MASS TRANSFER ACROSS A LIQUID-LIQUID INTERFACE
WITH AND WITHOUT
CHEMICAL REACTION

by

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TABLE OF CONTENTS

Page

PART II: UNSTEADY STATE MASS TRANSFER ACCOMPANIED BY A SLOW, IRREVERSIBLE SECOND ORDER CHEMICAL REACTION (WITHOUT STIRRING)

Page

ABSTRACT

The present study is divided into two parts. Part I was an attempt to investigate the steady state mass transfer across a liquid-liquid interface accompanied by a very slow, second order, irreversible chemical reaction using a glass vessel. Both liquid phases were well stirred and the lower phase was allowed to flow in and out of the reactor continuously. The system chosen for the study was ethyl acetate-sodium hydroxide solution. In order to simplify the transfer situation, the ethyl acetate phase was pre-saturated with water, so that the transfer became uni-directional, from the upper phase into the lower phase. Experimental runs were performed at 25°C, 40°C and 55°C temperature levels and at various sodium hydroxide concentrations ranging from 0.0002 N. up to 0.389 N. (while other experimental conditions, for example, stirrer speeds and lower phase flowrates were kept constant). In each run, transfer rate of ethyl acetate into the lower phase was measured and the mass transfer coefficient was calculated.

The results showed (a) Van Krevelen's film model for slow, second order, irreversible reaction system did not apply to ethyl acetate-sodium hydroxide because the reaction involved was too slow to cause any enhancement in mass transfer. (b) Mass transfer coefficient for reaction run was smaller than that for physical transfer into water; and the difference was accounted for by an interfacial resistance ($1/k_r$) apart from salt effect of sodium hydroxide and sodium acetate.

The resistance ($1/k_r$) varied directly as the concentration of sodium acetate, which, in turn, varied as a positive function of input sodium hydroxide concentrations in the bulk lower phase.

The cause of the retardation to transfer was still uncertain. However, it was speculated to be due to (a) Modification of hydrodynamic conditions near the interface by salt and reaction effect. (b) Formation of a surface barrier due to the presence of impurities. (c) Formation of an additional reaction zone or film due to a very slow chemical reaction.

In addition, an analogue study on concentration profiles of reactants and products in a film model was carried out. Also, J. B. Lewis' experiments were partly repeated and his method of evaluating physical mass transfer coefficients was discussed.

Part II was a study of unsteady state diffusion accompanied by a slow, second order, irreversible chemical reaction across unstirred liquid-liquid phases. The systems of ethyl formate-sodium hydroxide and ethyl acetate-sodium hydroxide were chosen.

The results of the schlieren investigation showed that when the ethyl ester, pre-saturated with water, was in contact with the sodium hydroxide phase, a zone was formed inside which reaction occurred. Turbulent liquid motion was observed in the zone which extended itself in course of time during the experiment.

A great part of the experimental work was spent in an effort to search for information about the zone. The Moire pattern was made use of in studying the zone propagation. Experiments were performed at room temperature, with each of the ethyl ester contacting sodium hydroxide solution at various concentrations (one concentration for each experiment).

The reaction zone thus formed was photographed at intervals. About 25 photographs were taken for each run. They were developed and analysed. In some runs, concentrations of reactants inside the zone were measured.

The results showed (a) The speed of zone propagation was higher in the ethyl formate-sodium hydroxide system than in the ethyl acetate-sodium hydroxide system. Within the system the speed increased with initial sodium hydroxide concentration used, then passed through a maximum, and decreased with increasing sodium hydroxide concentration. (b) Concentrations of both reactants inside the zone were low as compared to their initial concentrations.

A simple model was proposed to describe the zone propagation making use of the concept of eddy diffusivities.

INTRODUCTION

Ever since the development of chemical engineering, mass transfer across fluid-fluid interface has been one of the vital operations in the field. Important practical examples are numerous such as gas absorption of sulphur trioxide, nitrogen dioxide in the manufacture of acids. There are several operations in chemical industries involving the application of liquid-liquid extraction, for example, in the treatment of petroleum naphthas for purification and sulphur removal using caustic soda and added organic solvents.

Quite often these mass transfer processes involve simultaneous chemical reactions with the result that the transfer rates are affected to some extent. It is desirable to know how these reactions affect the transfer rates which are the key data for designing the equipment for the operation.

More work has been done in the field of gas absorption with all kinds of experimental apparatus such as liquid jets, bead columns or wetted wall columns, and the theories in concern are also rather well developed.

On the other hand, very little work has been done in the field of liquid-liquid mass transfer especially with chemical reaction. It was for this reason that the present investigation was carried out. The system of ethyl acetate-aqueous sodium hydroxide was chosen, where the reaction kinetics were not complex and which had been studied by many researchers. Both the steady state and unsteady state mass transfer experiments of the system were carried out.

The results in the preliminary investigation in steady state transfer showed that physical mass transfer of ethyl acetate into water was greater than into sodium hydroxide solution although the system involved a chemical reaction. The system was also investigated using a schlieren apparatus and it revealed that with sodium hydroxide solution as the lower phase, the interface became less agitated and the transfer of ethyl acetate into lower phase was observed qualitatively to be reduced as compared to the case of physical mass transfer into distilled water.

If there are two liquids "A" and "B" contacting each other as shown in figure (1) and considering that only "A" is going into "B" at a steady state. Generally the mass transfer rate depends on the properties of liquids such as solubility, diffusivity, density, viscosity and concentration gradient. If a physical mass transfer is accompanied by a chemical reaction, part of the substance transferred from the other phase will be used up by the reaction, thus the concentration gradient will be greater and a higher transfer rate will be observed. If the chemical reaction is a very rapid one, the concentration of "A" in compartment (2) becomes very small, and the process is diffusion controlled. On the other hand, if the chemical reaction rate is slow, some of "A" is left in compartment (2). In either case, the transfer rate is usually greater than the physical mass transfer rate.

In the preliminary investigation of unsteady state diffusion, a zone of reaction was observed shortly after the contact of the two phases. The zone was distinctly separated from the sodium hydroxide phase by a demarcation line which extended itself in course of time. Inside the reaction zone, turbulent liquid motion prevailed.

The results obtained in both of the preliminary investigations on the system of ethyl acetate-sodium hydroxide presented some interesting phenomena; some of them even contradicted the general idea that mass transfer was enhanced by chemical reaction. In view of this fact, a more extensive study was made.

BACKGROUND TO THEORETICAL STUDY

A) Transfer mechanism across the interface : -

1) Physical mass transfer

As early as 1904, Nernst (86)(87) extended the concept of Noyes and Whitney (89) and proposed the "diffusion layer theory". He visualized that during dissolution, say, of a solid in a liquid, a layer of constant thickness δ adhered to the surface of the solid and diffusion took place through this layer. On the other hand, he assumed that at every boundary between two phases, equilibrium was established with a practically infinite velocity. Based on experimental results, Nernst (87) and Brunner (9) showed that the rate of dissolution was proportional to the surface area exposed, to a concentration driving force, and a constant called transfer coefficient, which depended on the system and the operating conditions used. It was the study of this constant and its functional dependence on a number of variables which interested chemical engineers.

Following the advent of the "Nernst diffusion layer theory", a considerable number of workers (48)(110)(152) published their findings either in support or against the theory. Lewis and Whitman (71)(149) extended the concept of the diffusion layer to cover two films at a gas-liquid interface and derived the two-film theory of gas absorption. Their theory, together with Nernst's, were subjected to numerous discussions and investigations (9a)(106)(107)(126). Some investigators agreed or discarded the theories; while others, inspired by the theories, also developed some other new ideas (59)(83).

Recently, various mechanisms have been proposed in an attempt to give a realistic physical picture of transfer from an interphase into the stirred bulk of a liquid. The over-simplified two-film theory of Lewis and Whitman has been superseded by more elegant concepts such as the penetration theory of Higbie (49), the surface renewal theories of Danckwerts (15) and Kishinevski (61)(62)(63); the "film penetration" model, and recently, the "mixing model for transfer near a boundary" of Toor and Marchello (132)(132a). The Danckwerts' surface renewal theory was modified by Harriott (44a) by assuming that only part of the eddies which influenced the transfer rate came all the way to the interface. More recent development tended to favour the derivation of transfer rate based on the boundary layer theories first developed by Prandtl et al. (101)(143) . A comprehensive summary of the development was made by Marangozis (77). Furthermore, the effect of ions diffusing in mixed electrolytes has been discussed (121)(141) and in several cases, it has been combined with the existing theories (77)(121)(137)(141).

Theories on two component and multicomponent mass transfer have been developed by Toor and Sebulsky (133) and also by Roper et al (107a) on gas absorption. The mass transfer equations obtained differed in form from the usual binary components equations and predicted qualitative as well as large quantitative differences between binary and ternary transfer.

If the physical transfer rate equation for every theory is put into the form $N=k\Delta C$, then every theory can be compared with the film theory; different theories predict different values of transfer coefficient.

2) Mass transfer with chemical reaction

All of the above models concerning the mechanism of interphase mass transfer combined with chemical kinetics of a reaction can lead toward the prediction of the ratio of the rate of transfer with chemical reaction to the rate of pure physical transfer. Several cases have been treated. A detailed discussion of the cases was given by Marangozis (77) and comparison of the cases in film, penetration and surface renewal theories was presented by Vassilatos (137). Recently, a mathematical model based on the film-penetration concept, accompanied by a first order irreversible chemical reaction, has been formulated (53). Although most of the theories are proposed specifically for gas absorption, their extension to liquid-liquid systems do not involve assumptions differing significantly from those postulated for gas-liquid systems.

3) Comments on the models

The film theory is simple to apply and mostly used by design workers. However, it is proven by direct and indirect experimental evidence to be oversimplified. Probably the type of apparatus used (i.e. the flow pattern) is closely related to the theory chosen. For example, the film theory would be expected to work better for a gently stirred vessel, where steady state mass transfer across an unbroken interface occurs, than for a packed tower, where the liquid flows over a piece of packing for a very short period of time before being mixed and then flows to the next piece.

The penetration theory has been proven to work for apparatus such as wetted wall columns (37)(90)(95), laminar liquid jets (13)(113), disc column (2) and rotating drums (16).

Danckwerts (16a) has shown that neither the film theory nor the penetration theory is completely valid for packed towers. For such a kind of apparatus, the film-penetration model would be expected to work better. Applications of the film-penetration model to stirred vessel for liquid-liquid and gas-liquid systems have been recommended (138).

At present, although the Danckwerts surface renewal theory has been tested by absorption in a packed tower (16b), no direct proof has yet been available, and therefore, it still should be considered as tentative.

The laminar and turbulent boundary layer theories afford a rather vigorous, promising approach to the prediction of rates of interphase transfer from a knowledge of fundamental liquid mechanics and reaction data. The picture seems to be more realistic in many cases.

Though usually applied in cases where a fluid flows over a solid surface (77)(140a), the method has been extended by Potter (99) to include transfer between co-current liquid streams. The boundary layer theory has also been applied to physical transfer in drops (25)(58).

B) Transfer across liquid-liquid interface : -

1) Physical mass transfer

Notwithstanding the fact that measurements of diffusion across interfaces with the liquids being stirred were made by Sjolin (124), Hutchison (54) and Davies (19) as early as two decades ago, much more work has been done in the field of gas absorption and solid-liquid systems rather than liquid-liquid systems, mainly because the situation arising from liquid-liquid extraction is more complicated. The flow of components frequently involves both directions from the interface, and the surface properties are quite different from the gas-liquid or solid-liquid interfaces. As an example to demonstrate the complexity of liquid-liquid extraction, the Fick's diffusion equation for the rate of physical mass transfer is considered. In the case of gas absorption or solid dissolution, the experiments are usually conducted in such a way so that the concentration of the solute in the liquid phase is low. Consequently, the transfer coefficient as well as the diffusion coefficient are often assumed to be independent of the concentration of the solute without introducing serious error. However, in liquid-liquid extraction, the solute concentration frequently comes up to the range where the assumption of the constant diffusion coefficient is no longer valid. If the variation of the diffusion coefficient is taken into account by incorporating into the diffusion equation a suitable function of concentration, the equation becomes, in most cases, non-linear. Some solutions have been obtained by Fujita (31) and Raal (103).

Although the present existing theories for gas absorption are supposed to be applicable to liquid-liquid mass transfer, yet, comparisons of experimental results with theories often show large deviations. As a result, either the theoretical equations have to be modified or certain interfacial phenomena leading to the deviations have to be accounted for. Some investigators, based on the experimental results and dimensional analysis, proposed different mechanisms of mass transfer. Thus, J. B. Lewis (67)(68), in his studies of transfer across liquid-liquid interface in a stirred cell, proposed a correlation for individual mass transfer coefficients in terms of only Reynolds numbers and viscosities of the liquids. Although the proposed correlation represented the liquid-

liquid extraction results on a number of two-component systems fairly adequately, it appeared generally unable to give satisfactory predictions when applied to three-component systems. Sherwood (117) pointed out that the experimental results of Lewis actually did not exclude the possibility of correlating transfer coefficients with molecular diffusivities. Similar experiments were performed by Blokker (4) using several liquid systems and the results agreed with those of Lewis. More recently, Lewis experiments were repeated by Mayer (78) and McManamey (81) almost simultaneously. Both of them included a Schmidt group in their correlation as discussed in Appendix XI. Gordon and Sherwood (39) carried out experiments on the physical extraction of various solutes in water-isobutanol system. They were able to prove the theory of additivity of resistances first proposed by Whitman (71). Fujinawa et al (27) carried out the same type of experiments as Gordon and Sherwood except using water benzene as the two phases instead. They confirmed Gordon and Sherwood's results.

Liquid-liquid mass transfer phenomena were also studied in static diffusion cells by several workers (10)(123)(129)(134)(146). Equations predicting mass transfer rates were also derived.

Liquid-liquid extraction involving drops has been investigated by Johnson et al and many others (5)(25)(42)(58). A comprehensive literature survey on this subject has been made by Johnson and Hamielec (42). Several researchers have investigated, particularly, the ethyl acetate-water system (41a)(57a). Prediction of transfer rate usually involves either the application of the boundary layer theory or the derivation of concentration profiles from stream functions. Higher mass transfer rate, as compared to solid spheres, are usually obtained by both experimental measurements and theoretical predictions. The increase in transfer rate is believed to be due to internal circulation of the drop or interfacial turbulence, depending on the system under study. A recent paper by Thorsen and Terjesen (131) showed that both the internal circulation and the interfacial turbulence due to local variation in interfacial tension were not responsible for the higher rate of transfer. Instead, they proposed that the high transfer rate in pure liquid-liquid systems was due to interfacial turbulence set up in the continuous phase over the rear point of the drop. The turbulent motion was associated with the unstable liquid boundary and the point of separation where the primary disturbance was considered to arise. Their conclusions were quite different from the present existing explanation (33) for high transfer rate based on the thinning of the boundary layer caused by internal circulation. It should, however, be noted that the work of Terjesen et al involved only a few systems and at a certain range of Reynolds numbers (50-800). Whether the idea could be generalized or not still has to be confirmed by more experiments.

One of the difficulties encountered in liquid-liquid extraction is that mass transfer is sometimes associated with interfacial resistance or interfacial turbulence. It must be accepted, of course, that interfacial resistance may occur in gas absorption. Likewise, interfacial turbulence is also observed in gas absorption. Using schlieren and interferrometric techniques, Kroepelin and Prott (65) showed that the transfer of methanol vapor to water was an example of eruptive transfer.

Ward and Brooks (146) were the first to report the existence of spontaneous, highly localized interfacial agitation accompanying mass transfer across liquid-liquid interface. Since then, interfacial turbulence has been observed and studied in drops and flat interfaces both visually and photographically. Lewis et al (68)(70), in several cases of their liquid-liquid transfer studies, reported interfacial turbulence. Their observations were confirmed later by other workers (34)(46)(91)(122). Optical studies of interfacial turbulence were carried out by Gore (40) and Nelson (85). A rather complete literature survey on this subject had been given by Orell and Westwater (92). On the other hand, a mathematical model on interfacial turbulence based on the Marangoni effect, wherein movement in an interface was caused by longitudinal variation of surface tension, had been formulated by Sternling and Scriven (127). The model was tested by Orell and Westwater (92) using ethylene glycol-acetic acid-ethyl acetate system. It was found that the Sternling-Scriven model of interfacial turbulence could only explain part of the observed phenomenon.

2) Mass transfer with chemical reaction

Most of the experiments carried out so far in liquid-liquid mass transfer with chemical reaction are aimed at testing the film and penetration theories for rapid irreversible second order reaction. Comparison of available results leads to deviations. Thus Osborne (93), Searle and Gordon (115), Sherwood and Wei (122) extracted acetic acid from isobutanol using aqueous sodium hydroxide solution; the measured overall mass transfer coefficients appeared to be much higher than predicted by Hatta's theory (45), although Sherwood and Wei had taken the effect of ionic diffusion into account. At higher concentration levels of sodium hydroxide solution (1N - 3N), the transfer coefficients became irregular and non-reproducible. Other extraction experiments, namely, extraction of acetic acid from water by solutions of cyclohexylamine in isobutanol and extraction of n-butyric acid from benzene by aqueous sodium hydroxide were also performed by Sherwood and Wei (122); abnormally high values of transfer rates were obtained. They attributed the deviations to interfacial turbulence. On the contrary, Fujinawa et al (27)(28) carried out a large number of experiments on liquid-liquid extraction with chemical reaction, including the extraction of acetic acid from benzene by aqueous sodium hydroxide. In all the systems under study, chemical extraction rates were found to be constant in the range above some critical value of initial sodium hydroxide concentration. The conclusion was in support of the film theory.

Raal and Johnson (104) derived a non-linear differential equation on liquid extraction where the solute on absorption reacted to form a dimer through a rapid second order reversible reaction with the solvent. However, experimental results deviated from the predicted ones (103), probably due to interfacial turbulence or interfacial resistance.

Very little information concerning mass transfer with reaction involved is available. Nevertheless, extraction of acetic acid and butyric acid from various solvent drops by aqueous potassium hydroxide was carried out by Fujinawa and Nakaike (29). They found that in the case of acetic acid transfer from solvent drops, the transfer rates, in general, decreased with increasing potassium hydroxide concentration; while in the case of butyric acid transfer from solvent drops, the transfer rate, in general, slightly increased with increasing potassium concentration. Recently, mass transfer of ethyl acetate from a fixed drop into flowing aqueous sodium hydroxide solutions was measured by Watada of this Department (147). His preliminary results also indicated a decrease in transfer rate with increasing sodium hydroxide concentration.

Even less information can be obtained concerning unsteady state diffusion with chemical reaction in still fluids. In theory, only diffusion accompanied by an infinitely fast second order irreversible reaction has been worked out by Sherwood and Pigford (119) using the stagnant film model. This theory was generalized later by Scriven (114). The solution has also been worked out using both laminar boundary layer (24) and turbulent boundary layer models (117a). Mathematical solution of diffusion accompanied by a very fast, but not infinitely fast second order and third order irreversible reactions has been attempted by Friedlander (23). However, all the aforementioned workers have been, so far, trying to solve, one way or the other, the general mass balance equation (i.e.

$$\frac{\partial n_i}{\partial t} + \vec{v}\cdot\nabla n_i = \nabla\cdot D_{ii}\nabla n_i + G_i \quad)$$

C) Interfacial resistance : -

In recent years, considerable attention has been given to the phenomenon of interfacial resistance both in gas absorption and in liquid-liquid mass transfer. This kind of study is of fundamental importance in mass transfer. In essence, experimental mass transfer rates are compared with the theoretical predictions assuming a certain theory (such as the film or penetration theory). The interfacial resistance causes the transfer rates to be lower than the predicted values. This, of course, automatically involves the assumption that the mechanism chosen fits the transfer situation. Thus, many workers (13)(49)(76a)(142) have made the comparisons and have reported interfacial resistance of this type in physical gas absorption and evaporation (47). Similar type of interfacial resistance is also common in the liquid-liquid extraction without chemical reaction. The presence of interfacial resistance to the transfer of uranyl nitrate between water and solvents such as dibutyl carbitol and methyl isobutyl ketone was observed by Murdoch and Pratt (84) in a wetted wall column. Later, Smith et al (125) found that satisfactory agreement between experimental and predicted overall mass transfer coefficients for the transfer of uranyl nitrate between water and isobutyl ketones in a packed column could only be obtained by taking this interfacial resistance into account. J. B. Lewis (68)(69) studied the transfer of a variety of solutes (including uranyl nitrate) between water and a number of solvents in a stirred cell. The experimental overall transfer coefficients were compared with values predicted from individual transfer coefficients calculated by an empirical correlation previously determined (67). Interfacial resistance was observed in a number of cases. Blokker (4) carried out liquid extraction experiments in the same way as Lewis and he noted that deviations as high as ± 50% from calculated coefficients occurred. Gordon and Sherwood (39) reported interfacial resistance when they measured extraction rate of acetic acid from isobutanol by water in a stirred vessel.

Interfacial resistance was observed even in static diffusion cell. Thus, Sinfelt and Drickamer (123), Tung and Drickamer (134) could measure resistance in aqueous and non-aqueous liquid pairs using radioactive tracers. They also reported interfacial resistance in phenol-sulphuric acid-water system.

Very few data showing the interfacial resistance in chemical gas absorption or liquid-liquid extraction with chemical reaction are available. Jenny (57) carried out batchwise absorption of ethyl acetate vapor by sodium hydroxide solution. The absorption rate was found to be smaller than physical absorption rate. The liquid-liquid extraction work of Raal (103), Fujinawa et al (29) and Watada (147) as discussed previously all indicated the existence of interfacial resistance with mass transfer accompanied by a chemical reaction.

It is important to distinguish between the actual resistance and the apparent resistance due to (1) deviation from conditions of static equilibrium (2) presence of small traces of impurities (3) occurrence of a slow surface reaction.

1) Question of interfacial equilibrium

Kennedy (17) and many others suggested that the apparent resistance during absorption of carbon dioxide was due to departure from interfacial equilibrium. However, Lynn, Straatemeir and Kramers (76a) decided from their wetted wall column experiments that interfacial equilibrium existed in the sulphur dioxide system. Cullen and Davidson (13), Scriven and Pigford (112) concluded from jet absorption experiments and study on Knudsen's equation of gas kinetic theory that interfacial equilibrium existed in freshly formed, relatively clean carbon dioxide-water interface and the statement probably applied to the absorption of other slightly soluble gases in water. Less work was done in liquid-liquid mass transfer to prove this point. Scott, Tung and Drickamer (111) concluded from diffusion measurement involving the transfer of sulphuric acid between water and phenol that it was certainly not safe to assume equilibrium at the interface. Ward and Brooks (146) studied diffusion of acetic, propionic, n-butyric and n-valeric acids across the water toluene interface without stirring by Lamm scale method. They found that for all the acids, the concentration immediately next to the interface in the two layers remained constant throughout diffusion with a ratio equal to the distribution ratio. The extraction experiments of Terjesen et al (6)(7)(50)(72)(131) tended to favour the existence of interfacial equilibrium during mass transfer.

Strictly speaking, the interfacial equilibrium must be upset before any mass transfer can occur. For physical mass transfer experiments in gas absorption and liquid-liquid extraction, the assumption of interfacial equilibrium seems to be valid for many systems if the mass transfer rates are not very great. This assumption should not be generalized. With a reaction occurring at the interface, the existence of static equilibrium becomes less known and requires further investigations.

2) Presence of impurities at the interface

In mass transfer operations, particularly with pure liquid systems, the transfer rates are quite often reduced by the presence of traces of impurities or foreign material at the interface. There has been a huge amount of work devoted to investigating the effect of added surface active agents on the mass transfer rate. The general result, at the first glance, seems to be rather contradictory and confusing. Some investigators reported that the presence of surface active agents partially reduced the physical mass transfer rate; while others reported that surface active agents had no effect on the mass transfer rate.

a) Effect of surface active agents in gas absorption

The effect upon absorption of adding to water measurable quantities of surfactants, such as Teepol and Petrowet had been investigated by several workers (14)(22)(76a). The apparatus used were wetted wall columns or laminar jets. In the wetted wall columns, the addition of wetting agents markedly affected both the liquid flow regime, causing the disappearance of rippling in the falling films, and absorption rates, which were reduced. In the shorter columns or laminar jets, wetting agents were found to have no effect on absorption rates. Hammerton and Garner (43) demonstrated clearly that contamination of the surface of a rising bubble by surface active material initially present in trace amount could convert a mobile, free liquid surface into a rigid structure and that such a conversion was accompanied by a marked reduction in absorption rate.

b) Effect of surface active agents in liquid extraction

There are even more experiments done in liquid-liquid extraction with surface active material, particularly in drops. A comprehensive earlier literature survey on the effects of surfactants on extraction from drops was given by Garner et al (35). These workers, based on their experimental results together with some others, showed that extraction rates decreased with addition of surface active agents. In some cases, the extraction rate was reduced to over half of the original value. Terjesen (6)(7)(50)(72)(131) carried out extensive studies in liquid extraction with surface active agents soluble only in aqueous phase (mainly some sodium salts of sulphate or sulphonate) and they concluded that transfer rate was reduced by the agent. They first proposed that the role of surfactants on the decreasing extraction rate was due to their barrier behaviour hindering the transfer of solute travelling across the interface, an explanation different from the one proposed by Hutchinson (55) and Garner and Hale (36) that resistance was caused by some kind of interaction between the adsorbed film and the diffusing solute. An equation was derived relating the aqueous concentration of the surface active agent and the resistance (72). The derivation of the equation was based on the assumption that the interfacial resistance was proportional to the interfacial concentration of the surface active agent. However, Terjesen et al, in their later experiments (131) found that the action of surfactants on reducing transfer rate was due to their power of modifying the hydrodynamic conditions at or near the interface. Fujinawa et al (30) performed similar experiments as Terjesen and Garner and they found that the addition of very small amounts of surface active agents decreased the rates of extraction appreciably. In addition, they also found that the higher molecular substances had similar effect on transfer rate.

On the other hand, Lewis (67) carried out the extraction experiments in a stirred cell with long chain quarternary ammonium compound as surface active agent and with rigid protein film added respectively. He reported that while the ammonium compound which formed a mobile film at the interface had little effect, the rigid protein films caused a retardation of transfer, probably by damping interfacial turbulence. Gordon and Sherwood (39) carried out extraction experiments with addition of several commercial surface active agents respectively, they concluded that the effect of surface active agents on transfer rate was small. Davis and Mayers (20) repeated the experiments done by Lewis using a variety of surface active agents. They showed that the liquid-liquid mass transfer rate in a stirred cell was reduced in the presence of either soluble or insoluble surface active agents. These workers explained the nature of the surfactant films in terms of a "surface clearing " model which was related to the surface compression modulus of the film. In this way, they favoured the idea of the surface active agents acting like a barrier.

Conflicting results were found even in the study of static diffusion cell. Thus, Wiggill (151), Sinfelt and Drickamer (123) reported that the addition of a surface active agent had no effect on the transfer rate in the systems which they investigated. While Szpak (129) found the addition of "Aerosol OT" to water-acetic acid-benzene system slightly reduced the rate of extraction of acetic acid. At the same time, he noticed the disappearance of the interfacial turbulence associated with mass transfer when the system was pure.

Recently, Quinn and Jeanin (102) investigated the effect of surfactants (Tween 20) using a liquid-liquid laminar jet. They found no difference in transfer rates was detected between the runs with and without surface active agents.

The different results obtained by the workers are probably due to different types of surface active agents employed at various concentrations. Also it may be, to some extent, due to the choice of apparatus or system. For example, the laminar jet, whose geometry is well-defined, should be expected to be less affected than the liquid interface in a stirred cell, because of the more rapid formation of new surface in the former apparatus. The drop systems seem to be more easily affected by the surfactants, probably because the agents reduce the interfacial tension of the system, thus decreasing the internal circulation of the drop. On the other hand, it has also been shown, though not confirmed, that internal circulation does not affect the transfer rate. Despite the conflicting results, there is a general tendency to believe that the action of surface active agents on interphase mass transfer is more of a hydrodynamic rather than interfacial barrier nature.

3) Occurrence of slow surface reaction

Interfacial resistance can also be caused by a slow reaction happening at the phase boundary. Such reaction had been reported in the liquid extraction of inorganic nitrates by Murdoch and Pratt (84). Later, McManamey (82) repeated the experiments on inorganic nitrates extraction and showed that the metal nitrates might form a solvated complex at the interface and then pass into the solvent phase.

Since no direct proof of the existence of such interfacial reaction is available, the proposed cause of interfacial resistance must be reserved as tentative.

Summarizing the above discussions, it is clear that interfacial resistance arising in mass transfer experiments can be accounted for by the presence of impurities or foreign matters capable of modifying the hydrodynamic conditions at or near the interface. There are cases where the cause of interfacial resistance is due to employing an incorrect model or occurrence of an interfacial reaction and, in odd events, deviation from phase equilibrium (109).

True interfacial resistance is small if there is any (11)(13) (102) and can often be negligible except in the case of evaporation (47).

D) Note on the film theory : -

In the case of transfer between liquid and solid or gas and solid, the film is well-defined because of the rigidity of one phase and its thickness can be estimated experimentally quite accurately. Values as small as 10^{-4} cm have been measured (129). In the case of gas absorption by liquid, the concept of film is not as clearly defined. The liquid-liquid extraction operation requires even a closer examination of the film concept.

The actual transfer mechanism of the film theory, embodying the assumption of a thin stagnant liquid film adjacent to the interface in which steady state diffusion occurs, has long been open to question, particularly in cases where vigorous agitation at the interface occurs (for example, the packed tower). As pointed out by Lewis and Whitman themselves, the films were fictitious rather than realistic and the theory could neither predict the magnitude of the film thickness nor the mass transfer coefficient. Szpak (129) has demonstrated recently through experiments, that the classical concept of the film theory is incorrect. He proposed that mass transfer across liquid-liquid interface must be irregular and contributed separately by two factors, the random movement and the convective flux of the liquids.

Despite all the severe criticisms, the film theory survives and is still used in industrial design calculations mainly because of its simplicity.

Actually, the utility of the Whitman two-film theory does not depend on the existence of stagnant films but on the validity of three assumptions: (1) the rate of mass transfer within each phase is proportional to the difference in concentrations in the main body of the fluid and at the phase boundary or interface; (2) the phases are at equilibrium at the phase boundary; and (3) steady state diffusion occurs to the extent of negligible holdup of diffusing solute in the region near the phase boundary. The validity of assumption (2) has been discussed in the previous section. For the conditions of most applications, the first assumption is believed to hold well, though some investigators (105) found the molecular diffusion of water into n-butanol to be more nearly proportional to fugacity than to concentration difference.

In addition, it has been shown (8)(77)(137) that the effect of a reaction on the rate of pure physical mass transfer is nearly independent of the chosen model. This indicates that for any given type of equipment (which gives rise to various flow patterns) and provided the physical mass transfer is obtained, the film theory can always be applied to predict the transfer rate with reaction in the same equipment provided all the other conditions are kept constant.

PART I

STEADY STATE MASS TRANSFER ACCOMPANIED BY A SLOW, IRREVERSIBLE SECOND ORDER CHEMICAL REACTION

(WITH STIRRING)

THEORETICAL PRINCIPLES

A) Film theory : -

The following is the classical film theory describing the mass transfer across a liquid-liquid interface accompanied by a slow, second order irreversible chemical reaction. The situation is simplified by assuming that the transfer is uni-directional and from the upper phase into the lower phase. It is also assumed that the film in the upper phase offers no resistance to mass transfer. Thus, in this case, only the film in the lower phase is important.

Considering the following irreversible second order reaction

$$1 + 2 \longrightarrow 3 + 4 \qquad \ldots. (1)$$

taking place in a film of the lower phase between component 2 of the upper phase and component 1 of the lower phase. The rate of this reaction is given by

$$\frac{dC_1}{d\theta} = \frac{dC_2}{d\theta} = -kC_1C_2 \qquad \ldots. (2)$$

where k is the reaction rate constant, C_1 and C_2 are the concentrations of components 1 and 2 respectively, θ is the time. By a material balance in a differential volume element dx(1) of the liquid inside the film in steady state, the following equations can be written for the reactants: -

$$\frac{dC_1}{d\theta} = D_1 \frac{d^2C_1}{dx^2} - kC_1C_2 = 0 \qquad \ldots. (3)$$

$$\frac{dC_2}{d\theta} = D_2 \frac{d^2C_2}{dx^2} - kC_1C_2 = 0 \qquad \ldots. (4)$$

and for the products: -

$$\frac{dC_3}{d\theta} = D_3 \frac{d^2C_3}{dx^2} + kC_1C_2 = 0 \qquad \text{.... (5)}$$

$$\frac{dC_4}{d\theta} = D_4 \frac{d^2C_4}{dx^2} + kC_1C_2 = 0 \qquad \text{.... (6)}$$

with the following boundary conditions: -

at $x = 0$

$$\frac{dC_1}{dx} = 0$$

$$C_2 = C_{2i}$$

$$D_2 \frac{dC_2}{dx} = \text{transfer rate of } C_2$$

$$\frac{dC_3}{dx} = 0$$ (It is assumed that both components 1 and 3 cannot go into the upper phase.)

at $x = x_f$

$$C_1 = C_{1L}$$

$$C_2 = C_{2L}$$

$$C_3 = C_{3L}$$

$$C_4 = C_{4L}$$

where the D's refer to the molecular diffusivities of their corresponding components, x is the distance from the interface and x_f is the film thickness. C_{2i} represents the saturation concentration of 2 at the interface and C_{1L} is the concentration of 1 in the bulk of the liquid in the lower phase. All the diffusion coefficients are assumed to be constant throughout the film.

The simultaneous equations (3)(4) cannot be solved analytically as they are not linear. An attempt to obtain a numerical solution of the same equations has been made through the application of an analogue computer and the results are shown in Appendix IX. Analogue computer solution for the equations were also obtained by A. R. Gemmel (32) at the University of Toronto.

On the other hand, an approximate solution of equations (3) and (4) was first presented by Van Krevelen and Hoftijzer (136). They assumed that the concentration of component 1 was constant to a value C_{1i} throughout the proper reaction zone in the liquid film; and the concentration C_{2L} in the bulk lower phase was negligible. Figure (1) illustrates the concentration profiles after Van Krevelen's assumption. The constant concentration C_{1i} is related to C_{2i} by the equation

$$N_{2A} = \frac{D_2}{x_R}(C_{2i}) = \frac{D_1}{x_f - x_R}(C_{1L} - C_{1i}) \qquad .... (7)$$

where N_{2A} is the transfer rate of 2 from the upper phase

x_R is the thickness of the reaction zone

also, defining: -

mass transfer coefficient with reaction

$$k^{\circ}_{LA} = \frac{D_2}{x_R} = \frac{N_{2A}}{C_{2i}} \qquad .... (8)$$

mass transfer coefficient without reaction

$$k^*_{LA} = \frac{D_2}{x_f} \qquad \text{.... (9)}$$

$$\phi = \frac{k^\circ_{LA}}{k^*_{LA}} \qquad \text{....(10)}$$

$$q = \frac{D_2 C_{2i}}{D_1 C_{1L}} \qquad \text{....(11)}$$

$$M = \frac{k C_{1L} x_f^2}{D_2} \qquad \text{....(12)}$$

solution for equations (3) and (4) is

$$\phi = \frac{k^\circ_{LA}}{k^*_{LA}} = \frac{x_f}{x_R} = \frac{\sqrt{M(1 - q(\phi - 1))}}{\tanh\sqrt{M(1 - q(\phi - 1))}} \qquad \text{....(13)}$$

If the value of ϕ is greater than 1, the diffusion path for component 2 will be shortened because of the reaction. It should be noted that the thickness x_f of the film is assumed to be the same with and without reaction under the same hydrodynamic conditions. A solution for equation (13), obtained by trial and error calculations, was first presented by Van Krevelen and Hoftijzer as given in figure (2).

Another approximated solution of equations (3) and (4) was obtained by Peaceman (95) who assumed that the concentration of component 1 in the film varied linearly from a value of C_{1i} at the interface to C_{1L} in the bulk of the liquid.

B) Retardation to mass transfer : -

1) Mass transfer coefficient

Considering the general transfer equation of component 2 from the upper phase into the lower phase; and assuming the resistance to transfer in the upper phase is negligible,

$$N_2 = k_L \Delta C = k_L (C_{2i} - C_{2L}) \qquad \text{.... (14)}$$

where

N_2 = transfer rate of component 2

k_L = mass transfer coefficient

For the system of ethyl acetate-sodium hydroxide, the reaction rate is very slow so that ethyl acetate (C_2) can be assumed to diffuse into aqueous sodium hydroxide phase and react with sodium hydroxide (C_1) in the bulk homogeneously.

Writing a mass balance for NaOH in the lower phase

$$FCo - FC_1 = kC_1C_2V \qquad \text{.... (15)}$$

where

F = flowrate of the lower phase

Co = input concentration of NaOH

V = volume of the lower phase

k = reaction constant

also, writing a mass balance for ethyl acetate in the lower phase

$$T = FC_2 + kC_1C_2V \qquad \text{.... (16)}$$

where

T = transfer rate of ethyl acetate

From equations (15) and (16), C_1 and C_2 can be calculated which are equivalent to C_{1L} and C_{2L}.

Referring to equation (14), if N_2 and C_{2i} are known, k_L can be calculated.

2) Mass transfer resistance

In the reaction runs of the ethyl acetate-sodium hydroxide system, decreases in mass transfer rates are observed with increasing concentrations of sodium hydroxide solutions in the lower phase. This retardation may be due to the change in either the concentration gradient $(C_{2i} - C_{2L})$ or the transfer coefficient (k°_{L}) or both of them.

a) Change in concentration gradient

The decrease in concentration gradient is due to the change in the ethyl acetate solubility which, in turn, is due to the salt effect of sodium acetate and sodium hydroxide present at the interface.

There have been a number of qualitative and quantitative theories of salt effect, all with common underlying aspects but emphasizing different approaches to the problem. They can roughly be divided into four groups: the hydration theories (38), the electrostatic theories (21), the Van der Waals forces (64) and the internal pressure concept (80). Comparison of experimental data with the theoretical values showed that the internal pressure concept is the best explanation for salting out effect on non-polar nonelectrolytes; while the electrostatic theories give better results for polar nonelectrolytes.

On the other hand, the decrease in solubility produced by an electrolyte can often be described by the empirical relation (96)

$$\ln (S^{\circ}/S) = k_s C \qquad \text{.... (17)}$$

over a considerable range (up to approximately 4.0 molal). S is the solubility in the solution of electrolyte of concentration C. S° is the solubility in pure water, and k_s is a constant for each specific electrolyte when salting out a particular nonelectrolyte.

Salt effect of sodium acetate on ethyl acetate is easy to evaluate since it requires only a few simple experiments to get the data for equation (17). On the contrary, salt effect of sodium hydroxide on ethyl acetate cannot be measured experimentally since they react with each other. Furthermore, the salt effect of sodium hydroxide on the nonelectrolyte cannot be calculated using Kirkwood's (60) or Deybe's (21) methods due to limited thermodynamic data available. Nevertheless, comparison of a large group of experimental data on salt effects (44)(73) indicates that the salting coefficient of sodium hydroxide on ethyl acetate should be in the same order of magnitude as sodium acetate on ethyl acetate. In this work, it is assumed that salting coefficients for both sodium hydroxide and sodium acetate on ethyl acetate are the same.

b) Change in mass transfer coefficients

There are several factors, all speculative, responsible for the decrease in mass transfer coefficients in the reaction runs. They are outlined briefly below: (i) modification of hydrodynamic conditions near the interface (ii) formation of a surface barrier, covering up part of the interface (iii) presence of an additional film due to slow chemical reaction.

Let

k_L^* = mass transfer coefficient of ethyl acetate without reaction

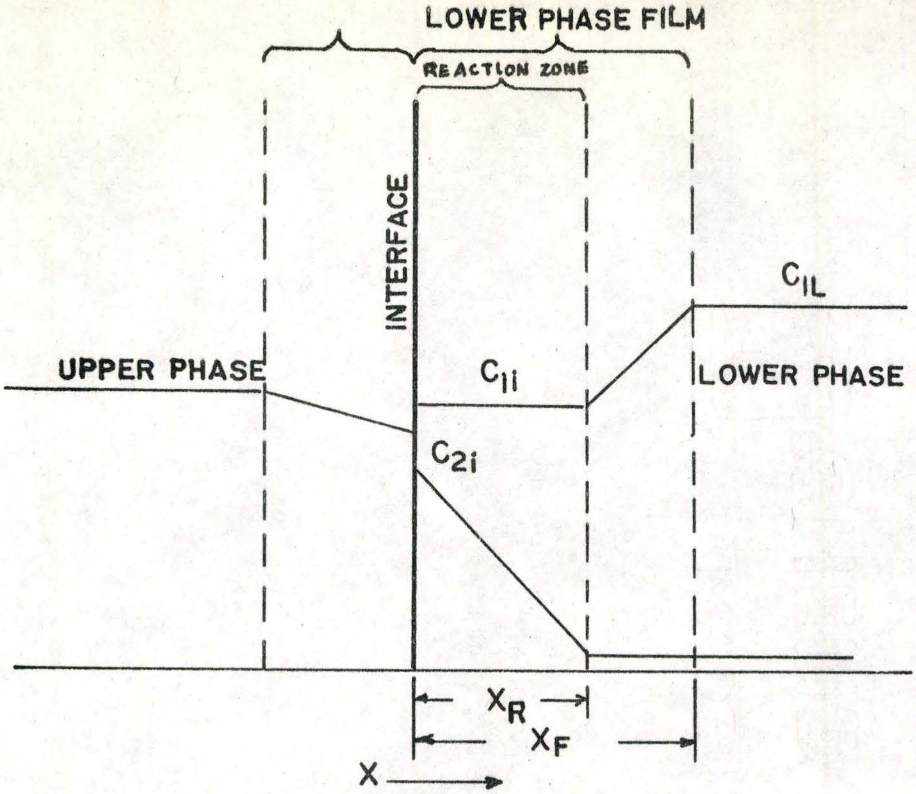
k_L° = mass transfer coefficient of ethyl acetate with reaction

$1/k_r$ = resistance

By the theory of additivity of resistances (71)(118),

$$1/k_L^\circ - 1/k_L^* = 1/k_r \qquad \text{.... (19)}$$

Concentration profiles of reactants are as shown in figure (3).



FIG·1 CONCENTRATION PROFILES IN THE LOWER PHASE FILM

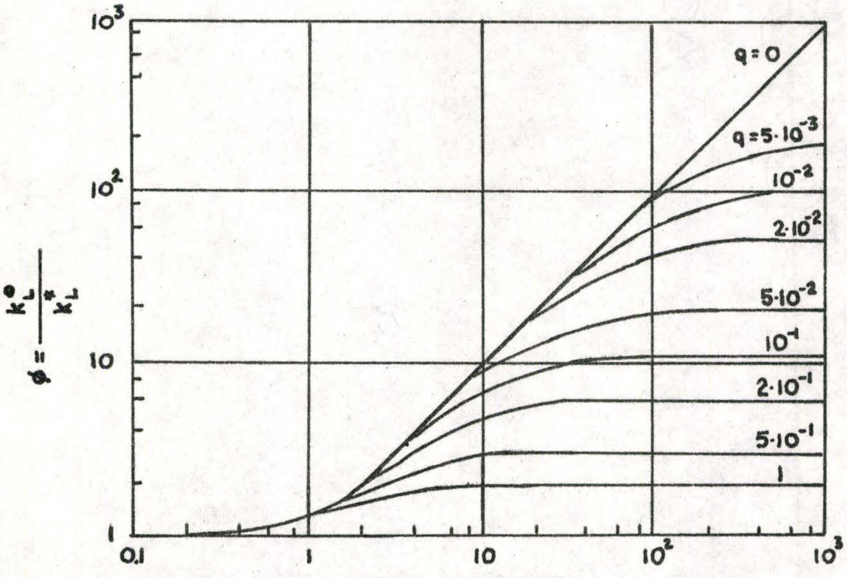


FIG. 2 SOLUTION OF EQUATION (13)

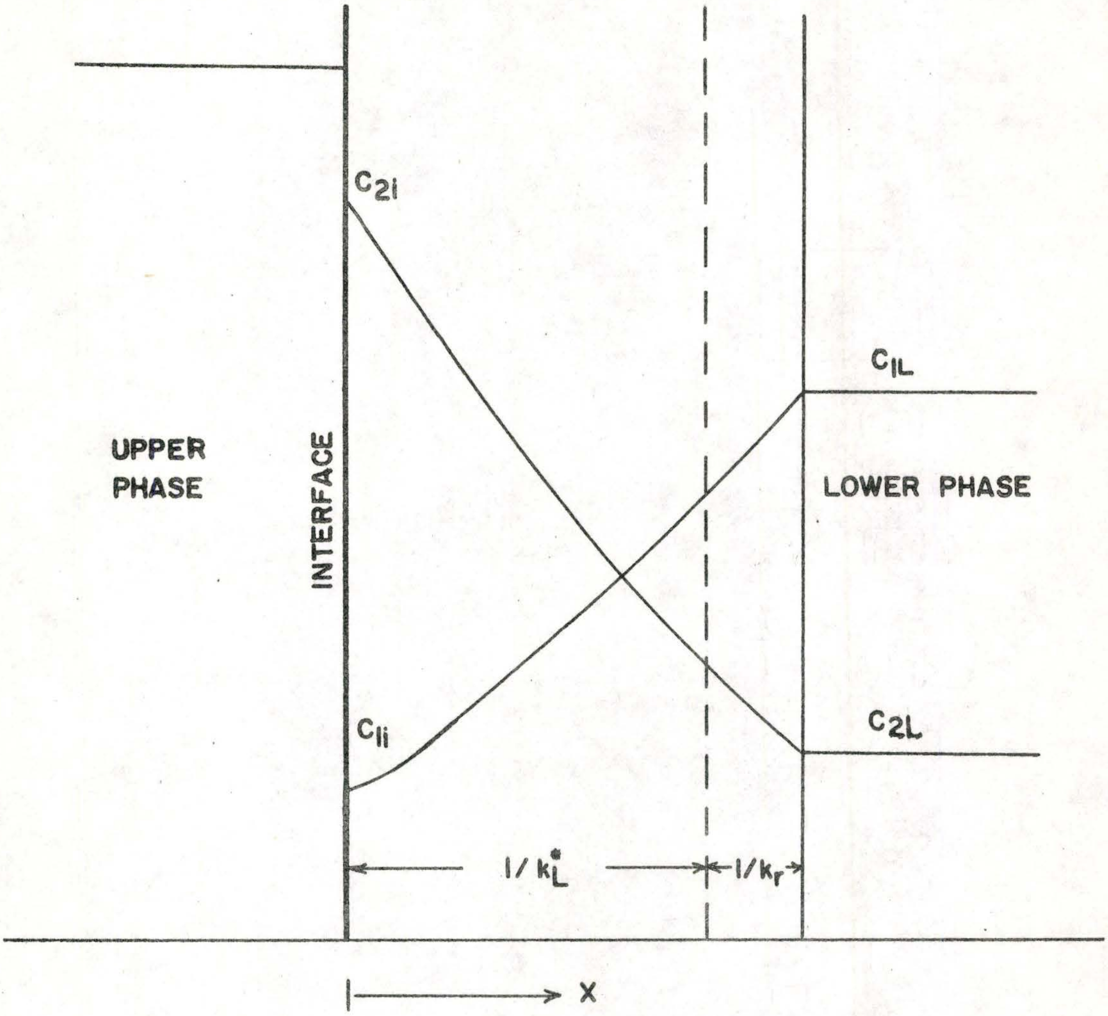


FIG. 3 CONCENTRATION PROFILES IN THE LOWER PHASE FILMS (WITH AN ADDITIONAL FILM)

EXPERIMENTAL DETAILS

A) Experimental : -

1) The flow sheet (Numbers in the following description refer to Figure (4))

The lower phase was introduced to surge tank (a 5-litre aspirator) and flowed into a constant head device (3). The outlet flow from the constant head device was regulated by an adjustable pinch clamp 13. The volumetric flow rate was metered by an FP flowmeter, tube #FP-1/8-12-G-5. The solution was then adjusted to the desired temperature by letting it flow through a round glass coil (6) immersed in a 12" diameter glass water bath (7). The outlet flow from the reactor was conducted through another constant head device (16) again and then to drain.

2) Experimental run

To start an experiment, pinch clamp (15) was closed. The ethyl acetate, pre-saturated with distilled water at the temperature of the experiment, was introduced into the reactor through the stopcock (16a) at the bottom of the lower compartment. Then the lower phase was let flow into the lower compartment very slowly so that mixing of the two phases was practically avoided. As more of the lower phase got into the lower compartment, ethyl acetate gradually rose into the upper compartment. When the interface reached the tip of the hook gauge and the ethyl acetate level reached about 1 cm. from the top of the upper compartment, pinch clamp(15) was screwed open and the stirrer started at 141 r.p.m. Then the flowrate was adjusted to the 12th division on the FP flowmeter which was about 1.5 litres/hour and has a range of ± 0.1 litre/hour, depending on the temperature of the experiment. This stirrer speed as well as the flowrate were pre-determined in the preliminary investigation.

The experiment was run at least for 20 minutes before taking any measurement in order that the system could come to steady state (retention time was approximately 4 minutes). Each experimental run lasted for at least 5 hours.

At the beginning and end of each experiment, the whole apparatus was flushed with distilled water for at least half an hour.

3) Measurement of transfer rate

At steady state, the interface was right at the tip of the hook gauge and the experiment was started. During the run, the upper phase was transferred into the lower phase. Therefore the volume of the upper phase decreased. The hydrodynamic equilibrium in the system was upset and the interface went up. A small amount of the upper phase liquid (1 to 2 ml) was added in at short intervals using a 5 ml syringe #H7608 manufactured by Becton, Dickinson and Company, U.S.A. This addition was to keep the level of the interface always at the tip of the hook gauge. The amount added would be equal to the amount transferred, if there was no other loss; thus the transfer rate could be calculated if the time between additions were known.

