SOME ANALYTICAL STUDIES

ON

NICKEL SALICYLALDOXIMATE

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By

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SCOPE AND CONTENTS:

Conditions for the precipitation of nickel salicylaldoximate from homogeneous solution were examined and procedures were recommended for the determination of nickel when present alone or mixed with some diverse ions.

The reaction between salicylaldehyde and hydroxylamine was studied in aqueous solution and some of the reaction parameters were evaluated.

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INTRODUCTION

General

The present study was undertaken as part of a general scheme with the following objectives in view: 1) the development of a suitable analytical method for a chosen metal-chelate system involving the technique of precipitation from homogeneous solution (PFHS); 2) a study of the nucleation process, and 3) a study of the mechanism of the co-precipitation process.

The technique of precipitation from homogeneous solution is adopted because it allows definite and reproducible data to be obtained in a precipitation process. The PFHS technique is a vastly improved method of controlling the rate of addition of the precipitant. It permits near equilibrium to be established between the solid (forming precipitate) and solution (mother liquor). This is a valuable feature which makes PFHS well suited for the study of the nature and extent of a co-precipitation process.

It is believed that precipitation occurs in two stages, the first involving 'nucleation' and the second a growth process. To study nucleation in a PFHS system it is essential to have a knowledge of kinetics of the reactions involved. In the present case, the kinetics of generation of salicylaldoxime is to be investigated. Hence, it is intended to study the reaction kinetics and try to establish the presence of intermediates, if any, in the reaction between salicylaldehyde and hydroxylamine. Nucleation could then be studied with nickel ion present in the reaction mixture.

The oximation reaction has been studied by several investigators. Recently, Jencks[91] showed that it is a two-step process. Either of these steps -- addition to the carbonyl group or dehydration of the adduct -- could be rate determining depending on the pH of the reaction mixture. Hileman and Gordon[93] have shown that the biacetyl-hydroxylamine reaction proceeds through formation of two carbinolamine intermediates and the slow dehydration of the initially formed intermediate determines the rate of the overall process. When nickel is also present in the system they found that formation of Ni-dimethylglyoximate proceeded by two independent paths making the nickel-dimethylglyoxime system too complex for rigorous nucleation studies. It is hoped that the nickel-salicylaldoximate system might be amenable to fruitful investigation. These kinetic and nucleation studies could be used to establish a complete model for the PFHS process which would ultimately help in the investigation of co-precipitation.

Precipitation from homogeneous solution

A precipitate produced by the conventional method of adding the reagent directly to the solution is usually voluminous, and there is possibility for excessive co-precipitation due to localised concentration gradients in the reaction mixture. If the resulting precipitates are gelatinous in nature as in the case of hydroxides of Fe, Al or Mn, they present problems in filtering and washing. It was recognised long ago[1] that slow addition of a dilute precipitant with constant stirring produced precipitates which were easy to handle analytically. The technique of precipitation from homogeneous solution evolved from such observations.

Willard and co-workers were the first to study PFHS systematically. They reported that the hydrolysis of urea or hexamine can be employed to bring the pH of the reaction mixture slowly to a desired value. For example, urea was used successfully for the separation of the basic salts[2] of aluminium, gallium, thorium , iron, lead, zirconium, tin and bismuth. However, Willard and co-workers showed that the precipitation of these basic salts depends not only on the control of pH but on the anion as well.[3] The hydrolysis reaction was also used in the precipitation of calcium as oxalate from solutions of dolomite.[4]

In recent years,a considerable amount of research was carried out on the technique of PFHS. Conditions for the precipitation from homogeneous solution may be approached in several ways. They are:

1) gradual change of pH to decrease the solubility of the desired compound;
2) generation *in situ* of the precipitant by using a controlled reaction;
3) gradual removal of one of the solvents from a mixed solvent system;
4) breakdown of a soluble complex to produce an insoluble species (ligand exchange or a redox process).

Hydrolysis of a suitable ester to produce the desired anion was successfully employed in many cases. Willard and co-workers[3] used triethyl phosphate and trimethyl phosphate for the fractional separation of zirconium and hafnium. Ross and Hahn[4] developed a method for the precipitation of bismuth as phosphate and applied this for the estimation of Bi in fusion alloys.

Methyl oxalate served as a source of oxalate for the precipitation of thorium and rare earth oxalates.[5,6] The precipitation of oxalates from homogeneous solution has resulted in better separation of the rare earth mixtures. The generation of sulphate ion is possible via hydrolysis of sulphamic acid[7,8] or potassium methyl sulphate or dimethyl sulphate.[9] Elving and Van Atta[10] reported the separation and determination of calcium, strontium and barium using dimethyl sulphate. A similar method was worked out also for the estimation of lead.[9]

Thioacetic acid or thioacetamide, on hydrolysis produces hydrogen sulphide which is employed to precipitate the sulphides of several metals qualitatively as well as quantitatively. Flashka[11] stated that the precipitates thus obtained are coarse, crystalline and easy to filter. The inherent risk of precipitating sulphur has restricted the use of this technique for the quantitative precipitation of sulphides.[12] However, conditions which permit the easy estimation of many elements have been worked out[13] carefully. Procedures for qualitative analysis[11] have also been recommended incorporating thioacetamide.

In recent years, the technique of producing the precipitant by hydrolysis of a suitable compound has been extended to the generation of chelating agents. Thus, 8-hydroxyquinoline[14], 8-hydroxyquinaldine, N-benzoylphenylhydroxylamine have been prepared by hydrolysis reactions and analytical methods developed for the estimation of many metals.

Procedures have also been worked out for the actual *in situ* synthesis of the chelating reagents. These include dimethylglyoxime,[15] cupferron,[16] furfuraldoxime, salicylaldoxime,[17] indane 1,2-dioxime, 1-nitroso,2-naphthol and quercetin. Existing data on this has been collected in a review by Firsching.[18]

Recently Jones and Newman[19] have recommended a procedure involving hydrolysis of acetamide to maintain an optimum pH for the estimation of nickel as nioxime complex. Heyn and Dave[20] have extended the technique of in situ preparation of cupferron for the estimation of copper and titanium.

Many years ago Wilson and Wilson[21] reported that highly crystalline silver halides could be produced by adding excess ammonia and simply allowing the ammonia in the reaction mixture to escape slowly into atmosphere. Recently Firsching[22] employed this method for the determination of iodide, bromide and chloride in a mixture of the three. The method was later extended to the determination of phosphate.

A variation of this procedure would be to start with mixed solvents such as alcohol-water or acetone-water in which the chelate would dissolve completely and then allowing the organic component to volatalise slowly. Howick and Jones[23] succeeded in precipitating oxinates of several metals in this way.

Thermal decomposition of peroxy complexes of Nb, Ta, W and Ti was shown[24] to be more convenient than the classical method for precipitating the hydrous acids of these metals. A change in the oxidation state of the metal could result in the breakdown of a soluble complex thus providing conditions for PFHS. Newman[25] described a procedure for precipitating cuprous thiocyanate from a Cu(11) solution.

Cartwright[26] discovered that oxidation of EDTA by hydrogen peroxide could be controlled by introducing certain metal oxides which cause decomposition of hydrogen peroxide. He utilised this method to precipitate dense and easily filterable phosphates of Bi, Fe, Pb, Ca and Ba. Release of a metal ion for precipitation can also be achieved by competing complexation. Barium was precipitated as the chromate, from a mixture of Ba, Ca, Sr and Pb present in solution as the EDTA complexes, by adding a magnesium salt solution.

By a clever use of two complexing agents HEDTA and DTPA to magnify the differences in stability of metal chelates, Firsching[28] was able to obtain an excellent separation of rare earths. Starting with equal amounts of La and Pr he showed that a 70 percent yield of Pr could be obtained in 99 percent purity in a single precipitation of the iodate.

A new method has been suggested by Klein and Fontal[29] to generate sulphate ion. The electrolytic reaction

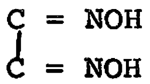
$$SCN^- + 4\ H_2O = SO_4^{--} + HCN + 7H^+ + 6e^-$$

yielded sulphate ion with hundred percent efficiency over a wide range of pH.

Many of these new approaches[30] for bringing about the conditions for PFHS appear very promising. In particular, the application of electrolysis, method of competing complexation and the method of removal of one of the solvents might be expected to result in significant developments in this field.

Oximes in analysis

Since the first report on the reactivity of dimethylgloxime[31] (DMG), many oximes have been found to possess valuable analytical properties. Most of the metal oximes obtained are colored and usually insoluble in water. The oximes may be classified as the dioximes, of which only the vicinal ones are important, the acyloin oximes, the ortho-hydroxy oximes and monoximes.

A great majority of the papers published so far in this field pertain to the use of dimethylgyloxime and this reagent has become universally accepted as the reagent for the determination of nickel. Gravimetric, colorimetric, volumetric as well as polarographic procedures have been worked out utilising DMG. The group  $\begin{array}{l} \mathrm{C = NOH} \\ | \\ \mathrm{C = NOH} \end{array}$ has been established as specific for nickel and palladium. Of the three stereo isomers of DMG (syn, anti and amphi) only the 'anti' form yields the red 1:2 chelate with nickel. The 'amphi' variety yields a yellow or greenish yellow (1:1) compound. The 'syn' form does not complex with nickel. The major disadvantage in the use of DMG is its near-insolubility in water thus requiring alcoholic solutions to be used. This presents an inherent danger of reagent contamination of the precipitates. It has also been noted that the nickel chelate becomes appreciably soluble in alcohol-water mixtures. However, methods have been devised for the determination of several metals, e.g. Ni, Pd, Co, Cu, Fe, Au, Pb and Re.[32,33]

1,2 -cyclohexanedionedioxime (nioxime)[34,35] and α-furildioxime[36] are two water soluble analogs of DMG. These reagents give red precipitates with nickel and their sensitivity to nickel is equal to that of DMG. The higher molecular weights and their solubility in water make these reagents valuable in analysis; several papers have appeared dealing with the gravimetric[37,38] and colorimetric[39] determination of metals.

4-methylnioxime and 4-isopropylnioxime have been introduced by Banks, et al.[40] as reagents for gravimetric estimation of Ni and Pd. The methyl derivative has more favourable properties than any of the vicinal dioximes studied so far. It is highly soluble in water. Nickel could be precipitated quantitatively even at low pH (3.0) and the precipitate does not creep and is very easy to handle. The 4-isopropylnioxime is shown to be more suitable for determining low amounts of nickel.[41,42] Banks[43,44] has reviewed the analytical chemistry of these reagents.

Results with cyclopentanedionedioxime were not satisfactory, but the procedures developed by Banks, et al. using heptoxime (cycloheptanedionedioxime) for the gravimetric determination of nickel were excellent. Perhaps the main disadvantage is that the preparation of the reagent is extremely difficult.

α-Benzildioxime, which is almost insoluble in water, was also recommended as a reagent for determination of Ni, Pd, Cu and Re. Both colorimetric[45,46,47] and gravimetric[48] procedures have been worked out.

Oxalene diamidoxime[49,50] and oxalene diuramidoxime[51,52] have also been tried by a few investigators. These reagents are sparingly soluble in water and have not shown any advantage over those already mentioned.

α-Benzoin oxime has received the most attention of the acyloin oxime group. It was shown[53] to react with Cu, Mo, W, Pd, Pt and Rh. The acyloin group is specific for copper provided the stereochemistry of the reagent molecule allows the formation of a chelate ring. It was found that pentanol 2-one-4-oxime does not form a water insoluble complex with copper; however, the β-oxime yields a brown complex. Procedures have been worked out for the estimation of Cu,[54] Mo,[55] W,[56] Pd,[57] Pt and Rh using the α-benzoin oxime.

Synthesis of 4-dimethylamino benzoinoxime was reported recently by Amillar[58] and the results of quantitative work are awaited.

Ephraim introduced salicylaldoxime[59] as a reagent for the detection and determination of copper and nickel. Since then this reagent and many of its derivatives have been investigated for the estimation of such metals as Zn, Cd, V, Fe, Pd, Pb and Bi.[60,61] None of the derivatives studied (5-nitro, 5-chloro, 5-methyl and 5-bromo) offer any advantage over the easily available salicylaldoxime. However, the colors of the different metal chelates with the oximes are markedly different and permit their use as reagents for detection of some of these metals. This is illustrated in the following table.

Colors of the metal chelates:

	Salicylaldoxime	5-Nitro Oxime	5-Chloro Oxime
Ag+	yellowish white	red	yellow
Au+++	brown	yellow	brown
Co++	brown	green	brown
Cu++	greenish yellow	greenish yellow	light brown
Pb++	yellow	orange	yellow
Fe+++	red	violet	blue
Ni++	green	brownish yellow	green
Bi+++	bright yellow	orange	yellow
Pd++	yellow	yellow	yellow

Howe and Mellon used salicylaldoxime for the spectrophotometric determination of iron.[62] Procedures for the determination of Pd[63] and separation of Pd[64] from the platinum metals, Ni, Fe, and Pb, have also been worked out. Spectrophotometric and solvent extraction characteristics of the Pd chelate have been studied by Martin.[65] Recently, Kiss and Ripan reported[66] a spectrophotometric study of the uranyl-salicylaldoxime system. The 1:1 chelate is orange in color and has its maximum absorption in alkaline solution (pH 8.6) at 460 mμ. Banerjee[67] found that the complex of salicylaldoxime with titanium could be extracted quantitatively into isobutanol without interference from Ca, Co, Mg, Ni, U(VI) and Cu over the pH range 4.5 to 7.0. However, Fe(III), Mo, W, and V(III) interfere in the determination of Ti.

Apart from a few initial investigations, very little interest has been shown in studying the usefulness of other hydroxy oximes such as resacetophenoneoxime,[68] respropiophenoneoxime,[69] 2-hydroxy, 5-methyl acetophenoneoxime[70] and resorcylaldoxime.[71] All these reagents are recommended for the determination of nickel and copper and the separation of copper from nickel. However, they are not in any way advantageous over the simple salicylaldoxime. Acyltetrahydronaphthaloxime has been recently synthesised and is expected[72] to be tried as a reagent for some of the bivalent metal ions.

Monoximes

Formaldoxime, the simplest in this class, forms water soluble complexes with many metals and the reaction has been exploited by many workers.

The nickel and copper complexes were studied spectrophotometrically by Bighi[73], Oaki *et al.*[74] and Sacco[75] and others. The molecular formula of the nickel complex is reported as $(CH_2NO)_6Ni\ Na_2$. The compound is insoluble in many organic solvents but highly soluble in water.

