DIFFUSION AND THERMODYNAMIC STUDIES IN AMIDE SOLUTIONS

Atusaye Kayana Sichali

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DIFFUSION AND THERMODYNAMIC STUDIES IN AMIDE SOLUTIONS

A THESIS

Submitted to the University of St. Andrews

for the degree of DOCTOR OF PHILOSOPHY

by

Atusaye Kayana Sichali B.Sc.

Supervisor

Dr. C.A. Vincent

September 1973.

DECLARATION

I declare that this thesis is my own composition, that the work therein has been carried out by me and that it has not been submitted in any previous application for a Higher degree.

The thesis describes results of research carried out at the Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. C.A. Vincent from 1st October, 1970 to 30th September, 1973.

Atusaye K. Sichali

CERTIFICATE

I hereby certify that Atusaye Kayana Sichali has spent eleven terms of research work under my supervision, has fulfilled the conditions of ordinance No. 12 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

C.A. Vincent
Director of Research

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SUMMARY

(A) Diffusion Studies

A study has been made on the effects of some selected halide salts on the structure of formamide by measuring molecular diffusion coefficients. A neutral molecule, ferrocene was allowed to diffuse in pure formamide and in halide salts solutions of formamide and its diffusion coefficients were determined. A test molecule was chosen rather than a test ion in order to avoid electrostatic effects due to ion-ion and ion-dipole interactions. Graphs of diffusion coefficient versus concentration of salts were drawn and the shapes of these curves have been discussed in terms of the "microscopic" and "macroscopic" effects of these salts on formamide structure.

Use of two diffusion techniques was made - (i) an electrochemical diffusion method based on the Cottrell equation and (ii) a diaphragm-cell method based on steady-state diffusion. Only the latter was successful.

A number of experimental methods were investigated in order to find a suitable analytical method for determining ferrocene (necessary for the diaphragm-cell measurements). A method for preparing radioactive ferrocene and a successful radiometric analytical technique were developed.

(B) Thermodynamics Studies

In this section the vapour pressures of binary mixtures of water-formamide, water-N-methylformamide and water-dimethylformamide were measured using a Zimmerli manometric gauge over several temperatures. The graphs of partial pressures of water (determined by a transpiration technique) versus mole fractions of water are given and explained in terms of the nature of interactions of water and the amides. By means of the Clausius-Clapeyron equation the enthalpies of vaporization of water were calculated and the results versus water mole fractions are shown in graphs. In the case of water-formamide, the enthalpies of vaporization and the enthalpies of viscous flow are compared.

(A) DIFFUSION SECTION

DIFFUSION OF FERROCENE IN PURE FORMAMIDE AND IN FORMAMIDE SOLUTIONS OF SELECTED HALIDE SALTS.

INTRODUCTION

With the development of better methods of measurement, the study of diffusion in solution has been considerably advanced in the last thirty years. Much has been done to use the diffusion properties of ions or molecules in the liquid phase to understand their general behaviour in solution and their effects on the structure of solvents, and to test theories of the liquid state. However the majority of diffusion work in electrochemistry has been confined to electrolytes in aqueous or mixed-aqueous media.

It was the aim in the present work to use diffusion measurements to study the effects of some selected halide salts on the structural properties of formamide. The technique was to measure the diffusion coefficient of a neutral (uncharged) molecule, ferrocene in this solvent and in salt solutions in formamide. The uncharged molecule was used in order to avoid the electrostatic effects; that is the electrophoretic and relaxation effects which occur in ionic diffusion due to the ionic atmosphere around the ion. This would enable the investigation of microscopic viscosity.

Experiments were also planned to investigate the effect of mutual diffusion of a salt and ferrocene in order to evaluate any drag effects.

Formamide with the high dielectric constant of approximately 109 [1,2] is a good solvent for many inorganic and organic salts[3,4]. It also has a low freezing point 2.51°C [1] and a high boiling point, 218°C [5], which give it a wide range in the liquid phase although its instability particularly at high temperature[4] is an inhibiting factor. While a great deal of work has been undertaken on the conductances, mobilities and transport numbers of electrolytes in formamide[6,7,8,9] very little has been done so far on the diffusion of electrolytes or molecular solutes in formamide.