4) Interface adjustment

The interface was always kept constant to the indented point of the reactor: this was indicated very clearly by the tip of the hook gauge.

The interface level could be adjusted by the constant head device mounted on a vernier scale.

5) Temperature control

The experiments were performed at 3 temperature levels 25°C, 40°C and 55°C.

The temperature of the reactor was kept constant using a water jacket which was also made of pyrex glass with an outside diameter of 9.13 cm.

The water was kept at the desired temperature level to a range of ± 0.05°C by a Universal Thermostat, manufactured by Haake Company, Germany.

6) Vapor loss determination

Since the top of the reactor was open to the atmosphere, evaporation of the ethyl acetate was bound to occur. The stainless steel cup helped to reduce the evaporation but could not totally eliminate it. Consequently, part of the ethyl acetate added during the experiment was lost to the atmosphere instead of being transferred.

Experiments determining the rate of evaporation of ethyl acetate in the reactor were carried out at 25°C, 40°C and 55°C.

The reactor was filled with ethyl acetate up to the mark on the stem which was 1 cm. down from the top of the reactor. The stirrer was started at 141 r.p.m. and temperature was maintained at the desired level. In course of time, ethyl acetate vaporized and the level of ethyl acetate was kept constant at the mark by continuously adding fresh water-saturated ethyl acetate. The amount added per hour was taken as the evaporation rate at that temperature level.

7) Solubility measurements

Solubility of ethyl acetate in water was measured at three temperature levels (25°C, 40°C and 55°C). Water and ethyl acetate were mixed and shaken vigorously in a separatory funnel and then put into a water bath in which the temperature could be maintained at a desired level to within 0.05°C. Solubility measurements from both initially super-saturated and under-saturated solutions were made. The ethyl acetate-water mixture was maintained at that temperature for 24 hours and was well shaken at intervals. Both phases were then separated as quickly as possible to ensure against any change in temperature. The concentration of ethyl acetate in water was analysed in a gas chromatograph (Beckman GC-2A) using a carbowax column.

Duplicate runs were performed, and the results were within 5% deviation.

8) Salt effect

It was observed that when sodium acetate was added into a system of ethyl acetate-water in equilibrium condition, the condition in the water phase was disturbed and droplets of ethyl acetate were seen salting out.

The salt effect of sodium acetate in this work was determined experimentally at 25°C and 40°C and 55°C.

To 250 ml. of water, saturated with ethyl acetate at a certain temperature (for example, 25°C), a known amount of sodium acetate was added and the mixture was put into a water bath of the same temperature and well shaken at intervals. The top of the containing flask was coated with paraffin wax as to ensure against vapor loss. After 24 hours, the container was taken out and the amount of excess ethyl acetate salted out was measured; thus the decrease in solubility could be calculated. The experiment was repeated at other sodium acetate concentrations and then at other temperature levels.

9) Ideal concentration profile across the film

An analogue study was carried out in an attempt to solve the differential equations (3), (4), (5) and (6). The detailed procedure was as shown in Appendix IX.

10) Checking the assumption of homogeneous reaction in the lower bulk phase

The calculation of concentrations of ethyl acetate and sodium hydroxide in the lower phase involved the assumption of a homogeneous reaction throughout the lower phase. This assumption was checked by two experiments at 25°C and 55°C.

The experiment was performed as the normal run. At about 300 minutes, the transfer rate of ethyl acetate was recorded. The feed (sodium hydroxide solution) was shut off, the stirrer was stopped and the output line of the reactor was also clamped as to avoid the backflow of the liquid from the constant head device. The lower phase was then drained, through the stopcock at the bottom of the reactor, to about 2/3 of its original volume to a beaker. 25 ml. of the solution was pipetted to 30 ml. of HCl solution of known normality, so that the NaOH in the solution was neutralized with a little excess of HCl. The whole operation required 1.2 minutes to finish. The excess HCl was back titrated with standard solution of NaOH again. Brom thymol blue was used as indicator.

B) Number of mass transfer experiments performed: -

1) Ethyl acetate-aqueous sodium hydroxide system

More than 80 experiments were performed at three temperature levels and at various NaOH concentrations. The transfer rate for each run was measured. These experiments can be divided roughly into three groups.

The first group consisted of 36 runs was experimented with ethyl acetate prepared by Fisher Scientific Company some time ago. The second group consisted of 29 runs was experimented with ethyl acetate prepared more recently by the same company; this fact about ethyl acetate was known through the lot number of the drums purchased. In the third group of experiments, ethyl acetate used was purified by redistillation in the way as described in Appendix IV.

2) Ethyl acetate-water system

Physical transfer rates of ethyl acetate into water were also measured at the three temperature levels. All three types of ethyl acetate classified in the preceding section were used.

3) Ethyl acetate-aqueous potassium hydroxide system

Three runs at 55°C were performed with potassium hydroxide solution as the lower continuous flowing phase. The input potassium hydroxide concentration for each run was varied. The mass transfer rates of the ethyl acetate obtained were compared to that of sodium hydroxide runs.

4) Other mass transfer experiments

In order to study the effect of products on the transfer rates, 5 runs at 55°C using sodium acetate solution at various concentrations were performed. One run was performed at 55°C with ethanol solution as the lower phase. Besides, two runs were performed using sodium propionate solution as the lower phase, one with ethanol being added to the same concentration as that of sodium propionate. Apart from all these, duplicate runs at 55°C using sodium butyrate as the lower phase were also performed and the results were found to be reproducible.

In all of the experiments, mass transfer rates of ethyl acetate into the lower phase were measured.

C) Method of calculation: -

1) Mass transfer rates of ethyl acetate

In each run, time required for each 5 ml. of ethyl acetate to transfer into the lower phase was noted. These time intervals were plotted against time after the start of the experiment, (i.e. after the first measurement was taken). Typical plots were shown in figures (5), (6) and (7).

In some of the runs, steady state could not be obtained and therefore a certain time (for example, 300 minutes after the start of the experiment) was arbitrarily taken as a standard. Therefore transfer rates at 300 minutes for all the runs were obtained from the graphs. These results were corrected for vapor loss by subtracting the corresponding evaporation rates.

2) Mass transfer coefficients

Solving the simultaneous equations of (15) and (16) in the theoretical section, the concentrations of ethyl acetate (C_2) and sodium hydroxide (C_1) for the runs could be calculated.

The mass transfer coefficients with reaction (k_L°) could be evaluated from equation (14) with the solubility of ethyl acetate into water (C_{2i}) corrected for salt effect.

The entire calculations were done in a Bendix G-15 digital computer employing Algo programming.

3) Concentration of sodium hydroxide in the check run

(refer to Section A (10))

It should be noted that the concentration of sodium hydroxide obtained from titrations did not agree with the ones predicted from equations (15) and (16) mainly because there was a time lag of 1.2 minutes. During that period, the reaction still went on. The sodium hydroxide concentration, after 1.2 minutes, could be calculated by the following reasoning:

As soon as the flow of the lower phase was stopped, steady state condition in the lower compartment was no longer applicable. Since it was 1.2 minutes between the time when steady state ceased to exist and the time when the solution was neutralized , the condition at that 1.2 minutes became batchwise. The concentration of sodium hydroxide at the end of 1.2 minutes could be calculated using the following equation: (144)

$$\frac{1}{n_{20} - n_{10}} \ln \frac{n_{11} (n_{20} - (n_{10} - n_{12}))}{n_{12} (n_{20} - (n_{10} - n_{11}))} = k(t_2 - t_1) \quad .... (20)$$

where

n_{10} = original concentration sodium hydroxide

n_{11} = concentration of sodium hydroxide at the start of sampling

n_{12} = concentration of sodium hydroxide at the time of titration

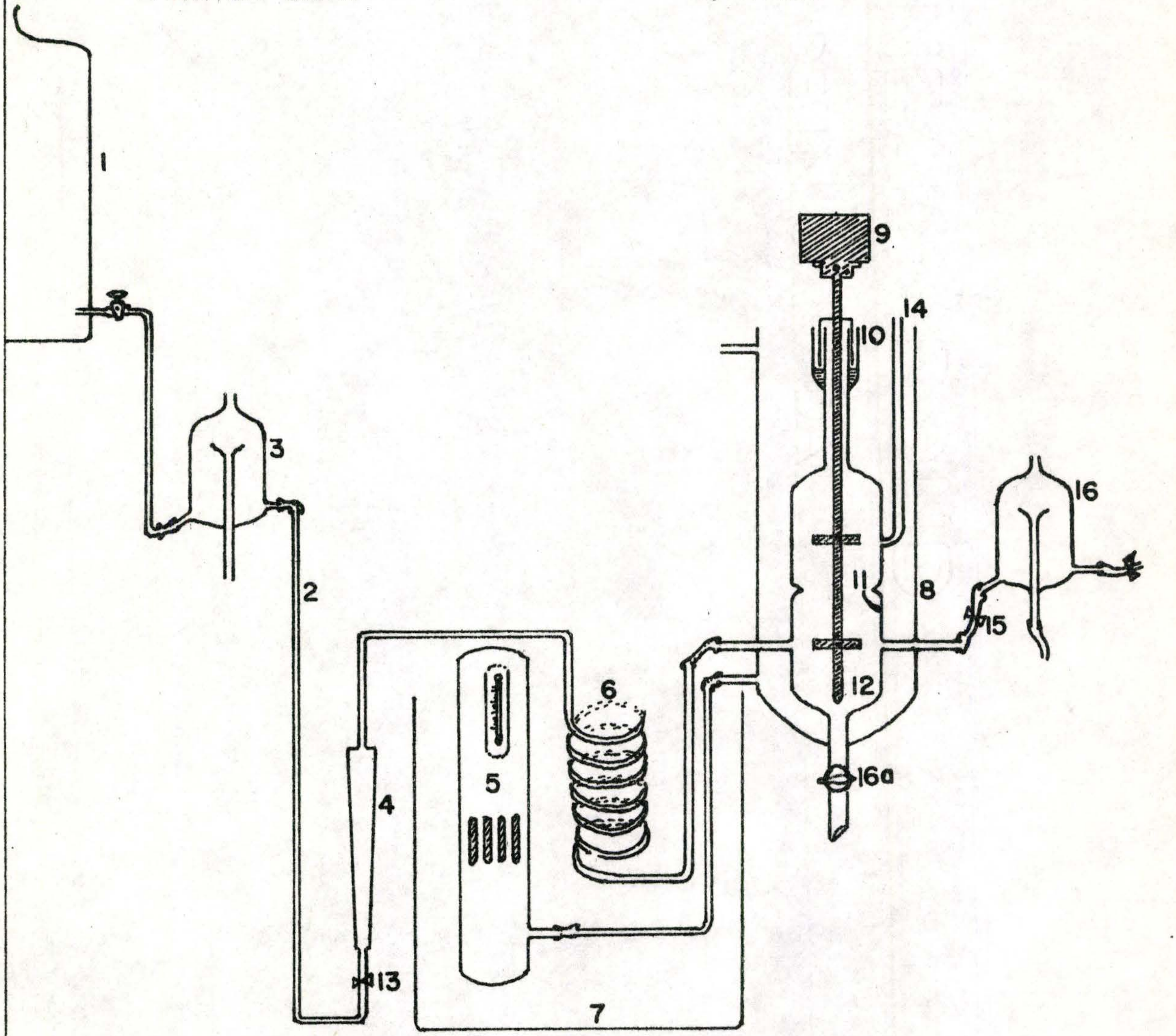
n_{20} = original concentration of ethyl acetate (if no reaction occurs) in the lower phase

k = reaction constant

$(t_2 - t_1)$ = time between the beginning of sampling and the titration

FIG. 4 STEADY STATE TRANSFER APPARATUS

1. RESERVOIR
2. TYGON OR GLASS TUBING
3. CONSTANT HEAD DEVICE
4. FLOWMETER
5. TEMP. CONTROLLER
6. GLASS COIL
7. WATER BATH
8. OUTER GLASS JACKET
9. CONSTANT SPEED MOTOR
10. MERCURY CUP
11. GLASS HOOK GAUGE
12. REACTOR
13. FLOW REGULATOR
14. STEM



RESULTS

1) A few samples of the detailed experimental data for the mass transfer runs for Group III of the ethyl acetate-sodium hydroxide runs were tabulated in Appendix V.

For the first group of the ethyl acetate-sodium hydroxide experiments, steady state was achieved almost right after the start of the experiment. Table 3 showed the variation of transfer rates (already corrected for vapor loss) with the initial input sodium hydroxide concentration in the continuous flowing lower phases. The physical transfer rates of ethyl acetate into water for this group were also included. Results in Table 3 were plotted on a semi-log scale graph as shown in figure (8).

For the second group of the ethyl acetate-sodium hydroxide experiments, steady state was reached about 100 minutes after the start of the experiment. Table 4 and figure (9) showed the variation of mass transfer rates of ethyl acetate with input sodium hydroxide concentrations. The physical transfer rates for this group were again included.

For the experiments performed with re-distilled ethyl acetate, steady state could hardly be attained even 300 minutes after the start of the experiments. Table 5 and figure (10) showed the transfer rates of ethyl acetate at 300 minutes versus input sodium hydroxide concentrations. Despite the scattering of data, all points on 55°C runs could be correlated by a straight line with a mean deviation of 10.7%. There was not much difference in the transfer rates for the 25°C and 40°C runs at the same input sodium hydroxide concentrations, and all the data in these runs could be correlated by a single straight line with a mean deviation of 13%.

The values of mass transfer rates for subsequent calculations were taken from the smoothed graph.

Results obtained for the runs with potassium hydroxide as the lower phase were tabulated in Table 6 and plotted in figure (11).

2) Using the experimental mass transfer rates, initial lower phase concentrations, flowrates and some other physical properties, the concentrations of ethyl acetate, sodium hydroxide, sodium acetate, and the mass transfer coefficient corrected for salt effect for each run were calculated and tabulated in Appendix VI.

Tables VII, VIII, IX showed the variation of the resistance $1/k_r$ with sodium acetate concentration in the lower bulk phase at the three temperature levels (values of $1/k_L^\circ$ were already corrected for salt effect). These results were also plotted in figure (13).

Mass transfer rates were also found to be retarded by the presence of sodium acetate, propionate and butyrate. Tables X and Xa showed the data obtained from these runs. Values of $1/k_r$ versus sodium acetate concentrations for ethyl acetate-sodium acetate solutions were recorded in Table Xa.

3) Solubility data for ethyl acetate in water were obtained and presented in Table I. Three samples were analysed in the gas chromatograph for each solubility determination and the average value was taken. Deviations between the values for each determination were less than 2%. The data were, on the average, about 10% higher than those recorded in the literature (56)(116). The data from the literature were used for

all calculations in this work.

4) Salt effect on solubility of ethyl acetate in solution of sodium acetate was described in Table II. Figure (12) showed the plot of solubility of ethyl acetate in sodium acetate solution versus concentration of sodium acetate.

5) The analogue study of concentration profiles across the film gave the results as shown (in the case of no enhancement of transfer rate by chemical reaction, and no effect of products on transfer rate):

Concentration	NaOH		NaAc		EtOAc	
	C_i	C_e	C_i	C_e	C_i	C_e
Run #85 0.11 N. NaOH at 55°C	.0364	.0398	.0758	.0702	.7500	0.121
Run #83 0.11 N. NaOH at 25°C	.0578	.0594	.0532	.0507	.8500	0.118

C_i = concentration at the interface in gm. moles/litre

C_e = concentration at the other end of the film in gm. moles/litre

The results were shown in figures (14) and (15).

6) For the two "check runs" performed at 25°C and 55°C, concentration of sodium hydroxide measured during the experiment agreed fairly well with the predicted value. Data obtained were shown as follows:

Run	measured NaOH conc. in the bulk lower phase	predicted NaOH conc. in the bulk lower phase	% deviation
25°C	0.0521 moles/litre	0.0565 moles/litre	7.8%
55°C	0.0528 moles/litre	0.0557 moles/litre	5.2%

TABLE I

SOLUBILITY DATA OF ETHYL ACETATE IN WATER

Temperature	Solubility of ethyl acetate in water (experimental)	Solubility of ethyl acetate in water (lit.)
25°C	0.980 moles/litre	0.850
40°C	0.844 moles/litre	0.773
55°C	0.822 moles/litre	0.750

TABLE II

VARIATION OF SOLUBILITY OF ETHYL ACETATE WITH SODIUM ACETATE CONCENTRATION

Temperature	Solubility of EtAc in 0.042 moles/litre NaAc solution	Solubility of EtAc in 0.085 moles/litre NaAc solution	Solubility of EtAc in 0.167 moles/litre NaAc solution	k_s
25°C	0.8224 moles/litre	0.7956 moles/litre	0.7642 moles/litre	0.369
40°C	0.7525 moles/litre	0.7362 moles/litre	0.7035 moles/litre	0.296
55°C	0.7359 moles/litre	0.7192 moles/litre	0.6948 moles/litre	0.230

TABLE III

VARIATION OF TRANSFER RATE OF ETHYL ACETATE WITH INPUT CONCENTRATION OF NaOH IN THE LOWER PHASE (GROUP I)

Conc. of NaOH Temperature	0 (water)	.0002 N	.00083 N	.0021 N	.105 N	.205 N	.389 N	1.001 N	2.41 N
25°C	15.76		4.38	4.41	4.51	4.24	3.78	2.99	1.65
	15.80					4.41	3.96	2.97	1.58
40°C	16.67		5.68	5.59	5.49	5.39	4.92	4.34	2.78
	16.97				5.52	5.40	5.01	4.41	2.61
							5.22		
55°C	18.70	16.80	10.43	7.91	6.63	7.17	6.27	6.27	4.30
						7.11	6.61	6.04	4.28

Note: Transfer rate of ethyl acetate saturated with water is in ml/hr

TABLE IV

VARIATION OF TRANSFER RATE OF ETHYL ACETATE WITH INPUT CONCENTRATION OF NaOH IN THE LOWER PHASE (GROUP II)

Conc. of NaOH Temperature	0 (water)	.00045 N	.00098 N	.00488 N	.0099 N	.051 N	.105 N
25°C	16.53	12.17	7.53 8.0	4.86	4.23 4.44	4.33 4.43	4.33
40°C	17.82	14.10	11.41 11.20	6.95	6.21 6.00	5.67	5.58 5.60
55°C	18.65	18.42	18.20 18.30	10.96	9.05 8.85	6.85 6.86 6.76	8.04 8.70

Note: Transfer rate of ethyl acetate saturated with water is in ml/hr

TABLE V

VARIATION OF TRANSFER RATE OF ETHYL ACETATE WITH INPUT CONCENTRATION OF NaOH IN THE LOWER PHASE (GROUP III)

Conc. of NaOH Temperature	0 (water)	.0002 N	.001 N	.0057 N	.01 N	.051 N	.11 N	.389 N
25°C	16.80	14.93	13.13	13.13		13.07	12.00	10.92
40°C	18.47		14.17	11.77 11.21		12.97		11.17
55°C	20.00	19.55	18.05	14.86	15.15	15.18		13.20

Note: Transfer rate of ethyl acetate saturated with water is in ml/hr.

TABLE VI

VARIATION OF TRANSFER RATE OF ETHYL ACETATE WITH INPUT CONCENTRATION OF KOH IN THE LOWER PHASE

Conc. of KOH Temperature	0 (water)	0.095 N	0.343 N	0.755 N
55°C	20.00	18.75	13.85	11.55

Note: Transfer rate of ethyl acetate saturated with water is in ml/hr

TABLE VII

VARIATION OF $1/k_L^o$ AND $1/k_r$ WITH SODIUM ACETATE CONCENTRATION IN THE LOWER BULK PHASE

ETHYL ACETATE - AQUEOUS SODIUM HYDROXIDE SYSTEM

(GROUP III) AT 25°C

Conc. of input NaOH (normality	.0001	.0002	.001	.0057	.01	.051	.11	.389
$1/k_L^o(1/hr)^{-1}$	5.110	5.217	5.488	5.833	5.957	6.314	6.361	5.582
$1/k_r(1/hr)^{-1}$	.703	.810	1.081	1.426	1.550	1.907	1.954	1.175
conc. of NaAc (normality)	.00007294	.0001451	.0007145	.003967	.006847	.03014	.05065	.07122

TABLE VIII

VARIATION OF $1/k_L^o$ AND $1/k_r$ WITH SODIUM ACETATE CONCENTRATION

IN THE LOWER BULK PHASE

ETHYL ACETATE - AQUEOUS SODIUM HYDROXIDE SYSTEM

(GROUP III) AT 40°C

Conc. of input NaOH (normality)	.0001	.0002	.001	.0057	.01	.051	.11	.389
$1/k_L^o$ (litres/hr)$^{-1}$	4.687	4.784	5.041	5.371	5.491	5.915	6.050	5.476
$1/k_r$ (litres/hr)$^{-1}$	1.073	1.170	1.427	1.757	1.877	2.301	2.436	1.862
conc. of NaAc (normality)	.00008576	.0001709	.0008481	.004757	.008255	.03696	.05847	.06957

TABLE IX

VARIATION OF $1/k_L^o$ AND $1/k_r$ WITH SODIUM ACETATE CONCENTRATION IN THE LOWER BULK PHASE

ETHYL ACETATE - AQUEOUS SODIUM HYDROXIDE SYSTEM

(GROUP III) AT 55°C

Conc. of input NaOH (normality)	.0001	.0002	.001	.0057	.01	.051	.11	.389
$1/k_L^o$ $(\text{litre/hr})^{-1}$	3.331	3.448	3.746	4.144	4.294	4.884	5.181	5.006
$1/k_r$ $(\text{litre/hr})^{-1}$	.097	.214	.512	.910	1.060	1.650	1.947	1.772
conc. of NaAc (normality)	.00009380	.0001874	.0009320	.005263	.009179	.04341	.07020	.07580

TABLE X

VARIATION OF TRANSFER RATE OF ETHYL ACETATE WITH INPUT CONCENTRATION OF SODIUM ACETATE, OR SODIUM PROPIONATE, OR SODIUM BUTYRATE SOLUTION IN THE LOWER BULK PHASE

conc. of solution(N.) Temperature	NaAc .0122	NaAc .0366	NaAc .112	NaAc .461	Na Propionate .397	Na Butyrate .402
55°C	19.37	18.50	17.25	15.54	15.37	7.05
					15.35	7.14

Note: Transfer rate of ethyl acetate saturated with water is in ml/hr

TABLE Xa

VARIATION OF $1/k_L^*$ AND $1/k_r$ WITH SODIUM ACETATE CONCENTRATION IN THE LOWER BULK PHASE

ETHYL ACETATE – SODIUM ACETATE SOLUTION SYSTEM AT 55°C

Conc. of NaAc Solution (normality)	.0122	.0366	.112	.461
k_L^* (litre/hr)	.2978	.2822	.2599	.2303
$1/k_L^*$ $(\text{litre/hr})^{-1}$	3.362	3.545	3.856	4.341
$1/k_r$ $(\text{litre/hr})^{-1}$	.128	.311	.622	1.107
k_L^* (litre/hr) corrected for salt effect	.3002	.2871	.2758	.2960
$1/k_L^*$ $(\text{litre/hr})^{-1}$	3.332	3.481	3.630	3.410
$1/k_r$ $(\text{litre/hr})^{-1}$ corrected for salt effect	.098	.247	.396	.176

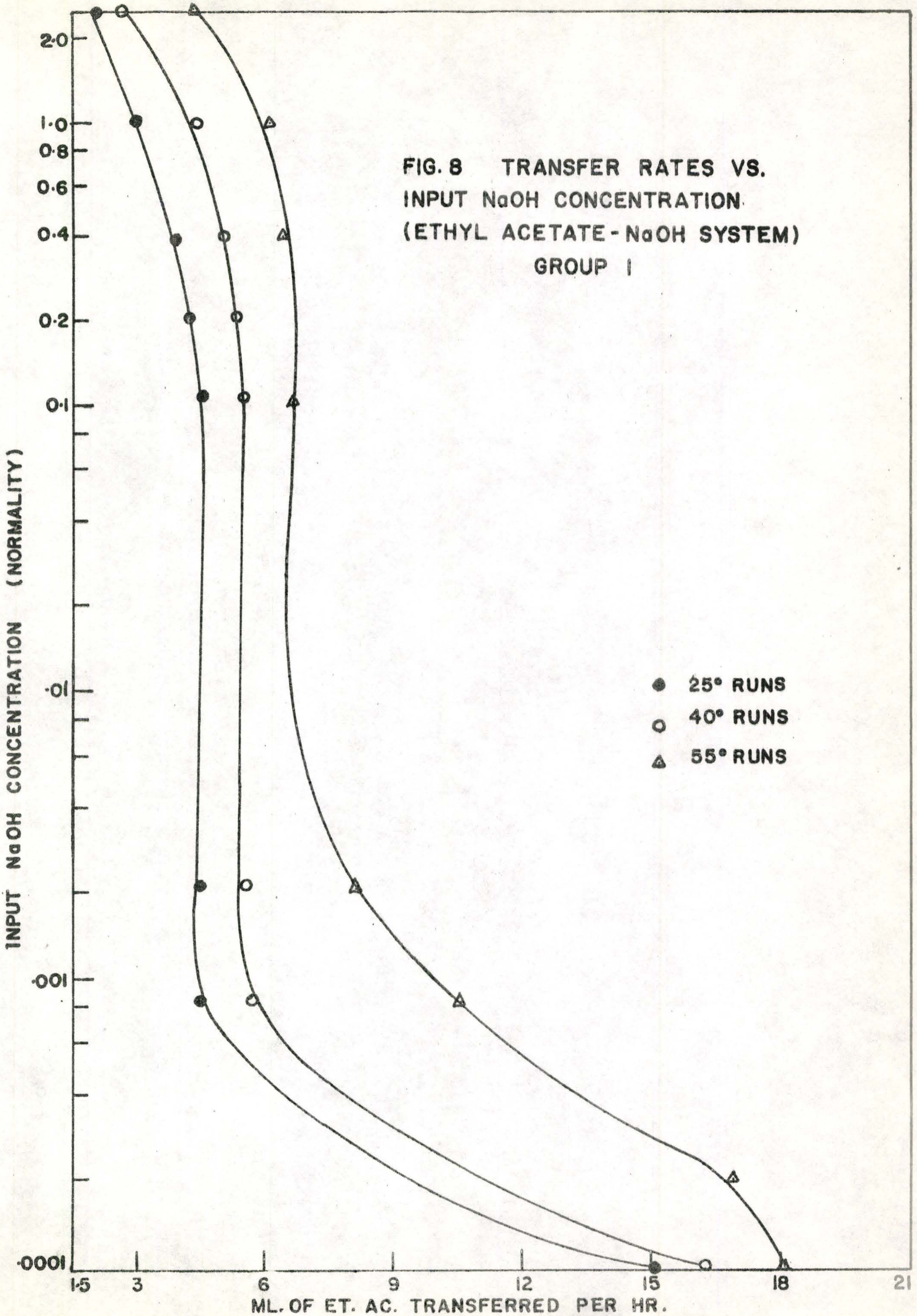


FIG. 8 TRANSFER RATES VS. INPUT NaOH CONCENTRATION (ETHYL ACETATE-NaOH SYSTEM) GROUP I

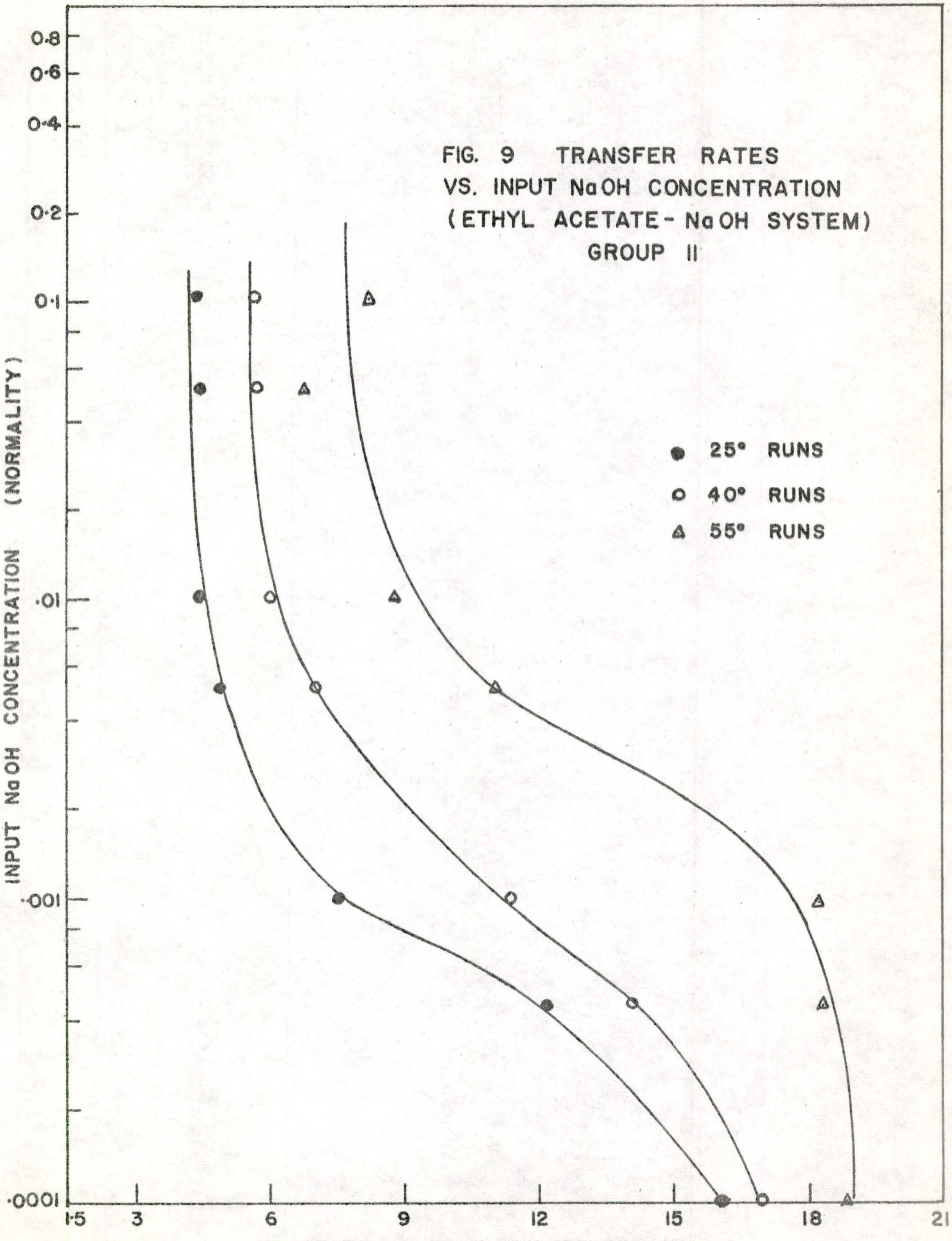


FIG. 9 TRANSFER RATES VS. INPUT NaOH CONCENTRATION (ETHYL ACETATE - NaOH SYSTEM) GROUP II

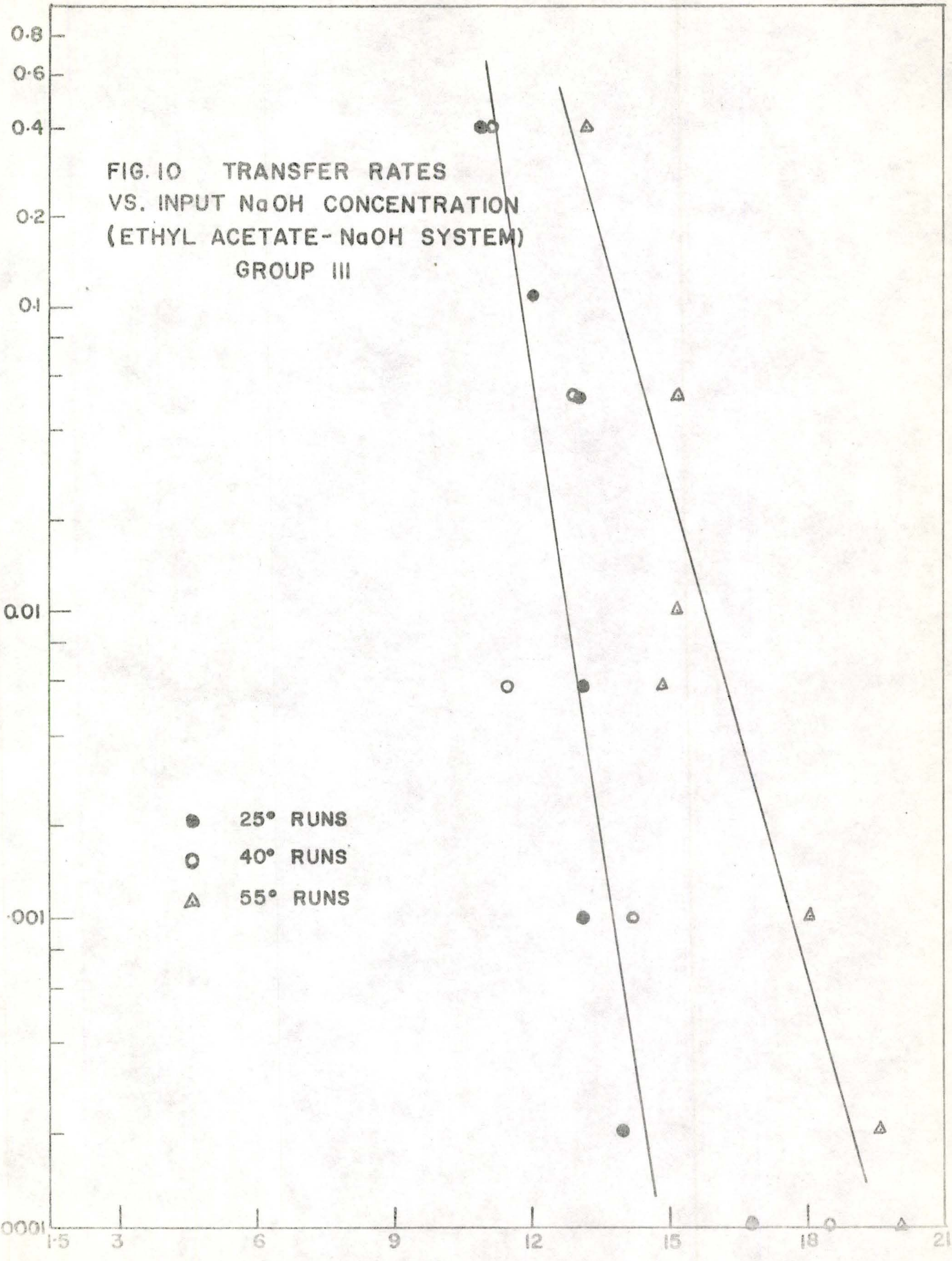


FIG. 10 TRANSFER RATES
VS. INPUT NaOH CONCENTRATION
(ETHYL ACETATE-NaOH SYSTEM)
GROUP III
● 25° RUNS
○ 40° RUNS
△ 55° RUNS
INPUT NaOH CONCENTRATION (NORMALITY)
0·8
0·6
0·4
0·2
0·1
0.01
·001
·0001
1·5
3
6
9
12
15
18
21
ML. OF ET. AC. TRANSFERRED PER HR.

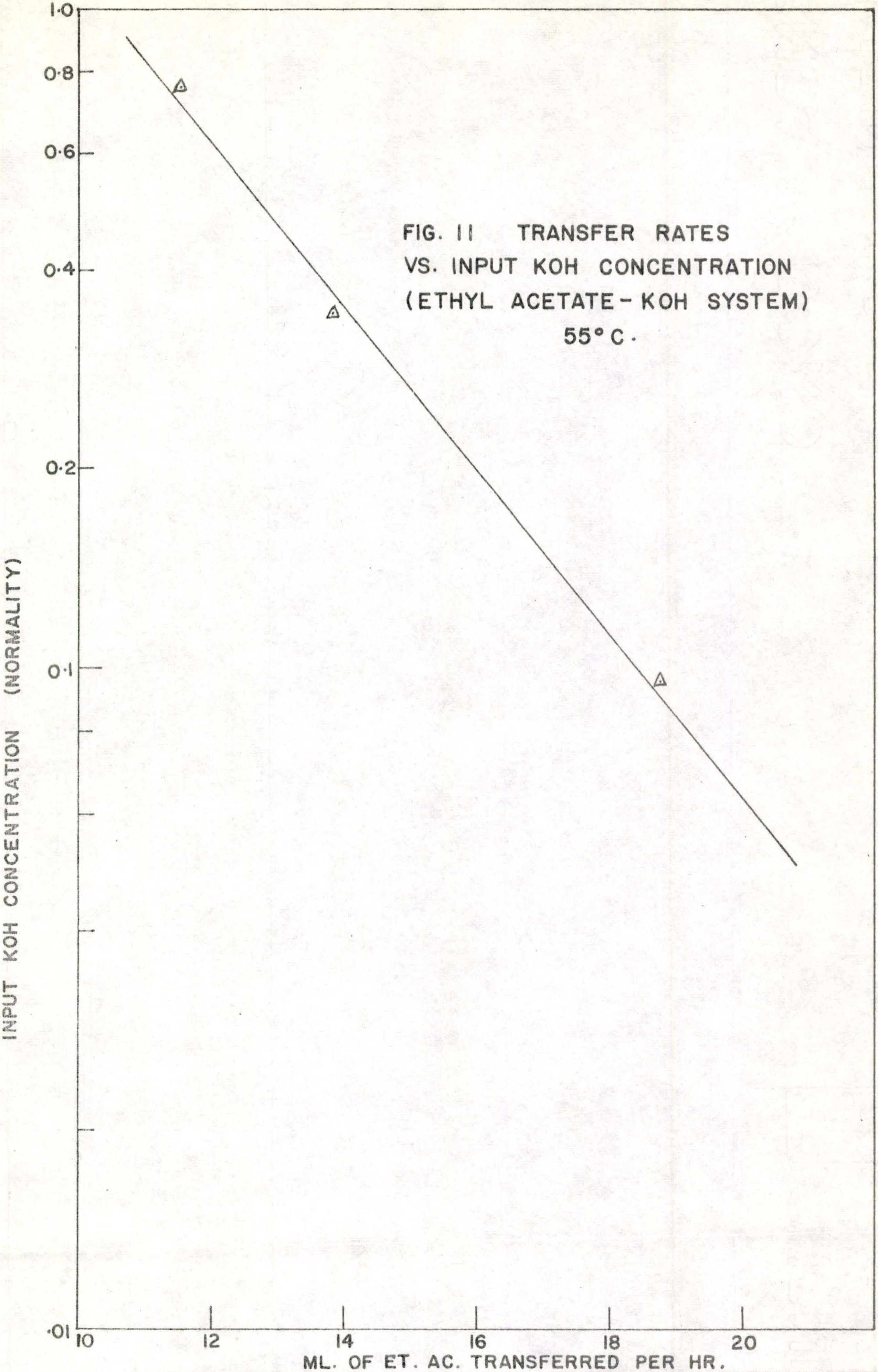


FIG. 11 TRANSFER RATES
VS. INPUT KOH CONCENTRATION
(ETHYL ACETATE - KOH SYSTEM)
55° C.
1·0
0·8
0·6
0·4
0·2
0·1
·01
10
12
14
16
18
20
INPUT KOH CONCENTRATION (NORMALITY)
ML. OF ET. AC. TRANSFERRED PER HR.

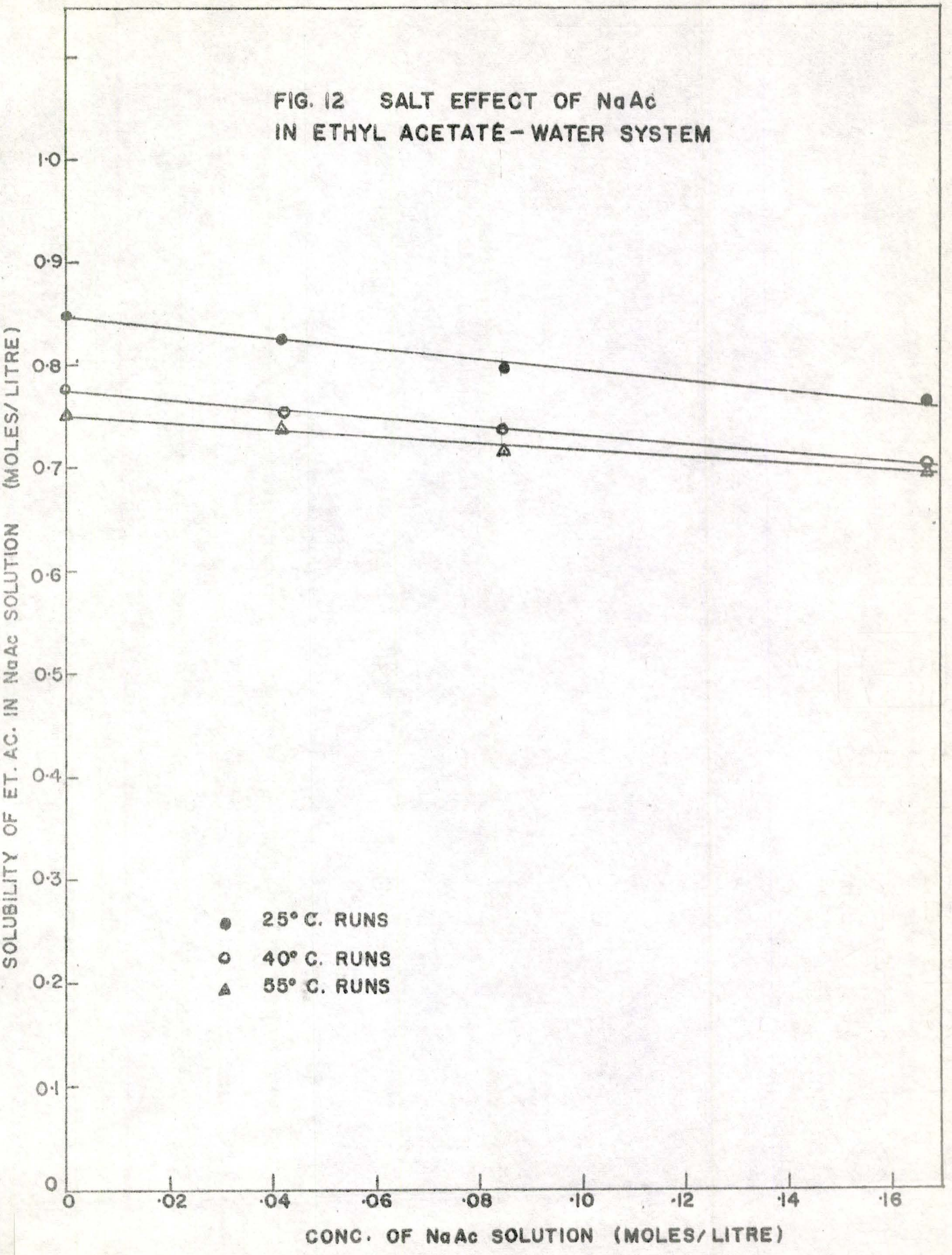


FIG. 12 SALT EFFECT OF NaAc IN ETHYL ACETATE-WATER SYSTEM

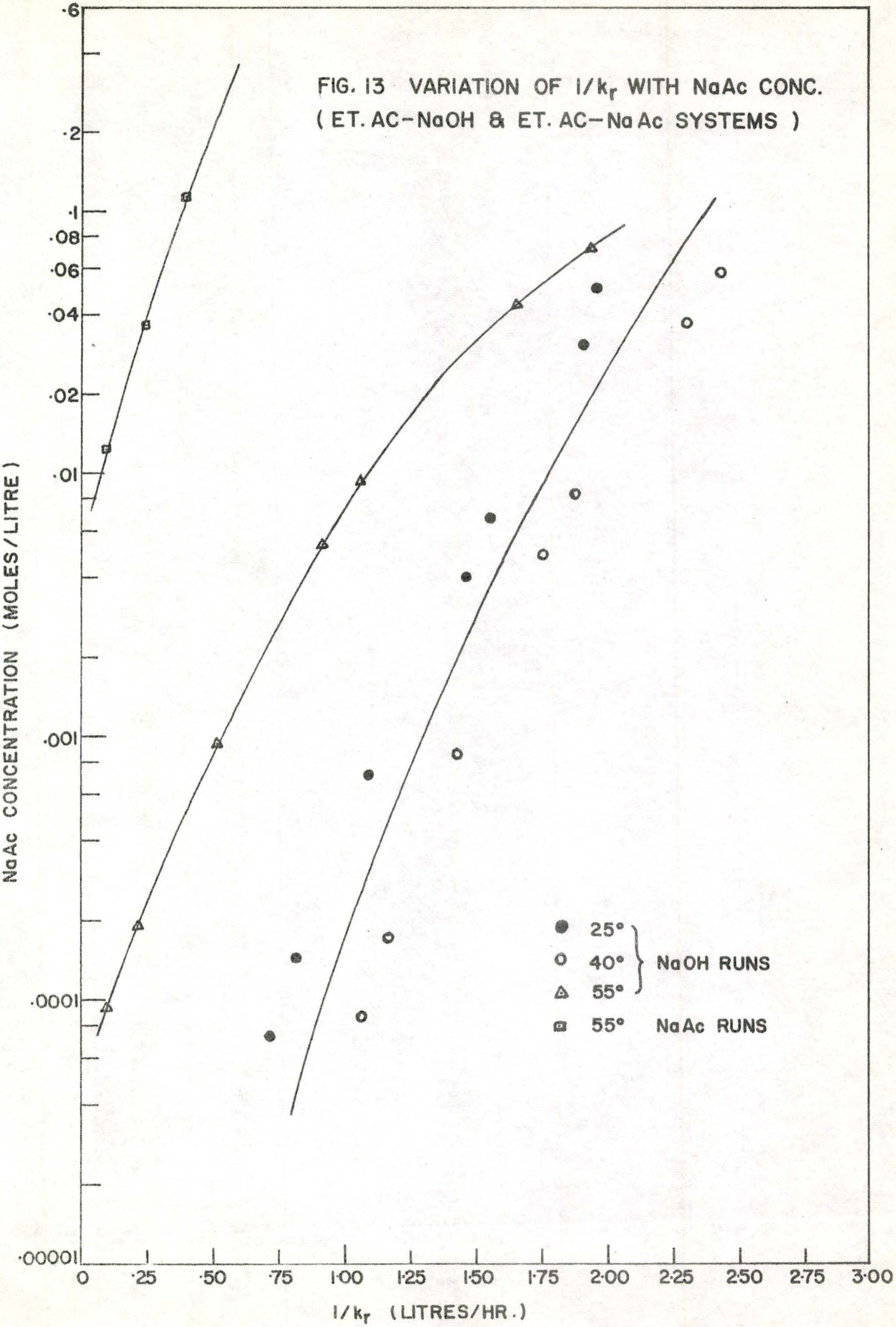


FIG. 13 VARIATION OF $1/k_r$ WITH NaAc CONC. (ET. AC−NaOH & ET. AC−NaAc SYSTEMS)

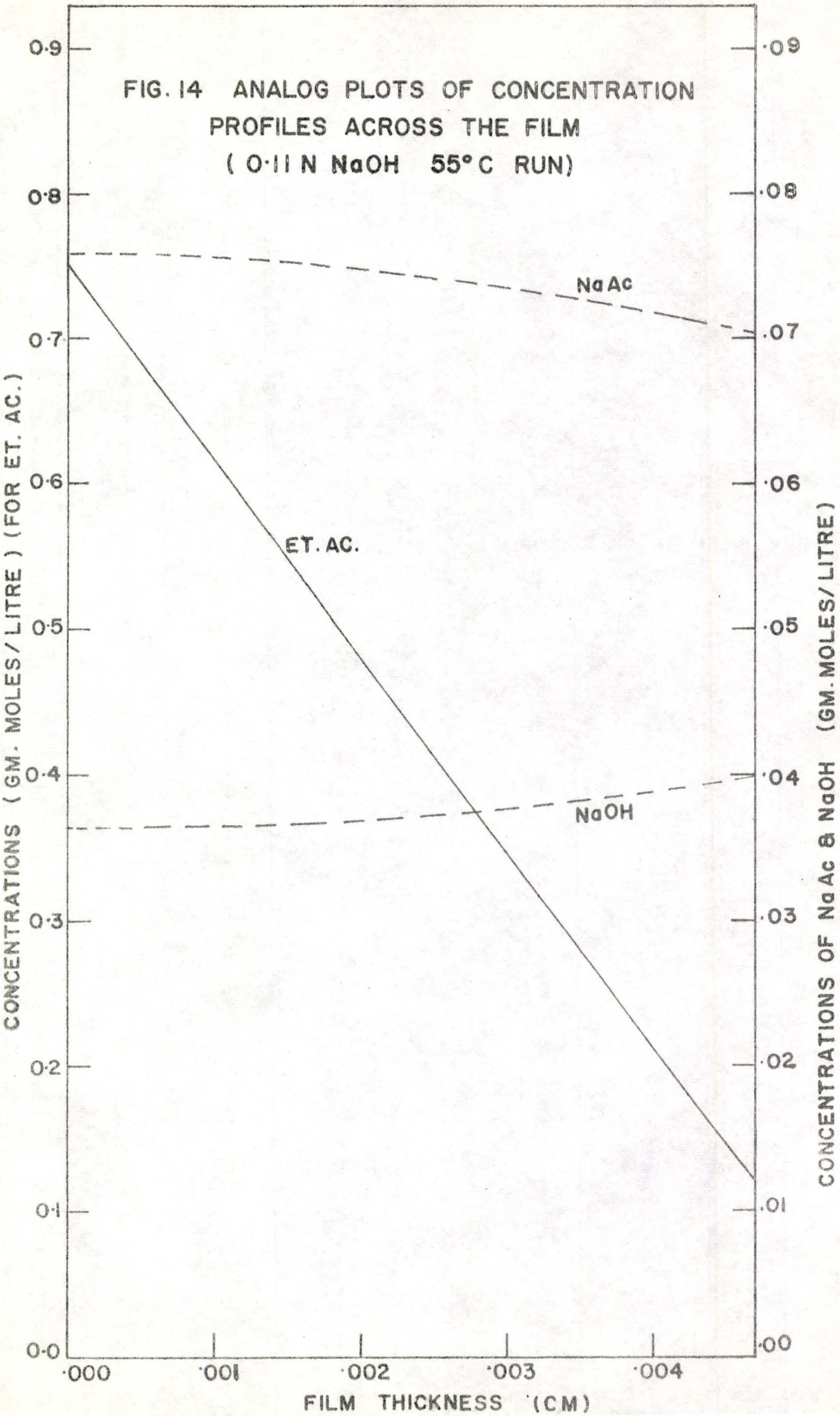


FIG. 14 ANALOG PLOTS OF CONCENTRATION PROFILES ACROSS THE FILM (0·11 N NaOH 55°C RUN)

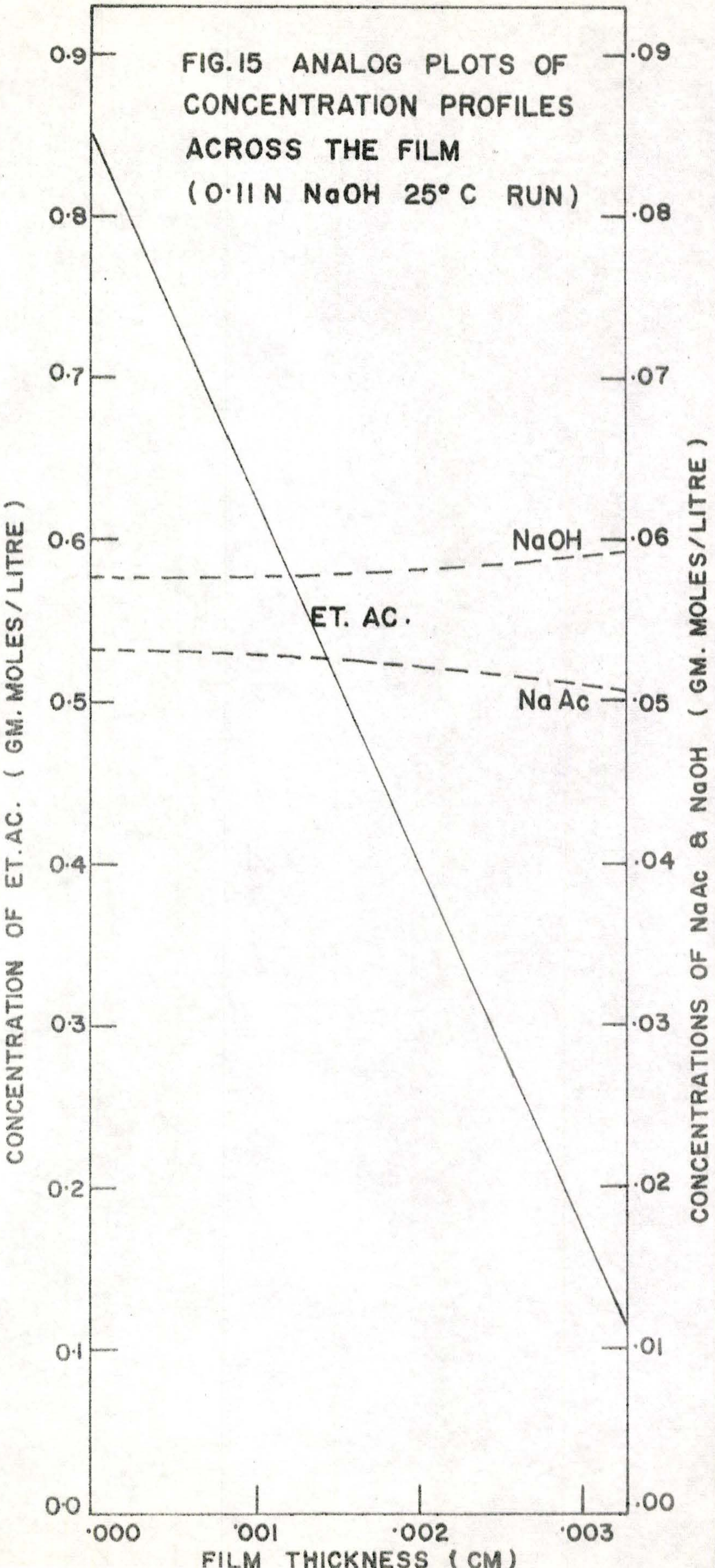


FIG. 15 ANALOG PLOTS OF CONCENTRATION PROFILES ACROSS THE FILM (0·11 N NaOH 25° C RUN)

DISCUSSION OF RESULTS

1) The chemical reaction involved in the system of ethyl acetate-sodium hydroxide

The saponification of ethyl acetate can be described by the following reaction equation

$$NaOH + CH_3COOC_2H_5 = CH_3COONa + C_2H_5OH \quad \text{.... (21)}$$

This reaction is second order and irreversible. A large amount of data on reaction constants in homogeneous phase can be obtained from literature, as shown in Appendix VIIIc. It is found that these data are generally consistent.