2-Thiophenetransaldoxime[76] was found to be very selective for Pd. The reagent is very stable and sufficiently soluble in water for analytical use. The precipitation of Pd is quantitative over a wide range of acidity and so close control of pH is not necessary.

Chelates of Pyridine 2-aldoxime (PAM) with copper Cu(I) and Cu(II) have been studied[77] by Daodrio and Arryo and procedures have been worked out for determination of copper.

β-Furfuraldoxime was recommended by Pshenitsyn et al.[78] and Hayes and Chandlee[79] for determining large amounts of Pd.

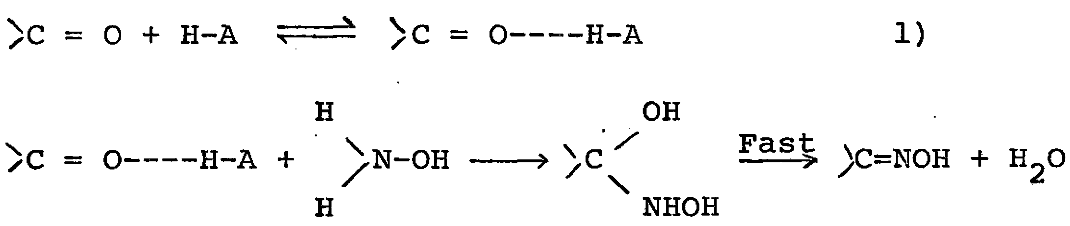
More recently, a new oxime, di-2-thienylketoxime, was introduced[80] as a reagent for the determination of Pd. Many other monoximes have been used in the extractive separation and determination of metals such as Ni, Co, Cu, Fe and Pd. α-Furilmonoxime was recommended for the determination of Co[81]. Di-1-naphthyldiketone monoxime was shown[82] to be useful for estimation of cobalt especially in the presence of large amounts of nickel and iron.

Phenyl 2-pyridylketoxime was found to be a good reagent for Pd[83] and Fe[84]. A procedure using quinoline 2-aldoxime for the extraction into chloroform, and colorimetric determination of palladium was recommended by Oi[85]. The method is particularly advantageous since many metals, e.g. Fe, Co, Ni, Ir, Ru, Rh, Pt and Cu(II) do not interfere. The same reagent could be used for extraction of the Cu(I)-chelate quantitatively. Tripathi and Banerjee[86] have recommended nicotinamidoxime for estimation of nickel.

In spite of the numerous 'oximes' already on the list for the gravimetric and colorimetric determination of many metals, efforts are still continuing to develop new procedures employing new oximes. It is, however, to be seen whether this search would bring out anything as fundamental as dimethylglyoxime itself.

Kinetics of oximation

The classical experiments of Barrett and Lapworth,[87] Olander,[88] Conant and Bartlett[89] and Westheimer[90] demonstrated that the reaction of carbonyl compounds with such nitrogen bases as hydroxylamine and semicarbazide exhibit a maxima in their pH-rate profiles. These studies have also shown that the reactions follow second order kinetics, being first order in the nitrogen base and first order in the carbonyl compound. The exact mechanism of the oximation process, however,has been the subject of active investigation and controversy. Hine proposed the following sequence of reactions.

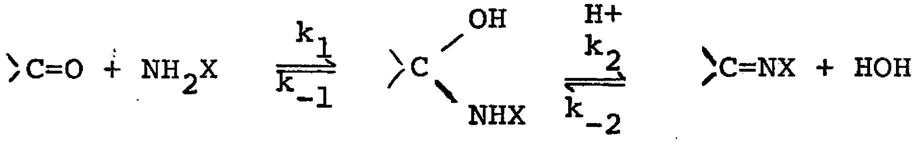


$$>C=O + H\text{-}A \rightleftharpoons\ >C=O\text{----}H\text{-}A \qquad 1)$$

$$>C=O\text{----}H\text{-}A + \underset{H}{\overset{H}{>}}N\text{-}OH \longrightarrow\ >C\begin{matrix}OH\\ NHOH\end{matrix} \xrightarrow{Fast}\ >C=NOH + H_2O$$

The increase in the overall rate of the reaction with increasing acidity was attributed to the increased concentration of the adduct in 1). At much higher acidity, more and more of the nitrogen base would get protonated thus decreasing the effective concentration of the free base. Jencks[97] studied the kinetics and mechanism of oximation with benzaldehyde, furfural, acetone, cyclohexanone and pyruvate ion, by following the changes in the UV absorption of the carbonyl compound. An initial rapid drop followed by a gradual increase in the absorption of the carbonyl compound was noticed and attributed to the formation of a carbinolamine intermediate. The addition compound might become stabilised by hydrogen bonding.

It has been suggested that at neutral pH the attack of the nitrogen base on the carbonyl compound is fast so that the overall rate is dependent on the equilibrium concentration of the addition compound and on the rate of its dehydration. The following scheme of reactions represents the situation adequately:



$$>C=O + NH_2X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\ >C\begin{matrix}OH\\ NHX\end{matrix} \underset{k_{-2}}{\overset{H+\ k_2}{\rightleftharpoons}}\ >C=NX + HOH$$

Recently, Gordon and co-workers[92,93] have studied the reaction of hydroxylamine with biacetyl. Direct proof of the presence of the intermediate was obtained by observing an absorption maximum which was not associated with either the reactants or the final products. When nickel was also present in the system, it was revealed that the intermediate formed a complex with nickel ion. This study was particularly useful in understanding the nucleation of nickel dimethylglyoximate.

In the present investigation, the kinetics of the reaction between hydroxylamine and salicylaldoxime was examined as a step in the study of the nucleation of nickel salicylaldoximate from aqueous solutions.

Also, as an integral part of this scheme, conditions for the quantitative precipitation of nickel salicylaldoximate from homogeneous solution have been studied and the method has been, incidentally, adopted for the gravimetric determination of nickel in the presence of some ferrous and nonferrous metals.

In the following pages, the results of these investigations are presented and discussed.

II

PRECIPITATION OF NICKEL SALICYLALDOXIMATE FROM HOMOGENEOUS SOLUTION

One of the objectives of the present study was the development of a gravimetric method for the determination of nickel by precipitation of nickel salicylaldoximate from homogeneous solution. The reaction between salicylaldehyde and hydroxylamine in the presence of nickel(II) was used to effect the precipitation of the chelate.

A. Experimental

1. Apparatus

A Mettler semimicro balance and calibrated pipets were used throughout the investigation. pH measurements were made with a Radiometer pH meter model 28, using a glass electrode type 202C and a saturated calomel electrode. The pH meter was calibrated with Beckman standard buffer solutions before use. Colorimetric determinations were made with a Spectronic 20 colorimeter.

2. Reagents and Solutions

A stock solution of nickel(II) was prepared by dissolving about 8.0 g of $Ni\ Cl_2 \cdot 6\ H_2O$ (Mallinckrodt. Co. New York) in one litre of distilled water. An aliquot of this solution was suitably diluted to give a working solution containing about 1 mg of nickel(II) per ml. The latter solution was standardized employing the method of Salesin and Gordon.[15] A portion of the stock solution was diluted to prepare the 5 x 10^{-5}M solution used as a spectrophotometric standard.

Solutions of other metal ions were prepared so as to contain about 5 mg of cation per ml by dissolving suitable amounts of the metal chlorides or sulphates in distilled water. All solutions were filtered before use.

A salicylaldehyde solution was prepared by dissolving about 8.0 g of the reagent in two litres of distilled water. To ensure complete dissolution, the mixture was stirred for about six hours. This solution was found to be stable for at least 48 hours.

A solution (0.02M) of quinoxaline 2,3-dithiol (Eastman Kodak Co., Rochester, N.Y.) was prepared by dissolving ~0.39 g of the reagent in 100 ml of ammonia (14M).

3. Procedures

(a) Precipitation of nickel salicylaldoximate from pure nickel salt solutions:

Preliminary investigations were conducted to determine the appropriate concentration of reagents, the temperature of reaction, the time allowed and the pH which would result in quantitative precipitation of the nickel chelate. The following procedure was found to be satisfactory.

Place an aliquot containing 2 to 75 mg of nickel(II) in a 400-ml beaker. Add an aqueous solution of ammonium chloride (1-2 g), and enough of a hydroxylamine hydrochloride solution so that about nine to twenty-five times the stoichiometric amount with respect to nickel has been added. Adjust the pH to 5.9 - 6.8 using a filtered dilute ammonia solution. Next, add a few ml of the salicylaldehyde solution and wait until a turbidity appears. Then add enough of the reagent solution so that a 3 to 15 fold excess of reagent is present in the reaction mixture. Set the mixture aside for about 4 hours at room temperature. Filter off the precipitate using a medium porosity sintered glass crucible, wash the precipitate thoroughly with distilled water and dry it at 110°C to constant weight.

(b) Precipitation of nickel Salicylaldoximate from nickel(II) solutions containing diverse ions:

The sequence of addition of the reagents is the same as that given above except that tartaric acid (2.0 g) must be added before the pH is adjusted. The amounts of hydroxylamine and salicylaldehyde have to be increased proportionately, taking into account the consumption of the reagent by the cations of metals such as zinc, manganese, vanadium, chromium, aluminium and iron, which form soluble complexes with salicylaldoxime.

(c) Determination of nickel in a steel sample:

The procedure described above yielded analytical recovery of the nickel and stoichiometric precipitates of the chelate only when small amounts (~20 mg) of Fe(II) were present in the reaction mixture. However, in the presence of large amounts (~100 mg) of iron the separation of nickel became more complicated. Preliminary studies on the effect of iron have lead to the following procedure for the determination of nickel in a steel sample.

Weigh out accurately a suitable amount of the steel sample into a porcelain dish and dissolve it in a mixture of hydrochloric and nitric acids. Wait until a clear solution is obtained and then transfer the contents carefully to a 500-ml volumetric flask and dilute to volume with distilled water. Pipet out twenty-five or fifty millilitre portions of this solution into separate beakers. To each of these, add aqueous solutions of 3 - 3.5 g of tartaric acid, 2 g of ammonium chloride and depending on the aliquot, about 2.5 or 5.0 g of hydroxylamine hydrochloride, in that order. Adjust the pH of the resulting solution to 6.0-6.5 using filtered dilute ammonia. Then add enough of a freshly prepared aqueous solution of salicylaldehyde so that the reagent is in 20-25 fold excess. Allow the reaction mixture to stand for 14-16 hours at room temperature. Filter off the precipitate using a medium porosity sintered glass crucible, wash with about 100 ml of distilled water and dry it at 110°C to constant weight.

(d) Conventional procedure for the precipitation of nickel salicylaldoximate:

A few estimations were carried out using a procedure similar to that recommended by Riley.[94] Two,ten and twenty millilitre aliquots of the nickel(II) solution (~1 mg/ml) were transferred into separate 400-ml beakers. About 50 ml of distilled water were added to each and the pH of each solution was then adjusted to ~6.5 using dilute ammonia. Then a freshly prepared solution of salicylaldoxime was added to the metal solution in an amount such that the reagent was about two-fold in excess of the stoichiometric requirement. The total volume of the solution was brought to about 200 ml with distilled water. The mixture was stirred well and allowed to stand for 3 hours. It was then filtered into a medium porosity sintered glass crucible. The precipitate was washed with distilled water and then dried at 110°C to constant weight.

(e) Determination of nickel(II) content of the filtrate:

A few representative filtrates were collected and treated in the following manner. The filtrate was first evaporated to dryness. The organic content of the residue was then destroyed by repeated addition of nitric acid and evaporation to dryness. The resulting residue was dissolved in distilled water and made up suitably in a volumetric flask. The nickel content of this solution was estimated colorimetrically.

A Beer's law plot was first prepared using the following procedure. Different aliquots of the spectrophotometric standard solution of nickel were transferred into several 25-ml volumetric flasks. Ten millilitres of ammonia and three millilitres of the reagent (quinoxaline 2,3-dithiol) solution were pipetted into each flask and the solution was made up to the mark with distilled water. The absorbance of each of these solutions was measured at 520 mμ. The blank solution was prepared in the same manner except that the nickel(II) was not added.

Test solutions prepared from the filtrate samples were treated as described above and the absorbances were noted. The nickel content of these solutions was then estimated from the Beer's law plot.

B. Results and Discussion

A preliminary study of the precipitation of nickel salicylaldoximate from homogeneous solution was undertaken to select the optimum conditions for quantitative recovery of nickel. The investigation consisted of obtaining data on the effect of each of the variables--temperature, pH, reaction time, and reagent excess--on the yield of the nickel chelate.

It was found that when the reaction was carried out in hot solution the recovery of nickel was not complete and the precipitate was difficult to handle as it had a tendency to adhere to the container. The low yield was probably due to loss of salicylaldehyde by decomposition and/or evaporation. Hence all subsequent experiments were conducted at room temperature.

Based on the procedure outlined in section II, the effect of pH on the recovery of nickel was studied. The results are shown in Fig. 1. As can be seen, the precipitation was quantitative in the pH range 5.9 - 6.9. The recovery of nickel was low on either side of this range. The sharp rise on the acidic side of the curve would indicate that control of pH is more critical on the acidic side than on the basic side. Also it can be seen from the two curves that the quantitative range of precipitation could be extended to pH 7.5 by increasing the reaction time to 12 hours. However, a prolonged reaction time did not have any effect on the yield of the nickel chelate when precipitation was made at pH 5.8 to 6.5. The pH range for the quantitative yield of nickel chelate also coincides with the nearly neutral conditions recommended by Riley[94] and by Flagg and Furman.[60]

The effect of reaction time on the precipitation of nickel was studied and some of the results are collected in Table I. In this study, all other reaction variables such as pH, excess reagent and temperature were kept the same for each experiment and only the reaction time was varied. The results showed that a time of about 3 hours is required for complete precipitation of nickel.

The effect of varying the amount of reagent in the reaction mixture on the precipitation of nickel chelate was studied. The results are shown in Fig. 2.

Fig. 1. Percent precipitation versus pH for the precipitation of nickel salicylaldoximate.

○ - Standing time 4-6 hr.

△ - Standing time 12 hr.

