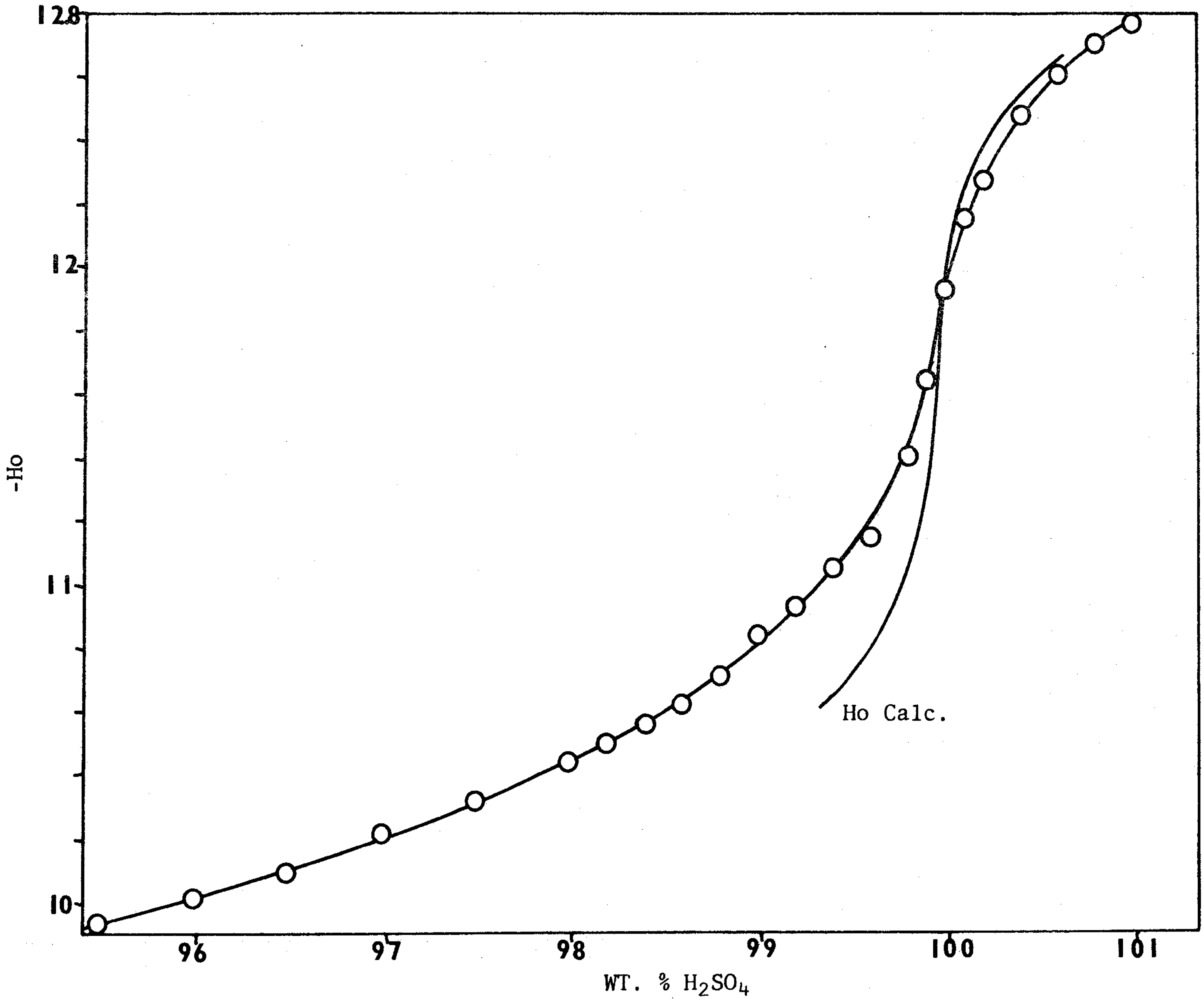

Figure 7. Ho Values Near 100% H_2SO_4

TABLE XI

IONIZATION RATIOS OF p-FLUORONITROBENZENE IN H_2SO_4-SO_3

ξ_B = 600 ξ_{BH^+} = 16,500 pK_{BH^+} = -12.44

mole % SO_3	ξ	log I
1.0	6,800	0.19
2.0	8,530	0.00
3.0	9,660	-0.12
4.0	10,550	-0.22
5.0	11,230	-0.30
6.0	11,790	-0.38
7.0	12,230	-0.44
8.0	12,650	-0.50
9.0	12,990	-0.55
10.0	13,300	-0.60
12.0	13,820	-0.69
14.0	14,250	-0.78
16.0	14,600	-0.87
18.0	14,840	-0.93
20.0	15,130	-1.02
22.5	15,360	-1.11
25.0	15,550	-1.20
27.5	15,670	-1.26
30.0	15,790	-1.33

TABLE XII

IONIZATION RATIOS OF p-CHLORONITROBENZENE IN H_2SO_4-SO_3

ξ_B = 400 ξ_{BH^+} = 21,800 pK_{BH^+} = -12.70

mole % SO_3	ξ	log I
1.0	6,850	0.36
2.0	8,500	0.22
3.0	9,750	0.11
4.0	10,750	0.03
5.0	11,570	-0.04
6.0	12,310	-0.10
7.0	12,990	-0.16
8.0	13,580	-0.20
9.0	14,120	-0.25
10.0	14,630	-0.30
12.0	15,480	-0.38
14.0	16,180	-0.45
16.0	16,750	-0.51
18.0	17,250	-0.57
20.0	17,700	-0.62
22.5	18,200	-0.69
25.0	18,650	-0.76
27.5	19,100	-0.84
30.0	19,480	-0.92
32.5	19,800	-0.99
35.0	20,100	-1.06
37.5	20,370	-1.14
40.0	20,580	-1.22

TABLE XIII

EXTINCTION COEFFICIENTS OF m-CHLORONITROBENZENE IN H_2SO_4-SO_3

mole % SO_3	λ_{max} (nm)	ξ	mole % SO_3	λ_{max} (nm)	ξ
6.0342	341	4,595	33.6004	349	10,302
6.0342	341	4,613	33.6004	350	10,989
9.1328	342	5,469	34.8321	350	11,129
9.1328	342	5,739	34.8321	350	11,569
10.0778	343	5,651	35.9076	350	10,134
10.0778	343	5,791	35.9076	349	12,138
13.6007	345	6,098	38.1852	350	12,049
13.6007	345	6,498	38.6897	350	11,973
17.2995	346	7,450	38.6897	350	12,246
17.2995	346	7,850	39.5457	350	11,229
19.0188	347	8,135	39.5457	350	12,229
21.3523	346	8,816	42.0854	350	11,751
21.3523	347	9,623	42.1879	351	11,546
23.1502	347	9,755	43.4902	350	11,892
23.1612	347	8,268	43.7431	351	12,460
23.1612	347	8,368	43.7431	351	13,560
25.2272	348	9,979	50.0000	353	11,093
26.1772	347	10,136	50.0000	352	11,127
26.4399	349	9,093	50.0000	353	11,264
28.4509	347	10,252	50.0000	353	12,664
30.5445	348	11,398	51.0006	353	12,405
30.5445	349	10,547	57.6594	354	13,501
33.0841	350	10,119	63.8338	353	11,886
33.0841	350	10,519	74.1176	353	12,721

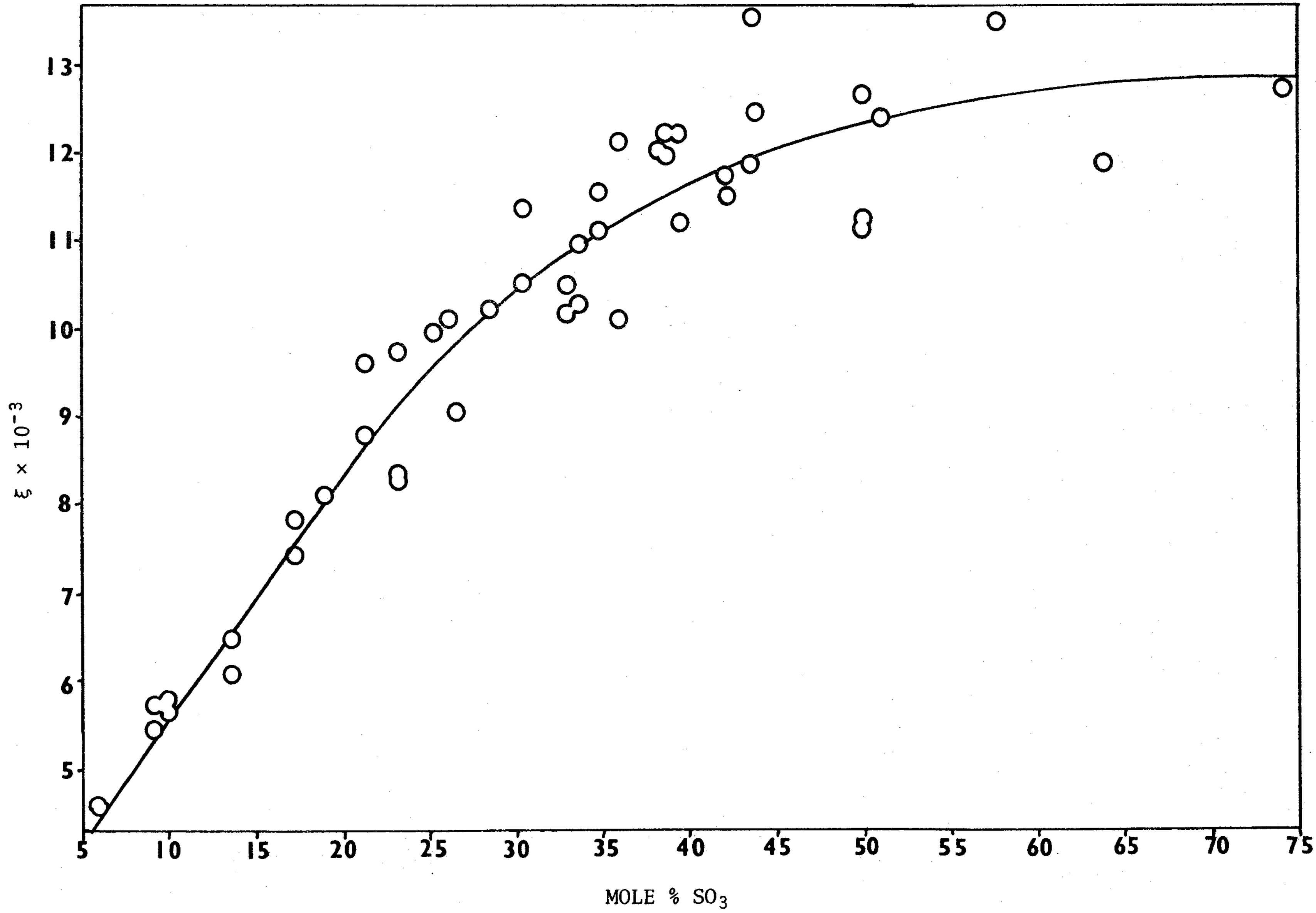

Figure 8. Extinction Coefficients of m-Chloronitrobenzene in H_2SO_4-SO_3

TABLE XIV

IONIZATION RATIOS OF m-CHLORONITROBENZENE IN H_2SO_4-SO_3

$\xi_B = 440$ $\xi_{BH+} = 12,850$ $pK_{BH+} = -13.16$

mole % SO_3	ξ	log I
6.0	4,330	0.34
7.0	4,700	0.28
8.0	5,000	0.24
9.0	5,270	0.20
10.0	5,550	0.15
12.0	6,180	0.06
14.0	6,660	0.00
16.0	7,250	-0.08
18.0	7,800	-0.16
20.0	8,350	-0.24
22.5	8,950	-0.34
25.0	9,520	-0.44
27.5	9,980	-0.52
30.0	10,400	-0.61
32.5	10,810	-0.71
35.0	11,160	-0.80
37.5	11,420	-0.88
40.0	11,660	-0.97

TABLE XV

EXTINCTION COEFFICIENTS OF 2,4-DINITROTOLUENE IN H_2SO_4-SO_3

mole % SO_3	λ_{max}	ξ
19.0188	325	5,812
23.1502	325	6,916
28.4509	328	8,128
33.6004	332	8,809
38.1852	332	10,044
42.0854	336	10,676
44.7460	335	11,018
47.0518	335	11,937
50.0000	336	11,802
50.0000	336	12,087
50.0000	335	12,140
57.6594	337	12,780
63.8338	337	12,389
74.1176	339	13,630
85.1885	344	13,808

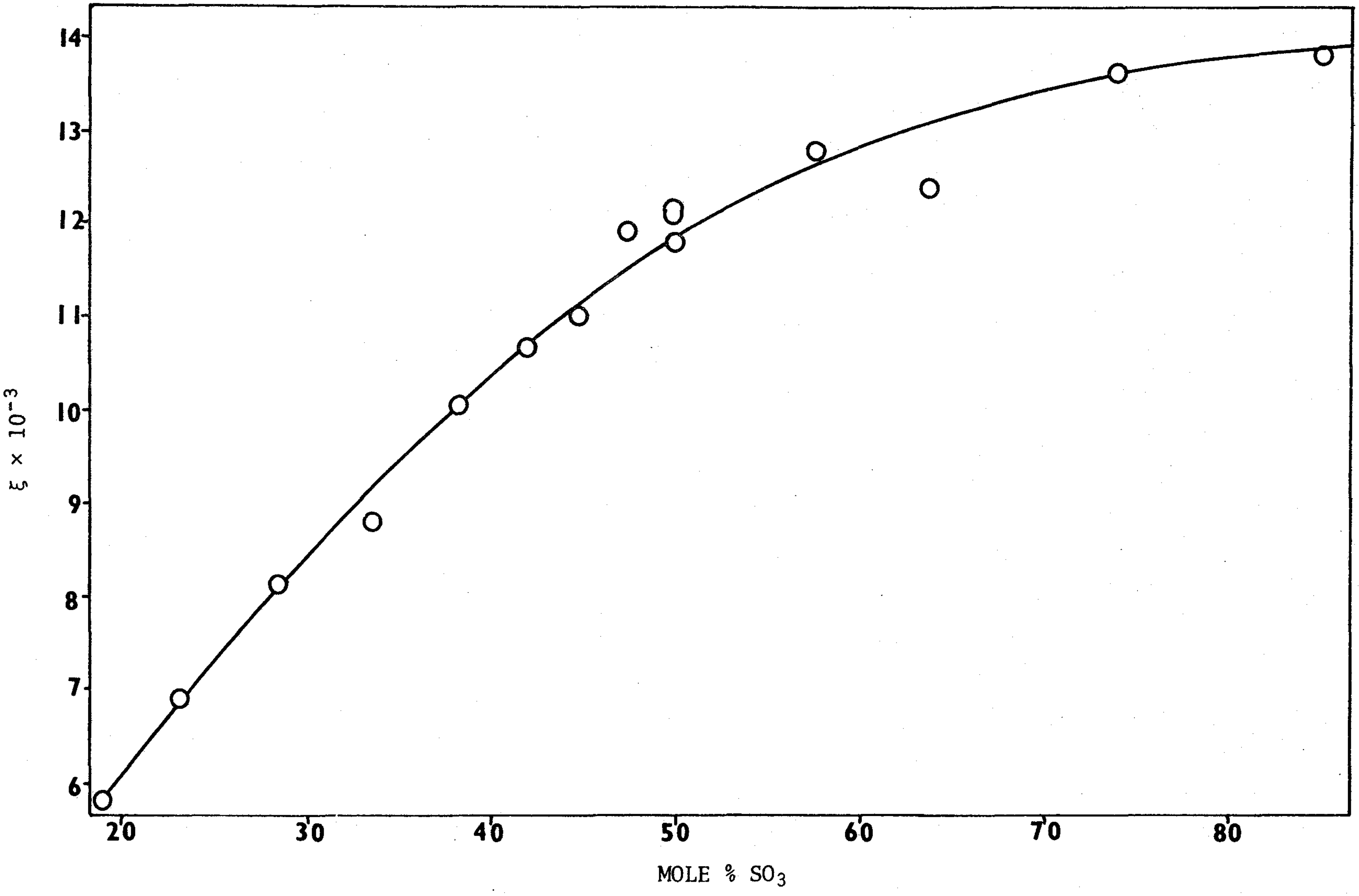

Figure 9. Extinction Coefficients of 2,4-Dinitrotoluene in H_2SO_4-SO_3

TABLE XVI

IONIZATION RATIOS OF 2,4-DINITROTOLUENE IN H_2SO_4-SO_3

$\xi_B = 1{,}700$ $\xi_{BH^+} = 13{,}900$ $pK_{BH^+} = -13.75$

mole % SO_3	ξ	log I
20.0	6,020	0.26
22.5	6,640	0.17
25.0	7,260	0.08
27.5	7,850	-0.01
30.0	8,380	-0.08
32.5	8,890	-0.16
35.0	9,380	-0.24
37.5	9,840	-0.30
40.0	10,300	-0.38
42.5	10,760	-0.46
45.0	11,200	-0.55
47.5	11,570	-0.63
50.0	11,890	-0.70
52.5	12,160	-0.78
55.0	12,410	-0.86
57.5	12,610	-0.93
60.0	12,780	-1.00
62.5	12,880	-1.04
65.0	12,990	-1.09

TABLE XVII

EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE IN H_2SO_4-SO_3

WAVE LENGTH (nm)	mole % SO_3 19.0188	23.1502	28.4509	33.6004	38.1852	42.0854
	EXTINCTION COEFFICIENTS					
210	13,675	-	-	-	-	-
220	13,676	12,764	-	-	-	-
230	>16,184	15,663	-	-	-	-
240	>16,184	16,381	-	-	-	-
250	>16,184	16,309	-	15,895	14,840	-
260	14,889	14,855	14,484	13,845	13,020	-
270	12,138	12,252	11,828	11,294	10,360	10,145
280	9,104	9,424	9,012	8,700	7,840	7,878
290	6,474	6,956	6,679	6,567	6,090	6,291
300	4,548	5,125	5,125	5,354	5,488	5,877
310	3,237	3,815	4,136	4,676	5,432	6,002
320	2,273	2,881	3,380	4,191	5,222	6,138
330	1,732	2,316	2,832	3,723	4,844	5,894
340	1,359	1,885	2,333	3,162	4,200	5,271
350	979	1,418	1,786	2,460	3,290	4,222
360	664	987	1,199	1,665	2,268	2,890
370	388	610	700	920	1,288	1,655
380	202	359	346	435	644	799
390	105	224	177	176	280	363
400	48	161	80	67	112	159
410	-	117	56	25	28	68
λ_{max} (nm)	320	320	320	320	320	320
ξ	2,273	2,881	3,380	4,191	5,222	6,138

TABLE XVII (cont.)

EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE IN H_2SO_4-SO_3

WAVE LENGTH (nm)	mole % SO_3					
	44.7460	47.0518	50.0000	57.6594	62.4590	62.4590
	EXTINCTION COEFFICIENTS					
250	-	13,196	11,075	-	10,280	9,970
260	-	11,876	10,235	-	8,009	8,626
270	9,200	9,801	8,372	-	6,495	7,029
280	7,268	7,481	6,346	-	5,069	5,323
290	5,938	6,300	5,394	-	4,510	4,715
300	5,712	6,513	5,834	4,886	5,492	5,705
310	5,997	7,290	7,165	7,171	7,568	7,950
320	6,197	8,077	8,209	9,171	9,593	10,185
330	6,038	8,045	8,495	10,058	10,561	11,234
340	5,503	7,279	7,983	9,697	10,385	11,018
350	4,508	5,981	6,755	8,299	9,100	9,783
360	3,220	4,289	4,811	6,134	6,865	7,352
370	1,882	2,501	2,845	3,623	4,084	4,500
380	945	1,277	1,412	1,804	2,007	2,225
390	468	628	604	827	845	970
400	209	309	256	376	352	402
410	100	170	102	165	158	176
λ_{max} (nm)	322	327	328	331	334	334
ξ	6,214	8,173	8591±75	10,073	10,614	11,273

TABLE XVII (cont.)

EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE IN H_2SO_4-SO_3

WAVE LENGTH (nm)	mole % SO_3 76.8803	76.8803	85.1885
	EXTINCTION COEFFICIENTS		
270	2,056	4,932	5,976
280	2,698	3,995	4,429
290	2,962	3,818	3,984
300	3,962	5,037	5,065
310	5,961	7,513	7,078
320	8,074	9,846	9,303
330	9,206	11,136	10,426
340	9,225	11,172	10,490
350	8,319	9,934	9,536
360	6,508	7,601	7,459
370	3,962	4,808	4,704
380	1,981	2,439	2,395
390	905	1,061	1,166
400	377	406	508
410	170	141	297
λ_{max} (nm)	335	336	336
ξ	9,432	11,330	10,617

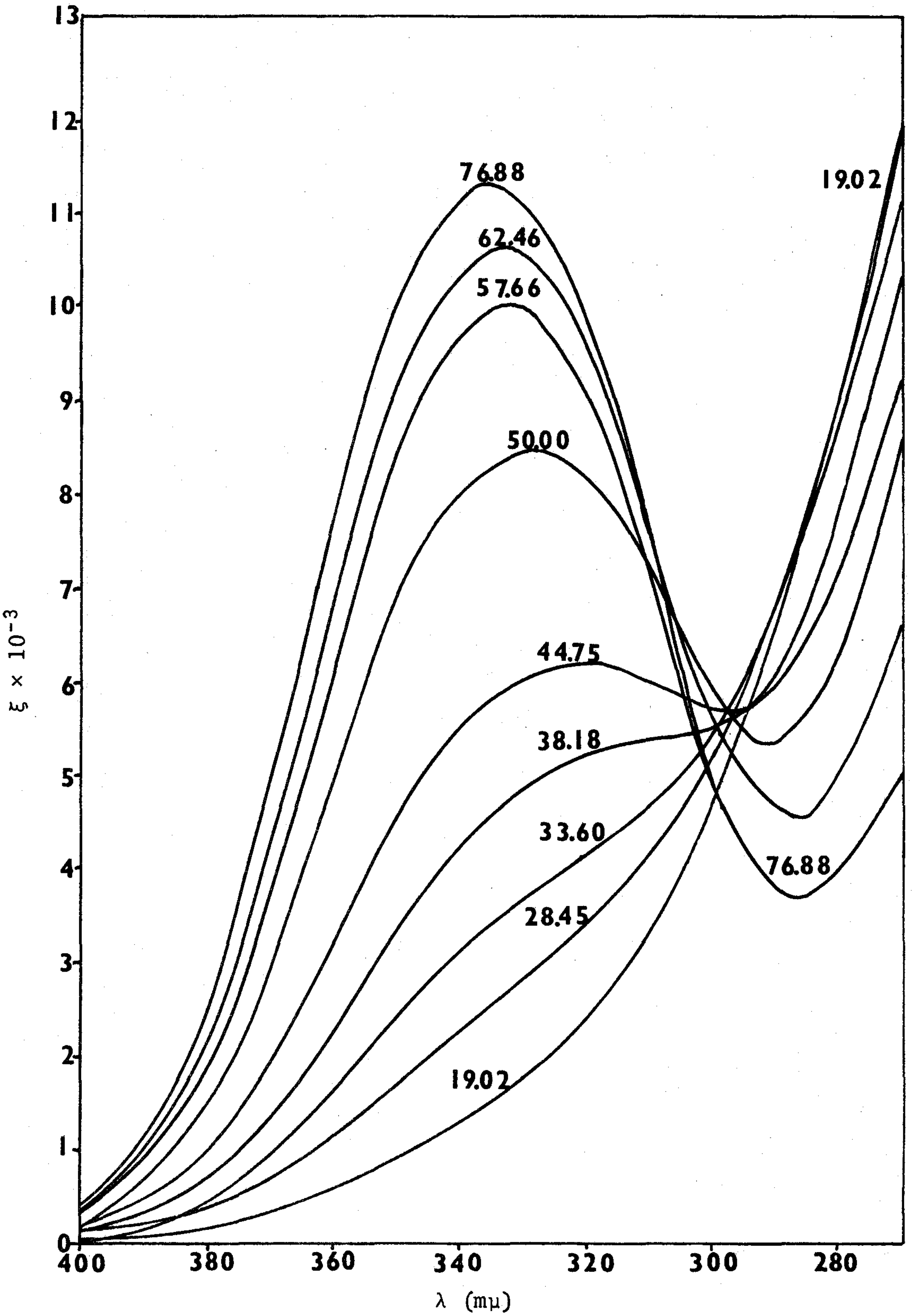

Figure 10. Representative Absorption Spectra of 2,4-Dinitrofluorobenzene in H_2SO_4-SO_3

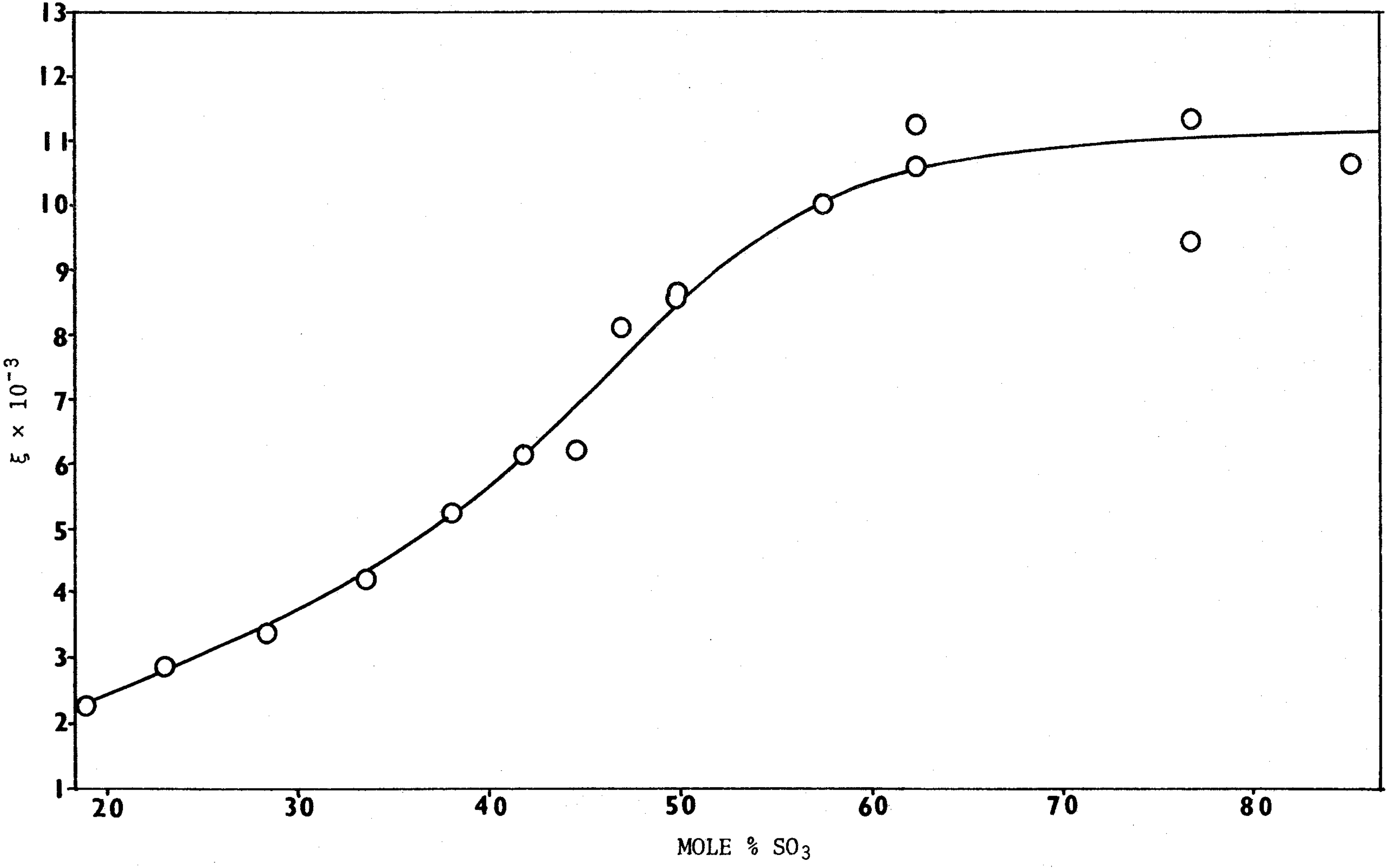

Figure 11. Extinction Coefficients of 2,4-Dinitrofluorobenzene in H_2SO_4-SO_3

TABLE XVIII

IONIZATION RATIOS OF 2,4-DINITROFLUOROBENZENE IN H_2SO_4-SO_3

ξ_B = 920 ξ_{BH^+} = 12,100 pK_{BH^+} = -14.03

mole % SO_3	ξ	log I
20.0	2,430	0.81
25.0	3,000	0.64
30.0	3,720	0.48
35.0	4,590	0.31
40.0	5,580	0.15
45.0	6,890	-0.04
50.0	8,470	-0.33
55.0	9,660	-0.55
60.0	10,370	-0.74
65.0	10,700	-0.84
70.0	10,860	-0.90
75.0	10,940	-0.94

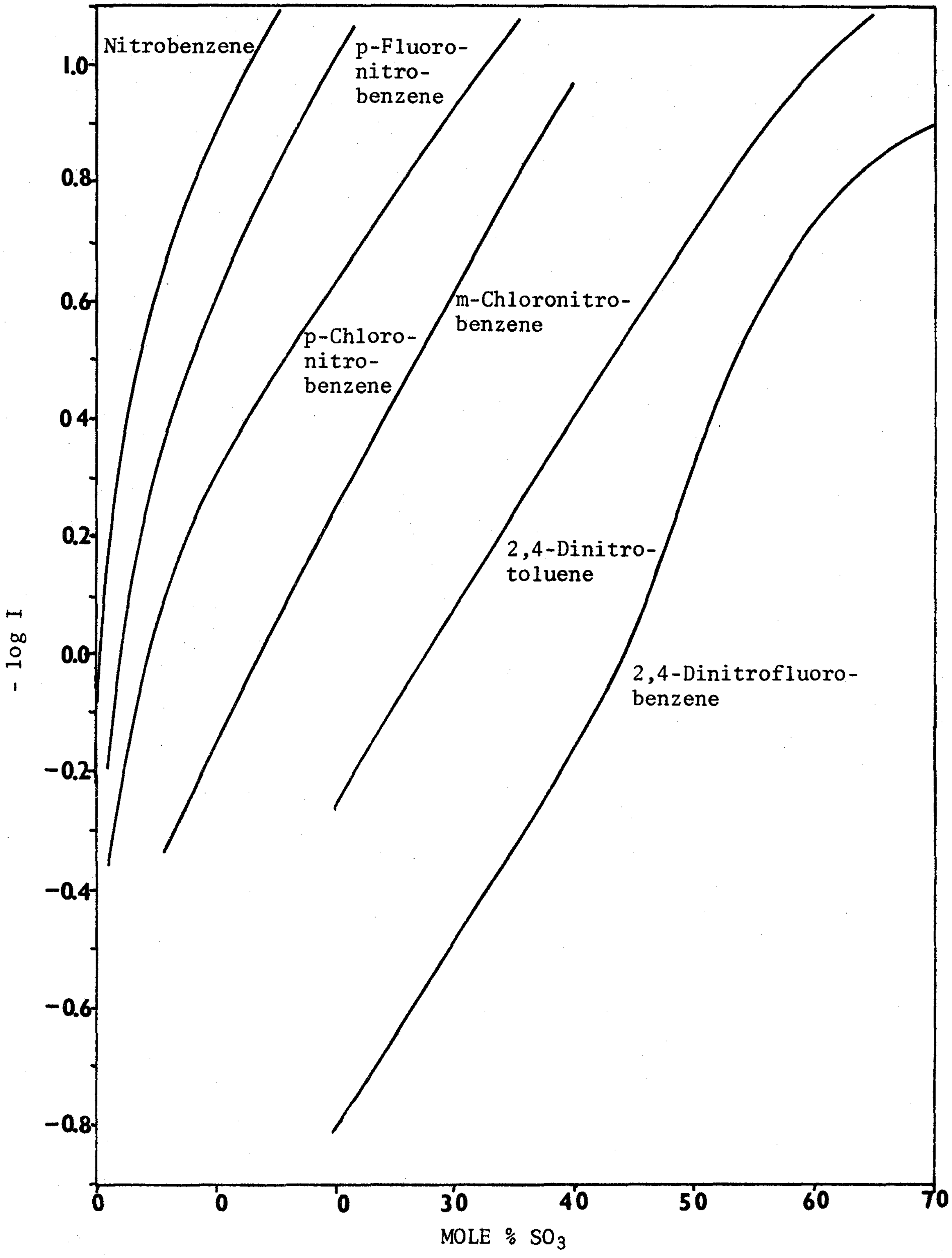

Figure 12. Ionization Ratios in H_2SO_4-SO_3

TABLE XIX

H_2SO_4-SO_3 SYSTEM

-Ho VALUES

mole % SO_3	NITROBENZENE	p-FLUORONITROBENZENE	p-CHLORONITROBENZENE	m-CHLORONITROBENZENE	2,4-DINITROTOLUENE	2,4-DINITROFLUOROBENZENE	AVERAGE
0.0	11.95	11.80	11.93				11.93
1.0	12.28	12.24	12.31				12.28
2.0	12.45	12.43	12.46				12.45
3.0	12.58	12.57	12.57				12.57
4.0	12.67	12.66	12.66				12.66
5.0	12.75	12.74	12.73				12.74
7.5	12.89	12.91	12.88	12.94			12.90
10.0	13.01	13.04	13.00	13.04			13.02
12.5	13.12	13.15	13.10	13.15			13.13
15.0	13.22	13.26	13.18	13.24			13.22
20.0		13.46	13.33	13.44	13.48		13.43
25.0			13.46	13.63	13.66		13.58
30.0			13.62	13.82	13.81		13.75
35.0				14.00	13.98		13.99
40.0				14.17	14.13		14.15
45.0					14.29		14.29
50.0					14.44		14.44
55.0					14.60	14.59	14.60
60.0					14.73	14.77	14.75
65.0					14.82	14.87	14.84
70.0						14.93	14.93
75.0						14.96	14.96