2) Comparison of transfer rates between Groups I, II, III of ethyl acetate-sodium hydroxide system

Comparison of results on Groups I and II of the reaction transfer runs on ethyl acetate-sodium hydroxide system reveals that transfer rates of Groups I and II runs are not the same even at identical input sodium hydroxide concentration; although reproducible results are obtained within each individual group. Generally, as seen in figures (8) and (9), mass transfer rates for the first group are lower than that of the second group. Incidentally, ethyl acetate used for Group II runs is more recently prepared than that used for Group I. It is, therefore, logical to suspect that some contaminants formed in the ethyl acetate during storage time. These contaminants may accumulate at the interface during the experimental run and act as a sort of resistance helping to reduce the interphase mass transfer. More contaminants may form in the ethyl acetate as the storage time increases.

There are some speculations on the nature of these contaminants which may be surface active agents or compounds of higher molecular weights. If the speculations are right, these contaminants should have high boiling points. The ethyl acetate used for Group III of the reaction runs is purified by re-distillation. It is expected that after re-distillation, contamination in ethyl acetate is reduced to a minimum if not completely elimimated; and for this reason, only the results in this group are considered for further calculations and discussion.

The results in Group III, as seen in figure (10), show that the transfer rates of the purified ethyl acetate into sodium hydroxide solution are much higher than those of Groups I and II. In spite of this, the transfer rates for all the reaction runs are still lower than the physical mass transfer rates into water at the same experimental temperature.

It should be noted, on the other hand, that for some of the experiments in this group, steady state cannot be reached even when the experiments are run up to 300 minutes —— the time when transfer rates for the runs are recorded. For this reason, the steady state equations for calculating C_{1L} and C_{2L} are not strictly valid. Fortunately, by observing figures (6) and (7), it is obvious that the change in transfer rates with time are so slow that steady state can be assumed without too great a sacrifice in accuracy.

3) Ethyl acetate-potassium hydroxide system

Table VI and figure (11) of the ethyl acetate-potassium hydroxide runs at 55°C show a similar trend of retardation in mass transfer as those of the ethyl acetate-sodium hydroxide system although the transfer rates obtained between two corresponding experiments are not quite the same. The difference in transfer rates is probably due to different experimental conditions, such as density, viscosity, interfacial tension and diffusivity of the liquids in concern. The reaction constants for the two systems are almost the same.

4) Calculation of $1/k_r$ in ethyl acetate-sodium hydroxide system

The retardation in transfer for each run is evaluated in terms of a resistance ($1/k_r$) as explained in equation (19). The term $1/k_L^\circ$ is calculated from equation (14) which includes the concentration term C_{2L}. Calculation of the concentration of ethyl acetate in the bulk lower phase involves the assumption of homogeneous reaction happening in the bulk lower phase. The two "check runs" performed at 25°C and 55°C indicate that this assumption is quite close to the actual situation.

5) Application of the "film theory" to the ethyl acetate-sodium hydroxide system

As seen from the reaction constant, the rate of reaction for the system under study is very slow. Van Krevelen and Hoftijzer's model for slow, second order, irreversible reaction is applied to this system and the enhancement factor ϕ is found to be practically equal to 1. The theoretical enhancement of transfer rate by this chemical reaction is very small if not negligible.

Results for the application are tabulated as shown: (refer to figure (2) in the "Theoretical Principles" chapter)

Variables	q	$\frac{(kD_2C_{1L})^{1/2}}{k^*_{LA}}$	ø
Run #85 0.11 N. NaOH 55°C	10.75	0.169	1
Run #88 0.389 N. NaOH 55°C	1.36	0.474	1.12 (approx.)
Run #86 0.389 N. NaOH 25°C	1.63	0.208	1

It is concluded that Van Krevelen's model does not apply to this reacting system, at least, not in the sodium hydroxide concentration range taken in this study.

6) Comparison of results on ethyl acetate-sodium hydroxide system obtained by other workers

Semi-batchwise absorptions of ethyl acetate vapor in caustic solutions were carried out by Jenny (57). Both phases were stirred during the experiment and the mixture of the ester with air was fed continuously to the gas space.

Also, transfer of the ester from a fixed ethyl acetate drop into the flowing sodium hydroxide solution was measured by Watada of this Department (147).

Data from both of them confirm that retardation to mass transfer rates occurs when ethyl acetate transfers into sodium hydroxide solutions instead of into water.

7) Possible factors governing the retardation

a) Effect of experimental conditions

The experimental conditions between the physical and reaction mass transfer runs may be different due to changes in density and viscosity. Usually, this change can be correlated using the stirrer Reynolds number.

$$Re = \frac{r \times d^2 \times \rho}{\mu}$$

where r is the number of revolutions per unit time, d the diameter of the stirrer, ρ the density and μ the viscosity of the liquid, respectively.

The concentrations of the input sodium hydroxide solution for all the Group III reaction runs are so low that the stirrer Reynolds number between the reaction runs and the physical runs are practically the same.

As an example, "Re" for Run #86 (0.389 N. NaOH at 25°C) is compared to that of the physical transfer run at the same temperature.

Stirrer Reynolds number for reaction run (maximum case):

$$Re = \frac{141/60 \times (2.4)^2 \times 1.015}{1.08/100} = 1275$$

Stirrer Reynolds number for physical run:

$$Re = \frac{141/60 \times (2.4)^2 \times 1}{1/100} = 1354$$

Deviation is only 5.8%.

NOTE: Data for ρ and μ are taken from International Critical Tables.

b) Back transfer of ethanol

During the reaction, ethanol is produced as a product. The ethanol formed diffuses back into the upper ethyl acetate phase; thus the transfer rate measured is lower than the actual transfer rate.

As a practical example, Run #85 (0.11 N. NaOH at 55°C) is considered. Ethanol formed is equivalent to the amount of sodium acetate formed according to the mass balance in the reaction equation: this is 0.0702 moles/litre. Assume steady state is reached at 300 minutes after the start of the experiment, the equilibrium concentration of ethanol in the upper phase is approximately 0.047 moles/litre. This means that $0.047 \times 46 \times 1/0.78 \times 0.11 = 0.305$ ml/(5 hours) of ethanol is back transferred into the upper phase.

From the above result, the back transfer is, of course, negligible.

c) Effect of back transfer of ethanol on the rate of ethyl acetate transfer

It has just been shown, in the preceding section, that the volume of ethanol diffusing back may introduce error in the measurement of ethyl acetate transfer.

However, the process of back diffusing of ethanol might reduce the transfer rate of ethyl acetate to some extent. Furthermore, the presence of ethanol may affect the properties, for example, the interfacial tension of the system. In order to check this point, transfer rates of ethyl acetate into ethanol solution and ethanol, sodium propionate solution were measured. Results indicate that ethanol has no effect on transfer rates.

d) Back transfer of sodium acetate and sodium hydroxide

It is suspected that the transfer rate of ethyl acetate may be altered by the back diffusion of sodium acetate and sodium hydroxide into the upper phase.

In the case of experiments performed at 55°C level, and according to solubility data, approximately 4.2% by weight of water is in the upper phase, that is about 4.3 ml. This amount can, at least theoretically, dissolve 0.15 gm. moles of sodium hydroxide and 0.07 gm. moles of sodium acetate. However, the actual situation in the upper phase may be very complicated: whether the water in ethyl acetate actually can dissolve any sodium hydroxide or sodium acetate or not is very doubtful.

Ethyl acetate in the upper phase after experimental runs was tested for the presence of sodium hydroxide by phenolphthalein indicator. Then the whole phase was evaporated to dryness to see if there was any white residue. Neither sodium acetate nor sodium hydroxide was found in the upper phase in each run.

It may be speculated that during the run, some of the sodium hydroxide diffuses into the upper phase and reacts with the ethyl acetate. The sodium acetate formed largely goes back to the interface or the lower bulk phase so that analysis of the upper phase shows no trace of sodium ions.

e) Effect of sodium acetate and sodium hydroxide

Two compounds are formed as products of the chemical reaction. One is ethanol which has been proven to have no effect on the transfer rate; the other is sodium acetate.

Mass transfer rates of ethyl acetate into sodium acetate solution at 55°C were measured and the results showed a positive retardation to transfer as a function of sodium acetate concentration. The retardation thus obtained was expressed in terms of resistance $(1/k_r)$. Part of the resistance calculated was due to salt effect, and the values of $(1/k_r)$, after being corrected for salt effect, were plotted against sodium acetate concentration in the lower phase as shown in figure (13). As observed, the resistance due to the presence of sodium acetate in the bulk lower phase accounted for only a small part of the resistance in the reaction run.

Just how the sodium acetate can decrease the ethyl acetate transfer is unknown. Visual observations in physical transfer runs show that it does act, to some extent, like a surface active agent stablizing the interface. Similar action would be expected for the sodium hydroxide.

In addition, physical transfer results of sodium propionate and sodium butyrate runs indicate that higher members of the homologous series do have a greater retardation effect to transfer rates.

Another speculation for the cause of resistance is to assume that adsorption of sodium acetate happens at the interface. Experiments were carried out to measure interfacial tension change as shown in Appendix VIII, B. Results obtained were not accurate enough to prove the existence of either an adsorption or desorption.

Also, the situation at the interface when with a chemical reaction is expected to be quite different to the one without. There may be some factors associated only with the chemical reaction, causing the retardation; these factors cannot be duplicated in physical transfer runs.

It should also be noted that the effect of sodium acetate and chemical reaction on the transfer rate are counter-balancing each other. The more rapid the reaction, the greater is the enhancement on transfer, but, at the same time, more sodium acetate is formed which causes the retardation.

f) Additional film

Additional resistance arises due to the formation of an extra film in the bulk lower phase. This is more fully discussed in Appendix X.

g) Effect of contaminants

In the same way as the contaminants found in the ethyl acetate, it is possible that sodium hydroxide used for the experiments may also have traces of contaminants which cause retardation in transfer. On the other hand, the ethyl acetate may still contain contaminants which cannot be separated by re-distillation.

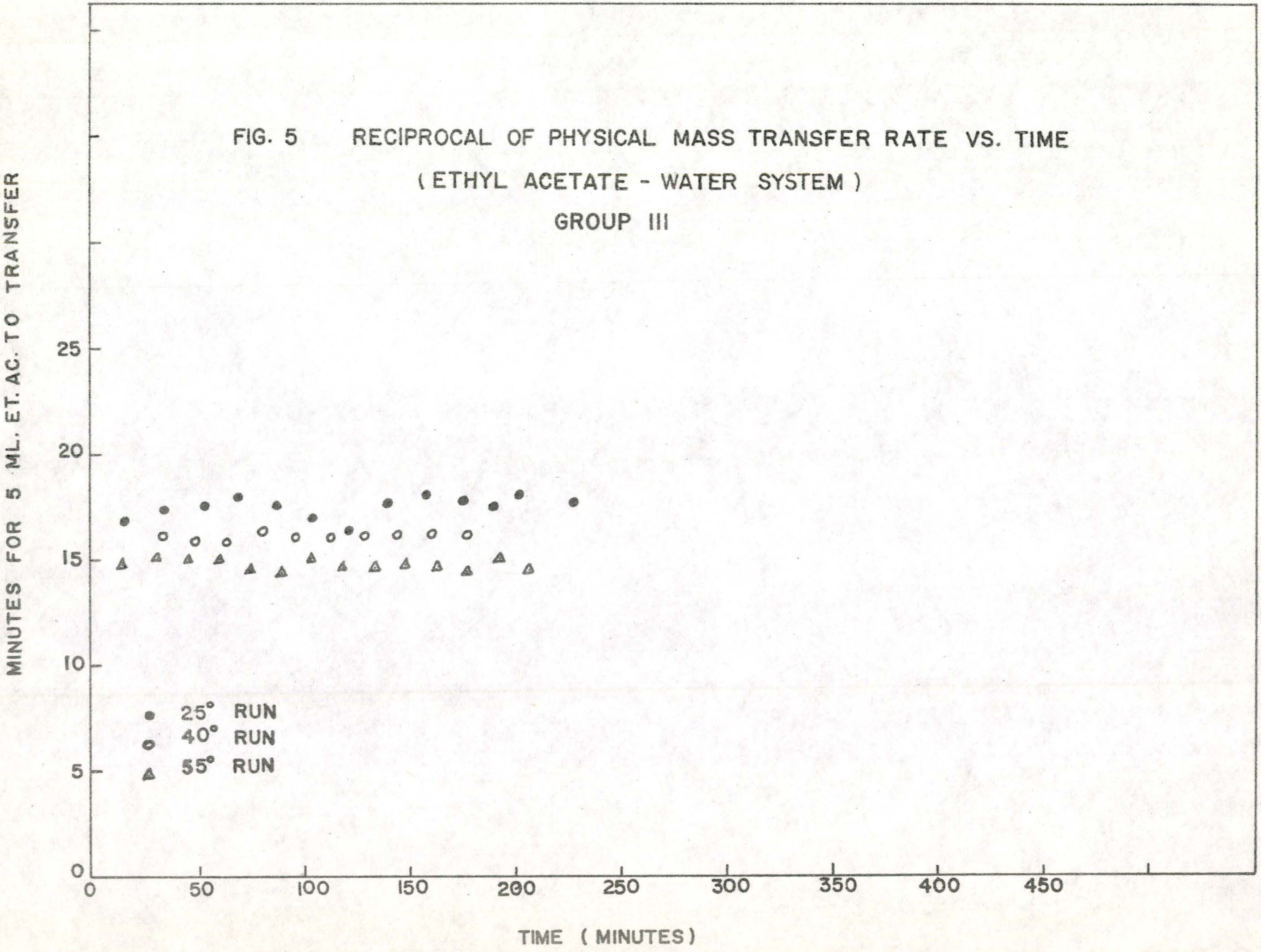


FIG. 5 RECIPROCAL OF PHYSICAL MASS TRANSFER RATE VS. TIME

(ETHYL ACETATE - WATER SYSTEM)

GROUP III

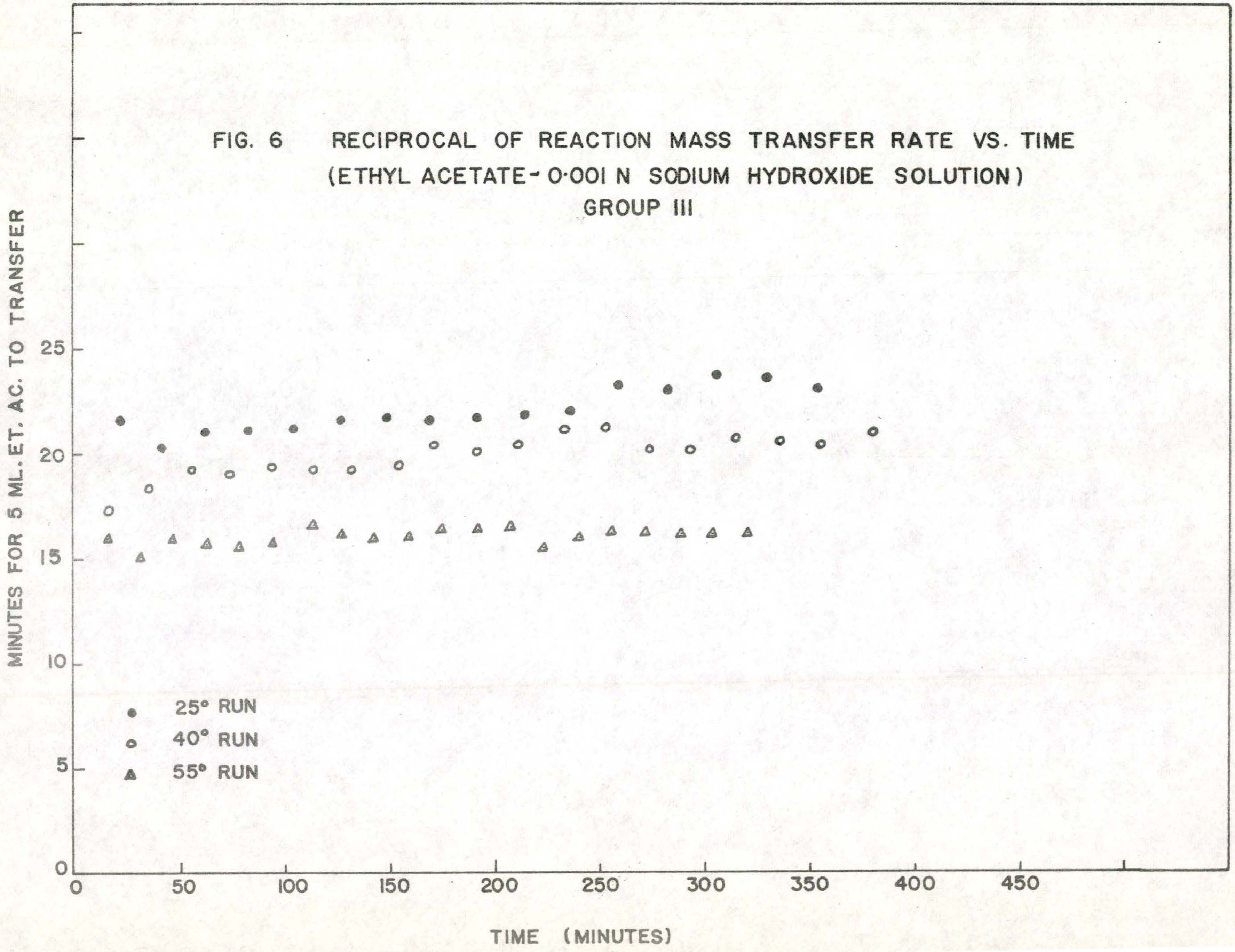


FIG. 6 RECIPROCAL OF REACTION MASS TRANSFER RATE VS. TIME (ETHYL ACETATE- 0·001 N SODIUM HYDROXIDE SOLUTION) GROUP III

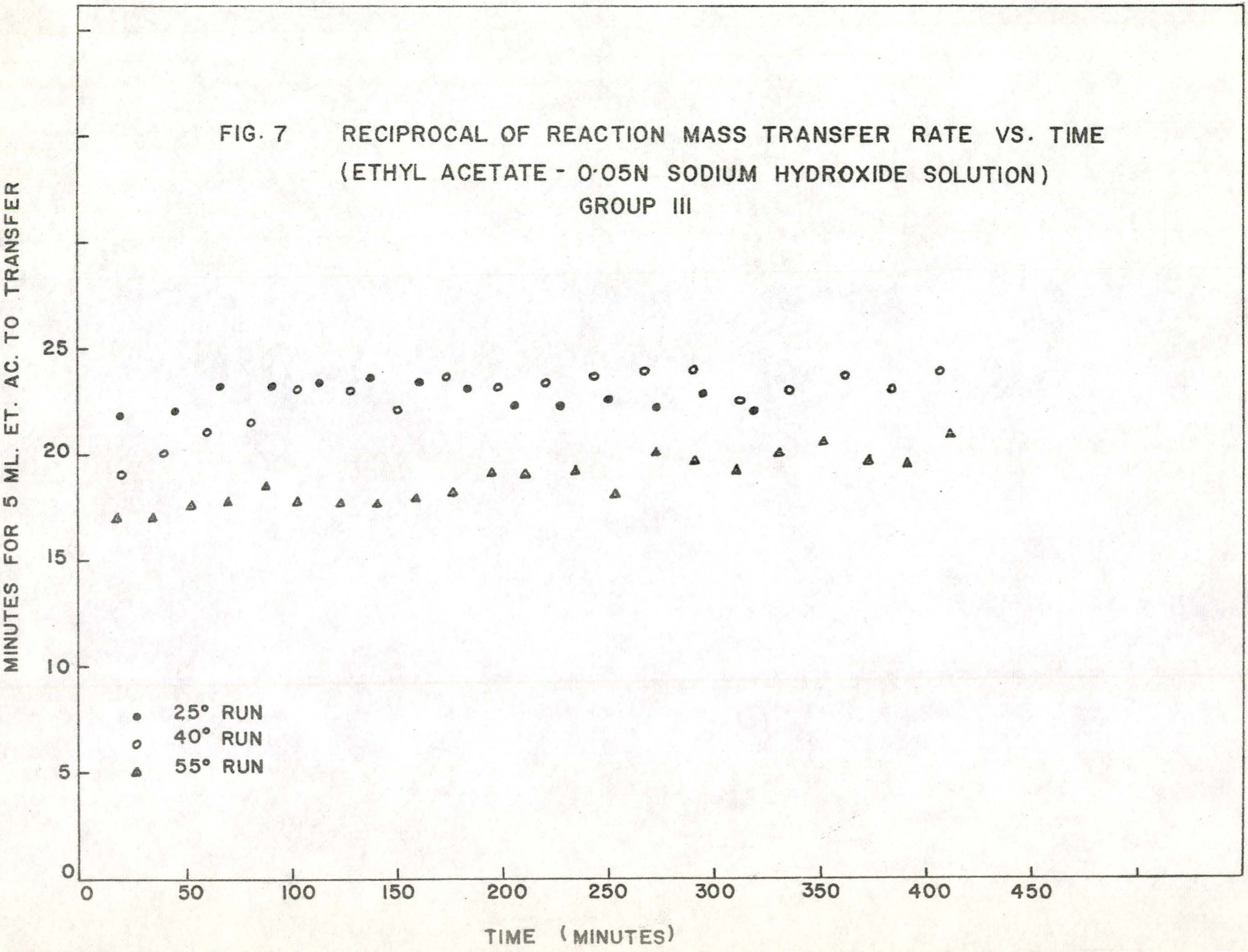


FIG. 7 RECIPROCAL OF REACTION MASS TRANSFER RATE VS. TIME
(ETHYL ACETATE - 0·05N SODIUM HYDROXIDE SOLUTION)
GROUP III

CONCLUSIONS

1) Mass transfer of ethyl acetate into aqueous sodium hydroxide is accompanied by a very slow second order irreversible chemical reaction. Theoretically, very little enhancement in transfer rate can be obtained. The concentration profiles for the reactants and products across the film are only slightly affected by the reaction, which is sufficiently slow to permit ethyl acetate to diffuse largely through the film before reacting. This conclusion is in agreement with those of Jenny, Viallard (139) and Watada.

2) Reduced transfer rate was observed with ethyl acetate transferring into sodium hydroxide solution instead of into water. Part of the retardation was proved to be due to salt effect.

3) Interfacial resistance ($1/k_r$) occurring in transfer of ethyl acetate into sodium hydroxide is speculated to be due to

a) modification of hydrodynamic conditions near the interface by the presence of sodium acetate and sodium hydroxide.

b) formation of a surface barrier due to impurities.

c) formation of an additional film in the lower phase and near the interface, as a result of the slow chemical reaction.

RECOMMENDATIONS

1) It is evident that much work is left to be done in order to fully understand the factors governing the interfacial resistance which occurs during the reaction run of the ethyl acetate-sodium hydroxide system. Particularly, more runs should be performed with esters of other members of the homologous series (for example, ethyl formate, ethyl propionate and ethyl butyrate) in order to study the stearic effect of molecules to mass transfer rates. Also, runs with other esters such as methyl propionate should be performed. Some runs should be performed with more pure material such as purified sodium hydroxide (100) and repeatedly re-distilled ethyl acetate so that the effect of contaminants on mass transfer rates can be understood.

In all the runs, concentrations of reactants and products should be measured instead of calculated, and the transfer rates should be measured with a more accurate syringe.

2) The three zones model as described in Appendix X seems to be quite specific and,so far, only observed in saponification of ester. Before starting to generalize the idea, more mass transfer experiments should be performed with other systems.

3) In the present system (ethyl acetate-sodium hydroxide) the reaction is so slow that Van Krevelen's model for slow second order reaction does not apply. A more rapid reaction is required for studying the Van Krevelen's model.

4) In mass transfer studies, the field of interfacial resistance is relatively untouched, particularly in theoretical aspects. If the resistance is generally attributed to the modification of hydrodynamic conditions at the interface, then establishment of some theory concerning the criterion for interfacial resistance to occur (similar to the criterion of instability for interfacial turbulence (127)) may be worthwhile to try.

5) Fujinawa (29) also reported interfacial resistance occurring in liquid-liquid extraction of acetic acid in benzene drops by aqueous potassium hydroxide solution. However, this particular system did not show any three zones phenomena under the schlieren apparatus. (With reference to Appendix X and Part II) At the present moment, it may be speculated that the reaction rate in the system used by Fujinawa is rapid; and a high concentration of sodium acetate thus formed causes the hydrodynamic condition at the interface to be modified. This speculation should be further investigated by experiments.

APPENDIX I

PRELIMINARY INVESTIGATION

A system with slow chemical reaction such as the saponification of esters was chosen for this study. Ethyl acetate was considered. Mutual solubility of ethyl acetate and water was reasonably high and a distinct interface could be seen between the two liquids.

A semi-continuous flow apparatus was devised similar to the one described in the "experimental section" and the procedure for measuring the transfer rates was also the same as described in the "experimental section".

Eleven runs on ethyl acetate-water system and ethyl acetate-aqueous sodium hydroxide system were performed at various temperatures and stirrer speeds; but the flowrate into the lower phase was kept constant in each run. Mass transfer rates versus stirrer r.p.m. with temperature as parameter were plotted and as shown in figure (16). It could be seen that at higher temperatures there was less effect of stirrer speed on transfer rate. Probably, the higher molecular diffusivity played a more important role in the transfer at high temperature runs. In any case, under similar conditions, the transfer of ethyl acetate in 0.95N sodium hydroxide was found appreciably lower than the physical transfer rate. Duplicate runs were done and results were reproducible.

Results for reaction runs at 0.95N sodium hydroxide and at 141 stirrer r.p.m. were also plotted as shown in figure (16). Mass transfer rate at 55°C was much higher than that of the 25°C and 40°C runs.

The preliminary investigation showed that for the present apparatus under study, in order to have a reasonably high mass transfer rate as well as a stable liquid-liquid interface, satisfactory operating conditions were found to be such that the lower phase flowrate was approximately 1.5 litres/hour and stirrer r.p.m. was 141.

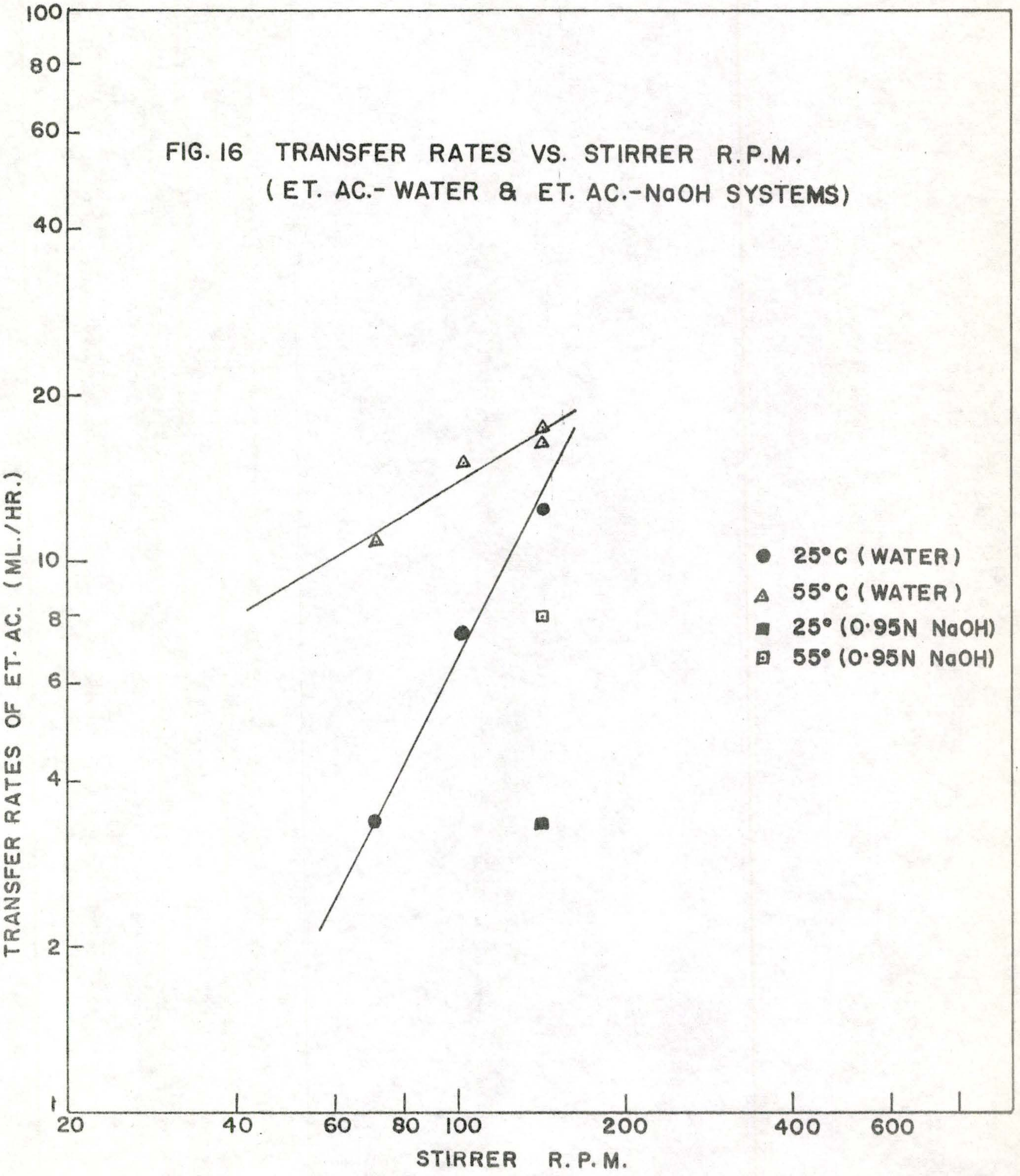


FIG. 16 TRANSFER RATES VS. STIRRER R.P.M.
(ET. AC.- WATER & ET. AC.-NaOH SYSTEMS)

APPENDIX II

DETAILED DESCRIPTION OF THE APPARATUS USED FOR STEADY STATE MASS TRANSFER EXPERIMENTS

1. Reactor

The reactor itself ,consisted of a cylindrical pyrex glass vessel , was indented as to give two compartments of approximately the same volume. The top of the upper compartment was narrowed and extended and ended with a mercury-seal device. There was an inlet and outlet in the lower compartment, so that continuous flow of the lower phase could be achieved. A glass hook gauge was installed for the purpose of indicating the interface level.

Precise dimensions of the reactor were difficult to obtain because it was curved in shape. The lower compartment was 5.8 cm in diameter and 3.7 cm in height, and had a volume of 98 c.c. The extended part of the upper compartment had a diameter of 1.4 cm and a height of 12.3 cm. The indented part just above the tip of the hook gauge had a diameter of 4.8 cm and an area of 18.1 sq. cm.

2. Stirrer (refer to figure 17a)

The stirrer was made of stainless steel (type 316) driven by an a-c motor type D-37-40 manufactured by SA Company and supplied by Canlab.

The stirrer was of paddle type with the blades 2.4 cm in diameter and 3.9 cm apart.

When not in motion, the paddles could stay inside the rod and remain in a vertical position. When the rod started to rotate, the two paddles were flung out in horizontal position. This device facilitated the insertion and removal of the stirrer into the reactor through the narrow neck.

3. Constant head device (refer to figure 17b)

Constant flow of the lower phase liquid was maintained by constant head device constructed as shown in the figure. The liquid flowed into the device through 1, and out through 3. Excess liquid was drained or recycled through 2.

4. Mercury-seal (refer to figure 17c)

The original purpose of the mercury-seal was to seal off the top compartment and minimized the vapor loss of the upper phase (ethyl acetate) during the experimental run. However, later experiments, particularly at higher temperature runs, showed that vapor pressure of ethyl acetate built up inside the seal during the experimental run; thus the interface between two liquids was depressed and erratic transfer rate measurements resulted.

The idea of using mercury-seal was therefore abandoned. Nevertheless, the stainless steel cup could still be used as a lid in the manner as shown in figure (17d) to reduce part of the vapor loss.

FIG. 17a STIRRER

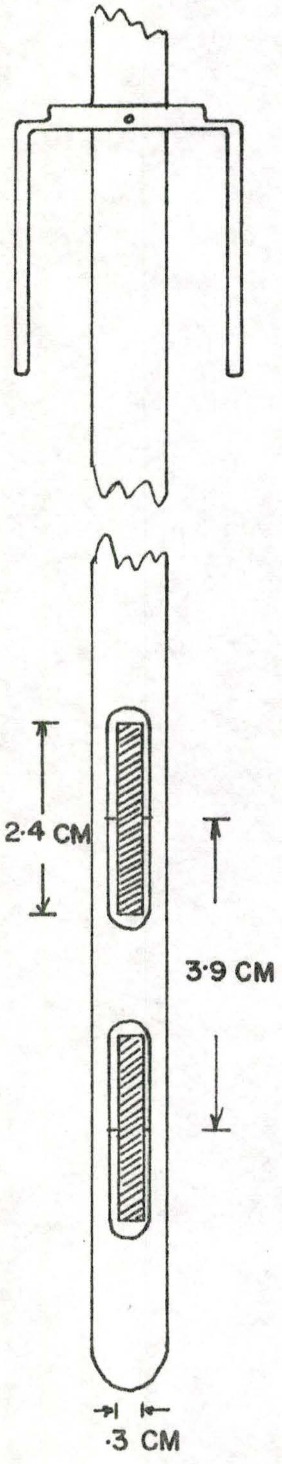
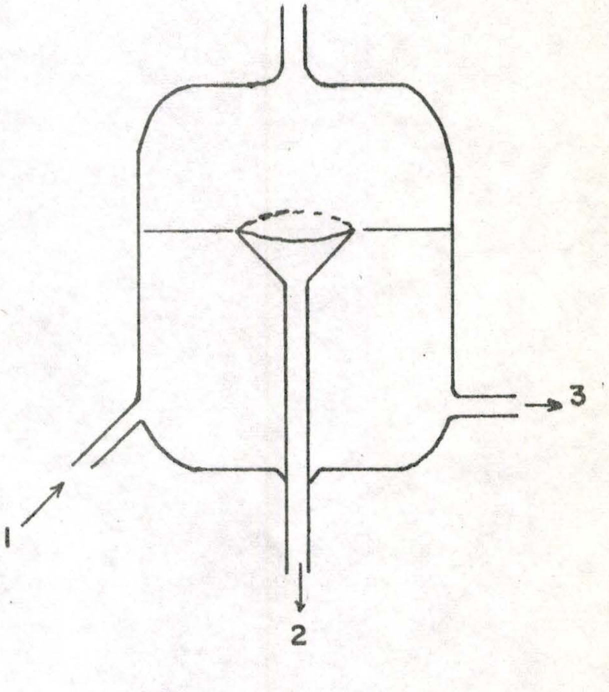


FIG. 17b. CONSTANT HEAD DEVICE



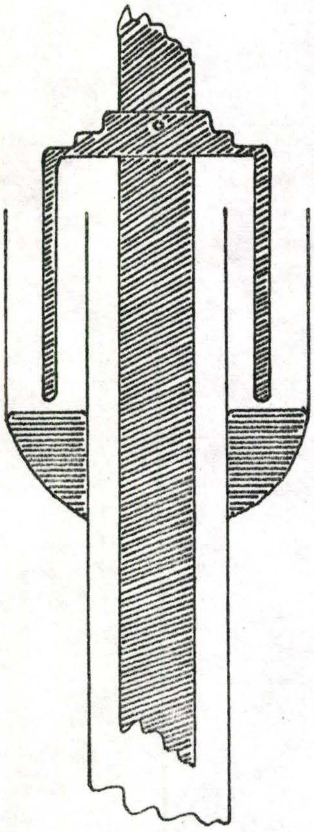
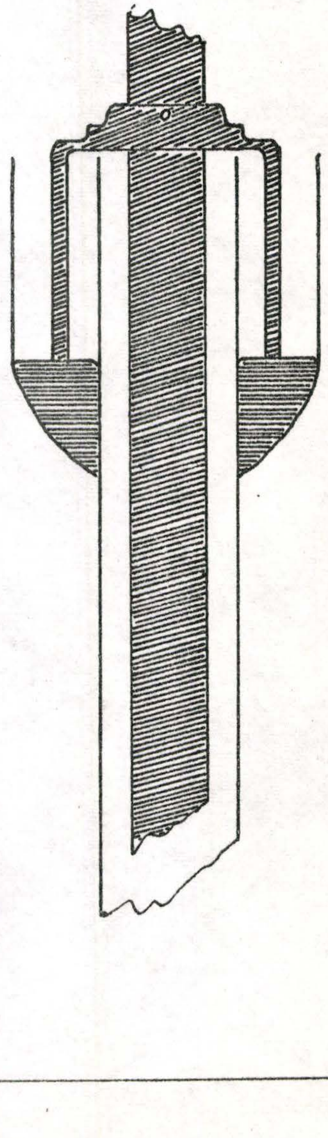


FIG. 17d MERCURY SEAL

FIG. 17c



APPENDIX III

SAMPLE CALCULATION (For Part I)

A) Salting coefficient of sodium acetate and sodium hydroxide : -

Referring to Table II, 25°C and 0.042 N. NaAc solution,

solubility of ethyl acetate in 0.042 N. NaAc: 0.8224 moles/litre.

Apply $\ln (\frac{S°}{S}) = k_s C$ .... (17)

and assuming NaAc is completely ionized

$$\ln \frac{0.850}{0.822} = k_s \; 2 \times 0.042$$

$$k_s \; \frac{0.03345}{0.08400} = 0.3980$$

Averaging the values of three runs at different concentrations of NaAc at 25°C,

$$k_s = 0.369$$

B) Ethyl acetate-sodium hydroxide system : -

1) Concentrations of reactants and products

Data are taken from run No. 83

0.11 N. input NaOH at 25°C (Co)

flowrate of lower phase (F): 1.41 litres/hr.

Reaction constant at 25°C (k): 374.4 $(\text{moles/litre})^{-1}$ hr^{-1}

Transfer rate (T): 11.903 ml/hr. (already corrected for vapor loss)

Volume of the lower phase (V): 0.098 litre

Water-saturated ethyl acetate contains 96.76 of ethyl acetate at 25°C,

$\therefore$ transfer rate = $\frac{96.76}{110.74} \times \frac{11.903}{88.108}$ = 0.1181 moles/hr of ethyl acetate

Let $B = (F^2 + kVT - FCokV)$

Substituting the values into the equation

$$B = ((1.41)^2 + 374.4 \times 0.098 \times 0.1181 - 1.41 \times 0.11 \times 374.4 \times 0.098)$$

$$= (1.9881 + 4.3330 - 5.6908)$$

$$= 0.6303$$

$$C_{NaOH} = \frac{-B + (B^2 - (-4(FkV)(F^2Co)))^{1/2}}{2(FkV)}$$

$$= \frac{-0.6303 + (0.3973 + 45.256)^{1/2}}{2 \times 51.734}$$

$$= \frac{6.1407}{103.47}$$

$$= 0.05935 \text{ moles/litre}$$

Substitute the values of C_{NaOH} into equation

$$C_{EtAc} = \frac{F\ (Co - C_{NaOH})}{kVC_{NaOH}}$$

$$= \frac{1.41 \times 0.05065}{374.4 \times 0.098 \times 0.05935}$$

$$= 0.032794 \text{ moles/litre}$$

Substitute the values of C_{NaOH} and C_{EtAc} into equation

$$C_{NaAc} = C_{EtOH} = \frac{kC_{NaOH}C_{EtAc}V}{F}$$

$$= \frac{374.4 \times 0.05935 \times 0.032794 \times 0.098}{1.41}$$

$$= \frac{0.071415}{1.41}$$

$$= 0.050649 \text{ moles/litre}$$

2) Mass transfer coefficient

Data are taken from run No. 83

0.11 N. input NaOH at 25°C and assuming the salting coefficients for both sodium acetate and sodium hydroxide are the same

substituting data into the equation

$$N = k^{\circ}_{L}\ (Cai_{EtAc} - C_{EtAc})$$

$$0.1181 = k^{\circ}_{L}\ \left(\frac{C_{EtAc\ (water)}}{e^{k_s \times 0.11 \times 2}} - C_{EtAc} \right)$$

$$\therefore\ k^{\circ}_{L} = \frac{0.1181}{0.7512} = 0.15722 \text{ litre/hr}$$

$$\frac{1}{k^{\circ}_{L}} = 6.361 \text{ hr/litre}$$

3) Resistance

Mass transfer coefficient without chemical reaction at 25°C:

$$\frac{1}{k^{*}_{L}} = 4.407 \text{ hr/litre}$$

$$\frac{1}{k_r} = \frac{1}{k^{\circ}_{L}} - \frac{1}{k^{*}_{L}} = 1.954 \text{ hr/litre}$$

C) Check run calculation : -

Referring to check run No. 2

Temperature: 25°C

Transfer rate: 11.0 ml/hr

Input sodium hydroxide concentration: 0.116 N.

Calculated sodium hydroxide concentration at steady state: 0.066995 N.

Calculated ethyl acetate concentration at steady state: 0.028109 N.

Substitute into equation (20)

$$\frac{1}{0.038886} \ln \frac{0.066995\,(0.077114 - 0.116 + n_{12})}{n_{12}\,(0.077114 - 0.116 + 0.066995)} = \frac{374.4}{60} \times 1.2$$

n_{12} = 0.0565 (corrected to 3 significant figures) gm. moles/litre

From titration n_{12} = 0.0521 gm. moles/litre

$$\% \text{ deviation} = \frac{0.0044}{0.565} \times 100$$

$$= 7.78$$

D) <u>Estimation of diffusion coefficient</u>: -

<u>Sodium hydroxide diffusing into water</u>

Referring to Appendix VIII, **limiting ionic conductances in water at** 25°C:

for Na^+ = 50.1; for OH^- = 197.6 amp/(cm^2)(volt/cm)(g.equiv./cm^3)

using equation (22)

$$D^o_{(25^oC)} = \frac{2RT}{(1/\lambda^o_+ + 1/\lambda^o_-)\,Fa^2}$$

$$= \frac{2 \times 8.316 \times 298}{(1/50 + 1/198)(96500)^2} = 2.141 \times 10^{-5} \text{ cm}^2/\text{sec}$$

using equation (23)

$$D_{(T)} = \frac{T}{334\,\mu_s}$$

$$D^o_{(55^oC)} = 2.141 \times 10^{-5} \times \frac{328}{334 \times 0.5064} = 4.142 \times 10^{-5} \text{cm}^2/\text{sec.}$$

E) <u>Pendant drop</u>: -

Referring to Appendix VIII,

Water drop suspended in ethyl acetate (saturated with water)

$$d_e = 0.375 \text{ cm.}$$

$$S = \frac{d_s}{d_e} = 0.871$$

$$\frac{1}{H} = 0.455$$

effective density = 0.097 gm/cm^3

Using equation (25)

$$\gamma = \frac{g(\rho_1 - \rho_2)\, d_e^2}{H}$$

$$= (0.455)(0.097)(980.4)(0.375)^2$$

$$= 6.085 \text{ dynes/cm}$$

F) Error analysis : -

1) Errors involved in the calculation of sodium hydroxide conc.

Data are taken from run No. 83

variables involved are,

$F \pm dF = 1.41 \pm 0.001$ litres/hr.

$V \pm dV = 0.098 \pm 0.001$ litres

$k \pm dk = 374.4 \pm 0.6$ (moles/litre $)^{-1}$ hr.$^{-1}$

$T \pm dT = 0.118 \pm 0.002$ moles/hr.