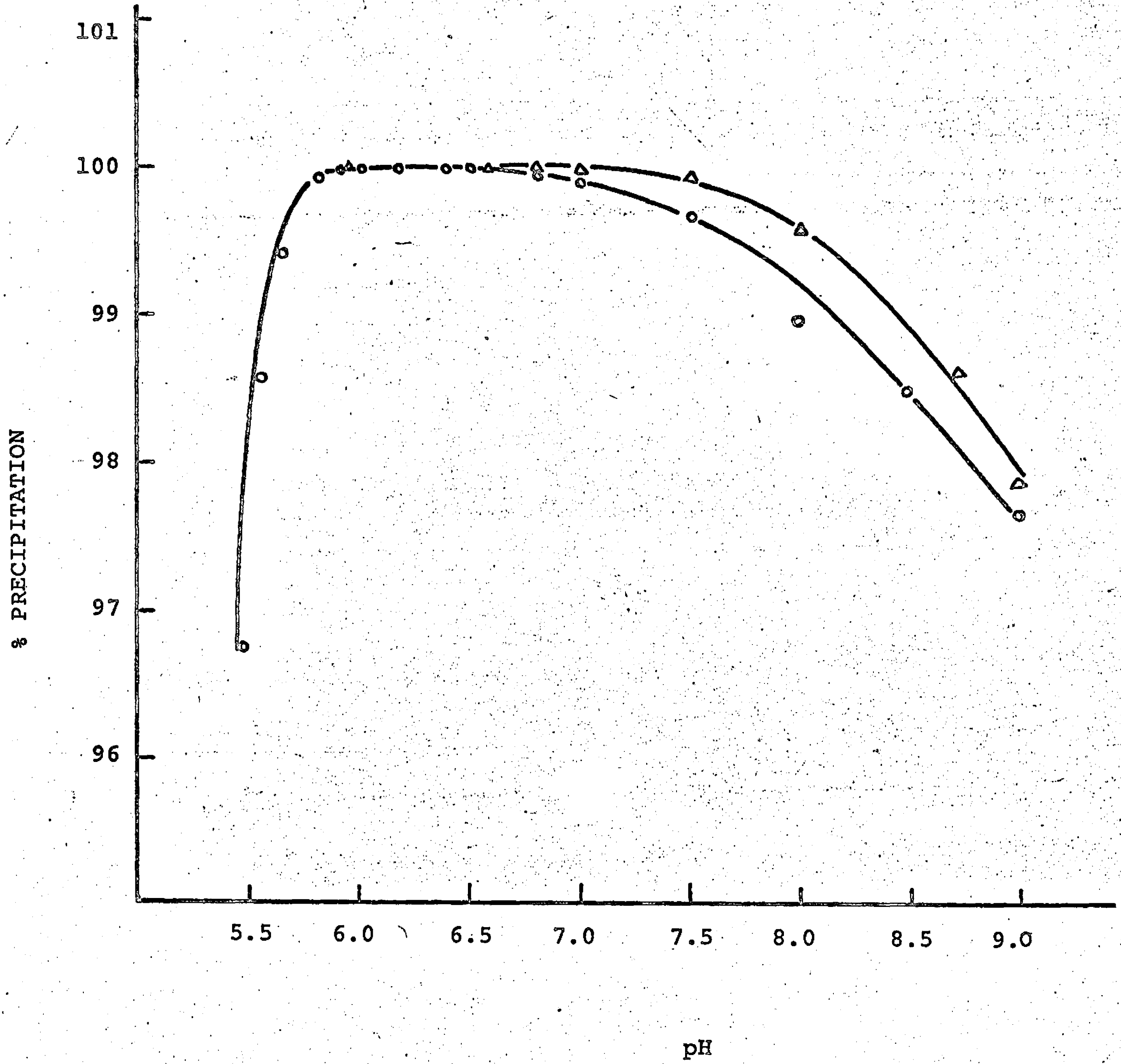
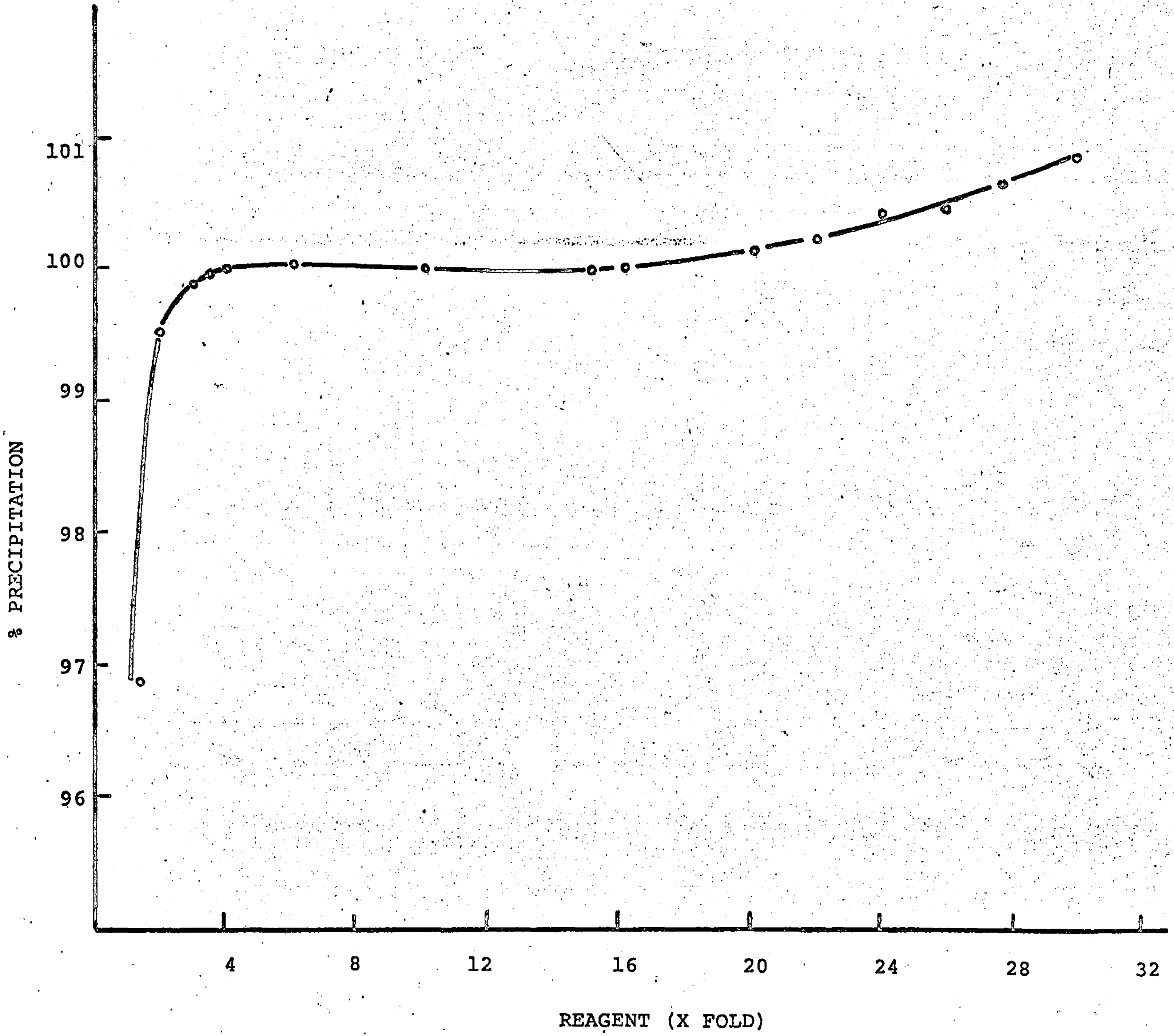

101
100
99
98
97
96
% PRECIPITATION
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
pH

TABLE 1

Effect of Reaction Time on Yield of Nickel Chelate

Time (min.)	Nickel Obtained (%)	Reaction Conditions:
60	94.00	The precipitations were made at room temperature from solutions containing salicylaldehyde in three fold excess and hydroxylamine hydrochloride in nine fold excess. The pH was adjusted to 6.3 in each case.
120	98.90	
150	99.50	
180	99.92	
200	99.96	
600	100.00	
1000	99.99	

Fig. 2. Percent precipitation versus reagent excess for the precipitation of nickel salicylaldoximate.


% PRECIPITATION
101
100
99
98
97
96
4
8
12
16
20
24
28
32
REAGENT (X FOLD)

As can be seen from the graph, the precipitation was complete over a wide range of reagent concentration. In the analytically useful range of the reagent excess, two possibilities may give rise to the plateau. First, the recovery of the nickel may be complete. Second, a compensation of errors resulting from loss of nickel due to solubility of the chelate in excess reagent balanced by coprecipitation of the reagent could produce a precipitate with the correct weight. In order to decide between these two possibilities, some of the filtrates were analyzed to determine their nickel content. This was done by using 2,3-quinoxaline-dithiol[95] as a colorimetric reagent. The results are shown in Table II. It can be seen that the nickel was quantitatively precipitated under these experimental conditions. After establishing the conditions for quantitative precipitation of nickel salicylaldoximate, the procedure described in Section II-A-3 was employed to separate nickel(II) from some of the common metal ions.

Salicylaldoxime forms complexes with many metals, for example, Ni, Cr, V, Mn, Zn, Al, Fe, Cd, Co, Cu and Pd. These complexes differ widely in their stability, solubility in water and the pH of incipient precipitation. Hence in computing the amount of salicylaldehyde required for precipitating nickel from any mixture of metals, allowance must be made for reagent consumption by the diverse ions.

TABLE II

Estimation of Nickel Content of Some Filtrates

Excess Reagent Employed (X Fold)	Amount of Nickel Taken (mg)	Nickel Found in the Filtrate (mg)
3	10.06	0.01 0.02
4	10.06	0.02 0.02
6	21.12	0.06 0.04 0.04
8	21.12	0.03 0.05 0.04

The initial attempts to separate nickel from the diverse ions were not successful. Accordingly, EDTA, citric acid and tartaric acid were tried as masking agents for the interfering ions. While EDTA and citric acid prevented, to a large extent, the precipitation of nickel salicylaldoximate, it was found that tartaric acid eliminated the interference of other metal ions. Some results of these studies are shown in Table III. Analysis of the precipitates indicated that the nickel chelate obtained was nearly free of contamination from all ions except cobalt and copper.

Although tartaric acid was found suitable as a masking agent in most cases, it could not be used when cadmium was present due to the formation of an insoluble cadmium tartrate salt. To overcome this difficulty, a more detailed study of the effect of pH on the precipitation of cadmium salicylaldoximate was undertaken. The pH of incipient precipitation of the cadmium chelate was found to be 6.5. Further experiments showed that nickel could be separated from cadmium if the pH of the solution was kept below 6.3.

Separation of nickel from copper or cobalt was not successful. Copper salicylaldoximate is known to precipitate from solutions in varying amounts over a wide range of pH (2.8 - 8.5). So it would appear that prior removal of copper, say by electrolysis, is necessary. Cobalt also behaves in a similar manner but it was not investigated in detail.

TABLE III

Effect of Some Diverse Ions on the Precipitation of Nickel-Salicylaldoximate

Foreign ion:	Tartrate	Mn	Zn	Al	Cd	Cr	Cu		Co
Amount of foreign ion taken (mg):	2000	50	100	100	50	50	10	50	20
Error in amount of nickel found (mg):	-0.02	-0.02	-0.01	-0.02	+0.01	-0.02	+1.0	+5.0	+3.0
	-0.01	-0.03	±0.00	+0.01	-0.03	-0.02	+1.2	+4.9	+3.1
	+0.01	±0.00	+0.02	-0.01	-0.02	+0.02			

(a) Amount of nickel taken in each case was 10.62 mg.

(b) Two grams of ammonium tartrate used in all except cadmium.

(c) pH was adjusted between 6.0 - 6.3 when cadmium was present. In other cases it was 6.0 - 6.8.

Tartaric acid prevented interference from small amounts (<20 mg) of iron but the situation became complicated when large amounts of iron (~100 mg) were present. It was found that when iron was present in the system the amount of nickel chelate precipitated depended on the amount of hydroxylamine hydrochloride present, excess reagent employed, reaction time allowed and the amount of tartaric acid added to the reaction mixture.

Results of some of these investigations are shown in Table IV. The presence of iron has a retarding effect on the reaction. At least 14 hours of reaction time was needed in contrast to the 3 hours required in the absence of iron. Salesin and Gordon[15] reported similar observations in their study of the precipitation of nickel dimethylglyoximate from homogeneous solution. A reaction time of 24 hours was found necessary when iron was present in the solution whereas a 2-3 hour period sufficed in its absence.

The general procedure developed during this study of separation of nickel from iron was then adopted to analyze a steel sample. The results of the analysis are presented in Table V. An average value of 11.12 percent nickel with a standard deviation of 0.054 was obtained when 50-ml aliquots were used. This analysis compares favourably with the certificate value of 11.14 percent nickel in the sample. When small aliquots (containing about 5 mg Ni) were employed the results were slightly lower.

TABLE IV

Precipitation of Nickel Salicylaldoximate in Presence of Iron

Excess Reagent[d] Added (X fold)	Tartaric Acid Added (g)	Error in Amount of Nickel Obtained (mg)[a]	Iron Found in the ppt. (mg)[b]
15	3.0	−0.12	0.00
20	2.5	+0.01	0.08
		+0.06[c]	0.05
20	3.0	−0.06	0.01
20	3.5	−0.06	0.00
20	4.0	−0.09	0.00
24	3.0	−0.05	0.06
25	2.5	+0.10	0.10
25	3.5	−0.06	0.02
25	6.0	−0.20	0.00

(a) Amount of nickel taken was 9.92 mg. About 100 mg of Fe^{+3} were present in each case.

(b) Iron was estimated colorimetrically by thiocyanate method.[96]

(c) A reaction time of 18 hours was allowed. All other determinations were within 15 hours.

(d) Hydroxylamine hydrochloride was in 200 to 300 fold excess.

TABLE V

Determination of Nickel in a Steel Sample

(NBS No.121b)

Vol. of Sample* Solution Taken (ml)	Nickel Obtained† (calc. as percent)	Iron Content in the ppt. (mg)
25.0	11.06	0.00
	11.05	0.00
	11.08	0.02
50.0	11.06	0.00
	11.12	0.04
	11.18	0.06
	11.19	0.06
	11.12	0.02
	11.09	0.09
50.0**	11.00 (a)	0.08
	10.04	0.08
	11.89 (b)	0.65
	11.91	0.68

---

* 1.00 g. of steel was dissolved and made up to one litre.

** Results obtained with the conventional procedure employing

(a) standing time of 6 hours.
(b) standing time of 16 hours.