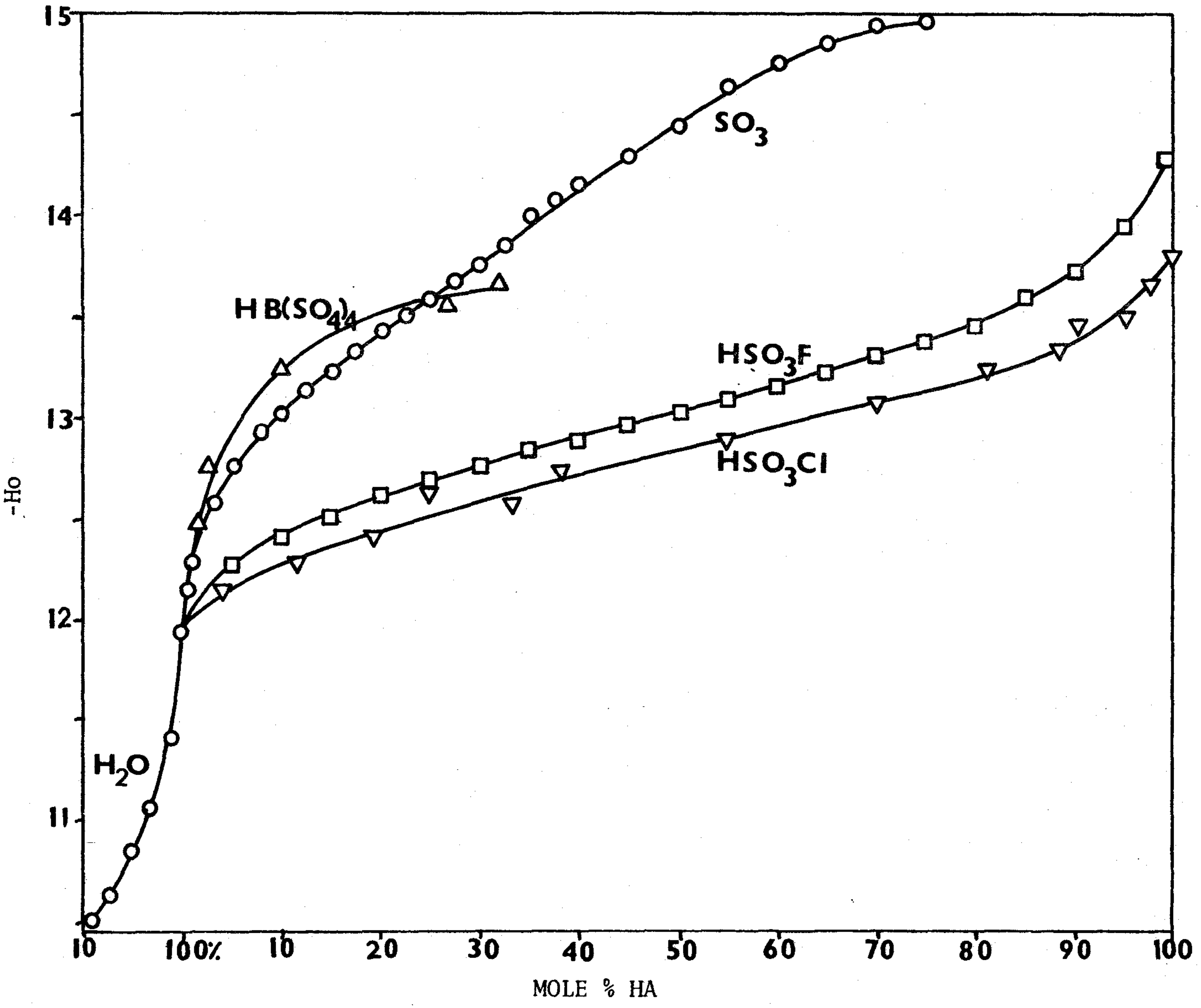

Figure 13. Ho Values for the H_2SO_4 Systems

TABLE XX

IONIZATION RATIOS OF p-CHLORONITROBENZENE IN H_2SO_4-HSO_3F

ξ_B = 400 ξ_{BH+} = 24,350 pK_{BH+} = -12.70

mole % HSO_3F	ξ	log I
5.90	6,560[60]	0.46
10.77	8,960[60]	0.25
13.1209	8,820	0.27
19.2433	11,870	0.04
22.4294	13,620	-0.09
24.05	10,150[60]	0.16
24.8382	10,160	0.16
26.3358	13,000	-0.04
27.0189	14,726	-0.17
34.51	13,800[60]	-0.10
37.1897	15,270	-0.21
44.9549	15,445	-0.23
55.85	17,300[60]	-0.38
60.4483	18,436	-0.48
81.8272	21,201	-0.82
85.5096	22,509	-1.05

TABLE XXI

IONIZATION RATIOS OF m-CHLORONITROBENZENE IN H_2SO_4-HSO_3F

$\xi_B = 440$ $\xi_{BH^+} = 14{,}380$ $pK_{BH^+} = -13.16$

mole % HSO_3F	ξ	log I
5.90	2,330[60]	0.80
10.77	2,890[60]	0.67
22.4294	3,612	0.53
34.51	4,790[60]	0.34
47.2671	6,785	0.08
55.85	6,790[60]	0.08
60.4483	8,017	-0.08
65.8733	7,981	-0.07
71.0363	9,226	-0.23
71.9369	9,192	-0.23
81.8272	10,013	-0.34
85.5096	10,944	-0.48
92.2844	12,448	-0.79

TABLE XXII

IONIZATION RATIOS OF 2,4-DINITROTOLUENE IN H_2SO_4-HSO_3F

ξ_B = 1,700 ξ_{BH^+} = 13,900 pK_{BH^+} = -13.75

mole % HSO_3F	ξ	log I
44.9549	3,350	0.80
60.4483	4,364	0.55
65.8733	4,345	0.55
71.0363	4,920	0.45
71.9369	5,151	0.40
81.8272	6,063	0.25
85.5096	6,480	0.19
92.2844	7,912	-0.02
95.6015	8,375	-0.08
99.539	11,280[61]	-0.56

TABLE XXIII

IONIZATION RATIOS OF 2,4-DINITROFLUOROBENZENE IN H_2SO_4-HSO_3F

$\xi_B = 920$ $\xi_{BH^+} = 12,100$ $pK_{BH^+} = -14.52$

mole % H_2SO_4 in HSO_3F	mole % HSO_3F in H_2SO_4	ξ	log I
22.9824	77.2176	1,720	1.11
15.0020	84.9980	1,954	0.99
7.7156	92.2844	2,933	0.66
4.938	95.062	3,050[61]	0.63
4.0666	95.9334	3,069	0.63
3.7582	96.2418	3,033	0.63
1.7668	98.2332	4,041	0.41
1.3756	98.6244	4,036	0.41
1.0601	98.9399	4,648	0.30
0.9139	99.0861	4,551	0.32
0.6374	99.3626	4,915	0.25
0.580	99.420	4,830[61]	0.27
0.343	99.657	5,620[61]	0.14
0.2668	99.7332	6,151	0.05
0.1432	99.8568	6,777	-0.04

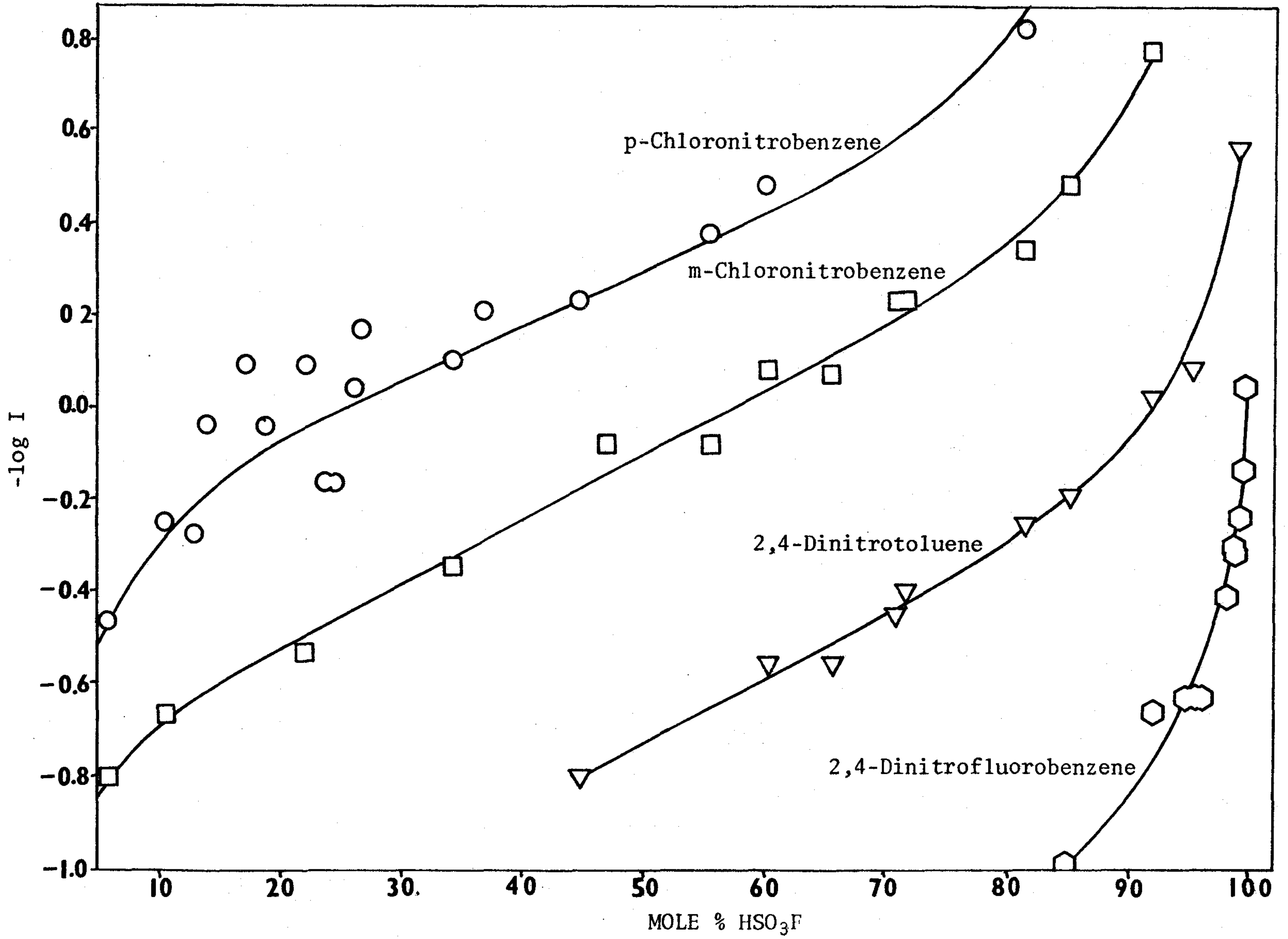

Figure 14. Ionization Ratios in H_2SO_4-HSO_3F

TABLE XXIV

-Ho VALUES FOR THE H_2SO_4-HSO_3F SYSTEM

mole % HSO_3F	p-CHLORONITRO-BENZENE	m-CHLORONITRO-BENZENE	2,4-DINITRO-TOLUENE	2,4-DINITROFLUORO-BENZENE	AVERAGE
5.0	12.18	12.29			12.24
10.0	12.37	12.42			12.40
15.0	12.50	12.51			12.50
20.0	12.61	12.59			12.60
25.0	12.69	12.66			12.68
30.0	12.76	12.74			12.75
35.0	12.82	12.81			12.82
40.0	12.88	12.88			12.88
45.0	12.94	12.95	12.96		12.95
50.0	13.00	13.02	13.03		13.02
55.0	13.06	13.09	13.09		13.08
60.0	13.12	13.15	13.16		13.14
65.0	13.20	13.23	13.22		13.22
70.0	13.27	13.30	13.30		13.29
75.0	13.37	13.37	13.37		13.37
80.0	13.50	13.46	13.46	13.44	13.46
85.0	13.68	13.58	13.57	13.54	13.59
90.0		13.77	13.71	13.68	13.73
95.0			13.94	13.95	13.95
99.0				14.21	14.21

TABLE XXV

IONIZATION RATIOS FOR THE SYSTEM H_2SO_4-$HSO_3C\ell$

m-NITROTOLUENE

ξ_B = 1,200 ξ_{BH^+} = 16,100 pK_{BH^+} = -11.99

mole % $HSO_3C\ell$	ξ[60]	log I	-Ho
18.99	11,500	-0.35	12.34
32.80	12,700	-0.53	12.52

NITROBENZENE

ξ_B = 900 ξ_{BH^+} = 16,175 pK_{BH^+} = -12.14

mole % $HSO_3C\ell$	ξ[60]	log I	-Ho
18.99	11,100	-0.30	-12.44

p-NITROCHLOROBENZENE

ξ_B = 400 ξ_{BH^+} = 23,075 pK_{BH^+} = -12.70

mole % $HSO_3C\ell$	ξ	log I	-Ho
4.1	5,200[79]	0.57	12.13
11.1	7,650[79]	0.33	12.27
24.8	10,900[79]	0.06	12.64
32.8	10,500[60]	0.09	12.60
37.9	12,100[79]	-0.03	12.73
54.6	14,050[79]	-0.18	12.88
69.8	16,150[79]	-0.36	13.06
81.0	17,850[79]	-0.52	13.22
88.2	18,750[79]	-0.63	13.33
90.3	20,550[60]	-0.90	13.60

TABLE XXV (cont.)

m-NITROCHLOROBENZENE

$\xi_B = 440$ $\xi_{BH^+} = 13{,}615$ $pK_{BH^+} = -13.16$

mole % HSO_3Cl	ξ^{60}	log I	-Ho
90.3	8,360	-0.18	13.34
100.0	11,100	-0.63	13.79

2,4-DINITROTOLUENE

$\xi_B = 1{,}700$ $\xi_{BH^+} = 13{,}900$ $pK_{BH^+} = -13.75$

mole % HSO_3Cl	ξ	log I	-Ho
90.3	5,390[60]	0.36	13.39
95.0	6,000[79]	0.26	13.49
97.5	7,000[79]	0.11	13.64
100.0	7,900[79]	-0.01	13.76
100.0	8,340[60]	-0.08	13.83

TABLE XXVI

Ho VALUES FOR THE SYSTEM H_2SO_4-HSO_3Cl

mole % HSO_3Cl	-Ho	mole % HSO_3Cl	-Ho
0.00	11.93	69.8	13.06
4.10	12.13	81.0	13.22
11.10	12.27	88.2	13.33
18.99	12.39	90.3	13.44
24.80	12.64	95.0	13.49
32.80	12.56	97.5	13.64
37.90	12.73	100.0	13.79
54.60	12.88		

TABLE XXVII

IONIZATION RATIOS FOR THE H_2SO_4-$HB(HSO_4)_4$ SYSTEM

m-NITROTOLUENE

$\xi_B = 1{,}200$ $\xi_{BH^+} = 16{,}100$ $pK_{BH^+} = -11.99$

mole % $HB(HSO_4)_4$	ξ^{60}	log I	-Ho
1.56	9,900	-0.15	12.14

NITROBENZENE

$\xi_B = 900$ $\xi_{BH^+} = 16{,}175$ $pK_{BH^+} = -12.14$

mole % $HB(HSO_4)_4$	ξ^{60}	log I	-Ho
1.56	11,500	-0.36	12.40
2.21	12,000	-0.42	12.56
10.06	15,300	-1.22	13.36

p-NITROCHLOROBENZENE

$\xi_B = 400$ $\xi_{BH^+} = 23{,}075$ $pK_{BH^+} = -12.40$

mole % $HB(HSO_4)_4$	ξ^{60}	log I	-Ho
1.56	12,600	-0.07	12.77
2.21	14,100	-0.18	12.98

2,4-DINITROTOLUENE

$\xi_B = 1{,}700$ $\xi_{BH^+} = 13{,}900$ $pK_{BH^+} = -13.75$

mole % $HB(HSO_4)_4$	ξ^{60}	log I	-Ho
2.21	2,620	1.09	12.66
10.06	4,060	0.62	13.13
27.0	6,490	0.19	13.56
32.0	7,110	0.10	13.65

TABLE XXVIII

-Ho VALUES FOR THE $HB(HSO_4)_4$-H_2SO_4 SYSTEM

mole % $HB(HSO_4)_4$	-Ho
1.56	12.47
2.21	12.73
10.06	13.24
27.0	13.56
32.0	13.65

TABLE XXIX

EVALUATION OF OVERLAP OF NITRO INDICATORS IN THE H_2O-H_2SO_4-SO_3 SYSTEM

INDICATORS	$a_{i,i-1}$	$\Pi a_{i,i-1}$
2,4,6-trinitroaniline—p-nitrotoluene	1.03	1.03
p-nitrotoluene—m-nitrotoluene	1.00	1.04
m-nitrotoluene—nitrobenzene	0.93	0.97
nitrobenzene—p-fluoronitrobenzene	0.94	0.91
p-fluoronitrobenzene—p-chloronitrobenzene	1.14	1.04
p-chloronitrobenzene—m-chloronitrobenzene	1.11	1.15
m-chloronitrobenzene—2,4-dinitrotoluene	0.94	1.08

TABLE XXX

EVALUATION OF OVERLAP OF NITRO INDICATORS IN THE H_2SO_4-HSO_3F SYSTEM

INDICATORS	$a_{i,i-1}$	$\Pi a_{i,i-1}$
p-chloronitrobenzene—m-chloronitrobenzene	1.00	1.04
m-chloronitrobenzene—2,4-dinitrotoluene	1.00	1.04
2,4-dinitrotoluene—2,4-dinitrofluorobenzene	0.91	0.95

CHAPTER IV

THE FLUOROSULFURIC ACID SOLVENT SYSTEM

A. HISTORICAL INTRODUCTION

Fluorosulfuric acid was first prepared by Kirman and Thorpe[85] in 1892 by the reaction of hydrogen fluoride with sulfur trioxide. Since then other preparative methods have been used usually involving the reaction of an inorganic fluoride, such as potassium or ammonium fluoride, with oleum or chlorosulfuric acid[86]. Fluorosulfuric acid is a highly corrosive, colourless, fuming liquid which must be handled at all times with extreme caution. It is unreactive to glass and some fluorinated hydrocarbons and thus may be conveniently handled in apparatus constructed from these materials. The highly hygroscopic nature of fluorosulfuric acid requires that it be handled in a completely dry environment.

This strong acid rapidly gained importance as measured by the number of patents involving its use. It has been used as a catalyst in a number of processes including alkylation reactions[87-91], acylation reactions[92,93], polymerization reactions[94-98], the hydrofluorination of olefins[99], and condensation reactions[100-103]. It has also proved useful in various processes such as the refining of lubricating oil[104], the removal of metals from crude petroleum[105], and the stabilization of cracked gasolines[106]. Fluorosulfuric acid has been used as a reagent or a solvent for a wide number of organic and inorganic reactions of industrial importance. The fluorosulfuric acid solvent system has been the subject of a large number of investigations; a number of reviews[86,107-110] have been written discussing various aspects of this superacid medium.

Fluorosulfuric acid has a wide liquid range, 251.4°C; a low viscosity[65], 1.72 centipoise at 25°C; and a high dielectric constant[65], ∿120, making it an ideal superacid solvent. Its low freezing point[111], -88.98°C, has enabled n.m.r. spectra to be obtained at temperatures low enough for proton transfer reactions to be slowed up sufficiently that signals can be obtained from the acidic protons of the conjugate acids of a large number of weak bases. This technique was used, for example, to show[112] that, in fluorosulfuric acid, acetamide is protonated on the oxygen atom rather than the nitrogen. It was also found[113] that phenol is protonated on the aromatic ring at the para position and not on the oxygen atom. Many other protonation studies have been carried out in 100% HSO_3F.

The properties of fluorosulfuric acid have been studied in some detail by a number of workers. As in the sulfuric acid solvent system it is convenient to make use of the solvent system concept for defining acids and bases. Acids of the fluorosulfuric acid solvent system ionize to give the $H_2SO_3F^+$ ion, i.e.,

$$HA + HSO_3F \rightleftharpoons H_2SO_3F^+ + A^- \qquad \text{(IV-1)}$$

Bases ionize to give the SO_3F^- ion, i.e.,

$$B + HSO_3F \rightleftharpoons BH^+ + SO_3F^- \qquad \text{(IV-2)}$$

The ions $H_2SO_3F^+$ and SO_3F^- are the characteristic autoprotolysis ions of the solvent just as $H_3SO_4^+$ and HSO_4^- are in the sulfuric acid solvent system.

Electrical conductivity of solutions of acids and bases in fluorosulfuric acid occurs very largely by proton transfer involving the ions $H_2SO_3F^+$ and SO_3F^-, respectively[65]. The conductivity of pure fluorosulfuric acid has been shown[65] to arise, in part, from the ions produced in the autoprotolysis reaction.

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \qquad \text{(IV-3)}$$

The autoprotolysis constant, $K_{ap} = 3.8 \times 10^{-8}$ mole^{2}kg^{-2}, is considerably smaller than the corresponding constant in H_2SO_4.

Ions other than $H_2SO_3F^+$ and SO_3F^- may be present in very low concentrations in fluorosulfuric acid although it is not certain what these are or how they arise. A cryoscopic study of the system HF-HSO_3F-SO_3 showed that freshly distilled fluorosulfuric acid generally contains a very small excess of SO_3[111]. This presumably arises from the weak dissociation of the acid, at its boiling point, into HF and SO_3, with a small excess of SO_3 remaining in the distillate.

$$HSO_3F \rightleftharpoons HF + SO_3 \qquad \text{(IV-4)}$$

This does not prove, however, that at 25°C any significant amount of self-dissociation occurs. At -88.98°C, any such reaction must have an equilibrium constant[111] of less than 3×10^{-7} moles^{2}kg^{-2}.

Fluorosulfuric acid has been found[114] to sulfonate benzene and it was suggested that self-dissociation according to 5 occurs to a small extent with the HSO_3^+ ion acting as the sulfonating agent. However,

$$HSO_3F \rightleftharpoons HSO_3^+ + F^- \qquad \text{(IV-5)}$$

as monomeric SO_3, or a solvate of it, is more likely to be the active species in sulfonation[115], this may not be regarded as evidence for (IV-5)

As in the case of sulfuric acid it is a simple matter to find bases of the fluorosulfuric acid solvent system. The alkali and alkaline earth fluorosulfates dissolve as fully dissociated electrolytes in fluorosulfuric acid.

$$MSO_3F \rightleftharpoons M^+ + SO_3F^- \qquad \text{(IV-6)}$$

Salts of other weaker acids that are weak acids of the HSO_3F solvent system also act as bases in fluorosulfuric acid, e.g.,

$$KF + HSO_3F \rightleftharpoons K^+ + SO_3F^- + HF \qquad \text{(IV-7)}$$

$$KC\ell + HSO_3F \rightleftharpoons K^+ + SO_3F^- + HC\ell \qquad \text{(IV-8)}$$

$$K_2SO_4 + 2HSO_3F \rightleftharpoons 2K^+ + 2SO_3F^- + H_2SO_4 \qquad \text{(IV-9)}$$

All protonation reactions produce basic solutions in fluorosulfuric acid according to Equation IV-2. It was mentioned in Chapter III that HSO_3F acts as a weak acid in solutions in sulfuric acid. It is thus expected that H_2SO_4 must act as a weak base in fluorosulfuric acid.

$$H_2SO_4 + HSO_3F \rightleftharpoons H_3SO_4{}^+ + SO_3F^- \qquad \text{(IV-10)}$$

An equilibrium constant of approximately 10^{-4} has been found[65].

A large number of more complex reactions produce basic solutions in fluorosulfuric acid. Among these are the oxidation-reduction reactions which produce solutions of polyatomic cations. Peroxydisulfuryldifluoride, $S_2O_6F_2$, is a convenient oxidizing agent in fluorosulfuric acid which reacts[116,117] readily with such elements as iodine, bromine, selenium, tellurium, and sulfur to produce polyatomic cations such as I_2^+, Br_3^+, Se_8^{+2}, Te_4^{+2}, S_8^{+2}, e.g.,

$$8Se + S_2O_6F_2 \rightleftharpoons Se_8^{+2} + 2SO_3F^- \qquad \text{(IV-11)}$$

Although HSO_3F is a very acidic solvent it was of interest to see if a still more acidic medium could be produced by the addition of suitable solutes, i.e., acids of the fluorosulfuric acid solvent system. As in the case of sulfuric acid it was found[118,119] that SO_3 reacted with HSO_3F to form polymeric fluorosulfuric acids such as HS_2O_6F, HS_3O_9F, etc.

$$(n-1)SO_3 + HSO_3F \rightleftharpoons HS_nO_{3n}F \qquad \text{(IV-12)}$$

Although these solutions are nonconducting and thus the acids $HS_nO_{3n}F$ are too weak to be measurably ionized, sulfur trioxide does exhibit very weak acid properties[60] in that it decreases the conducitivity of solutions of KSO_3F due, presumably, to the reaction

$$SO_3F^- + SO_3 \rightleftharpoons S_2O_6F^- \qquad \text{(IV-13)}$$

Since all other known protonic acids act either as bases or non-electrolytes in fluorosulfuric acid it is necessary to study another class of acids, Lewis acids, in order to find materials capable of increasing the acidity of fluorosulfuric acid. Woolf[114] reported that the inorganic fluorides AuF_3, TaF_5, PtF_4 and SbF_5 all act as acids in fluorosulfuric acid. Thompson et. al.[120] reinvestigated the behaviour of SbF_5 in HSO_3F and studied the effect of addition of SO_3 to SbF_5 solutions in HSO_3F. They found that SbF_5 did act as an acid in the fluorosulfuric acid solvent system and that addition of SO_3 caused further increases in acidity as a result of the formation of a series of acids of the general formula $H[SbF_5\text{-}n(SO_3F)_1\text{+}n]$. The acid $HSbF_2(SO_3F)_4$ was found to be a strong acid of the fluorosulfuric acid solvent system. Gillespie et. al.[121] found that phosphorus, arsenic, bismith, niobium pentafluorides, and titanium tetrafluoride all acted as weak acids in fluorosulfuric acid increasing in strength according to the series $PF_5 \sim NbF_5 < TiF_5 \sim AsF_5 < BiF_5$. As in the case of SbF_5 it was found[121] that the acidity of AsF_5 solutions in HSO_3F could be increased by the addition of SO_3 resulting in the formation of a series of acids with the general formula $H[AsF_{5-n}(SO_3F)_{1+n}]$. The series of acid strengths in fluorosulfuric acid was thus continued: $BiF_5 < AsF_4(SO_3F) < SbF_5 < AsF_2(SO_3F)_3 < SbF_2(SO_3F)_3$. The acidic character of all of these inorganic fluorides and mixed fluoride-fluorosulfates is the result of their ability to accept the fluorosulfate anion SO_3F^-

$$MF_5 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + MF_5(SO_3F)^- \qquad \text{(IV-14)}$$

Of all the Lewis acids in fluorosulfuric acid the systems $HSO_3F\text{-}SbF_5$ and $HSO_3F\text{-}SbF_5\text{-}SO_3$ have been most studied. That antimony pentafluoride is not a strong acid of the fluorosulfuric acid system was demonstrated[120] by its conductimetric titration with the strong base KSO_3F. The curve passes through a minimum at $KSO_3F/SbF_5 \sim 0.4$-behaviour consistent with a weak acid-strong base titration. The mode of ionization of SbF_5 is not as simple as implied in Equation IV-14. It has been found[120] that there are two acid species present in solution, the monomeric acid $H[SbF_5(SO_3F)]$ and the dimeric acid $H[(SbF_5)_2(SO_3F)]$. The former is a weak acid with a dissociation constant of 3.7×10^{-3},

$$H[SbF_5(SO_3F)] + HSO_3F \rightleftharpoons SbF_5(SO_3F)^- + H_2SO_3F^+ \qquad \text{(IV-15)}$$

while the latter is a strong, fully-dissociated acid,

$$H[(SbF_5)_2(SO_3F)] + HSO_3F \rightleftharpoons (SbF_5)_2SO_3F^- + H_2SO_3F^+ \qquad \text{(IV-16)}$$

Monomer and dimer are in equilibrium and as the concentration of SbF_5 increases so the relative amount of the dimer increases. The equilibrium,

$$2H[SbF_5(SO_3F)] \rightleftharpoons (SbF_5)_2SO_3F^- + H_2SO_3F^+ \qquad \text{(IV- 7)}$$

has an equilibrium constant of 7×10^{-3}. Since the dimer is a much stronger acid than the monomer, the apparent degree of ionization of SbF_5 increases with concentration, contrary to normal behaviour for weak electrolytes.

The acid $H[SbF_5(SO_3F)]$ is just one of a series of acids of general formula $H[SbF_{5-x}(SO_3F)_{x+1}]$, where x = 0,1,2,3. A solution of the acid $H[SbF_2(SO_3F)_4]$ is obtained by mixing, in fluorosulfuric acid, SO_3 and SbF_5 in the mole ratio $SO_3/SbF_5 > 3$. It is a strong acid in fluorosulfuric acid as shown[120] by the fact that when titrated with KSO_3F the conductivity passes through a sharp minimum at $KSO_3K/H[SbF_2(SO_3F)_4] = 1.0$. Like SbF_5 the acid is present in both monomeric and dimeric forms, i.e., $HSbF_2(SO_3F)_4$ and $H[SbF_2(SO_3F)_3]_2SO_3F$; both forms are fully dissociated strong acids. The concentration of $H_2SO_3F^+$ depends upon the relative amounts of the monomer and dimer which are in equilibrium.

$$[SbF_2(SO_3F)_3]_2SO_3F^- + 2HSO_3F \rightleftharpoons 2SbF_2(SO_3F)_4^- + H_2SO_3F^+ \qquad \text{(IV-18)}$$

The equilibrium constant for (IV-18) has been estimated to be 4 × 10^{-3} moles^{2}kg^{-2}.

It has been found[122] that various ligand redistribution reactions occur in the SbF_5-HSO_3F system giving rise to ions such as $Sb_2F_{11}^-$, cis-$SbF_4(SO_3F)_2^-$, and higher polymeric, fluorosulfate-bridged species based upon the cis-$SbF_4(SO_3F)_2^-$ grouping. Trans-$SbF_4(SO_3F)_2^-$ and its polymers have also been proposed. These same species have been postulated for the HSO_3F-SbF_5-SO_3 system. The concentration and type of species present in any given solution is highly dependent upon the molar ratio of SbF_5 to SO_3, and their concentration in fluorosulfuric acid. The systems HSO_3F-SbF_5 and HSO_3F-SbF_5-SO_3 are thus very complex but they do produce solutions of the highest known acidity and thus have attracted much attention and use.

B. ACIDITY STUDIES IN FLUOROSULFURIC ACID SOLUTIONS

Some preliminary Ho measurements in the fluorosulfuric acid solvent system have been carried out by Barr[60], Birchall[61], and Gillespie and Janzen[78]. Using the aromatic nitro indicators introduced in Chapter III along with the compounds 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene they were able to extend the Ho scale, on the basis of a very few measurements, up to an acid composition of 6 mole % SbF_5 in HSO_3F. Their studies involved the acid systems H_2SO_4-HSO_3F, KSO_3F-HSO_3F, and HSO_3F-SbF_5. Unfortunately, as indicated in the preceeding chapter, the basis for their acidity scale and some of their ionization ratios is somewhat in error.

In this chapter the Ho function will be extended, by the use of aromatic nitro indicators, into the fluorosulfuric acid solvent system. Measurements have been carried out on the systems H_2SO_4-HSO_3F-SO_3, HSO_3F-AsF_5, HSO_3F-SbF_5, HSO_3F-SbF_5-xSO_3, and HSO_3F-SbF_5-$3SO_3$. The Ho function has also been calculated for the system KSO_3F-HSO_3F on the basis of measurements previously made[60,61].

B.1. THE H_2SO_4-HSO_3F-SO_3 SYSTEM

Ho measurements for most of the H_2SO_4-HSO_3F system have been discussed in Chapter III, B.3; the acidity function in the region of 100% HSO_3F was, however, incompletely treated. In order to define more carefully the Ho function in this region and to firmly establish the Ho of 100% HSO_3F the indicators 2,4-dinitrotoluene and 2,4,6-trinitrotoluene were studied in dilute solutions of H_2SO_4 in HSO_3F and in solutions of the very weakly acidic system HSO_3F-SO_3. It should be noted that it is not valid to attempt to measure the Ho of 100% HSO_3F directly. The concentration of the indicator, required for extinction coefficient measurements, is of the same order of magnitude as the concentration of the autoprotolysis ions and thus addition of the basic indicator will markedly alter the acidity of 100% HSO_3F. The Ho of pure fluorosulfuric acid must be found by an interpolation technique.

Table XXXI lists the extinction coefficients of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene in the H_2SO_4-HSO_3F-SO_3 system near 100% HSO_3F. These values are plotted in Figure 15 from which ξ values at regularly spaced concentrations were obtained. These values were then used to calculate the ionization ratios for the two indicators as shown in Tables XXXII and XXXIII and plotted in Figure 16. The ξ_B and ξ_{BH^+} values for 2,4-dinitrofluorobenzene, 920 and 12,100 respectively, were those previously used in the H_2SO_4-HSO_3F system. The ξ_B for 2,4,6-trinitrotoluene was found to be 960 in 100% H_2SO_4. An ξ_{BH^+} of 10,600 was found in the HSO_3F-SbF_5 system; this will be discussed in a later section. The pK_{BH^+}, -15.60, for 2,4,6-trinitrotoluene was found from the overlap with 2,4-dinitrofluorobenzene (pK_{BH^+} = -14.52) over the region 0.10 - 1.50 mole % SO_3.