$Co \pm dCo = 0.1100 \pm 0.0002$ moles/litre

The equation used is,

$$dC_{NaOH} = (\partial C_{NaOH}/\partial F)dF + (\partial C_{NaOH}/\partial V)dV + (\partial C_{NaOH}/\partial k)dk + (\partial C_{NaOH}/\partial T)dT + (\partial C_{NaOH}/\partial Co)dCo$$

By differentiation and substitution,

$$\begin{aligned} dC_{NaOH} = {} & ((-2F + CokV + (1/(2(B^2+4F^3kVCo)^{1/2}))(2B(2F-kVCo)+12F^2kVCo)) \\ & /(2FkV) - (-B + (B^2+4F^3kVCo)^{1/2})/(2F^2kV))\ dF \\ & +((-kT + FCok + (1/(2(B^2+4F^3kVCo)^{1/2}))(2B(kT-FCok)+4F^3kCo)) \\ & /(2FkV) - (-B + (B^2+4F^3kVCo)^{1/2})/(2FkV^2))\ dV \\ & +((-VT + FVCo + (1/(2(B^2+4F^3kVCo)^{1/2}))(2B(VT-FCoV)+4F^3VCo)) \\ & /(2FkV) - (-B + (B^2+4F^3kVCo)^{1/2})/(2FVk^2))\ dk \\ & +((-kV + (1/(2(B^2+4F^3kVCo)^{1/2}))(2BkV))/(2FkV))\ dT \\ & +((FkV + (1/(2(B^2+4F^3kVCo)^{1/2}))(-2BFkV+4F^3kV))/(2FkV))\ dCo \end{aligned}$$

Substituting the actual values,

$$\begin{aligned} dC_{NaOH(maximum)} &= 0.0000374 + 0.000152 + 0.0000219 + 0.0006436 + 0.0001504 \\ &= 0.0010053 \end{aligned}$$

Maximum % error in C_{NaOH} is

$$(dC_{NaOH(maximum)}/C_{NaOH})100 = 1.693$$

Taking the root mean square,

$dC_{NaOH(probable)} = 0.00067$

Probable % error in C_{NaOH} is 1.129

2) Errors involved in the calculation of ethyl acetate concentration

Data are taken from run No. 83

The equation used is,

$$dC_{EtAc} = (\partial C_{EtAc}/\partial F)dF + (\partial C_{EtAc}/\partial V)dV + (\partial C_{EtAc}/\partial k)dk + (\partial C_{EtAc}/\partial T)dT + (\partial C_{EtAc}/\partial Co)dCo$$

By differentiation and substitution, and denoting $C_{NaOH} = C_1$

$$\begin{aligned} dC_{EtAc} = {} & (((-FC_1-F(Co-C_1))/(kVC_1{}^2))(\partial C_1/\partial F) + (Co-C_1)/(kVC_1))\ dF \\ & + (((-FC_1-F(Co-C_1))/(kVC_1{}^2))(\partial C_1/\partial V) - (F(Co-C_1))/(kC_1V^2))\ dV \\ & + (((-FC_1-F(Co-C_1))/(kVC_1{}^2))(\partial C_1/\partial k) - (F(Co-C_1))/(k^2VC_1))\ dk \\ & + (((-FC_1-F(Co-C_1))/(kVC_1{}^2))(\partial C_1/\partial T))\ dT \\ & + (((-FC_1-F(Co-C_1))/(kVC_1{}^2))(\partial C_1/\partial Co)) + F/(kVC_1))\ dCo \end{aligned}$$

Substituting the actual values,

$$\begin{aligned} dC_{EtAc(maximum)} &= 0.0000216 + 0.0001503 + 0.0000261 + 0.0007716 + 0.000051 \\ &= 0.0010206 \end{aligned}$$

Maximum % error in C_{EtAc} is

$$(dC_{EtAc(maximum)}/C_{EtAc})100 = 3.112$$

Taking the root mean square,

$dC_{EtAc(probable)} = 0.000788$

Probable % error in C_{EtAc} is 2.403

3) Errors involved in the calculation of sodium acetate concentration

Data are taken from run No. 83

The equation used is

$$\begin{aligned} d_{NaAc} = {} & (\partial C_{NaAc}/\partial F)dF + (\partial C_{NaAc}/\partial V)dV + (\partial C_{NaAc}/\partial k)dk \\ & + (\partial C_{NaAc}/\partial T)dT + (\partial C_{NaAc}/\partial Co)dCo \end{aligned}$$

By differentiation and substitution, and denoting $C_{EtAc} = C_2$

$$\begin{aligned} dC_{NaAc} = {} & ((kC_2V/F)(\partial C_1/\partial F) + (kC_1V/F)(\partial C_2/\partial F) - kC_1C_2V/F^2)\ dF \\ & + ((kC_2V/F)(\partial C_1/\partial V) + (kC_1V/F)(\partial C_2/\partial V) + kC_1C_2/F)\ dV \\ & + ((kC_2V/F)(\partial C_1/\partial k) + (kC_1V/F)(\partial C_2/\partial k) + C_1C_2V/F)\ dk \\ & + ((kC_2V/F)(\partial C_1/\partial T) + (kC_1V/F)(\partial C_2/\partial T))\ dT \\ & + ((kC_2V/F)(\partial C_1/\partial Co) + (kC_1V/F)(\partial C_2/\partial Co)\ dCo \end{aligned}$$

Substituting the actual values,

$$\begin{aligned} dC_{NaAc(maximum)} & = 0.0000387 + 0.000154 + 0.0000222 + 0.000658 + 0.0000486 \\ & = 0.0009215 \end{aligned}$$

Maximum % error in C_{NaAc} is

$$(dC_{NaAc(maximum)}/C_{NaAc})100 = 1.819$$

Taking the root mean aquare,

$$dC_{NaAc(probable)} = 0.000657$$

Probable % error in C_{NaAc} is 1.297

APPENDIX IV

THE CHEMICALS USED IN THE EXPERIMENTS

A) Ethyl acetate

Fisher certified, A.C.S.

F.W. 88.108

Boiling range: 76.8 - 77.3°C

Density: 0.893 to 0.895 gm./ml. at 25°C

Lot No. (for Group I experiments) 712431

Lot No. (for Group II experiments) 720520

Lot No. (for Group III experiments) 720520

B) Sodium hydroxide pellets

Fisher certified, A.C.S.

F.W. 39.999

Lot No. 713084

C) Potassium hydroxide pellets

Fisher certified, A.C.S.

F.W. 56.108

Lot No. 714291

D) Sodium acetate

Fisher certified, fused anhydrous

F.W. 82.037

Lot No. 720310

E) Sodium propionate

Fisher N.F.

F.W. 96.064

Lot No. 713377

F) Sodium butyrate

Matheson Coleman and Bell Division,

The Matheson Co. Inc.,

F.W. 110.09

Lot No. 299026

G) Redistilled ethyl acetate

The batchwise apparatus for the purification of ethyl acetate was as shown in figure (17e).

Approximately 2 litres of fresh ethyl acetate was put into a 2-litre round bottom flask surrounded by a Glas-col hemispherical heating mantle, "series O". Fractionation was done in a 24" long column packed with small helical glass rings. The column was equipped with a nichrome wire heating coil. Both the pot and the column was electrically heated, and the power supply was regulated by powerstats. Ethyl acetate vapor overhead was cooled by a cold-finger type condenser.

During the purification, the column was operated at 78°C which was a little above the boiling point of ethyl acetate. Reflux ratio of 1:1 was used until ethyl acetate vapor at constant boiling temperature (76.8°C) was obtained. Zero reflux ratio was then used.

H) Test of purity on ethyl acetate

It was suspected that different batches of ethyl acetate purchased contained different amounts of contaminants. Several experiments were carried out to clear the point.

(a) Both samples of ethyl acetate used for the Group I and Group II experiments were passed through the gas chromatograph (Beckman GC-2A, using a paraplex column). No traces of volatile impurities were detected.

(b) Samples of ethyl acetate used for Group II and Group III (redistilled) experiments were analysed in a Infraed Spectrophotometer (Beckman IR5). No traces of impurities were detected.

(c) Refractive index of ethyl acetate used for all of the three Groups of experiments were checked separately with an Abbe Refractometer for the difference. Negative results were obtained.

I) Ethyl formate

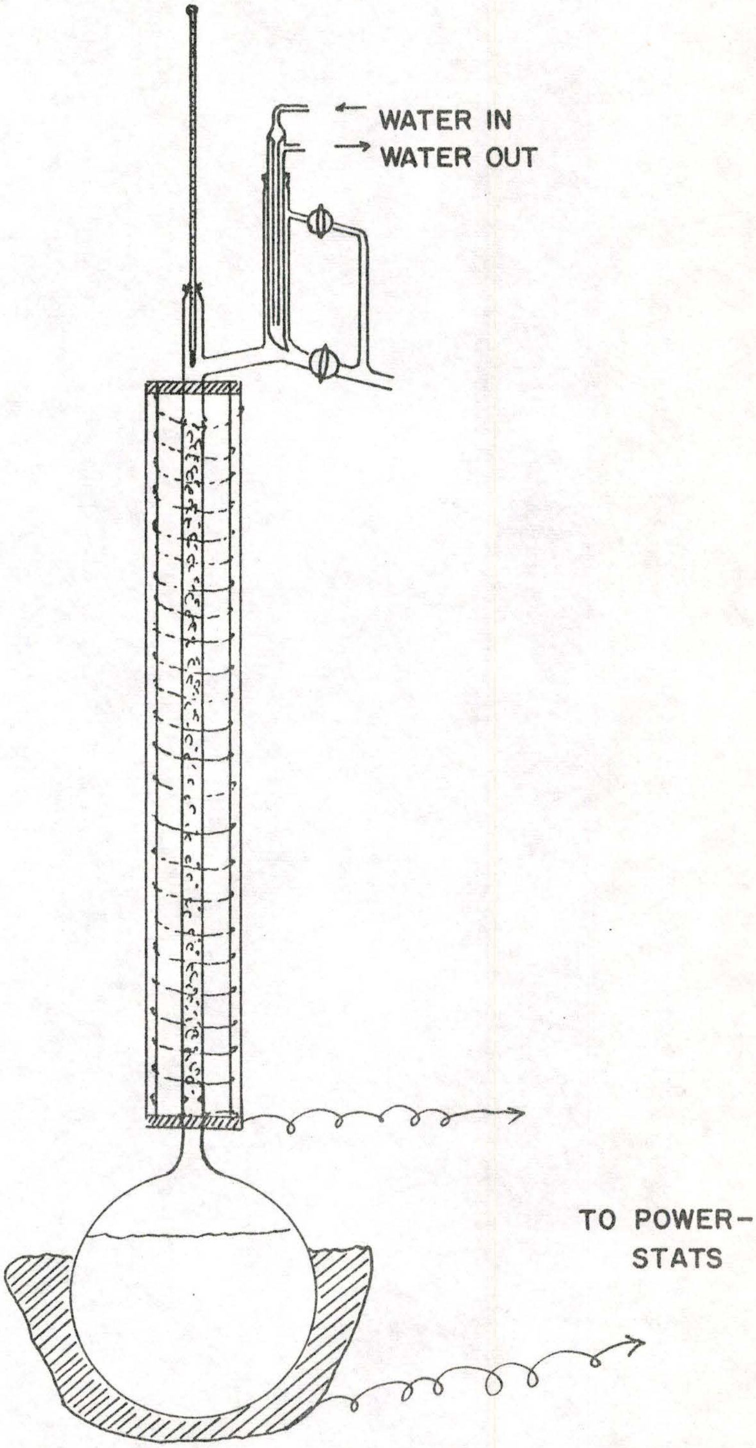
Baker analysed reagent

F.W. 74.081

Density: 0.917 gm./ml. at 25°C

Lot No. 24231

FIG. 17e APPARATUS FOR THE REDISTILLATION OF ET. AC.



APPENDIX V

SAMPLES OF EXPERIMENTAL DATA FOR TRANSFER RUNS

Run No. 66

Upper phase: ethyl acetate saturated with water at 40°C.

Lower phase: distilled water at 40°C.

Temperature: 40°C.

R.P.M. : 141

Flowrate : 1.53 litres/hr. (lower phase)

Time(in minutes)	ml added	Time required for adding 5 ml.
0	2	
8.6	2	
14.0	1	
16.7	2	16.7
23.6	2	
29.8	1	
32.8	2	16.1
39.0	2	
45.4	1	
48.6	2	15.8
55.2	2	
61.4	1	
64.4	2	15.8
71.0	1	
74.3	2	

Time (in minutes)	ml added	Time Required for adding 5 ml
80.7	2	16.3
87.1	2	
93.5	1	
96.7	2	16.0
103.4	2	
109.9	1	
112.7	2	16.0
119.5	2	
126.0	1	
128.8	2	16.1
135.2	2	
141.6	1	
144.8	2	16.0
151.6	2	
157.8	1	
161.0	2	16.2
167.5	2	
173.5	1	
177.1	2	16.1
184.1	2	
190.1	1	
193.6	2	16.5
200.1	2	
206.2	1	
209.7	2	16.1

Time (in minutes)	ml added	Time Required for adding 5 ml
216.1	2	
222.7	1	
226.0	2	16.3
232.0	2	
238.6	1	
241.9	2	15.9
248.3	2	
254.3	1	
257.8	2	15.9
264.2	2	
270.6	1	
273.8	2	16.0
280.2	2	
286.7	1	
290.0	2	16.2
296.3	2	
302.6	1	
305.9	2	15.9

Run No. 83

Upper phase: ethyl acetate saturated with water at 25°C

Lower phase: 0.110 N NaOH.

Temperature: 25°C

R, P. M. : 141

Flow rate : 1.41 litres/hr.

(lower phase)

Time (minutes)	ml added	Time required for adding 5 ml
0	2	
9	2	
18.5	1	
23.2	2	23.2
32.8	2	
42.0	1	
46.8	2	23.6
56.4	2	
65.8	1	
70.5	2	23.7
80.1	1	
85.0	2	
94.1	1	23.6
99.4	2	
110.0	2	

Time (minute)	ml added	Time required for adding 5 ml
119.4	2	25.3
128.5	2	
137.7	1	
142.5	2	23.1
152.0	1	
157.2	2	
166.4	2	23.9
175.9	2	
185.4	1	
190.2	2	23.8
200.3	1	
205.2	2	
214.8	2	24.6
224.5	2	
234.4	1	
239.1	2	24.3
248.0	2	
257.0	1	
261.4	2	22.3
271.1	1	
275.8	2	
286.1	2	24.7
295.0	2	
304.9	1	
309.8		23.7

Run No. 94

Upper phase: ethyl acetate saturated with water at 55°C

Lower phase: 0.112 N. NaAc.

Temperature: 55°C.

R. P. M. : 141

Flow rate : 1.608 litres/hr.
(lower phase)

Time (minutes)	ml added	Time required for adding 5 ml
0	2	
6	2	
12.5	1	
15.8	2	15.8
22.7	2	
29.5	1	
32.7	2	16.9
39.4	2	
46.3	1	
49.5	2	16.8
56.3	2	
63.3	1	
66.6	2	17.1
72.9	2	
79.1	1	

Time (minutes)	ml added	Time required for adding 5 ml
83.0	1	16.4
86.5	2	
93.1	2	
99.9	1	16.9
103.3	2	
110.2	2	
117.3	2	17.4
123.8	2	
130.6	1	
133.9	2	16.6
140.7	1	
144.2	2	
150.9	2	17.0
157.8	2	
164.5	1	
168.0	2	17.1
174.8	2	
181.7	1	
185.1	2	17.1
192.2	2	
198.7	1	
202.2	2	17.1
209.2	2	
216.1	1	
219.6	2	17.4

Time (minutes)	ml added	Time required for adding 5 ml
226.4	2	
233.5	1	
236.8	2	17.2
243.6	2	
250.4	1	
254.1	2	17.3
261.2	1	
264.1	2	
271.2	2	17.1
278.1	2	
285.2	1	
288.4	2	17.2
295.2	2	
301.9	1	
305.4	2	17.0
312.2	2	
318.7	1	
322.2	2	16.8
328.7	2	
335.7	1	
339.1		16.9

APPENDIX VI

COMPUTER RESULTS FOR ETHYL ACETATE - SODIUM HYDROXIDE SYSTEM

(GROUP III)

A) Transfer rates data for 25°C and 40°C

All the transfer rates obtained from these runs (taken at 300 minutes after the start of each experiment) were plotted against input NaOH normalities as shown in figure 10. These data could be correlated by a single straight line by means of the least square method. The mean deviation was 13%. The smoothed data were as follows:

Input NaOH (normality)	Transfer rate (ml/hr)
0.0001	14.762
0.0002	14.479
0.0010	13.822
0.0057	13.112
0.0100	12.882
0.0510	12.217
0.1100	11.903
0.3890	11.388

B) Transfer rates data for 55°C

Least square method was also applied to the results of the 55°C runs and a straight line relationship between input NaOH concentrations and transfer rates could be drawn with a mean deviation of 10.7%. The smoothed data were tabulated as follows:

Input NaOH (normality)	Transfer rate (ml/hr)
0.0001	19.516
0.0002	18.956
0.0010	17.657
0.0057	16.252
0.0100	15.798
0.0510	14.483
0.1100	13.862
0.3890	12.843

C) Computer results (Bendix G - 15)

With the aid of data obtained from the preceding sections, concentrations of reactants and products in the bulk phase were calculated using equations (15) and (16). Also, mass transfer coefficients were calculated using equation (14). Salt effect of both sodium acetate and sodium hydroxide was accounted for in estimating the solubility of ethyl acetate in the reacting solution.

TABLE XIa

COMPUTER RESULTS OF 25°C RUNS

Input NaOH (normality)	C_{NaOH} gm.moles/litre	C_{EtAc} gm.moles/litre	$C_{NaAc} = C_{EtOH}$ gm.moles/litre	k_L^o litre/hr.
0.0001	0.000027061	0.10358	0.000072939	0.19571
0.0002	0.000054933	0.10148	0.00014507	0.19168
0.0010	0.00028551	0.096170	0.00071449	0.18221
0.0057	0.0017332	0.087950	0.0039668	0.17143
0.01	0.0031528	0.083459	0.0068472	0.16787
0.051	0.020863	0.055509	0.030137	0.15838
0.11	0.059350	0.032795	0.050650	0.15722
0.389	0.31778	0.0086128	0.071221	0.17914

TABLE XIb

COMPUTER RESULTS OF 40°C RUNS

Input NaOH (normality)	C_{NaOH} gm.moles/litre	C_{EtAc} gm.moles/litre	$C_{NaAc}=C_{EtAc}$ gm.moles/litre	k_L^o litre/hr.
0.0001	0.000014237	0.094656	0.000085763	0.21338
0.0002	0.000029088	0.092325	0.00017091	0.20901
0.001	0.00015189	0.087735	0.00084811	0.19839
0.0057	0.00094274	0.079290	0.0047573	0.18617
0.01	0.0017453	0.074319	0.0082548	0.18212
0.051	0.014043	0.041352	0.036957	0.16907
0.11	0.051531	0.017828	0.058468	0.16530
0.389	0.31943	0.0034224	0.069573	0.18261

TABLE XIc

COMPUTER RESULTS OF 55°C RUNS

Input NaOH (normality)	C_{NaOH} gm.moles/litre	C_{EtAc} gm. moles/litre	$C_{NaAc}=C_{EtOH}$ gm.moles/litre	k_L^o litre/hr.
0.0001	0.00000620	0.11687	0.0000938	0.30025
0.0002	0.000012582	0.11507	0.00018742	0.29004
0.001	0.000068018	0.10585	0.00093198	0.26697
0.0057	0.00043710	0.093014	0.0052629	0.24129
0.01	0.00082114	0.086353	0.0091789	0.23289
0.051	0.0075909	0.044177	0.043409	0.20476
0.11	0.039797	0.013627	0.070203	0.19302
0.389	0.31320	0.0018695	0.075797	0.19978

APPENDIX VII

DATA ON ETHYL ACETATE-SODIUM HYDROXIDE SYSTEM OBTAINED BY OTHER WORKERS

A) Jenny's data (57) are presented in the following table

TABLE XII

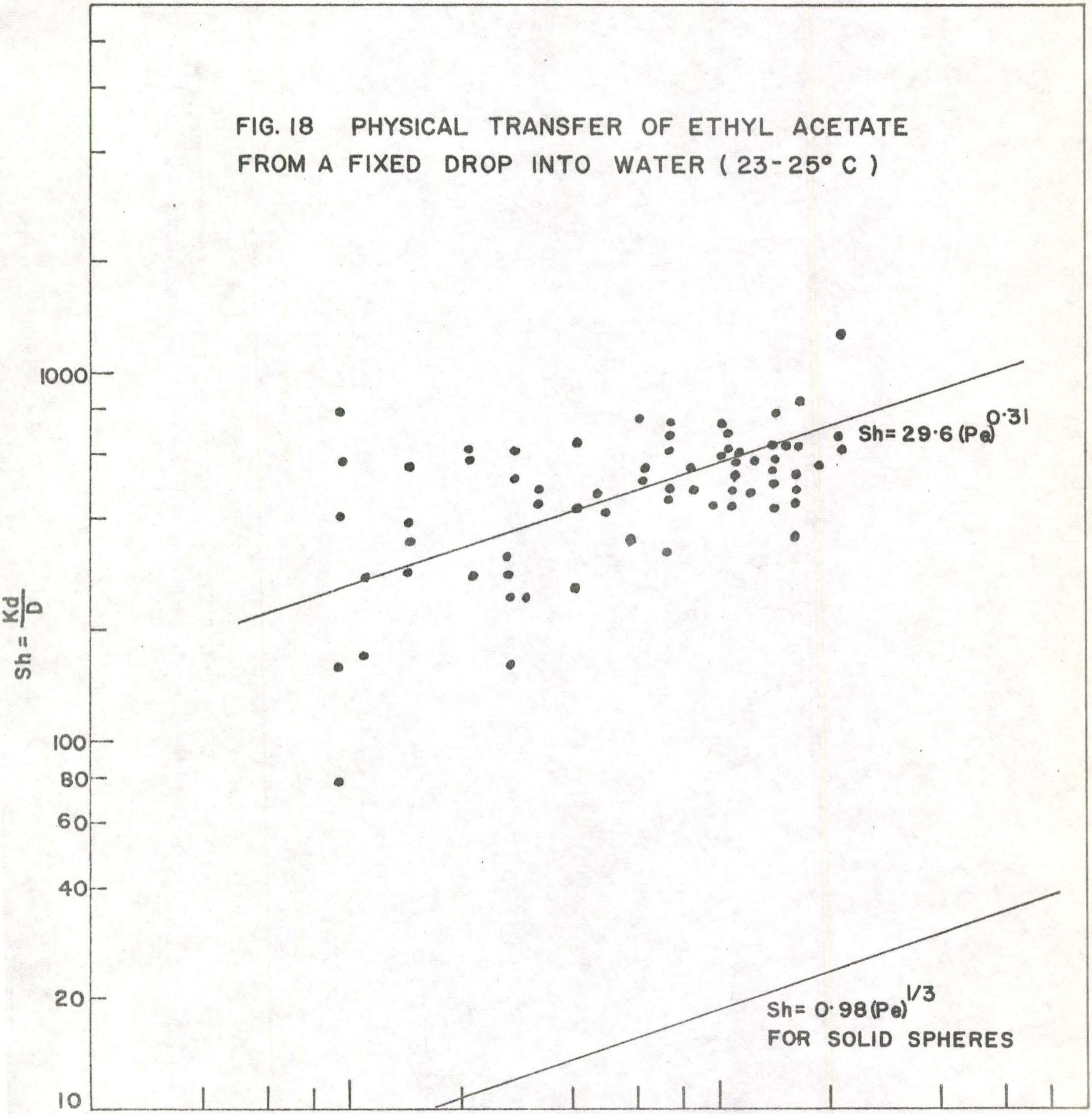
RATE OF ABSORPTION OF ETHYL ACETATE VAPOR BY SODIUM HYDROXIDE SOLUTIONS

Initial sodium hydroxide conc. (normality)	Partial pressure of solute in gas (atm.)	Absorption rate lb.moles/hr.ft.^{2}
0 (water)	0.095	0.00294
0.5	0.095	0.00258
1.0	0.092	0.00274

B) Watada's data (147) are best presented as shown in figures (18) and (19).

It should be noted that the lines were drawn through a large amount of scattered data. In spite of this, retardation of transfer rates in the same order of magnitude as those obtained in this study was observed with the ethyl acetate-sodium hydroxide system as compared to ethyl acetate-water system.

FIG. 18 PHYSICAL TRANSFER OF ETHYL ACETATE FROM A FIXED DROP INTO WATER (23-25° C)



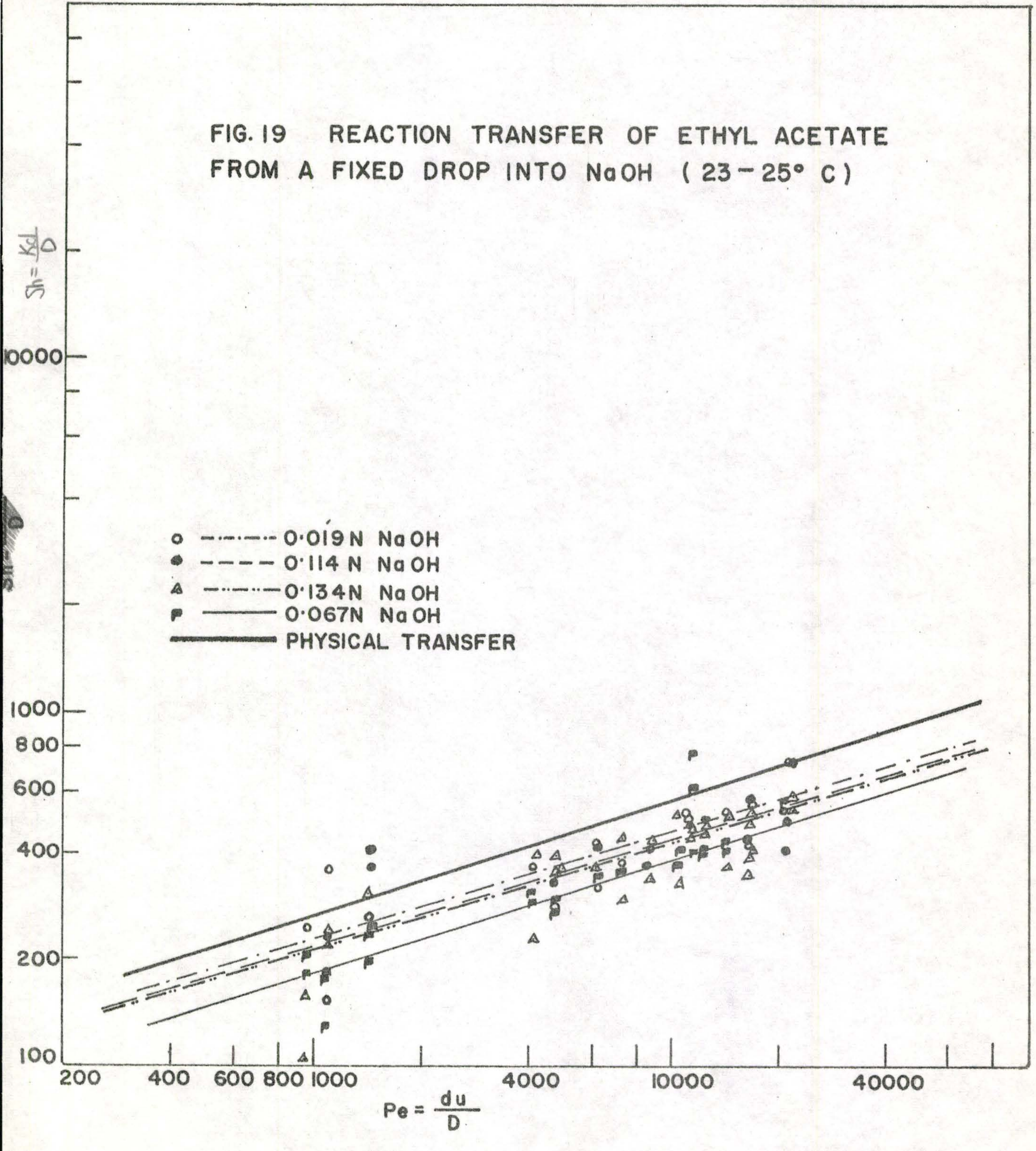


FIG. 19 REACTION TRANSFER OF ETHYL ACETATE FROM A FIXED DROP INTO NaOH (23 - 25° C)

APPENDIX VIII

PHYSICAL PROPERTIES

A) Diffusion coefficient determinations : -

In order to study the concentration profiles of reactants and products across the film for the ethyl acetate-sodium hydroxide system, diffusion coefficients of the components involved were required. They were measured using a diaphragm cell as shown in figure (20a). The procedure for the measurement was a standard one as described in the text and reference (135) (128).

Diffusion coefficient of ethyl acetate in water at 25°C was first measured. The results obtained did not agree with the value recorded in the literature; and furthermore, not reproducible. Diffusion coefficients calculated from equations based on well-known references were used instead.

1. Ethyl acetate

Since ethyl acetate was organic in nature, it was assumed to be non-ionic. The molecular diffusivity was obtained from the correlation proposed by Stokes-Einstein as given by Wilke (153) to be 1.02×10^{-5} $cm^2/sec.$ at 25°C as compared to 1.14×10^{-5} $cm^2/sec.$, extrapolated from J. B. Lewis' (66) results. The diffusion coefficient at 55°C (using $\frac{T}{D\mu}$ = constant) was found to be 2.21×10^{-5} $cm^2/sec.$ Dilute solution was assumed.

2. Sodium hydroxide

The diffusion coefficient D^o in very dilute solution of complete ionized simple univalent electrolytes was given by the Nernst equation

$$D^o = \frac{2RT}{(1/\lambda_+^{\,o} + 1/\lambda_-^{\,o})\ Fa^2} \qquad \ldots\ (22)$$

and

$$D_{(T)} = D^o \frac{T}{334\mu_s} \qquad \ldots\ (23)$$

where μ_s = viscosity of water at T^oC in centipoise. The diffusion coefficient of sodium hydroxide calculated in this way was found to be 2.14×10^{-5} cm^2/sec. at 25^{o}C and 4.14×10^{-5} cm^2/sec. at 55^{o}C. Dilute solution was assumed.

The situation was complicated if the presence of sodium acetate in the solution was included. In this case, diffusion in mixed electrolytes was concerned and the expression giving the diffusion of anions was, (121) (141)

$$n_-N_- = -\frac{RT}{Fa^2}\frac{\lambda_-}{n_-}\left(G_- + n_-c_-\frac{\sum\lambda_+G_+/n_+ - \sum\lambda_-G_-/n_-}{\sum\lambda_+c_+ + \sum\lambda_-c_-}\right) \qquad \ldots\ (24)$$

where

n = valence of the ion

N = mass transfer rate, gm.moles sec^{-1}cm^{-2}

R = gas constant, 8.315 joules/^{o}K (gm.mole)

T = temperature ^{o}K

Fa = Faraday, 96500 coulombs/gm. equivalent

λ = ion mobility, amp/(cm^2)(volt/cm)(gm.equivalent/cm^3)

G = concentration gradient of the ion gm. equivalent cm^{-4}

C = concentration of ion gm. equivalent cm^{-3}

Σ = sum

+ = refers to cations

- = refers to anions

However, for the present qualitative analogue computer study, a maximum limit for concentration profiles was enough, and for this reason, diffusion coefficient for single electrolyte diffusing in water was used. (Diffusivity of hydroxyl ions in the film were enhanced about 50% by the presence of other ions (138).)

3. Sodium acetate

Diffusion coefficient for sodium acetate in water was also calculated, based on Nernst equation. D^o was 1.20×10^{-5} cm^2/sec. for 25°C and 2.325×10^{-5} cm^2/sec. for 55°C.

B) Interfacial tension measurement : -

There was a suspicion, although not likely, that sodium acetate, which exhibits retardation to transfer rate, might accumulate at the interface during the run owing to the slow reaction. The excess amount at the interface could be described by the Gibbs isotherm.

$$\Gamma = \frac{a}{RT}\frac{d\gamma}{da} \qquad \text{.... (25)}$$

where

Γ = excess amount of sodium acetate at interface moles/cm^2

a = concentration of sodium acetate moles/litre

R = gas constant for a mole

T = temperature ^{o}K

γ = interfacial tension dynes/cm

It could be seen that the accumulation, if there was any, could be determined by measuring the change of interfacial tension. Pendant drop method by Andreas was used for this interfacial tension measurement (1).

The drop formed at the end of the glass nozzle was photographed with the aid of an electronic flash light as to reduce the heat effect. The photograph was then developed and printed. The two dimensions "d_e" and "d_s" as shown in figure (20b) were measured.

Drops of sodium acetate solution at 0.0306 moles/litre, 0.0706 moles/litre and 0.0965 moles/litre were suspended in pure ethyl acetate, saturated with water. It should be noted that photographs for each drop must be taken at the same time after the formation, because the local concentration and the interfacial tension changed with time. The γ found between ethyl acetate and water, 0.0306 N., 0.0706 N., 0.0965 N. sodium acetate solution were 6.085 dynes/cm., 6.312 dynes/cm., 6.119 dynes/cm. and 5.903 dynes/cm., respectively. It was therefore concluded that there was no accumulation of sodium acetate at the interface, or else, the change of γ was so small that this method was not suitable for the measurement.

C) <u>Reaction constants for the system of ethyl acetate-sodium hydroxide</u> : -

Homogeneous reaction was assumed in the lower phase and the reaction constants were taken from the literature (52) (100) (140).

A curve of reaction constant versus temperature was drawn as shown in figure (20).

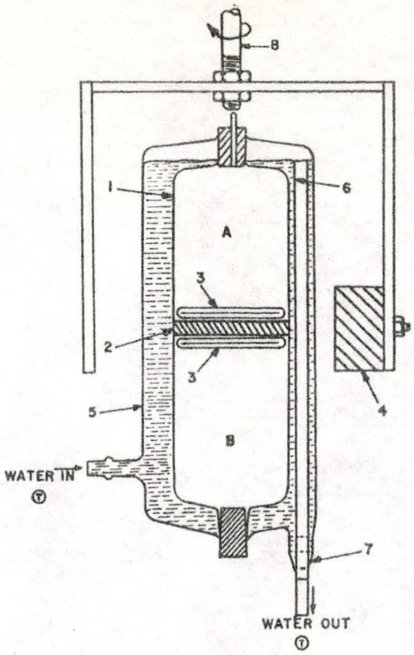
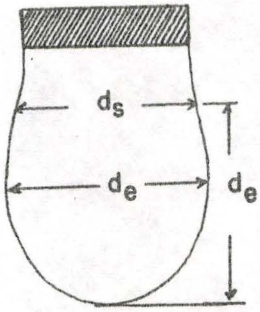


FIG. 20 a –Schematic diagram of diaphragm diffusion cell.

1. diffusion cell	5. jacket
2. diaphragm	6. overflow tube
3. stirrer	7. rubber joint
4. magnet	8. rotating shaft

FIG. 20b PENDANT DROP



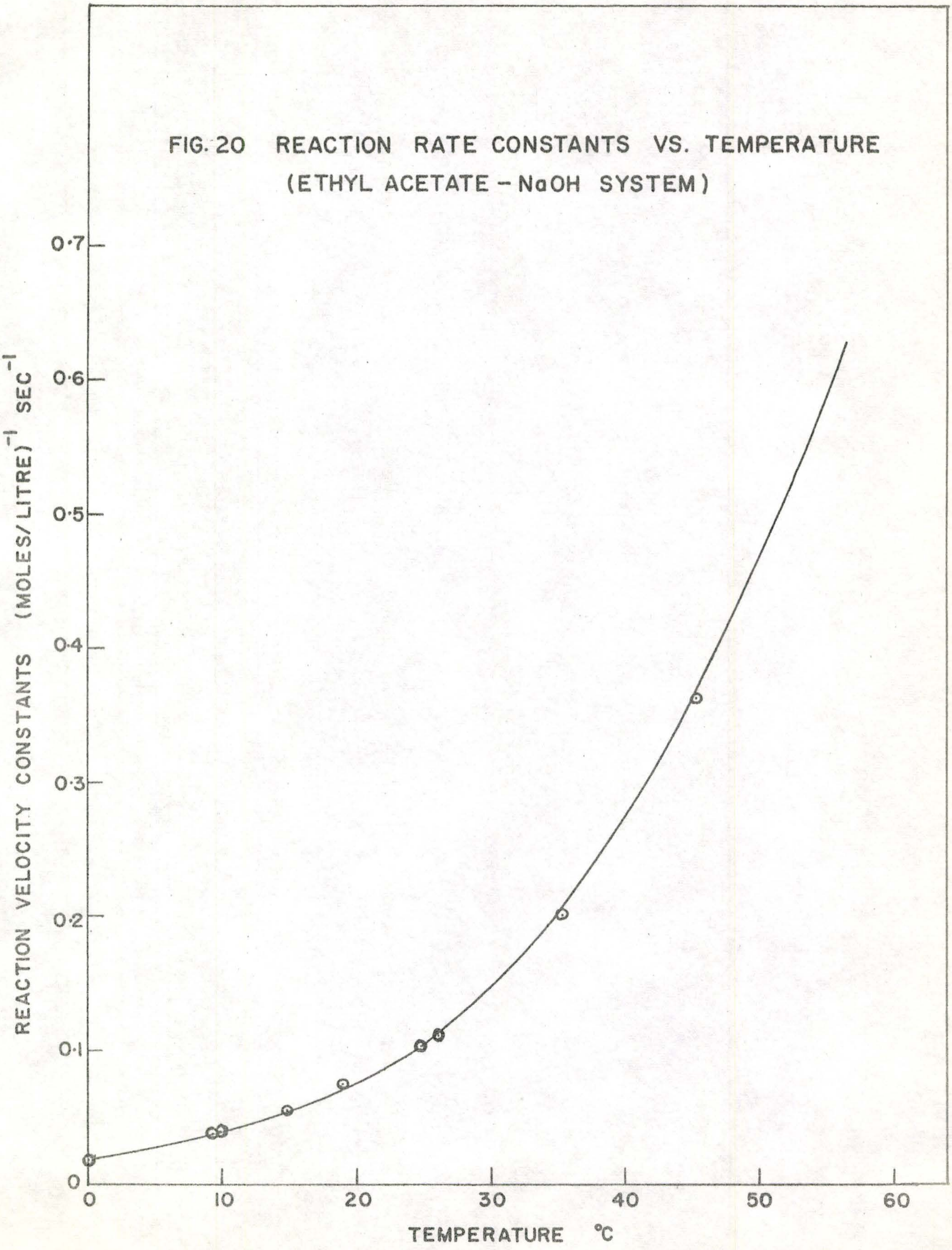


FIG. 20 REACTION RATE CONSTANTS VS. TEMPERATURE (ETHYL ACETATE - NaOH SYSTEM)

APPENDIX IX

ANALOGUE STUDY

An analogue study was also carried out with the aid of a TR - 10 computer manufactured by Electronics Associates Inc., and a variplotter. There are three objects for doing this study: (a) to establish the concentration profiles of the reactants and products for the system of ethyl acetate and sodium hydroxide solution across the film, (b) to evaluate the retardation to mass transfer in the system of ethyl acetate-sodium hydroxide, and (c) to simulate the concentration profiles of reactants and products across the film of a system with some boundary conditions given.

A) Concentration profiles of reactants and products across the film for the system of ethyl acetate-sodium hydroxide

If the film model is assumed for this system, the concentration profiles of the reactants and products across the film at steady state can be obtained by solving equations (3) (4) (5) and (6). For the present study, only sodium acetate as the product was concerned.

Perhaps, one of the troublesome part in applying a TR - 10 analogue computer is in scaling. Since the computer can produce a maximum voltage of only 10, every numerical value has to be scaled so that the corresponding representing voltage is less than 10. An example for the scaling is given below with data taken from Run No. 85:

input sodium hydroxide concentration = 0.11 N.

temperature = 55°C

diffusivity of NaOH (55°C) = 4.14×10^{-5} cm^2/sec.

diffusivity of EtAc (55°C) = 2.21×10^{-5} cm^2/sec.

diffusivity of NaAc (55°C) = 2.325×10^{-5} cm^2/sec.

reaction constant (55°C) = 0.59 (moles/litre)$^{-1}$sec.$^{-1}$

The film thickness as calculated from physical mass transfer rate is 4.7×10^{-3} cm. Let λ (machine constant) be 10^{-3}; the solution time (τ) will be 4.7 sec.

Let C_1 = concentration of NaOH

C_2 = concentration of EtAc

C_3 = concentration of NaAc

A table can be set up.

	machine variable	max. value across the film	representing voltage
C_1	$100C_1$	0.0398 moles/litre	3.98
C_2	$10C_2$	0.712 moles/litre	7.12
C_3	$100C_3$	0.0702 - 0.08 moles/litre	7.02 - 8
$\frac{dC_2}{dx}$		0.197 moles/hr.	
x		4.7×10^{-3}cm.	

The $\frac{k}{D}$ values are calculated as follow: -

substitute the values into equation (3)

$$\frac{d^2(100C_1)}{d\tau^2} = 10^2 \times \frac{10^{-6} \times 0.59}{10^{-5} \times 4.14} \times \frac{10}{10^2 \times 10} \frac{(10^2C_1)\ (10C_2)}{10}$$

$$\frac{k}{D_1} = 0.0143$$

substitute the values into equation (4)

*

*

$$\frac{d^2((100/2.5)C_2)}{d\tau^2} = \frac{10^2}{2.5} \times 10^{-6} \times \frac{0.59}{4.14 \times 10^{-5}} \frac{10}{10^2 \times 10} \frac{(10^2C_1)(10C_2)}{10}$$

$$\frac{k}{D_2} = 0.0107$$

substitute the values into equation (5)

$$\frac{d^2(100C_3)}{d\tau^2} = 10^2 \times 10^{-6} \times \frac{0.59}{2.33 \times 10^{-5}} \frac{10}{10^2 \times 10} \frac{(10^2C_1)(10C_2)}{10}$$

$$\frac{k}{D_3} = 0.02532$$

The transfer rate, which is the initial condition for integrator No. 5, is calculated from the equation: $N_2 = D_2A \frac{dc}{dx}$.

*

* NOTE:

In order to reduce $\frac{d((100/2.5)C_2)}{d\tau}$ into $\frac{d(10C_2)}{d\tau}$ the output from integrator No. 5 is multiplied by a factor of 0.25 through a potentiometer.

Assuming a physical transfer rate, which is rather true in ideal case,

$$\left(\frac{dc}{dx}\right)_{x=0} = .136\ (\text{moles/c.c.})\text{cm}^{-1} = 136\ (\text{moles/litre})\text{cm}^{-1}$$

$$\therefore \frac{d(10^2 C_2 25)}{d\tau} = 10^2 \times 10^{-3} \times \frac{136}{2.5} = 5.44 \text{ volts}$$

The circuit diagram was as shown in figure (21). The analogue plots were as shown in figures (14) and (15).

By observing the concentration profiles, it was certain that the assumption of homogeneous reaction in the lower phase was close to the actual situation.

B) Evaluation of the retardation to mass transfer in reaction runs for the system of ethyl acetate-sodium hydroxide

Considering equation (14), $N = \frac{DA}{x} (\Delta C) = k_L^o (\Delta C)$

if the transfer rate was reduced, the retardation could be evaluated in terms of either one or both of the variables. In the theoretical section, the retardation was explained, apart from salt effect, in terms of "k" by adding one more resistance as "$1/k_r$". In this section, it was shown that the retardation could also be evaluated in terms of ΔC. The decrease in ΔC due to retardation to transfer could easily be obtained by an analogue computer.

The same circuit was used as in section(A) and the data were taken from Run No. 85 (0.11 N. NaOH and 55°C) as an example. The boundary conditions were the same as those for Run No. 85 except the initial condition for integrator No. 6 was adjusted (solubility of ethyl acetate) so that C_2 at the other side of the film coincided with the bulk concentration measured. In this run, the equivalent retardation was found to be a decrease in solubility of 0.147 moles/litre.

C) Simulation of concentration profiles of reactants and products across the film for a given system

Considering a system similar to ethyl acetate and sodium hydroxide, the reaction equation was

$$A + B \longrightarrow C + D.$$

Since all the components involved were mono-molecular, the concentration of C and D was the same.

There were actually two main factors controlling the shape of the profiles; the transfer rate and the reaction constant. The solubility was also fairly important. As a practical example for demonstration, the physical transfer rate for the system of ethyl acetate and sodium hydroxide at 55°C was again taken and for the sake of simplicity, $\frac{k}{D_1} = \frac{k}{D_2} = \frac{k}{D_3}$ was assumed.

The idea was to find the $\frac{\text{"}k\text{"}}{D}$ and transfer rate of a system whose physical transfer rate was equivalent to that of ethyl acetate - sodium hydroxide system and whose concentration profiles satisfied the film model.

If the transfer rate was kept constant at 8 volts, which was equivalent to 200(moles/litre)$(\text{cm})^{-1}$, and the value of $\frac{k}{D}$ was varied, a set of computer plots could be obtained as shown in figure (21a). The profile of C_2 was getting more and more curved. If the $\frac{k}{D}$ value was increased beyond 5.5, C_2 at the end of the film had a higher value than the physical transfer one and retardation occurred. Therefore, the system having $\frac{k}{D}$ values of more than 5.5 should have a transfer rate of higher than 200(moles/litre)(cm)$^{-1}$ in order to satisfy the conditions of the film model.

On the other hand, the system could also be studied by keeping $\frac{k}{D}$ constant and varying the transfer rate instead. Figure (21b) showed the variation of concentration profiles with transfer rate keeping $\frac{k}{D}$ constant at 10.

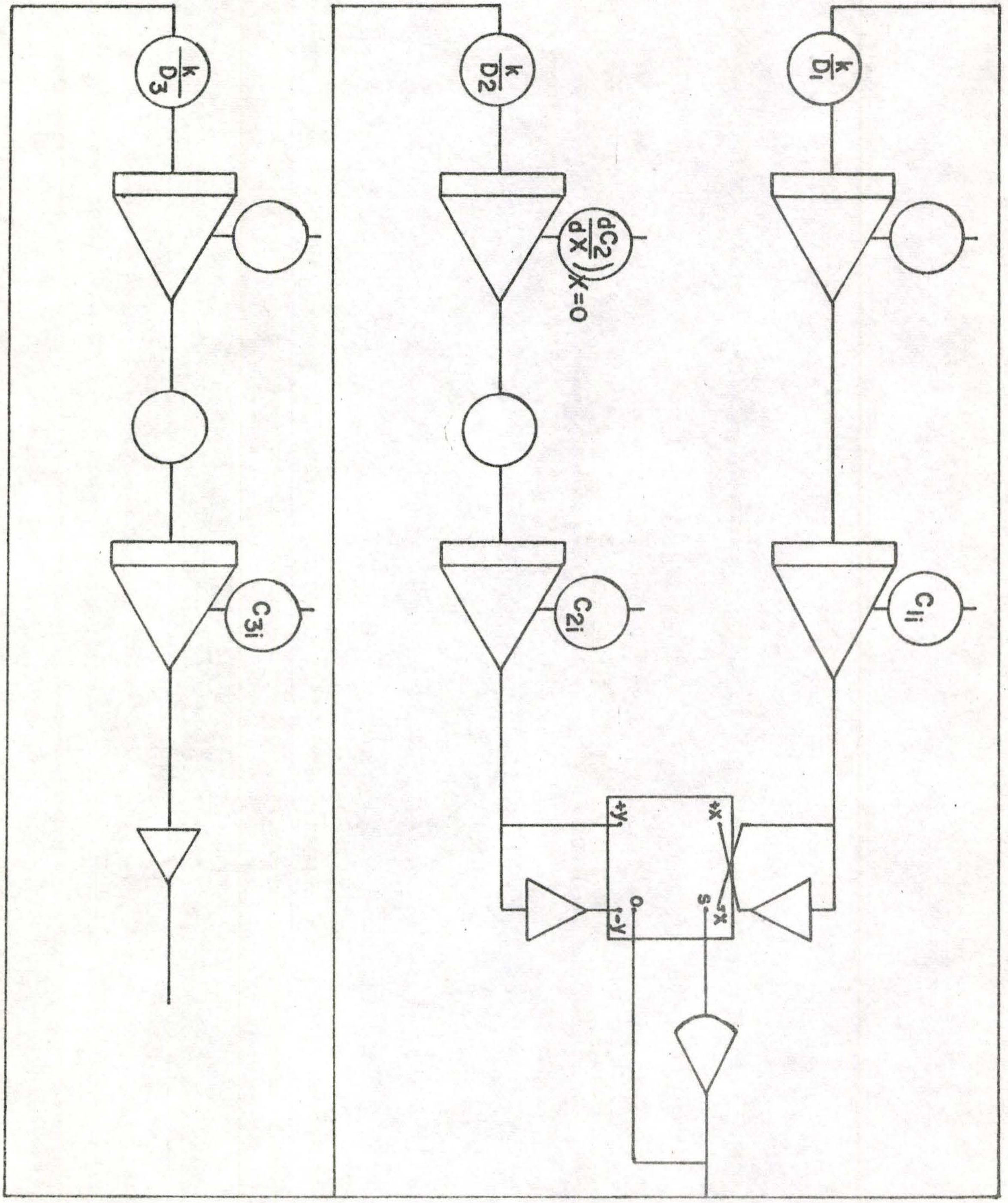


FIG. 21 ANALOG CIRCUIT DIAGRAM

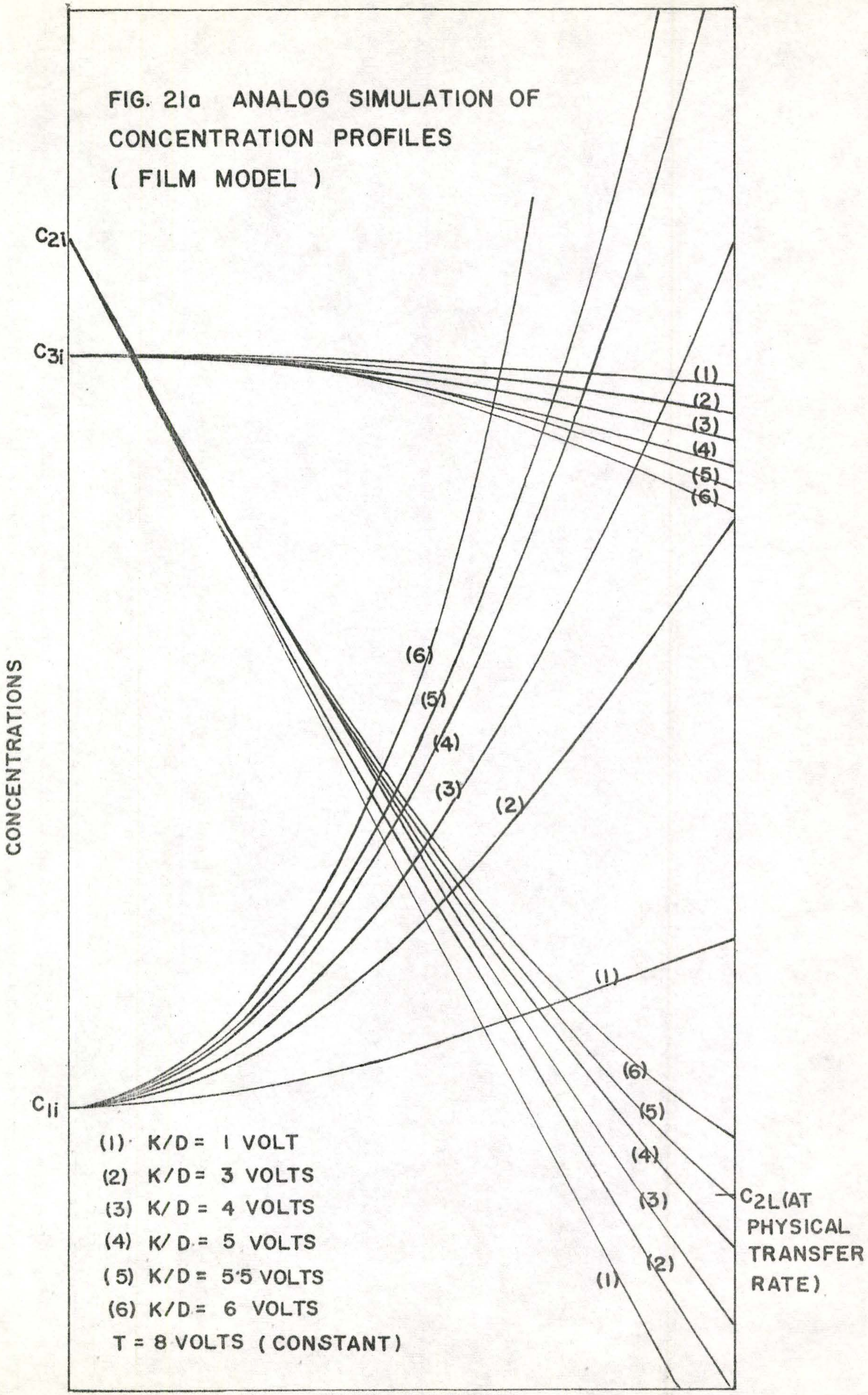


FIG. 21a ANALOG SIMULATION OF CONCENTRATION PROFILES (FILM MODEL)

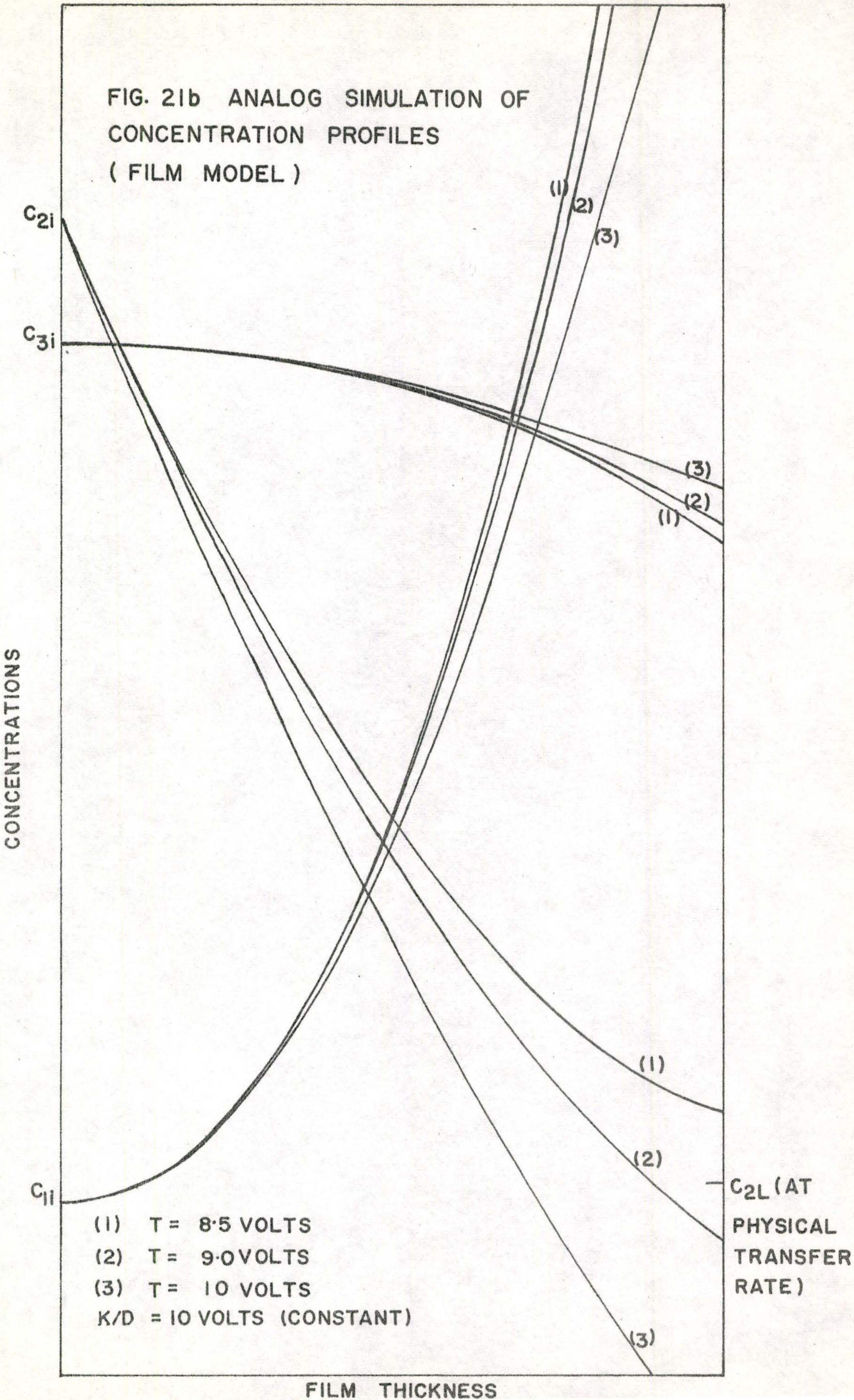


FIG. 21b ANALOG SIMULATION OF CONCENTRATION PROFILES (FILM MODEL)

APPENDIX X

A) The three zones model (with reference to Part II) : -

If the optical cell situation for ethyl acetate-sodium hydroxide system as observed in Part II is modified; and sodium hydroxide is passed in and out the well-sitrred lower phase continuously, a steady state will eventually be reached where three zones separated by two boundaries exist. If the liquid inside the reaction zone is assumed to be well mixed, then the concentration profiles of the reactants can be sketched as shown in figure (22).