DIFFUSION

It should be stated that discussion of diffusion in this work shall only refer to the liquid phase. Diffusion at its simplest can be described as the decrease of a difference in concentration by mass transport due to molecular motion. It is a spontaneous and irreversible, entropy driven process which leads to an equilibration of concentration within a single phase. Like conductance and viscosity to which it is related the coefficient of diffusion is a significant property of substances in solutions.

Eyring and his co-workers[10,11] have treated diffusion in liquids as a rate process. The pure liquid at rest is considered to be continually undergoing rearrangements in which one molecule at a time escapes from its "cage" into an adjoining empty "hole" and that the molecules thus move in each of the cartesian coordinate directions in jumps over energy barriers. If a solute is then allowed to diffuse under influence of gradient of concentration in this liquid it is easy to visualize from the above conception that the process of flow will be by these jumps over energy barriers, and that the direction of flow will be determined by the frequency or probability of the forward and backward jumps.

J, the diffusional flow or flux of a substance in a mixture with other substances may be defined as the amount of this substance passing perpendicularly through a reference surface of unit area during unit time. Fick's first law states that the flux is proportional to the concentration gradient, that is, that

$$J \ \alpha \ \frac{\partial c}{\partial x}$$

where c is the concentration of the substance, x is the distance in the direction of diffusion and $\frac{\partial c}{\partial x}$ is the concentration gradient. This means that the amount of flow of a substance is inversely proportional to the distance from the source of the substance and directly proportional to the amount of the substance per unit volume. The concentration gradient, $\frac{\partial c}{\partial x}$, is the rate of increase of concentration with distance measured in the direction of the flow. It is usual in diffusion experimental work to confine diffusion in one dimension in the positive direction of x and until the present time to use c.g.s. units of measurement.

Two situations are generally defined in diffusion; (a) steady-state and (b) non-steady state diffusion. A steady state is assumed to exist when $\frac{\partial c}{\partial x}$ is considered not to change with time, t, and is defined as

$$J = -D\frac{\partial c}{\partial x} \qquad \ldots\ldots\ 1$$

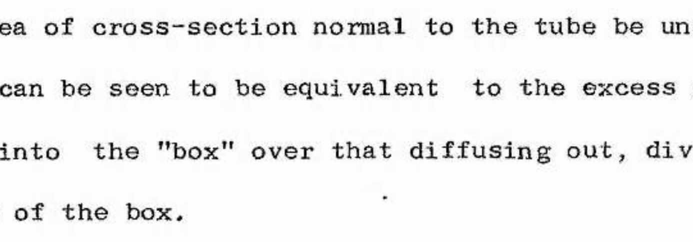
where D is the "diffusion coefficient" for the substance under consideration. The negative sign indicates that the flow measurement is in the positive x-direction from the region of higher to the region of lower concentration so that D has a positive value. Partial differentials are used because in general c is dependent on time as well as distance.

The non-steady state situation takes into account the variation of c with both time and distance. In such cases the flux $J = -D\frac{\partial c}{\partial x}$ is converted into a second order partial differential equation connecting c, x and time t.

$$J\,(x,t) = \frac{dN(x,t)}{dt} = D\,\frac{\partial c(x,t)}{\partial x}$$

i.e. rate of diffusion at position x and time t is proportional to the concentration gradient existing at x at time t. The two quantities J(x,t) and c(x,t) are functions of two variables. At time $t = o$ the concentration is uniform throughout the solution. Thus t is taken to be the time elapsed since the beginning of the diffusion or electrolysis. x is the distance normal to the diffusion column or electrode surface.

Consider the section of solution between x and (x + dx)



Let the area of cross-section normal to the tube be unity. $\frac{\partial c(x,t)}{\partial t}$ can be seen to be equivalent to the excess of material diffusing into the "box" over that diffusing out, divided by the volume of the box.