Table XXXIV lists the (pK_{BH^+} + log I) values for the two indicators along with the average -Ho values. Figure 17 shows the -Ho function for the systems H_2SO_4-HSO_3F-SO_3 near 100% HSO_3F. As indicated previously in the H_2SO_4-HSO_3F system the slope of the -Ho curve near 100% HSO_3F begins to increase rapidly as the concentration of the weak base, H_2SO_4, decreases. This behaviour is similar to that found near 100% $HSO_3C\ell$, H_2SO_4 and H_2O and represents, in the case of fluorosulfuric acid, the increasing $H_2SO_3F^+$ concentration as determined by the autoprotolysis equilibrium. An Ho value of -15.07 was found for 100% HSO_3F from the intersection of the H_2SO_4-HSO_3F and HSO_3F-SO_3 acidity function curves. This value represents the Ho of pure HSO_3F with no solute present and is therefore only valid under such conditions.

It is apparent from Figure 17 that the SO_3, or more accurately $HS_nO_{3n}F$, is indeed acting as a very weak acid as suggested by Barr[60]. The small autoprotolysis constant[64] for fluorosulfuric acid ($K_{A.P.}$ = 4×10^{-8} mole^{2}kg^{-2}) indicates that a large change in acidity should result even from the addition of a very small quantity of a weak acid. The slight increase for the case of SO_3 indicates that it is indeed an extremely weak acid. The -Ho curve levels off above 2 mole % SO_3 indicating that it is probably only the acid HS_2O_6F that is acidic in HSO_3F and that higher polymers are either not formed to any significant extent or do not increase in acidity as in the case of the H_2SO_4-SO_3 system.

B.2. THE KSO_3F-HSO_3F SYSTEM

Potassium fluorosulfate, like all alkali metal fluorosulfates, has been found to act as a fully dissociated strong base in fluorosulfuric acid[65]. In order to evaluate the Ho function for the system KSO_3F-HSO_3F Barr[60] and Birchall[61] measured the extinction coefficients of a number of aromatic nitro indicators in solutions of various concentrations of KSO_3F in HSO_3F. Their ξ values for the indicators p-chloronitrobenzene, m-chloronitrobenzene, 2,4-dinitrotoluene, and 2,4-dinitrofluorobenzene are listed in Table XXXV along with the calculated ionization ratios. The ξ_B, ξ_{BH^+}, and pK_{BH^+} values, also shown in Table XXXV, are those introduced in Chapter III. Figure 18 shows the ionization ratios as a function of the mole % KSO_3F present. From these curves the (pK_{BH^+} + log I) values for each indicator were calculated, along with the average -Ho values, at regularly spaced concentration intervals. The results are given in Table XXXVI and Figure 17.

Figure 17 shows the -Ho function for the KSO_3F-HSO_3F system. As expected from the relatively small autoprotolysis constant for fluorosulfuric acid, the acidity function decreases very sharply with increasing KSO_3F concentration. As previously explained no measurements were made in the pure solvent; however the Ho value of -15.07 for 100% HSO_3F, found in the H_2SO_4-HSO_3F-SO_3 system, is consistent with an extrapolation of the -Ho curve for the KSO_3F-HSO_3F system.

B.3. THE HSO_3F-AsF_5 SYSTEM

Ho measurements of the weakly acidic, in terms of fluorosulfuric acid chemistry, HSO_3F-AsF_5 system have been carried out up to an AsF_5 concentration of 5 mole %. Very approximate vapour pressure measurements indicate that above this concentration the vapour pressure of the HSO_3F-AsF_5 solutions increases rapidly. AsF_5 is a gas at room temperature and must be condensed into HSO_3F, by the use of a vacuum system, in order to prepare the acid solutions. Solutions of the indicators for Ho measurements were prepared in a large dry box resulting in some loss of AsF_5 from the concentrated solutions. This meant that the concentration of AsF_5 in solutions initially more concentrated than 5 mole % was not certain.

Table XXXVII lists the observed extinction coefficients of 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene which are plotted as a function of the AsF_5 concentration in Figure 19. Tables XXXVIII and XXXIX list the ionization ratios for the two respective indicators at regularly spaced acid concentrations. The ξ_B, ξ_{BH^+}, and pK_{BH^+} values for 2,4,6-trinitrotoluene were those used in the H_2SO_4-HSO_3F-SO_3 system. An ξ_B of 800 was found for 1,3,5-trinitrobenzene in 100% H_2SO_4. The ξ_{BH^+}, 10,700, and pK_{BH^+}, -16.04, were found in the HSO_3F-SbF_5 system to be discussed in the next section.

Table XL lists the (pK_{BH^+} + log I) values for the HSO_3F-AsF_5 system along with the average -Ho values which are plotted in Figure 17 as a function of the AsF_5 concentration. The -Ho curve for the system HSO_3F-AsF_5 behaves as would be expected for a weak acid of the fluorosulfuric acid solvent system. After an initial, relatively rapid, increase, the slope of the Ho curve increases at a somewhat slower rate. This is presumably a result of the weakly acidic nature of AsF_5 and, because of the high vapour pressures, the uncertainty of the AsF_5 concentration in the more concentrated solutions.

B.4. THE HSO_3F-SbF_5 SYSTEM

A limited number of acidity function measurements for the system HSO_3F-SbF_5 have been carried out by previous workers[60,61,78] who made use of the aromatic nitro indicators 2,4-dinitrofluorobenzene, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene. These measurements were, however, felt to be insufficient to properly define an acidity function for the HSO_3F-SbF_5 system. Their results were initially disregarded for the purpose of this study and then later compared with the results found here. Even after correcting their results by using our new pK_{BH^+} values for the various indicators the two Ho curves were different in magnitude although of the same general shape. Their limited results were thus disregarded for the purpose of defining an Ho function for the HSO_3F-SbF_5 system.

Figure 20 shows the extinction coefficients of 2,4-dinitrofluorobenzene over the acid composition range of 0-1 mole % SbF_5. It should be remembered that 2,4-dinitrofluorobenzene was found to be partially protonated in dilute solutions of H_2SO_4 in HSO_3F and is thus protonated to a considerable extent in 100% HSO_3F. The addition of the acid SbF_5 to HSO_3F would be expected to cause a continual increase in acidity; however, the ξ values of 2,4-dinitrofluorobenzene appear, after a short initially rapid increase, to level off and remain constant, at 12,100, over the range of 0.05 to 0.2 mole % SbF_5. They then slowly begin to increase above the acid concentration of 0.2 mole % SbF_5. This second increase is accompanied by a shift to shorter wavelengths of the position of the absorption maximum assigned to the protonated nitro group of 2,4-dinitrofluorobenzene. It is concluded that the level portion of this curve represents the extinction coefficient of the fully mono-protonated indicator, i.e., ξ_{BH^+} for 2,4-dinitrofluorobenzene is 12,100. The second increase is the result of the protonation of the second nitro group of the indicator. Details of this diprotonation will be discussed later in this section.

Table XLI lists the extinction coefficients of 2,4,6-trinitrotoluene found in the HSO_3F-SbF_5 system. ξ values over the acid composition range 0-1 mole % SbF_5 are plotted in Figure 21. The resulting curve rises rapidly from 100% HSO_3F (extrapolated value taken from Figure 15) and appears to level off at an ξ value of 10,600. This value is taken to be the ξ_{BH^+} for 2,4,6-trinitrotoluene.

As in the case of 2,4-dinitrofluorobenzene, and all other polynitro aromatic indicators studied, the second rise in ξ values, as a function of increasing acid strength, is assigned to the diprotonation of the indicator. This diprotonation stage is characterized by a shift of the observed λ_{max} to shorter wavelengths. The monoprotonation stage was found to have a characteristic shift of the λ_{max} to slightly longer wavelengths as the degree of protonation increased. Di- and even triprotonation of indicators, or bases, in this highly acidic medium have been previously observed. Brand's[57] acidity function measurements for the H_2SO_4-SO_3 system and Levy's[123] ketone basicity measurements, which will be discussed more fully in Chapter V, both have examples of multiple protonation.

Table XLII lists the ionization ratios for the monoprotonation of 2,4,6-trinitrotoluene in dilute solutions of SbF_5 in HSO_3F. ξ values were taken from Figure 21 at regularly spaced SbF_5 concentrations. The ξ_B value of 960 was found, as previously mentioned, in 100% H_2SO_4. The resulting log I values are plotted versus mole % SbF_5 in Figure 32 and will be discussed later.

Table XLIII lists the observed extinction coefficients of 1,3,5-trinitrobenzene as found in the HSO_3F-SbF_5 system. Figure 22 shows the ξ values as a function of SbF_5 concentration over the range of 0-1 mole % SbF_5. As in the previous case of 2,4,6-trinitrotoluene, the extinction coefficients rise rapidly with increasing SbF_5 concentration and then level off, at an acid concentration of approximately 0.4 mole % SbF_5, at an ξ value of 10,700. This ξ value is taken as the ξ_{BH^+} for 1,3,5-trinitrobenzene. Table XLIV lists the calculated log I values using ξ values obtained from Figure 22 at regularly spaced SbF_5 concentrations. The ξ_B value of 800 was found in 100% H_2SO_4. The log I values are plotted in Figure 32 for dilute solutions of SbF_5; they will be discussed later.

The observed extinction coefficients of 2,4,6-trinitrochlorobenzene in the HSO_3F-SbF_5 system are tabulated in Table XLV and plotted versus mole % SbF_5 in Figure 23. As in the cases of the previous two indicators the extinction coefficients initially rise rapidly with increasing SbF_5 concentration and then level off, in this case with an ξ value of 11,600. The ξ_{BH^+} for 2,4,6-trinitrochlorobenzene was thus taken to be 11,600. Although it is not indicated in Figure 23 the ξ values do increase for a second time, accompanied with the characteristic shift in the absorption maximum to shorter wavelengths, at still higher SbF_5 concentrations. Table XLVI lists the ionization ratios for the monoprotonation of 2,4,6-trinitrochlorobenzene in the HSO_3F-SbF_5 system. The log I values were calculated from ξ values obtained from Figure 23, the ξ_B value of 700 was found in 100% H_2SO_4. Figures 32 and 33 show the log I values as a function of the SbF_5 concentration; these curves will be discussed later.

Table XLVII lists the observed extinction coefficients, at the λ_{max}, for 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system. A representative number of complete absorption spectral data are tabulated in Table XLVIII and five of these curves are plotted in Figure 24. Figure 10, of the previous chapter, shows a representative number of complete absorption spectra for 2,4-dinitrofluorobenzene in the H_2SO_4-SO_3 system. It was found that as the SO_3 concentration increased, or the acidity increased, that a new peak, in the region of 330 nm, appeared in the spectrum of the unprotonated indicator. This new peak increased in intensity and shifted slightly to longer wavelengths as the acidity further increased. The increase in the observed extinction coefficient was taken as a measure of increased protonation of the indicator. Figure 24 shows similar changes in the absorption spectrum of the monoprotonated 2,4-dinitrofluorobenzene except that as the acidity is increased the wavelength of maximum absorption shifts to the ultra-violet region of the spectrum rather than to longer wavelengths. It was found that the absorption spectrum of the indicator, where the extinction coefficient is greater than that assigned as the ξ_{BH^+} (12,100), can be satisfactorily explained by the presence of two peaks, one at about 335 and another at about 300 nm.

The presence of two absorptions making up the observed spectra is apparent from the unsymmetrical nature of the curves of Figure 24. Figures 25 and 26 show two examples of how the composite absorption curves may be broken down into their two components. A Dupont 510 Curve Resolver accompanied by a Dupont Curve Plotter was used to separate the two components. Standard gaussian shaped curves were generated by the instrument and then electronically added together in order to produce the observed absorption curve. In most cases a total of three individual gaussian curves were required to exactly copy the experimental curve. The positions of the maximum absorptions for the three curves were found to be approximately 335, 300 and less than 230 nm; the exact position of the low wavelength peak could not be determined because of a strong absorption by the solvent in this region.

The absorption spectra may be resolved into the peaks resulting from the nitro group first protonated (335 nm), the second nitro group being protonated (300 nm), and the remaining amount of the second nitro group which has not yet been protonated (<230 nm). All three peaks may be seen at any degree of ionization between just barely diprotonated to full diprotonation. Brand[57] pointed out that the absorptions of each nitro group of a dinitro aromatic indicator, or for that matter any polynitro aromatic indicator, are quite independent in that the transitions appear to be localized in the individual nitro groups and do not involve the electronic structure of the aromatic ring itself. Brand used the example of the absorption spectra of fully monoprotonated

2,4-dinitrochlorobenzene and indicated the peak resulting from the $ArNO_2H^+$ group and that of the $ArNO_2$ group. He also predicted the disappearance of the $ArNO_2$ peak upon complete diprotonation and the formation of a new peak as a result of the second protonated nitro group.

As the SbF_5 concentration is increased the 300 nm peak in the absorption spectra of 2,4-dinitrofluorobenzene increases at the expense of the peak below 230 nm. At an SbF_5 concentration of 10.08 mole % or greater the peak below 230 nm has essentially disappeared and the 300 nm peak has greatly increased in intensity. Thus Brand's[57] prediction of the behaviour of the absorption spectra of a dinitro indicator has been verified; above 10.08 mole % SbF_5 2,4-dinitrofluorobenzene is diprotonated. The relative changes in intensity of the 300 nm peak may be used to calculate ionization ratios of the protonation of the second nitro group.

In order to calculate ionization ratios from an observed absorption spectrum by means of the relationship

$$I = \frac{\xi_{BH^+} - \xi}{\xi - \xi_B}$$

it is necessary to show that the extinction coefficients measured be representative of the absorption resulting from the protonated and unprotonated forms of the indicator only. That is ξ, the observed extinction coefficient must be the sum of ξ_{BH^+} and ξ_B only. If another peak is present but remains constant throughout the complete protonation range then the absorption of that peak alone, once determined, must be subtracted from the observed absorption before the ionization ratio may be calculated. In the case of the monoprotonation of all the indicators studied no other peaks were present in the region of interest and thus this problem did not arise.

In the case of 2,4-dinitrofluorobenzene the 335 nm peak of the first nitro group to be protonated gives rise to a marked absorption in the region of 300 nm where the second protonated nitro group has its absorption. It was found, by the use of the Dupont Curve resolver, that the intensity of the 335 nm peak decreased somewhat as the 300 nm peak increased. As the 335 nm peak decreased its width increased and its position shifted slightly more to longer wavelengths. It is felt that these changes are the result of solvent effects and do not represent changes in the degree of protonation of the fully protonated first nitro group. These changes in peak height, width and position resulted in a variation of the absorption, resulting from the first protonated nitro group, in the region of 300 nm. In order to calculate ionization ratios it was thus necessary to separately analyze each absorption spectrum and subtract the absorption resulting from the first protonated nitro group.

The use of the Dupont Curve resolver for the quantitative work required in subtracting one peak from an observed composite absorption spectra requires a great deal of care. The large number of variables, such as peak height, width and position for each individual absorption curve making up the observed spectra, requires that the electronically produced curve must be very carefully fitted to that found experimentally. Very close attention must be paid to the long wavelength tail resulting mainly from the absorption of the first protonated nitro group at 335 nm.

Over a period of two years it was found that the adjusted extinction coefficients at approximately 300 nm, found by subtracting the absorption of the first protonated nitro group from the observed absorption curve, were reproducible to within better than 10%. Each curve was analysed at least twice and the average of all independently determined ξ values were reported.

Table XLIX lists the adjusted extinction coefficients for the diprotonation of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system. These values are plotted in Figure 27 where the typical behaviour of the extinction coefficients for the protonation of an aromatic nitro indicator may be seen. A rapid rise in ξ values in dilute solutions of SbF_5 in HSO_3F is followed by a gradual decrease in the slope of the curve as the SbF_5 concentration is increased. This behaviour is consistent with the expected behaviour of the acidity function for the HSO_3F-SbF_5 system.

The calculation of ionization ratios was carried out by the use of the relationship

$$I = \frac{\xi_{BH_2{}^{+2}} - \xi}{\xi - \xi_{BH^+}} \qquad \text{(IV-19)}$$

where $\xi_{BH_2{}^{+2}}$ is the adjusted extinction coefficient of the fully diprotonated indicator at its λ_{max}, ξ is the observed adjusted extinction coefficient at the wavelength of the diprotonated species, and ξ_{BH^+} is the adjusted extinction coefficient of the fully monoprotonated indicator at the wavelength of the second nitro group's absorption. An ξ_{BH^+} of 900 was found in very dilute solutions of SbF_5 in HSO_3F where 2,4-dinitrofluorobenzene is not being diprotonated.

The $\xi_{BH_2^{+2}}$ of 20,450 was found in the HSO_3F-SbF_5-SO_3 system and is approached in the HSO_3F-SbF_5 system. ξ values were taken at regularly spaced SbF_5 concentrations from Figure 27. Table L lists the ionization ratios for the diprotonation of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system. These are plotted in Figure 33 which is discussed later.

The observed extinction coefficients of 2,4,6-trinitrotoluene in HSO_3F-SbF_5 have been previously tabulated in Table XLI. Table LI lists the complete absorption spectra for a representative number of solutions of 2,4,6-trinitrotoluene in concentrated SbF_5 solutions. Figure 28 shows some of these curves. It is apparent from Figure 28 that a new peak, assigned to the absorption of a second protonated nitro group, increases in intensity as the SbF_5 concentration is increased. As in the case of 2,4-dinitrofluorobenzene the observed spectra may be resolved into a number of individual absorptions resulting from the first protonated nitro group (325 nm), the second protonated nitro group (300 nm), and the unprotonated nitro groups (below 230 nm). Figures 29 and 30 indicate how two of these curves have been resolved into their components.

As in the case of 2,4-dinitrofluorobenzene it was found necessary to subtract the peak resulting from the absorption of the first protonated nitro group, from the observed absorption curve, in order that the ionization ratios for 2,4,6-trinitrotoluene could be calculated. Table LII lists the adjusted extinction coefficients which are plotted in Figure 31. The curve of Figure 31 is typical for the protonation of an aromatic nitro indicator in this superacid medium. The adjusted absorption curve for 2,4,6-trinitrotoluene in dilute solutions of SbF_5 in HSO_3F, where diprotonation is not taking place, showed no absorption in the region of 300 nm and thus the ξ_{BH^+} value was found to be zero. The $\xi_{BH_2^{+2}}$ of 14,500 was obtained from the HSO_3F-SbF_5-SO_3 system to be discussed in a later section. Apparently the acidity of the HSO_3F-SbF_5 system over the concentration range studied is not high enough to fully diprotonate this indicator.

Table LIII lists the ionization ratios for the diprotonation of 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system. These were calculated by the use of Equation IV-19 using ξ values taken at regularly spaced SbF_5 concentrations from Figure 31. Figure 33 shows these log I values as a function of the SbF_5 concentration.

Although Table XLII indicated that numerous measurements of extinction coefficients of 1,3,5-trinitrobenzene have been made in the HSO_3F-SbF_5 system in the region where it is being diprotonated it was not possible to make effective use of these measurements. As will be shown later, it was not possible to determine the $\xi_{BH_2^{+2}}$ for this indicator and thus ionization ratios could not be calculated. It should, however, be noted that the general behaviour of this indicator was consistent with that of 2,4,6-trinitrotoluene in the region in which it undergoes diprotonation.

The ionization ratio curves of Figure 32 represent the monoprotonation of the indicators 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, and 2,4,6-trinitrochlorobenzene in dilute solutions of SbF_5 in HSO_3F. It is readily apparent that they behave in a reasonably uniform manner up to a concentration of 0.12 mole % SbF_5; above this concentration the slope of the -log I curves for 1,3,5-trinitrobenzene and 2,4,6-trinitrochlorobenzene are not equal. Using the overlap technique and the pK_{BH^+} of 2,4,6-trinitrotoluene (-15.60), as found in the HSO_3F-SO_3 system, the ionization constant for 1,3,5-trinitrobenzene was found to be -16.04. The quantitative evaluation of the degree of parallelism for these two curves and those to follow will be discussed later. A pK_{BH^+} of -16.12 was found for 2,4,6-trinitrochlorobenzene by overlap with 1,3,5-trinitrobenzene.

Figure 33 shows the log I curves for the monoprotonation of 2,4,6-trinitrochlorobenzene and the diprotonation of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system. Using the pK_{BH^+} of -16.12 for 2,4,6-trinitrochlorobenzene, $pK_{BH_2^{+2}}$ values of -17.35 and -18.36 were found, by the overlap technique, for 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene respectively. The use of the difference between the monoprotonation log I curve of 2,4,6-trinitrochlorobenzene and the diprotonation curve of 2,4-dinitrofluorobenzene as the difference in their ionization constants is not entirely valid because of the positive charge present on the latter indicator. Fortunately, however, the behaviour of the nitro groups of polynitro aromatic indicators is quite independent and thus such an overlap technique may be at least partly justified. Without this overlap it would not be possible to determine the $pK_{BH_2^{+2}}$ for the indicators 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene and thus the acidity function in superacid systems could not otherwise be extended to higher acidities than those measured by 2,4,6-trinitrochlorobenzene. It may be possible to find weaker nitro bases than 2,4,6-trinitrochlorobenzene; however, none were studied in this investigation.

The (pK_{BH^+} + log I) or ($pK_{BH_2^{+2}}$ + log I) values for the indicators studied in the HSO_3F-SbF_5 system are listed in Table LIV along with their average values. The average values above a concentration of SbF_5 greater than 0.10 mole %, where the diprotonation results are first used, have been referred to as Ho values although they should strictly be classified as H+ values where

$$H+ = pK_{BH_2^{+2}} + \log \frac{[BH^+]}{[BH_2^{+2}]} \qquad \text{(IV-20)}$$

The degree of parallelism between the first protonation of 2,4,6-trinitrochlorobenzene and the second protonation of 2,4-dinitrofluorobenzene, to be discussed quantitatively in a later section, is not as good as found between other nitro indicators. It appears, however, to be good enough to allow the use of the symbol Ho in describing the acidity function generated by the diprotonation of the indicator 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene. Figure 34 shows the resulting -Ho function for the HSO_3F-SbF_5 system over the composition range of 0-11 mole % SbF_5.

The -Ho curve for the HSO_3F-SbF_5 system initially increases rapidly upon the addition of small amounts of the moderately weak acid ($K_a = 3.7 \times 10^{-3}$ moles kg^{-1})[121] SbF_5 to HSO_3F. The relatively small autoprotolysis constant for fluorosulfuric acid indicates that even dilute solutions of weak acids should produce relatively large changes in acidity. As previously mentioned the species $SbF_5SO_3F^-$ and $(SbF_5)_2SO_3F^-$ are formed even in relatively dilute solutions. The K_a of 3.7×10^{-3} refers to the acid $HSbF_5SO_3F$ initially formed while

$H(SbF_5)_2SO_3F$, formed as the SbF_5 concentration is increased, is a strong acid of the HSO_3F solvent system.

The low temperature (-54°C) ^{19}F n.m.r. spectra of a 22.45 mole % SbF_5 in HSO_3F solution was found to be essentially identical to that reported by Dean and Gillespie[41] for a 47.9 mole % solution of SbF_5 in HSO_3F except that the relative intensities of the peaks were not the same because the relative concentration of the polymeric species was somewhat greater at higher SbF_5 concentrations. The formation of the numerous polymeric species such as $Sb_2F_{11}^-$, polymeric cis and trans $SbF_4(SO_3F)_2^-$, and $FSO_3\cdot SbF_4\cdot FSO_3\cdot SbF_5$, which were shown to be present would slow down the rate of increase of the -Ho curve with increasing SbF_5 concentration. The very few measurements of the absorption spectra of indicators above an SbF_5 concentration of 11 mole % indicate that this is probably the case.

The acid mixture of equal molar amounts of SbF_5 and HSO_3F has been used extensively by a number of workers[124] for the study of carbonium ions in solution. This solvent, termed magic acid, is estimated to have an Ho of between -19.5 and -20 on the basis of investigations reported here.

B.5. THE HSO_3F-SbF_5-xSO_3 SYSTEM

The effect of the addition of SO_3 upon the acidity of the HSO_3F-SbF_5 system was studied with the use of the indicators 2,4-dinitrofluorobenzene and 1,3,5-trinitrobenzene. Table LV lists the extinction coefficients of these two indicators as a function of the SbF_5:SO_3 molar ratio in a solution containing 2 mole % SbF_5 in HSO_3F. The ξ values are plotted, as a function of the SbF_5:SO_3 molar ratio, in

Figure 35.

It is apparent from the increase in ξ values of the two indicators as the SO_3 concentration is increased that the acidity of the solutions must also be increasing. Unfortunately, it is not possible to calculate the actual changes in -Ho values as a function of the $SbF_5:SO_3$ molar ratio. 2,4-Dinitrofluorobenzene, while initially only partially diprotonated, quickly becomes fully diprotonated and thus ionization ratios cannot be calculated. 1,3,5-Trinitrobenzene does not become fully diprotonated; however, the $\xi_{BH_2^{+2}}$ for this indicator could not be determined and thus ionization ratios could not be calculated.

It is, however, apparent that the acidity increases with increasing SO_3 concentration until a molar ratio of somewhat less than 1:3 is reached. Above this ratio further addition of SO_3 produced no change in the extinction coefficients and thus no change in the acidity. This is consistent with the electrical conductivity measurements of Thompson et. al.[120] who found that the conductivity of SbF_5 solutions in HSO_3F reached a maximum upon the addition of 3 moles of SO_3 per mole of SbF_5 present. A maximum increase in acidity of 0.96 -Ho units was found for the 2 mole % SbF_5 solutions upon the addition of SO_3. This value is obtained from the difference in -Ho's of 2 mole % SbF_5 (17.60) and 2 mole % $SbF_5 \cdot 3SO_3$ (18.56), the latter value being taken from the results of the next section.

A ^{19}F n.m.r. investigation of the species present in solutions of various $SbF_5:SO_3$ molar ratios in HSO_3F has been previously carried out by Thompson et. al.[120]. Their paper shows typical spectra for these solutions which were similar to those found in this work. The assignment of the peaks observed in this work is in full agreement with those of Thompson et. al. As indicated in the last section, the species present in solutions of SbF_5 in HSO_3F are mainly $SbF_5SO_3F^-$ and $(SbF_5)_2SO_3F^-$ with traces of cis and trans $SbF_4(SO_3F)_2^-$ and $Sb_2F_{11}^-$. As the SbF_5:SO_3 molar ratio is increased to approximately 1:1 the concentrations of $SbF_5SO_3F^-$ and $(SbF_5)_2SO_3F^-$ decrease, the peak resulting from $Sb_2F_{11}^-$ disappears, while the concentration of cis and trans $SbF_4(SO_3F)_2^-$ and their polymers increases. Some traces of $SbF_3(SO_3F)_3^-$ may also be seen.

As the molar ratio is increased to slightly more than 1:2.0 SbF_5:SO_3 the peaks resulting from $SbF_5SO_3F^-$ and $(SbF_5)_2SO_3F^-$ disappear and the concentration of the species $SbF_4(SO_3F)_2^-$ decreases. Cis and trans $SbF_3(SO_3F)_3^-$, and presumably their polymers, increase in concentration while new peaks assigned to cis and trans $SbF_2(SO_3F)_4^-$ are present. At molar ratios in excess of 1:3 SbF_5:SO_3 cis and trans $SbF_2(SO_3F)_4^-$ and their polymers are most prevalent although $SbF_3(SO_3F)_3^-$ and some free SO_3 are also present.

It was found that as the $SbF_5 \cdot 3SO_3$ concentration was increased the apparent concentration of the $SbF_2(SO_3F)_4^-$ species increased with respect to the $SbF_3(SO_3F)_3^-$ species. This is presumably the result of further polymerization. It is readily apparent that solutions containing large amounts of $SbF_5 \cdot 3SO_3$ form complicated mixtures with the presence of $SbF_2(SO_3F)_4^-$ as the most predominant species. It has been found[120] that dilute solutions of $H[SbF_2(SO_3F)_4]$, at both room and low temperatures, act as strong acids of the fluorosulfuric acid system.

B.6. THE HSO_3F-SbF_5-$3SO_3$ SYSTEM

Acidity function measurements of the system HSO_3F-SbF_5 containing a molar ratio of SbF_5:SO_3 in excess of 1:3 were carried out by the use of the indicators 2,4-dinitrofluorobenzene, 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene. As was fully explained in the study of the HSO_3F-SbF_5 system, these indicators undergo diprotonation and thus the acidity function for this system should be called H+; however, as before, the symbol Ho will be used. Ionization ratios were calculated from adjusted extinction coefficients as explained in the HSO_3F-SbF_5 system.

Table LVI lists the observed and adjusted extinction coefficients for the diprotonation of 2,4-dinitrofluorobenzene in the system HSO_3F-SbF_5-$3SO_3$. The observed ξ values are plotted in Figure 36 and show that after an initially rapid increase they level off indicating that full diprotonation has taken place. Table LVII lists the complete absorption spectra for a representative number of solutions; five of these are plotted in Figure 37. It is apparent, as found in the HSO_3F-SbF_5 system, that diprotonation is taking place with the formation of a new peak at about 300 nm as the result of the protonation of the second nitro group. This family of absorption curves is identical to those shown in Figure 24 for the diprotonation of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5 system indicating that identical processes are taking place in the two acid systems.

Figure 38 shows the adjusted extinction coefficients for the diprotonation of 2,4-dinitrofluorobenzene as a function of the $SbF_5 \cdot 3SO_3$ concentration. The $\xi_{BH_2^{+2}}$ value of 20,450 was determined from the upper level portion of this curve. Table LVIII lists the ionization ratios for the diprotonation of 2,4-dinitrofluorobenzene in the HSO_3F-SbF_5-$3SO_3$ system. These were calculated using ξ values taken from Figure 38 at regularly spaced $SbF_5 \cdot 3SO_3$ concentrations, an ξ_{BH^+} value of 900 as previously determined, and the $\xi_{BH_2^{+2}}$ of 20,450.

Table LIX lists the observed and adjusted extinction coefficients for the diprotonation of 2,4,6-trinitrotoluene in the HSO_3F-SbF_5-$3SO_3$ system. The observed ξ values are plotted in Figure 36 where it may be seen that the ξ values initially increase rapidly and then appear to level off. A similar curve for 1,3,5-trinitrobenzene, to be discussed later, is increasing in the region of 11.5 mole % $SbF_5 \cdot 3SO_3$ while that of 2,4,6-trinitrotoluene is beginning to level off. The acidity of the system must be continuing to rise, as measured by the increasing ξ values of 1,3,5-trinitrobenzene, and thus the levelling off of 2,4,6-trinitrotoluene's curve indicates that full diprotonation has been reached.

Typical absorption spectra for 2,4,6-trinitrotoluene in HSO_3F-SbF_5-$3SO_3$ are listed in Table LX and shown in Figure 39. This family of curves is identical to those of Figure 28, as found for the diprotonation of 2,4,6-trinitrotoluene in the HSO_3F-SbF_5 system, except that higher ξ values are obtained at high concentrations of $SbF_5 \cdot 3SO_3$ in HSO_3F. It is concluded that identical processes are taking place in both acid systems.

Figure 38 shows the adjusted extinction coefficients of 2,4,6-trinitrotoluene where the peak resulting from the first protonated nitro group has been subtracted from the observed spectra. An $\xi_{BH_2^{+2}}$ value of 14,500 was obtained at high $SbF_5 \cdot 3SO_3$ concentrations. The ionization ratios for the diportonation of 2,4,6-trinitrotoluene are listed in Table LXI. As for previous indicators these were calculated from ξ values obtained at regularly spaced $SbF_5 \cdot 3SO_3$ concentrations from Figure 38. The ξ_{BH^+} value of 0 as found in the HSO_3F-SbF_5 system was used.

Figure 36 shows the extinction coefficients of 1,3,5-trinitrobenzene in the HSO_3F-SbF_5-$3SO_3$ system. As the $SbF_5 \cdot 3SO_3$ concentration is increased the absorption resulting from the solvent shifts to longer wavelengths. At about 11.5 mole % $SbF_5 \cdot 3SO_3$ it has completely obscured the λ_{max} of 1,3,5-trinitrobenzene, which is at ∿285 nm, and thus the diprotonation behaviour of this indicator cannot be determined. It is thus not possible to obtain an $\xi_{BH_2{}^{+2}}$ for the indicator in the HSO_3F-SbF_5-$3SO_3$ system with the result that acidity measurements using this indicator must be of a qualitative nature.

It was earlier pointed out that the ξ values of 1,3,5-trinitrobenzene increase with increasing $SbF_5 \cdot 3SO_3$ concentration thus indicating that the acidity was increasing. The shape of the ξ versus mole % $SbF_5 \cdot 3SO_3$ curve of Figure 36 is quite similar to that of 2,4,6-trinitrotoluene, until the latter indicator's curve levels off as a result of complete diprotonation, indicating that the behaviour of these two indicators is quite similar.

Table LXII lists the average ($pK_{BH_2{}^{+2}}$ + log I) values for the diprotonation of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene along with the average Ho values. These are plotted in Figure 34 showing that the HSO_3F-SbF_5-$3SO_3$ system is the most acidic of all systems studied. As would be expected for solutions of a strong acid in fluorosulfuric acid the -Ho curve increases very rapidly at low solute concentrations. The -Ho curve increases more slowly at higher $SbF_5 \cdot 3SO_3$ concentrations as a result of the formation of polymeric species in solution. The -Ho of 19.35 for a 7 mole % $SbF_5 \cdot 3SO_3$ solutions in HSO_3F represents the highest Ho value measured.

C. DISCUSSION

The Ho function has been extended into the fluorosulfuric acid solvent system by the use of the aromatic nitro indicators 2,4-dinitrofluorobenzene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, and 2,4,6-trinitrochlorobenzene. It was shown in Chapter III that the monoprotonation behaviour of 2,4-dinitrofluorobenzene was similar to that of other nitro indicators and the aniline indicators, used[46] to determine the Ho function for the H_2O-H_2SO_4 system. Johnson's[48] method for the evaluation of the degree of parallelism, as discussed in Chapter III, gave a value for the product $\Pi a_{i,i-1}$ of 0.95 for all Ho indicators up to and including 2,4-dinitrofluorobenzene. A product of unity would indicate that all indicators were, on the average, behaving in the same way to acidity changes.