Method of obtaining the concentration profiles is outlined as follows. The differential equations of (3) and (4) are again used.

$$D_1 \frac{d^2C_1}{dx^2} = D_2 \frac{d^2C_2}{dx^2} = kC_1C_2$$

C_1 refers to the concentration of sodium hydroxide

C_2 refers to the concentration of ethyl acetate

The boundary conditions are: for $0 \leqslant x \leqslant x_1$

at $x = 0$ $\qquad C_1 = C_{1i}$

$$\left.\frac{dC_1}{dx}\right)_{x=0} = 0$$

$$D_2 \left.\frac{dC_2}{dx}\right)_{x=0} = N_{2o} \quad (\text{moles/cm}^2 \text{ sec.})$$

at $x = x_1$

$C_1 = C_{12}$

$C_2 = C_{22}$

for $x_2 \leqslant x \leqslant x_3$

at $x = x_2$

$C_1 = C_{12}$

$C_2 = C_{22}$

$$D_2 \left.\frac{dC_2}{dx}\right)_{x = x_2} = N_{22} \text{ (moles/cm}^2\text{ sec.)}$$

at $x = x_3$

$C_1 = C_{1L}$

$C_2 = C_{2L}$

in the region $x_1 \leqslant x \leqslant x_2$

rate of reaction = $(x_2 - x_1)(1)kC_{12}C_{22}$

in the region $x_3 \leqslant x$, mass balance on sodium hydroxide yields

$$FCo - FC_{1L} = kC_{1L}C_{2L}V + A\left(-D_1\left(\frac{dC_1}{dx}\right)_{x = x_3}\right) \quad .... (24)$$

and mass balance on ethyl acetate yields

$$- FC_{2L} + A\left(-D_2\left(\frac{dC_2}{dx}\right)_{x = x_3}\right) - kC_{1L}C_{2L}V = 0 \quad .... (25)$$

also

$$N_{2o} = \int_0^{x_1} kC_1C_2dx + kC_{12}C_{22}(x_2 - x_1) + N_{22} \quad .... (26)$$

where k is in $(\text{moles/litre})^{-1}\text{sec.}^{-1}$; F is in (litres/sec);

A is in (cm^2)

Integrating equations (3) and (4) and substituting the boundary conditions, the following expressions are obtained:

for the first film,

$$D_2 \ (C_2 - C_{22}) - D_1 \ (C_1 - C_{12}) = N_{2o} \ (x_1 - x)$$

or

$$D_2 \ (C_{2i} - C_{22}) - D_1 \ (C_{1i} - C_{12} = N_{2o} \ (x_1 - 0) \qquad \dots . \ (47)$$

similarly, for the second film,

$$D_2 \ (C_{22} - C_{2L}) - D_1 \ (C_{12} - C_{1L}) = N_{22} \ (x_3 - x_2) \qquad \dots . \ (28)$$

On the other hand, if the concentration C_1 is assumed to be constant across the film and equal to the average of the boundary values,

$D_2 \dfrac{d^2C_2}{dx^2} = kC_1C_2$ can be integrated to the form of

$$C_2 = K_1 e^{\sqrt{\frac{k}{D_2}C_{\bar{1}}}\,x} + K_2 e^{-\sqrt{\frac{k}{D_2}C_{\bar{1}}}\,x} \qquad \dots . \ (29)$$

where

K_1, K_2 are integration constants

$C_{\bar{1}}$ is the average value of component 1 between boundaries of one film.

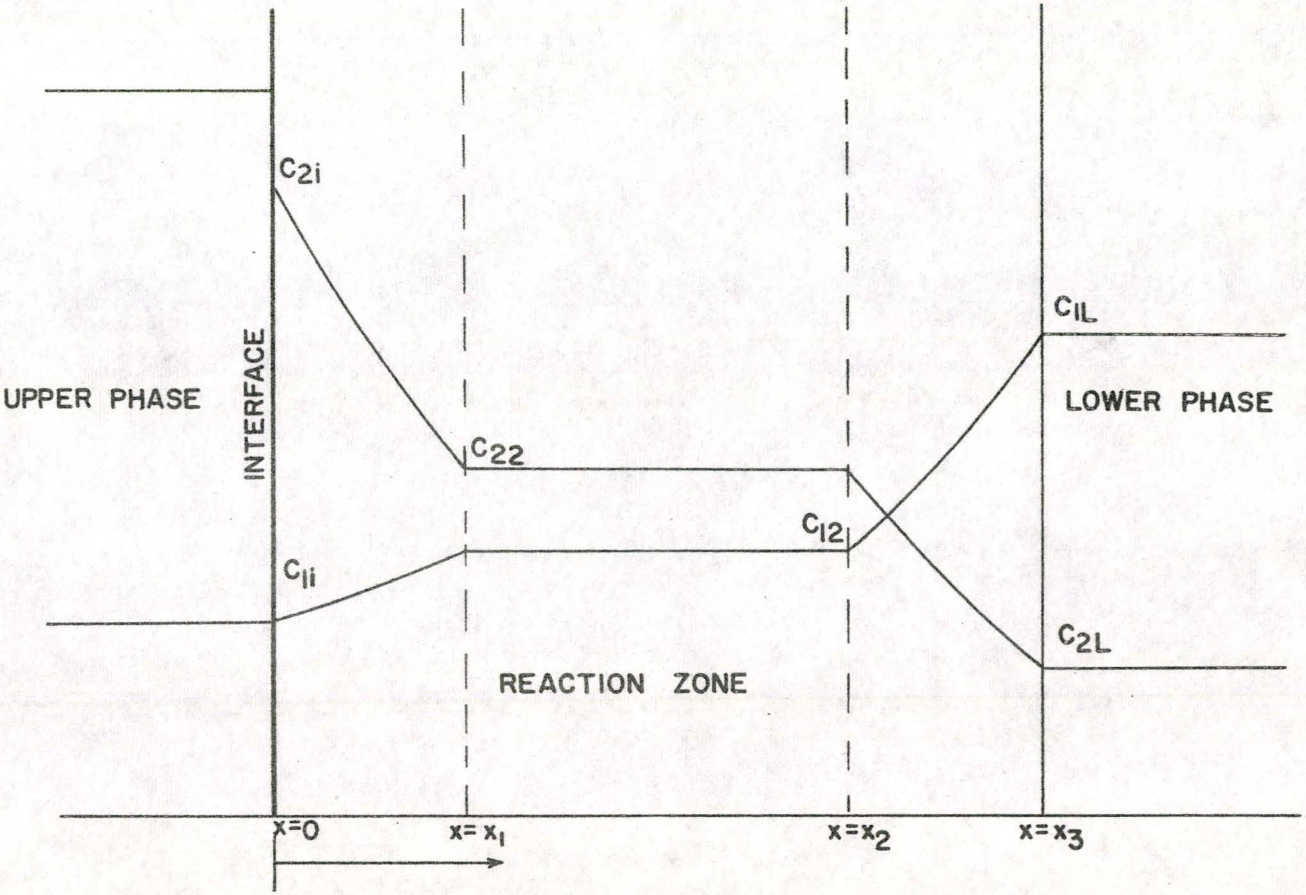
With the above equations, concentration profiles of the reactants can be set up by trial and error method.

B) Simplification of the three zones model : -

The thickness of films and reaction zone depends on the stirrer speed as well as the flowrate of the lower phase. For the reaction runs in the present study, it may be speculated that the reaction zone is so small that its presence can practically be neglected and the situation is simplified to two adjacent films at the interface.

If the reaction inside the films is so slow that the concentration of sodium hydroxide is essentially unchanged throughout the films and equal to that of the bulk lower phase, the films act as pure resistances and the situation is further simplied to that as described in the "Theoretical Principles" section.

FIG. 22 CONCENTRATION PROFILES IN THE FILMS (THE THREE ZONES MODEL)



APPENDIX XI

REPETITION OF J. B. LEWIS' EXPERIMENTS

There is still another way of determining the concentration of sodium acetate at the interface (C_{ai}) apart from either solving equation (5) or measuring the interfacial tension of the system as described in Appendix VIII, section (B).

A reaction run of the ethyl acetate-sodium hydroxide system is considered. It is assumed that only one film exists at the interface. At steady state, material balance on sodium acetate across the film yields the following equation:

$$N_a = k_a \left(C_{ai} - \frac{k C_{1m} C_{2m} V}{F} \right) \quad \ldots. (30)$$

where

C_{ai} = concentration of sodium acetate at the interface (gm.moles/litre)

k_a = physical mass transfer coefficient of sodium acetate across the film into the lower phase (litres/hr.)

C_{1m} = measured concentration of sodium hydroxide in the bulk lower phase (gm.moles/litre)

C_{2m} = measured concentration of ethyl acetate in the bulk lower phase (gm.moles/litre)

N_a = amount of sodium acetate formed inside the film per unit time; theoretically this is equal to measured ((sodium acetate concentration in the lower phase) x (flowrate)) - (kC_1C_2V) (moles/hr.)

C_1, C_2 = calculated sodium hydroxide, ethyl acetate concentrations in the lower phase, assuming negligible reaction rate inside the film (gm.moles/litre)

If k_a is known, C_{ai} can easily be evaluated.

In 1954, J. B. Lewis published a paper concerning the mechanism of mass transfer of solutes across liquid-liquid interfaces (67). According to his idea, individual physical mass transfer coefficients for any binary systems were related only to Reynolds numbers and physical properties of the two phases by the expression (units were referred to his paper):

$$60\ k_1/\nu_1 = 6.76 \times 10^{-6}\ (Re_1 + Re_2\mu_2/\mu_1)^{1.65} + 1 \qquad \ldots. (31)$$

In his second paper concerning a single solute transferring from one phase to another (68), he compared the measured overall transfer coefficient with the predicted one, which was obtained by acquiring individual transfer coefficients from equation (31) and adding them up, using the equation (solute travels from phase 1 to 2):

$$1/K_{o2} = 1/k_2 + m/k_1 \qquad \ldots. (32)$$

In some cases, good agreements were observed; while in some others, as high as 30 fold differences were reported between the observed and the predicted results.

The validity of the expression (31) is therefore doubtful, and some of his experiments were repeated as a check.

The apparatus used was a cell, similar to the one used by Lewis, and as shown in figure (23). Two identical halves of the cell were made of 6 inches internal diameter thick-walled glass column. They were bolted together on both sides of a central stainless steel plate. The interface was restricted to an annular gap between a central circular baffle and a circumferential wall baffle. The purpose of the baffle was to reduce cavitation and possible irregular wall effects and, in general, to give greater stability to the interface. Two stirrers were driven by synchronising motors through two concentric shafts. The speeds of the stirrers were regulated by "Zero-max" variable speed torque converters. The driving unit and the cell could be detached; and in the experimental runs, they were connected only by the concentric shafts. In this way, the transmission of the mechanical vibration from the motors to the cell was reduced to the minimum. Temperature of the cell was kept at a desired level to ± 0.05°C using a constant temperature water bath.

Three systems were chosen for this study at 20°C. They were:

(a) iso-butanol-water (mutual saturation runs)

20 runs were performed at various stirrer speeds.

(b) ethyl acetate-water (mutual saturation runs)

7 runs were performed at various stirrer speeds.

(c) toluene-water, already mutually saturated (acetic acid transferring from toluene to water)

4 runs were performed at slightly different initial acetic acid concentration.

The procedure and method of calculation were the same as those used by J. B. Lewis. An Abbe refractometer was used for analysing the concentration of iso-butanol in water, ethyl acetate in water and water in iso-butanol. A gas chromatograph (paraplex column) was used to determine the concentration of water in ethyl acetate. Titration method was used to determine the concentration of acetic acid in both the toluene and water phases.

All of the mutual saturation runs were fairly reproducible. Mass transfer coefficients of 4 runs on iso-butanol-water system with identical conditions showed a maximum deviation of 6%. The results on acetic acid transferring from toluene to water were more scattered. Transfer coefficients on three similar runs showed a maximum deviation of 20%.

All the least square calculations were processed on an I.B.M. 1620 digital computer. The results for systems (a) and (b) were plotted, similar to Lewis' form and as shown in figure (24). Even the units for k was (cm/min) this time instead of (cm/sec) as used by Lewis, 15 k values for transfer of water into iso-butanol phase still could not be included because they were so small that "$60\ k_1/\nu_1 - 1$" became negative. By the least square method, the data in figure (24) could be correlated by the expression (with an average deviation of 8.9%):

$$60\ k_1/\nu_1 = 2.84 \times 10^{-6}\ (Re_1 + Re_2\mu_2/\mu_1)^{2.37} + 1 \qquad \text{....}\ (33)$$

or

$$k_1/\nu_1 = 4.73 \times 10^{-8}\ (Re_1 + Re_2\mu_2/\mu_1)^{2.37} + 0.0167 \qquad \text{....}\ (34)$$

Only one average result is obtained in system (c); and more than a 5-fold difference was obtained between the predicted overall transfer coefficient (0.0009 cm/min) and the measured one (0.0049 cm/min).

It was, therfore, concluded that Lewis' correlation was very empirical and restricted to a particular cell. In order to generalize the expression (31), some more terms were required, for example, Sherwood number.

Recently, Lewis' experiments were repeated by two more researchers, and they proposed the following correlations, which were more reasonable: (reference 78)

$$k_1 d/D_1 = \beta \, (Sc)^{5/6} \, (Re_1 Re_2)^{0.5} \qquad \ldots . \, (35)$$

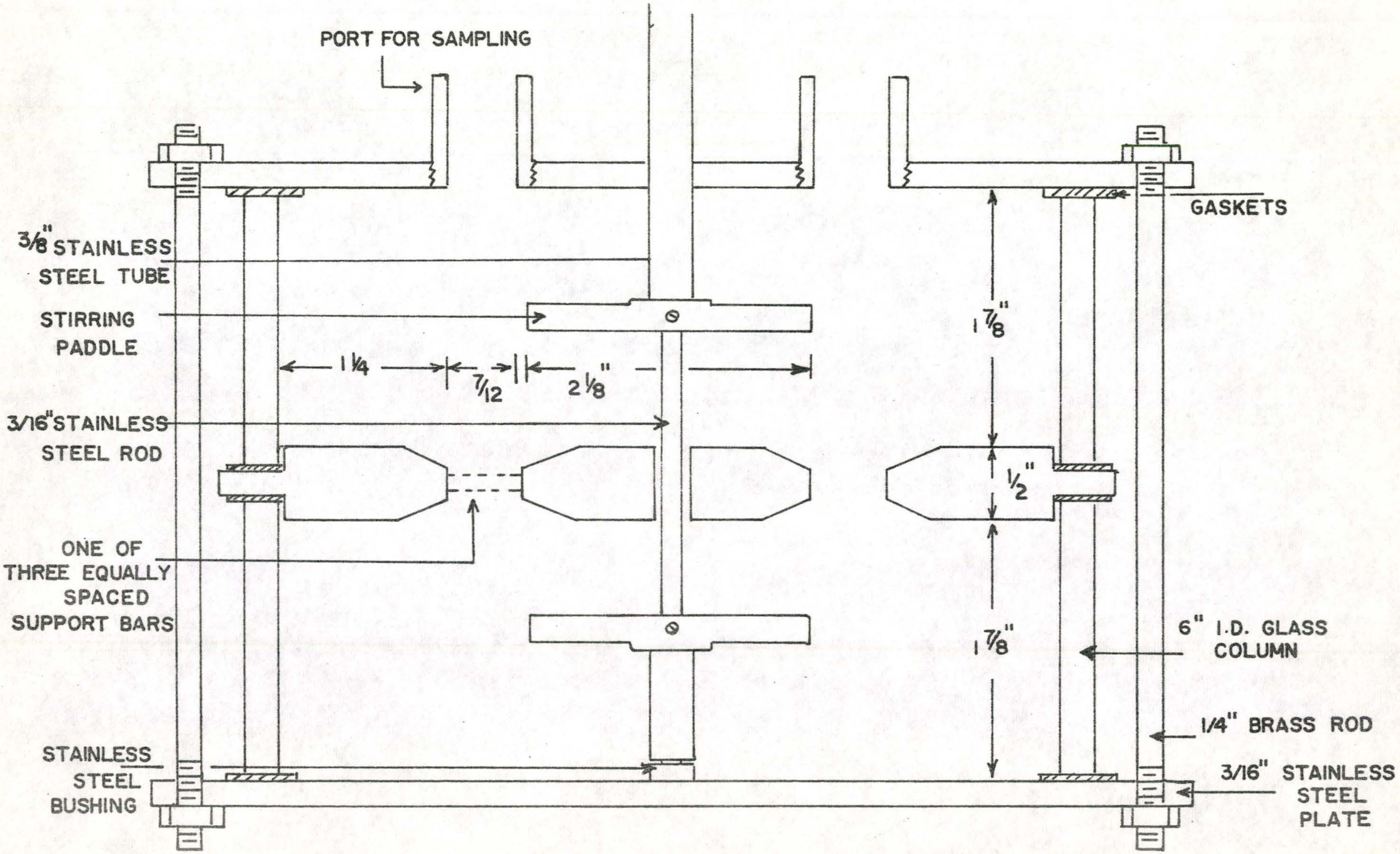
and (reference 81)

$$60 \, k_1/\nu_1 = \alpha \, (Sc)^{-0.37} \, (Re_1)^{0.9} \, (1 + \mu_2 Re_2/\mu_1 Re_1) \qquad \ldots . \, (36)$$

α is a constant

β is a function of μ_2/μ_1

FIG. 23 EXTRACTION CELL



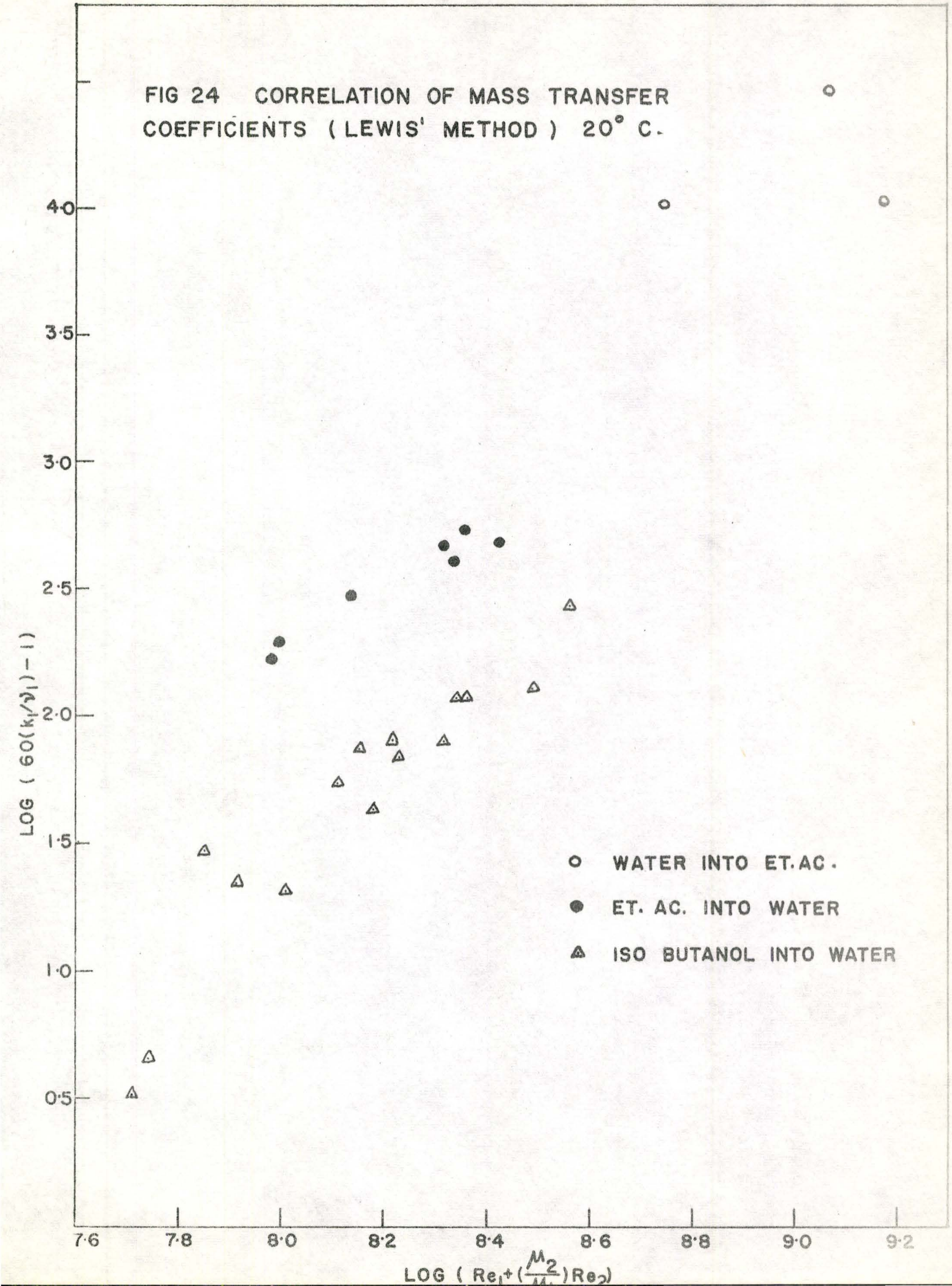


FIG 24 CORRELATION OF MASS TRANSFER COEFFICIENTS (LEWIS' METHOD) 20° C.

PART II

UNSTEADY STATE MASS TRANSFER
ACCOMPANIED BY A SLOW
IRREVERSIBLE SECOND ORDER
CHEMICAL REACTION
(WITHOUT STIRRING)

EXPERIMENTAL DETAILS

A) Schlieren investigation : -

1) Apparatus

The schlieren arrangement was as shown in figure (25). The schlieren principle has been reviewed quite extensively (74)(75)(97). Various modifications on the apparatus have been made. The arrangement used in this experiment was most conventional. It consisted of five components: the light source, the optical unit, the test cell and the knife edge, all aligned and mounted on a 3 meter long optical bench. The phenomenon observed in the test cell was recorded in motion pictures. A detailed description of the apparatus was given in Appendix XII.

2) Experimental run

25 ml. of re-distilled ethyl acetate pre-saturated with distilled water at room temperature was let contact with approximately 90 ml. of sodium hydroxide solution. The liquid-liquid interface thus formed was closely studied with the aid of the schlieren apparatus. The experiment was carried out at room temperature (24° ± 2°C) and repeated at various concentration levels of sodium hydroxide solution. Duration of the experiment ranged from two hours to over ten hours.

B) Measurement of concentration distribution of reactants inside the reaction zone : -

1) Apparatus

The apparatus consisted of a test cell, a "phase contactor" and long hypodermic needles as shown in figure (26). (A detailed description of the apparatus was given in Appendix XII.) A cathetometer was used to position accurately the needle-tips from the ethyl acetate-sodium hydroxide interface.

2) Experimental

a) Experimental run (Numbers in the following description refer to figure (26))

Four long sampling needles (3) were put into the cell (1). The needles were equally spaced within the cell and their relative vertical distances with respect to each other were measured using a cathetometer. Ethyl acetate pre-saturated with water was poured into the test cell, filling one-eighth of its volume. Then, the phase contactor (2) containing approximately 1½ litres of sodium hydroxide at the desired concentration level was lowered into the cell until the fritted glass disc just touched the bottom of the cell. After the cell top was tightly covered with clean aluminum foil to avoid evaporation of the upper phase, the sodium hydroxide solution was let out slowly through the sintered glass disc and under the ethyl acetate phase. The flowrate was controlled by the pipette filler. In this way, a smooth and rather undisturbed interface between the light phase and the heavy phase was formed. As more and more of the sodium hydroxide solution was introduced into the cell, the interface moved up gradually to a pre-determined level which was 1 mm. above the tip of the highest needle. Zero time for the experiment began as soon as the sodium hydroxide started to be introduced. Duration of the experiment was 100 minutes. During the experimental run, four samples were taken at intervals from each sampling needle; and 2 ml. of the solution was drawn for each sample. The "phase contactor" was left inside the cell throughout the experiment.

After each experiment, both the test cell and the "phase contactor" were cleaned with warm concentrated sodium hydroxide-ethanol solution and concentrated chromic acid respectively. The sampling needles were flushed with a large amount of distilled water.

b) Temperature control

All the experiments were carried out at room temperature (24° ± 2°C). Temperature variation within each individual experiment was within 1°C.

c) Sample analysis

Each sample freshly drawn from the cell was quickly put into an erlenmeyer flask containing 25 ml. of distilled water. The dilution helped to slow down the reaction occurring in the sample. Then, the solution was titrated immediately with 0.1 N. HCl to the end point using phenolphthalein as indicator.

A known amount of sodium hydroxide was then added to the titrated solution. The top of the erlenmeyer flask was sealed with paraffin wax, while the lower half of the flask was immersed in water at constant temperature of 70°C for three hours until the hydrolysis was completed. The original amount of ethyl acetate present in the sample was determined by back titration with the acid.

C) Measurement of zone propagation : -

1) Apparatus

The apparatus consisted of a light source, a test cell, a "phase contactor", Moiré plates and photographic equipment. They were arranged as shown in figure (27) (A detailed description of the apparatus was given in Appendix XII.)

2) Experimental

a) Experimental run (Numbers in the following description refer to figure (27))

45 ml. of re-distilled ethyl acetate saturated with water was first introduced into the cell (1); then the "phase contactor", containing approximately 100 ml. of the sodium hydroxide solution at desired concentraction level, was lowered to the optical cell until the fritted glass disc just touched the bottom of the cell. The pair of Moiré plates (2) were placed in position. The top of the cell was covered with a pair of glass plates in order to eliminate the turbulence induced by evaporation of the light phase. Sodium hydroxide solution was introduced into the cell in the similar way as described in Section (B) 2. The time for the beginning of the experiment was taken as soon as the heavy phase started to enter. Duration of the experiment was arbitrarily set to be 100 minutes. During each run, about 25-30 pictures of the reaction zone were photographed with the camera (4). The "phase contactor" was left inside the cell throughout the run.

At the end of each experiment, the cell, the "phase contactor" and the cover plates were carefully washed with concentrated sodium hydroxide-ethanol solution, concentrated chromic acid and a large amount of distilled water.

b) The Moiré pattern (41)(76)(94)(108)

In order to get a Moiré pattern of the solution under test, one plate with the ruled lines in horizontal direction was attached to one side of the cell. On the other side of the cell, the other plate was attached in such a way that the lines of the two plates intersected at a small angle (8° 32'). A ground glass plate was inserted between one side of the cell and the Moiré plate. The resulting pattern was a set of vertical straight Moiré lines if there were no concentration gradient of any component within the solution inside the test cell. The spacing of the lines depended on the angle at which the two plates intersected. At the angle of intersection used for this work, the spacing was 16 lines/inch. The Moiré lines became curved wherever a concentration gradient existed, and the degree of curvature was usually proportional to the concentration gradient.

c) Temperature control

All the experiments were performed at room temperature (24° ± 2°C). Temperature variation within each experimental run was less than 1°C.

d) Measurement of zone propagation

The pictures taken during each run were developed. Most of the negatives were made into slides which were subsequently projected. Dimensions of the reaction zone for each slide were recorded. Measurement of the transfer rate for each experimental run was also attempted by noting the changing of ethyl acetate-sodium hydroxide interface level with respect to the bottom of the cell.

D) <u>Number of diffusion experiments performed</u> : -

1) <u>Ethyl acetate-aqueous sodium hydroxide system</u>

Ten experiments on the measurement of the propagation of reaction zone were performed at room temperature and at various sodium hydroxide concentrations. Experiments at 0.5 N. sodium hydroxide concentration level were repeated twice to check the reproducibility.

On the other hand, only three experiments were performed at different sodium hydroxide concentrations on probing the concentration distribution of the reactants inside the reaction zone.

More than ten experiments were performed on the schlieren investigation.

The ethyl acetate used was purified by re-distillation in the way as described in Appendix IV.

2) Ethyl acetate-water system

Physical diffusion of ethyl acetate into water was studied at room temperature, using both the schlieren apparatus and the Moiré plates.

3) Ethyl formate-aqueous sodium hydroxide system

More than ten experiments were performed on the measurement of the propagation of reaction zone at room temperature and at various sodium hydroxide concentrations ranging from 0.05 N. to 2.0 N. Experiments were repeated at three sodium hydroxide concentration levels to check the reproducibility.

The ethyl formate used was of the analytical grade supplied by J. T. Baker Chemical Co. Owing to the shortage of supply, the ethyl formate was not purified by re-distillation.

4) Ethyl formate-water system

The diffusion phenomenon of ethyl formate into water was investigated at room temperature, using the Moiré plates.

E) Method of calculation : -

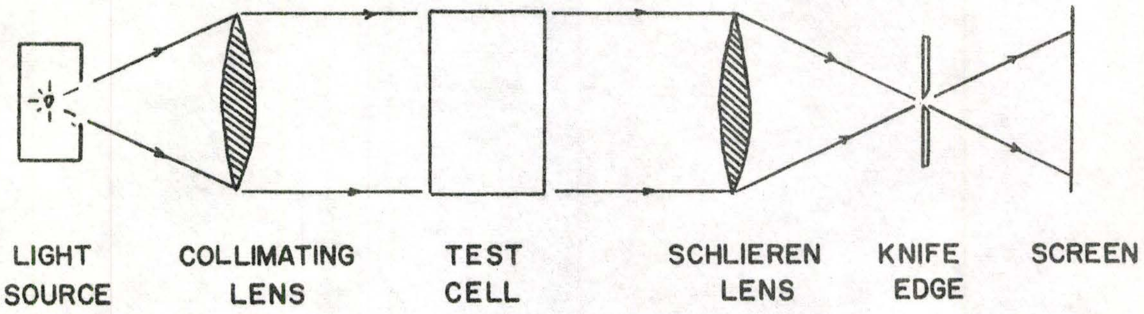
1) Measurement of zone thickness

The photographic slides for each run were projected on the wall consecutively. The image of the reaction zone on each negative was enlarged in order to reduce error in measurement. The magnification, in this case, was 11.354 times the actual dimensions.

For each slide, the thickness of the reaction zone was measured three times on three different locations. Each of the measured zone thickness was divided by 11.354 (the magnification number) so that it could be converted back to its actual experimental value. The three values thus obtained were averaged, and the square of the averaged zone thickness was also calculated.

All the calculations were done in a Bendix G-15 computer.

FIG. 25 SCHLIEREN APPARATUS



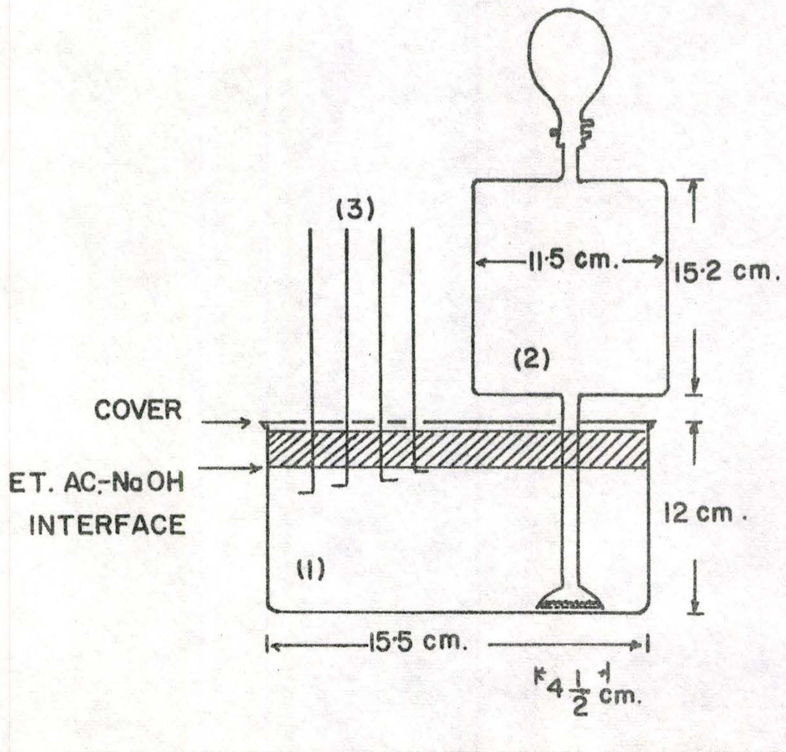
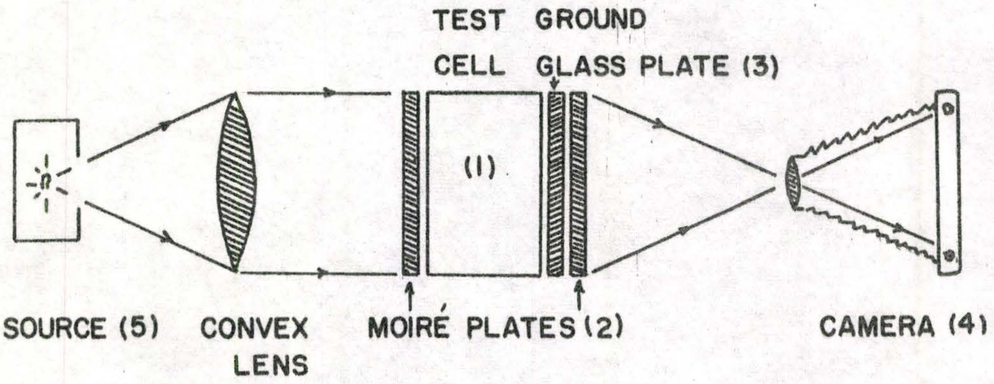


FIG. 26 APPARATUS FOR CONCENTRATION MEASUREMENTS

FIG. 27 APPARATUS FOR THE MEASUREMENT OF ZONE PROPAGATION
(TOP VIEW)



RESULTS AND OBSERVATIONS

A) Schlieren investigation : -

1) Ethyl acetate-sodium hydroxide system

(The following description refers to figure (28)

Right after the contact of the two phases, ethyl acetate was seen diffusing into the lower phase through the interface "AB" which appeared on the screen as a thick, dark line due to its meniscus on the cell wall. The diffusing ethyl acetate reacted with sodium hydroxide on its way into the lower phase forming a reaction zone, inside which turbulent liquid motion was observed. The zone was separated distinctly from the lower sodium hydroxide phase by a boundary "CD" which also was revealed on the screen as a thick, dark line. Down from the boundary "CD", small but numerous streaks protruded slowly into the lower phase. These streaks were found to be sodium acetate and ethanol by an experiment described in the "Preliminary Investigations" (Appendix XIII). In the course of time, the reaction zone extended itself further down, while the turbulent motion within the zone gradually died out. The speed of zone extension was faster with lower normality of the initial sodium hydroxide concentration.

2) Ethyl acetate-water system

No reaction zone was observed with the system, and the transfer of ethyl acetate into water was gentle and slow.

B) Concentration distribution of the reactants inside the reaction zone : -

Data for the three runs on ethyl acetate-sodium hydroxide system were presented in Tables XII, XIII and XIV respectively (Appendix XV). These data were plotted with concentration of sodium hydroxide and ethyl acetate versus time for each needle position. The graphs were shown in figures (29), (30) and (31). In the three graphs, if the time was kept constant, the concentration of reactants as a function of distance from the interface for each initial sodium hydroxide concentration could be obtained. Two graphs of such a kind were drawn at 20 minutes and 40 minutes after the beginning of the experiments. They were presented in figures (32) and (33).

C) Measurement of zone propagation : -

Pictures taken during each run were analysed. Besides the measurement of zone thickness on each picture, the accompanying Moiré pattern was also noted.

1) Ethyl acetate-sodium hydroxide system

At the beginning of the run, straight Moiré lines were observed extending from the bottom of the cell up to near the liquid interface between the reaction zone and the bulk lower phase. Inside the reaction zone, turbulent liquid motion was noticed and no Moiré lines were observable. Just below the demarcation line between reaction zone and sodium hydroxide, curved Moiré lines were observed. With low initial sodium hydroxide concentration, the strip where the lines curved themselves was quite narrow. On the other hand, with more concentrated sodium hydroxide solution, the curved-line portion was perhaps wider. Typical pictures of the Moiré pattern for some runs were shown in plate numbers 1, 2, 3, 4 and 5.

In course of time, liquid motion inside the reaction zone became less turbulent and the speed of zone propagation slowed down. The reaction zone stayed at a certain thickness for some time, and shrank subsequently at a very, very slow rate, at the same time, the demarcation line became diffused. In the experiments with higher initial sodium hydroxide concentrations, streaks of sodium acetate were seen diffusing out of the reaction zone and blurring the Moiré pattern below the interface; thus rendering both the observation and measurement difficult.

Nevertheless, measurements of zone thickness from the photographs for each run were made as a function of time. An example of the measurements was shown in plate No. 2. The data, after being converted back to the actual zone thickness, were recorded in Appendix XVI. It should be noted that the calculation was done in a computer which gave out the results in five significant figures. Due to the precision of the measuring instrument, any figures beyond two decimal places were of no significant value.

For each experiment, a curve of zone thickness versus time was plotted. This set of curves was shown in figure (34).

Also, for each experiment, $(\text{zone thickness})^2$ was plotted against time, and the set of straight lines was shown in figure (35). The slope of each line in figure (35) was plotted against the initial sodium hydroxide concentration of the particular experiment at which the line was obtained. The resulting graph was shown in figure (36).

2) Ethyl acetate-water system

No reaction zone was observed throughout the entire physical diffusion experiment. The Moiré lines were straight all the way up from the bottom of the cell, until near the ethyl acetate-water interface, where the lines were curved. A typical Moiré pattern was shown in plate No. 6.

3) Ethyl formate-sodium hydroxide system

The observation was generally similar to that of ethyl acetate-sodium hydroxide runs with a few exceptions. The speed of zone propagation was much faster than that of the ethyl acetate-sodium hydroxide system, and the turbulence inside the reaction zone was more vigorous.

In the runs with low initial sodium hydroxide concentration, the reaction zone was found to be extending itself down to the bottom of the cell within a short period of time. Motion of liquid within the reaction zone was observed to be vigorous and cycling convection current was set up as illustrated in figure (37). (also plate #8)

With high initial sodium hydroxide concentration, for example, 1.5 N. and 2.0 N., the propagation of the zone was much slower and only to a certain thickness. Turbulent and cycling liquid motion was observed around the parimeter of the zone. Furthermore, the zone movement was not even. Quite often, approximately one-quarter of the interfacial area, particularly the reaction zone and the bulk sodium hydroxide phase, travelled slower than the rest: this caused the zone thickness measurement to be difficult. A typical Moiré pattern was shown in plate No. 9.

Data obtained were treated in the same way as for ethyl acetate-sodium hydroxide system. Computer results and graphs were shown in

Appendix XVI and figures (38), (39) and (40) respectively.

Zone propagation for one of the runs (0.1 N. sodium hydroxide solution) was recorded with 16 mm. motion pictures taken at 8 frames/sec.

4) Ethyl formate-water system

No reaction zone was observed in this system. However, a rather interesting phenomenon was observed when ethyl formate was transferring into water. The diffusion mechanism, instead of by the conventional diffusion gradient setting up at the interface, was by eruptive transfer. Streaks of ethyl formate streamed down towards the bottom of the cell as shown in plate No. 7. As a result, more ethyl formate was found at the bottom than at the upper portion of the water phase. The Moiré lines were observed to be curved at the bottom part of the lower phase.

5) Reproducibility of the experiments

Comparison of data on repeated runs in ethyl formate-sodium hydroxide system showed that the reproducibility for the runs under test ranged from a minimum deviation of 3% to as high as 9%.

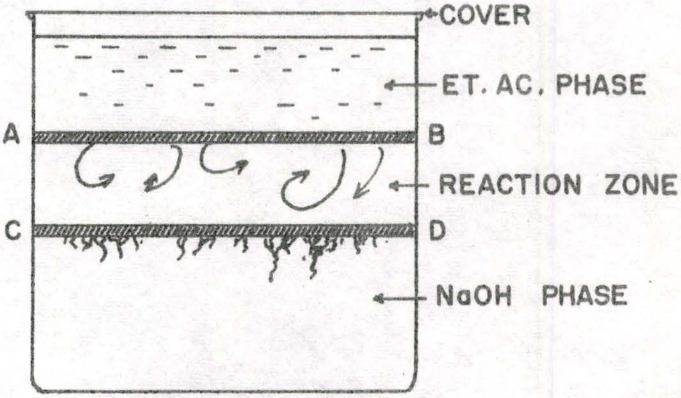
Results of three repeated runs in ethyl acetate-sodium hydroxide system (0.5 N. sodium hydroxide) were plotted as shown in figure (41).

6) Measurement of transfer rate

Measurement of transfer rate of the upper phase in each run was attempted. The levels of the interface (between the light phase and the heavy phase) at the beginning and at 100 minutes of each experiment were recorded with reference to the bottom of the cell. The difference between the two measured levels multiplied by the area of the cell gave the volume of the upper phase transferred in 100 minutes.

The measurements were found to be inaccurate due to the small amount of the upper phase transferred. The attempt was unsuccessful.