† NBS certificate value for nickel content was 11.14 percent.

All the PFHS procedures reported in literature so far, with a few exceptions, have been shown to be significantly better than the conventional procedures of precipitating the metal chelate. In the case of copper-salicylaldoximate, however, it was noted that the conventional procedure yielded better results particularly when copper was mixed with other ions. Hence, in the present investigation, it was felt that a comparative study of the two procedures was in order.

Riley[94] recommended a procedure using salicylaldoxime for separating copper and nickel in which he employed 'sufficient' reagent to be in slight excess and precipitated the copper chelate at pH$\sim$3.0. Then the filtrate was almost neutralised with ammonia and the solution was either left overnight or stirred to coagulate the nickel precipitate. In the present study a two-fold excess of reagent was used. The total volume of reaction mixture as well as the total reagent concentration were kept identical in both the procedures. The results obtained by using the procedures outlined in section II-A are shown in Table VI. It can be seen that the conventional procedure gave rise to positive errors indicative of contamination of the precipitate. It might have been possible to obtain more quantitative and acceptable results by employing less amount of reagent such as 11/10 - 15/10 fold excess.

The results of the estimation of the nickel content in the steel sample by the conventional procedure are shown

TABLE VI

Comparison of the Conventional and PFHS Procedures for Precipitating Nickel Salicylaldoximate

Amount of Nickel Taken (mg)	Error in Amount Found (mg)	
	Conventional	PFHS
2.12	-0.06	-0.01
	-0.06	-0.02
	-0.07	-0.01
10.62	+0.05	-0.01
	+0.06	±0.00
	+0.08	-0.03
	+0.08	-0.01
21.24	+0.08	-0.01
	+0.08	-0.02
	+0.10	±0.00

in Table V. When a standing time of 6 hours was allowed, the precipitation was far from complete while after a 16 hour period there was considerable coprecipitation. Thus it was very difficult to separate nickel from iron when the conventional method was adopted. These observations have confirmed the expected superiority of the PFHS techniques over the conventional method in producing precipitates of desirable quality.

III

STUDIES ON THE OXIMATION REACTION OF SALICYLALDEHYDE

This part of the investigation was conducted in order to study the kinetics of the reaction between salicylaldehyde and hydroxylamine. The reaction conditions were similar to those used in the gravimetric procedure for nickel salicylaldoximate outlined in section II. As aqueous solutions of salicylaldehyde and salicylaldoxime have characteristic spectra in the ultra violet region, progress of the reaction was followed by observing the changes in absorbance of the reaction mixture as a function of time.

A. Experimental

1. Apparatus

A Bausch and Lomb 'Spectronic 600' spectrophotometer was used to obtain all spectrophotometric data. The instrument has a tungsten lamp for the visible region and a deuterium lamp for the 200 - 340 mμ range.

A Sargent model SRL Recorder was used in conjunction with the spectrophotometer. The instrument can record either percent transmission or absorbance and has three chart drive speeds.

A constant temperature bath FORMA-TEMP (Sargent Co., Toronto) was used for temperature control. Glass syringes (Hamilton Co., Whittier, Calif.) of one, two and five millilitre capacity were used for transferring the solutions into the reaction cell.

Two types of quartz absorption cells were used in these experiments. One was square with an optical path length of one centimeter. The other was cylindrical in shape with an optical path length of five centimeters. The latter cell was water jacketed to facilitate temperature control.

2. Reagents and Solutions

Salicylaldehyde (Fisher Scientific Co., Fairlawn, N.J.) was purified by vacuum distillation. Salicylaldoxime was purified by re-crystallising from alcohol. Hydroxylamine hydrochloride was purified by re-crystallising from alcohol containing a few millimeters of distilled water.

An aqueous solution ($\sim 4 \times 10^{-4}$M) of salicylaldoxime was prepared by dissolving ~60 mg in one litre of filtered distilled water.

This solution was kept in the constant temperature bath for at least 12 hours before use. Aqueous solutions of salicylaldehyde which had aged for periods longer than 48 hours were not used.

3. Procedures

(a) Determination of some characteristics of the ultraviolet spectra of salicylaldehyde and salicylaldoxime:

Salicylaldehyde solutions of suitable dilution were taken in a 1.0 cm quartz cell and the spectrum was recorded over the 200 - 340 mμ range using distilled water in the reference cell. The absorption maxima were located and the effect of pH and salt concentration on these peaks were studied.

Ten-millilitre aliquots of the salicylaldehyde stock solution were pipetted into several 100-ml volumetric flasks and diluted with distilled water almost up to the mark. Then, varying amounts of very dilute ammonia were added to each flask and the solutions were brought to volume. The pH of each of these solutions was noted. Absorption spectra were recorded for these solutions. Next, another set of solutions was prepared in 100-ml volumetric flasks each containing 10 ml of salicylaldehyde stock solution and 10 to 30 ml of ammonium chloride solution (4M and the pH adjusted to 7.0 with dilute ammonia). Spectra were recorded for these solutions against appropriate blank solution. Later, a few solutions were prepared which contained the same amount of salicylaldehyde stock solution and the pH was adjusted to 6.0 - 7.5 using a dilute sodium hydroxide solution. Absorption spectra were obtained for these solutions using distilled water as the blank solution.

Procedures which were identical to those mentioned above were adopted to study the spectral characteristics of aqueous salicylaldoximate solutions.

(b) Determination of the isosbestic point of the salicylaldehyde-salicylaldoxime system:

Equimolar solutions of salicylaldehyde and salicylaldoxime were prepared by diluting appropriate amounts of the stock solutions in separate 100-ml volumetric flasks. A solution of ammonium chloride (4M) was prepared and the pH was adjusted to 7.00± 0.02 using dilute ammonium hydroxide. A set of volumetric flasks of ten-millilitre capacity was taken and one ml of the ammonium chloride solution was placed in each flask. Then aliquots of 9, 7, 6, 3, 2 millilitres of salicylaldoxime solution were transfered into five of the flasks. Next, complementary amounts of salicylaldehyde solution were pipetted into each flask making up the volume to 10 ml in each case. The solutions were mixed thoroughly and the absorption spectrum of each solution was recorded in the ultraviolet region.

(c) Determination of the kinetics of the reaction at 304 and 325 mμ:

The oximation reaction was followed by observing the changes in the absorption maxima of the reaction mixture with time. The following procedure was adopted.

The absorption cells were cleaned thoroughly and matched before use. The stock solution of hydroxylamine hydrochloride was diluted(ten-fold) and used as a blank solution in the reference cell. The recorder was kept ready by selecting the chart speed and setting the zero position of the pen. Two millilitres of salicylaldehyde stock solution were transfered into the reaction cell. The wavelength selector on the B&L 600 was set at 325 mμ. Then one ml of hydroxylamine solution was quickly transferred into the reaction cell and the recorder was started. After mixing the solutions thoroughly, the cell was placed in the cell compartment and the absorbance was recorded as a function of time. After a lapse of 30 seconds, the wavelength was dialed to 304 mμ and the absorbance was again recorded. From then on, by switching between these two wavelengths at suitable intervals of time, a composite record of absorbances at 325 mμ and 304 mμ was obtained as a function of time. The same procedure was repeated several times to test the reproducibility of the spectral records obtained. Next, a salicylaldehyde solution of different concentration (6.5×10^{-5}M) was used and, employing the same procedure, absorbance versus time data were obtained.

(d) Determination of the kinetics of the oximation reaction at the isosbestic point:

The following procedure was adopted to obtain data on change in absorbance of the reaction mixture at the isosbestic point.

Working solutions of 2.25×10^{-5}M salicylaldehyde were prepared by suitably diluting an aliquot of the stock solution. These solutions were kept in a constant temperature bath for about 12 hours before use. A cylindrical cell with a 5.0 cm path length and an outer jacket to circulate thermostated water was used in all the experiments. The reference cell was filled with diluted (1:10) hydroxylamine stock solution.

Using a 5-ml syringe, exactly 2.5 ml of salicylaldehyde solution were transferred into the reaction cell. Thermostated water (14.9°C) was allowed to circulate through the reaction cell during the entire experiment. Exactly 0.3 ml of the hydroxylamine stock solution was transferred into the reaction cell using the 1-ml syringe. The recorder was turned on simultaneously. The solutions in the cell were mixed well by gently shaking the cell. The absorbance was recorded continuously for about thirty minutes and later at intervals. Then salicylaldehyde solutions of different concentrations (2.45×10^{-5} and 2.80×10^{-5}M) were employed and the absorbance versus time data were obtained in each case in the manner described above.

The above experiments were then repeated employing the constant temperature bath adjusted to different temperatures (20.1° and 24.9°C ± 0.1). Results of these studies are presented and discussed in the following pages.

B. Results and Discussion

The absorption spectra of aqueous solutions of salicylaldoxime and salicylaldehyde revealed that each has three absorption peaks in the ultra violet region. These spectra are shown in Fig. 3. Sone[97] and Lemon[98] have previously reported the absorption spectra of these compounds in alcoholic solutions. They were able to locate two peaks, one at 260 mμ and another at 305 mμ, for

Fig. 3. Spectra of salicylaldehyde (A) and salicylaldoxime (B). (Discontinuity in B was due to change in scale.)

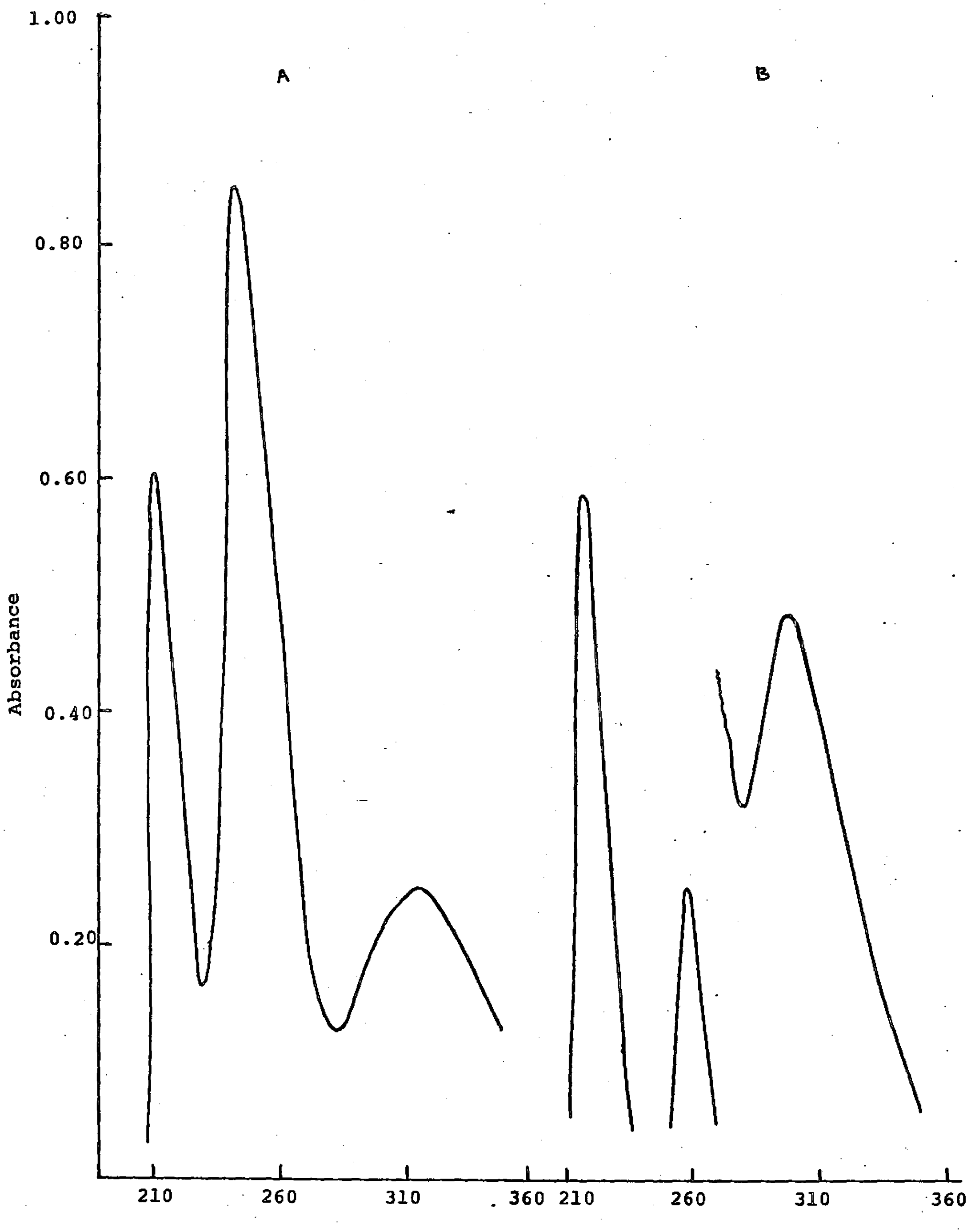

1.00
0.80
0.60
0.40
0.20
Absorbance
A
B
210
260
310
360
210
260
310
360
Wavelength mμ

Fig. 3

salicylaldoxime and ~260 mμ and 325 mμ for salicylaldehyde, but missed the ~210 mμ peak as they studied the spectra only in the 230 - 340 mμ range. The results of the present study are in general agreement with their observations.

Further study showed that the absorption maxima for salicylaldehyde were sensitive to the ammonium ion concentration and to the pH of the solution. The peak at 326 mμ was shifted toward shorter wavelengths when the solution contained ammonium salts. The peak height also was reduced in such solutions. Hence it was necessary to obtain the apparent extinction coefficients of the various peaks at the pH and ionic concentrations which were to be used in the study of the salicylaldehyde-hydroxylamine reaction.

The absorption maxima of salicylaldoxime solutions did not show any sensitivity to changes in pH or ammonium ion concentration in the ranges studied. The absorption peak at 304 mμ was selected to follow the changes in the salicylaldoxime concentration because it was sufficiently separated from the aldehyde peak at 325 mμ that minimum interference was anticipated.

The extinction coefficients obtained from this study are as follows:

Salicylaldehyde E_{325} 2495 and E_{304} 1535
Salicylaldoxime E_{325} 850 and E_{304} 3320

Experiments were then conducted to collect data on the concentrations of salicylaldehyde and salicylaldoxime in the reaction mixture as a function of time. This was done by mixing known amounts of salicylaldehyde and hydroxylamine solutions and noting the absorbances of the mixture at 325 mμ and 304 mμ at various times. A section of the plot of absorbance versus time for one such experiment is shown in Fig. 4.