The degree of parallelism, or overlap, of the new indicators was evaluated as previously outlined. Table LXIII lists the individual $a_{i,i-1}$ values along with the overall products. The degree of parallelsim is within the range of values found for the aniline indicators; however the overlap between the monoprotonation of 2,4,6-trinitrochlorobenzene and the diprotonation of 2,4-dinitrofluorobenzene is particularly poor. This would be expected as a result of the effect of a localized positive charge in the area of the nitro group undergoing protonation. The diprotonation behaviour of aromatic nitro indicators is thus similar, but not identical, to monoprotonation behaviour. The two indicators undergoing diprotonation were included in the set of aromatic nitro indicators because their behaviour is similar to that of indicators undergoing monoprotonation and because this gave a means for extending the acidity scale to higher levels of acidity.

The behaviour of the -Ho curves of Figure 34 is consistent with the order of acidity previously proposed on the basis of conductivity measurements; $SO_3 < AsF_5 < SbF_5 < SbF_2(SO_3F)_3$. Solutions of SO_3 were found to be extremely weakly acidic in fluorosulfuric acid while $SbF_2(SO_3F)_3$ solutions are the most acidic of all systems studied and presumably are the most acidic solutions known.

As demonstrated in the system H_2O-H_2SO_4-SO_3 the Ho function may be calculated if it is assumed that it is a measure of the concentration of the most acidic species present. In the region of 100% HSO_3F the most acidic species possible is $H_2SO_3F^+$. Equation IV-21 was derived from the observed Ho of 100% HSO_3F (-15.07) and the concentration of $H_2SO_3F^+$ present as a result of the autoprotolysis reaction.

$$\mathrm{Ho} = -\log[H_2SO_3F^+] - 18.55 \qquad \text{(IV-21)}$$

The calculated Ho function behaves much as it does in the region of 100% sulfuric acid. The agreement between the calculated and experimental curves for fluorosulfuric acid is, however, somewhat better than that found in the sulfuric acid system. A 0.1 mole % KSO_3F solution is calculated to have an Ho of -13.35 while a value of -13.67

has been found. A similar concentration of $SbF_5 \cdot 3SO_3$ was calculated to produce a solution of H_o = -16.79; an experimental value of -16.77 has been found. It is apparent that the H_o function near 100% HSO_3F can be calculated with reasonable accuracy by the use of the above relationship. The dashed lines of Figures 17 and 34 indicate that the experimental and calculated H_o's are identical over a range of approximately 3 H_o units. At higher concentrations of KSO_3F or $SbF_5 \cdot 3SO_3$ the calculated H_o function is somewhat lower than that experimentally found. Activity coefficient effects may account for some of the difference between the observed and calculated H_o values at high solute concentrations.

TABLE XXXI

EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE AND 2,4,6-TRINITROTOLUENE IN H_2SO_4-HSO_3F-SO_3

mole %	2,4-DINITROFLUOROBENZENE	
H_2SO_4	ξ	λ_{max} (nm)
1.7668	4,041	330
1.3756	4,036	330
1.0601	4,648	330
0.9139	4,551	330
0.6374	4,915	329
0.2668	6,151	329
0.1432	6,777	330
0.1411	6,950	330

mole %	2,4-DINITROFLUOROBENZENE		2,4,6-TRINITROTOLUENE	
SO_3	ξ	λ_{max} (nm)	ξ	λ_{max} (nm)
0.1539	9,940	332	3,507	315
0.6328	10,570	332	4,313	318
1.2714	10,985	331	4,953	320
2.1190	11,005	332	5,344	320
2.4768	11,600	333	5,273	320
3.2398	11,973	332	5,692	320
3.4387	12,100	332	5,342	320
3.8160	11,324	332	5,235	320
5.0754	11,326	332	5,274	320
7.4060	11,459	331	5,037	320
9.3641	10,763	332	4,485	320
9.6036	11,885	332	5,682	321

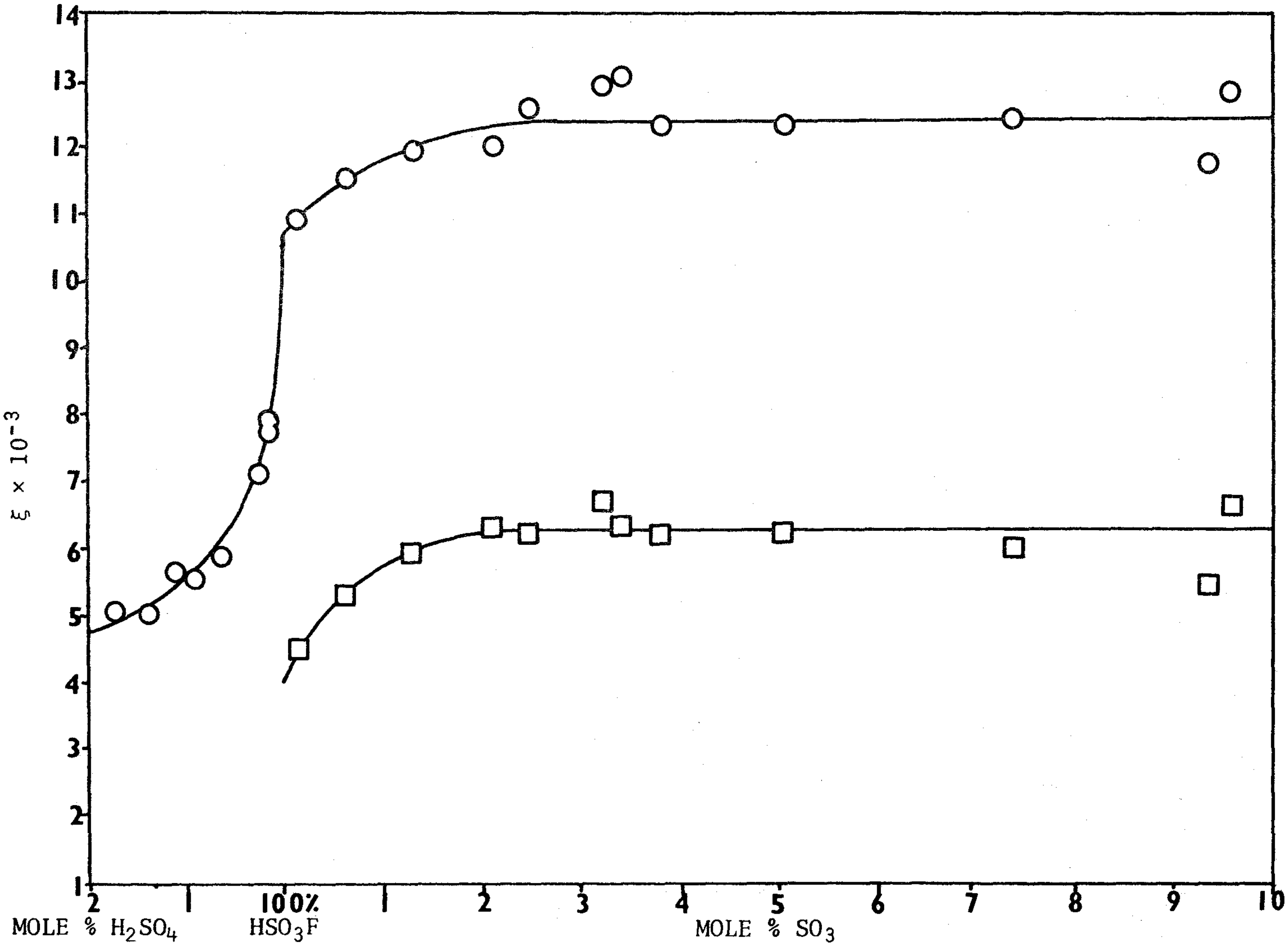

Figure 15. Extinction Coefficients of 2,4-Dinitrofluorobenzene (○) and 2,4,6-Trinitrotoluene (□) in H_2SO_4-HSO_3F-SO_3

TABLE XXXII

IONIZATION RATIOS OF 2,4-DINITROFLUOROBENZENE IN H_2SO_4-HSO_3F-SO_3

$\xi_B = 920$ $\xi_{BH^+} = 12,100$ $pK_{BH^+} = -14.52$

mole % H_2SO_4	ξ	log I
2.00	3,800	0.46
1.50	4,100	0.40
1.00	4,570	0.31
0.50	5,430	0.17
0.25	6,300	0.03
0.10	7,500	-0.15
0.00	9,600	-0.54

mole % SO_3	ξ	log I
0.10	9,900	-0.61
0.25	10,110	-0.66
0.50	10,420	-0.75
1.00	10,840	-0.90
1.50	11,090	-1.00

TABLE XXXIII

IONIZATION RATIOS OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SO_3

ξ_B = 960 ξ_{BH^+} = 10,600 pK_{BH^+} = -15.60

mole % SO_3	ξ	log I
0.00	3,200	0.52
0.10	3,420	0.46
0.25	3,740	0.39
0.50	4,180	0.30
1.00	4,750	0.19
1.50	5,100	0.12
2.00	5,220	0.10
3.00	5,310	0.08
4.00	5,310	0.08
5.00	5,310	0.08
7.50	5,310	0.08
10.00	5,310	0.08

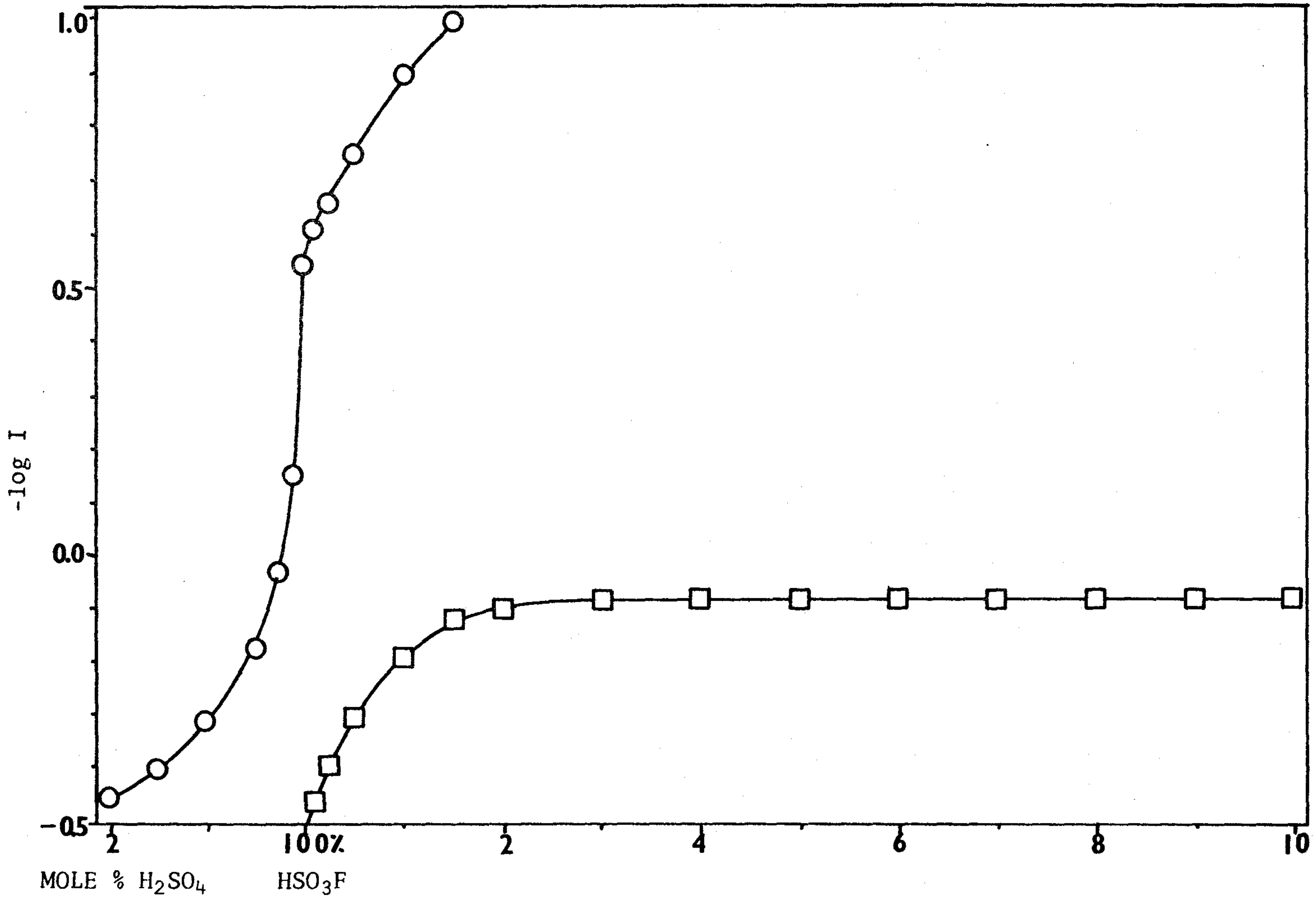

Figure 16. Ionization Ratios for 2,4-Dinitrofluorobenzene (○) and 2,4,6-Trinitrotoluene (□) in H_2SO_4-HSO_3F-SO_3

TABLE XXXIV

-Ho VALUES FOR THE SYSTEM H_2SO_4-HSO_3F-SO_3

mole % H_2SO_4	-Ho
2.00	14.06
1.50	14.12
1.00	14.21
0.50	14.35
0.25	14.49
0.10	14.68

mole % SO_3	2,4-DINITROFLUOROBENZENE	2,4,6-TRINITROTOLUENE	AVERAGE
0.00	15.06	15.08	15.07
0.10	15.13	15.14	15.14
0.25	15.18	15.21	15.19
0.50	15.27	15.30	15.28
1.00	15.42	15.41	15.42
1.50	15.52	15.48	15.50
2.00		15.50	15.50
3.00		15.52	15.52
4.00		15.52	15.52
6.00		15.52	15.52
8.00		15.52	15.52
10.00		15.52	15.52

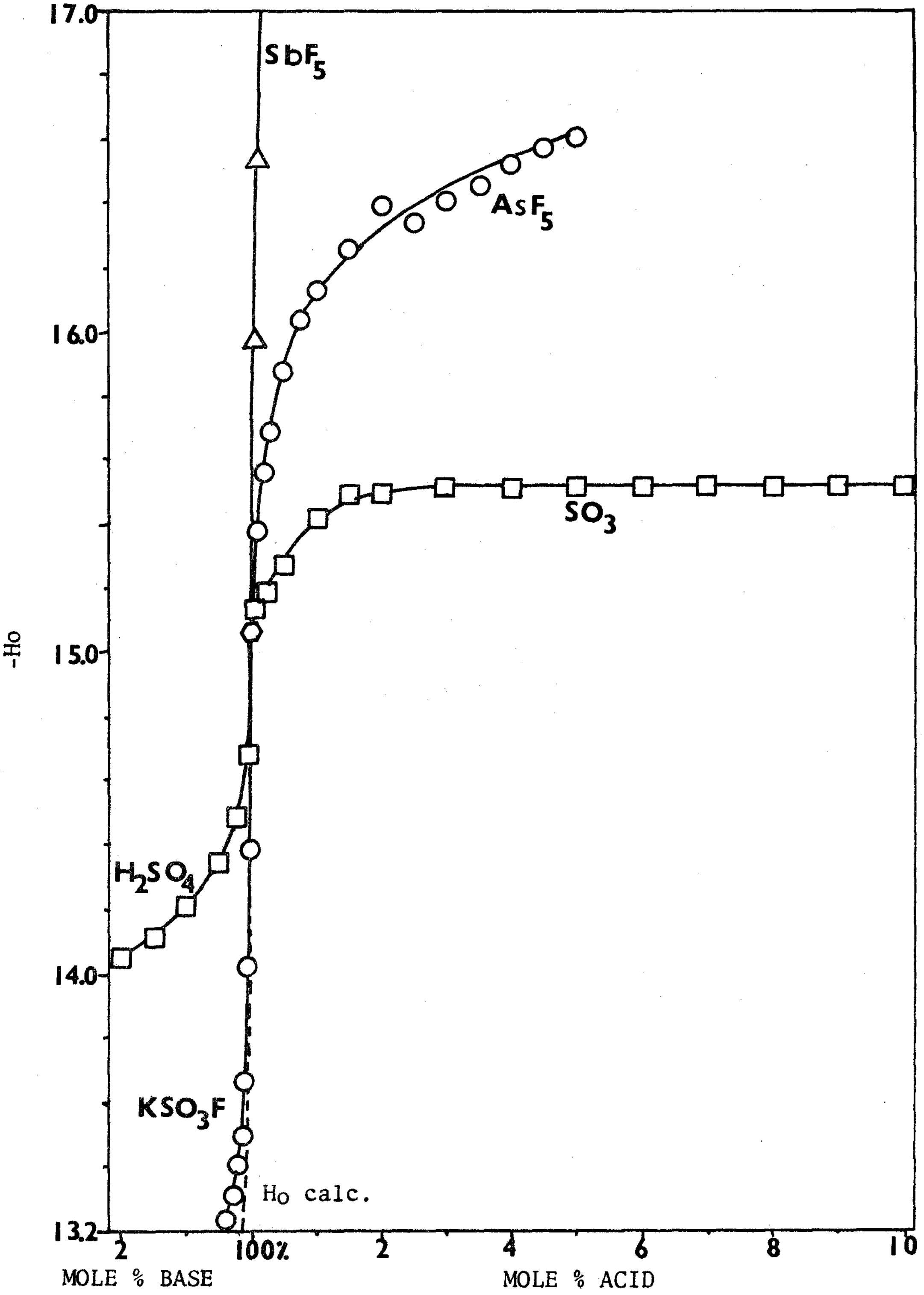

Figure 17. -Ho Function Near 100% HSO_3F

TABLE XXXV

EXTINCTION COEFFICIENTS AND IONIZATION RATIOS IN KSO_3F-HSO_3F

mole % KSO_3F	ξ	log I
	p-CHLORONITROBENZENE	
$\xi_B = 400$	$\xi_{BH^+} = 24{,}350$	$pK_{BH^+} = -12.70$
0.3927	19,650*	-0.61
0.1449	20,400*	-0.70
0.0786	21,800*	-0.92
	m-CHLORONITROBENZENE	
$\xi_B = 440$	$\xi_{BH^+} = 14{,}380$	$pK_{BH^+} = -13.16$
0.1449	10,590*	-0.43
0.0786	11,100*	-0.51
	2,4-DINITROTOLUENE	
$\xi_B = 1{,}700$	$\xi_{BH^+} = 13{,}900$	$pK_{BH} = -13.75$
0.3927	4,320*	0.56
0.1449	6,150*	0.24
0.0786	7,140*	0.09
	2,4-DINITROFLUOROBENZENE	
$\xi_B = 920$	$\xi_{BH^+} = 12{,}100$	$pK_{BH^+} = -14.52$
0.156	2,560†	0.76
0.047	4,470†	0.33
0.022	4,520†	0.32

*Ref. 60.

†Ref. 61.

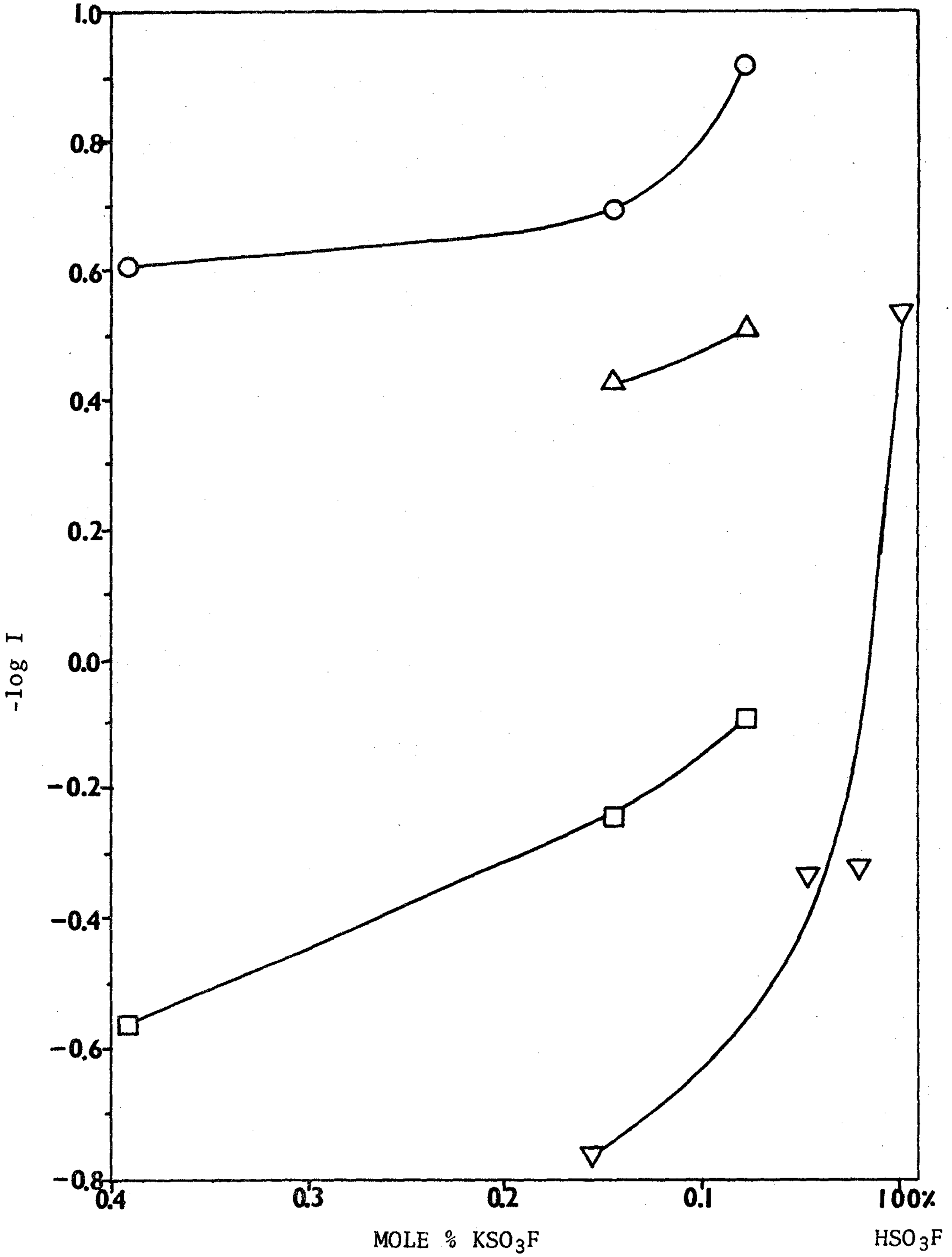

Figure 18. Ionization Ratios of p-Chloronitrobenzene (○); m-Chloronitrobenzene (△); 2,4-Dinitrotoluene (□); and 2,4-Dinitrofluorobenzene (▽) in KSO_3F-HSO_3F

TABLE XXXVI

-Ho VALUES FOR THE SYSTEM KSO_3F-HSO_3F

mole % KSO_3F	p-CHLORONITROBENZENE	m-CHLORONITROBENZENE	2,4-DINITROTOLUENE	2,4-DINITROFLUOROBENZENE	AVERAGE
0.400	13.30		13.17		13.24
0.350	13.32		13.23		13.28
0.300	13.33		13.29		13.31
0.250	13.34		13.36		13.35
0.200	13.36		13.43		13.40
0.150	13.40	13.58	13.50	13.76	13.56
0.100	13.52	13.64	13.59	13.89	13.66
0.075	13.65	13.69	13.67	13.98	13.75
0.050				14.11	14.11
0.025				14.35	14.35
0.000				15.07	15.07

TABLE XXXVII

EXTINCTION COEFFICIENTS OF 2,4,6-TRINITROTOLUENE AND 1,3,5-TRINITROBENZENE IN HSO_3F-AsF_5

mole %	2,4,6-TRINITROTOLUENE		1,3,5-TRINITROBENZENE	
AsF_5	ξ	λ_{max} (nm)	ξ	λ_{max} (nm)
0.0982	4,146	318	2,784	295
0.2538	5,381	322	3,503	298
0.3749	7,139	323	4,196	300
0.4958	7,545	322	4,706	300
0.5804	7,774	323	5,377	300
0.6598	8,200	323	5,364	301
0.7601	8,178	323	5,427	301
0.8627	8,622	325	4,972	302
0.9845	8,681	324	5,988	302
1.4715	8,796	324	6,541	302
2.9508	10,042	324	7,690	303
4.3167	10,621	322	8,462	303

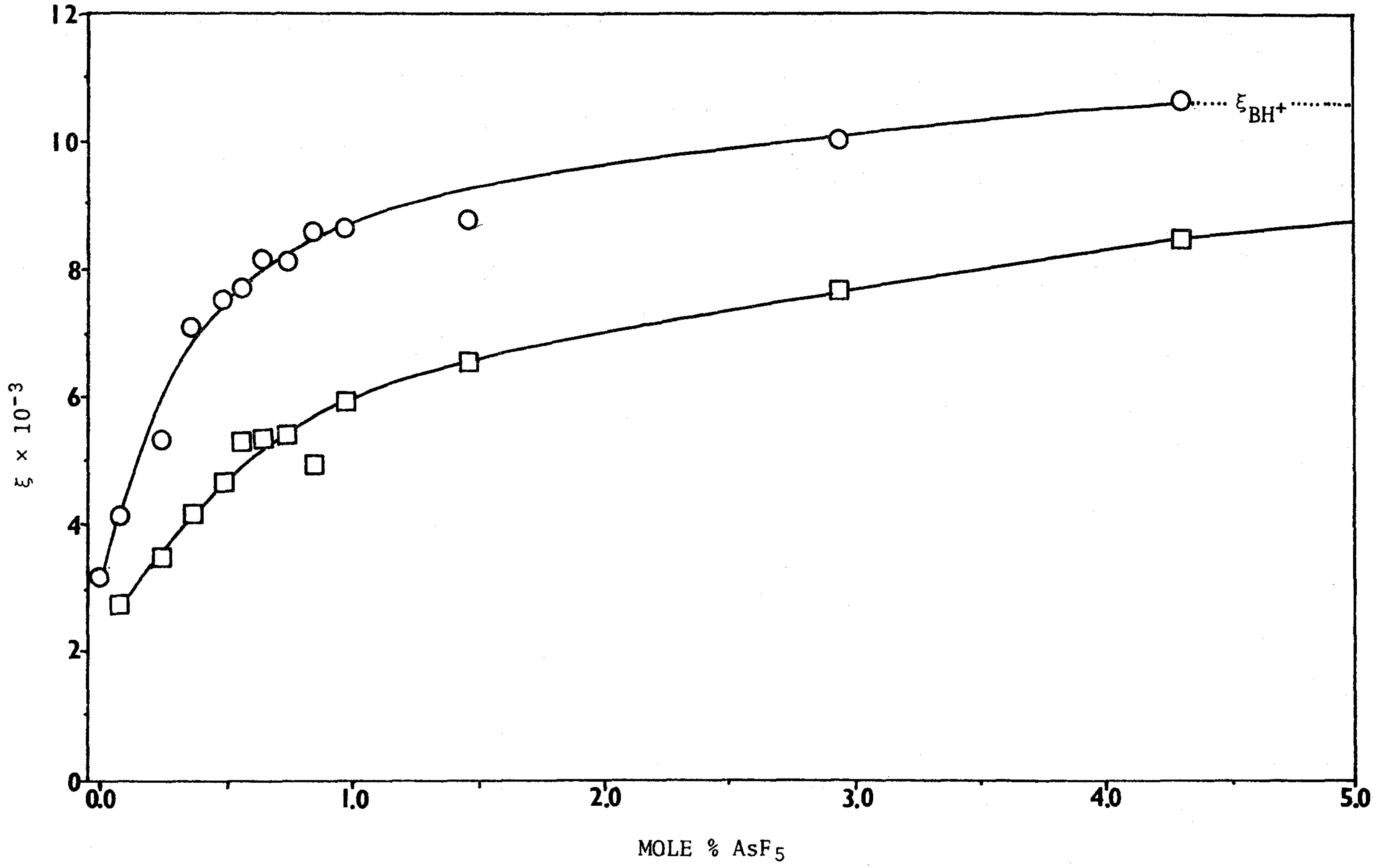

Figure 19. Extinction Coefficients of 2,4,6-Trinitrotoluene (○) and 1,3,5-Trinitrobenzene (□) in HSO_3F-AsF_5

TABLE XXXVIII

IONIZATION RATIOS OF 2,4,6-TRINITROTOLUENE IN HSO_3F-AsF_5

$\xi_B = 960$ $\xi_{BH+} = 10,600$ $pK_{BH+} = -15.60$

mole % AsF_5	ξ	log I
0.10	4,420	0.25
0.20	5,450	0.06
0.30	6,280	-0.09
0.40	6,940	-0.21
0.50	7,450	-0.31
0.75	8,190	-0.48
1.00	8,600	-0.58
1.25	8,900	-0.67
1.50	9,150	-0.75
2.00	9,580	-0.93

TABLE XXXIX

IONIZATION RATIOS OF 1,3,5-TRINITROBENZENE IN HSO_3F-AsF_5

ξ_B = 800 ξ_{BH^+} = 10,700 pK_{BH^+} = -16.04

mole % AsF_5	ξ	log I
0.10	2,700	0.62
0.20	3,300	0.47
0.30	3,840	0.35
0.40	4,320	0.26
0.50	4,750	0.18
0.75	5,520	0.04
1.00	5,980	-0.04
1.25	6,300	-0.09
1.50	6,560	-0.14
2.00	7,020	-0.23
2.50	7,420	-0.31
3.00	7,720	-0.37
3.50	8,010	-0.42
4.00	8,290	-0.49
4.50	8,500	-0.54
5.00	8,600	-0.57

TABLE XL

-Ho VALUES FOR THE SYSTEM HSO_3F-AsF_5

mole % AsF_5	2,4,6-TRINITROTOLUENE	1,3,5-TRINITROBENZENE	AVERAGE
0.10	15.35	15.42	15.38
0.20	15.54	15.57	15.56
0.30	15.69	15.69	15.69
0.40	15.81	15.78	15.80
0.50	15.91	15.86	15.88
0.75	16.08	16.00	16.04
1.00	16.18	16.08	16.13
1.25	16.27	16.14	16.20
1.50	16.35	16.18	16.26
2.00	16.53	16.27	16.40
2.50		16.34	16.34
3.00		16.41	16.41
3.50		16.46	16.46
4.00		16.53	16.53
4.50		16.58	16.58
5.00		16.61	16.61

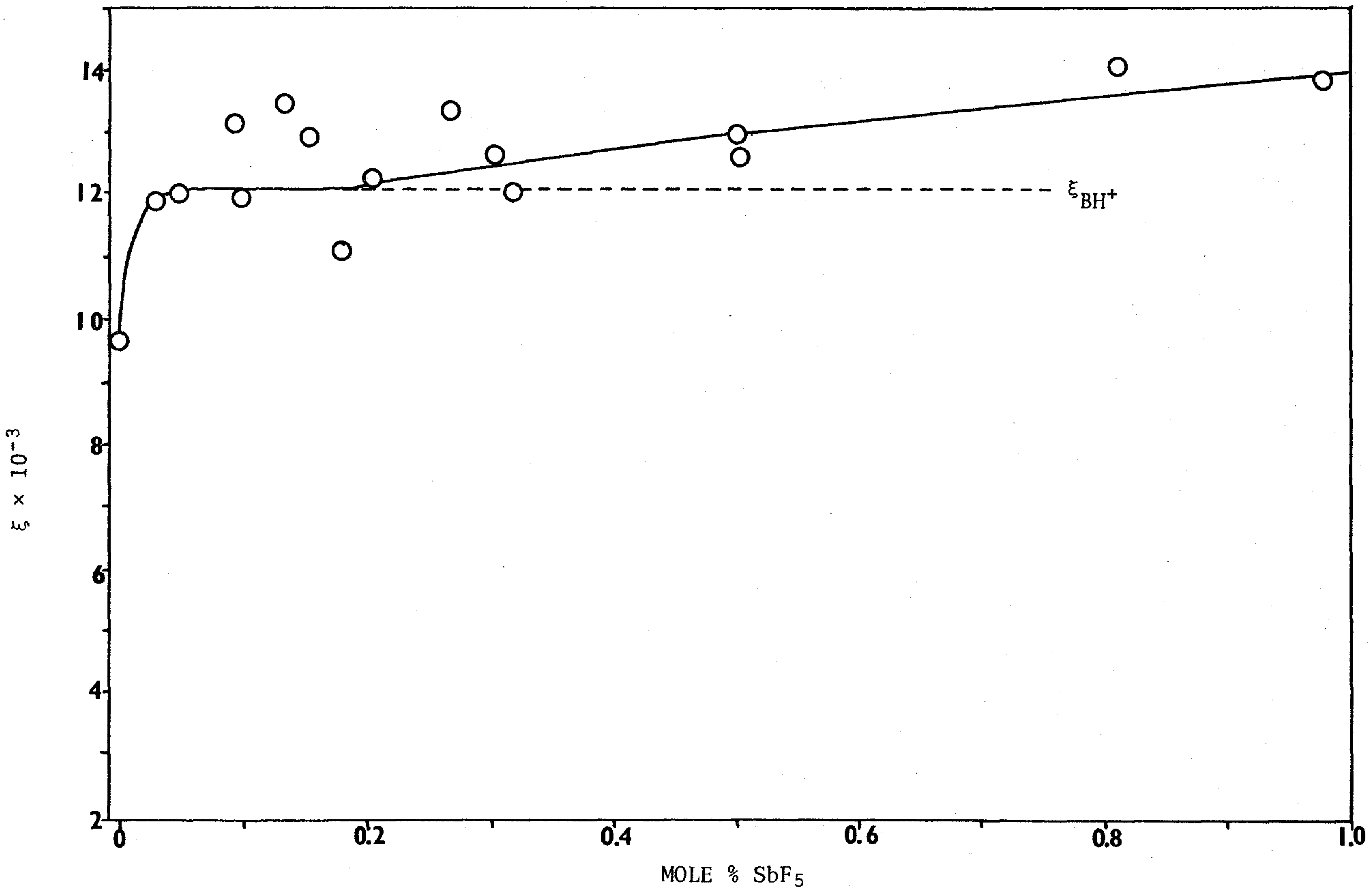

Figure 20. Extinction Coefficients of 2,4-Dinitrofluorobenzene in Dilute Solutions of SbF_5 in HSO_3F