FIG. 28 SCHLIEREN PICTURE OF THE REACTION ZONE (ETHYL ACETATE-NaOH SYSTEM)



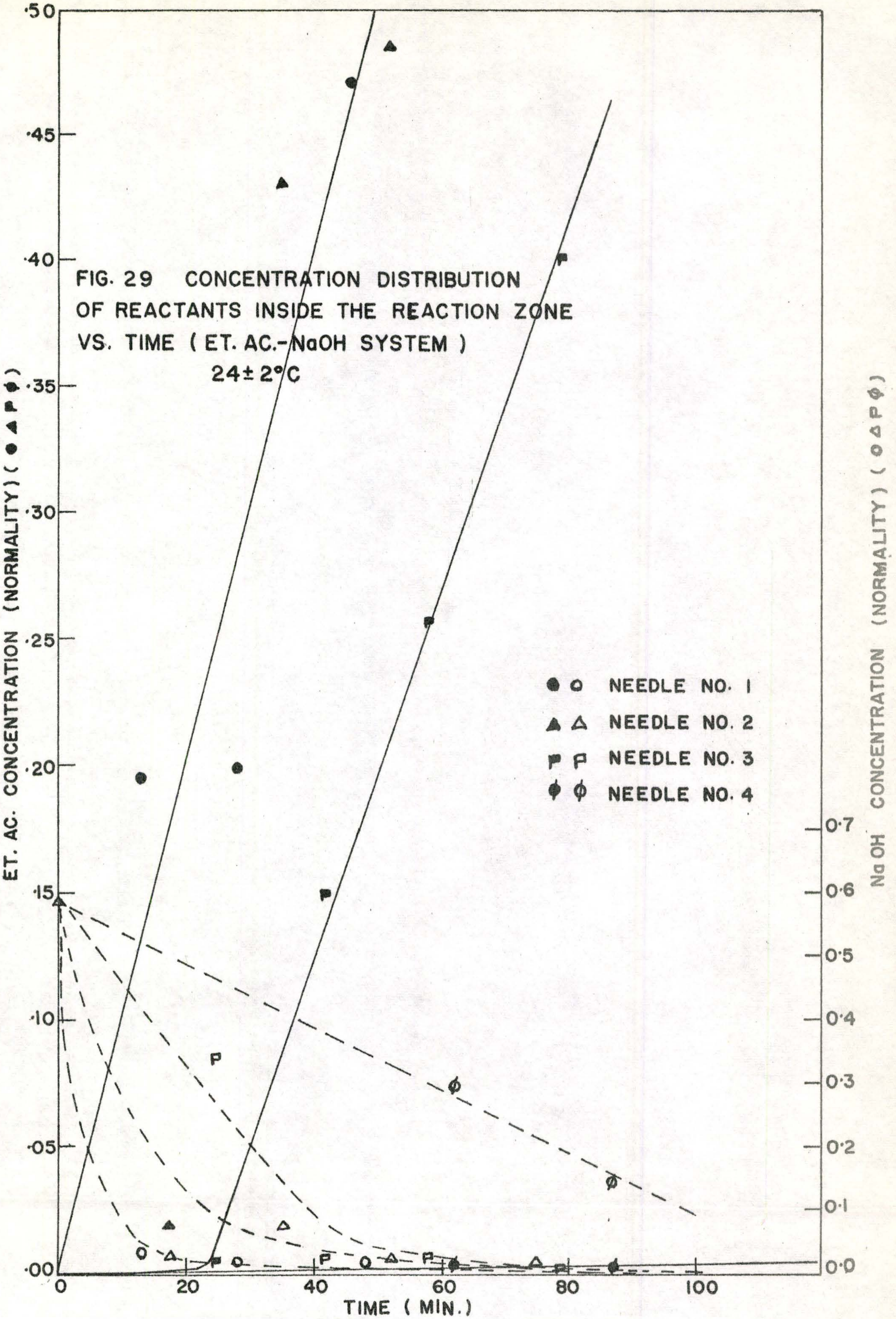


FIG. 29 CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE VS. TIME (ET. AC.-NaOH SYSTEM) 24± 2°C

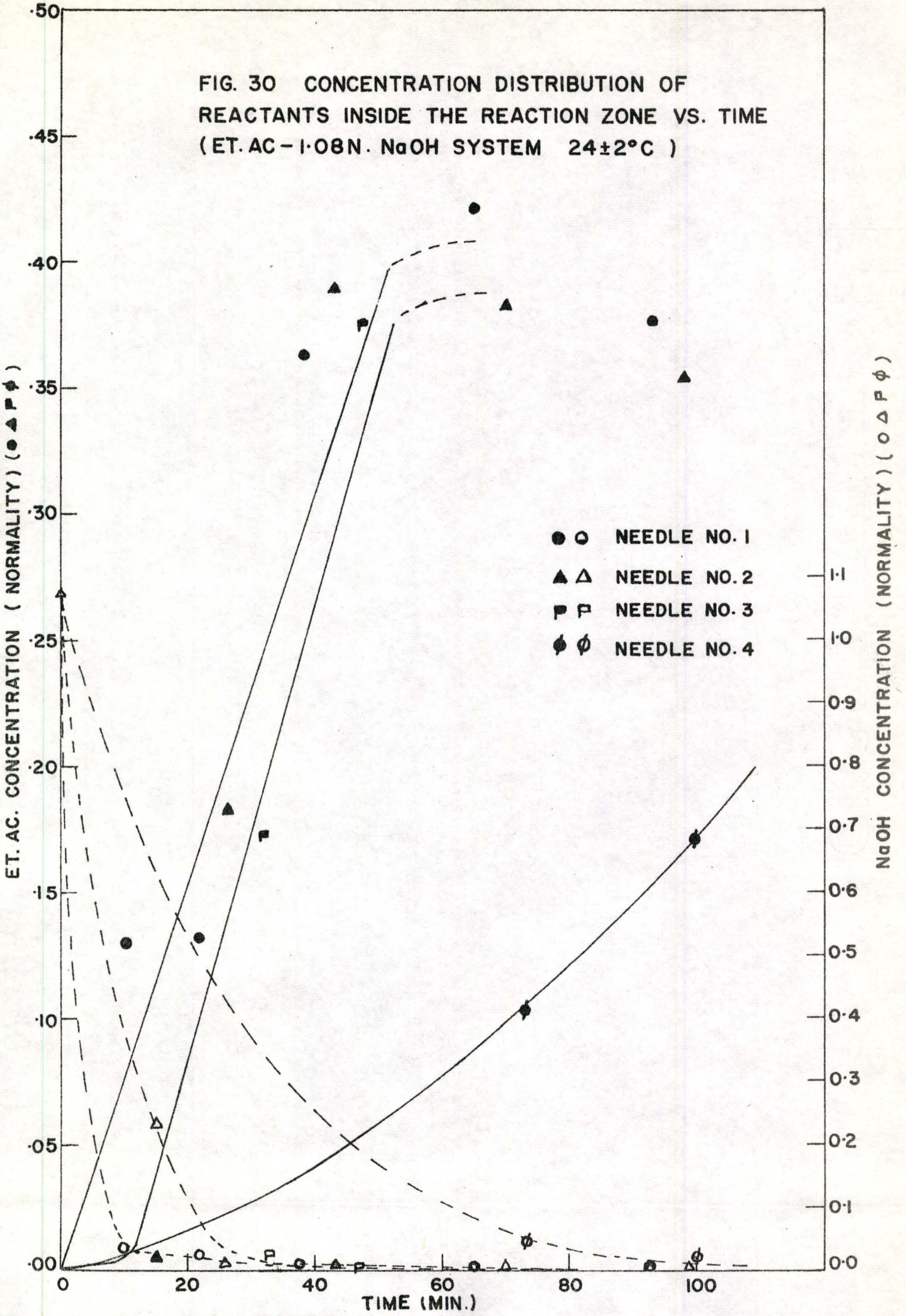
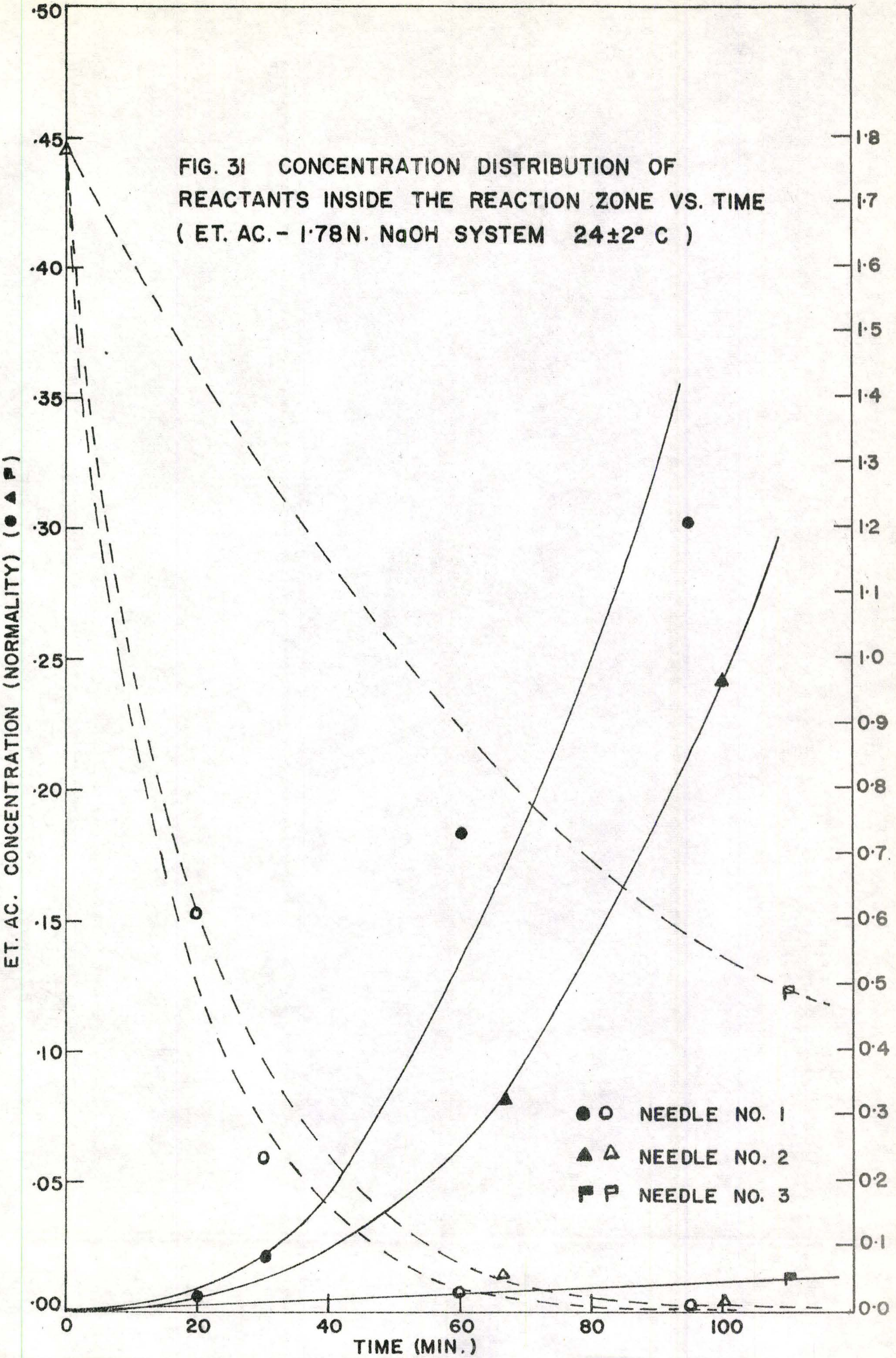


FIG. 30 CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE VS. TIME (ET. AC – 1·08N. NaOH SYSTEM 24±2°C)

FIG. 31 CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE VS. TIME (ET. AC. - 1·78 N. NaOH SYSTEM 24±2° C)



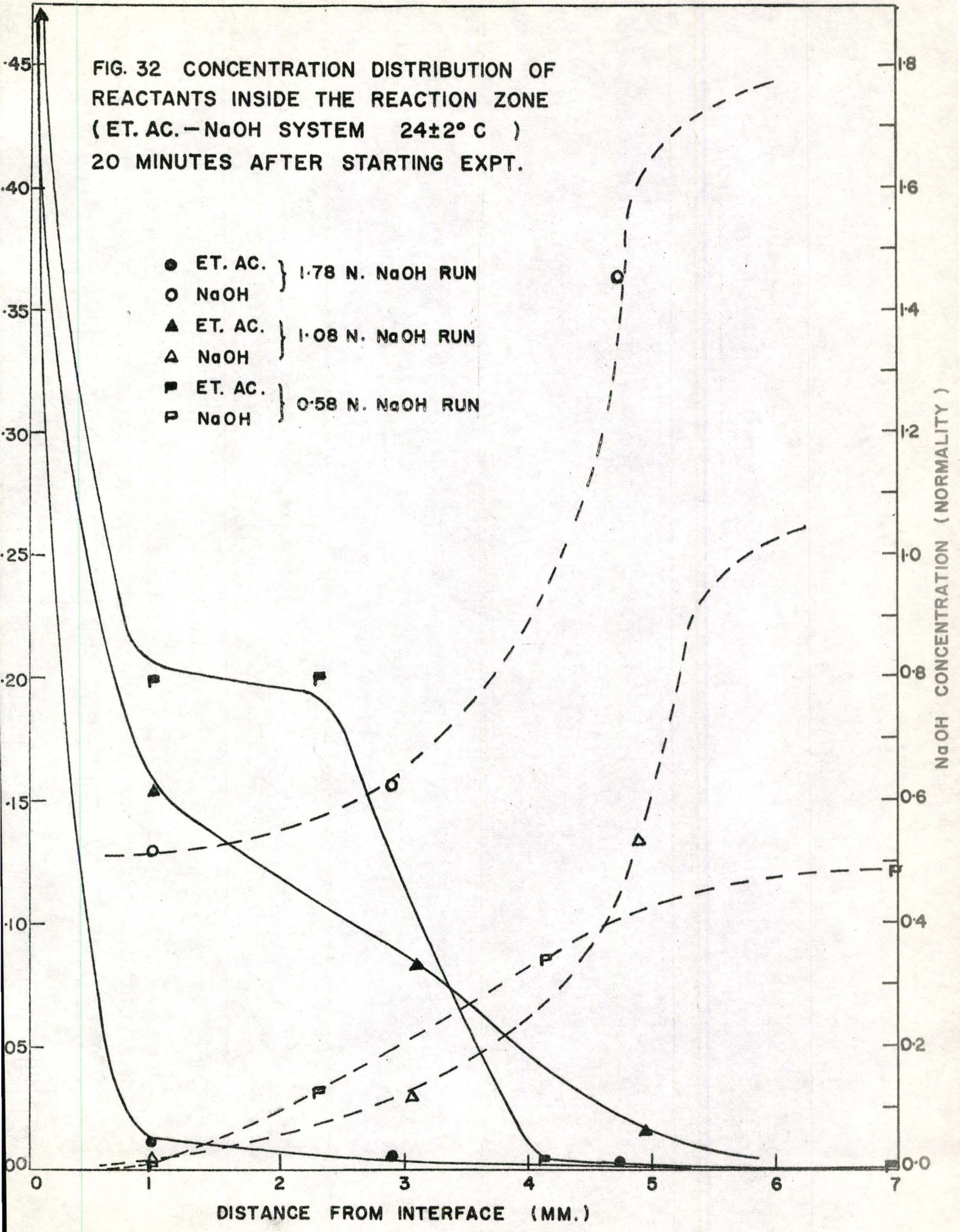


FIG. 32 CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE (ET. AC. — NaOH SYSTEM 24±2° C) 20 MINUTES AFTER STARTING EXPT.

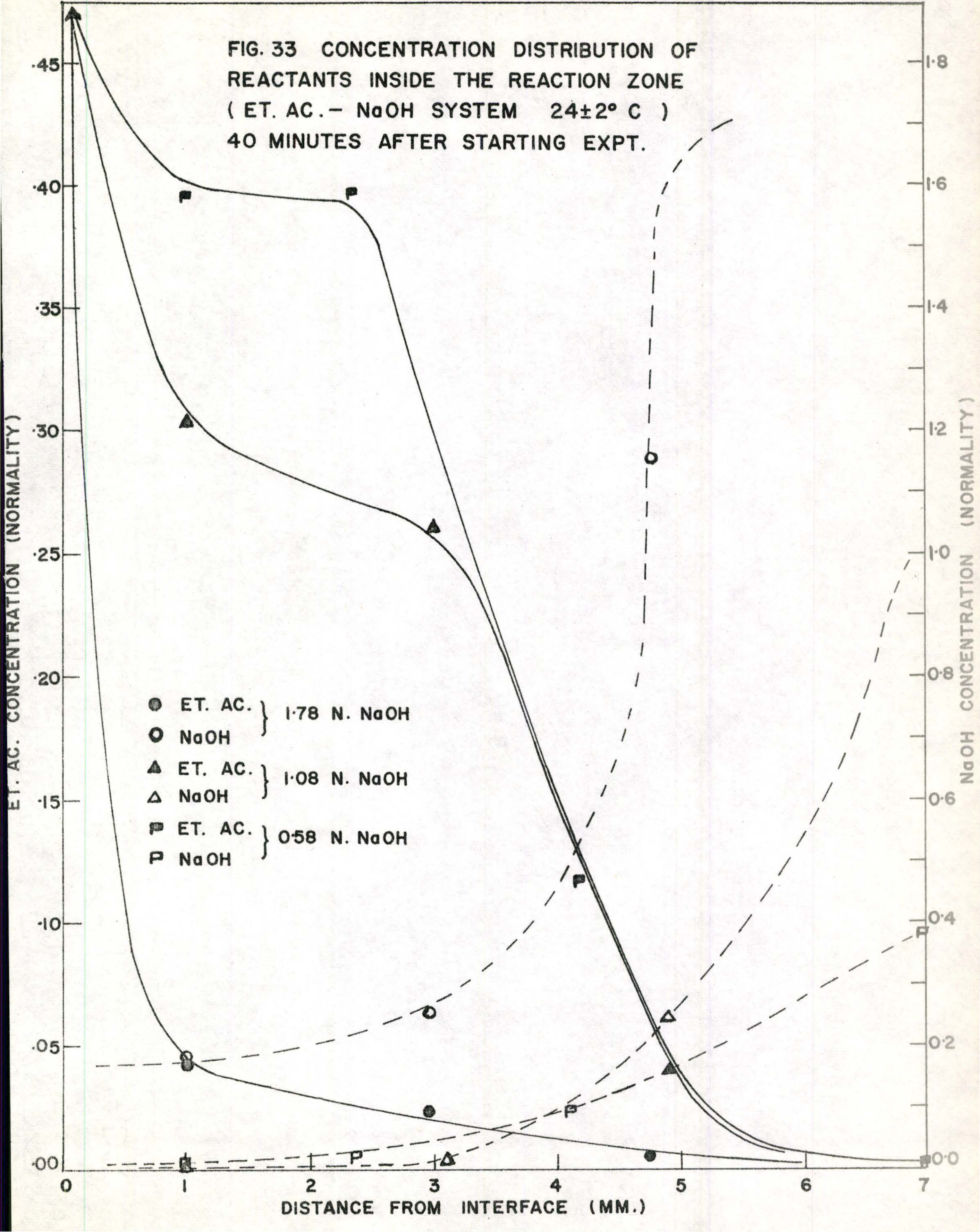
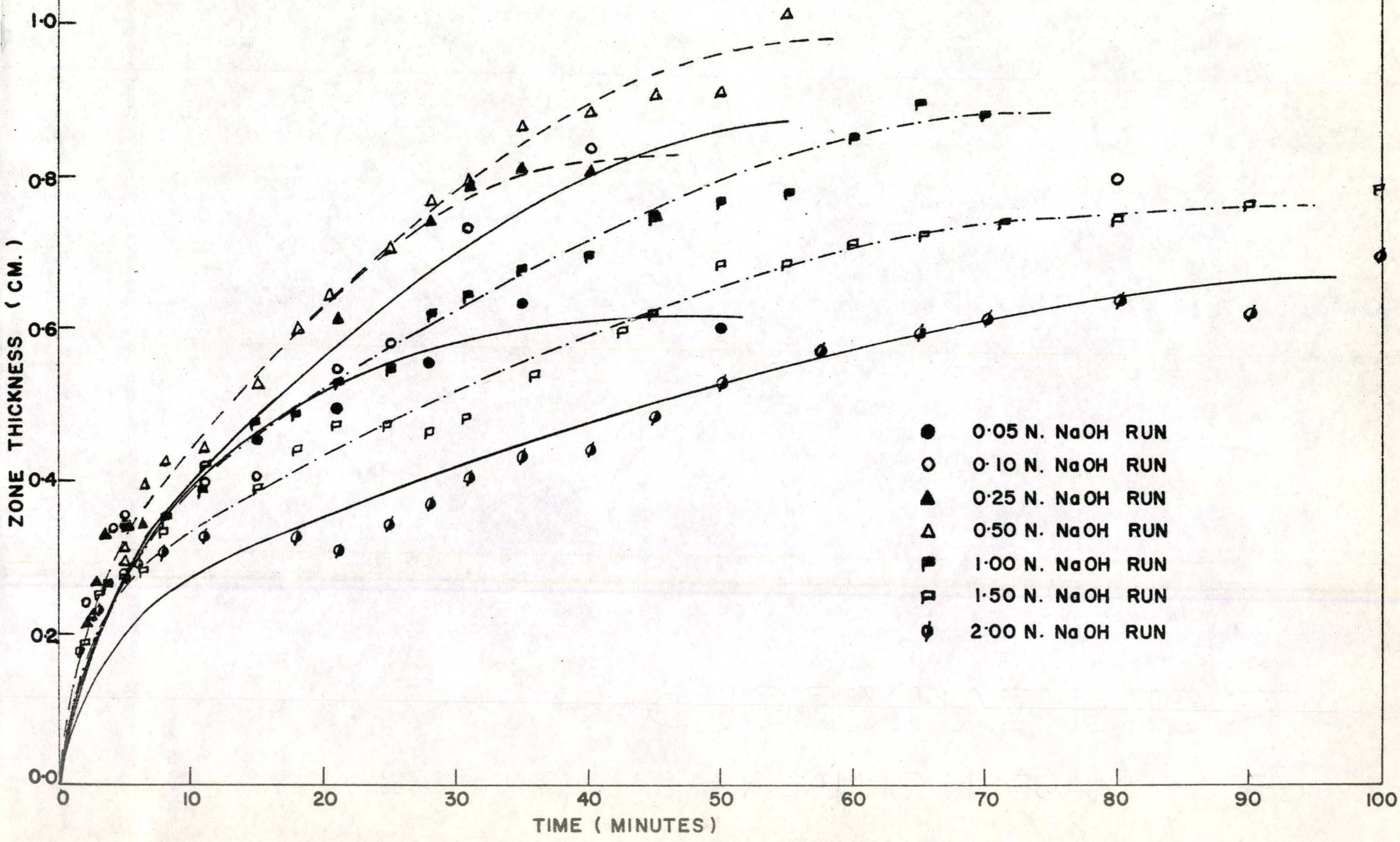


FIG. 33 CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE (ET. AC. – NaOH SYSTEM 24±2° C) 40 MINUTES AFTER STARTING EXPT.

FIG. 34 REACTION ZONE THICKNESS VS. TIME (ET. AC.-NaOH SYSTEM 24±2° C)



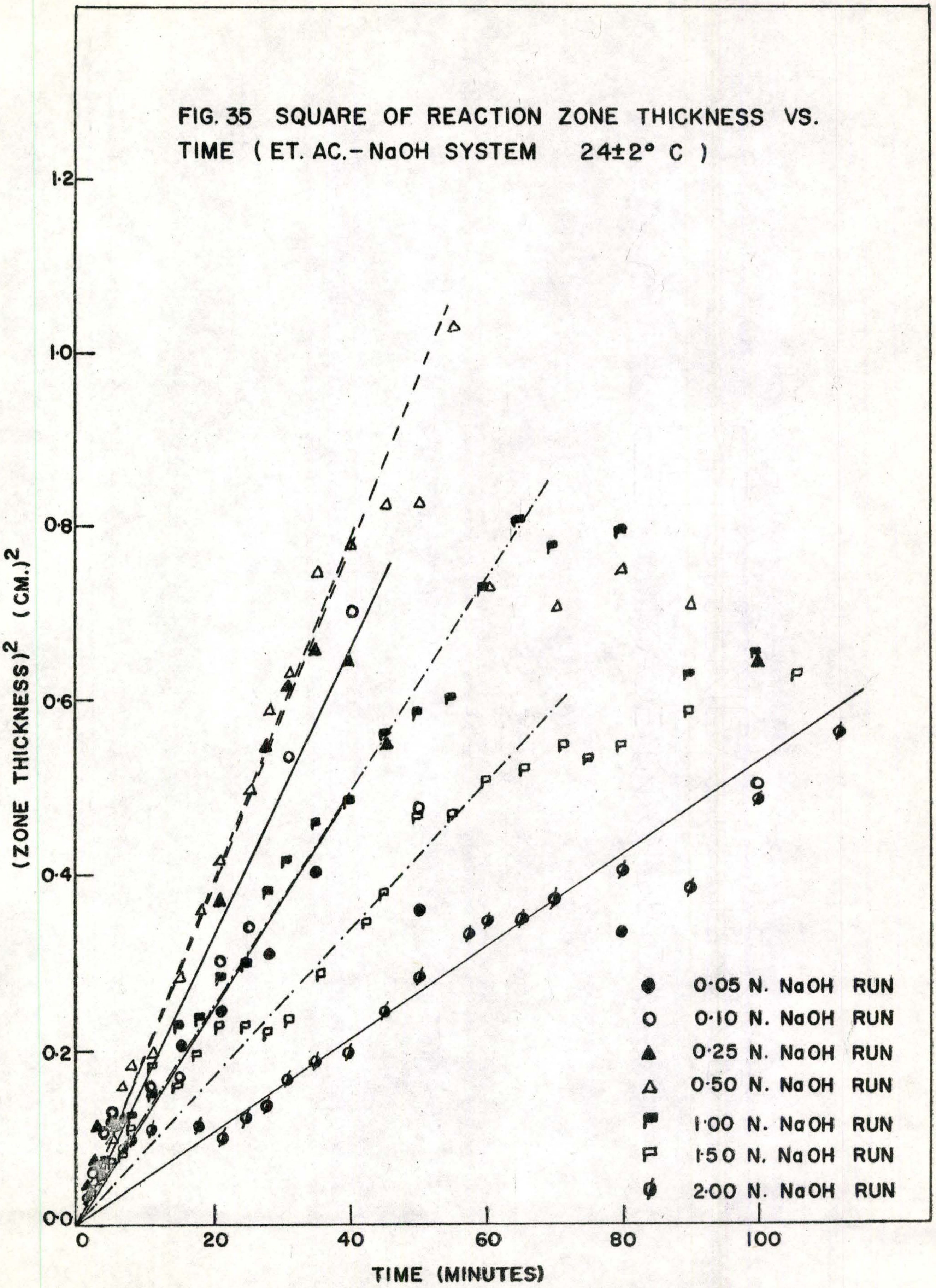


FIG. 35 SQUARE OF REACTION ZONE THICKNESS VS. TIME (ET. AC.- NaOH SYSTEM 24±2° C)

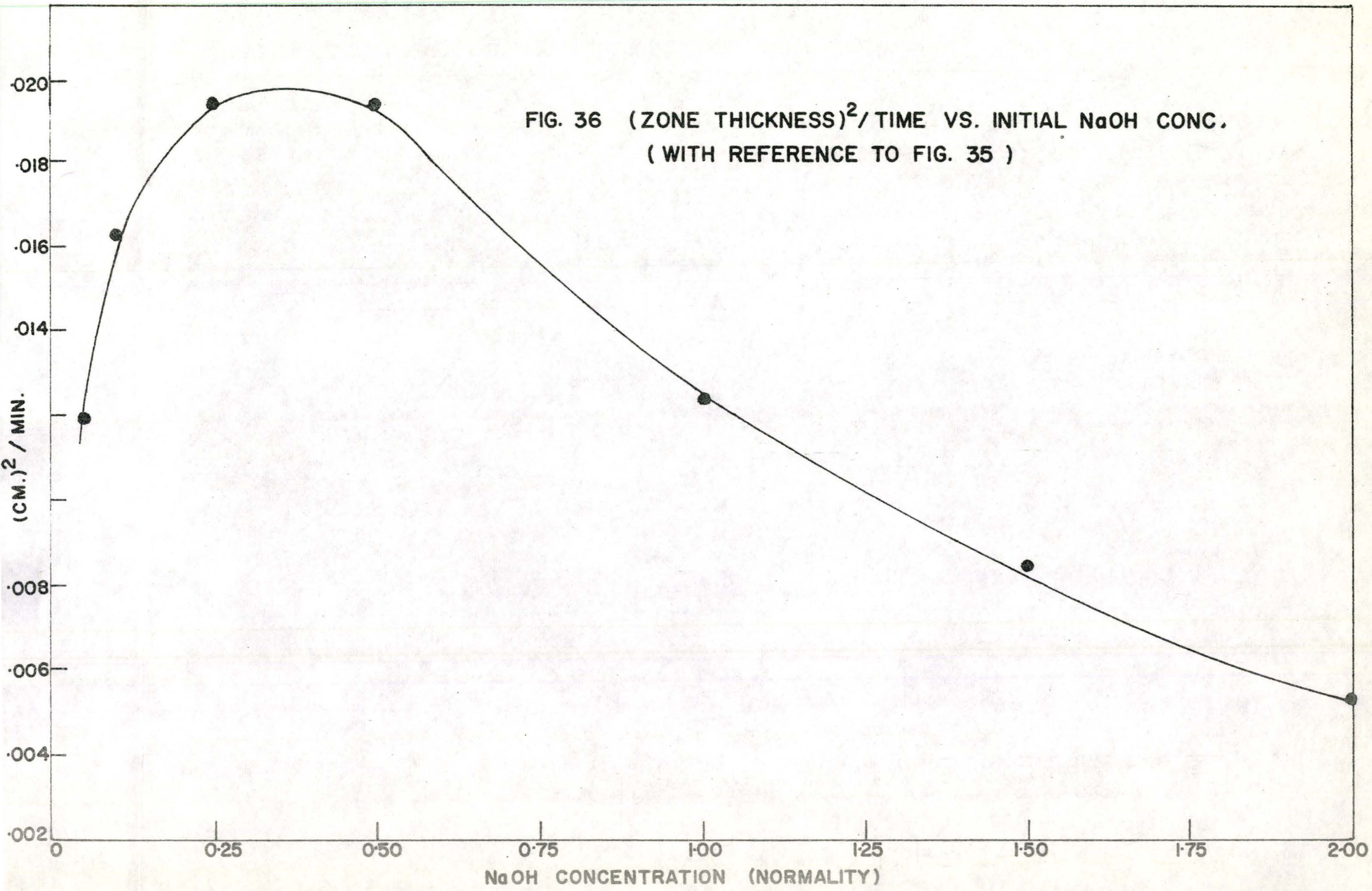
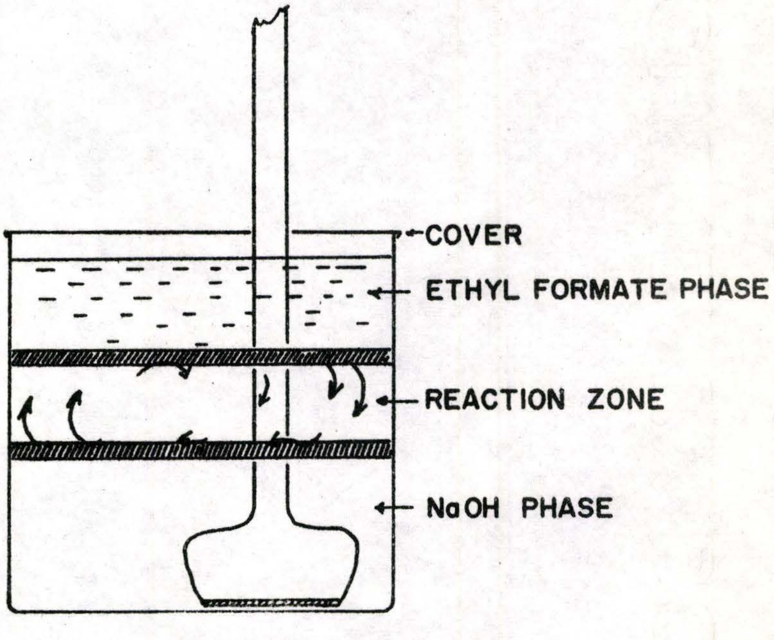


FIG. 36 (ZONE THICKNESS)^2/ TIME VS. INITIAL NaOH CONC.
(WITH REFERENCE TO FIG. 35)

FIG. 37 PICTURE OF THE REACTION ZONE
(ETHYL FORMATE - NaOH SYSTEM)



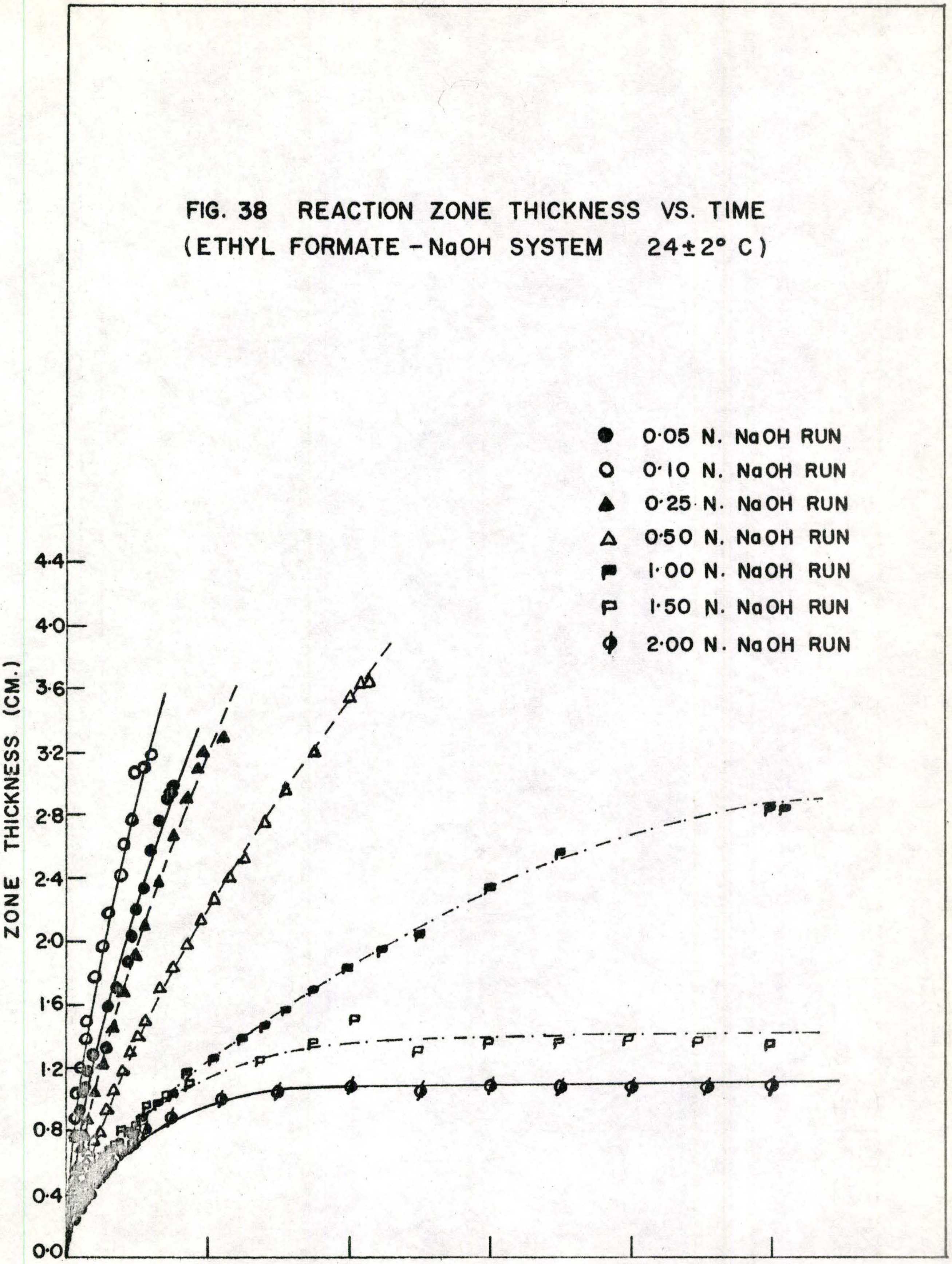


FIG. 38 REACTION ZONE THICKNESS VS. TIME (ETHYL FORMATE - NaOH SYSTEM 24±2° C)

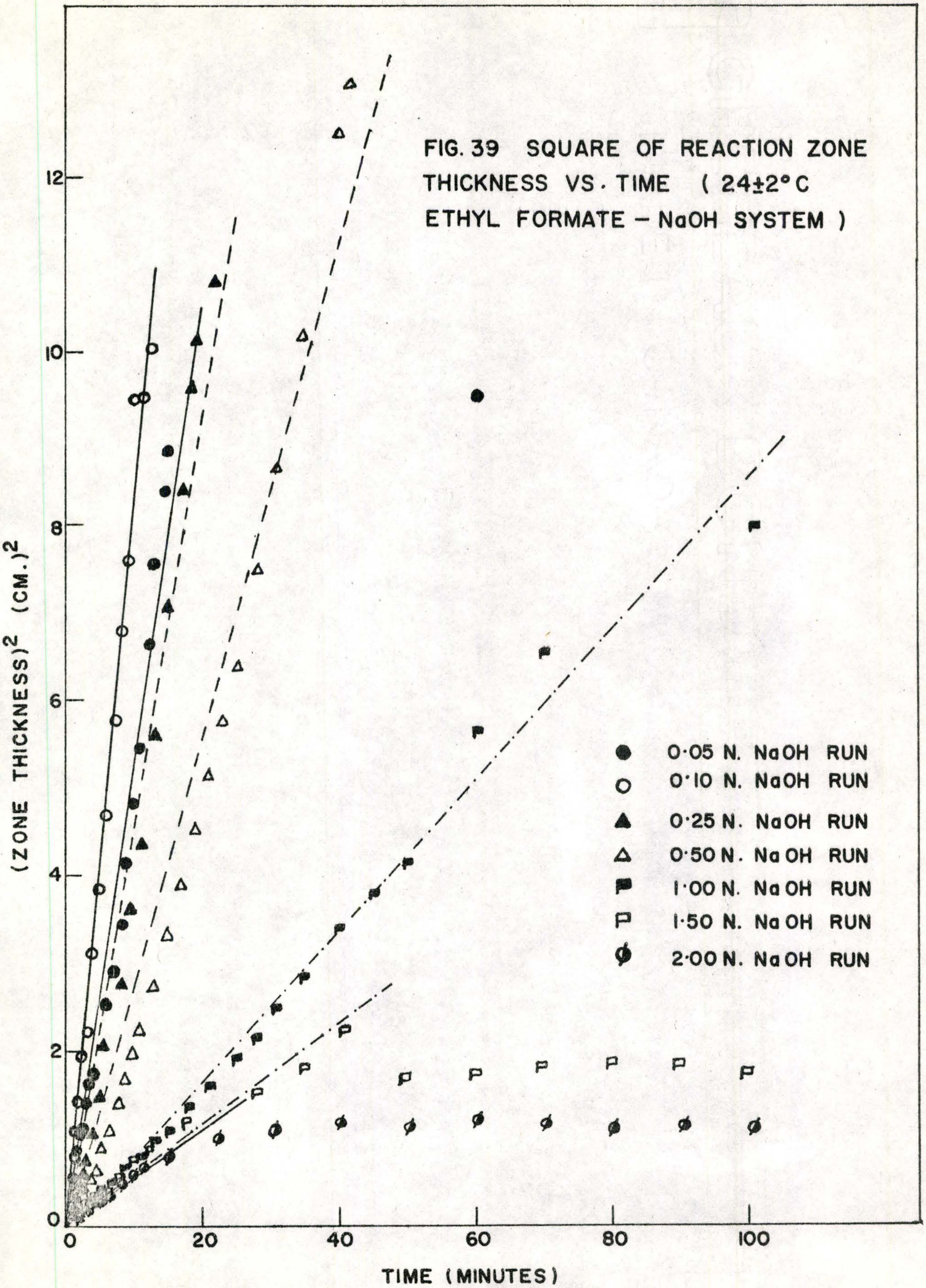


FIG. 39 SQUARE OF REACTION ZONE THICKNESS VS. TIME (24±2°C ETHYL FORMATE – NaOH SYSTEM)

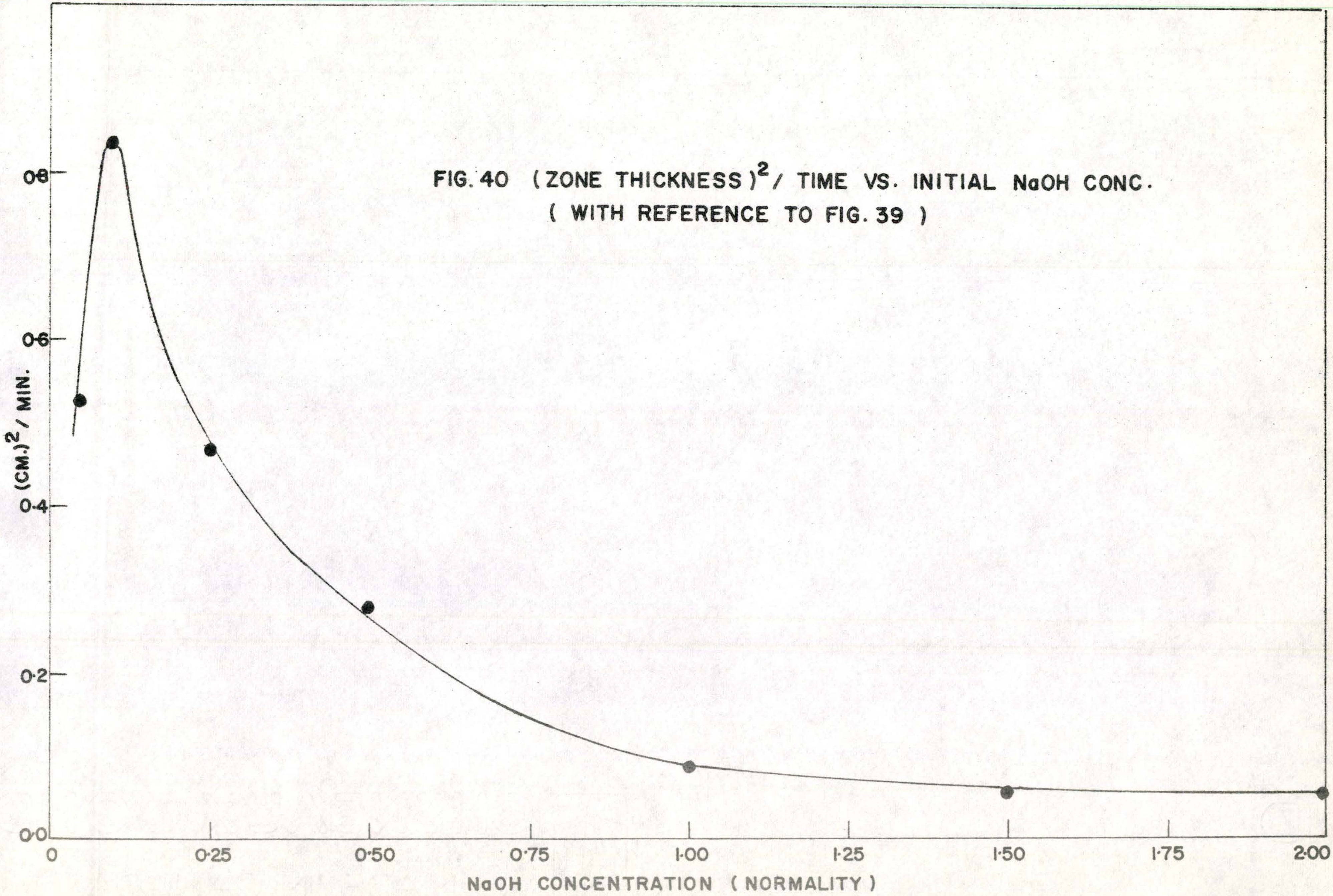


FIG. 40 (ZONE THICKNESS)^2/ TIME VS. INITIAL NaOH CONC.
(WITH REFERENCE TO FIG. 39)

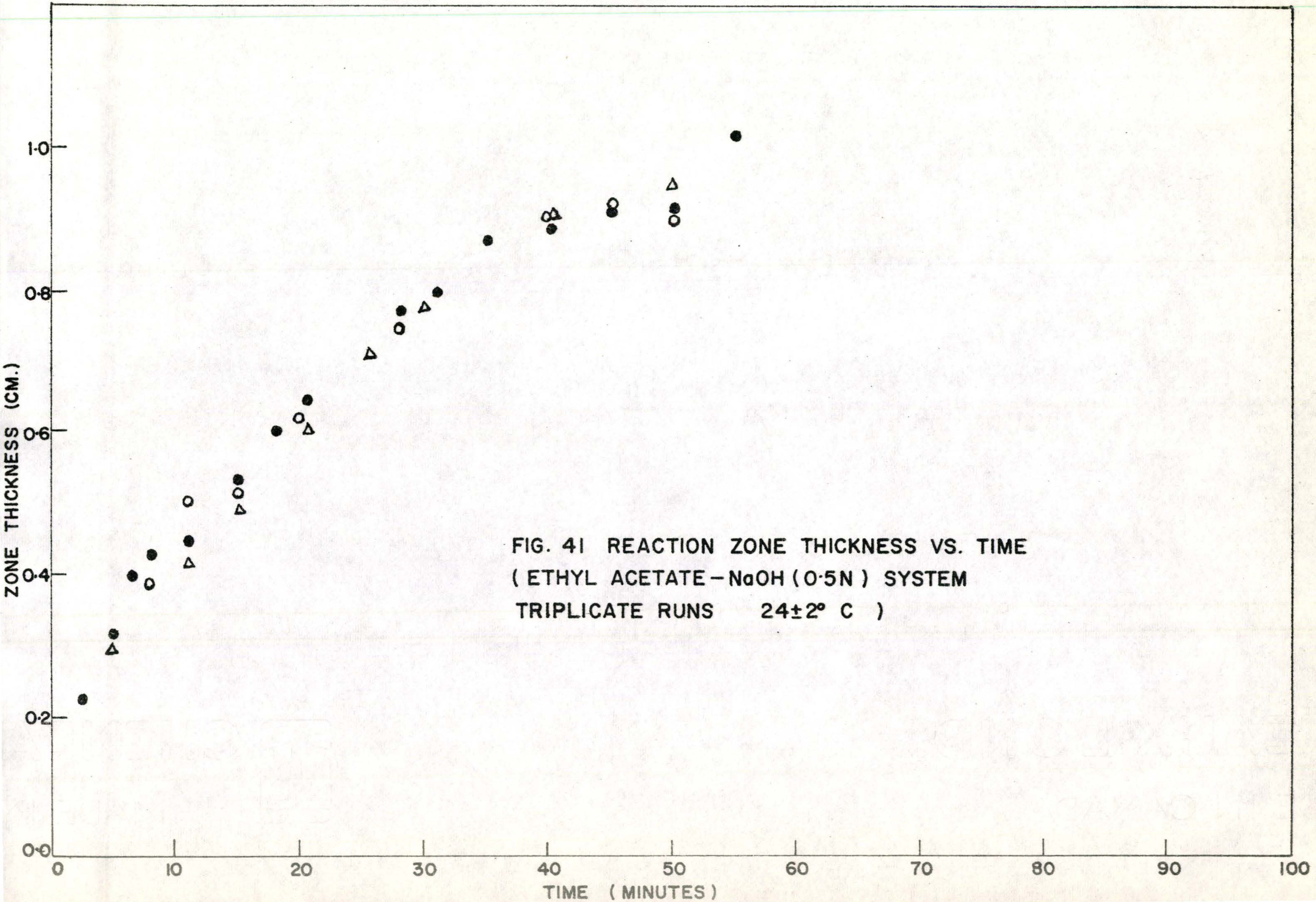


FIG. 41 REACTION ZONE THICKNESS VS. TIME
(ETHYL ACETATE – NaOH (0·5N) SYSTEM
TRIPLICATE RUNS 24±2° C)

DISCUSSION OF RESULTS

A) Schlieren investigation : -

1) Ethyl acetate-aqueous sodium hydroxide system (with reference to figure (28))

The schlieren picture is interpreted in the following way. Ethyl acetate transferring from the upper phase through the interface "AB" reacts with sodium hydroxide in the reaction zone, which can be distinguished visually because of its difference in refractive index from the other phases. Sodium acetate and ethanol formed as the reaction products inside the reaction zone diffuse into the lower phase through the interface "CD". In course of time, more and more of the sodium hydroxide in the zone is reacted while ethyl acetate (which is in excess) from the upper phase keeps on diffusing down. As a result, more and more of the diffused ethyl acetate is unreacted and the zone pushes itself down. The speed of extension depends, of course, on the available sodium hydroxide.

Explanations for the zone formation are numerous but uncertain. Up to the present stage, zone formation is mainly attributed to the occurrence of (a) slow chemical reaction and its accompanying effects such as (b) temperature (c) reaction products (d) interfacial tension.

a) Zone formation due to slow chemical reaction has just been discussed in the preceding paragraph.

b) Due to the heat of reaction, which is calculated to be 13.141 k.cal/mole for ethyl acetate-sodium hydroxide and 15.649 k.cal/mole for ethyl formate-sodium hydroxide, (Refer to Sample Calculations) a temperature gradient may set up in the lower phase. This temperature difference causes the local physical properties of the liquid to change, and this in turn, causes the refractive index of the liquid to alter.

c) The reaction products also cause a change in the refractive index of the portion in which they are present.

d) The reaction zone is also characterized by the presence of turbulence. It has long been suggested that in liquid-liquid systems, the interfacial turbulence commonly observed is caused mainly by the change of interfacial tension as a result of localized concentration changes of components at the interface. These concentration changes may be due to the movement of liquids or the presence of a chemical reaction. The theory of interfacial turbulence has been discussed quite adequately by Scriven and Sternling (127), and is particularly applicable to liquid-liquid systems.

B) Concentration distribution of the reactants inside the reaction zone : -

Based on the data obtained, the following statements are deduced:

a) The reactants inside the reaction zone are not uniformly distributed; instead, concentration gradients are observed as shown in figure (32) and figure (33).

b) With dilute initial sodium hydroxide solution and at the beginning of the run (0 to approximately 40 minutes), concentrations of both reactants inside the zone are rather low as compared to their original concentrations. Outside the zone in both phases, the concentrations of ethyl acetate and sodium hydroxide are constant and equal to their original concentrations. Very sharp concentration gradients are expected across the boundaries on both sides of the zone. At the later part of the experiment, concentration of sodium hydroxide inside the zone remains substantially constant at a low value, while the concentration of ethyl acetate in the zone increases. Also, the concentration gradients across the boundaries become more gentle.

Similar process is also developed in experiments with higher initial sodium hydroxide concentrations except in longer time.

The above statements must be considered as approximate. Afterall, each sample drawn out for analysis is from a certain area rather than from a point. Consequently, the analysis represents the average concentration of a certain area in the zone rather than a particular point. There is also another kind of error involved in the analysis of samples. Between the sampling and the titration, there is a time gap, during which time the solution undergoes further reaction. Although precautions have been taken, such as diluting the sample solutions immediately after sampling and making the sampling procedure standard, no allowance has been made to compensate the error introduced.

C) Measurement of zone propagation : -

1) Ethyl acetate-aqueous sodium hydroxide and ethyl formate-aqueous

sodium hydroxide systems

a) Straight line relationship

From figure (35), it can be seen that in ethyl acetate-sodium hydroxide system, the plot of (zone thickness)^2 versus time for each experiment yields a straight line for some time. The higher the initial sodium hydroxide concentration is, the longer will the straight line relationship hold.

Similar plots are obtained with the ethyl formate-sodium hydroxide system as shown in figure (39)

b) Speed of the zone propagation

From graph (36), it is evident that for ethyl acetate-sodium hydroxide system, the speed of zone propagation increases with initial sodium hydroxide concentration, passes through a maximum at about 0.37 N., and decreases with increasing initial sodium hydroxide concentration.

With the ethyl formate system the speed is much higher (graph 40). Yet, a similar trend is observed as in the ethyl acetate-sodium hydroxide system except that the maximum speed occurs at 0.1 N. sodium hydroxide concentration.

c) Possible factors governing the speed of reaction zone propagation

(i) Turbulence

It is highly probable that the speed of zone propagation depends mainly on the degree of turbulence within the reaction zone. The more turbulent the zone, the faster it extends.

(ii) Physical properties

The zone turbulence is closely related to the physical properties of the solution inside. Concentrated sodium hydroxide solution which has greater density and viscosity can reduce the degree of turbulence and slow down the speed of zone propagation.

(iii) Heat of reaction

The heat effect is of two folds. Because of the temperature increase, the viscosity of the liquid inside the zone becomes less. Convection current of liquid inside the zone also sets up as a result of temperature gradient. All these lead to the enhancement of the turbulence.

On the other hand, the density of the liquid inside the zone is reduced (although may be to a small extent) as a result of temperature increase, and a buoyancy effect is set up: this helps to slow down the speed of zone propagation.