The concentrations of salicylaldehyde and salicylaldoxime in the reaction mixture were calculated from this data utilizing the following equations:

$$A^{325} = E_{s}^{325}\,[s]\,1 + E_{ox}^{325}\,[ox]\,1$$

$$A^{304} = E_{s}^{304}\,[s]\,1 + E_{ox}^{304}\,[ox]\,1$$

where

A = absorbance of the solution at the wavelenths (mμ) indicated by superscript.

E = extinction coefficient for the species indicated by the subscript at the wavelength noted as superscript.

s = salicylaldehyde

ox = salicylaldoxime

[ ] = concentration of the species within brackets.

The results of some of these calculations are shown in Table VII.

It can be seen from Table VII that the sum of the salicylaldehyde and salicylaldoxime concentrations at any time during the reaction was not equal to the initial

Fig. 4. Absorbance versus Time for the salicylaldehyde-hydroxylamine system. (Curve A at 304 mμ and curve B at 325 mμ. Both were recorded simultaneously on the same chart.)

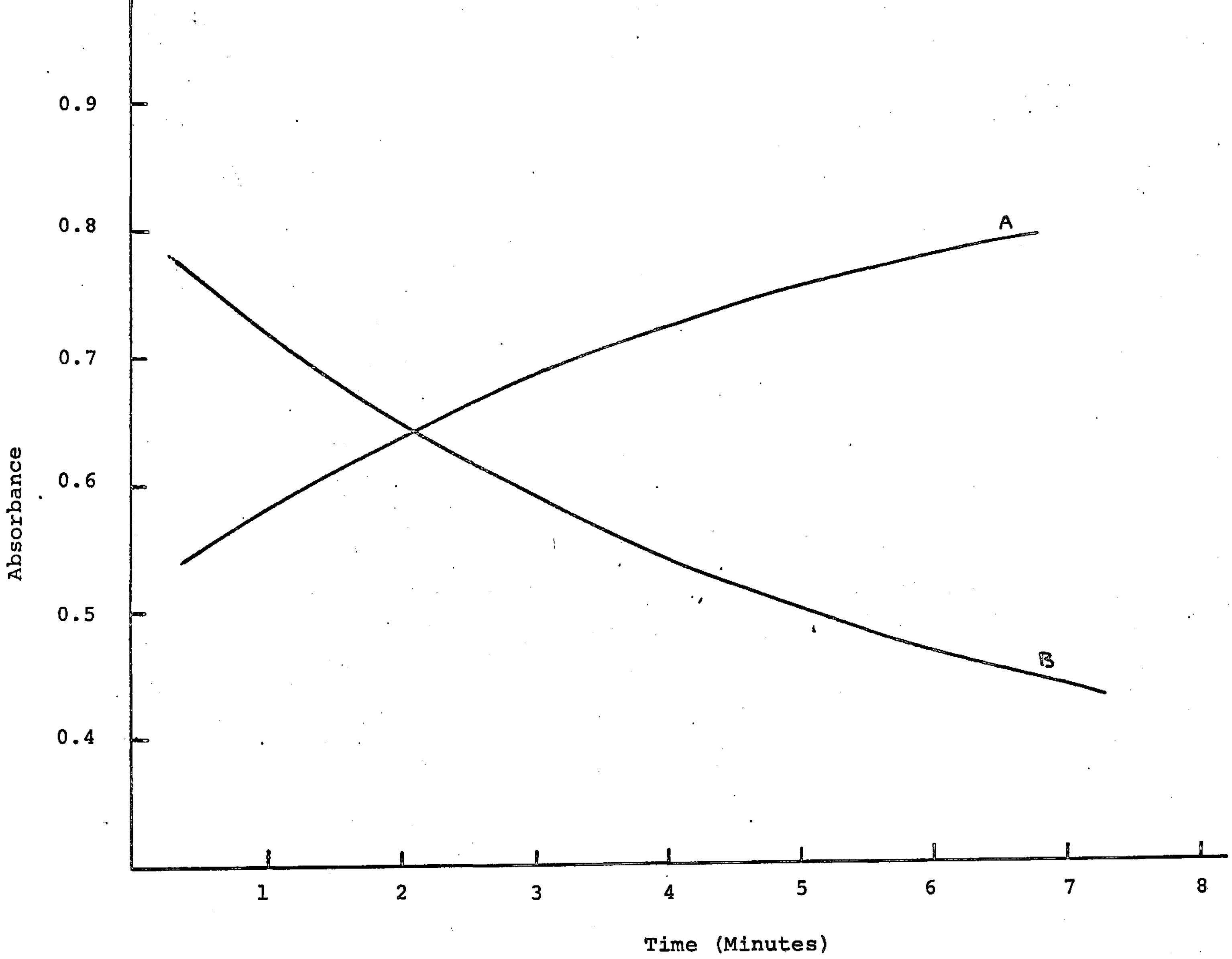


Fig. 4

TABLE VII

Results of Calculation of the Amounts of Salicylaldehyde and Salicylaldoxime in the Reaction Mixture

		Concentration of absorbing species			
	Time (minutes)	Aldehyde	Oxime	Total	
Set 1.					
	0	3.28	0.00	3.28	(x 10^4M)
	0.5	2.93	0.31	3.24	
	1.0	2.70	0.52	3.22	
	1.5	2.51	0.68	3.19	
	2.0	2.27	0.89	3.16	
	3.0	1.95	1.19	3.14	
	3.5	1.70	1.40	3.10	
Set 2.					
	0	6.56	0.00	6.56	(x 10^5M)
	0.5	5.91	0.61	6.51	
	1.0	5.47	1.02	6.49	
	1.5	5.15	1.31	6.46	
	2.0	4.92	1.53	6.45	
	2.5	4.70	1.72	6.42	
	3.0	4.53	1.87	6.40	
	3.5	4.34	2.05	6.39	

salicylaldehyde concentration. This lack of mass balance clearly pointed to the formation, in the reaction mixture, of a third species which may or may not absorb in the 300 - 330 mμ region. A new series of experiments was then initiated to obtain information about this compound.

The salicylaldehyde-salicylaldoxime system was studied closely to detect an isosbestic point in their spectra. This was done in the following manner. Mixtures containing complementary amounts of equimolar solutions of salicylaldehyde and salicylaldoxime were prepared such that the total volume and total molarity was the same in each mixture. Absorption spectra were then recorded for each of these solutions in the 200 - 330 mμ range. A composite record of these spectra is shown in Fig. 5. An isosbestic point is evident at 321.4 mμ.

By definition, the absorbance of a reaction mixture containing salicylaldehyde, hydroxylamine and salicylaldoxime, at the isosbestic point, must remain constant as long as the total molarity of the salicylaldehyde and salicylaldoxime is constant. Any deviation from this necessarily indicates the presence of an extra species formed in the reaction mixture. Thus, if the progress of the reaction between salicylaldehyde and hydroxylamine was followed by noting the absorbance at the isosbestic point as a function of time, it would be possible to confirm the formation of a new species in the reaction mixture.

Fig. 5. Absorption spectra of various mixtures of salicylaldehyde and salicylaldoxime solutions.

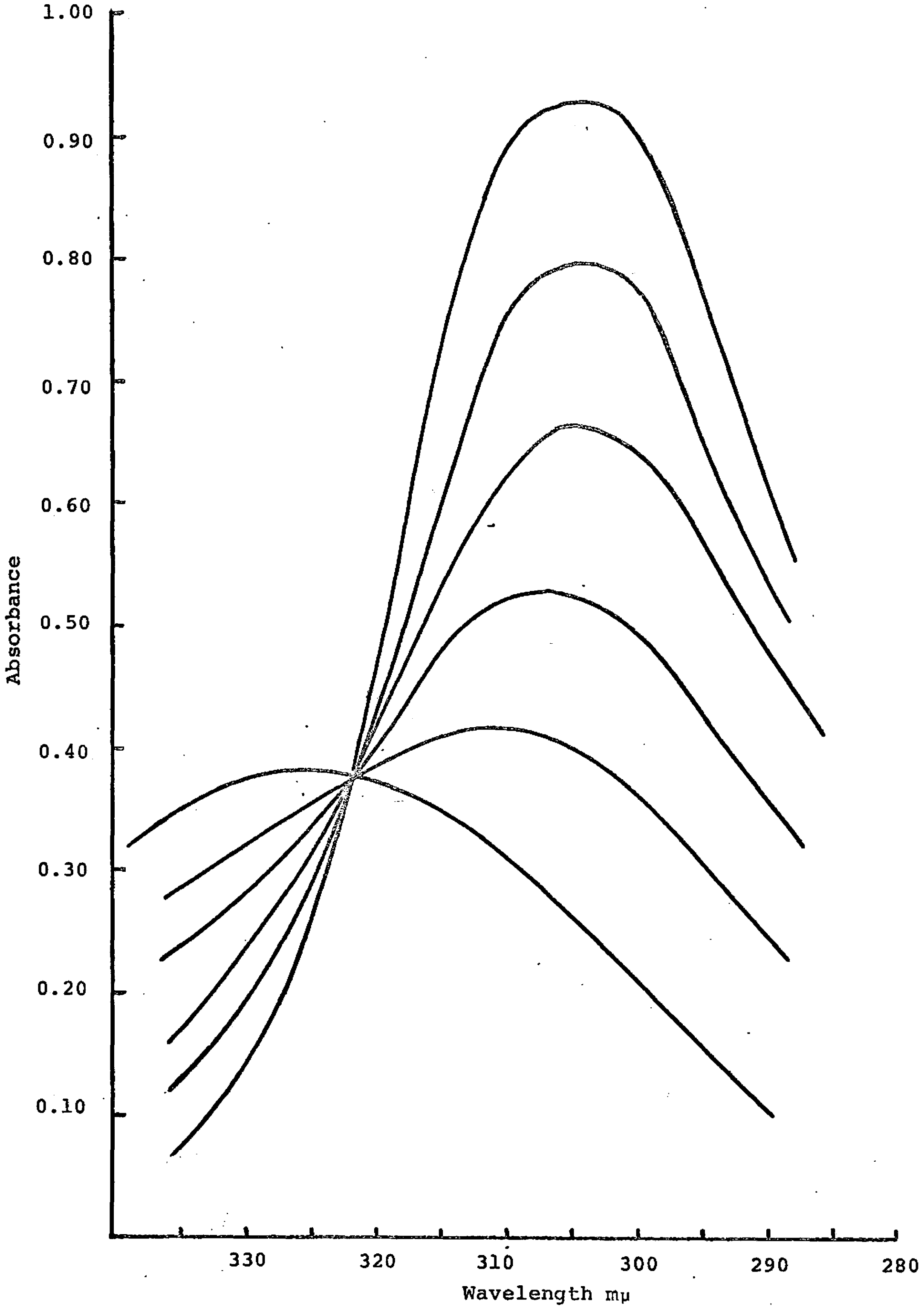
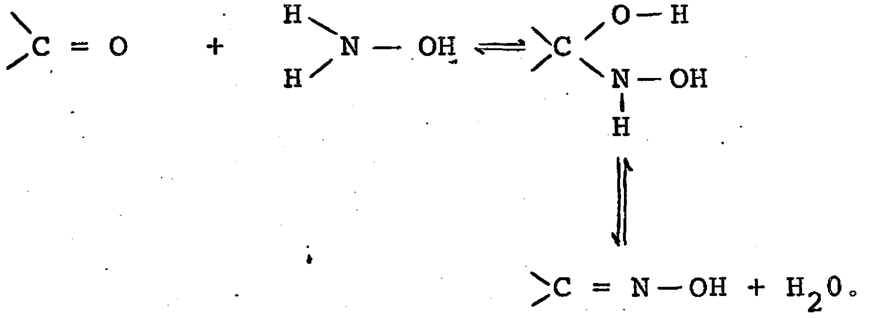

1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
Absorbance
330
320
310
300
290
280
Wavelength mμ

Fig. 5

Experiments were conducted along these lines and the results are presented in part in Figs. 6 and 7. The steady decrease of the absorbance of the reaction mixture with time confirmed the conclusions drawn from the earlier experiments.

Jencks[91] studied the reaction between hydroxylamine and several aldehydes and ketones in alcoholic solutions and reported the formation of an additional compound in each case. He represented the reaction sequence by the following equations:



Similar observations were also reported by Knorr[99].

Following these conclusions, it was assumed that only one intermediate compound formed during the reaction in this study. In such case, the difference between the observed and expected values of absorbance of the reaction mixture must be related to the concentration of the intermediate formed during the reaction.

In order to interpret the experimental results obtained from the spectrophotometric kinetic study it was necessary to derive expressions which related the absorbance with the rate constants of the reactions involved.

Fig. 6. Initial parts of the Absorbance versus Time charts.