TABLE XLI

EXTINCTION COEFFICIENTS OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SbF_5

mole % SbF_5	ξ	λ_{max} (nm)
0.03007	6,087	322
0.09515	10,259	323
0.1567	13,421	320
0.1812	10,350	324
0.2707	11,725	320
0.3059	10,861	322
0.5053	10,781	322
0.8118	10,324	321
1.3054	10,008	320
1.4792	11,300	318
1.7750	10,880	317
1.9238	11,873	316
3.3872	11,896	310
3.5454	13,610	308
5.2531	14,364	304
6.8557	15,752	300
7.0268	16,301	302
9.3710	15,960	302
10.0810	16,583	300

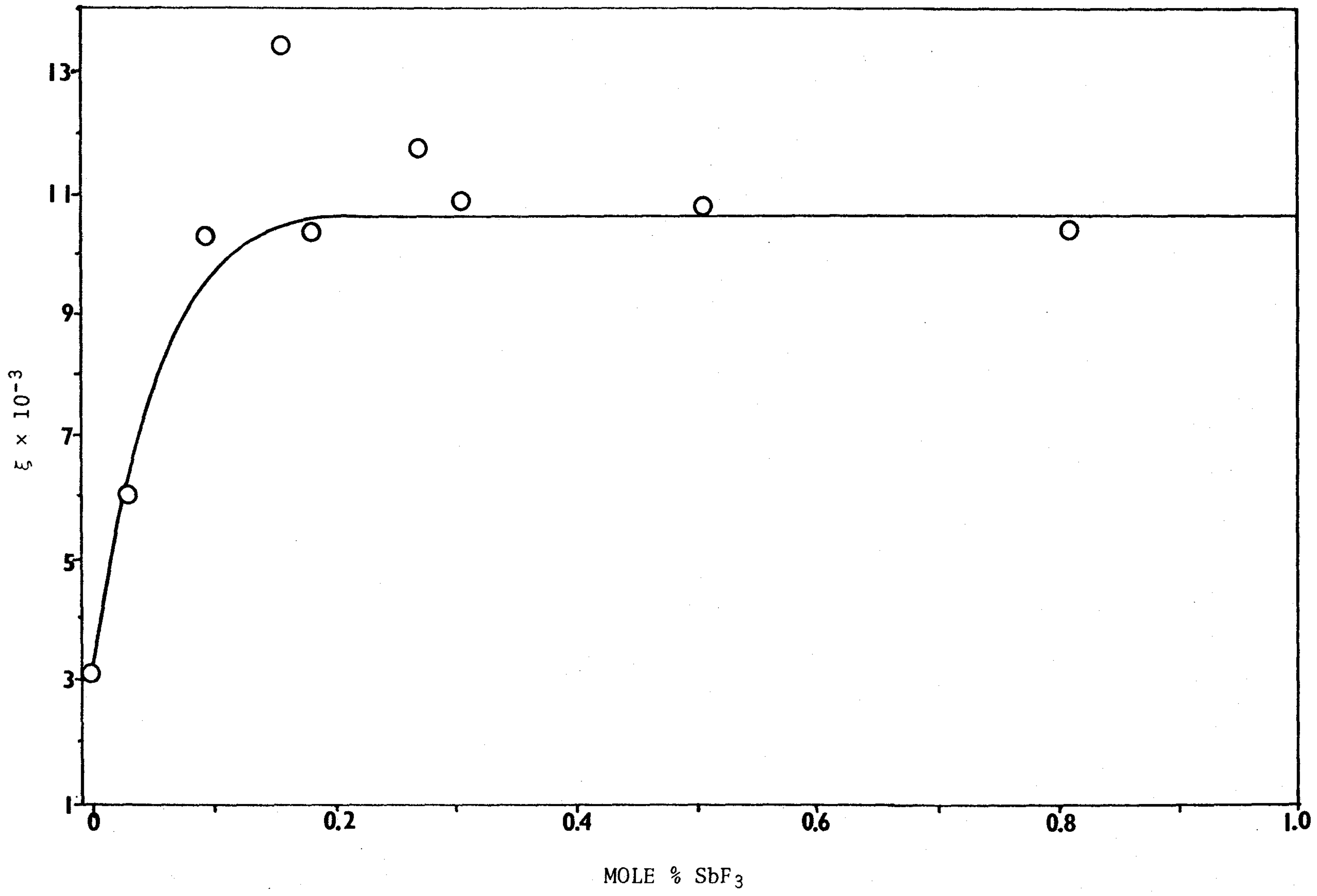

Figure 21. Extinction Coefficients of 2,4,6-Trinitrotoluene in Dilute Solutions of SbF_5 in HSO_3F

TABLE XLII

IONIZATION RATIOS OF 2,4,6-TRINITROTOLUENE IN DILUTE SOLUTIONS OF SbF_5 IN HSO_3F

$\xi_B = 960$ $\xi_{BH^+} = 10,600$ $pK_{BH^+} = -15.60$

mole % SbF_5	ξ	log I
0.010	4,150	0.31
0.020	5,150	0.11
0.030	6,100	-0.06
0.040	6,920	-0.21
0.050	7,630	-0.35
0.075	8,890	-0.67
0.100	9,600	-0.94
0.125	10,200	-1.36

TABLE XLIII

EXTINCTION COEFFICIENTS OF 1,3,5-TRINITROBENZENE IN HSO_3F-SbF_5

mole % SbF_5	ξ	λ_{max} (nm)
0.03007	3,080	300
0.09515	8,260	302
0.1567	11,224	305
0.1812	9,241	302
0.2707	10,403	302
0.3059	10,325	303
0.5053	10,717	302
0.8118	10,821	300
1.3054	9,526	304
1.4792	11,188	301
1.6861	10,329	300
1.7750	10,299	302
1.9238	11,486	300
2.5863	9,785	298
3.8970	13,604	296
6.7391	13,229	290
9.2229	14,151	288

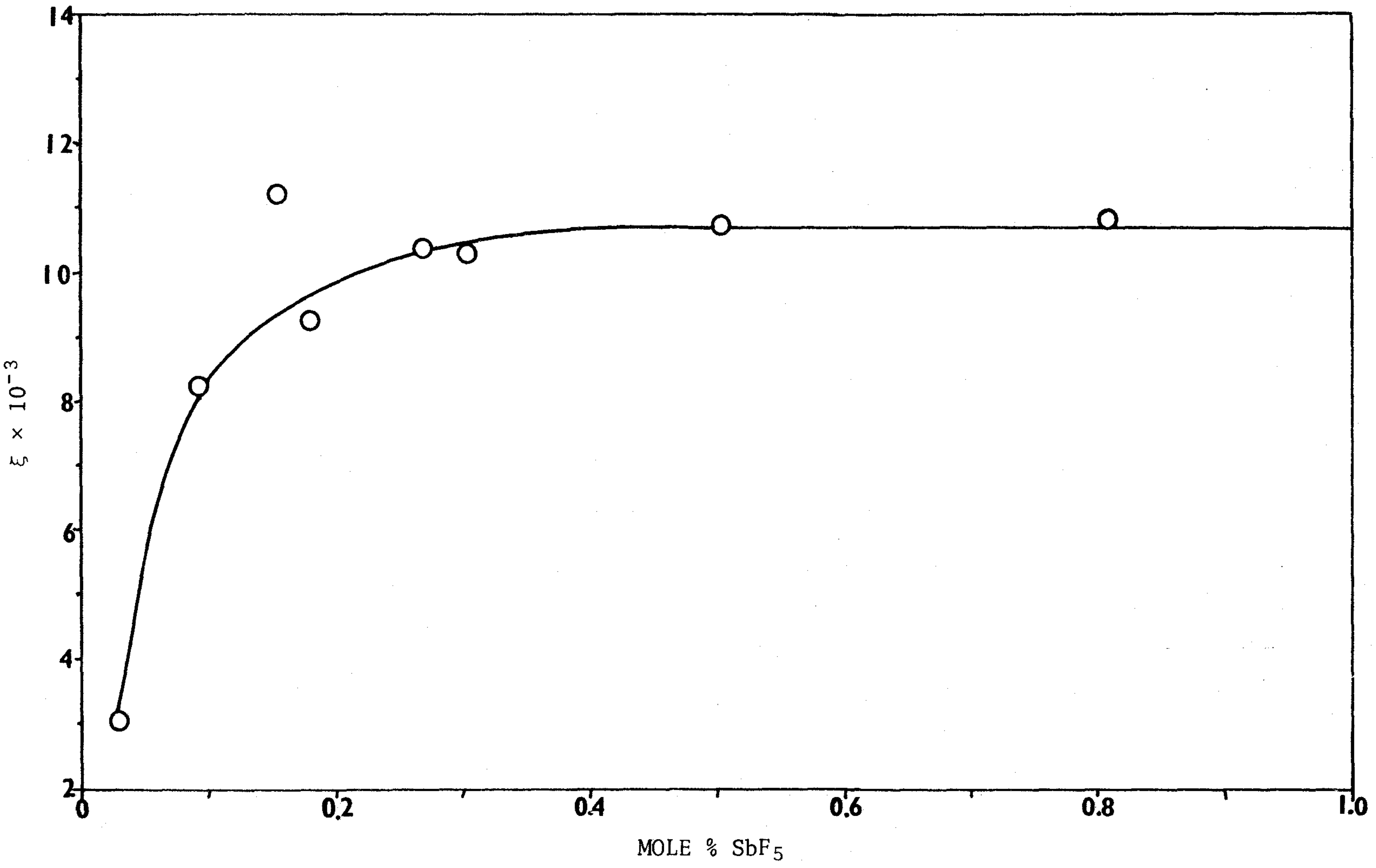

Figure 22. Extinction Coefficients of 1,3,5-Trinitrobenzene in Dilute Solutions of SbF_5 in HSO_3F

TABLE XLIV

IONIZATION RATIOS OF 1,3,5-TRINITROBENZENE IN DILUTE SOLUTIONS OF SbF_5 IN HSO_3F

$\xi_B = 800$ $\xi_{BH^+} = 10,700$ $pK_{BH^+} = -16.04$

mole % SbF_5	ξ	log I
0.030	3,200	0.50
0.040	4,300	0.26
0.050	5,360	0.07
0.060	6,220	-0.08
0.070	7,000	-0.22
0.080	7,550	-0.33
0.090	8,000	-0.42
0.100	8,360	-0.51
0.125	8,890	-0.65
0.150	9,260	-0.77
0.175	9,580	-0.89
0.200	9,830	-1.02

TABLE XLV

EXTINCTION COEFFICIENTS OF 2,4,6-TRINITROCHLOROBENZENE IN HSO_3F-SbF_5

mole % SbF_5	ξ	λ_{max} (nm)
0.03007	3,008	340
0.04267	7,958	338
0.1210	9,749	339
0.2707	9,806	340
0.3059	9,764	340
0.5053	10,396	338
0.8118	10,950	338
1.4792	11,254	336
1.7750	11,534	336
1.9238	11,338	337
3.5148	11,954	334
4.1807	11,258	332
7.0268	12,715	326

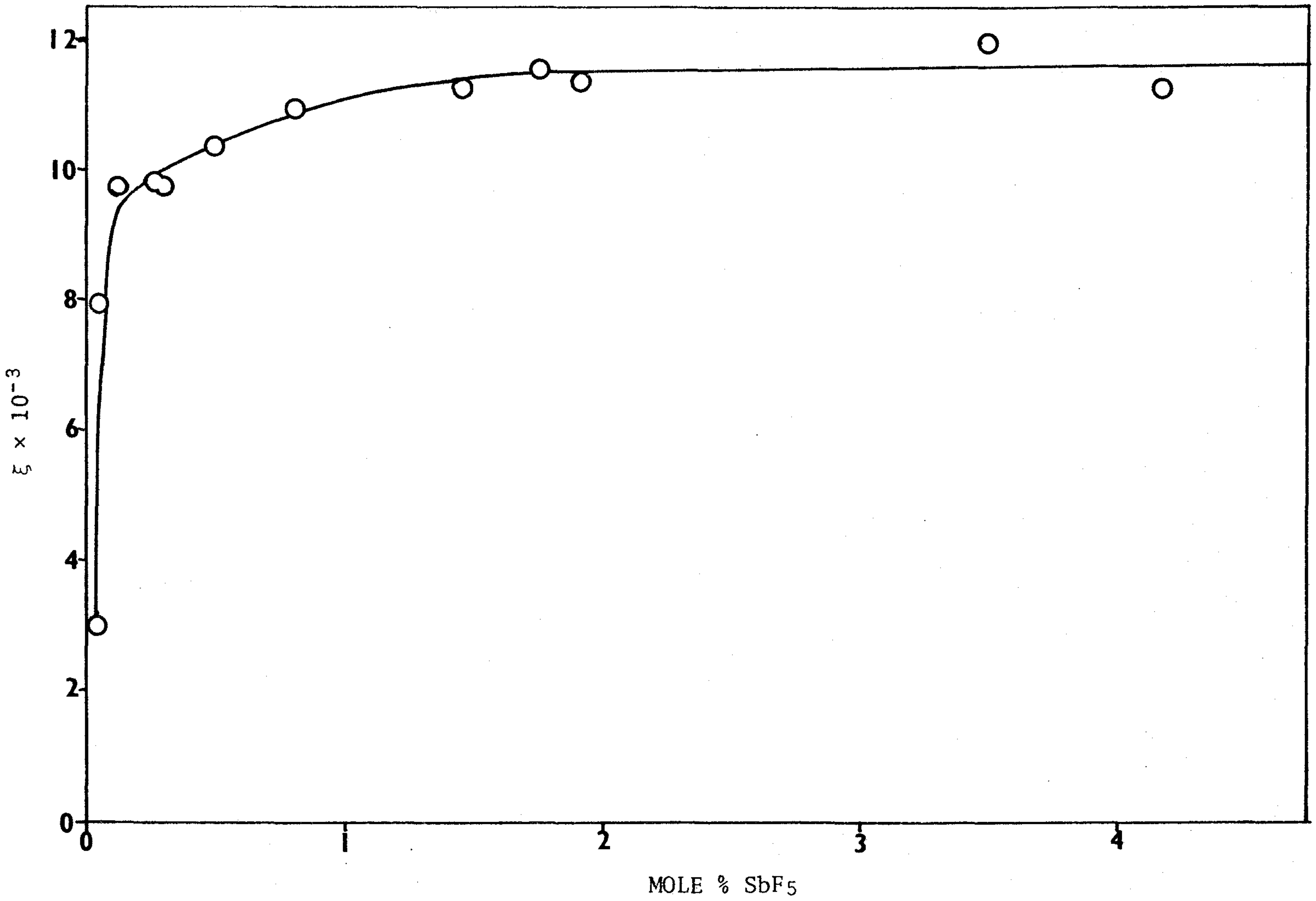

Figure 23. Extinction Coefficients of 2,4,6-Trinitrochlorobenzene in HSO_3F-SbF_5

TABLE XLVI

IONIZATION RATIOS OF 2,4,6-TRINITROCHLOROBENZENE IN DILUTE SOLUTIONS OF SbF_5 IN HSO_3F

$\xi_B = 700$ $\xi_{BH^+} = 11,600$ $pK_{BH^+} = -16.12$

mole % SbF_5	ξ	log I
0.030	3,300	0.50
0.040	4,500	0.27
0.060	6,600	-0.07
0.080	8,000	-0.31
0.100	8,850	-0.47
0.120	9,240	-0.56
0.140	9,480	-0.62
0.160	9,630	-0.66
0.180	9,780	-0.70
0.200	9,900	-0.73
0.224	10,000	-0.76
0.249	10,060	-0.78
0.274	10,110	-0.80
0.299	10,140	-0.81
0.349	10,220	-0.84
0.398	10,300	-0.87
0.497	10,480	-0.94
0.563	10,610	-1.00

TABLE XLVII

EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE IN HSO_3F-SbF_5

mole % SbF_5	ξ	λ_{max} (nm)
0.03007	11,931	332
0.04963	12,029	331
0.09510	13,153	331
0.09908	11,975	327
0.1355	13,494	325
0.1567	12,984	328
0.1812	11,108	327
0.2061	12,291	322
0.2707	13,389	325
0.3059	12,640	323
0.3195	12,036	322
0.5021	12,956	313
0.5053	12,601	317
0.8118	14,035	309
0.9778	13,823	304
1.2326	16,252	305
1.3054	12,974	308
1.4792	13,604	304
1.7750	15,900	302
1.9238	16,788	302
2.4377	16,896	302
3.5148	19,379	300
3.5454	16,803	301
3.5904	18,953	300
4.1807	19,705	300
5.1752	19,420	300
5.2531	19,265	299
6.8557	20,406	299
7.0268	21,283	300
8.7379	19,830	300
10.0810	21,856	300
19.8718	20,441	298
23.6052	21,172	298
49.1353	22,246	300

TABLE XLVIII

REPRESENTATIVE ABSORPTION SPECTRA OF 2,4-DINITROFLUOROBENZENE IN HSO_3F-SbF_5

mole % SbF_5	0.3059	0.5053	0.8118	1.3054	1.4792	1.7750	1.9238
λ (nm)	ξ	ξ	ξ	ξ	ξ	ξ	ξ
200	9,600	8,510	9,820	-	-	-	-
210	8,920	8,090	8,550	7,340	6,680	13,450	10,780
220	8,880	8,180	8,000	6,570	5,970	9,470	7,900
230	8,720	7,890	7,500	5,680	5,330	7,000	6,300
240	7,560	6,830	6,330	4,230	4,440	5,440	5,030
250	6,590	5,970	5,580	3,070	3,990	3,600	4,480
260	6,020	5,650	5,650	2,880	4,470	3,630	5,240
270	5,880	5,890	6,450	4,050	6,033	5,360	7,500
280	6,640	7,140	8,620	6,810	8,870	8,910	11,130
290	8,540	9,480	11,420	10,260	12,070	13,370	15,100
300	10,450	11,350	13,550	12,550	13,490	15,770	16,740
310	11,910	12,410	14,010	12,970	13,190	15,360	16,060
320	12,600	12,560	13,420	12,120	11,940	13,690	13,940
330	12,400	12,140	12,530	11,060	10,480	11,920	12,080
340	11,360	11,040	11,080	9,520	9,010	9,950	10,160
350	9,280	8,990	8,810	7,370	6,980	7,480	7,610
360	6,520	6,300	5,980	4,980	4,660	4,870	5,030
370	3,760	3,570	3,300	2,730	2,530	2,580	2,740
380	1,790	1,650	1,570	1,260	1,180	1,210	1,270
390	810	720	670	510	450	490	520
400	320	260	250	200	140	160	210
410	160	120	110	100	40	60	100
420	90	30	50	50	-	20	-
λ_{max}	323	317	309	308	304	302	302
ξ_{max}	12,640	12,600	14,040	12,970	13,600	15,900	16,790

TABLE XLVIII (cont.)

mole % SbF_5	3.5148	3.5454	4.1807	5.2531	6.8557	7.0268	10.0810
λ (nm)	ξ	ξ	ξ	ξ	ξ	ξ	ξ
220	6,860	6,500	6,510	5,710	5,640	6,580	5,650
230	6,140	5,770	5,180	4,530	4,600	5,170	4,400
240	4,630	4,200	3,800	3,230	3,200	3,700	2,860
250	4,360	3,560	3,450	3,120	3,200	3,470	2,470
260	5,440	4,400	4,680	4,550	4,920	5,050	4,240
270	8,690	6,690	8,110	8,210	8,490	8,950	8,390
280	13,380	10,640	12,830	13,270	13,550	14,370	14,120
290	17,870	14,930	17,660	17,670	18,460	19,640	19,740
300	19,380	16,780	19,700	19,270	20,390	21,280	21,860
310	18,090	15,660	18,030	17,190	18,390	18,900	19,420
320	14,880	13,160	14,640	13,890	14,500	14,660	15,180
330	12,490	11,030	12,020	11,180	11,850	11,830	11,950
340	10,310	8,990	9,710	8,980	9,230	9,300	9,230
350	7,540	6,660	7,100	6,460	6,700	6,580	6,530
360	4,900	4,120	4,370	4,080	4,120	4,050	3,870
370	2,930	2,350	2,380	2,230	2,160	2,280	1,980
380	1,560	1,200	1,160	1,040	1,100	1,200	1,010
390	810	700	500	460	530	660	450
400	540	500	240	240	300	440	260
410	350	340	130	140	180	330	180
420	190	250	90	70	80	210	110
λ_{max}	300	301	300	299	299	300	300
ξ_{max}	19,380	16,800	19,700	19,270	20,410	21,280	21,860

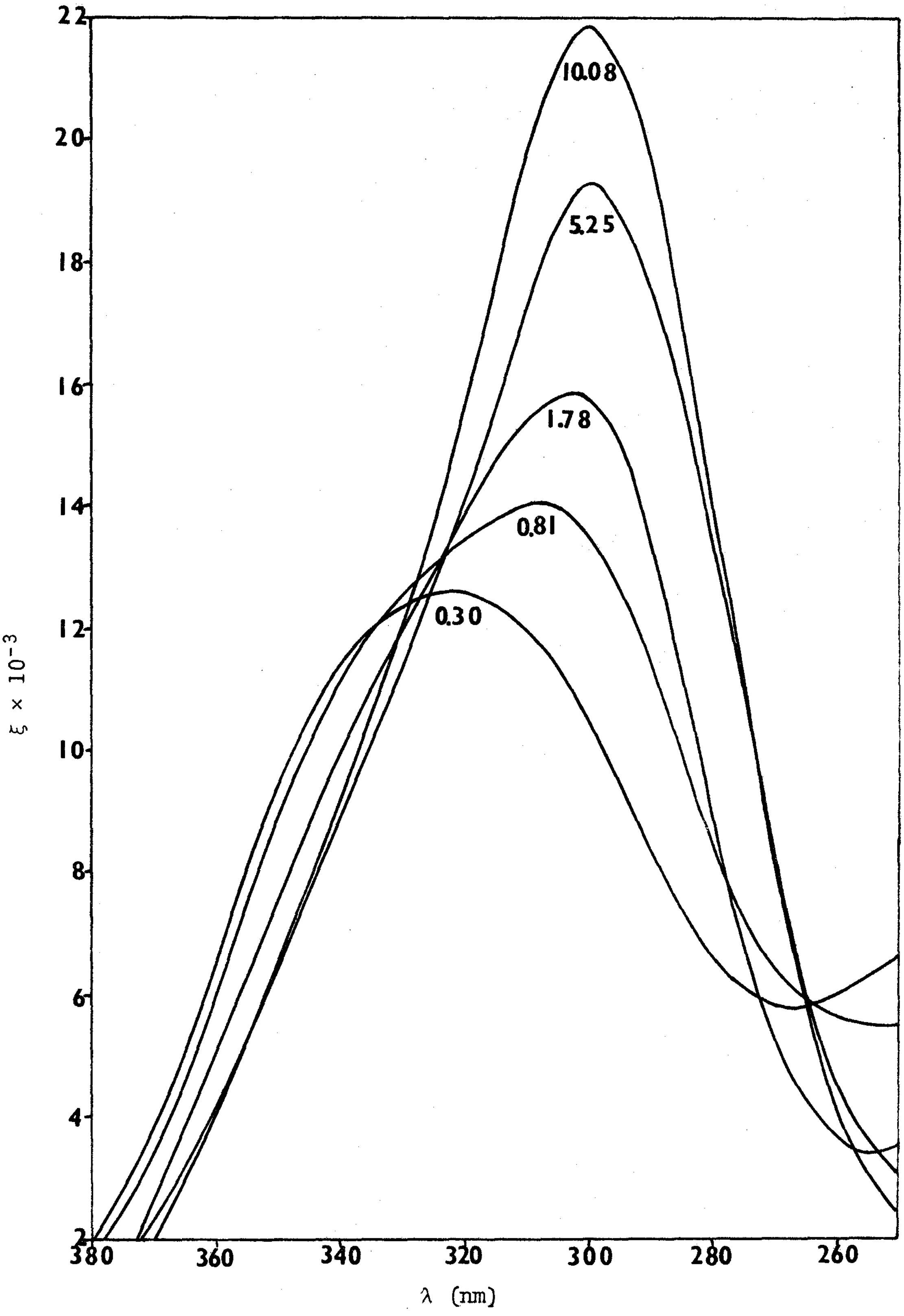

Figure 24. Representative Absorption Spectra of 2,4-Dinitrofluorobenzene in HSO_3F-SbF_5

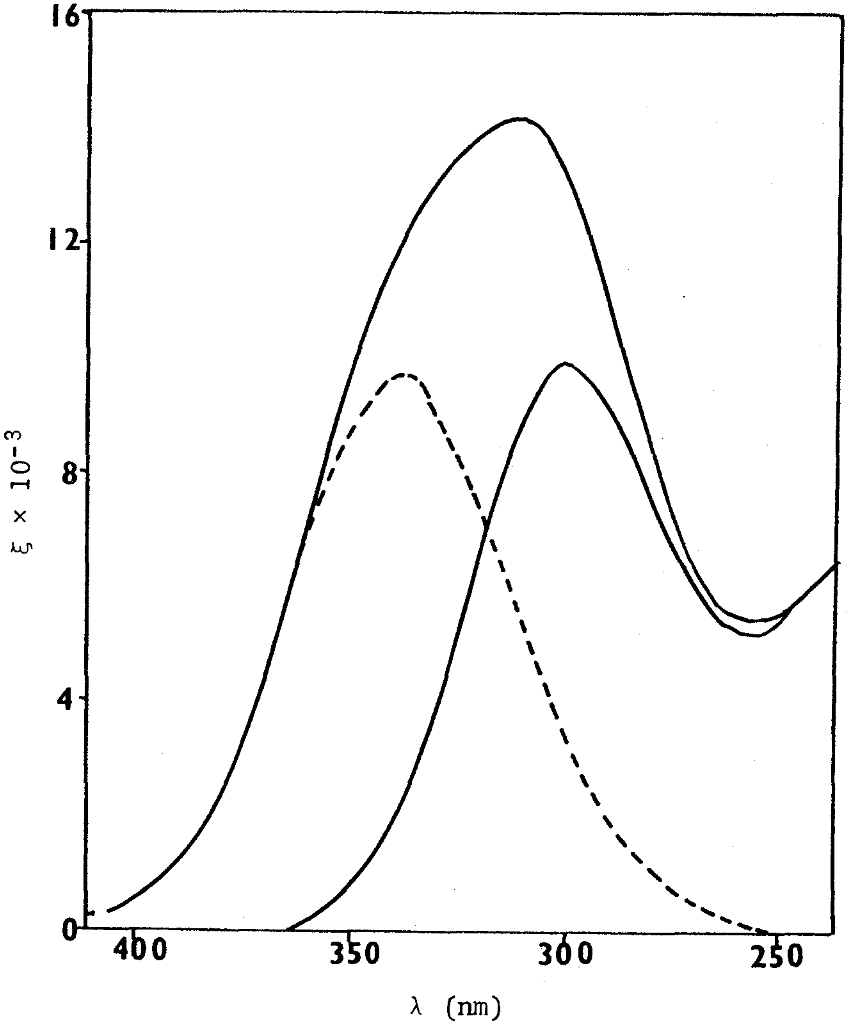

Figure 25. Absorption Spectra of 2,4-Dinitrofluoro benzene in 0.8118 mole % SbF_5

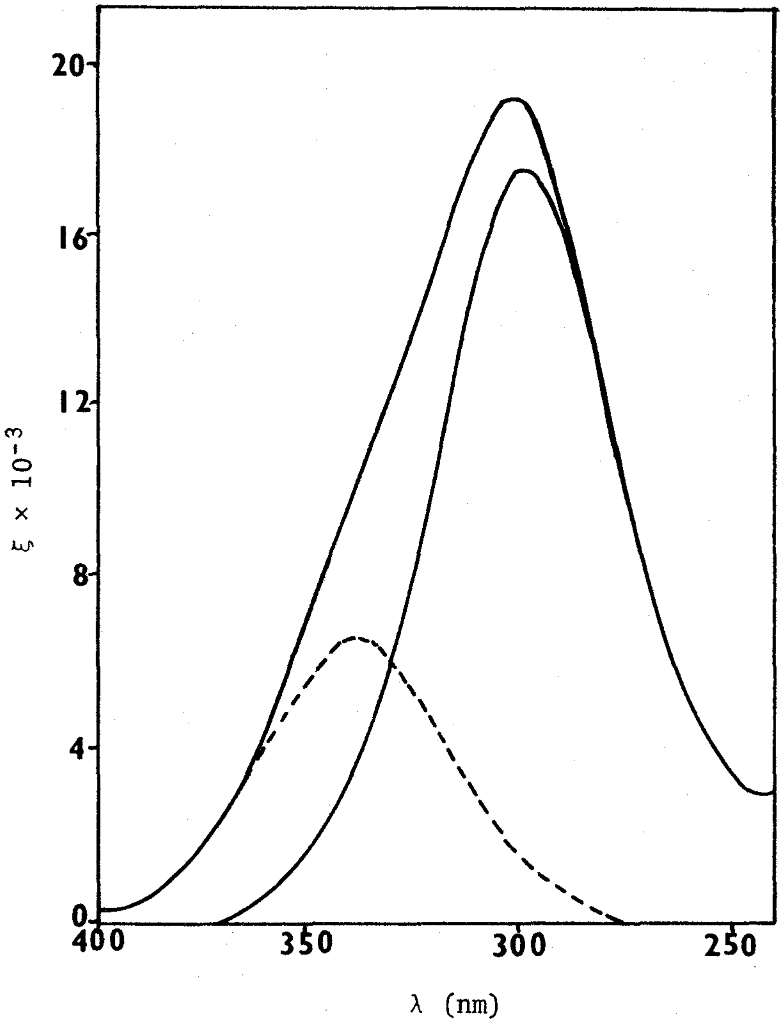

Figure 26. Absorption Spectra of 2,4-Dinitrofluorobenzene in 5.2531 mole % SbF_5

TABLE XLIX

ADJUSTED EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE IN HSO_3F-SbF_5

mole % SbF_5	ξ	λ
0.04963	900	300
0.09908	4,300	300
0.2061	5,550	300
0.3059	6,750	300
0.3195	5,700	300
0.5021	7,650	300
0.5053	7,800	300
0.8118	9,800	300
0.9778	10,950	300
1.2326	11,180	300
1.3054	9,850	300
1.4792	11,450	299
1.7750	13,600	299
1.9238	15,400	299
2.4377	12,950	300
3.5148	18,600	299
3.5454	14,900	299
3.5904	17,200	300
4.1807	18,800	299
5.1752	18,200	298
5.2531	18,000	299
6.8557	18,950	298
7.0268	20,300	297
8.7379	18,700	297
10.0810	20,350	297
19.8718	19,550	297
23.6052	20,700	298
49.1353	21,000	299

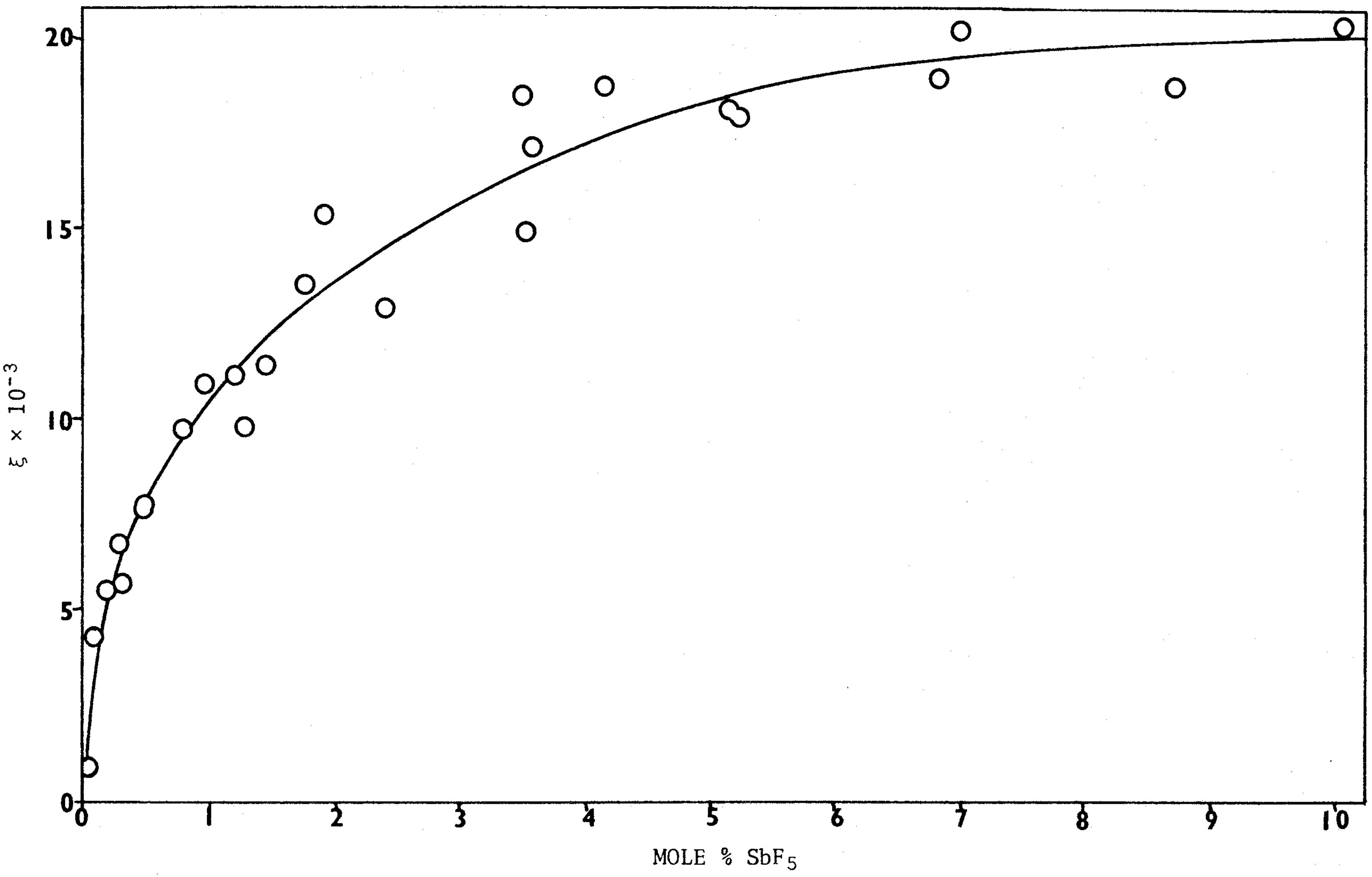

Figure 27. Adjusted Extinction Coefficients of 2,4-Dinitrofluorobenzene in HSO_3F-SbF_5