(iv) Salt effect

Salt effect of sodium acetate and sodium hydroxide at a higher sodium hydroxide concentration run is expected to be great inside the reaction zone. Under such a condition, the solubility of the upper phase, thus the transfer rate, is reduced: this helps to slow down the speed of zone propagation.

Referring back to curves (36) and (40), the indication is: At high sodium hydroxide concentration runs, the turbulence generated by chemical reaction is over-balanced by the effects of concentration, buoyancy, physical properties and salt; thus the speed of zone propagation decreases with increasing sodium hydroxide concentration.

d) Zone thickness

It is quite interesting to note that in ethyl acetate-sodium hydroxide system, and also ethyl formate-sodium hydroxide system with high initial sodium hydroxide solution, reaction zone extends itself only to a certain thickness. Probably, with the presence of sodium acetate inside the zone, a quasi-equilibrium is set up so that the transfer of both reactants to the zone is extremely slow. The turbulence is thus reduced, accordingly, to the minimum.

In the case of ethyl formate-sodium hydroxide system with dilute initial sodium hydroxide solution, the reaction rate is so fast that an equilibrium cannot be established.

e) The model

Based on the experimental observations obtained so far, a very simple model is proposed for the ethyl ester-sodium hydroxide system. With reference to figure (42),

let

the concentration of the light phase inside the reaction zone at time "t" = C_2 moles/litre

the concentration of the heavy phase (NaOH) inside the reaction zone at time "t" = C_1 moles/litre

the saturation concentration of the light phase = C_{2i} moles/litre

the original concentration of the heavy phase = C_{10} moles/litre

the distance of the reaction zone-NaOH interface from the ethyl ester-reaction zone interface (zone thickness) at time "t"=x cm.

The following were observed;

1. Rather abrupt concentration gradients occur across the interfaces on both sides of the reaction zone.

2. Concentrations of both reactants inside the zone at time "t" are low

and may be considered constant without too large a sacrifice in accuracy. The mean values of C_1 and C_2 are approximately equal and inversely proportional to the zone thickness.

$$\therefore \quad C_2 \propto C_{2i}/x \quad ; \quad C_1 \propto C_{10}/x$$

and

$$C_2 = \frac{D_2'C_{2i}}{x} \quad ; \quad C_1 = \frac{D_1'C_{10}}{x}$$

where

D_2' and D_1' are proportionality constants which include the average eddy diffusivities of the upper phase (C_2) and the lower phase (C_1) respectively.

At the lower edge of the reaction zone, the rate of removal of the reactant(sodium hydroxide) is, for unit area $(C_{10} - C_1) \frac{dx}{dt}$

By overall material balance on the reaction zone and assuming the lower phase removed is being used up by the reaction,

$$(C_{10} - C_1) \frac{dx}{dt} = kC_1C_2x = k \frac{D_2'C_{2i}}{x} \frac{D_1'C_{10}}{x} x \qquad \ldots. (37)$$

or, according to the second observation,

$$(C_{10} - C_1) \frac{dx}{dt} = k \frac{D_1'^2 C_{10}^2}{x} \qquad \ldots. (38)$$

where k = reaction constant; t = time

Integrating equation (38) between time "0" and "t"

$$x^2 = \frac{kD_1'^2 C_{10}^2}{C_{10} - C_1} \; t$$

Since C_1 is small, $(C_{10} - C_1) = C_{10}$

$$\therefore \quad x^2 = C_{10} k D_1'^2 t$$

The model works only if the experimental conditions are the same as the two observations. This is the case at the beginning portion of each experiment.

At the later part of each experiment, the turbulence inside the zone gradually dies out and concentrations of reactants increase. Under such conditions, $C_1 \neq C_2$

equation (37) is used

$$(C_{10} - C_1) \frac{dx}{dt} = k \frac{D_2'C_{2i} \quad D_1'C_{10}}{x}$$

again, if C_1 is small as compared to C_{10} ,

$$\frac{dx}{dt} = k \frac{D_2'C_{2i}D_1'}{x}$$

on integration,

$$x^2 = kD_2'D_1'C_{2i}t$$

No doubt the picture is much more complicated, with the interfacial tension and heat of reaction effects playing a role.

f) Application of the model to experimental results

(i) From figures (35) and (39), it can be seen that for each experiment, a straight line is obtained for some time. The slope of the line is equal to "$kC_{10}D_1'^2$" of that particular experiment. Different slopes indicate different values of "$C_{10}D_1'^2$" between experiments since "k" is a constant.

(ii) From figures (36) and (40), it is observed that maximum values of the curves lie at approximately 0.37 and 0.1 N. respectively: this indicates that the maximum value of eddy diffusivity of sodium hydroxide for ethyl acetate-sodium hydroxide system and ethyl formate-sodium hydroxide system lies in 0.37 N. sodium hydroxide and 0.1 N. sodium hydroxide respectively.

The above statement is in agreement with the visual observation, particularly with the ethyl formate-sodium hydroxide system.

2) Ethyl acetate-water; and, ethyl formate-water systems

The Moiré pattern for ethyl acetate-water system is quite normal. The curved Moire lines indicate the presence of concentration gradient at the interface. From the degree of curvature of the lines, a concentration gradient can be calculated. A complete theory on the Moiré pattern was given by Lord Raleigh (76) in 1874. His theory was discussed by Guild (41). Recently, the method was applied by Sato et al who developed a technique which could measure the concentration gradient directly out of the geometry of the Moiré lines (108).

The phenomenon observed in ethyl formate diffusion is rather unusual. At first, it is thought that the eruptive transfer is a result of the density flow. However, a check on the literature shows that the density of ethyl formate at 25°C is 0.917, and the explanation is hardly possible.

On the other hand, it must be realized that ethyl formate hydrolizes in water at a fairly large rate. As an example, ethyl formate is shaken well with water and form two phases. The mixture is let stand for two days, and the ethyl formate is found to be hydrolyzed completely. From this point of view, the eruptive transfer phenomenon may be due to hydrolysis reaction.

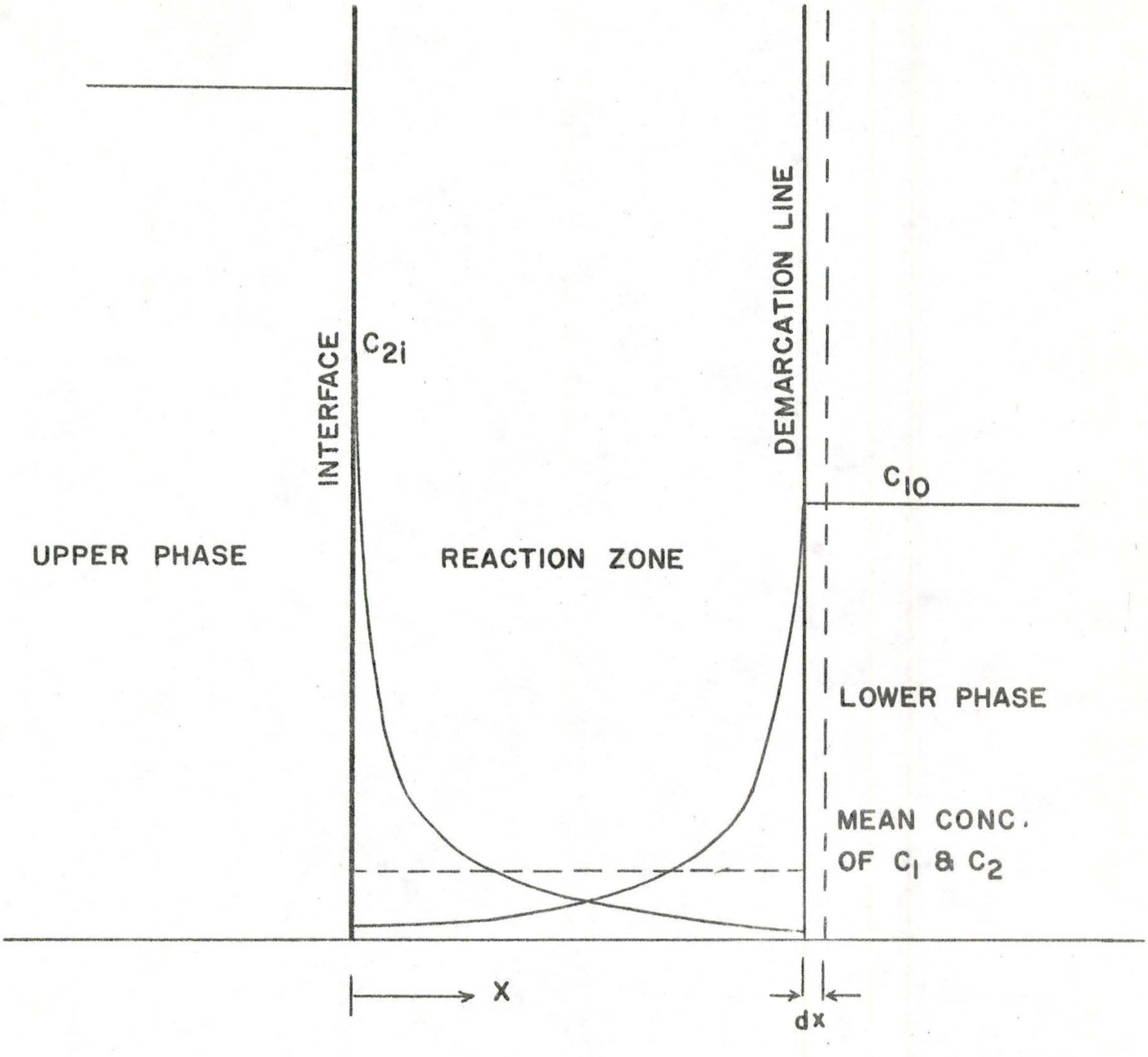


FIG. 42 CONCENTRATION PROFILES IN THE REACTION ZONE (THE PROPOSED MODEL)

CONCLUSIONS

1) When ethyl ester is transferring into a limited amount of aqueous sodium hydroxide solution —— a case of unsteady state mass transfer accompanied by a slow chemical reaction, a zone of reaction is distinctly formed; inside which, turbulent liquid motion prevails. The reaction zone extends itself in course of time. Studies of this phenomenon apparently have not been reported in the literature.

2) The speed of zone propagation depends on the eddy diffusivity of the lower phase (sodium hydroxide) which in turn depends on the system and on the initial sodium hydroxide concentration used for the experiment. The speed of zone extension is higher with ethyl formate-sodium hydroxide system than with ethyl acetate-sodium hydroxide system. Within the system, the speed increases with initial sodium hydroxide concentration used, then passes through a maximum, and decreases with increasing initial sodium hydroxide concentration.

3) Concentrations of both reactants inside the zone are low as compared to their initial concentrations. Outside the reaction zone in the lower phase, the concentration of sodium hydroxide is constant and equal to the original concentration.

4) A simplified model is proposed to describe the zone propagation and predict qualitatively the eddy diffusivity of the heavy phase.

5) Eruptive transfer was observed in physical diffusion of ethyl formate into water.

RECOMMENDATIONS

The recommendations can roughly be grouped into two sections according to their nature: (a) to obtain better experimental results (b) to obtain more information about the phenomenon.

A) Recommendations for obtaining better results : -

1) Measurement of concentration distribution of reactants inside the reaction zone

a) Micro-analysis

Some of the disadvantages in the titration method adopted for the measurement lie in sampling. It is difficult to obtain a reasonable size sample (2 ml.) representing a very localized area. Moreover, sampling loss, in this case, may introduce error. Both of the disadvantages can be eliminated if micro-analysis techniques are developed.

It would even be better if delicate instruments were devised and inserted into the reaction zone to detect the concentration of the reactants without sampling. One type of instrument suggested for measuring the sodium hydroxide concentration is an accurate pH meter, capable of readings up to 0.01 pH and a very fine electrode (for example, Beckman Special model electrode, which has a sensitive tip of ½ mm. both in length and in diameter).

With the aid of the refined method of analysis, (such as the micro-analysis or the pH meter) experiments should be planned with zone propagation and reactant concentrations measured at the same time.

2) Zone measurement

a) Design of diffusion cell

At the present stage, the apparatus for measuring the speed of zone propagation is rather crude. The use of sintered glass disc did reduce mixing, induced when contacting the two phases, to a considerable amount; but further improvement would be desirable. Furthermore, when applying the method for filling the cell in the lower phase, there is a time lag of about 1 minute. The apparatus is therefore not suitable for zone measurement, particularly with experimental systems having high reaction constants and fast zone propagation speeds.

A new diffusion cell with improved design should be constructed. In fact, a modified Claesson cell (8) has been devised. A brief description of the cell is given in the following, with reference to figure (43). It has the shape and dimensions as shown. The cell consists mainly of two blocks of stainless steel, one (block B), being smaller, is enclosed by the other. The smaller block can also slide smoothly onto the other. Both the front and the back of the larger steel block (A) are mounted with optically flat glass plates. When the cell is in use, one half of the cell proper (E_2) in block (A) is filled with the heavy phase. Then the other half (E_1) in block (B) is filled with the light phase through the opening (C). Block (B) is then pushed to the right by the lever (D) until the half cell proper (E_1) is exactly above the other half (E_2); and the normal diffusion run begins.

b) Cleaning of the apparatus

The reproducibility of experimental results depends, to a large extent, on the cleanliness of the apparatus. Experimental evidence indicates that measurement of zone propagation in apparatus not carefully cleaned gives the speed about 50% lower than those measured in clean apparatus.

A standard procedure should, therefore, be developed for the cleaning. One method suggested is that the apparatus should be washed in soap solution for general cleaning purposes, then, in warm sodium hydroxide—ethanol solution to remove any grease and silicone derivatives, and finally in concentrated chromic acid to destroy any organic impurities. In between the treatment of cleaning solutions, the apparatus should be rinsed with a large amount of distilled water.

c) Temperature control

The reproducibility of experimental results is also affected by the precision of the temperature control. Within each experiment, a temperature fluctuation may cause a variation of reaction rate, which in turn, may cause a variation of degree of zone turbulence.

Thus the cell should be thermostated at a desired temperature level throughout each experimental run.

d) Flattening of the interface

It is evident that the precision of the measurement of zone propagation is largely reduced due to the presence of meniscuses at the "demarcation line" and at the ethyl acetate reaction zone interface. These meniscuses appear as thick dark lines on the photographs and render the zone thickness measurement to be difficult.

Further efforts are worthwhile to be spent on eliminating the meniscuses by coating the cell walls with some compounds other than silicone derivatives.

"Fluoro Glide" was found from preliminary investigation to be opaque if too thick a layer was sprayed on. Its application to the cell was required after each experimental run. Despite the aforementioned disadvantages, if a skillful spraying technique together with a suitable binder to the teflon suspension can be developed, it is not impossible to obtain a good coating of "Fluoro Glide" which does not dissolve in the liquids under test, and is capable of reducing the thickness of the meniscuses; and, at the same time, is transparent enough to enable the tracing of liquid movement inside the cell optically.

In addition, another chemical compound, "Vinylidene Fluoride" (supplied by Research Lab., Canadian Westinghouse Co., Hamilton) is recommended for the coating. This compound is colourless and gives a transparent coating which may be suitable for the liquid systems used.

e) Measurement of zone propagation by the colourimetric method

Besides the schlieren and Moiré pattern techniques currently employed to trace the reaction zone propagation in this work, some other types of experiment which can be performed more easily to serve the same purpose should also be tried out.

Measurement of zone propagation making use of the pH change of the liquid systems as a result of reaction should be carried out. The pH of sodium hydroxide solution is about 12.4; and the pH of the liquid inside the reaction zone is around 10.1. If an indicator, which will change its colour between 10.1 and 12.4, is added to the lower phase (sodium hydroxide) prior to the beginning of the experimental run, the zone propagation may easily be traced by observing the colour change.

B) Recommendations for obtaining further information about the phenomenon : -

1) Extension of the present experimental work

In addition to the measurement of ethyl acetate, sodium hydroxide concentrations inside the reaction zone, the distribution of sodium acetate and ethanol formed as reaction products should be probed so that the effect of salt and alcohol to zone propagation can be more fully understood. Also, the distribution of reaction products reflects the areas where most of the reaction takes place.

In order to learn more about the reaction zone, still a great number of experiments should be done; such as repeating the experiments on ethyl acetate-sodium hydroxide, ethyl formate-sodium hydroxide systems at higher temperature levels. Experiments should also be performed with esters of higher members of the homologous series (for example, ethyl propionate, ethyl butyrate and methyl propionate) and also with other kinds of alkaline solutions (for example, potassium hydroxide). All these experiments will help to reveal the importance of reaction rate as well as heat of reaction to the reaction zone turbulence.

2) Temperature measurement of liquid systems

Previous temperature measurements of ethyl acetate-sodium hydroxide systems (refer to Preliminary Investigation, Appendix XIII) indicate temperature differences ranging from ½ to 1°C were found within the reaction zone. These numbers were rather doubtful since the measurements were carried out at room temperature, and the liquid systems were not temperature controlled.

More precise temperature measurements should be made in liquid systems under investigation. Very fine chromel-alumel thermocouples with O.D of 0.34 mm. are available for the purpose (Thermocoax,supplied by the Philips Electronics Co.). It is expected that very localized temperature measurements within and outside the reaction zone can be obtained. These temperature data may help to realize the effect of temperature on zone turbulence.

3) Measurement of zone turbulence

The proposed model on zone propagation (refer to "Discussion of Results") predicts from the available experimental data that ethyl acetate-sodium hydroxide and ethyl formate-sodium hydroxide systems have maximum eddy diffusivities at initial sodium hydroxide concentrations of 0.37 N. and 0.1 N. respectively. This prediction, although has been verified qualitatively by optical observation, may also be tested experimentally. A hot-wire anemometer is available for the purpose.

4) Interfacial tension measurement

In order to disclose the importance of liquid-liquid interfacial tension to the zone turbulence, an experiment should be performed with ethyl acetate vapor-sodium hydroxide solution system. If the Scriven and Sternling Theory (127) is correct, zone turbulence should be partly or entirely eliminated in the presence of a gas-liquid interface.

5) Mathematical manipulation

It is quite obvious that the model proposed for zone propagation is over-simplified. If a more refined model is to be set up, the following effects, at least, should be included: (a) turbulence caused by interfacial tension change; (b) turbulence caused by reaction inside the zone; (c) free convection of liquids inside the zone as a result of temperature difference,

which, in turn, is caused by the heat of reaction; (d) change of physical properties of liquids such as density and viscosity inside the zone as a result of temperature as well as concentration changes; (e) concentration of both reactants inside the reaction zone are small but substantial and a concentration gradient exists just below the "demarcation line"; (f) the effect of reaction products, particularly the salt effect.
The mathematics may become too difficult to handle if all the effects mentioned are taken into account. It is expected that some of the effects can be combined together, while others may be negligible. Nevertheless, the appropriate selection can only be made possible from the results of many experiments.

Another mathematical approach, besides setting up a model, is by dimensional analysis.

On the other hand, there is, of course, the differential equation describing the concentration gradients of components across the interface by the use of mass and heat balance.

6) Simulation of the reaction zone

One of the most common ways to find out the dominating factors contributing to the zone propagation is to study and distinguish all the possible factors. Separate experiments should be conducted as to simulate the experimental situation governed by individual factors. To make the statement clear, two examples are given in the following:

a) It is suspected that the zone turbulence, to some extent, is caused by free convection and change of physical properties of liquids as a result of temperature difference which is roughly determined to be in the range of ½ to 1°C. This speculation can be tested by performing an experiment with the system of ethyl acetate-sodium acetate solution. Heating elements are immersed into the sodium acetate solution at a distance from the interface equivalent to the ordinary zone thickness (½ to 1 cm.). The liquid around the elements is heated to about ½ to 1°C higher than that at the interface. Turbulence thus induced can be studied under the schlieren apparatus or by the hot-wire anemometer.

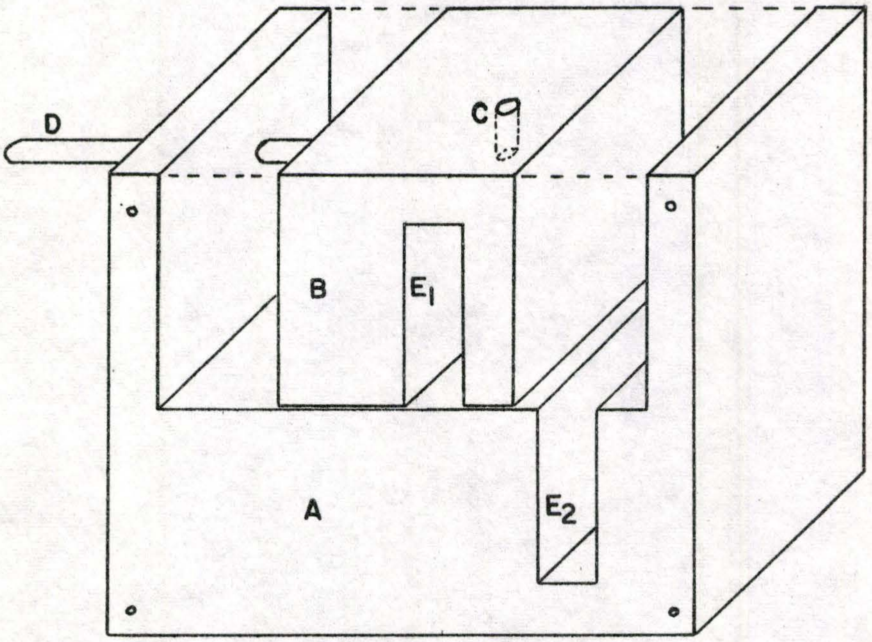
b) It is also speculated that the presence of sodium acetate inside the reaction zone is one of the main causes for the retardation of zone propagation at high sodium hydroxide concentration runs. In order to clear this point, an experiment should be performed with the ethyl acetate-sodium hydroxide system at dilute initial sodium hydroxide concentration. During the run, a known amount of sodium acetate is added to the reaction zone. The speed of zone propagation thus measured is compared with that obtained from the run at same initial sodium hydroxide concentration but without the injection of sodium acetate.

7) Miscellaneous investigations

Quite a number of interesting phenomena were observed during the diffusion experimental runs. Some of them may be worthwhile to pursue, for example, the eruptive transfer of ethyl formate into water. Also in the reaction runs, the curved section of Moiré lines observed just below the "demarcation line" may be made use of to calculate the concentration gradient.

Moreover, in the ethyl acetate-sodium hydroxide system, the Moiré lines were found curving to the left in experiments performed with initial sodium hydroxide concentration up to 1 N. In reaction runs with initial sodium hydroxide concentration higher than 1 N., the Moiré lines curved to the right (examples are shown in plates Numbers 1, 2, 3, 4 and 5).

FIG. 43 SCHEMATIC DIAGRAM OF THE PROPOSED DIFFUSION CELL



APPENDIX XII

Detailed description of the apparatus used for unsteady state diffusion experiments:

A) Apparatus for schlieren investigation: -

1) The light source

The light source was a mercury super pressure lamp for direct current (HBO 100 W/2) supplied by Osram Com., Germany. The lamp was housed in the centre of a cylindrical metal container, 18 cm. in diameter and 24 cm. high, with a hole of 1.2 cm. diameter on the wall to let the light out.

2) The optical unit

The optical unit contained two 80 mm. convex lenses which served as the schlieren and the collimating lens respectively. Both lenses were mounted and were free to travel along the optical axis of the system.

3) The test cell

The test cell was an ordinary optical cell (4.8 cm. long, 4.9 cm. wide and 5.5 cm. high) supplied by Fisher Co. (cat. no. 4-732). It was made of glass plates fused together with an acid-resistant glass frit. The sides and bottom of the cell were ground; the front and back were clear and plane.

4) The knife edge

The knife edge was made of two metal pieces which were separated by a gap. One of the pieces was sharpened at one end like a single-edged razor blade. The slit could be adjusted by micrometer arrangement to cut off the desired amount of light.

5) The camera

Interfacial activity observed in each experiment was photographed in motion picture by a 16 mm. Bolex Paillard camera.

B) Apparatus for measuring the concentration distribution of components inside the reaction zone : -

1) The cell

In order to reduce the error arising from sampling loss, a big cell was used. It was made out of the lower half of a 4-litre pyrex beaker. The cell was 12 cm. high and 15.5 cm. in diameter.

2) The phase contactor

The phase contactor was made out of the design and dimensions as shown in figure (26). The reservoir had a capacity of 1½ litres. A pipette filler at the top was used to control the flowrate of the lower phase liquid through the sintered glass disc (pyrex coarse grade).

3) Hypodermic needles

Four long needles were made out of stainless steel tube (type 304) with outside diameter of 28/1000 inch. One end of each tube was fitted into a hypodermic needle (No. 18), so that liquid sample could be drawn through the needle into a syringe.

C) Apparatus for measurement of zone propagation : -

The test cell, the convex lens and the light source used for experiments had been discussed in Section (A).

1) The phase contactor

The phase contactor was made out of the design and dimensions as shown in figure (44). The reservoir had a capacity of 100 ml.

2) Moiré plates

The Morié plates were consisted of a pair of optically flat glass plates; each plate was 6 cm. square and etched with equidistant horizontal lines, 100 lines per inch. The plates were obtained from Professor Kazuo Sato, Department of Chemical Engineering, Tokyo Institute of Technology, Japan.

3) Photographic equipment

A Pentax camera was used with close-up extension tubes Numbers 1 and 2. Pictures were taken with Kodak plus-X film.

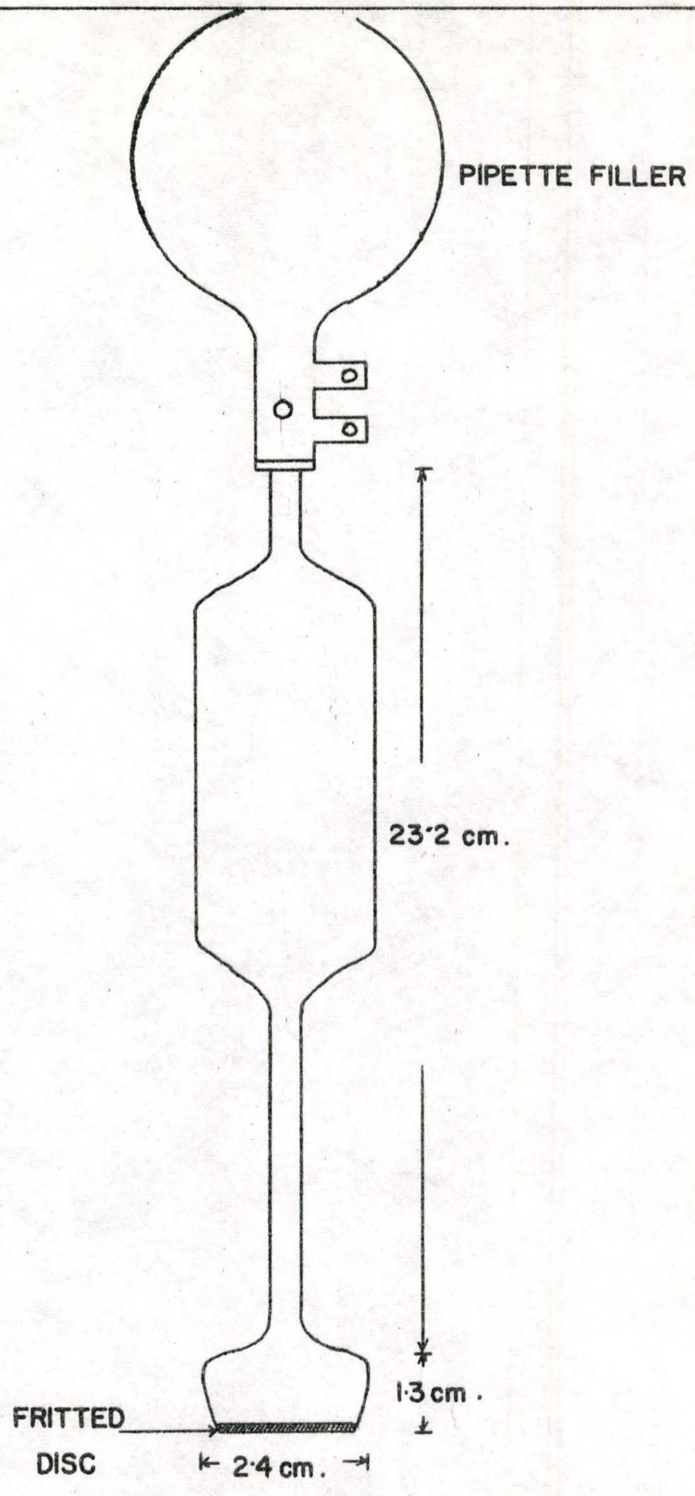


FIG. 44 THE PHASE CONTACTOR

APPENDIX XIII

PRELIMINARY INVESTIGATION

A) Schlieren investigation : -

Some experiments were performed at the earlier stage of this work using the schlieren apparatus. The object of these experiments was to develop and get familiar with the experimental procedure and try to solve any experimental difficulties encountered.

1. Liquid systems under investigation

Besides the ethyl acetate - sodium hydroxide system, some diffusion experiments were performed on ethyl acetate - potassium hydroxide, ethyl formate - sodium hydroxide and acetic acid in benzene - sodium hydroxide.

It was found that the same kind of schlieren picture was observed in the ethyl acetate - potassium hydroxide system as in ethyl acetate - sodium hydroxide. This result was in agreement with the expectation, since the reaction constants of both systems were almost equal. A more turbulent reaction zone was observed with the ethyl formate - sodium hydroxide system. However, with the acetic acid in benzene - aqueous sodium hydroxide system, no reaction zone was observable.

2. Contact of two phases

Although great care was exercised when ethyl acetate phase was poured freely on top of the sodium hydroxide solution, yet a great disturbance of the interface was observed as a result of mechanical mixing. This disturbance was very undesirable because it might modify the original interfacial condition which was obtained when the two phases contacted each other smoothly. Several attempts had been made to improve the technique of contacting the phases. They were described briefly as follows:

(a) The light phase was put into the cell first. The heavy phase in a syringe was then injected into the cell slowly through a hypodermic needle under the light phase. This method was found to be unsatisfactory even with the application of the interface sharpening technique of Kahn and Polson (98).

(b) The heavy phase was put into the cell first, then a partition diaphragm (sheets of filter paper or bond paper or saran wrap or aluminum foil), which fitted the cell inner walls quite snugly, was placed on top which sealed the liquid surface. The light phase was poured on top of the diaphragm, filling the cell to the desired level. The diaphragm was then pulled out at an extremely slow rate to permit the formation of a calm, unperturbed interface. This method was workable, provided that a suitable kind of material for the diaphragm could be obtained. In view of the long period of time required to pull the sheet out carefully, the zero time as well as the initial interfacial area were rather uncertain.

(c) The light phase was first put into the cell; then, the heavy phase was introduced through a "phase contactor" as shown in figure (44). The method was modified from that of McBain et al (79) (88), who used similar kinds of apparatus to measure diffusion coefficients of components in one phase solution. This method was found, so far, to be the most suitable.

3. Schlieren photography

Schlieren pictures of the reaction zone were taken for each experimental run using a 16 mm movie camera together with a time lapse device. Several ways had been tried in order to obtain sharp pictures.

The methods are outlined as follows:

(a) The camera, with lens removed, was placed at the end of the optical bench. The schlieren pictures were taken by focussing the image of the test cell directly onto the film.

(b) The schlieren pictures were projected onto a screen first. The movie camera, with lens on, was aimed at the screen and the pictures were taken.

(c) The schlieren pictures were projected onto a piece of ground glass instead; and the movie was taken with the camera, shooting directly at the back of the ground glass.

None of the above methods were satisfactory.

4. Interface flattening

When the schlieren picture of the liquid system in the test cell was projected onto a screen, two thick, dark lines were seen sandwiching the reaction zone. These lines represented the "meniscuses" of the two boundaries; one was the interface between the ethyl acetate phase and the reaction zone, and the other was a demarcation line between the reaction zone and the bulk sodium hydroxide solution. Since the presence of these "meniscuses" could block the vision on a portion of the interfacial area, their elimination would be quite desirable. Attempts were made to reduce the thickness of the phase separation meniscus by coating the cell walls with a layer of anti-wetting agent. The compounds tried, so far, for the coating were of silicone derivatives; such as "Dow Corning 1208" (a mixture of methyltrichlorosilane and dimethyldichlorosilane) and "ReleasaGen" (a silicone derivative with spray application, supplied by

General Mills Co., U.S.A.). The silicone derivative coating gave satisfactory performance on air-water interface, but dissolved in both sodium hydroxide solution and ethyl acetate. Other compound for the coating was also tried; such as "Fluoro Glide" which was a suspension of teflon particles to be sprayed on the apparatus under test (The material was manufactured by Chemplast Inc., U.S.A.). The spraying was difficult to carry out because if too thick a layer of coating was applied, the cell became opaque, and if the coating was too thin, the meniscuses could not be eliminated. Furthermore, the teflon coating adhered loosely to the cell wall and could easily be washed away during cleaning. As a result, spraying had to be applied after each experiment. The method was not suitable. Therefore, no coatings were applied to the test cell for the experiments performed in this work.

B) Measurement of concentration distribution of reactants inside the reaction zone : -

1. Methods of analysis

There are several methods being considered for use in analysing the concentration of either one of the reactants inside the reaction zone. They are the optical method, the conductometric method (145) (130), the high frequency method (148), the spectrophotometric method (26), the pH method, the gas chromatograph method and the ordinary titration method (100). Apart from the spectrophotometric method (for the determination of ethyl acetate) and the high frequency method (for the determination of sodium hydroxide) which require equipment not readily available, the rest of the methods are quite conventional.

The optical method involves measuring the concentration of a component inside the solution by noting the refractive index change. The conductometric method involves determining the sodium hydroxide by measuring the electrical conductivity of the solution. These two methods require calibration, and the presence of more than one component in the zone causes the calibration to be impossible for specific components.

The pH method involves the measurement of the hydrogen ion concentration. It is not a good way to determine the sodium hydroxide quantitatively because the pH is not sensitive to the change of the sodium hydroxide concentration.

The gas chromatograph is handy for the analysis of volatile mixture. However, if a solution containing ethyl acetate, ethanol, sodium hydroxide and sodium acetate is injected into the gas chromatograph, the ethyl acetate and ethanol will vaporize while the sodium hydroxide and the sodium acetate are non-volatile and stay inside the column.

The only workable method is titration which has been discussed more fully in the "Experimental Detail" section.

2. Preliminary experiments

A few experiments were performed with the ethyl acetate-sodium hydroxide system on probing the concentration of reactants inside the zone. The experiments were performed in a small optical cell. Due to the limited amount of liquid available inside the reaction zone, only one sample (2 c.c.) or, at the most, two could be drawn from each run. Results of the sample analyses showed that the concentration of reactants inside the zone were low as compared to their concentrations outside the zone respectively.

C) Measurement of zone propagation : -

Early measurement on zone propagation involved tracing the zone movement on time-lapse movie, and later measured the zone thickness on developed film using a "photo comparator". Some of the experiments were carried out using a cathetometer to measure the zone propagation. One run was performed using both devices for the measurement.

Results of three experiments performed on ethyl acetate-sodium hydroxide system using a cathetometer as measuring device were plotted. Figure (45) showed the relationship of zone thickness versus time. Results of the run using both the time-lapse movie and cathetometer for measurement were shown in figure (46). It was clear that the readings obtained from the"photo comparator"were not as good as from the cathetometer.

In addition, it was also found that no reaction zone could be observed in the ethyl ester-sodium hydroxide system when the initial sodium hydroxide concentration was lower than 0.05N.

D) The pH measurement : -

An experiment was designed to show that, for the ethyl acetate-sodium hydroxide system inside the optical cell, the streaks diffusing into the lower phase from the reaction zone were sodium acetate. This involved the use of a pH meter capable of taking pH measurement continuously (Beckman Zeromatic 9600).

First of all, pH of individual components were measured and the results were:

0.06 N. NaOH	pH: 12.2
1.5 N. NaAc	pH: 8.2
0.06 N. NaOH and 1 N. NaAc	pH: 12.3
ethyl acetate saturated with water	pH: 5.8

Two phases in the optical cell are then contacted and the electrodes were placed in the lower phase near the bottom of the cell, and pH value of 12.2 was observed, indicating the presence of pure sodium hydroxide. Some time later, as the streaks passed down to the electrodes, pH value of the solution was still in the range of 12.1 to 12.2. However, as soon as the reaction zone extended itself into the region where the electrodes stood, pH value dropped gradually to 10.1.

E) The temperature measurement : -

Copper-constantan thermocouple and a potentiometer (Type K-3 manufactured by Leeds & Northrup Co.) were used to measure the temperature difference of the ethyl acetate-sodium hydroxide system inside the optical cell. The thermocouple was insulated up to the region very close to the hot junction so that very localized temperature measurement could be obtained.

Results were shown in the following tables, XIa and XIb. It must be realized that the dipping of the hot junction into different zones respectively was a manual operation and therefore subject to position error and non-reproducibility. Consequently, the data should be treated qualitatively. The order of magnitude rather than the actual values should be considered. On the other hand, since the experiment was performed with the optical cell uncovered, evaporation of the ethyl acetate did help to cool down the temperature of the upper phase. As a result, the measured one degree difference should actually be less. Perhaps, a 1/2°C temperature difference was more reasonable (after examining the data).

Judging from the results, it was evident that the "hottest region" for ethyl acetate-sodium hydroxide system was at the "demarcation line" between the reaction zone and the lower sodium hydroxide phase.

As far as acetic acid in benzene-aqueous sodium hydroxide system was concerned, reaction was rapid, and turbulent liquid motion helped to spread the temperature evenly throughout the system in a short time.

TABLE XIa

TEMPERATURE MEASUREMENTS

Upper phase: ethyl acetate saturated with water at room temperature

Lower phase: 0.4 N. sodium hydroxide solution

Time after the start of expt. (mins.) Position of thermocouple Temp. °C	2	5	9	18	27
Upper phase	21.46	21.45	21.33	21.22	21.05
Upper			21.09	21.16	21.78
Zone Middle	22.28	22.43	21.38	22.10	21.98
Lower			22.35	22.35	22.21
Lower phase	21.93	22.01	22.09	22.10	22.09

TABLE XIb

TEMPERATURE MEASUREMENTS

Upper phase: 0.4 N. acetic acid in benzene saturated with water

Lower phase: 0.06 N. sodium hydroxide solution

Time after the start of expt. (mins.) / Position of thermocouple / Temp. °C	1	5
Upper phase	21.75	22.12
Interface	22.33	22.25
Lower phase	22.50	22.25

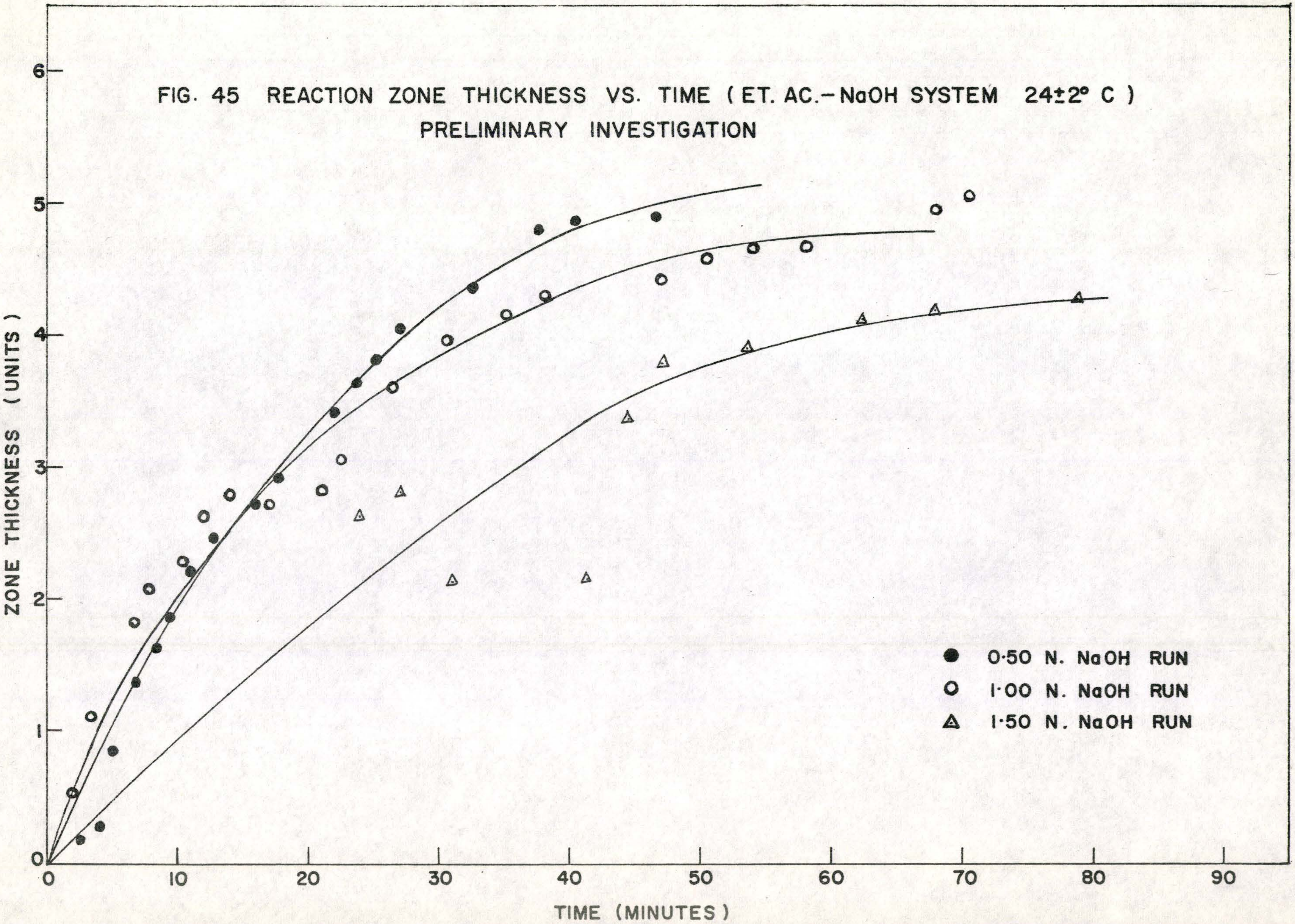


FIG. 45 REACTION ZONE THICKNESS VS. TIME (ET. AC.-NaOH SYSTEM 24±2° C)
PRELIMINARY INVESTIGATION

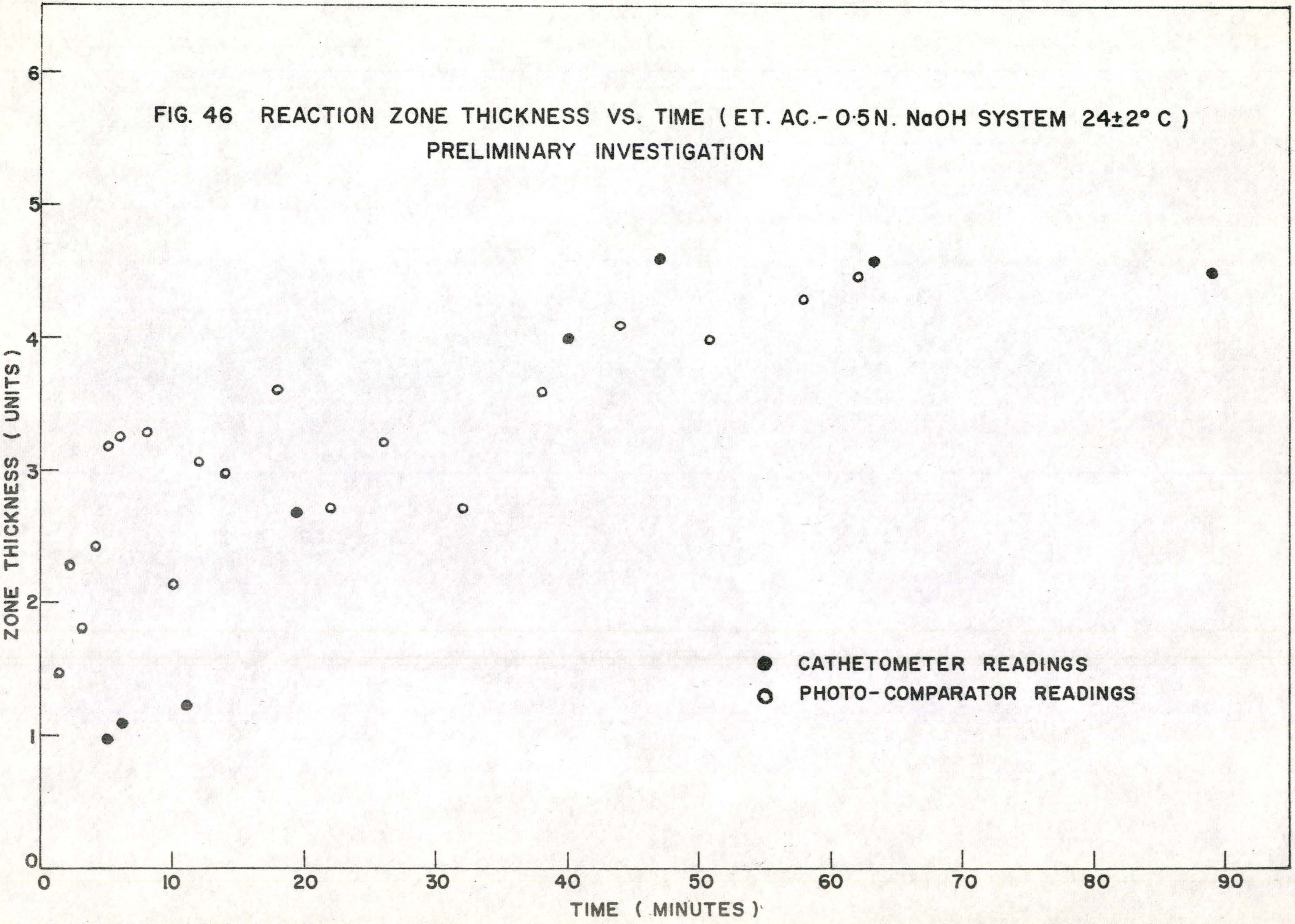


FIG. 46 REACTION ZONE THICKNESS VS. TIME (ET. AC.- 0·5 N. NaOH SYSTEM 24±2° C)
PRELIMINARY INVESTIGATION

APPENDIX XIV

SAMPLE CALCULATION (For Part II)

A) **Concentration distribution of reactants inside the reaction zone** : -

Referring to Table XII, Appendix XV,

initial sodium hydroxide concentration: 0.58 N.

temperature: 24° ± 0.5°C

2 ml sample taken from needle No. 1 at 13 minutes

amount of 0.1 N. HCl required for the titration = 0.6 ml

$$\therefore \text{ NaOH concentration in the sample} = \frac{2 \times 0.1}{0.6}$$

$$= 0.033 \text{ N.}$$

4 ml of 0.0985 N.NaOH was added to the solution which was then refluxed for three hours

amount of 0.1 N. HCl required to neutralize the excess NaOH = 0.05 ml

∴ amount of 0.1 N. NaOH required to react with ethyl acetate in the sample = (4 x 0.0985 - 0.05 x 0.1) / 0.1

= 3.890 ml

$$\therefore \text{ ethyl acetate concentration in the sample} = \frac{3.890 \times 0.1}{2}$$

$$= 0.199 \text{ N.}$$

B) **Measurement of zone propagation**: -

Referring to run No. 4, Appendix XVI

initial NaOH concentration: 0.5 N.

temperature: 23.5 ± 0.5°C

picture No. 10 was taken at 25 minutes

the three measurements of the zone thickness were 7.8 cm, 8.1 cm and 8.0 cm

the actual thickness of the zone:

$$7.8 \times 4.8/54.5 = 0.68697 \text{ cm}$$

$$8.1 \times 4.8/54.5 = 0.71339 \text{ cm}$$

$$8.0 \times 4.8/54.5 = 0.70459 \text{ cm}$$

$\therefore$ average zone thickness = 0.70165 cm

$\therefore$ square of average zone thickness = 0.49231 cm^2

C) Calculation of heat of reaction of ethyl acetate-sodium hydroxide system: -

$\Delta H_{(combustion)}$ data were obtained from references (56)(51)

$CH_3COOC_2H_5 + 5O_2 = 4CO_2 + 4H_2O$ . . . $\Delta H_c = -538760$ cal. .... (41)

$4H_2 + 2O_2 = 4H_2O$ . . . $\Delta H_c = -68317 \times 4$ cal. .... (42)

$4C + 4O_2 = 4CO_2$ . . . $\Delta H_c = -94051 \times 4$ cal. .... (43)

equation (43) + equation (42) - equation (41)

$4C + 4H_2 + O_2 = CH_3COOC_2H_5$ . . . $\Delta H_f = -110712$ cal.

in a similar way,

$2C + 3H_2 + 1/2\ O_2 = C_2H_5OH$ . . . $\Delta H_f = -66053$ cal.

from references (56)(51)

ΔH_f for NaOH = - 112000 cal.

ΔH_f for $NaCOOC_2H_5$=-175800 cal.

$\therefore$ $\Delta H_{(reaction)}$ =-13.141 k.cal./mole

which agreed well with the literature value (3) of 13.08 k.cal./mole

APPENDIX XV

TABLE XII

CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE

INITIAL NaOH CONCENTRATION = 0.58 N.

Time (mins.)	Distance from interface (mm.)	NaOH conc. (normality)	EtAc conc. (normality)
13	1.00 (needle #1)	0.033	0.199
17.5	2.35 (needle #2)	0.160	0.017
24.6	4.15 (needle #3)	0.340	0.002
27.9	1.00	0.015	0.198
35	2.35	0.070	0.430
42	4.15	0.013	0.148
46	1.00	0.002	0.471
52	2.35	0.002	0.486
58	4.15	0.020	0.256
61.8	6.95 (needle #4)	0.290	0.020
70	1.00	0.002	0.579
75	2.35	0.002	-
79	4.15	0.003	0.399
87	6.95	0.140	0.007
107	1.00	0.002	0.524

TABLE XIII

CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE

INITIAL NaOH CONCENTRATION = 1.08 N.