That is $$\frac{\partial c(x,t)}{\partial t} = \frac{1}{dx}\left[+\,D\left(\frac{\partial c}{\partial x}\right)_{x+dx} - D\left(\frac{\partial c}{\partial x}\right)_{x}\right]$$

But $$\left(\frac{\partial c}{\partial x}\right)_{x+dx} = \left(\frac{\partial c}{\partial x}\right)_{x} + \frac{1}{dx}\left(\frac{\partial c}{\partial x}\right)dx$$

Therefore $$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad \ldots\ldots 2$$

This is Fick's second law.

To solve differential equations of this nature one must define initial and boundary conditions in order to obtain explicit solutions, that is expressions for the flux at any time t and any position x.

If c.g.s. units for measurement of length and time are used and J, the flux is expressed in moles cm^{-2} sec^{-1} and x in cm; c will be expressed in moles cm^{-3}. The diffusion coefficient D can then be recognised as the amount of solute that diffuses across a one square cm area in one second under the influence of a concentration gradient $\frac{\partial c}{\partial x}$. The diffusion coefficient may vary with the concentration of the solute in a solvent and it is a measure of the diffusing tendency of the solute for a given solvent at a given temperature. It is these characteristics which make the diffusion coefficient an important tool in understanding the interactions of electrolytes and solvents in electrochemistry.

Perhaps one of the most important ways in which measured diffusion coefficient values of large, uncharged molecules have been used has been to test Stokes law and the Einstein equation. When a molecule diffuses through a medium, a frictional force sets into balance this diffusion force when some constant velocity is reached. The frictional force exerted by a viscous fluid of viscosity η was derived for a macroscopic sphere of radius r by Stokes as:

Frictional force (F) = $6\pi r\eta v$ where v is velocity of the sphere.

The Einstein equation $D = \frac{kT}{6\pi r\eta}$, where D is the diffusion coefficient, k the Boltzmann Constant and T the absolute temperature, is a direct result of Stokes law. Although Einstein's equation applies only to uncharged colloidal particles and large spheres the relationship is important both in electrolyte and non-electrolyte solutions. Edward[12] has pointed out that it is possible to produce an empirical correction factor for the Stokes-Einstein equation to enable one to apply it to small molecules down to 2Å in radius. A number of workers[13,14,15,16,17] have tried to explain some diffusion properties of ions and molecules in terms of viscosity. The general theme among these workers has been that although the diffusion coefficients of solutes increase with decreasing viscosity of the solution the extent to which this happens is not as great as represented by the Einstein equation. In their study of diffusion of electrolytes, non-electrolytes and colloidal electrolytes McBain and Liu[18] in 1931 combined the Nernst equation ($D = \frac{2RT}{\frac{1}{u}+\frac{1}{v}}$ where u and v are ionic mobilities at infinite dilution), which applies to the diffusion of electrolytes at extreme dilution, and the Einstein equation into one equation which they stated held good for all concentrations, even for such a complex case as solutions of soap. They were also able to calculate from their equations, the size of the sucrose molecule from its diffusion coefficients in 0.05 N solution, by assuming it to be a spherical particle with the density of solid sucrose and found the molecular weight to be 388 as compared with its formula weight of 342. The difference they said would be equivalent to a hydration of about two molecules of water. Another serious attempt at studying this hydration and shape of molecules was that of Wang[19] in 1954. He tried a new method of studying the hydration and shape of protein molecules by measuring the self-diffusion of water in protein solutions.

Ion-pair formation and complex formation of species in solutions are an important occurence in solution chemistry. In their study of diffusion of zinc and magnesium sulphates in aqueous solutions Harned and Hudson[20] found that their diffusion coefficients were not only abnormally high but deviated from theory. After correcting for ion-pair formation the results led to constant values for the mobility of the ion-pair. Stokes and Reilly[21] have tried to explain the diffusion of cadmium chloride in aqueous medium in terms of the complexes formed in the solution.