Curves 1, 2 and 3 are taken at 24.9°C

Curves A, B and C „ at 20.1°C

add Equilibrium values for the absorbance:

0.168		0.172			0.182	
0.180	(24.9°C),	0.186	(20.1°C)	and	0.190	(14.9°C)
0.192		0.200			0.205	

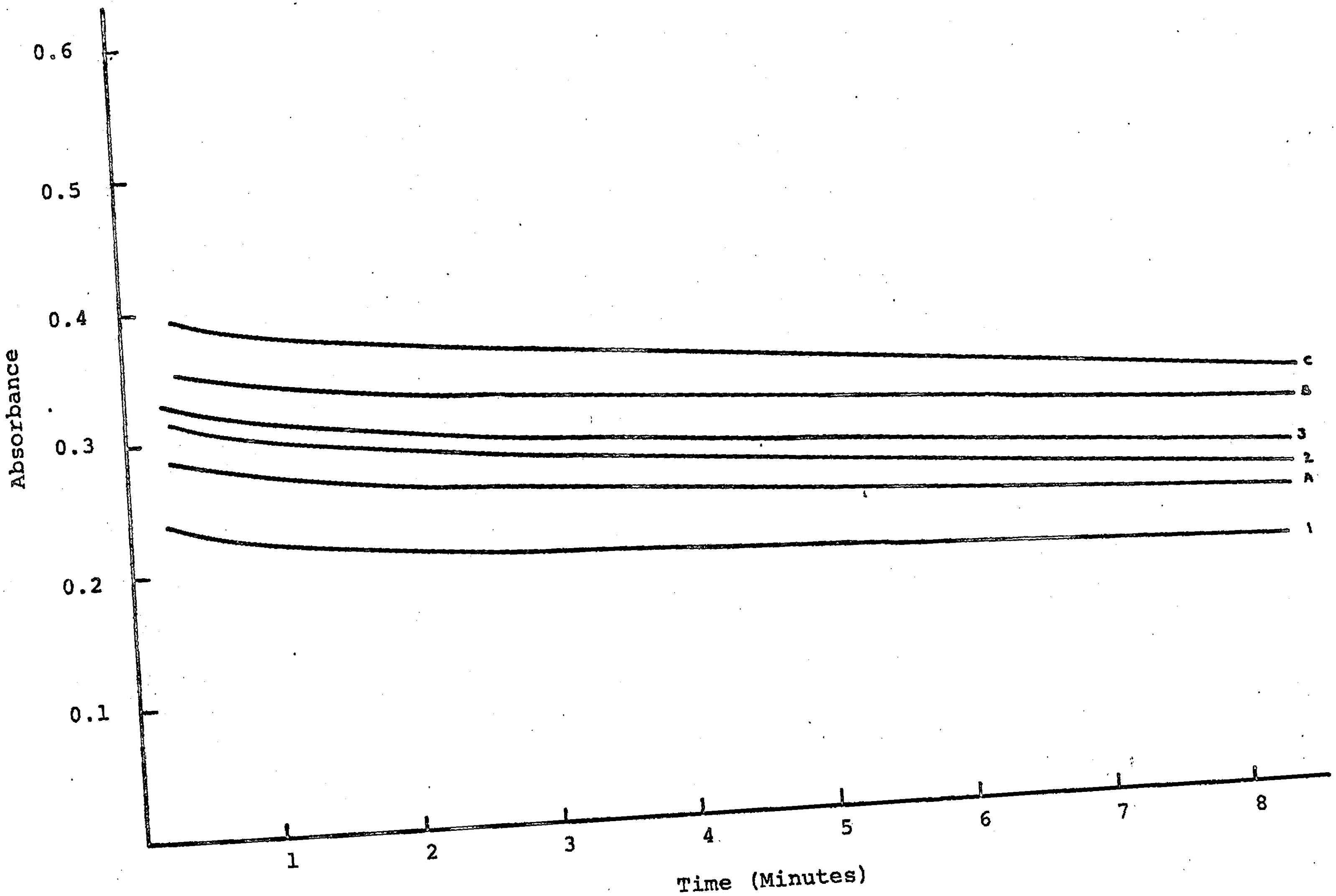


Fig. 6

Fig. 7. Initial parts of the Absorbance versus Time charts taken at 14.9°C. (The broken line is for the system containing nickel.)

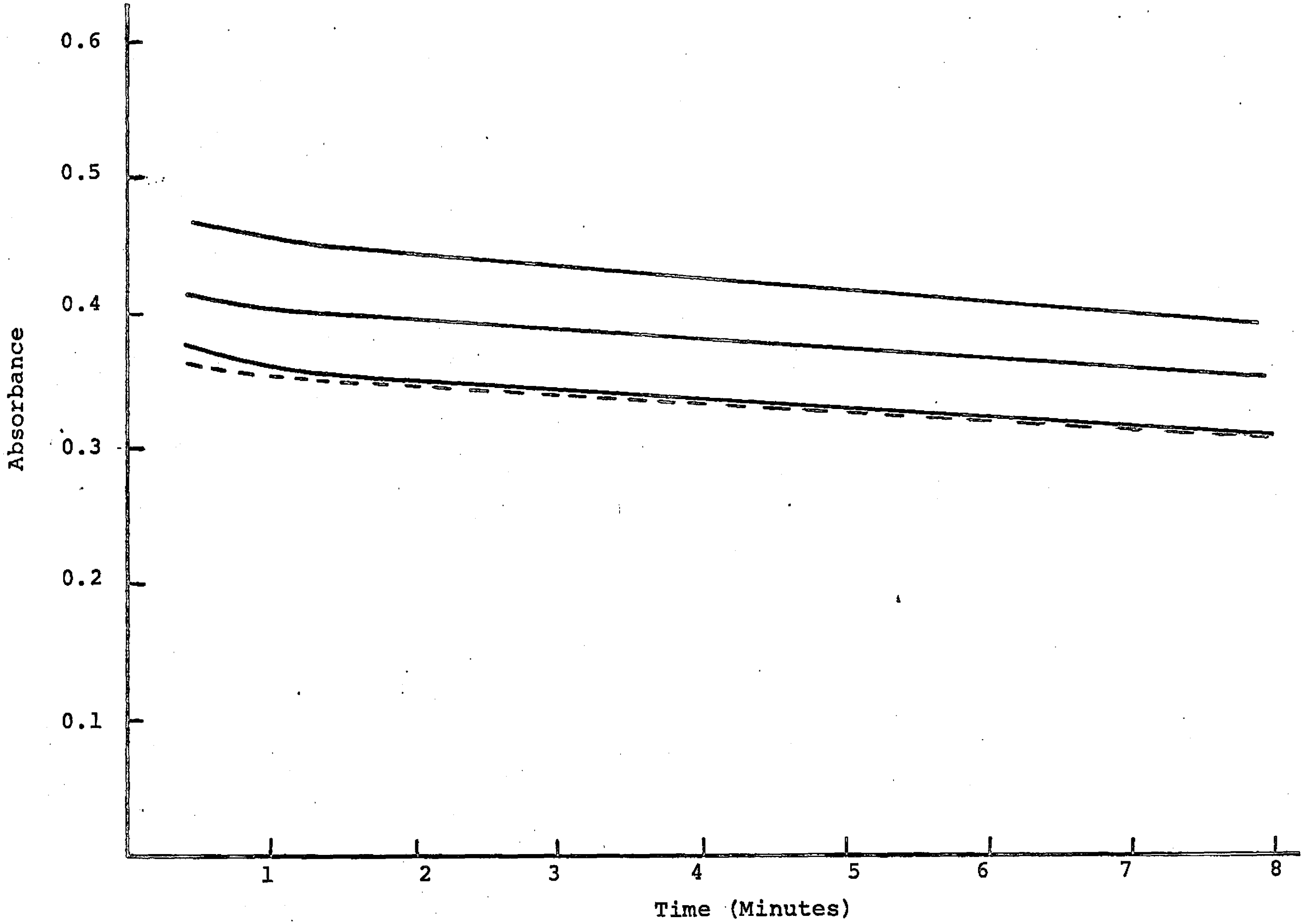


Fig. 7

The following reaction mechanism was proposed:

$$S + Hx \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ox + H_2O. \qquad \ldots. \quad (1)$$

Symbols used:

S - Salicylaldehyde

Hx - Hydroxylamine

I - Reaction intermediate

Ox - Salicylaldoxime

E_C - Extinction coefficient for salicylaldehyde (321.4 mμ)

E_N - Extinction coefficient for salicylaldoxime (321.4 mμ)

E_I - Extinction coefficient for intermediate (321.4 mμ)

A - Absorbance of the reaction mixture at any time t

A_i - Absorbance of the reaction mixture at t = o

k - Rate constant for the reaction

K - Equilibrium constant

[ ] - Denotes the concentration of the species within brackets.

1 - Optical path length of the absorption cell

If no intermediate is formed during the reaction, the absorbance of the reaction mixture must be given by:

$$A = E_C [S] 1 + E_N [Ox] 1 \qquad \ldots..(2)$$

But if an intermediate is rapidly formed according to equation (1) and if it also absorbs in that wavelength region, the absorbance of the mixture at the isosbestic point is given by

$$A = E_C [S] l + E_N [Ox] l + E_I [I] l \qquad \ldots(3)$$

If E_I is less than E_N, the absorbance of the mixture decreases initially and then reaches an equilibrium value depending on the final concentrations of the species involved. As the experimental results followed this pattern it can be concluded that E_I is small compared to E_N or E_C.

A mass balance in the reaction mixture following equation (1) gives

$$[S_i] = [S] + [I] + [Ox] \qquad \ldots(4)$$

where the subscript denotes the initial concentration of the species.

Then

$$A_i - A = \Delta A = E_C [S_i] l - E_C [S] l - E_I [I] l - E_N [Ox] l . \qquad \ldots(5)$$

Substitution of equation (4) and simplification gives

$$\Delta A = (E_C - E_I) [I] l$$

$$= G [I] l \qquad \ldots(6)$$

where $G = (E_C - E_I)$.

Now, in the reaction sequence given in (1) it can safely be assumed that the rate of the reverse reaction in the first step is negligibly small. This assumption is based on the observation reported by Jencks, that the carbonyl compound is almost completely converted into the carbinolamine intermediate within a short time.

Then, the rate of disappearance of salicylaldehyde is given by the equation typical for a second order reaction.

$$-\frac{d[S]}{dt} = k_1 [S] [Hx]. \qquad \ldots(7)$$

But if the concentration of hydroxylamine in the reaction mixture is maintained so high that its consumption during the reaction is relatively negligible then pseudo first order kinetics, with respect to salicylaldehyde, will result. In such case, the rate of disappearance of salicylaldehyde can be written as

$$-\frac{d[S]}{dt} = k_1^1 [S] \qquad \ldots(8)$$

where k_1^1 is the 'apparent' rate constant for the reaction. Again, in the initial period of the reaction when it can be assumed that the build up of salicylaldoxime concentration is negligible,

$$[S] = [S_i] - [I]$$

and

$$[I] = \frac{\Delta A}{G \cdot 1}.$$

Equation (8) after substitution and integration yields

$$\ln \left\{ \frac{S_i G \cdot 1 - \Delta A}{G \cdot 1} \right\} = -k_1^1 t + \ln [S_i] \qquad \ldots(9)$$

and a plot of $\ln \left\{ \frac{S_i G \cdot 1 - \Delta A}{G \cdot 1} \right\}$ versus time should give a straight line with a slope equal to $-k_1^1$.

However, equation (9) contains two unknown parameters k_1^1 and G and so is not solvable as such. For this reason, another equation using the same quantities is obtained. Since

$$[S] = [S_i]\, e^{-k_1^1 t} \qquad \ldots(10)$$

and

$$[S_i] - [S] = [I] = [S_i]\left(1 - e^{-k_1^1 t}\right)$$

it follows

$$\frac{\Delta A}{G \cdot l} = [S_i]\left(1 - e^{-k_1^1 t}\right) \qquad \ldots(11)$$

Now, using the equations (9) and (11) values for the apparent rate constant k_1^1 can be calculated.

From this the rate constants for the reaction may easily be obtained since, $k_1^1 = k_1 [Hx]$.

The data obtained from the absorbance versus time charts was processed as mentioned above and part of the results are presented in Table VIII. Each figure represents the average of six fairly reproducible runs conducted in each experiment. Plots of $\log\left(S_i - \frac{\Delta A}{G \cdot l}\right)$ versus time are shown in Figs. 8, 9 and 10.

It can be seen that only the initial experimental points were considered in drawing the best straight line graphs in Figs. 8-10. This is justifiable since the assumption made in deriving the equations, that the concentration of the oxime is negligibly small, will be progressively invalidated during the reaction. Values of k_1^1 were then calculated from the slopes of these graphs.

TABLE VIII

Results of Calculation of $-\log S_i - \frac{\Delta A}{G \cdot l}$ from the Absorbance Versus Time Data

Temperature (°C)[2]	24.9		20.1		14.9	
Time (Minutes)	ΔA	$-\log\left(S_i - \frac{\Delta A}{G \cdot l}\right)$	ΔA	$-\log\left(S_i - \frac{\Delta A}{G \cdot l}\right)$	ΔA	$-\log\left(S_i - \frac{\Delta A}{G \cdot l}\right)$
0	0.000	4.648(a)	0.000	4.648	0.000	4.648
	0.000	4.611(b)	0.000	4.611	0.000	4.611
	0.000	4.553(c)	0.000	4.553	0.000	4.553
0.5	0.009	4.665	0.008	4.663	0.008	4.663
	0.014	4.636	0.009	4.627	0.009	4.627
	0.015	4.577	0.009	4.567	0.010	4.569
1.0	0.016	4.680	0.016	4.680	0.014	4.674
	0.024	4.656	0.018	4.643	0.013	4.634
	0.027	4.597	0.019	4.583	0.016	4.579
1.5	0.020	4.689	0.022	4.693	0.020	4.684
	0.031	4.670	0.024	4.656	0.019	4.644
	0.035	4.611	0.024	4.593	0.021	4.587
2.0	0.024	4.697	0.028	4.705	0.023	4.693
	0.036	4.680	0.029	4.665	0.024	4.654
	0.040	4.620	0.030	4.602	0.025	4.594
2.5	0.026	4.701	0.032	4.714	0.028	4.703
	0.039	4.686	0.032	4.672	0.028	4.661
	0.044	4.627	0.034	4.611	0.030	4.602
3.0	0.029	4.708	0.035	4.721	0.032	4.710
	0.043	4.695	0.034	4.676	0.032	4.669
	0.046	4.631	0.039	4.618	0.035	4.611

/cont'd......

TABLE VIII (Cont'd)

Temperature (^{o}C)^{2}	24.9		20.1		14.9	
Time (Minutes)	ΔA	$-\log\left(S_i - \frac{\Delta A}{G \cdot 1}\right)$	ΔA	$-\log\left(S_i - \frac{\Delta A}{G \cdot 1}\right)$	ΔA	$-\log\left(S_i - \frac{\Delta A}{G \cdot 1}\right)$
3.5	0.031	4.712	0.038	4.726	0.034	4.714
	0.046	4.701	0.036	4.679	0.036	4.675
	0.049	4.636	0.042	4.623	0.039	4.620
4.0	0.033	4.717	0.040	4.730	0.036	4.718
	0.049	4.708	0.038	4.682	0.039	4.680
	0.052	4.642	0.045	4.633	0.043	4.626

(a) Results of experiments with 2.25 x 10^{-5}M salicylaldehyde.

(b) Results of experiments with 2.45 x 10^{-5}M salicylaldehyde.

(c) Results of experiments with 2.80 x 10^{-5}M salicylaldehyde.

(1) Each valve represents an average of six experimental determinations.

(2) Temperatures are maintained to ± 0.1°C.

Fig. 8. Plot of $\underline{-\text{Log}\left(S_i - \frac{\Delta A}{G \cdot l}\right)}$ versus <u>Time</u>

(Temperature 20.1°C.)