TABLE L

IONIZATION RATIOS OF 2,4-DINITROFLUOROBENZENE IN HSO_3F-SbF_5

$\xi_{BH^+} = 900$ $\xi_{BH_2^{+2}} = 20,450$ $pK_{BH_2^{+2}} = -17.35$

mole % SbF_5	ξ	log I
0.10	3,600	0.80
0.20	5,180	0.55
0.30	6,260	0.42
0.40	7,110	0.33
0.50	7,840	0.26
0.60	8,480	0.20
0.80	9,500	0.11
1.00	10,390	0.03
1.20	11,180	-0.04
1.40	11,910	-0.11
1.60	12,520	-0.17
1.80	13,040	-0.21
2.00	13,550	-0.26
2.50	14,700	-0.38
3.00	15,720	-0.50
3.50	16,570	-0.61
4.00	17,310	-0.72
4.50	17,880	-0.82
5.00	18,380	-0.95
5.50	18,770	-1.03

TABLE LI

REPRESENTATIVE ABSORPTION SPECTRA OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SbF_5

mole % SbF_5	0.5053	0.8118	1.4792	1.7750	1.9238	3.3872	3.5454
λ (nm)	ξ	ξ	ξ	ξ	ξ	ξ	ξ
200	15,220	14,150	-	-	-	-	-
210	16,030	14,740	16,070	18,320	18,560	-	-
220	16,580	15,000	16,200	16,540	17,420	15,210	16,960
230	14,620	13,280	13,820	13,260	14,150	12,760	14,500
240	11,450	10,570	10,660	9,830	10,890	9,540	10,810
250	9,360	8,620	8,730	7,420	9,000	7,680	8,790
260	7,800	7,250	7,640	5,950	7,950	7,130	7,930
270	6,160	6,070	6,730	5,090	7,420	7,250	8,040
280	5,450	5,740	6,800	5,490	7,950	8,170	9,370
290	6,260	6,660	8,150	7,210	9,350	9,790	11,420
300	7,920	8,210	9,670	9,210	10,850	11,220	13,140
310	9,810	9,660	10,970	10,500	11,750	11,900	13,580
320	10,760	10,300	11,240	10,850	11,620	11,050	12,750
330	10,280	9,660	10,310	9,820	10,510	9,400	11,000
340	8,750	8,180	8,650	8,080	8,600	7,380	8,760
350	6,740	6,290	6,530	6,100	6,530	5,550	6,620
360	4,720	4,410	4,590	4,230	4,660	3,840	4,710
370	2,910	2,750	2,820	2,570	2,900	2,300	3,050
380	1,660	1,570	1,520	1,450	1,620	1,320	1,940
390	870	830	800	740	850	660	1,160
400	400	400	300	340	380	290	780
410	200	170	160	150	200	-	500
420	90	70	90	70	110	-	360
λ_{max}	322	321	318	317	316	310	308
ξ_{max}	10,780	10,320	11,300	10,880	11,870	11,990	13,610

TABLE LI (cont.)

mole % SbF_5	5.2531	6.8557	7.0268	9.3710	10.0810
λ (nm)	ξ	ξ	ξ	ξ	ξ
220	15,780	15,950	16,420	15,310	15,070
230	13,180	13,480	13,560	14,930	12,340
240	9,750	9,970	10,040	9,910	8,970
250	8,110	8,330	8,330	8,890	7,240
260	7,900	8,350	8,500	9,250	7,460
270	8,830	9,650	10,090	10,530	9,430
280	10,700	11,900	12,490	12,410	12,460
290	12,920	14,590	15,020	14,860	15,350
300	14,240	15,750	16,300	15,920	16,580
310	14,050	15,020	15,470	15,430	15,580
320	12,630	13,220	13,420	13,110	12,950
330	10,360	10,620	10,570	10,300	10,040
340	8,090	8,250	8,160	7,820	7,460
350	5,910	5,980	5,970	5,510	5,320
360	4,150	4,240	4,210	3,870	3,580
370	2,600	2,760	2,780	2,770	2,290
380	1,550	1,780	1,690	1,880	1,270
390	850	990	1,000	1,290	650
400	420	590	620	990	340
410	230	410	430	-	180
420	110	300	240	-	110
λ_{max}	304	300	302	302	300
ξ_{max}	14,360	15,750	16,300	15,960	16,580

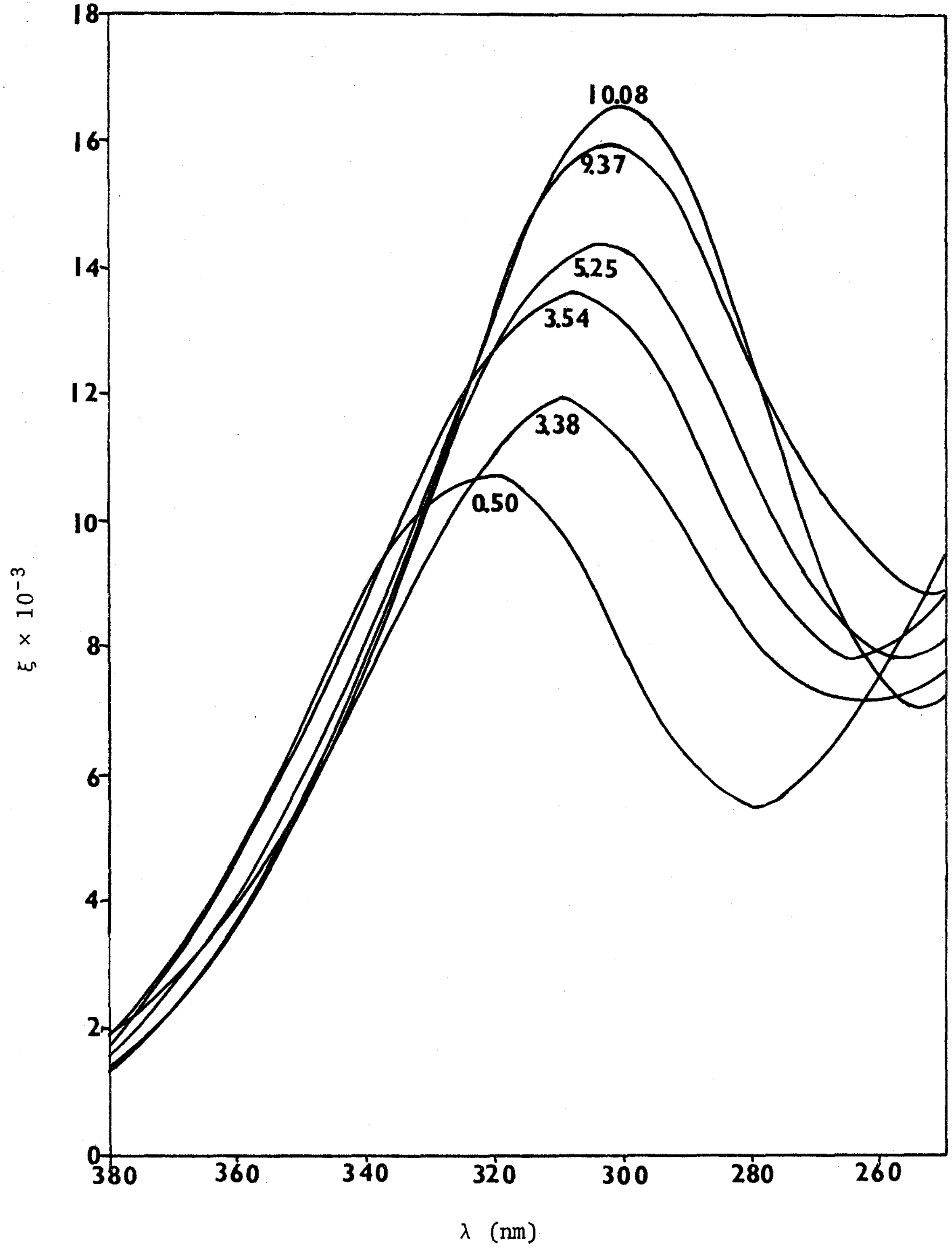

Figure 28. Representative Absorption Spectra of 2,4,6-Trinitrotoluene in HSO_3F-SbF_5

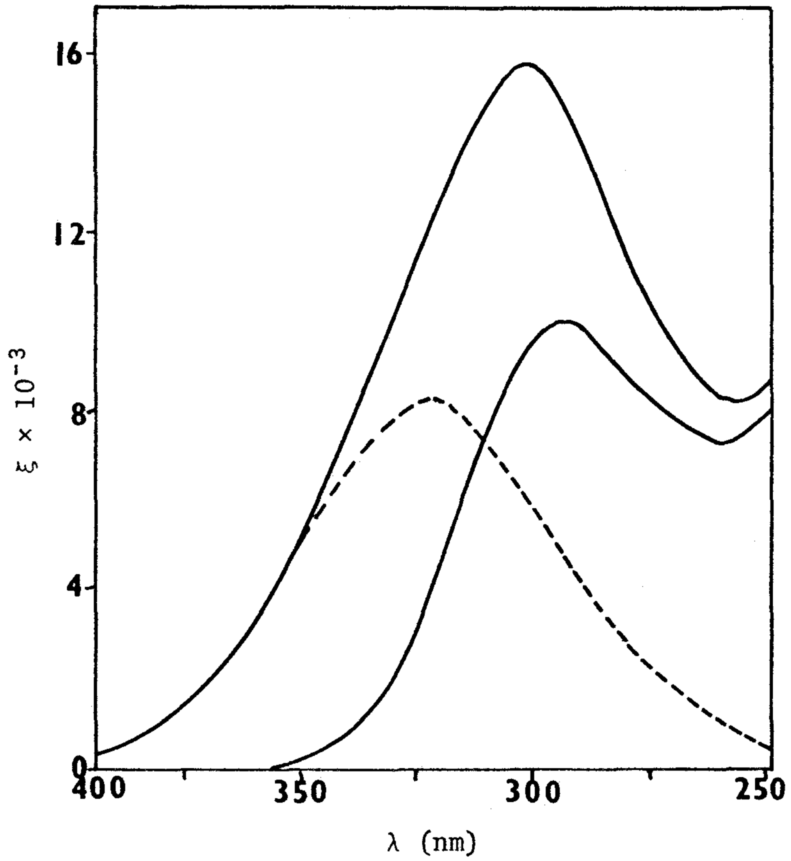

Figure 29. Absorption Spectra of 2,4,6-Trinitrotoluene in 6.8577 mole % SbF_5

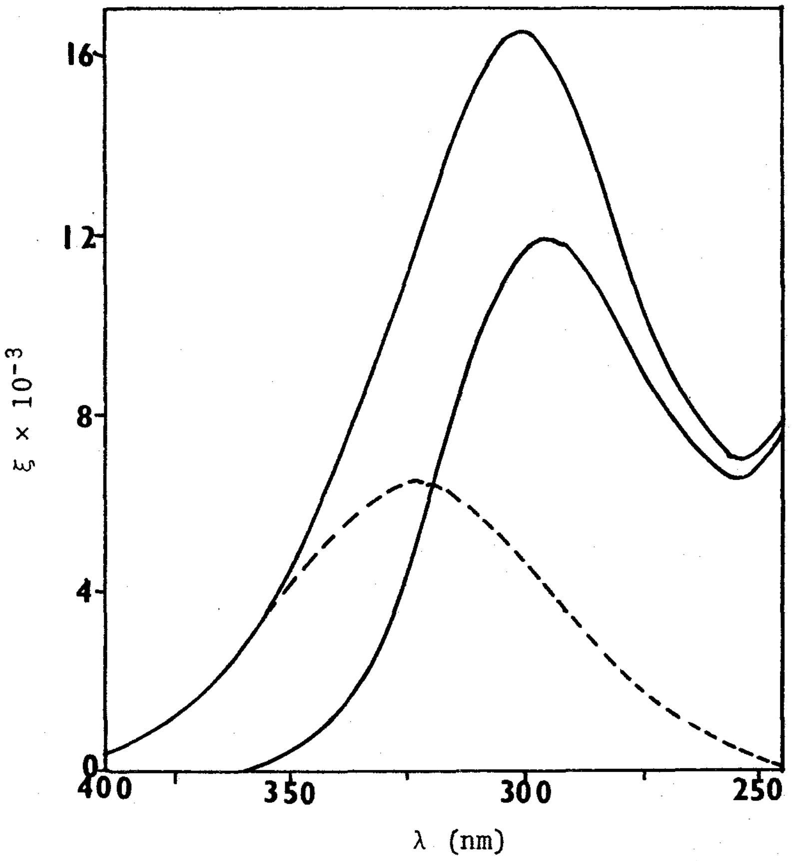

Figure 30. Absorption Spectra of 2,4,6-Trinitrotoluene in 10.0810 mole % SbF_5

TABLE LII

ADJUSTED EXTINCTION COEFFICIENTS OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SbF_5

mole % SbF_5	ξ	λ (nm)
0.5053	600	318
0.8118	0	300
1.4792	2,200	305
1.7750	990	306
1.9238	3,150	305
3.3872	3,450	306
5.2531	6,700	300
6.8557	10,000	298
7.0268	10,500	297
9.3710	10,400	300
10.0810	11,900	298

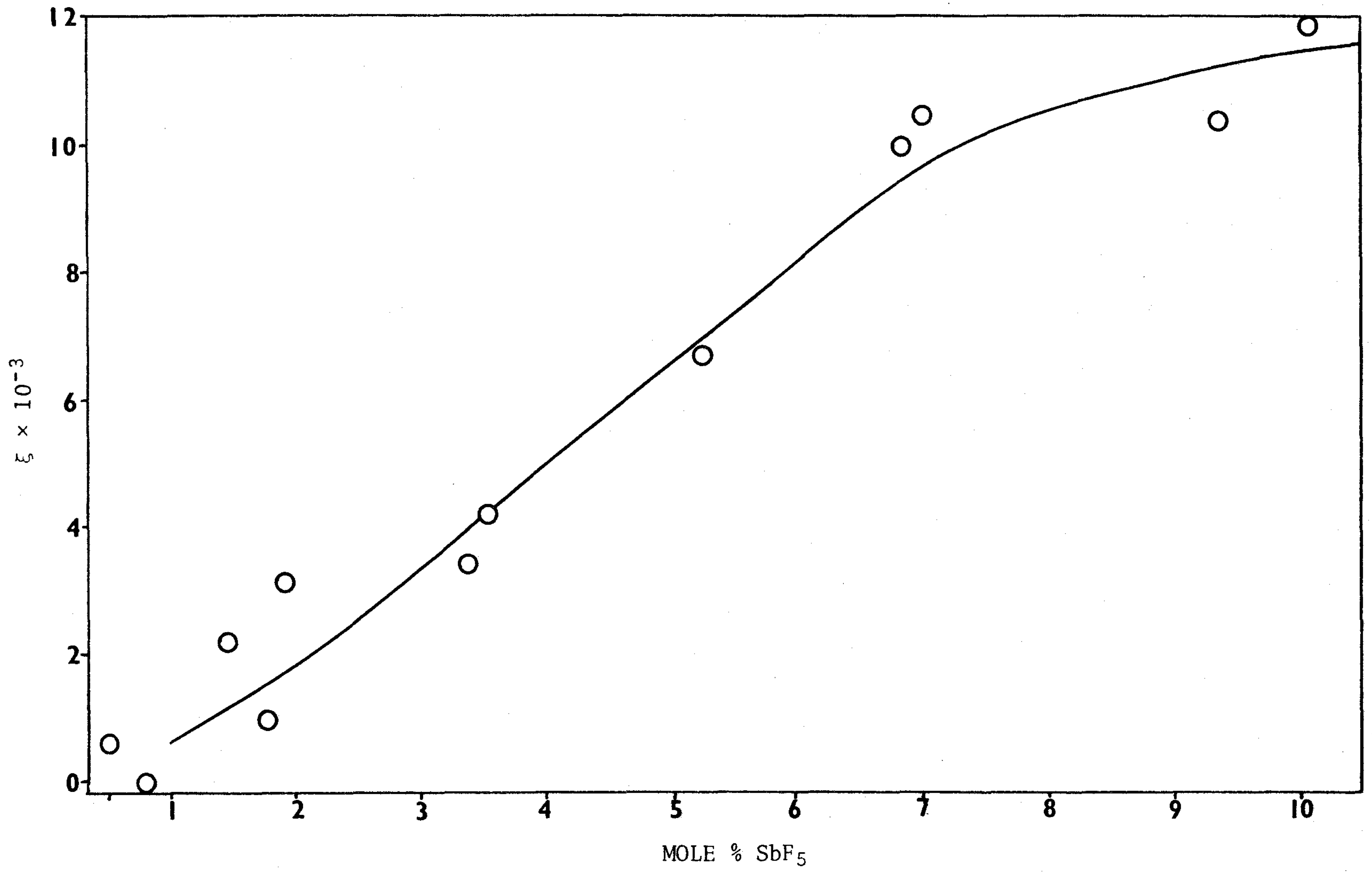

Figure 31. Adjusted Extinction Coefficients of 2,4,6-Trinitrotoluene in HSO_3F-SbF_5

TABLE LIII

IONIZATION RATIOS OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SbF_5

$\xi_B = 0$ $\xi_{BH^+} = 14{,}500$ $pK_{BH^+} = -18.36$

mole % SbF_5	ξ	log I
2.50	2,540	0.67
3.00	3,330	0.52
4.00	4,960	0.28
5.00	6,600	0.08
6.00	8,230	-0.12
7.00	9,710	-0.31
8.00	10,560	-0.43
9.00	11,120	-0.52
10.00	11,500	-0.58
11.00	11,770	-0.63

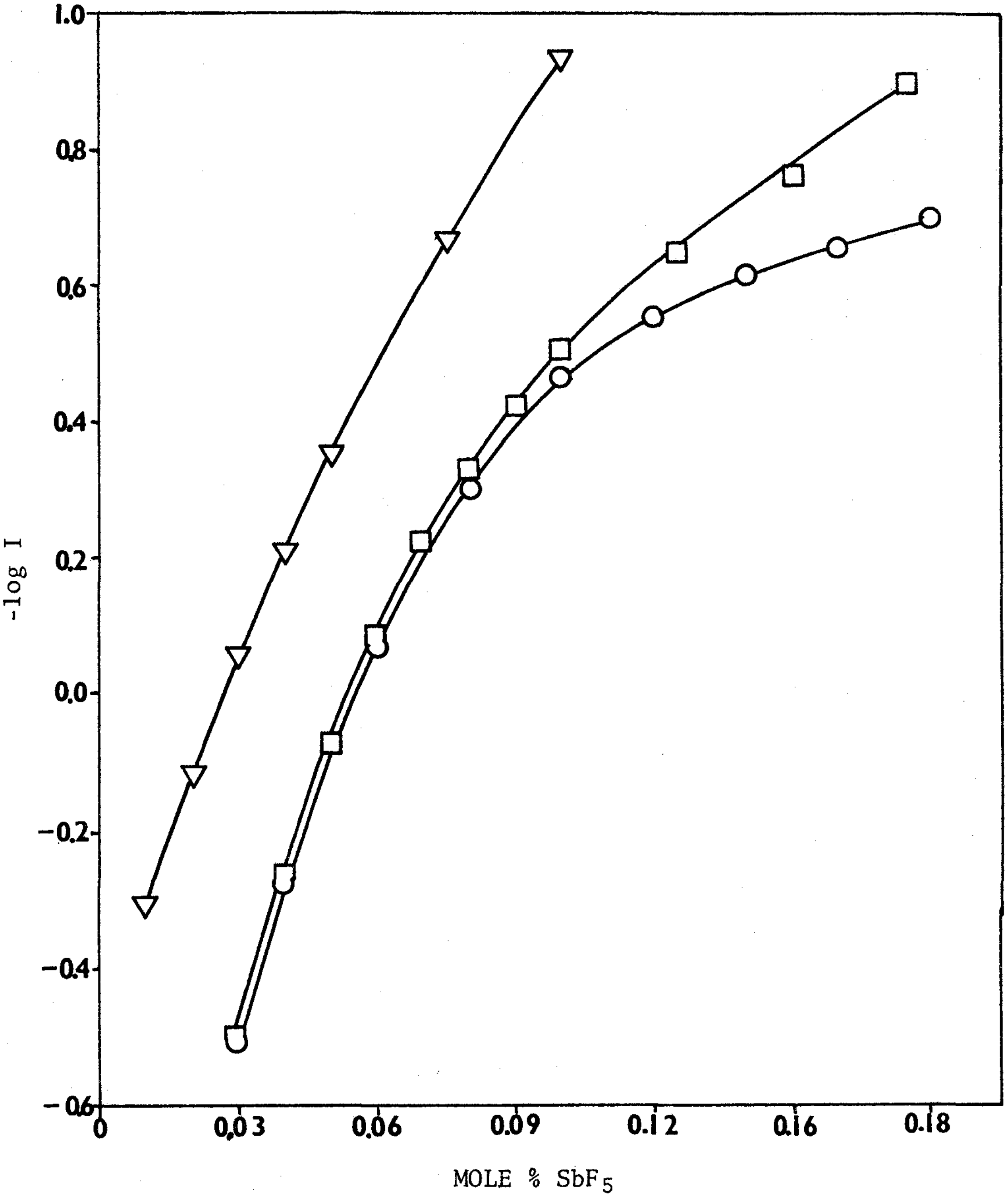

Figure 32. Ionization Ratios of 2,4,6-Trinitrotoluene (▽), 1,3,5-Trinitrobenzene (□), and 2,4,6-Trinitrochlorobenzene (○) in Dilute Solutions of SbF_5 in HSO_3F

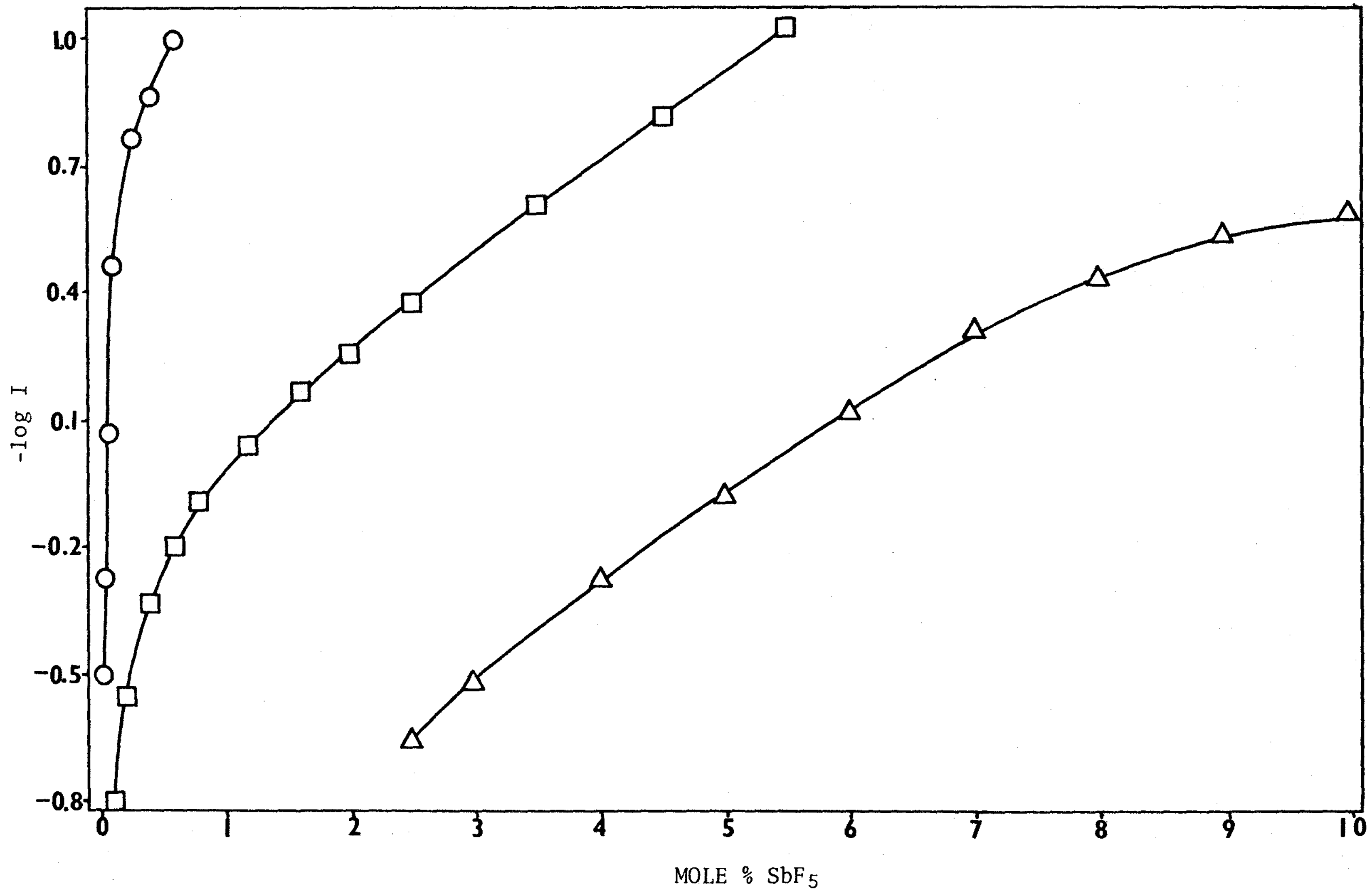

Figure 33. Ionization Ratios of 2,4,6-Trinitrochlorobenzene (○), Protonated 2,4-Dinitrofluorobenzene (□), and Protonated 2,4,6-Trinitrotoluene (△) in HSO_3F-SbF_5

TABLE LIV

-Ho VALUES FOR THE HSO_3F-SbF_5 SYSTEM

mole % SbF_5	2,4,6-TRINITRO-TOLUENE	1,3,5-TRINITRO-BENZENE	2,4,6-TRINITRO-CHLORO-BENZENE	PROTONATED 2,4-DINITRO-FLUORO-BENZENE	PROTONATED 2,4,6-TRINITRO-TOLUENE	AVERAGE -Ho
0.01	15.29					15.29
0.02	15.49					15.49
0.03	15.66	15.54	15.62			15.61
0.04	15.81	15.78	15.85			15.81
0.05	15.95	15.97	16.03			15.98
0.06	16.08	16.12	16.19			16.13
0.07	16.21	16.26	16.32			16.26
0.08	16.32	16.37	16.43			16.37
0.09	16.43	16.46	16.52			16.47
0.10	16.53	16.55	16.59	16.55		16.55
0.12		16.67	16.68	16.61		16.65
0.14		16.77	16.74	16.68		16.73
0.18			16.82	16.76		16.79
0.30			16.93	16.92		16.92
0.50			17.06	17.09		17.08
0.75				17.22		17.22
1.00				17.32		17.32
1.50				17.39		17.49
2.00				17.61		17.61
3.00				17.84	17.83	17.84
4.00				18.07	18.08	18.08
5.00				18.27	18.29	18.28
6.00					18.48	18.48
7.00					18.66	18.66
8.00					18.79	18.79
9.00					18.88	18.88
10.00					18.94	18.94
11.00					18.99	18.99

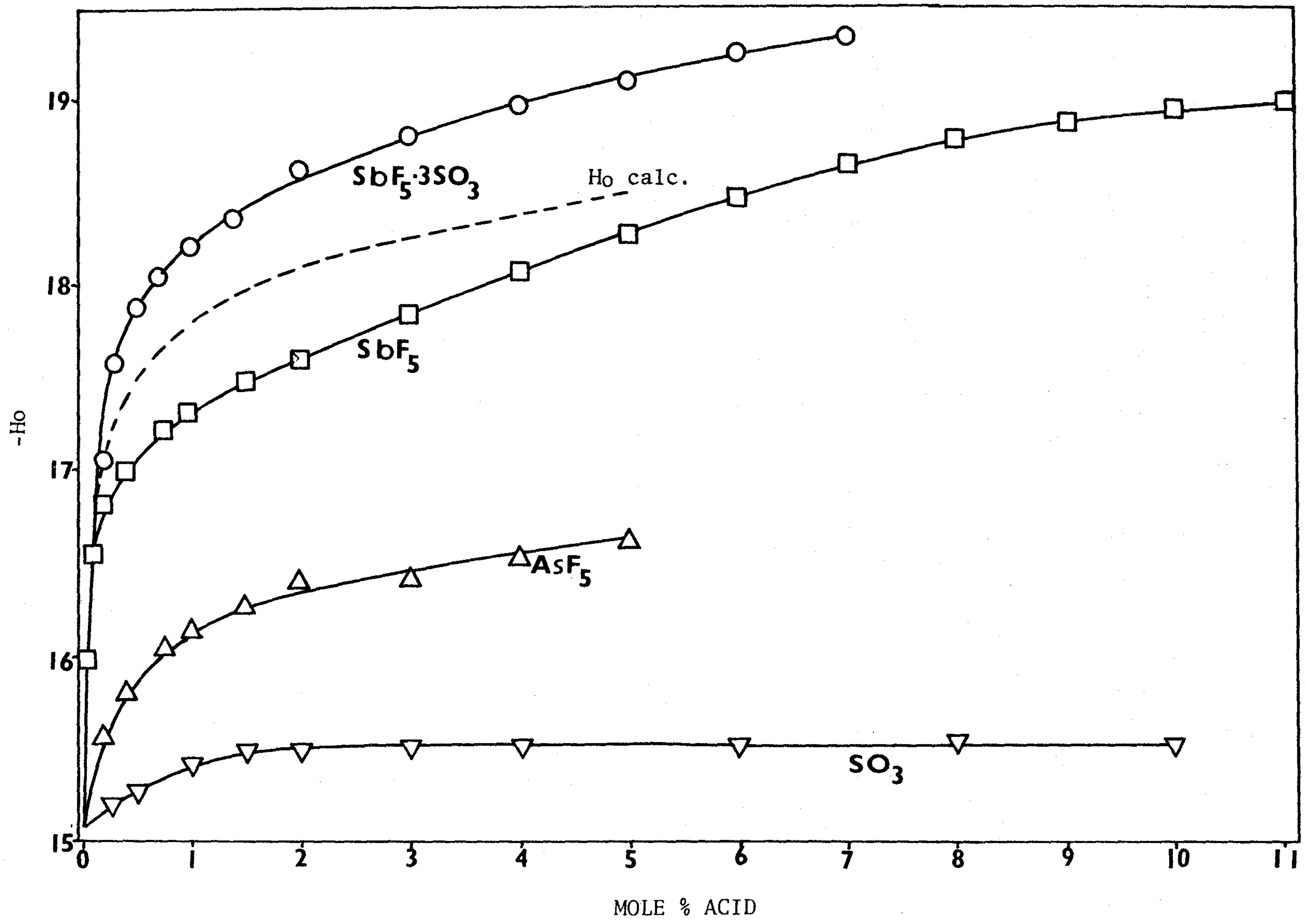

Figure 34. -Ho Values for Acids of the Fluorosulfuric Acid Solvent System

TABLE LV

EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE AND 1,3,5-TRINITROBENZENE AS A FUNCTION OF THE $SbF_5:SO_3$ MOLE RATIO

MOLE %	MOLE RATIO	2,4-DINITROFLUOROBENZENE		1,3,5-TRINITROBENZENE	
$SbF_5 \cdot xSO_3$	$SbF_5:SO_3$	ξ	λ_{max}	ξ	λ_{max}
2.00000	1:0.00000	16,300	302	10,700	300
2.00031	1:0.61110	18,025	302	12,370	299
2.00008	1:0.94665	17,530	300	11,410	298
2.00031	1:1.05151	20,810	299	14,645	293
1.99650	1:1.27542	18,410	302	12,360	294
1.99957	1:1.76394	20,590	300	13,610	294
1.99990	1:2.37051	21,120	300	14,070	292
1.99776	1:2.93001	21,270	300	14,740	294
1.99053	1:3.42401	21,620	300	14,420	292
1.99589	1:3.70011	20,540	300	14,870	291
1.99989	1:3.80769	19,290	300	14,405	290