Time (mins.)	Distance from interface (mm.)	NaOH conc. (normality)	EtAc conc. (normality)
10	1.00 (needle #1)	0.033	0.127
15	3.10 (needle #2)	0.230	0.004
22	1.00	0.020	0.130
26	3.10 (needle #2)	0.010	0.180
32	3.10 (needle #3)	0.030	0.172
38	1.00	0.003	0.362
43	3.10 (needle #2)	0.003	0.387
47	3.10 (needle #3)	0.003	0.374
65	1.00	0.003	0.420
70	3.10 (needle #2)	0.003	0.381
73	4.92 (needle #4)	0.040	0.102
93	1.00	0.001	0.375
98	3.10 (needle #2)	0.001	0.352
100	4.92	0.020	0.170
420	1.00	0.070	0.208
780	1.00	0.001	0.208
782	3.10 (needle #2)	0.005	0.173
787	4.92	0.060	0.020

TABLE XIV

CONCENTRATION DISTRIBUTION OF REACTANTS INSIDE THE REACTION ZONE

INITIAL NaOH CONCENTRATION = 1.78 N.

Time (mins.)	Distance from interface (mm.)	NaOH conc. (normality)	EtAc conc. (normality)
20	1.00 (needle #1)	0.610	0.005
30	1.00	0.237	0.020
60	1.00	0.030	0.183
67	2.97 (needle #2)	0.050	0.080
95	1.00	0.010	0.301
100	2.97	0.013	0.240
110	4.72 (needle #3)	0.490	0.013

APPENDIX XVI

EXPERIMENTAL DATA

Unsteady State Mass Transfer with Chemical Reaction

A) Ethyl acetate-sodium hydroxide system:

Run No. 1

Upper phase: ethyl acetate saturated with water.

Lower phase: 0.05 N. NaOH

Total No. of photographs taken: 20.

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm.)	Zone thickness Measurement No. 2 (cm.)	Zone thickness Measurement No. 3 (cm.)	Zone thickness Average (cm)	$(\text{Average Zone thickness})^2$ $(\text{cm.})^2$
4	5	0.35229	0.36110	0.31706	0.34348	0.11798
8	15	0.40514	0.44037	0.49321	0.44624	0.19913
10	21	0.45798	0.51082	0.50202	0.49027	0.24037
12	28	0.51963	0.55486	0.59890	0.55780	0.31114
14	35	0.59009	0.66936	0.64294	0.63413	0.40212
16	50	0.53725	0.61651	0.63413	0.59596	0.35517
18	80	0.56367	0.57248	0.58128	0.57248	0.32773

Run No. 2

Upper phase: ethyl acetate saturated with water.

Lower phase: 0.1 N. NaOH.

Total No. of photographs taken: 12.

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Zone thickness Average)^2 (cm)^2
1	2	0.22018	0.22018	0.26422	0.23486	0.05516
2	3.8	0.35229	0.32587	0.33468	0.33761	0.11398
3	5	0.29945	0.37872	0.37872	0.35229	0.12411
4	11	0.36991	0.41394	0.41394	0.39926	0.15941
5	15	0.38752	0.38752	0.44917	0.40807	0.16652
6	21	0.51082	0.55486	0.57248	0.54606	0.29818
7	25	0.51082	0.58128	0.63413	0.57541	0.33110
8	31	0.67816	0.72220	0.79266	0.73101	0.53438
9	40	0.77505	0.86312	0.87192	0.83670	0.70006
10	50	0.78385	0.66055	0.61651	0.68697	0.47193
11	60	0.68697	0.71339	0.73982	0.71339	0.50893

Run No. 3.

Upper phase: ethyl acetate saturated with water.

Lower phase: 0.25 N. NaOH.

Total No. of photographs taken: 27.

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Picture No.	Time (minutes)	Zone Thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone Thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	2	0.22018	0.22899	0.19376	0.21431	0.04593
2	2.7	0.26422	0.26422	0.26422	0.26422	0.06981
3	3.5	0.32587	0.32587	0.32587	0.32587	0.10619
4	5	0.29945	0.32587	0.38752	0.33761	0.11398
5	6.5	0.32587	0.34349	0.36991	0.34642	0.12001
10	21	0.51963	0.63413	0.67816	0.61064	0.37288
12	28	0.69578	0.74862	0.77505	0.73982	0.54733
13	31	0.73982	0.81027	0.79266	0.78092	0.60983
14	35	0.83670	0.81908	0.77505	0.81027	0.65655
15	40	0.81027	0.82789	0.77505	0.80440	0.64707
16	45.6	0.72220	0.75743	0.73982	0.73982	0.54733
24	100.	0.80147	0.80147	0.80147	0.8147	0.64235
26	101	0.79266	0.79266	0.79266	0.79266	0.62831

Run No. 4.

Upper phase: ethyl acetate saturated with water.

Lower phase: 0.5 N. NaOH.

Total No. of photographs taken: 23

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thicknes)^2 (cm)^2
2	2.3	0.22018	0.22018	0.22018	0.22018	0.04848
3	5.0	0.30826	0.31706	0.29945	0.30826	0.09502
4	6.5	0.41394	0.40514	0.36991	0.39663	0.15708
5	8	0.39633	0.37872	0.48440	0.41982	0.17625
6	11	0.44037	0.44037	0.33917	0.44330	0.19652
7	15	0.47560	0.56367	0.53725	0.52550	0.27615
8	18	0.58128	0.60771	0.59890	0.59596	0.35517
9	20.5	0.63413	0.65174	0.65174	0.64587	0.41715
10	25	0.68697	0.71339	0.70459	0.70165	0.49231
11	28	0.73101	0.77505	0.78385	0.76330	0.58263
12	31	0.76624	0.80147	0.81027	0.79266	0.62831
13	35	0.88954	0.84550	0.87192	0.86899	0.75514

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
14	40	0.85431	0.88073	0.89835	0.88780	0.77053
15	45	0.88073	0.89835	0.94238	0.90716	0.82293
16	50	0.89835	0.91596	0.91596	0.91009	0.82827
17	55	0.99523	1.02170	1.02170	1.01280	1.02590
18	60	0.87192	0.83670	0.84550	0.85138	0.72484
19	70	0.84550	0.82789	0.85431	0.84257	0.70992
20	80	0.86312	0.86312	0.87192	0.86606	0.75005
21	90	0.81027	0.86312	0.88954	0.85431	0.72985
22	100	0.85431	0.86312	0.86312	0.86018	0.73992
23	600	0.95119	0.95119	0.96000	0.95413	0.91036

Run No. 4A

Upper phase: ethyl acetate saturated with water.

Lower phase: 0.5 N. NaOH

Total No. of photographs taken: 23

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	$(\text{Average Zone thickness})^2$ $(\text{cm})^2$
3	8	0.36991	0.39633	0.36991	0.37872	0.14343
5	15	0.49321	0.45798	0.57248	0.50789	0.25795
7	20.5	0.59009	0.59890	0.66055	0.61651	0.38009
9	28	0.69578	0.74862	0.77505	0.73982	0.54733
12	40	0.86312	0.89835	0.95119	0.90422	0.81761
13	45	0.82789	0.92477	0.98642	0.91303	0.83362
14	50	0.83670	0.92477	0.93358	0.89835	0.80703
15	60	0.86312	0.73982	0.79266	0.79853	0.63765
16	65	0.82789	0.83670	0.89835	0.85431	0.72985

Run No. 4B

Upper phase: ethyl acetate saturated with water.

Lower phase: 0.5 N. NaOH

Total No. of Photographs taken: 14

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
2	5	0.26422	0.29945	0.29945	0.28771	0.08278
4	11	0.39633	0.38752	0.43156	0.40514	0.16414
5	15	0.47560	0.41394	0.56367	0.48440	0.23465
6	20.5	0.47560	0.63413	0.68697	0.59890	0.35868
7	25.6	0.63413	0.71339	0.77505	0.70752	0.50059
8	30	0.70459	0.79266	0.82789	0.77504	0.60069
9	40	0.82789	0.95119	0.95119	0.91009	0.82827
10	50	0.88954	0.97761	0.97761	0.94826	0.89919

Run No. 5.

Upper phase: ethyl acetate saturated with water

Lower phase: 1.0 N. NaOH

Total No. of Photographs taken: 25

Picture No.	(minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
2	3.1	0.23780	0.28183	0.26422	0.26128	0.06827
3	3.5	0.24660	0.25541	0.20257	0.23486	0.055160
4	5.0	0.26422	0.26422	0.26422	0.26422	0.069812
5	8.0	0.35229	0.35229	0.34349	0.34936	0.12205
6	11	0.36110	0.36110	0.44917	0.39046	0.15246
7	15	0.47560	0.48440	0.46679	0.47560	0.22619
8	18	0.44917	0.49321	0.50202	0.48147	0.23181
9	21	0.47560	0.52844	0.57248	0.52550	0.27615
10	25	0.45798	0.58128	0.60771	0.54899	0.30139
11	28	0.58128	0.62532	0.63413	0.61358	0.37648
12	31	0.58128	0.65174	0.68697	0.64000	0.40960

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	$(\text{Average Zone thickness})^2$ $(\text{cm})^2$
13	35	0.63413	0.68697	0.71339	0.67816	0.45991
14	40	0.63413	0.67816	0.77505	0.69578	0.48411
15	45	0.70459	0.77505	0.77505	0.75156	0.56484
16	50	0.73982	0.75743	0.81027	0.76917	0.59163
17	55	0.75743	0.76624	0.81027	0.77798	0.60525
18	60	0.81908	0.83670	0.93358	0.86312	0.74498
19	65	0.84550	0.91596	0.92477	0.89541	0.80176
20	70	0.85431	0.88073	0.91596	0.88367	0.78087
21	80	0.85431	0.90716	0.89835	0.88661	0.78607
22	90	0.79266	0.81027	0.75743	0.78679	0.61904
23	100	0.81908	0.81908	0.80147	0.81321	0.66131
24	102	0.81027	0.79266	0.81908	0.80734	0.65180

Run No. 6

Upper phase: ethyl acetate saturated with water.

Lower phase: 1.5 N. NaOH.

Total No. of photographs taken: 27.

Picture No.	Time (Minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	$(\text{Average Zone thickness})^2$ $(\text{cm})^2$
1	1.9	0.19376	0.18495	0.18495	0.18789	0.03530
2	3.5	0.26422	0.26422	0.24660	0.25835	0.06674
3	5.0	0.28183	0.27303	0.25541	0.27009	0.07294
4	6.5	0.26422	0.27303	0.29945	0.27890	0.07778
5	8.0	0.34349	0.33468	0.33468	0.33761	0.11398
6	11	0.44037	0.41394	0.41394	0.42275	0.17872
7	15	0.39633	0.39633	0.39633	0.39633	0.15708
8	18	0.48440	0.40514	0.44037	0.44330	0.19652
9	21	0.48440	0.45798	0.47560	0.47266	0.22341
10	25	0.48440	0.45798	0.49321	0.47853	0.22899
11	28	0.40514	0.48440	0.51082	0.46679	0.21789
12	31	0.50202	0.41394	0.53725	0.48440	0.23465
13	35.8	0.54605	0.51082	0.54605	0.53431	0.28549

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	$\left(\text{Average Zone thickness}\right)^2$ $(\text{cm})^2$
14	42.5	0.57248	0.58128	0.63413	0.59596	0.35517
15	45	0.59890	0.60771	0.64294	0.61651	0.38009
16	50	0.71339	0.67816	0.67816	0.68991	0.47597
17	55	0.67816	0.67816	0.69578	0.68404	0.46790
18	60	0.72220	0.67816	0.73101	0.71046	0.50475
19	65.8	0.72220	0.71339	0.72220	0.71927	0.51734
20	71.6	0.73101	0.73101	0.76624	0.74275	0.55168
21	75	0.70459	0.72220	0.75743	0.72807	0.53009
22	80	0.72220	0.73982	0.76624	0.74275	0.55168
23	90	0.73982	0.77505	0.77505	0.76330	0.58263
24	105.6	0.79266	0.79266	0.76266	0.79266	0.62831
25	152	0.66936	0.70459	0.66055	0.67816	0.45991
26	158	0.58128	0.55486	0.61651	0.58422	0.34131
27	160	0.54605	0.57248	0.62532	0.58128	0.33789

Run No. 7

Upper phase: ethyl acetate saturated with water.

Lower phase: 2.0 N. NaOH.

Total No. of photographs taken: 24

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	1.7	0.17615	0.17615	0.17615	0.17615	0.03103
2	3.5	0.25660	0.23780	0.20257	0.22899	0.05244
3	5.0	0.26422	0.28183	0.26422	0.27009	0.07294
4	6.5	0.30826	0.28183	0.29064	0.29358	0.08619
5	8.0	0.32587	0.29945	0.29064	0.30532	0.093221
6	11	0.32587	0.32587	0.33468	0.32881	0.10811
7	15	0.40514	0.40514	0.36991	0.39339	0.15476
8	18	0.33468	0.31706	0.31706	0.32293	0.10429
9	21	0.30826	0.29064	0.33468	0.31119	0.09684
10	25	0.33468	0.36110	0.33468	0.34349	0.11798
11	28	0.37872	0.36110	0.36110	0.36697	0.13467
12	31	0.41394	0.38752	0.40514	0.40220	0.16177

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
13	35	0.45798	0.41394	0.42275	0.43156	0.18624
14	40	0.44037	0.42275	0.45798	0.44037	0.19392
15	45	0.44917	0.48440	0.51963	0.48440	0.23465
16	50	0.51082	0.53725	0.54605	0.53138	0.28236
17	57.5	0.59890	0.55486	0.57248	0.57541	0.33110
18	60	0.57248	0.59009	0.59890	0.58716	0.34475
19	65	0.57248	0.58128	0.62532	0.59303	0.35168
20	70	0.59009	0.59009	0.65174	0.61064	0.37288
21	80	0.62532	0.61651	0.66055	0.63413	0.40212
22	90	0.57248	0.62532	0.65174	0.61651	0.38009
23	100	0.69578	0.68697	0.70459	0.69578	0.48411
24	112	0.72220	0.74862	0.78385	0.75156	0.56484

B) Ethyl formate - sodium hydroxide system:

Run No. 8

Upper phase: ethyl formate saturated with water.

Lower phase: 0.05 N. NaOH

Total No. of Photographs taken: 20

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	1.0	0.74862	0.75743	0.76624	0.75743	0.57370
2	1.5	0.91596	0.94238	0.94238	0.93358	0.87157
3	2.0	1.00400	1.03050	1.05690	1.03050	1.06180
4	2.5	1.05690	1.03930	1.04810	1.04810	1.09850
5	3.0	1.21540	1.14500	1.18900	1.18310	1.39980
6	3.7	1.28590	1.21540	1.35630	1.28590	1.65350
8	5.4	1.33870	1.28590	1.32110	1.31520	1.72980
9	6.0	1.59410	1.58530	1.60290	1.59410	2.54120
10	7.1	1.69980	1.70860	1.70860	1.70570	2.90940
11	8.3	1.86720	1.86720	1.84950	1.86130	3.46440
12	9.1	2.02570	2.03450	2.03450	2.03160	4.12720

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	$(\text{Average Zone thickness})^2$ $(\text{cm})^2$
13	10	2.17540	2.17540	2.25470	2.20180	4.84810
14	11	2.30750	2.34280	2.36040	2.33690	5.46100
15	12	2.51890	2.61580	2.58050	2.57170	6.61390
16	13	2.64220	2.86240	2.85360	2.78610	7.76210
17	14	2.80070	2.99450	2.82720	2.87410	8.26060
18	15	2.96810	2.99450	2.98570	2.98280	8.89680
19	60	3.00260	3.00260	3.00260	3.00260	9.00560

Run No. 9

Upper phase: ethyl formate saturated with water

Lower phase: 0.1 N. NaOH

Total No. of photographs taken: 23

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	1.2	0.85431	0.88954	0.87192	0.87193	0.76025
2	1.5	1.05690	1.00400	1.01280	1.02460	1.04980
3	2.0	1.20660	1.20660	1.11850	1.17720	1.38590
4	2.5	1.41800	1.33870	1.36510	1.37390	1.88770
5	3.0	1.51490	1.50610	1.40920	1.47670	2.18060
6	4.0	1.81430	1.75270	1.72620	1.76440	3.11310
7	5.0	1.98170	1.95520	1.93760	1.95820	3.83440
8	6.0	2.14020	2.14900	2.20180	2.16370	4.68150
9	7.3	2.37800	2.41320	2.43080	2.40730	5.79530
10	8.0	2.55410	2.64220	2.62460	2.60700	6.79630
11	9.0	2.77430	2.73030	2.77430	2.75960	7.61560

Picture No.	Time (minute)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
12	10	2.99450	3.12660	3.05610	3.05910	9.35800
13	10.5	3.04730	3.08260	3.09140	3.07380	9.44800
15	12	3.24110	3.12660	3.14420	3.17060	10.0530

Run No. 10

Upper phase: ethyl formate saturated with water.

Lower phase: 0.25 N. NaOH.

Total No. of photographs taken: 20

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	1.0	0.44917	0.42275	0.53725	0.46972	0.22064
2	1.5	0.59009	0.56367	0.62532	0.59303	0.35168
3	2.0	0.67816	0.66936	0.70459	0.68404	0.46790
4	2.5	0.75743	0.77505	0.78385	0.77211	0.59615
5	3.0	0.86312	0.86312	0.87192	0.86606	0.75005
6	4.0	1.07450	0.97761	1.03930	1.03050	1.06180
7	5.0	1.21540	1.18900	1.20660	1.20370	1.44880
8	6.5	1.47960	1.43560	1.40920	1.44150	2.07780
9	8.0	1.69100	1.67340	1.63820	1.66750	2.78060
10	9.5	1.93760	1.89360	1.86720	1.89950	3.60790
11	11	2.11380	2.04330	2.11380	2.09030	4.36920

Picture no.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	$(\text{Average Zone thickness})^2$ $(\text{cm})^2$
12	13	2.39560	2.37800	2.33390	2.36920	5.61300
13	15	2.64220	2.62460	2.70380	2.65690	7.05900
14	17	2.90640	2.87120	2.90640	2.89470	8.37920
15	18.5	3.10020	3.08260	3.08260	3.08840	9.5385
16	19	3.19710	3.19710	3.17060	3.18830	10.1650(0)
18	22	3.28510	3.26750	3.29390	3.28220	10.7730(0)

Run No. 11

Upper phase: ethyl formate saturated with water

Lower phase: 0.5 N. NaOH

Total No. of photographs taken: 31

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	1.4	0.44917	0.46679	0.54605	0.48734	0.23750
2	1.7	0.54605	0.54605	0.56367	0.55193	0.30462
3	2.0	0.59009	0.57248	0.57248	0.57835	0.33449
4	2.3	0.59890	0.57248	0.65174	0.60771	0.36931
5	2.6	0.61651	0.59890	0.59009	0.60183	0.36220
6	2.9	0.68697	0.66936	0.66936	0.67523	0.45593
7	3.6	0.73982	0.70459	0.74862	0.73101	0.53438
8	4.2	0.75743	0.75743	0.81908	0.77798	0.60525
9	5.3	0.96881	0.91596	0.90716	0.93064	0.86609
10	6.5	1.03050	1.03050	1.06570	1.04220	1.08620
11	8.0	1.16260	1.19780	1.17140	1.17720	1.38590
12	9.0	1.28590	1.30350	1.28590	1.29170	1.66860
13	10	1.40920	1.40040	1.38280	1.39740	1.95280

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
14	11	1.4708	1.50610	1.49720	1.49140	2.22420
15	13	1.65580	1.65580	1.65580	1.65580	2.74160
16	15	1.84950	1.83190	1.79670	1.82610	3.33450
17	17	1.98170	1.97280	1.95520	1.96990	3.88050
18	19	2.14900	2.14020	2.11380	2.13430	4.55530
19	21	2.29870	2.27230	2.22830	2.26640	5.13670
20	23	2.41320	2.43080	2.35160	2.39850	5.75300
21	25	2.55410	2.52770	2.49250	2.52480	6.37450
22	28	2.79190	2.74790	2.68620	2.74200	7.51870
23	31	2.99450	2.91520	2.90640	2.93870	8.63610
24	35	3.20590	3.19710	3.17060	3.19120	10.1840(0)
25	40	3.53170	3.54060	3.52290	3.53170	12.4730(0)
26	41	3.61100	3.49650	3.69030	3.59930	12.9550(0)

Run No. 12

Upper phase: ethyl formate saturated with water.

Lower phase: 1.0 N. NaOH

Total No. of Photographs taken: 29

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	0.8	0.30826	0.29945	0.30826	0.30532	0.09322
2	1.4	0.38752	0.38752	0.37872	0.38459	0.14791
3	1.7	0.40514	0.37872	0.40514	0.39633	0.15708
4	2.0	0.39633	0.37872	0.42275	0.39926	0.15941
5	2.3	0.50202	0.44037	0.45798	0.46679	0.21789
6	2.9	0.49321	0.54605	0.49321	0.51082	0.26094
7	3.2	0.52844	0.49321	0.51082	0.51082	0.26094
8	3.5	0.51082	0.49321	0.51963	0.50789	0.25795
9	4.0	0.55486	0.55486	0.58128	0.56367	0.31772
10	5.0	0.59890	0.60771	0.60771	0.60477	0.36575
11	6.0	0.65174	0.66055	0.69578	0.66936	0.44804
12	7.0	0.69578	0.69578	0.73101	0.70752	0.50059

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
13	9.0	0.78385	0.79266	0.84550	0.80734	0.65180
14	11	0.88073	0.88954	0.90716	0.89248	0.79651
15	13	0.93358	0.96881	0.99523	0.96587	0.93291
16	15	0.97761	1.04810	1.06570	1.03050	1.06180
17	18	1.14500	1.18900	1.18900	1.17430	1.37900
18	21	1.23300	1.27710	1.28590	1.26530	1.60100
19	25	1.32990	1.40920	1.43560	1.39160	1.93640
20	28	1.40920	1.47960	1.53250	1.47380	2.17200
21	31	1.54130	1.58530	1.61170	1.57940	2.49470
22	35	1.63820	1.69980	1.72620	1.68810	2.84960
23	40	1.83190	1.83190	1.87600	1.84660	3.40990
24	45	1.95520	1.93760	1.98170	1.95820	3.83440
25	50	1.94640	2.02570	2.14020	2.03740	4.15110
26	60	2.34280	2.37800	2.34280	2.35450	5.54360
27	70	2.55410	2.57170	2.55410	2.56000	6.55360
28	101	2.81830	2.86240	2.81830	2.83300	8.02600
29	102	2.81830	2.82720	2.80070	2.81540	7.92650

Run No. 13

Upper phase: ethyl formate saturated with water

Lower phase: 1.5 N. NaOH

Total No. of phtographs taken: 18

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	1.2	0.27303	0.24660	0.30826	0.27596	0.07616
2	1.5	0.29064	0.33468	0.34349	0.32293	0.10429
3	2.0	0.37872	0.38752	0.40514	0.39046	0.15246
4	3.5	0.47560	0.50202	0.53725	0.50495	0.25498
5	5.0	0.61651	0.61651	0.65174	0.62828	0.39471
6	8.0	0.78385	0.76624	0.79266	0.78092	0.60983
7	12	0.96000	0.94238	0.94238	0.94826	0.89919
8	18	1.07450	1.08330	1.11850	1.09210	1.19270
9	28	1.18900	1.25060	1.27710	1.23890	1.53490
10	35	1.25060	1.40920	1.42680	1.36220	1.85560
11	41	1.49720	1.49720	1.50610	1.50020	2.25060

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
12	50	1.27710	1.32110	1.32110	1.30640	1.70670
13	60	1.34750	1.32990	1.37390	1.35050	1.82370
14	70	1.34750	1.34750	1.35630	1.35050	1.82370
15	80	1.35630	1.37390	1.38280	1.37100	1.87970
16	90	1.34750	1.36510	1.37390	1.36220	1.85560
17	100	1.30350	1.33870	1.32110	1.32110	1.74530
18	120	1.18900	1.20660	1.21540	1.20370	1.44850

Run No. 14

Upper phase: ethyl formate saturated with water.

Lower phase: 2.0N. NaOH.

Total No. of photographs taken: 22

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
1	1.1	0.23780	0.23780	0.29064	0.25541	0.06524
2	2.2	0.33468	0.32587	0.35229	0.33761	0.11398
3	3.0	0.44037	0.40514	0.44917	0.43156	0.18624
4	4.0	0.50202	0.48440	0.47560	0.48734	0.23750
5	5.0	0.57248	0.54605	0.52844	0.54899	0.30139
6	6.0	0.62532	0.61651	0.61651	0.61945	0.38372
7	8.0	0.73982	0.70459	0.62532	0.68991	0.47597
8	9.5	0.79266	0.76624	0.76624	0.77504	0.60069
9	11	0.83670	0.81908	0.79266	0.81615	0.66610
10	15	0.92477	0.86312	0.84550	0.87780	0.77053
11	22	0.99523	1.01280	1.01280	1.00700	1.01400

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	$(\text{Average Zone thickness})^2$ $(\text{cm})^2$
12	30	1.02170	1.03050	1.06570	1.03930	1.08010
13	40	1.07450	1.09210	1.08330	1.08330	1.17350
14	50	1.04810	1.03930	1.05690	1.04810	1.09850
15	60	1.08330	1.07450	1.08330	1.08040	1.16720
16	70	1.04810	1.06570	1.09210	1.06860	1.14200
17	80	1.05690	1.05690	1.05690	1.05690	1.11700
18	90	1.04810	1.05690	1.07450	1.05980	1.12320
19	91	1.02170	1.05690	1.05690	1.04510	1.09230
20	100	1.03930	1.04810	1.05690	1.04810	1.09850
21	102	1.03930	1.04810	1.05690	1.04810	1.09850

Run No.143

Upper phase: ethyl formate saturated with water.

Lower phase: 2.0 N.

Total no. of photographs taken: 21

Picture No.	Time (minutes)	Zone thickness Measurement No. 1 (cm)	Zone thickness Measurement No. 2 (cm)	Zone thickness Measurement No. 3 (cm)	Zone thickness Average (cm)	(Average Zone thickness)^2 (cm)^2
15	45	1.10970	1.19780	1.28590	1.19780	1.43470
16	50	1.12730	1.11850	1.07450	1.10680	1.22500
17	60	1.10970	1.10970	1.08330	1.10090	1.21200
18	70	1.03930	1.03930	1.03930	1.03930	1.08010
19	80	1.13610	1.09210	1.08330	1.10390	1.21850
20	100	1.00400	1.04810	1.04810	1.03340	1.06790

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PLATE I ETHYL ACETATE - 0·1 N NaOH SYSTEM
25 MINUTES AFTER STARTING THE RUN

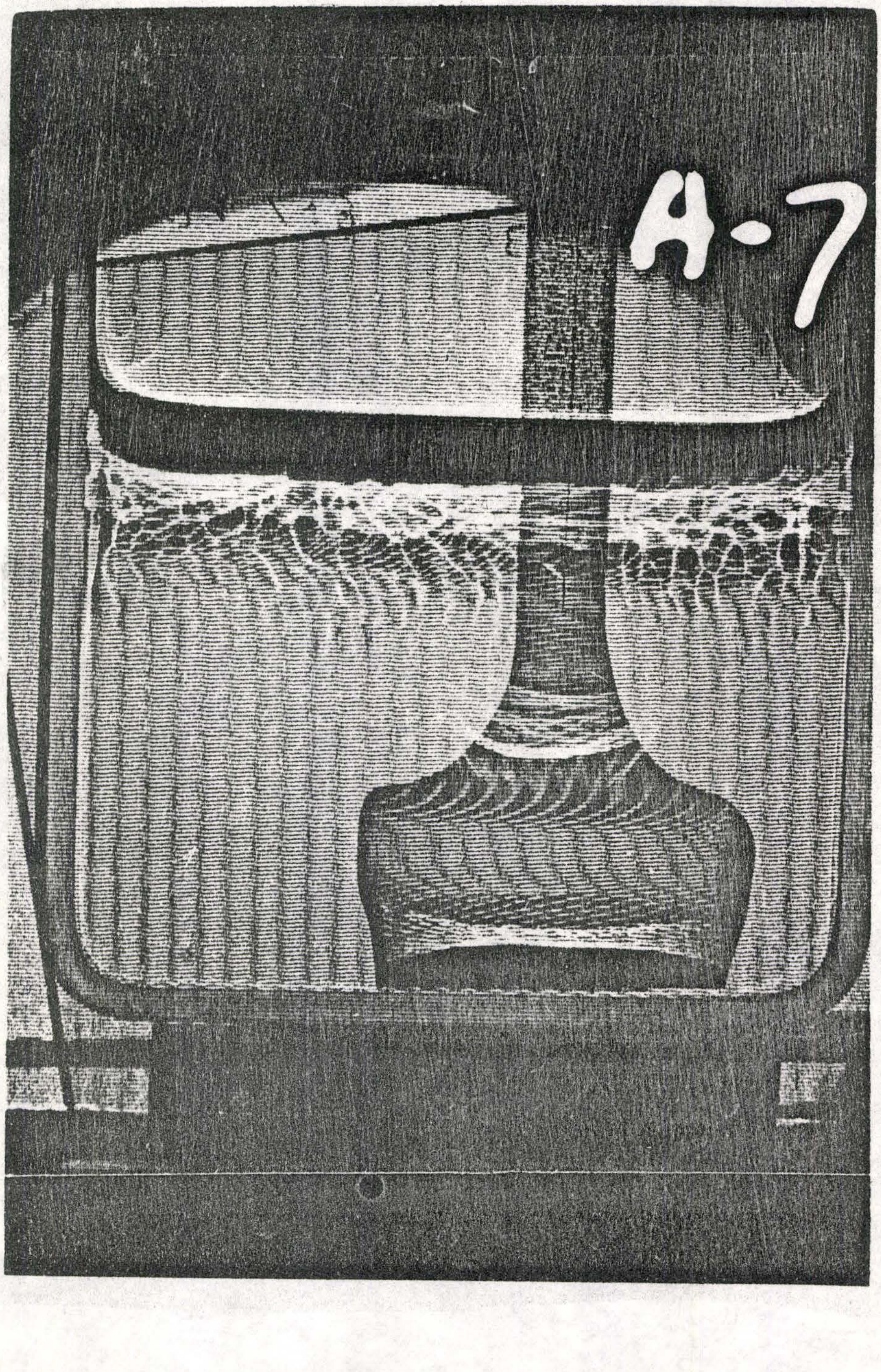

PLATE 2 ETHYL ACETATE - 0·5N NaOH SYSTEM
25 MINUTES AFTER STARTING THE RUN

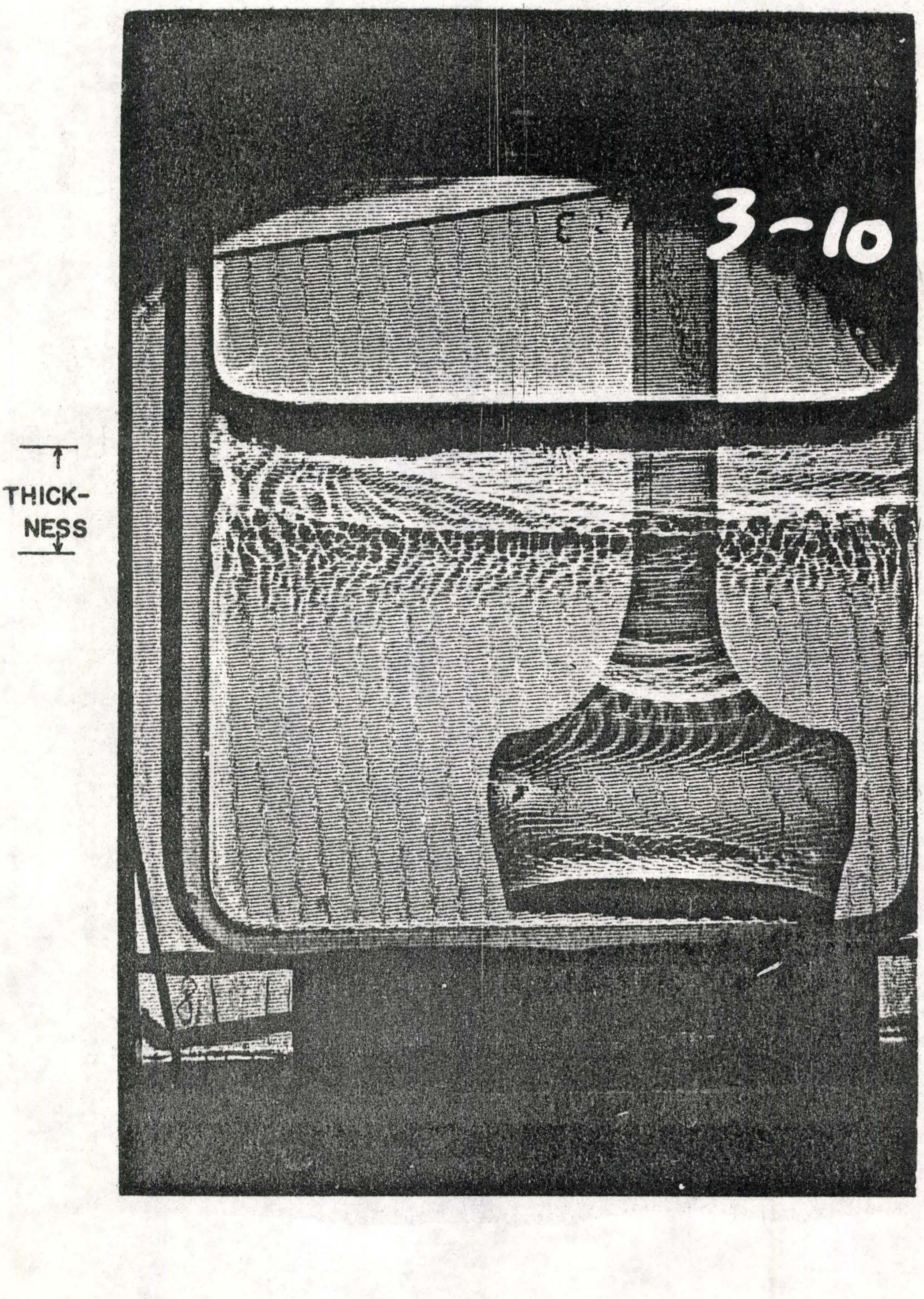

PLATE 3 ETHYL ACETATE – 1·0 N NaOH SYSTEM
25 MINUTES AFTER STARTING THE RUN

PLATE 4 ETHYL ACETATE – 1·5N NaOH SYSTEM
25 MINUTES AFTER STARTING THE RUN

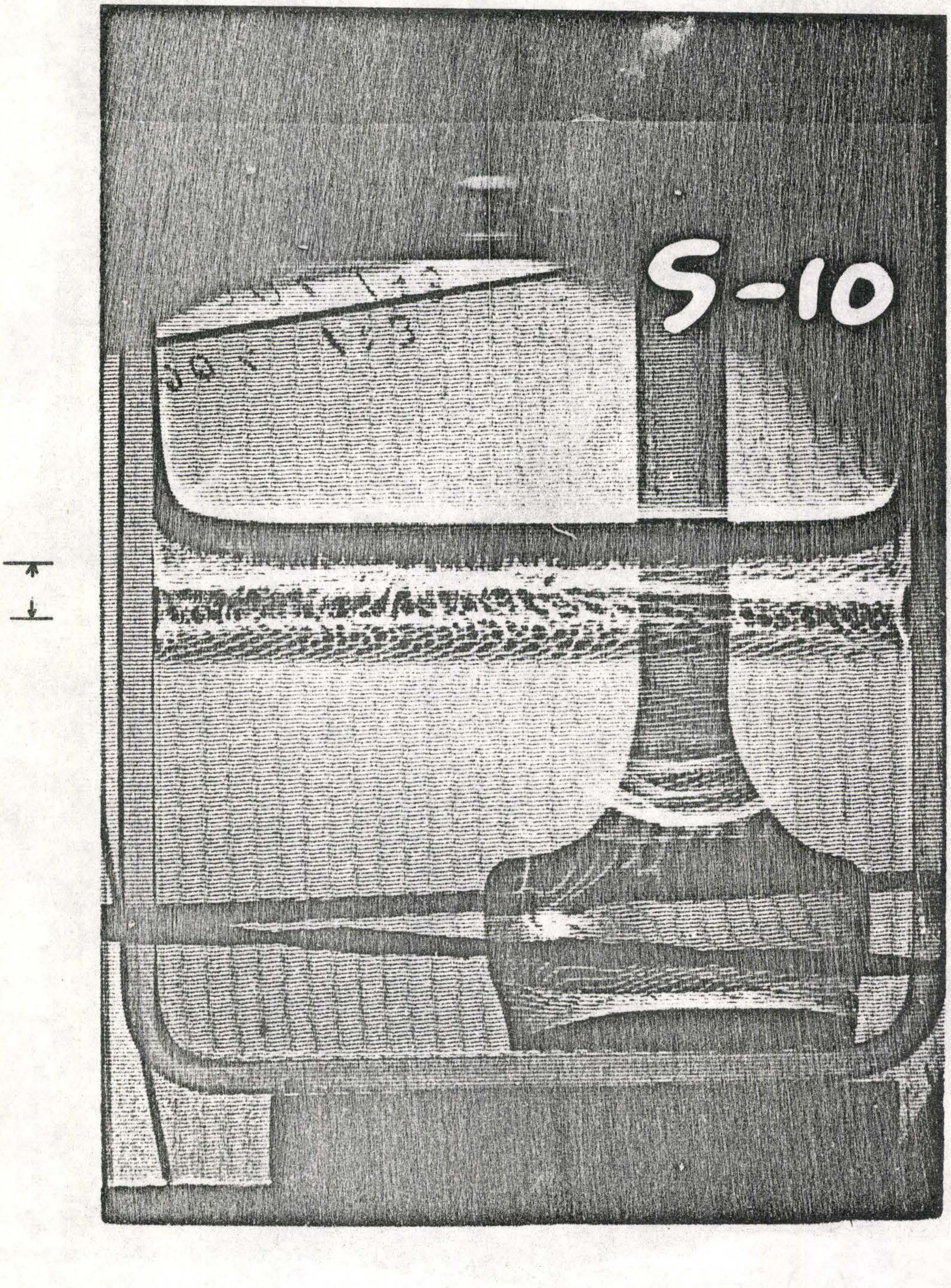

PLATE 5 ETHYL ACETATE - 2·0N NaOH SYSTEM
25 MINUTES AFTER STARTING THE RUN

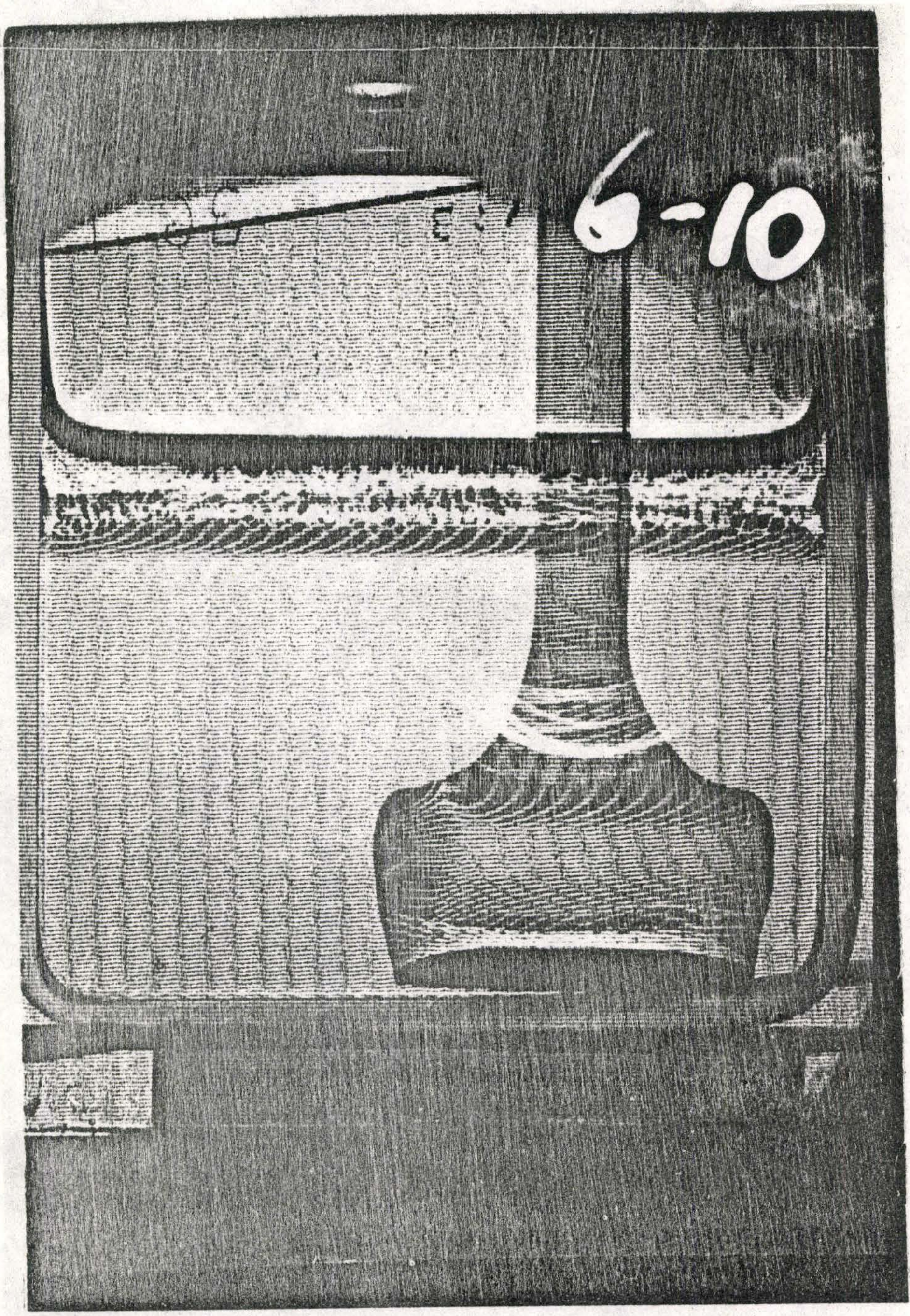

PLATE 6 ETHYL ACETATE - WATER SYSTEM
80 MINUTES AFTER STARTING THE RUN

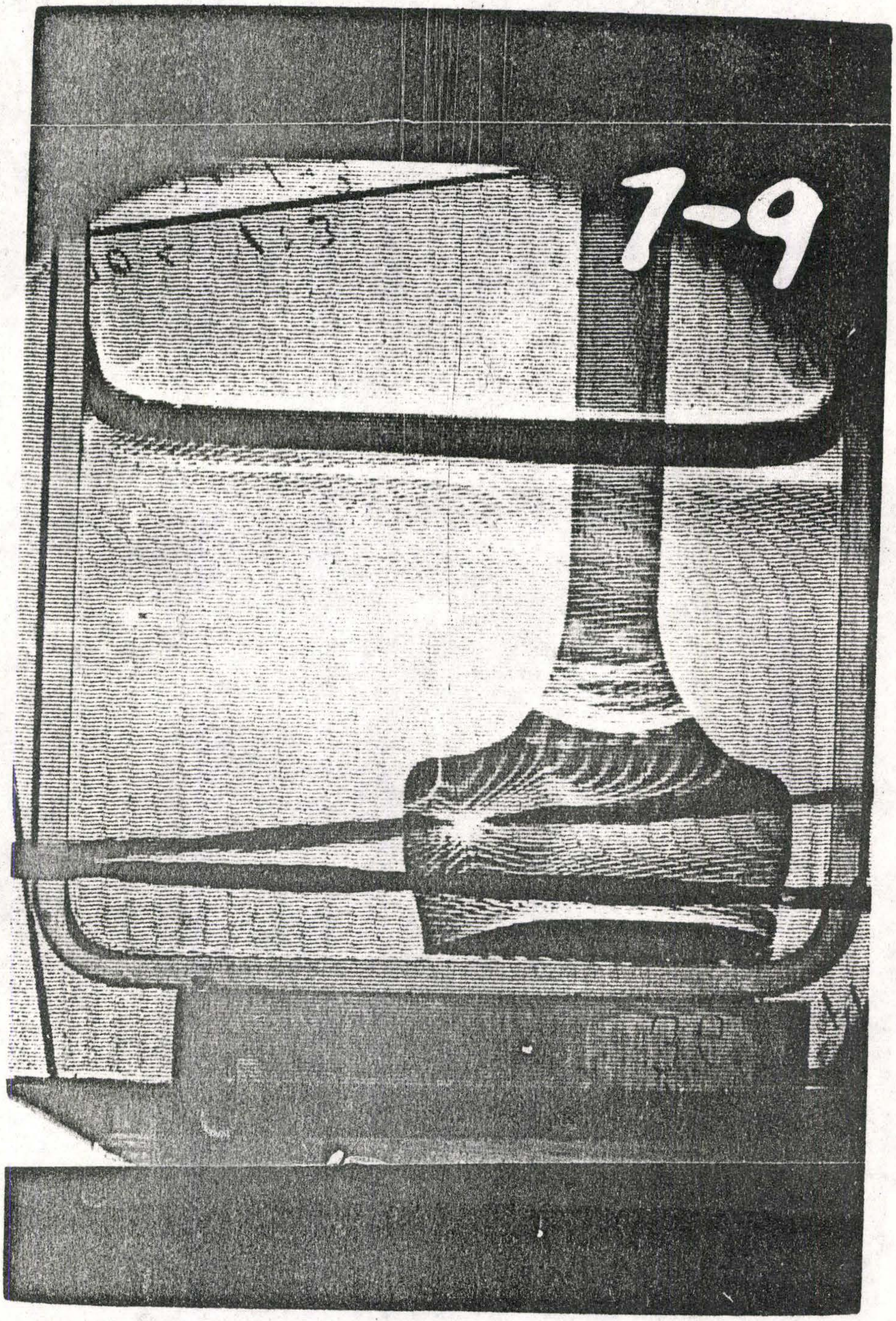

PLATE 7 ETHYL FORMATE—WATER SYSTEM
28 MINUTES AFTER STARTING THE RUN

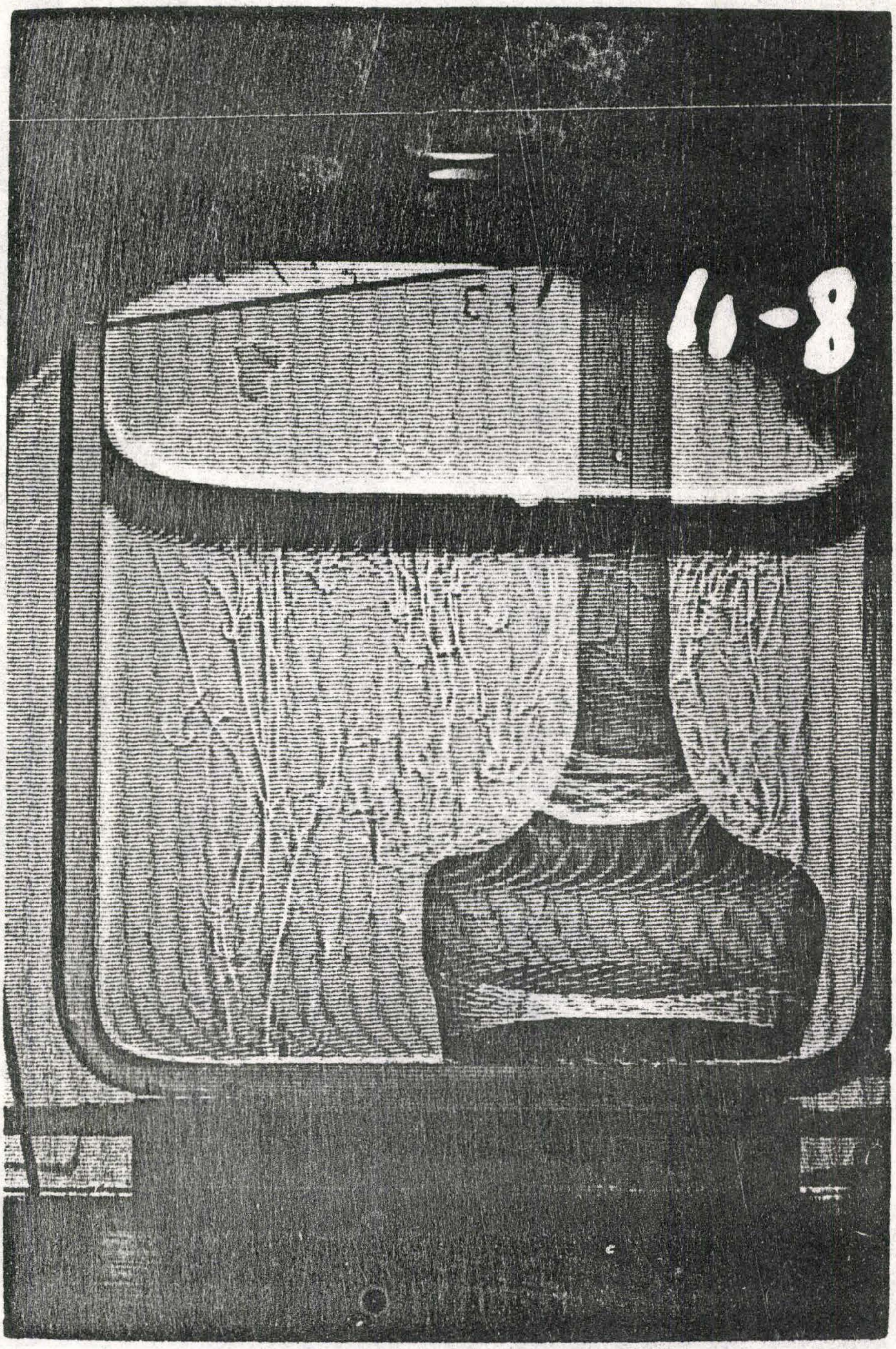

PLATE 8 ETHYL FORMATE – 0·1N NaOH SYSTEM
8 MINUTES AFTER STARTING THE RUN