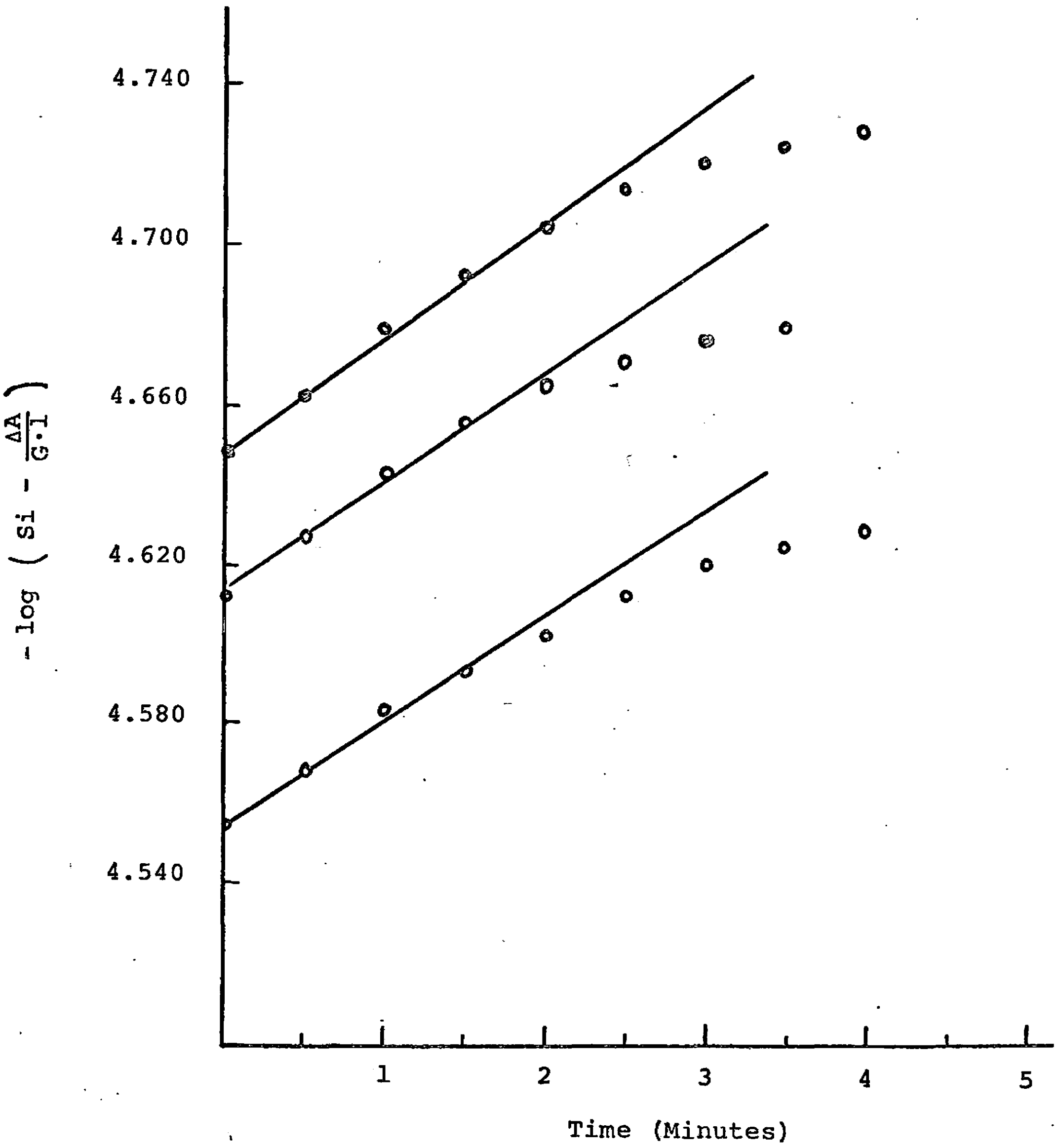

4.740
4.700
4.660
4.620
4.580
4.540
- log (Si - $\frac{\Delta A}{G \cdot 1}$)
1
2
3
4
5
Time (Minutes)

Fig. 8

Fig. 9. Plot of $\underline{-\mathrm{Log}\left(S_i - \frac{\Delta A}{G \cdot l}\right)}$ versus <u>Time</u>

(Temperature 24.9°C.)

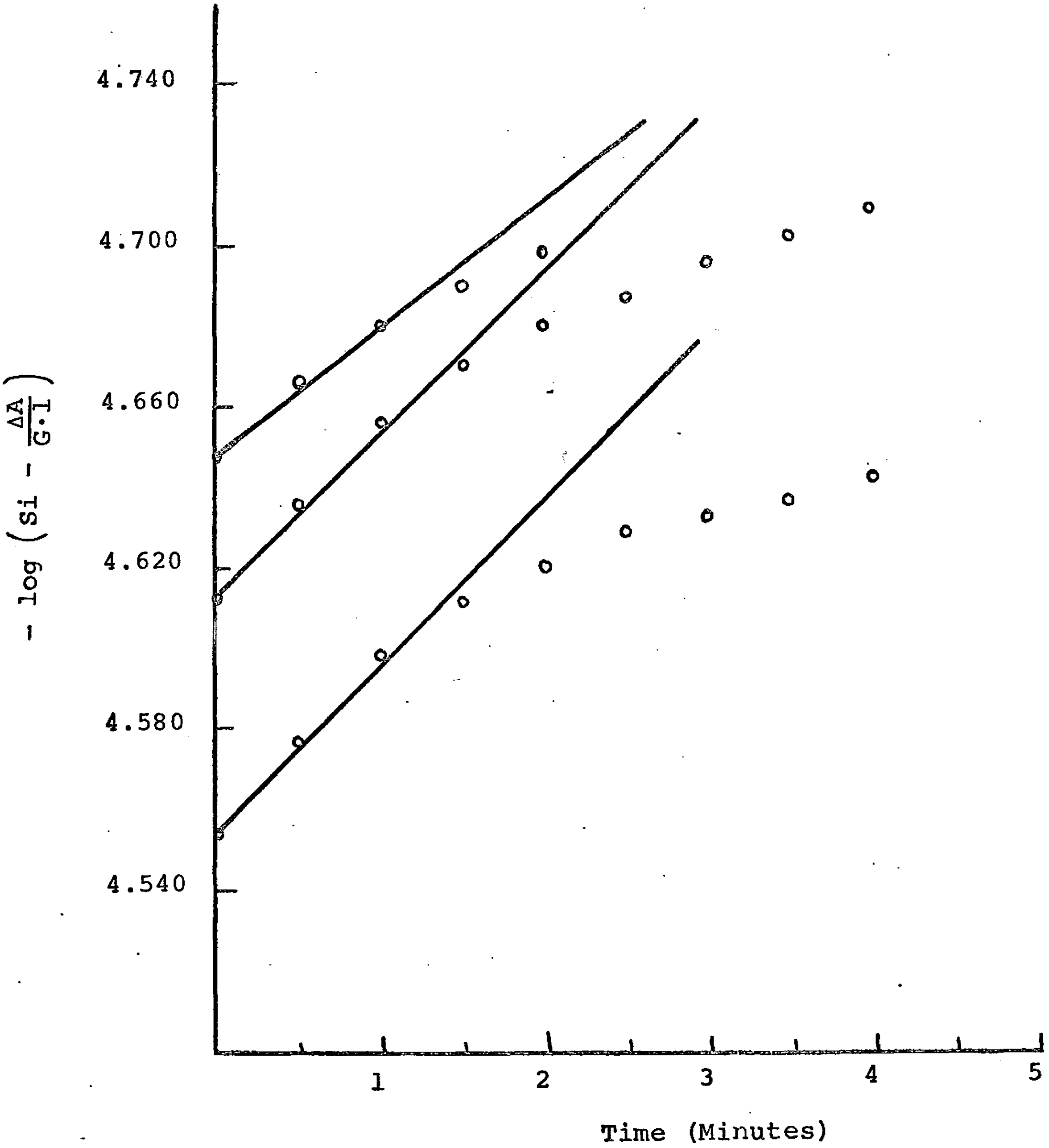

- log $\left(Si - \frac{\Delta A}{G \cdot I}\right)$
4.740
4.700
4.660
4.620
4.580
4.540
1
2
3
4
5
Time (Minutes)

Fig. 9

Fig. 10. Plot of $\underline{-\text{Log}\left(S_i - \frac{\Delta A}{G \cdot l}\right)}$ versus <u>Time</u>

(Temperature 14.9°C.)

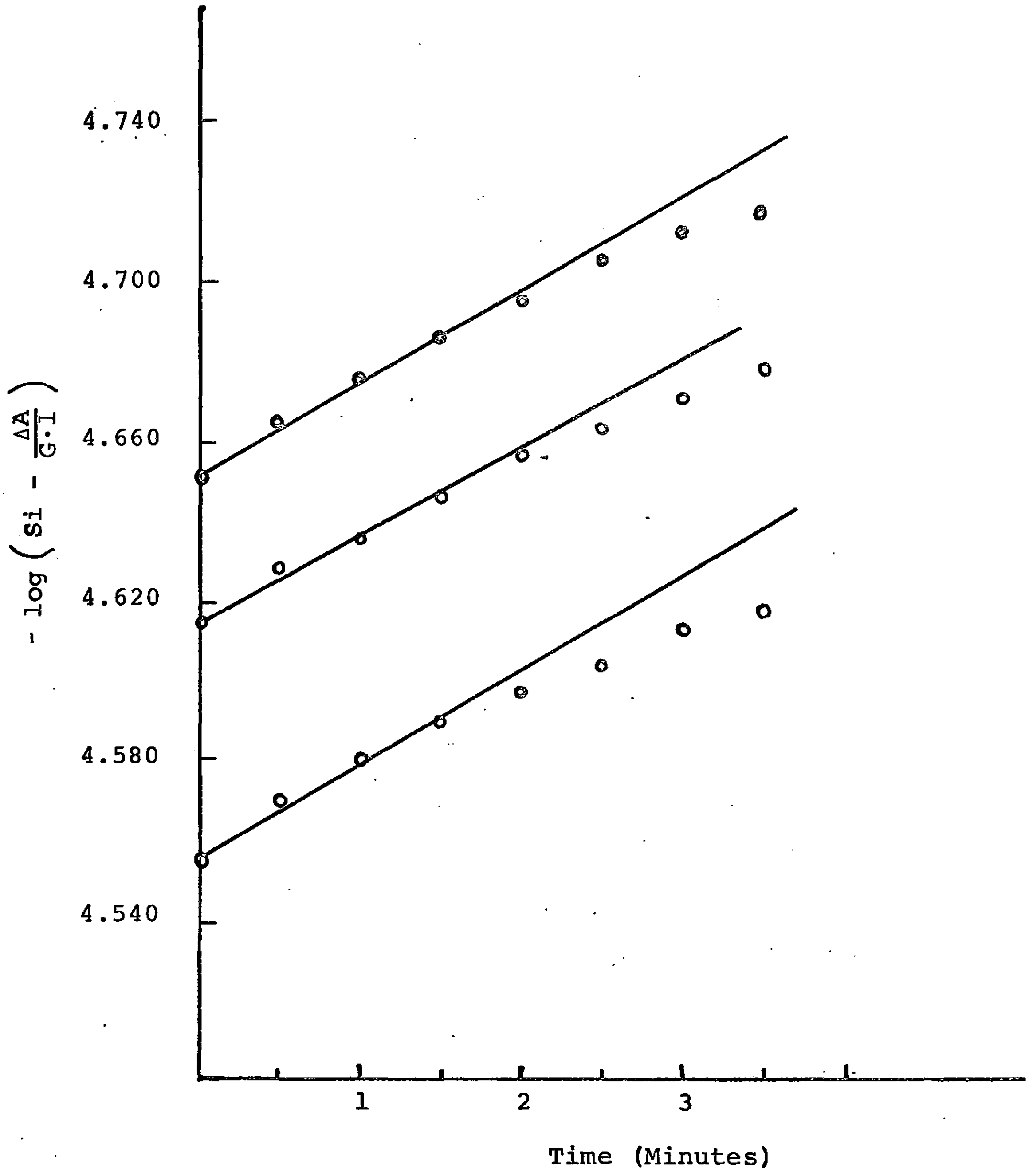


Fig. 10

The results of the calculation of the specific rate constants at three different temperatures are shown in Table IX. From these values an Arrhenius plot was constructed. The graph is shown in Fig. 11. Using the slope of the straight line the activation energy for the reaction was calculated to be 9.2 K cal.Mol^{-1}.

Also, the extinction coefficient of the carbinolamine intermediate was calculated to be 360 at 321.4 mμ. This is in agreement with Jencks'observations. He reported that measurements at high base concentration and extrapolation to infinite base concentration indicated that in most cases the absorbance of the addition compounds is very small (at 320 mμ.)

The second step in the reaction sequence (Eq.1) is the dehydration of the carbinolamine intermediate to form salicylaldoxime. The equilibrium constant for this step can be easily obtained from data already at hand. After sufficient lapse of time when the system reached equilibrium, the following equations may be derived.

$$A_{obs} = A_{eq} \qquad \Delta A = A_i - A_{eq}$$

$$K_1 = \frac{[I]_{eq}}{[S]_{eq}\,[Hx]_{eq}} \quad \text{or} \quad K_1^1 = \frac{[I]_{eq}}{[S]_{eq}} \qquad \ldots.(12)$$

and

$$K_2 = \frac{[Ox]_{eq}\,[H_2O]}{[I]_{eq}} \quad \text{or} \quad K_2^1 = \frac{[Ox]_{eq}}{[I]_{eq}}. \qquad \ldots.(13)$$

TABLE IX

Results of Calculation of the Rate Constant k_1

Temperature (°C)	k_1 Mol^{-1} Min^{-1}	
14.9	0.372	(a)
	0.320	(b)
	0.378	(c)
20.1	0.467	(a)
	0.481	(b)
	0.460	(c)
24.9	0.651	(a)
	0.550	(b)
	0.643	(c)

(a) Experiments with 2.45×10^{-5}M salicylaldehyde solution.

(b) Experiments with 2.25×10^{-5}M salicylaldehyde solution.

(c) Experiments with 2.80×10^{-5}M salicylaldehyde solution.

Fig. 11. Arrhenius plot for the rate constant k_1.