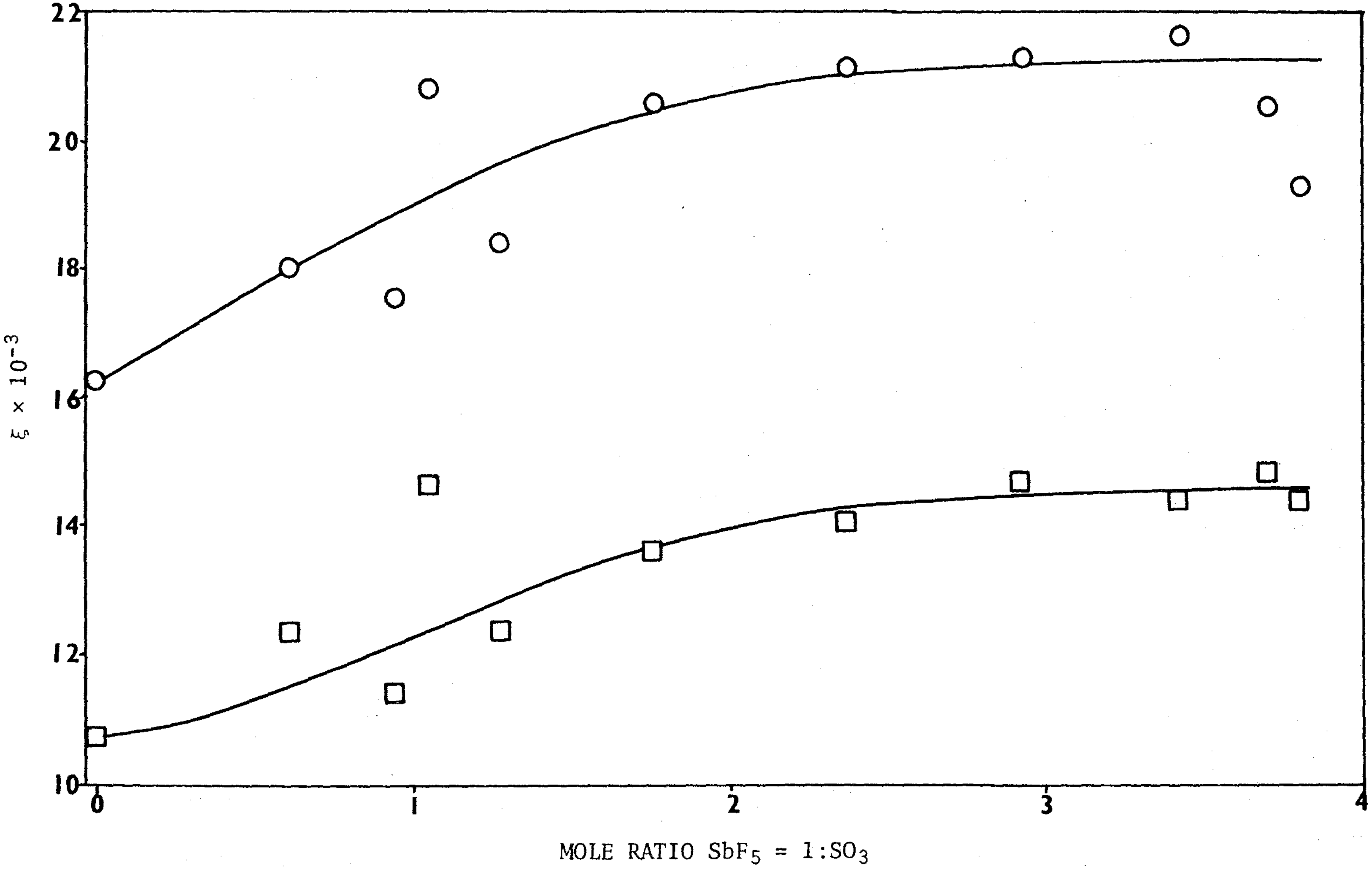

Figure 35. Extinction Coefficients of 2,4-Dinitrofluorobenzene (○) and 1,3,5-Trinitrobenzene (□) as a Function of the $SbF_5:SO_3$ Molar Ratio

TABLE LVI

OBSERVED AND ADJUSTED EXTINCTION COEFFICIENTS OF 2,4-DINITROFLUOROBENZENE IN HSO_3F-SbF_5-SO_3

MOLE % SbF_5-SO_3	MOLE RATIO SbF_5:SO_3	OBSERVED ξ	OBSERVED λ (nm)	ADJUSTED ξ	ADJUSTED λ (nm)
0.2016	1:3.48101	12,950	312	7,500	298
0.3722	1:3.80959	15,930	303	14.050	300
0.6602	1:3.29699	16,820	300	15,600	299
0.9836	1:3.27643	19,285	300	17,300	299
1.9959	1:3.70011	20,540	300	19,150	298
2.6936	1:3.27377	21,008	300	19,700	298
4.6674	1:3.32210	21,620	300	20,250	298
5.2543	1:3.31841	21,438	300	20,050	298
7.3032	1:3.27578	21,752	300	20,450	297
9.8280	1:3.50156	21,885	300	20,500	298
11.2654	1:3.30076	19,255	303	-	-
11.3512	1:3.26000	21,595	300	20,250	298
17.8938	1:3.29602	21,810	302	20,550	299

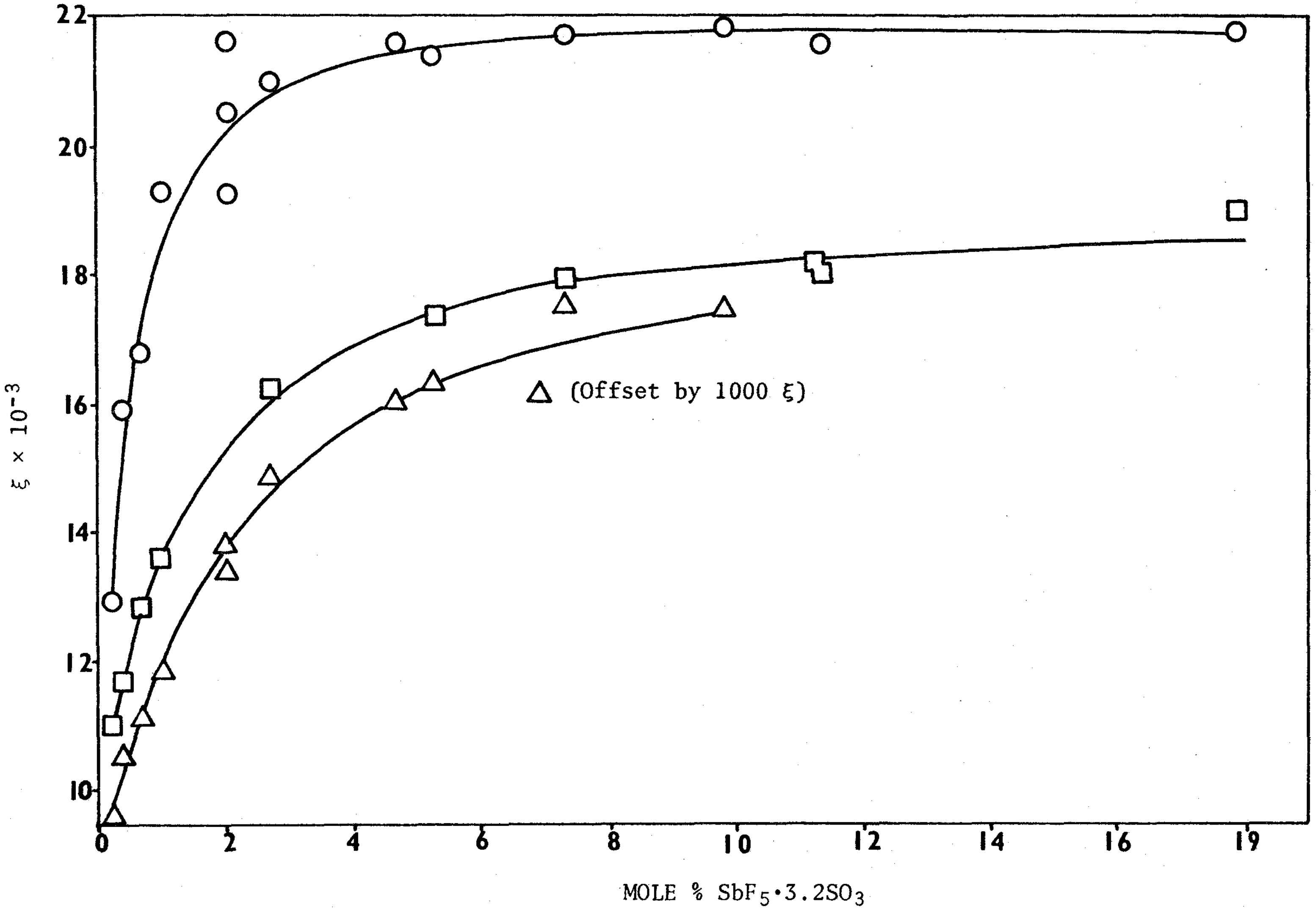

Figure 36. Observed Extinction Coefficients of 2,4-Dinitrofluorobenzene (○), 2,4,6-Trinitrotoluene (□), and 1,3,5-Trinitrobenzene (△) in HSO_3F-SbF_5-SO_3

TABLE LVII

ABSORPTION SPECTRA OF 2,4-DINITROFLUOROBENZENE IN HSO_3F-SbF_5-SO_3

MOLE % SbF_5-SO_3 MOLE RATIO $SbF_5:SO_3$ λ(nm)	0.2016 1:3.48101 ξ	0.3772 1:3.80959 ξ	0.6602 1:3.29699 ξ	0.9836 1:3.27643 ξ	1.9959 1:3.70011 ξ	2.6936 1:3.27377 ξ
230	7,550	-	-	-	-	-
240	6,840	5,450	-			
250	6,050	4,880	3,740	3,780	-	-
260	5,790	5,390	4,430	4,760	4,690	5,080
270	6,270	7,200	6,910	7,740	8,190	7,950
280	8,030	10,240	10,870	12,500	13,440	13,620
290	10,510	13,800	15,100	17,160	18,790	18,830
300	12,450	15,770	16,820	19,280	20,540	21,010
310	12,930	15,390	15,690	17,810	18,790	18,780
320	12,620	13,850	13,190	14,470	14,630	14,740
330	12,020	12,220	11,060	11,940	11,850	11,450
340	10,580	10,500	9,060	9,570	9,220	8,970
350	8,490	8,110	6,630	7,020	6,530	6,090
360	5,830	5,550	4,350	4,420	4,060	3,590
370	3,420	3,110	2,370	2,390	2,190	1,860
380	1,740	1,540	1,130	1,270	1,000	770
390	870	720	560	600	530	350
400	480	360	350	400	310	150
410	330	280	220	300	250	-
λ_{max}	312	303	300	300	300	300
ξ_{max}	12,950	15,930	16,820	19,280	20,540	21,010

TABLE LVII (cont.)

MOLE % SbF_5-SO_3	4.6674	5.2543	7.3032	9.8280	11.3512	17.8938
MOLE RATIO $SbF_5:SO_3$	1:3.32210	1:3.31843	1:3.27578	1:3.50156	1:3.26600	1:3.29602
λ(nm)	ξ	ξ	ξ	ξ	ξ	ξ
270	8,650	8,900	10,220	-	-	-
280	14,214	13,660	13,470	16,000	16,160	-
290	19,580	19,190	19,160	19,350	19,830	19,580
300	21,620	21,440	21,750	21,880	21,600	21,540
310	19,520	19,360	19,790	20,100	19,260	20.080
320	15,360	14,920	15,370	15,780	14,710	16,140
330	11,950	11,750	11,920	12,210	11,310	12,520
340	9,230	9,110	9,170	9,420	8,700	9,550
350	6,450	6,330	6,380	6,570	8,010	6,620
360	3,840	3,770	3,700	3,940	3,520	3,980
370	2,000	1,930	1,920	2,160	1,890	2,190
380	860	960	810	1,030	880	1,080
390	380	460	320	560	400	640
400	200	280	150	380	240	510
410	120	190	110	310	180	340
λ_{max}	300	300	300	300	300	302
ξ_{max}	21,621	21,438	21,750	21,880	21,600	21,810

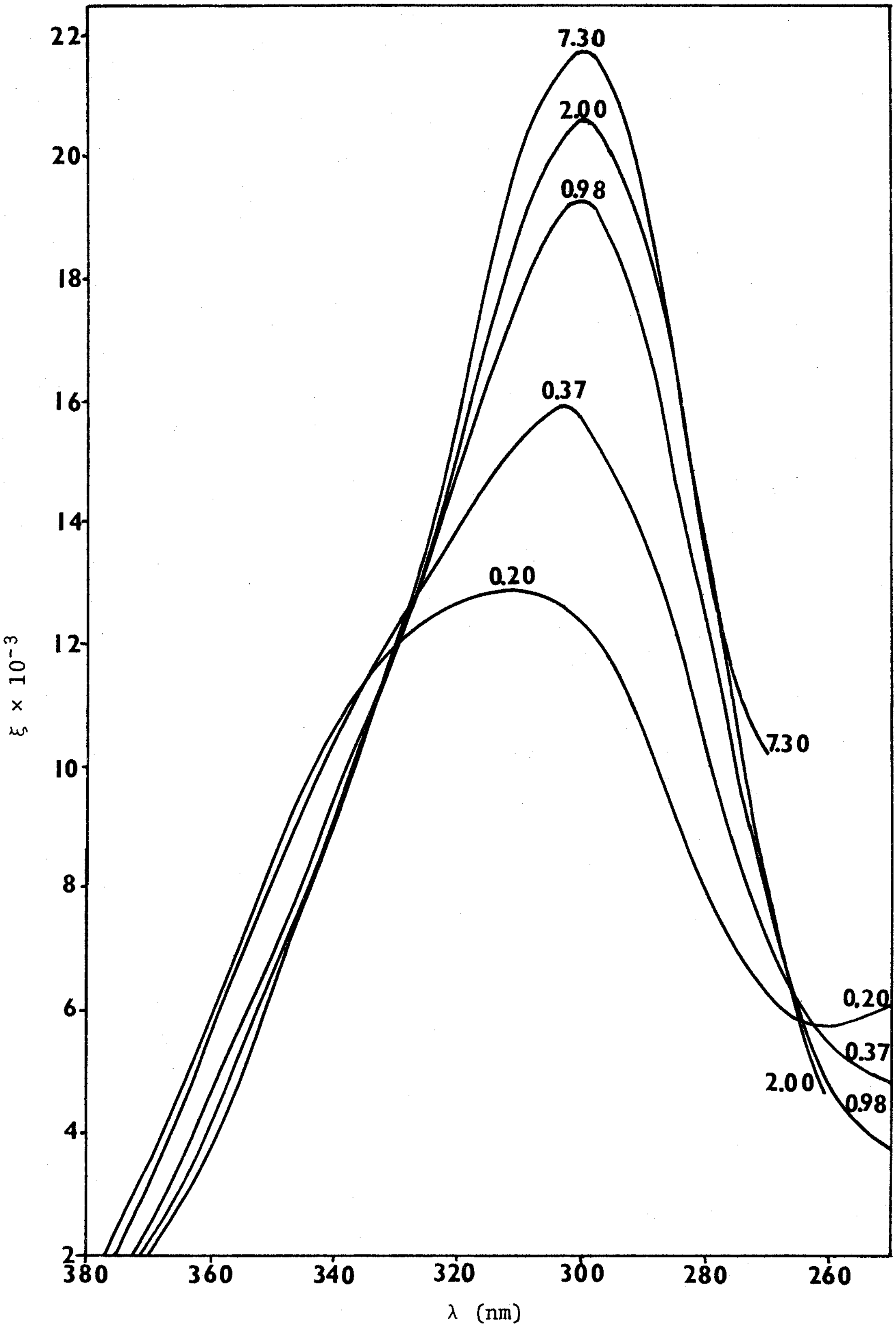

Figure 37. Representative Absorption Spectra of 2,4-Dinitrofluorobenzene in HSO_3F-SbF_5-SO_3

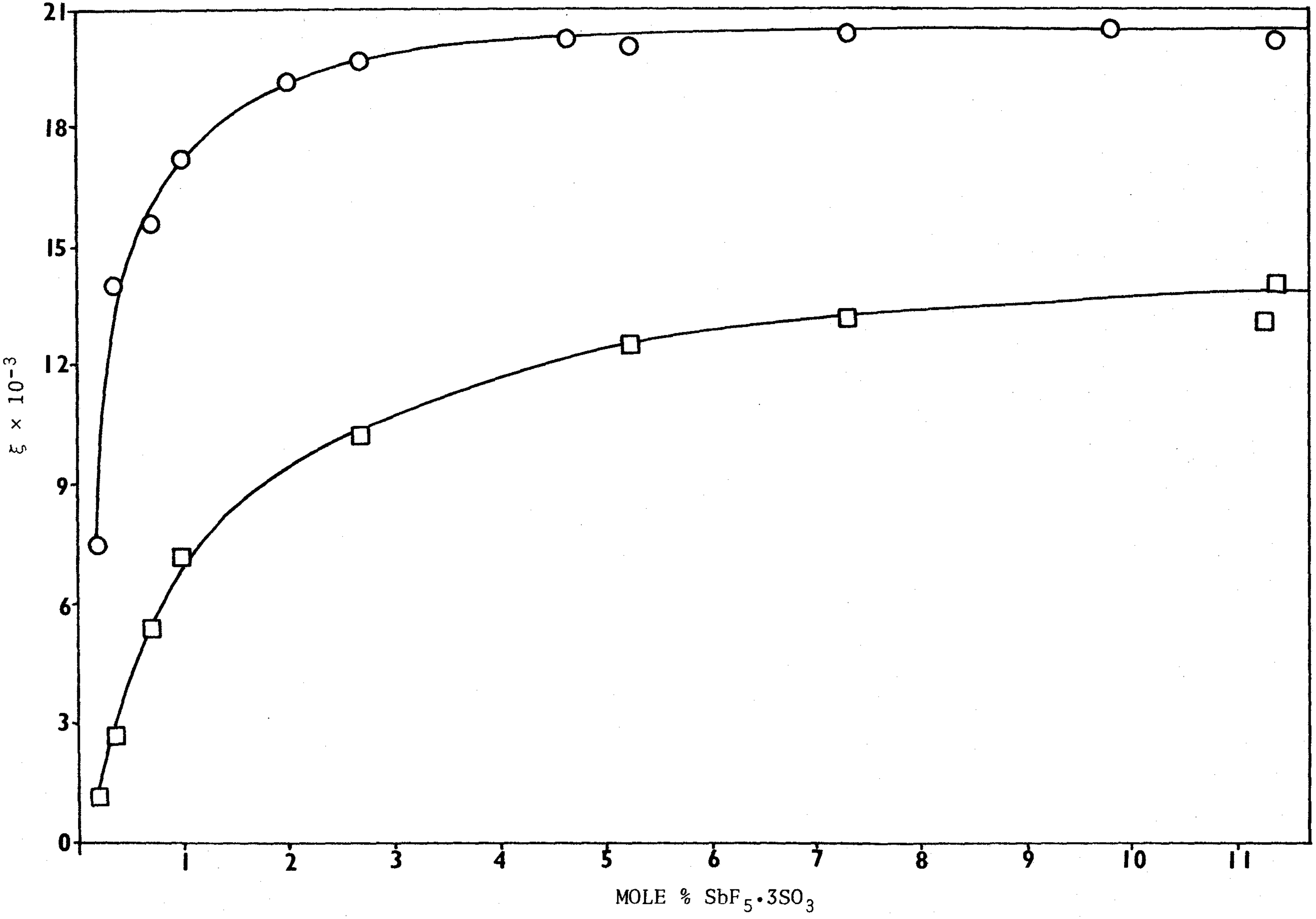

Figure 38. Adjusted Extinction Coefficients of 2,4-Dinitrofluorobenzene (○) and 2,4,6-Trinitrotoluene (□) in HSO_3F-SbF_5-SO_3

TABLE LVIII

EXTINCTION COEFFICIENTS AND IONIZATION RATIOS FOR THE DIPROTONATION OF 2,4-DINITROFLUOROBENZENE IN HSO_3F-SbF_5-SO_3

$\xi_{BH^+} = 900$ $\xi_{BH_2^{+2}} = 20{,}450$ $pK_{BH_2^{+2}} = -17.35$

MOLE % SbF_5-SO_3	ξ	log I
0.20	7,500	0.29
0.30	12,350	-0.15
0.40	14,100	-0.32
0.50	15,030	-0.42
0.60	15,690	-0.48
0.70	16,220	-0.56
0.08	16,620	-0.61
0.90	17,000	-0.68
1.00	17,300	-0.72
1.20	17,800	-0.80
1.40	18,230	-0.89
1.60	18,560	-0.97
1.80	18,870	-1.05

TABLE LIX

OBSERVED AND ADJUSTED EXTINCTION COEFFICIENTS OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SbF_5-SO_3

MOLE % SbF_5-SO_3	MOLE RATIO SbF_5:SO_3	OBSERVED ξ	OBSERVED λ_{max} (nm)	ADJUSTED ξ	ADJUSTED λ_{max} (nm)
0.2016	1:3.48101	11,010	321	1,150	307
0.3722	1:3.80959	11,690	317	2,700	309
0.6602	1:3.29699	12,824	311	5,400	300
0.9836	1:3.27643	13,627	307	7,250	301
2.6936	1:3.27377	16,257	302	10,300	299
5.2543	1:3.31841	17,384	300	12,550	298
7.3032	1:3.27578	17,967	299	13,150	299
11.2654	1:3.30076	18,255	302	13,100	300
11.3512	1:3.26600	18,026	301	14,150	298
17.8938	1:3.29602	19,014	298	15,100	295

TABLE LX

ABSORPTION SPECTRA OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SbF_5-SO_3

MOLE % SbF_5-SO_3	0.2016	0.3772	0.6602	0.9836	2.6936
MOLE RATIO SbF_5:SO_3	1:3.48106	1:3.80959	1:3.29699	1:3.27643	1:3.27377
λ (nm)	λ	λ	λ	λ	λ
230	13,540	-	-	-	-
240	11,540	10,670	-	-	-
250	9,490	9,080	8,680	-	-
260	7,980	7,740	7,780	7,410	7,510
270	6,500	6,820	7,780	7,800	8,840
280	5,920	6,800	8,710	9,280	11,680
290	6,750	8,200	10,610	11,480	14,720
300	8,520	9,930	12,350	13,110	16,230
310	10,200	11,200	12,820	13,520	15,620
320	11,010	11,690	12,220	12,480	13,560
330	10,520	10,720	10,690	10,690	10,600
340	8,830	9,080	8,470	8,450	8,040
350	6,830	6,980	6,330	6,260	5,750
360	4,690	4,980	4,410	4,320	3,960
370	2,970	3,190	2,900	2,740	2,560
380	1,800	1,870	1,720	1,590	1,580
390	1,010	1,060	920	850	850
400	520	550	530	450	480
410	280	330	260	260	320
420	200	260	-	-	230
λ_{max}	321	317	311	307	302
ξ_{max}	11,010	11,690	12,820	13,630	16,260

TABLE LX (cont.)

MOLE % SbF_5-SO_3	5.2543	7.3032	11.2654	11.3512	17.8938
MOLE RATIO SbF_5:SO_3	1:3.31841	1:3.27578	1:3.30076	1:3.26601	1:3.29602
λ (nm)	ξ	ξ	ξ	ξ	ξ
270	10,420	-	-	-	-
280	13,310	13,460	14,750	14,580	21,630
290	16,180	16,420	15,490	16,680	18,440
300	17,380	17,970	18,100	18,030	18,980
310	16,200	16,970	17,750	16,490	17,120
320	13,450	13,830	15,300	13,280	13,660
330	10,220	10,460	11,600	9,760	10,320
340	7,490	7,690	8,450	6,980	7,280
350	5,320	5,460	5,840	4,780	5,200
360	3,680	3,780	4,010	3,270	3,580
370	2,350	2,360	2,610	2,000	2,380
380	1,340	1,360	1,440	1,130	1,410
390	720	730	660	500	840
400	400	410	390	230	600
410	280	270	230	100	420
420	220	-	-	-	-
λmax	300	299	303	301	298
ξmax	17,380	17,930	18,260	18,030	19,010

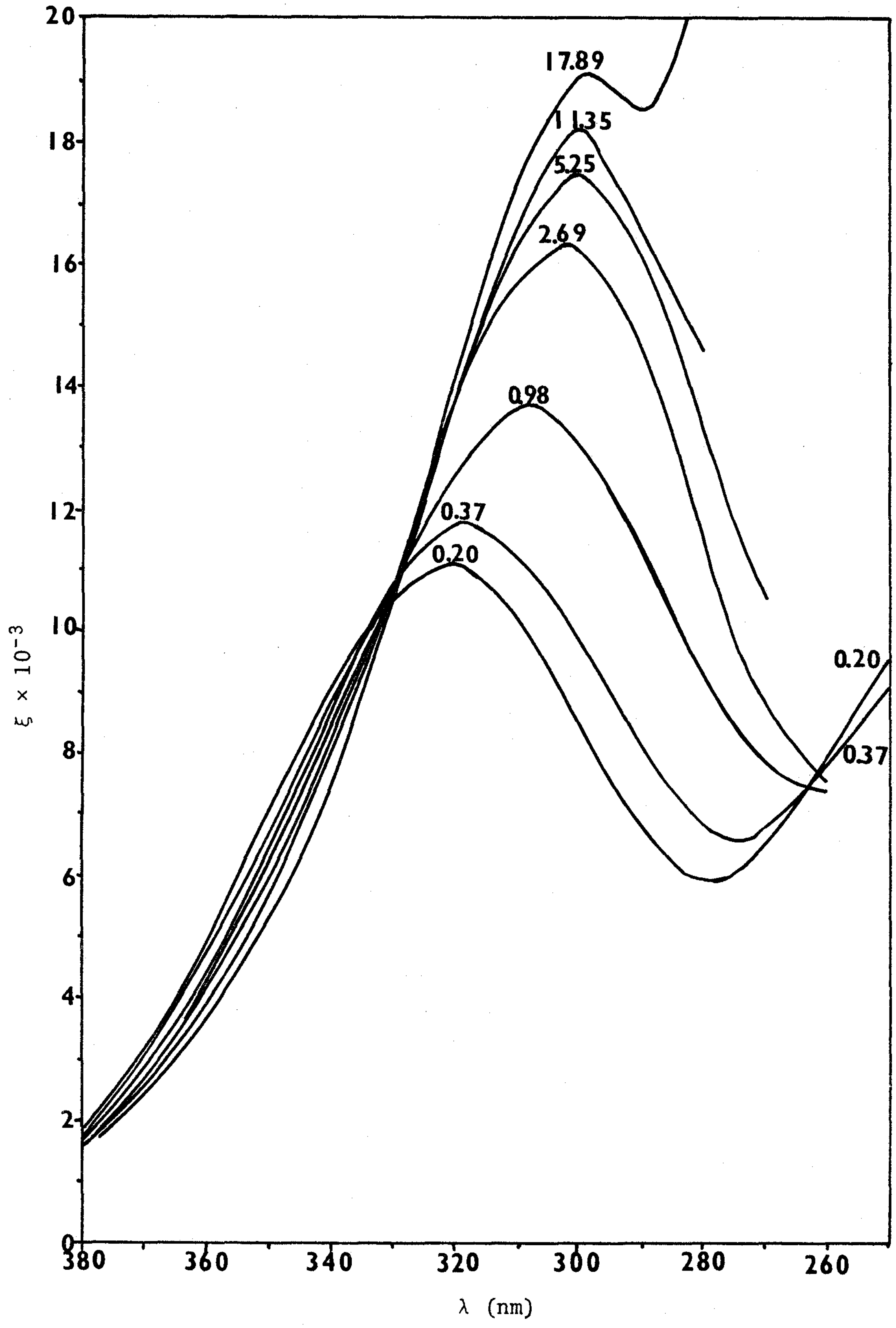

Figure 39. Representative Absorption Spectra of 2,4,6-Trinitrotoluene in HSO_3F-SbF_5-SO_3

TABLE LXI

EXTINCTION COEFFICIENTS AND IONIZATION RATIOS FOR THE DIPROTONATION OF 2,4,6-TRINITROTOLUENE IN HSO_3F-SbF_5-SO_3

$\xi_{BH^+} = 0$ $\xi_{BH_2^{+2}} = 14{,}500$ $pK_{BH_2^{+2}} = -18.36$

MOLE % SbF_5-SO_3	ξ	log I
0.30	2,400	0.70
0.40	3,420	0.51
0.50	4,350	0.37
0.60	5,220	0.25
0.70	5,850	0.17
0.80	6,400	0.10
0.90	6,800	0.05
1.00	7,180	0.01
1.20	7,800	-0.07
1.40	8,260	-0.12
1.60	8,620	-0.17
1.80	9,160	-0.23
2.00	9,320	-0.26
2.50	10,070	-0.36
3.00	10,700	-0.45
3.50	11,150	-0.52
4.00	11,570	-0.60
4.50	11,940	-0.67
5.00	12,290	-0.75
5.50	12,630	-0.83
6.00	12,870	-0.90
6.50	13,030	-0.95
7.00	13,150	-0.99

TABLE LXII

-Ho VALUES FOR $HSO_3F-SbF_5-3SO_3$

MOLE % $SbF_5 \cdot 3SO_3$	2,4-DINITROFLUOROBENZENE	2,4,6-TRINITROTOLUENE	AVERAGE
0.20	17.06		17.06
0.30	17.50	17.66	17.58
0.40	17.67	17.75	17.71
0.50	17.77	17.99	17.88
0.60	17.83	18.11	17.97
0.70	17.91	18.19	18.05
0.80	17.96	18.26	18.11
0.90	18.03	18.31	18.17
1.00	18.07	18.35	18.21
1.20	18.15	18.43	18.29
1.40	18.24	18.48	18.36
1.60	18.32	18.52	18.42
1.80	18.40	18.59	18.52
2.00		18.62	18.62
2.50		18.72	18.72
3.00		18.81	18.81
3.50		18.88	18.88
4.00		18.96	18.96
4.50		19.03	19.03
5.00		19.10	19.10
5.50		19.19	19.19
6.00		19.26	19.26
6.50		19.31	19.31
7.00		19.35	19.35

TABLE LXIII

EVALUATION OF OVERLAP OF NITRO INDICATORS IN THE FLUOROSULFURIC ACID SYSTEMS

Indicators	$a_{i,i-1}$	$\Pi a_{i,i-1}$
2,4-dinitrofluorobenzene—2,4,6-trinitrotoluene	1.08	1.02
2,4,6-trinitrotoluene—1,3,5-trinitrobenzene	0.87	0.89
1,3,5-trinitrobenzene—2,4,6-trinitrochlorobenzene	1.09	0.97
2,4,6-trinitrochlorobenzene—protonated 2,4-dinitrofluorobenzene	0.89	0.86
protonated 2,4-dinitrofluorobenzene—protonated 2,4,6-trinitrotoluene	0.97	0.84

CHAPTER V

DISCUSSION

A. AROMATIC NITRO INDICATORS

It has been demonstrated that the Hammett acidity function, H_0, can be extended into the superacid region by the use of a self-consistent set of aromatic nitro indicators. The protonation behaviour of these indicators was found to be similar to that of the aniline indicators and thus both sets of indicators may be used to generate a consistent H_0 scale extending from infinitely dilute solutions of acids in water to the highly acidic HSO_3F-$SbF_5 \cdot 3SO_3$ system, i.e., over a range of 20 H_0 units. By the use of these aniline and aromatic nitro indicators it is now in principle possible to measure the acidity of all known acid systems.

Table LXIV lists the various aromatic nitro indicators used in this study along with their ξ_B, ξ_{BH^+} and pK_{BH^+} values as found in each of the acid systems studied. The pK_{BH^+} values for m-nitrochlorobenzene and 2,4-dinitrotoluene were independently evaluated in two different acid systems; averages of the closely agreeing values were used in all acidity function calculations. It is recommended that these average pK_{BH^+} values be used in any future evaluation of the Hammett acidity function of highly acidic acid media. The ξ_{BH^+} values for two of the indicators were found to be dependent upon the acid system used in their evaluation and thus if these indicators were used in another acid system, such as the HF-SbF_5 system, their ξ_{BH^+} should be determined in that medium. Relatively small changes in an ξ_{BH+} value result in substantial changes in calculated ionization ratios and thus their accurate assessment is important. The difference in the Ho values for 100% H_2SO_4 as reported by Gillespie and Robinson[59], -12.08, and that reported in this thesis, -11.93, is a result of minor changes in the ξ_{BH+} values for some of the indicators. This shows the importance of accurate determination of the ξ_{BH+} values for indicators used in the evaluation of a medium's acidity.

The basic dissociation constants (K_b) of a number of aromatic nitro indicators have been evaluated from conductivity measurements, at 25°C, in the acidic solvents H_2SO_4[51] and HSO_3F[65]. K_b is defined as

$$K_b = \frac{[BH^+][X^-]}{[B]} \cdot \frac{f_{BH+} \cdot f_{X-}}{f_B} \tag{V-1}$$

where the square brackets represent molar concentrations and X^- is HSO_4^- or SO_3F^-. If it is assumed that the activity coefficient term can be neglected

$$\log K_b = \log \frac{[BH^+]}{[B]} + \log [X^-]$$

$$\text{but} \quad \log \frac{[BH^+]}{[B]} = pK_{BH+} - H_o$$

$$\text{thus} \quad \log K_b = pK_{BH+} - H_o + \log [X^-] \tag{V-2}$$

Substituting the experimental Ho value for sulfuric acid, -11.93, and the HSO_4^- concentration at 100% H_2SO_4, 8.98×10^{-4} molar[71], which results from the autoprotolysis of the solvent, (V-2) becomes

$$\log K_b = pK_{BH+} + 10.41 \tag{V-3}$$

A similar treatment using the H_0 of -15.07 and the SO_3F^- concentration of 3.36×10^{-4} molar[64] for 100% HSO_3F, gives

$$\log K_b = pK_{BH^+} + 11.60 \qquad \text{(V-4)}$$

Figure 40 shows the log K_b versus pK_{BH^+} values for p-nitrotoluene ($K_b = 0.174$), m-nitrotoluene ($K_b = 4.2 \times 10^{-2}$), nitrobenzene ($K_b = 1.8 \times 10^{-2}$), p-chloronitrobenzene ($K_b = 7.3 \times 10^{-3}$), and 2,4-dinitrotoluene ($K_b = 9.1 \times 10^{-4}$) in sulfuric acid where the K_b values have been converted to molar units from the molal K_b values given in reference 51. The straight line represents the calculated relationship according to (V-3). It is readily apparent that a satisfactory agreement is obtained between the calculated relationship and the observed values. Figure 40 also shows the log K_b versus pK_{BH^+} values of p-chloronitrobenzene ($K_b = 1.31$), m-chloronitrobenzene ($K_b = 0.136$), 2,4-dinitrotoluene ($K_b = 2.4 \times 10^{-2}$), 2,4-dinitrofluorobenzene ($K_b = 2.3 \times 10^{-3}$), and 1,3,5-trinitrobenzene ($K_b = 6.9 \times 10^{-5}$) in fluorosulfuric acid where the molal K_b values[65] have been converted to molar units. The straight line represents the calculated relationship according to (V-4) but the agreement is not as good as that found for sulfuric acid.

The constant in Equation V-4 depends in part on the value of the autoprotolysis constant for fluorosulfuric acid. The value of 1.08×10^{-7} mole^{2}l^{-2} reported by Thompson[64] was calculated from the mobilities of the autoprotolysis ions, SO_3F^- and $H_2SO_3F^+$, at infinite dilution, which are not known very precisely because they were obtained by an extrapolation resulting in an error of as much as 15% in the K_{ap}. This error produces an uncertainty of ∓ 0.05 in the constant of Equation V-4. The estimated error in the interpolated H_o of 100% HSO_3F is ∓ 0.05 H_o units resulting in an overall uncertainty in the constant of Equation V-4 of ∓ 0.10 units. The lower limit of this error brings the calculated relationship between log K_b and pK_{BH^+} closer to the observed values (dashed line) but does not completely account for their differences. The basic dissociation constants of highly ionized bases, such as p-chloronitrobenzene ($K_b = 1.31$), may be in error by as much as 30% with the magnitude of the error decreasing considerably as the bases become less ionized. This uncertainty may account for a further portion of the difference between the calculated relationship and the experimental values; however, it is also felt that neglect of the activity coefficient term in the derivation of the relationship between log K_b and pK_{BH^+} may not be justified.

B. THE H_o FUNCTION IN SUPERACID MEDIA

The extension of the Hammett acidity function, H_o, into the superacid region provides a quantitative measure of the relative acidity of the acid systems studied. Previous measurements of the dissociation constants of a number of weak bases have indicated[51,65] that HSO_3F is a more acidic medium than H_2SO_4. This difference in acidity may now be expressed quantitatively in terms of H_o values which are -11.93 for H_2SO_4 and -15.07 for HSO_3F indicating that fluorosulfuric acid is slightly more than 1000 times as acidic as sulfuric acid. Disulfuric acid, $H_2S_2O_7$, has also been used as an acid solvent and its acidity has been assessed[80] to be higher than HSO_3F on the basis of the behaviour of a number of weak bases which were studied by conductivity at 25°C.

The H_0 for a 50 mole % SO_3 solution in H_2SO_4, a composition corresponding to $H_2S_2O_7$, has been found to be -14.14 which is appreciably less than that of 100% HSO_3F. This apparent discrepancy may readily be explained by the behaviour of the H_0 curves in the region of $H_2S_2O_7$ and HSO_3F. The H_0 curve has a steep slope in the region of 100% HSO_3F as a result of the relatively small autoprotolysis constant while, in the region of 50 mole % SO_3, the H_0 curve increases very gradually. This gradual increase is the result of the complex nature of $H_2S_2O_7$ which contains[74] high concentrations of H_2SO_4, $H_2S_3O_{10}$, $H_2S_4O_{13}$, $H_3SO_4^+$ and $HS_3O_{10}^-$, all of which are highly acidic. The addition of a base to $H_2S_2O_7$ results in only a slight change in acidity as a result of changes in the equilibrium positions of the reactions involving the various species in $H_2S_2O_7$. It may thus be said that $H_2S_2O_7$ is a highly buffered acidic medium. The small autoprotolysis constant of fluorosulfuric acid offers little in the way of buffering action and there are no other acidic species present as in the case of disulfuric acid. The addition of even small amounts of a base to fluorosulfuric acid greatly decreases its acidity as may be seen in Figure 17 of Chapter IV which shows the sharp drop in $-H_0$ upon the addition of either H_2SO_4 or KSO_3F.

The higher H_0 value for HSO_3F as compared to $H_2S_2O_7$ thus indicates that 100% HSO_3F is more acidic than 100% $H_2S_2O_7$; however on addition of a base the H_0 of the fluorosulfuric acid decreases much more rapidly than that of a disulfuric acid solution. Fluorosulfuric acid does have the advantage that it is relatively nonoxidizing as compared to $H_2S_2O_7$ and is thus often more useful as a highly acid solvent medium.

The above example indicates the importance of remembering that the H_0 measurements reported in this thesis are for solutions containing only the various acidic species studied with no other components present. The addition of a base to any acid medium reduces its acidity to an extent dependent upon the properties of the solvent. In the superacid systems studied the acidity is particularly sensitive to additions of bases, in the region of 100% HSO_3F and $HSO_3C\ell$ and to a lesser extent, 100% H_2SO_4. If a measure of acidity of solutions of bases in these particularly sensitive solvents is desired then it is necessary to measure their acidity directly or calculate an approximate value using Equation III-17 near 100% H_2SO_4 and Equation IV-21 near 100% HSO_3F.

The acidity of fluorosulfuric acid can be greatly increased, as shown by the H_0 curves of Figure 34, by the addition of strong Lewis acids. A 10 mole % SbF_5 solution, on the basis of the difference in H_0 values, is nearly 10,000 times as acidic as fluorosulfuric acid. Concentrated solutions of SbF_5 or $SbF_5 \cdot 3SO_3$ appear to have the same buffering properties as $H_2S_2O_7$. This buffering effect is the result of the equilibrium between various polymeric species that have been shown[120] to be present in solution. The very high acidity and low basicity of these superacid systems account for their ability to stabilize the large number of extremely reactive species that have been produced and studied in these superacid solutions[110,125].

The relationship between the $H_2SO_3F^+$ concentration

$$H_0 = -\log\ [H_2SO_3F^+] - 18.79 \qquad \text{(V-5)}$$

and H_0, derived in Chapter IV, may be used to estimate the acid dissociation constants of SO_3, AsF_5, SbF_5 and $SbF_5 \cdot 3SO_3$ in fluorosulfuric acid. In this expression the $H_2SO_3F^+$ concentration is in molal units and the constant, -18.79, is determined from the H_0 of 100% HSO_3F and the $H_2SO_3F^+$ concentration in 100% HSO_3F at 25°C (1.90×10^{-4} molal[64]). The validity of (V-5) has been previously demonstrated for dilute solutions of strong acids and bases in HSO_3F. If it is assumed that any increase in H_0 is the result of an increased $H_2SO_3F^+$ concentration then the difference in H_0 between 100% HSO_3F and the solution in question represents the increased $H_2SO_3F^+$ concentration in that solution.

The acidic ionization of SbF_5 may be represented by the equation

$$SbF_5 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + SbF_5SO_3F^- \qquad \text{(V-6)}$$

where

$$K_a = \frac{[H_2SO_3F^+][SbF_5SO_3F^-]}{[SbF_5]} \qquad \text{(V-7)}$$

A 2 mole % solution of SbF_5 in HSO_3F is 0.204 molal in SbF_5 and has an acidity 2.53 H_0 units higher than that of 100% HSO_3F. This increase in H_0 corresponds to an increase in $H_2SO_3F^+$ concentration of 3.70×10^{-2} molal according to Equation V-5. Since $[SbF_5SO_3F^-] = [H_2SO_3F^+]$ we find $K_a = 8.20 \times 10^{-3}$ mole kg^{-1}. It must be remembered that the behaviour of SbF_5 in HSO_3F is not as simple as given in (V-6) because of the formation of polymeric species, even in dilute solutions. Similar K_a calculations were made for solutions containing 1 and 0.5 mole % SbF_5 resulting in K_a values of 4.6×10^{-3} and 3.2×10^{-3} respectively. These results were extrapolated to infinitely dilute solutions in fluorosulfuric acid to give a K_a of 2.2×10^{-3} moles kg^{-1} at room temperature; this may be compared to the literature[120] value of 3.7×10^{-3} mole kg^{-1}

found by a conductimetric method at 25°C. The reasonable agreement of the two values indicates the general validity of determining K_a values from H_o measurements.

Similar procedures were used to estimate the K_a values for SO_3, AsF_5 and $SbF_5 \cdot 3SO_3$. It was found that the K_a for AsF_5 ionizing according to

$$AsF_5 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + AsF_5SO_3F^- \qquad \text{(V-8)}$$

was 3.7×10^{-6} mole kg^{-1}. As the AsF_5 concentration is increased the K_a becomes larger, probably indicating, as in the case of SbF_5, the presence of polymeric species of higher acidity. A K_a of 4.61×10^{-7} mole kg^{-1} was found for SO_3 ionizing according to

$$SO_3 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + S_2O_6F^- \qquad \text{(V-9)}$$

However upon increasing the SO_3 concentration the K_a decreases somewhat. Apparently a limiting concentration of $S_2O_6F^-$ is quickly reached above which the species appears to be unstable. This would limit the concentration of $H_2SO_3F^+$ produced according to (V-9) thus accounting for the levelling of the H_o curve at high SO_3 concentrations. $SbF_5 \cdot 3SO_3$ was found to act as a completely dissociated strong acid as previously found[120]. Values for K_a of AsF_5 and SO_3 have not been previously published but the values given above are consistent with the previous qualitative conclusions from conductimetric studies.

C. USE OF N.M.R. IN THE DETERMINATION OF ACIDITY

The determination of acidity in highly acidic media is by no means limited to the use of the spectrophotometric technique as outlined in this thesis. Any property of an indicator that can be related to changes in the ionization ratio of the indicator can be used to evaluate the acidity of a medium. The accuracy of the resulting acidity scale will be dependent upon the sensitivity of the property being measured to changes in the ratio of protonated to unprotonated forms of the base, and the the degree to which making the measurements alters the acidity of the medium. The spectrophotometric technique has been the most widely used because, for suitable indicators, the ionization ratio can be measured quite accurately and the required concentration of the basic indicators is so small that it does not detectably alter the acidity of the system under study except in a few special cases such as 100% HSO_3F.

N.m.r. spectroscopy has been used by a number of workers[61,126-130] to evaluate the basicity of weak bases in highly acidic media. The technique uses changes in chemical shift of a substituent of the base in question as a measure of the degree of protonation of the base. The resulting ionization "constants" are referred to the acidity scale used to define the acidity of the solvent, most often the relationship $pK_a = H_o$ at half protonation is used even though the bases may not necessarily behave in a similar fashion to the indicators used to describe the acidity scale.

Levy et. al.[123] determined the ionization behaviour of a number of halogen substituted ketones by the n.m.r. method and found that a selected series of these had H_o values at half protonation ranging from 0.3 to approximately -17. The ionization "constants" of the stronger bases were based upon Jorgenson and Hartter's aniline indicator

H_o scale and those at high acidity were based upon preliminary H_o measurements obtained from this laboratory before completion of this thesis. Levy et. al. proposed that this series of ketone indicators could be used for acidity function measurements, by the n.m.r. technique, over the complete acid range from dilute aqueous solutions of strong acids to the high acidity of the HSO_3F-SbF_5 system.

The n.m.r. technique has the advantage that it may be used to determine medium acidity in multiphase systems and in systems which are highly coloured. The usual spectrophotometric technique may not be easily used to study these systems. The main disadvantage of the n.m.r. technique is that relatively high concentrations of the basic indicators are required in order that reliable spectra may be obtained. This disadvantage may, however, be overcome by future developments in the field of n.m.r. spectroscopy. In principle it is possible to select indicators whose chemical shifts on protonation are sufficiently large enough to allow for an accurate evaluation of ionization ratios and thus accurate acidity function measurements. If the set of indicators behave in a similar fashion to the indicators used to define the reference acidity function scale then the n.m.r. technique may, in principle, be satisfactorily used to determine the acidity of any acid system.

Levy et. al.[123] made use of a set of halogen substituted ketones whose ionization "constants" were based upon the H_o function although it has been shown[133] that some of the indicators more closely follow the H_A scale. It should also be noted that the preliminary H_o scale for the HSO_3F-SbF_5 system as used by Levy et. al. has been revised during the completion of this work with the result that their ionization "constants" of the weakly basic indicators should be altered accordingly. The chemical shift of ketone indicators upon protonation was found to be only about 1 ppm and essentially independent of the concentration of the indicator used ($\sim$0.15 molar). The concentration independence of the chemical shifts is surprising especially in the region of 100% HSO_3F where a 0.15 molar solution of base would cause a large change in acidity. Some preliminary measurements of the protonation behaviour of 2,4-dinitrofluorobenzene and other nitro indicators by the n.m.r. technique, made during the course of the present work, indicated that the chemical shift of the ring protons were highly concentration dependent well below the 0.15 molar solutions used by Levy et. al. It is suggested that the use of ketone indicators to measure the acidity of a medium, by the use of the n.m.r. technique, be fully reinvestigated with particular attention being paid to the effect of indicator concentration especially in the region of 100% HSO_3F.

The use of the n.m.r. technique for the evaluation of medium acidity can in principle be done with as much accuracy as the spectrophotometric technique and it may be used to study solutions which cannot be otherwise investigated. The n.m.r. technique is also useful for the determination of the relative basicity of a number of materials which do not have easily interpretable absorption spectral changes upon protonation. Other methods, such as the measurements of the heat of ionization as reported by Arnett et. al.[131,132] do, however, appear to be more generally applicable for basicity evaluations.

TABLE LXIV

ξ_B, ξ_{BH^+} AND pK_{BH^+} VALUES FOR THE AROMATIC NITRO INDICATORS

INDICATOR	H_2O-H_2SO_4-SO_3 SYSTEM			H_2SO_4-HSO_3F-SO_3 AND HSO_3F-MF_5 SYSTEMS			AVERAGE
	ξ_B	ξ_{BH^+}	$-pK_{BH^+}$	ξ_B	ξ_{BH^+}	$-pK_{BH^+}$	$-pK_{BH^+}$
p-nitrotoluene	2,100	19,200	11.35	-	-	-	11.35
m-nitrotoluene	1,200	16,100	11.99	-	-	-	11.99
nitrobenzene	900	15,150	12.14	-	-	-	12.14
p-fluoronitrobenzene	600	16,500	12.44	-	-	-	12.44
p-chloronitrobenzene	400	21,800	12.70	400	24,350	12.70	12.70
m-chloronitrobenzene	440	12,850	13.20	440	14,380	13.13	13.16
2,4-dinitrotoluene	1,700	13,900	13.74	1,700	13,900	13,76	13,75
2,4-dinitrofluorobenzene	920	12,100	(14.03)	920	12,100	14.52	14.52
2,4,6-trinitrotoluene	-	-	-	960	10,600	15.60	15.60
1,3,5-trinitrobenzene	-	-	-	800	10,700	16.04	16.04
2,4,6-trinitrochlorobenzene	-	-	-	700	11,600	16.12	16.12
(2,4-dinitrofluorobenzene)H^+	-	-	-	900	20,450	17.35	17.35
(2,4,6-trinitrotoluene)H^+	-	-	-	0	14,500	18.36	18.36

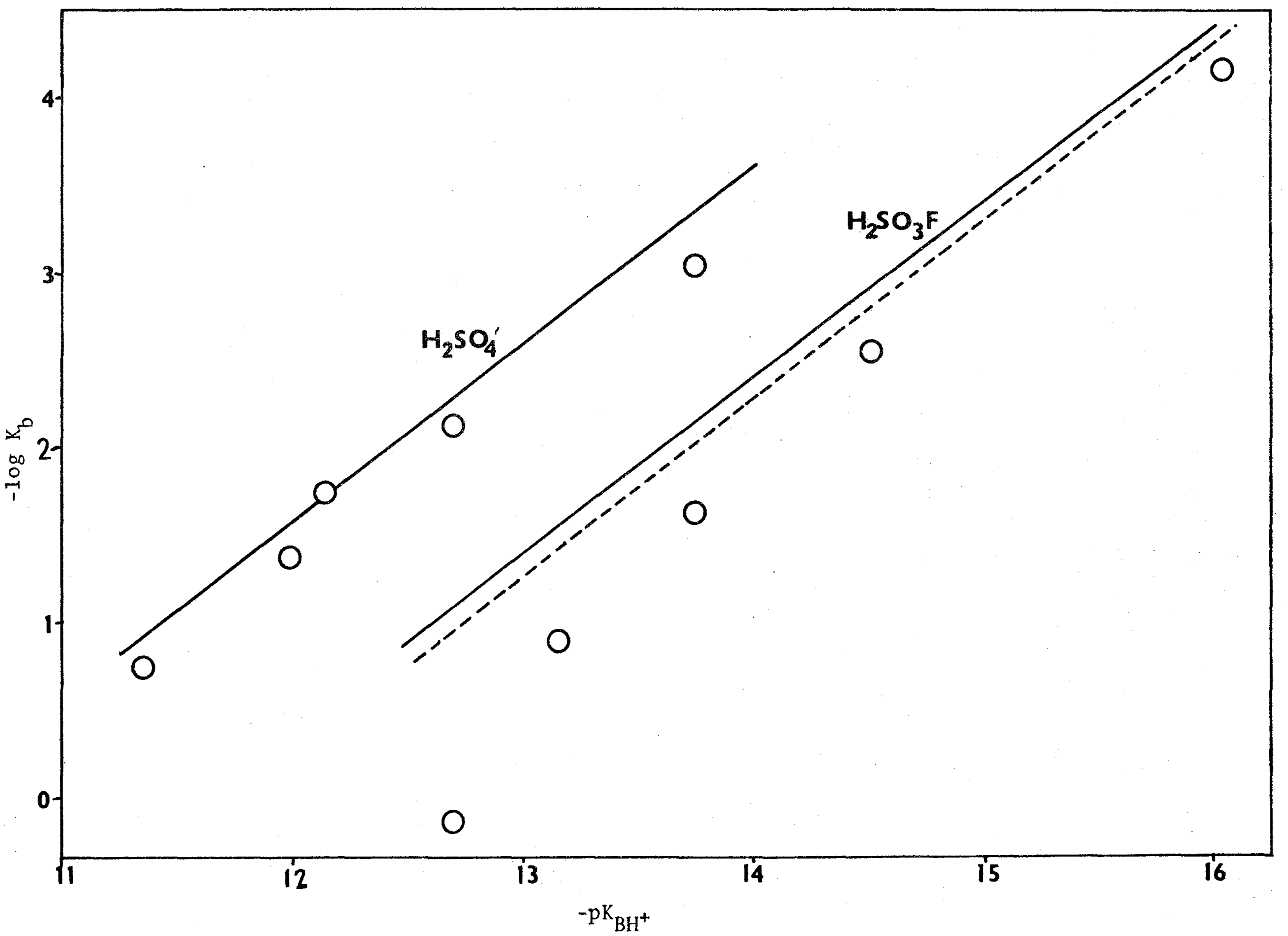

Figure 40. Relationship between log K_b and pK_{BH^+} in H_2SO_4 and HSO_3F.

APPENDIX I

ERROR LIMITS

The error of any one particular extinction coefficient measurement may be as high as ±500 ξ; however the large amount of data collected has allowed the use of graphical techniques to reduce this error. It is estimated that an error of ±200ξ may be present in extinction coefficients as taken from the various graphs. If ξ_{BH^+} and ξ_B are assumed to be 15,000 and 1000 respectively and the measured ξ is assumed to be 8000, a situation where the ionization ratio is most sensitive to changes in ξ, an error of ±200ξ in the measured extinction coefficient would produce an error of ±0.025 log I units or H_o units.

The degree of parallelism of the log I versus acid composition curves as measured by the $a_{i,i-1}$ values listed in Tables XXIX, XXX, and LXIII indicate the reliability of the overlap technique in estimating ionization constants for the various indicators. The H_o values given in this thesis have an overall error of ±0.04 H_o units as an upper limit.

REFERENCES

1. L. P. Hammett and A. J. Deyrup, J. Amer. Chem. Soc., 54, 2721 (1932).
2. L. P. Hammett and A. J. Deyrup, J. Amer. Chem. Soc., 54, 4239 (1932).
3. L. P. Hammett and M. A. Paul, J. Amer. Chem. Soc., 56, 827 (1934).
4. M. A. Paul, J. Amer. Chem. Soc., 76, 3236 (1954).
5. M. A. Paul and F. A. Long, Chem. Revs., 57, 1 (1957).
6. L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill Book Company, Toronto, (1970), pp 263-313.
7. T. G. Bonner and J. C. Lockhart, J. Chem. Soc., 2840 (1957).
8. K. Yates and H. Wai, J. Amer. Chem. Soc., 86, 5408 (1964).
9. K. N. Bascombe and R. P. Bell, J. Chem. Soc., 1096 (1959).
10. J. G. Dawber and P. A. H. Wyatt, J. Chem. Soc., 3589 (1960).
11. R. P. Bell, K. N. Bascombe, and J. C. McCoubrey, J. Chem. Soc., 1286 (1956).
12. H. H. Hyman, M. Kilpatrick and J. J. Katz, J. Amer. Chem. Soc., 79, 3668 (1957).
13. R. J. Gillespie, Chemistry in Canada, 19, 39 (1967).
14. T. F. Young and A. A. Krawetz, quoted by H. A. C. McKay, Trans. Faraday Soc., 52, 1568 (1956).
15. R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, New York, (1959), p 85.
16. E. M. Arnett and G. W. Mach, J. Amer. Chem. Soc., 86, 2671 (1964).
17. R. L. Hinman and J. Lang, J. Amer. Chem. Soc., 86, 3796 (1964).
18. A. R. Katritzky, Tetrahedron, 19, 465 (1963).
19. K. Yates, J. B. Stevens, and A. R. Katritzky, Can. J. Chem., 42, 1957 (1964).
20. K. Yates and J. B. Stevens, Can. J. Chem., 43, 529 (1965).

21. C. D. Johnson, A. R. Katritzky, and N. Shakir, J. Chem. Soc., B, 1235 (1967).

22. R. I. Zalewski and G. E. Dunn, Can. J. Chem., 46, 2469 (1968).

23. C. C. Greig and C. D. Johnson, J. Amer. Chem. Soc., 90, 6453 (1968).

24. N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, J. Amer. Chem. Soc., 77, 3044 (1955).

25. N. C. Deno, P. T. Groves, and G. Saines, J. Amer. Chem. Soc., 81, 5790 (1959).

26. E. M. Arnett and G. W. Mach, J. Amer. Chem. Soc., 88, 1177 (1966).

27. K. Yates and J. C. Riordan, Can. J. Chem., 43, 2328 (1965).

28. N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, J. Amer. Chem. Soc., 81, 2344 (1959).

29. J. Sierra, M. Ojeda, and P. A. H. Wyatt, J. Chem. Soc., B, 1570 (1970).

30. V. S. Shklyaev, Yu. S. Chekryshkin, and Yu. M. Chupina, Russ. J. Phys. Chem., 43, 1048 (1969).

31. P. Vetesnik, J. Bielavsky, and M. Vecera, Coll. Czech. Chem. Comm., 33, 1687 (1968).

32. D. Landini, G. Modena, G. Scorrano, and F. Taddei, J. Amer. Chem. Soc., 91, 6703 (1969).

33. J. F. Bunnett and F. P. Olsen, Can. J. Chem., 44, 1899 (1964).

34. P. Haake, R. D. Cooke, and G. H. Hurst, J. Amer. Chem. Soc., 89, 2650 (1967).

35. T. G. Bonner and J. Philips, J. Chem. Soc., B, 650 (1966).

36. R. L. Reeves, J. Amer. Chem. Soc., 88, 2240 (1966).

37. F. A. Long and M. A. Paul, Chem. Revs., 57, 935 (1957).

38. K. N. Bascombe and R. P. Bell, Disc. Faraday Soc., 24, 158 (1957).

39. P. A. H. Wyatt, Disc. Faraday Soc., 24, 162 (1957).

40. E. Hogfeldt, Acta Chem. Scand., 14, 1627 (1960).

41. J. C. D. Brand, J. Chem. Soc., 997 (1950).

42. N. C. Deno and R. W. Taft, J. Amer. Chem. Soc., 76, 244 (1954).

43. E. M. Arnett, Prog. Phys. Org. Chem., 1, 223 (1963).

44. N. C. Deno, "Survey of Progress in Chemistry", ed. A. F. Scott, Academic Press, New York, (1963), Vol. 2, p 155ff.

45. J. F. Edwards, Trans. Roy. Soc. Can., 4,2, sect. III, 313 (1964).

46. M. R. Jorgenson and D. R. Hartter, J. Amer. Chem. Soc., 85, 878 (1963).

47. E. Hogfeldt and J. Bigeleisen, J. Amer. Chem. Soc., 82, 15 (1960).

48. C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, J. Amer. Chem. Soc., 91, 6654 (1969).

49. P. Tickle, A. G. Briggs, and J. M. Wilson, J. Chem. Soc. B, 65 (1970).

50. A. Hantzsch, Z. Physikal Chem., 65, 41 (1908).

51. R. J. Gillespie and C. Solomons, J. Chem. Soc., 1796 (1957).

52. R. J. Gillespie and E. A. Robinson, J. Chem. Soc., 4233 (1957).

53. R. J. Gillespie and T. Birchall, Can. J. Chem., 43, 1045 (1965).

54. H. Hogeveen, Recueil, 87, 1320 (1968).

55. G. A. Olah and T. E. Kiovsky, J. Amer. Chem. Soc., 90, 6461 (1968).

56. G. A. Olah and T. E. Kiovsky, J. Amer. Chem. Soc., 90, 6461 (1968).

57. J. C. D. Brand, W. E. Horning, and M. B. Thornley, J. Chem. Soc., 1374 (1952).

58. R. J. Gillespie and E. A. Robinson, unpublished results.

59. R. J. Gillespie and E. A. Robinson, "Non-Aqueous Solvent Systems", ed. T. C. Waddington, Academic Press, New York, (1965), pp 157-161.

60. J. Barr, Ph.D. Thesis, University of London, (1959).

61. T. Birchall, Ph.D. Thesis, McMaster University, (1963).

62. R. J. Gillespie, J. V. Oubridge, and C. Solomons, J. Chem. Soc., 1804 (1957).

63. G. Jones and B. C. Bradshaw, J. Amer. Chem. Soc., 55, 1780 (1933).

64. R. C. Thompson, Ph.D. Thesis, McMaster University, (1962).

65. J. Barr, R. J. Gillespie, and R. C. Thompson, Inorg. Chem., 3, 1149 (1964).

66. Handbook of Chemistry and Physics, R. C. Weast ed., The Chemical Rubber Co., 47th edition, 1966-67.

67. R. J. Gillespie and J. A. Leisten, Quart. Revs., 8, 40 (1954).

68. R. J. Gillespie, Rev. Pure Appl. Chem. (Australia), 9, 1 (1959).

69. R. J. Gillespie and E. A. Robinson, "Advances in Inorganic and Radiochemistry", eds. H. J. Emeleus and A. G. Sharpe, Academic Press, New York, (1959), Vol. 1, p 385ff.

70. R. J. Gillespie, "Inorganic Sulphur Chemistry", ed. G. Nickless, Elsevier Publishing Company, New York, (1968), pp 563-586.

71. S. J. Bass, R. J. Gillespie, and E. A. Robinson, J. Chem. Soc., 821 (1960).

72. J. Barr, R. J. Gillespie, and E. A. Robinson, Can. J. Chem., 39, 1266 (1961).

73. R. J. Gillespie and E. A. Robinson, Can. J. Chem., 40, 658 (1962).

74. R. J. Gillespie and K. C. Malhotra, J. Chem. Soc., A, 1994 (1967).

75. A. Hantzsch, Z. Phys. Chem., 61, 257 (1907).

76. R. H. Flowers, R. J. Gillespie, and J. V. Oubridge, J. Chem. Soc., 1925 (1956).

77. R. J. Gillespie, R. Kapoor, and E. A. Robinson, Can. J. Chem., 44, 1197 (1966).

78. R. J. Gillespie, and A. Janzen, unpublished results.

79. V. A. Palm, Doklady Akad. Nauk. S.S.S.R., 108, 270 (1956).

80. R. J. Gillespie and K. C. Malhotra, J. Chem. Soc., C, 1933 (1968).

81. R. H. Flowers, R. J. Gillespie, E. A. Robinson, and C. Solomons, J. Chem. Soc., 4327 (1960).

82. S. J. Bass, R. J. Gillespie, and E. A. Robinson, J. Chem. Soc., 845 (1960).

83. J. R. Brayford and P. A. H. Wyatt, J. Chem. Soc., 3453 (1955).

84. E. A. Robinson and J. A. Ciruna, Can. J. Chem., 46, 1719 (1968).

85. W. Kirman and T. E. Thorpe, J. Chem. Soc., 921 (1892).

86. G. H. Cady, "Advances in Inorganic Chemistry and Radiochemistry", eds. H. J. Emeleus and A. G. Sharpe, Academic Press, New York, (1960), Vol. II, pp 123-127.

87. Standard Oil Development Co., British Patent 537,538 (1941); C.A., 36, 1328 (1942).

88. C. L. Thomas, U.S. Patent 2,313,103 (1943); C.A., 37, 5076 (1943).

89. V. N. Ipatieff and C. B. Linn, U.S. Patent 2,428,279 (1947); C.A., 42, 353 (1948).

90. C. A. Braidwood, British Patent 640,485 (1950); C.A., 45, 658 (1951).

91. Dominion Tar and Chemical Co. Ltd., British Patent 668,283 (1952); C.A., 47, 2212 (1953).

92. H. D. Hartough and A. I. Kosak, J. Amer. Chem. Soc., 69, 3093 (1947).

93. H. D. Hartough and A. I. Kosak, U.S. Patent 2,475,564 (1949); C.A., 43, 7966 (1949).

94. V. N. Ipatieff and C. B. Linn, U.S. Patent 2,421,946 (1947); C.A., 41, 5296 (1947).

95. A. K. Schneider, U.S. Patent 2,795,571 (1957); C.A., 51, 18699 (1957).

96. E. F. Sachara, U.S. Patent 2,745,869 (1956); C.A., 50, 12538 (1956).

97. C. A. Braidwood and A. G. Hovey, U.S. Patent 2,419,185 (1947); C.A., 41, 4658 (1947).

98. A. Bell, C. J. Kibler, J. G. Smith, T. E. Stanin, W. H. Steaton, and R. E. Gee, French Patent 1,365,778 (1964); C.A., 62, 10547 (1965).

99. J. D. Coffee and F. H. Bratton, U.S. Patent 2,462,359 (1949); C.A., 43, 3834 (1949).

100. W. H. C. Rueggebery and D. J. Torrans, Ind. Eng. Chem., 38, 211 (1946).

101. C. W. Gates, Canadian Patent 449,652 (1948); C.A., 42, 6983 (1948).

102. W. E. Kemp, Canadian Patent 445,094 (1947); C.A., 42, 2623 (1948).

103. J. H. Simons, H. J. Passino, and S. Archer, J. Amer. Chem. Soc., 63, 608 (1941).

104. P. H. Carnel, U.S. Patent 2,538,293 (1951); C.A., 46, 2290 (1952).

105. E. A. Coons, U.S. Patent 2,611,735 (1952); C.A., 47, 2969 (1953).

106. H. Beuther and W. C. Offutt, U.S. Patent 2,786,018 (1957); C.A., 51, 10047 (1957).

107. W. Lang, "Fluorine Chemistry", ed. J. H. Simons, Academic Press, New York, (1950), Vol. I, pp 167-182.

108. A. Engelbrecht, Angew. Chem. Intern. Ed. Engl., 4, 641 (1965).

109. R. C. Thompson, "Inorganic Sulphur Chemistry", ed. G. Nickless, Elsevier Publishing Company, New York, (1968), pp 587-606.

110. R. J. Gillespie, Accounts Chem. Research, 1, 202 (1968).

111. R. J. Gillespie, J. B. Milne, and R. C. Thompson, Inorg. Chem., 5, 468 (1966).

112. R. J. Gillespie and T. Birchall, Can. J. Chem., 41, 148 (1963).

113. T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, Can. J. Chem., 42, 1433 (1964).

114. A. A. Woolf, J. Chem. Soc., 433 (1955).

115. C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, (1953), p 300.

116. R. J. Gillespie and M. J. Morton, Quart. Revs., in press.

117. R. J. Gillespie and J. Passmore, Accounts of Chemical Research, in press.

118. R. J. Gillespie and E. A. Robinson, Can. J. Chem., 40, 675 (1962).

119. P. A. W. Dean and R. J. Gillespie, J. Amer. Chem. Soc., 92, 2362 (1970).

120. R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, Inorg. Chem., 4, 1641 (1965).

121. R. J. Gillespie, K. Ouchi, and G. P. Pez, Inorg. Chem., 8, 63 (1969).

122. P. A. W. Dean and R. J. Gillespie, J. Amer. Chem. Soc., 91, 7264 (1969).

123. G. C. Levy, J. D. Cargioli, and W. Raceba, J. Amer. Chem. Soc., 92, 6238 (1970).

124. G. A. Olah, Chem. Eng. News, 55, 76 (1967).

125. R. J. Gillespie and T. E. Peel, "Advances in Physical Organic Chemistry", ed. V. Gobd, Vol. 9, in press.

126. R. W. Taft, Jr., and P. L. Levins, Anal. Chem., 34, 436 (1962).

127. N. C. Deno and M. J. Wisotsky, J. Amer. Chem. Soc., 85, 1735 (1963).

128. D. G. Lee, Can. J. Chem., 48, 1919 (1970).

129. J. T. Edwards, J. B. Leane, and I. C. Wang, Can. J. Chem., 40, 1521 (1962).

130. E. Grunwald, A. Loewenstein, and S. Meiboom, J. Chem. Phys., 27, 641 (1957).

131. E. M. Arnett, R. P. Quirk, and J. J. Burke, J. Amer. Chem. Soc., 92, 1260 (1970).

132. E. M. Arnett, R. P. Quirk, and J. W. Larsen, J. Amer. Chem. Soc., 92, 3977 (1970).

133. R. I. Zalewski and G. E. Dunn, Can. J. Chem., 47, 2263 (1969).

134. C. H. Rochester, "Acidity Functions", Academic Press, New York, (1970), vi + 291.