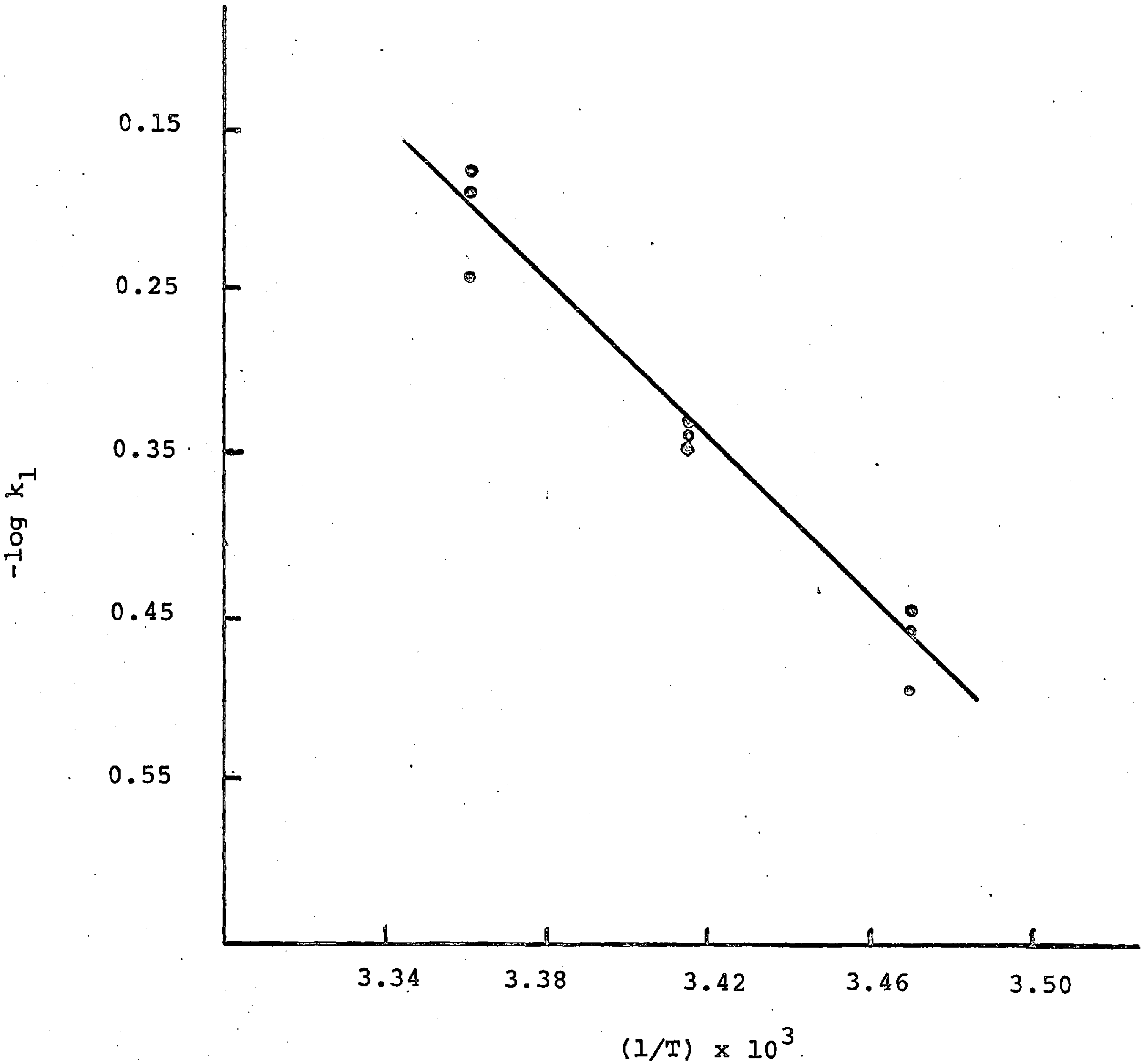


Fig. 11

The equilibrium concentration of salicylaldehyde may be assumed to be relatively negligible. This assumption is fair enough in view of the observations made by Jencks with other aldehydes. He pointed out that up to 95 percent of the aldehyde, in most cases, was converted into the addition product within a short period of the reaction.

In such case a mass balance equation ignoring the equilibrium salicylaldehyde concentration may be written as

$$[Ox]_{eq} = [S]_i - [I]_{eq} \qquad \ldots.(14)$$

and substituting for $[I]_{eq}$ from equation (6)

$$[Ox]_{eq} = [S]_i - \frac{\Delta A}{G \cdot l} \qquad \ldots.(15)$$

or

$$K_2^1 = \frac{[S_i] - \frac{\Delta A}{G \cdot l}}{\frac{\Delta A}{G \cdot l}} \qquad \ldots.(16)$$

Thus, the equilibrium constant is related to the following measurable quantities: the initial salicylaldehyde concentration, the initial absorbance of the reaction mixture and the absorbance at equilibrium. The value of G has already been obtained from earlier calculations. Hence, utilizing the data collected in the experiments described in Section III-A-3, the equilibrium constant for the dehydration step may be calculated. The results of these calculations are shown below.

Temperature (°C)	14.9	20.1	24.9
K_2^1 (mol^{-1})	1.66	2.00	2.22

In calculating these reaction constants, k_1 and K_2', it was assumed that (a) the only important reaction in the early moments is the formation of the carbinolamine intermediate and (b) the formation of this addition product is almost complete. Earlier reports by Jencks and others clearly pointed out that in neutral solution the addition equilibrium is rapidly established relative to the rate of dehydration. Also, the extent of carbinolamine formed is dependent on the concentration of the carbonyl compound in solution. In view of this, it could safely be concluded that the reaction constants obtained in this study are reasonably accurate. However, calculation of other constants k_{-1}, k_2 and K_{-2} was not successful at present, pointing the need for further work.

A few experiments were conducted in which the oximation reaction was followed using the reactant solution to which a little (0.03 mg) nickel had been added. A plot of the absorbance versus time is shown in Fig. 7 as a broken line. It can be seen that this graph closely follows the absorbance versus time graph which was obtained in the absence of nickel. This indicated that nickel(II) had apparently little effect on the reaction between salicylaldehyde and hydroxylamine. A thorough examination of this aspect would set the stage for nucleation and coprecipitation studies with nickel salicylaldoximate.

IV

SUMMARY

Precipitation of nickel as Ni(II) salicylaldoximate was quantitative in the pH range 5.8 - 7.0 when the reagent was generated *in situ* employing the salicylaldehyde-hydroxylamine reaction. While a minimum of three fold excess of salicylaldehyde was necessary for complete recovery of nickel(II) in a 4 hour reaction period, sufficiently large amounts (~16 fold excess) of the reagent were tolerated.

Interference due to diverse ions like Zn, Cr, V, Mn, Al, and Fe was eliminated by a suitable modification of the procedure involving addition of tartaric acid and increased amounts of the reagents. The procedure could not be applied to separate nickel from either copper or cobalt. However, it was adopted for the determination of nickel in steel samples.

The salicylaldehyde-hydroxylamine reaction was shown to proceed through the formation of a reaction intermediate and a suitable reaction mechanism was given. Parameters, such as the extinction coefficient of the carbinolamine intermediate and the rate constant of the addition step of the reaction sequence, were obtained. The Arrhenius plot for the rate constant was constructed over a temperature range 15 - 25°C from which the energy of activation was calculated. Also, an approximate value for the equilibrium constant of the dehydration step was obtained.

V

FUTURE WORK

A detailed study of the oximation reaction of salicylaldehyde in the presence of nickel should be carried out. This would provide a basis for the study of the nucleation process in the precipitation of nickel salicylaldoximate.

Utilizing the rate constant obtained in this study, and following the oximation reaction spectrophotometrically at several wavelengths, it should be possible to compute the absorption spectrum of the reaction intermediate. Such data might in turn be useful in refining the values of the constants obtained in this study.

A study of the solvent extraction behaviour and the spectrophotometric characteristics of nickel salicylaldoximate could result in a procedure for the determination of nickel in trace concentrations. It might also be possible to overcome the interference of copper and cobalt, by proper choice of extraction conditions, either by withholding the interfering ions in the aqueous phase or by complete extraction of the metal chelates followed by a simultaneous spectrophotometric determination.

APPENDIX

Solvent Extraction and Spectrophotometric Determination of Nickel

A Preliminary Report

The gravimetric procedure developed in the present investigation was found to be suitable for estimation of milligram quantities of nickel. However, smaller amounts of nickel could not be handled easily.

Nickel salicylaldoximate is soluble in many organic solvents yielding a green colored solution. It was thus intended to study the solvent extraction and spectrophotometric characteristics of the nickel chelate in order to develop a method for estimating small amounts of nickel. N-amyl acetate was chosen as the solvent. The solution of nickel salicylaldoximate in this solvent was found to exhibit an absorbance maximum at 385 mμ. The following procedure was adopted to investigate the extraction of the nickel chelate into n-amyl acetate.

The standard stock solution of nickel(II) was diluted suitably so as to contain 0.1 mg Ni per ml and 0.5, 1.0, 2.0, 3.0 and 4.0 ml aliquots of this solution were transferred into different separately funnels. Then

10.0 ml of an ammonium chloride solution (0.4M and the pH adjusted to 6.5 using 0.4M ammonium hydroxide) were added and the total volume in each flask was brought to 20.0 ml using distilled water. Later, 50 ml of n-amyl acetate solution of salicylaldoxime (0.02M) were added to each funnel and shaken vigorously. After about twenty minutes, with the layers well separated, the aqueous phase was collected in a beaker. A few ml of the organic phase solvent were then placed in a spectrophotometric cell (1.0 cm path length) and the absorbance was noted at 385 mμ using the reagent solution in the reference cell.

A graph of the absorbance versus amount of nickel was constructed and is shown in Fig. 12. It can be seen that the absorbance of nickel salicylaldoximate followed Beer's law. The aqueous phase collected in each case was tested for nickel using the procedure described in Section II-A. The results indicated that the extraction of nickel into the organic phase was complete.

Further study on the extraction of nickel chelate showed that:

(a) the procedure could be adopted for estimating sub-milligram amounts of nickel;

(b) tartrate ion did not interfere with the extraction of nickel;

(c) copper and cobalt interferes in the determination of nickel. The extraction of the copper chelate into the

Fig. 12. Beer's law plot for nickel-salicylaldoximate.

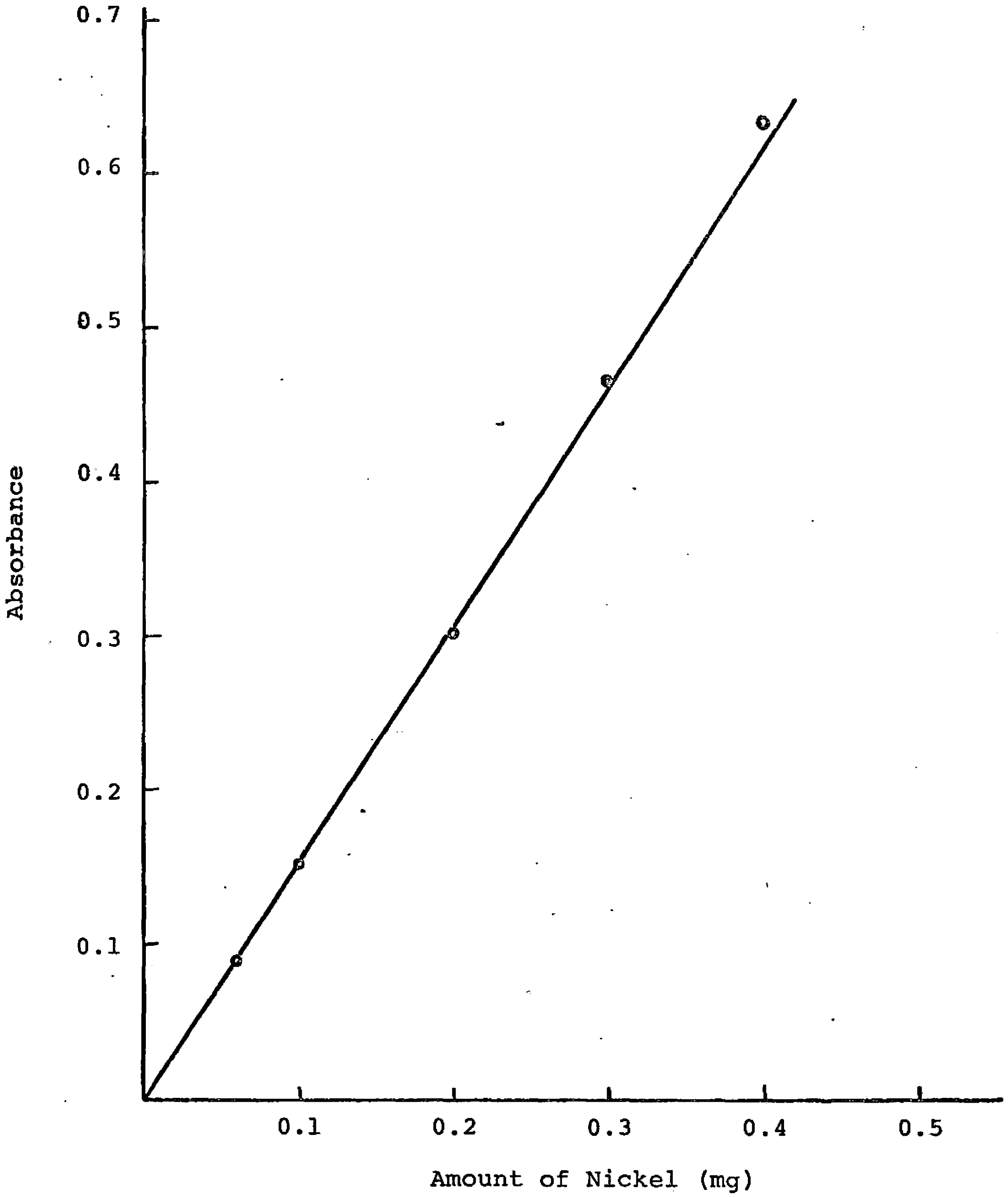

0.7
0.6
0.5
0.4
0.3
0.2
0.1
Absorbance
0.1
0.2
0.3
0.4
0.5
Amount of Nickel (mg)

Fig. 12

organic phase, under the conditions of the experiment, was complete. The copper chelate solution has an absorption maximum at 344 mμ and this would permit a simultaneous determination of copper and nickel when these metals are present together.

(d) Iron interferred seriously, due to the formation of a violet colored chelate. But tartrate ion eliminated this interference completely.

Further detailed study involving the effect of pH, reagent excess and salt concentration in the aqueous phase on the extraction of the nickel chelate into n-amyl acetate is in progress.

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