More recently numerous papers have appeared on diffusion and self-diffusion[22,23,24,25] of substances in liquid media. These workers have measured diffusion coefficients of a number of substances in different solutions and have tried to use them to test some theories of the liquid state and to try to improve on them.

While the interpretation of diffusion coefficients from diffusion measurements in different solvents and solutions is no simple problem a great deal of useful scientific information has emerged from them and more useful information will come out as the methods of studying the diffusive properties of substances improve and new theories of explaining them are developed.

The problems to determine diffusion coefficients as contained in Fick's laws, experimentally were no mean task and it took many years to develop reliable methods for measuring diffusion coefficients in both the steady state and the non-steady state. There are several modern methods for accurate determination of diffusion coefficients. These are the conductimetric method developed by Harned and his collaborators[26,27] in the 1940's; the Goüy Interference method as described by Kegeles and Gosting[28] in 1947; the diaphragm-cell method originated by Northrop and Anson[29] in 1928 and the electrochemical method based on the Cottrell equation. The first two and the last methods are based on Fick's second law (that is non-steady state conditions) and the diaphragm-cell method is based on Fick's first law (steady state conditions). In the work done here experiments were undertaken to measure diffusion coefficients under (a) the electrochemical method and (b) under conditions as expressed by Fick's first law. Only these two methods will be considered below.

(a) Chronoamperometry and the Cottrell Equation

If the redox potential of a system is known, use of the Nernst equation enables one to select a potential at which the equilibrium concentration of one of the components of the couple can be reduced virtually to zero. If the kinetics of the electron transfer are rapid then any electroactive molecule or ion reaching the solution layer in the immediate neighbourhood of the electrode will be electrolysed instantaneously.

Consider the reaction

$$A - \bar{e} \longrightarrow A^{+}$$

and let $c(x,t)$ be the concentration of A at x and t in mol cm^{-3} and C be the bulk concentration of A.

Boundary Conditions

(i) At $t = o$, $c(x,o) = C$ that is at any position, the concentration of A is C mol cm^{-3} prior to electrolysis.

(ii) Assuming that immediate depletion of A occurs when the potential is switched on, we have $C(o,t) = o$ for $t > o$

(iii) Assuming that the experiment is short enough for there to be negligible change in the concentration of A at distances far from the electrode surface,

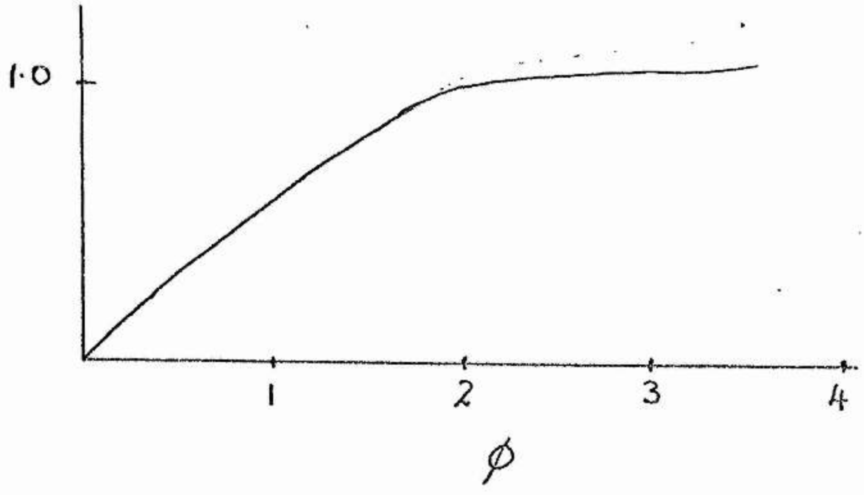
$$C(\infty,t) = C$$

The solution of this as given by Delahay[30] is

$$C(x,t) = C \text{ erf } \left(\frac{x}{2D^{\frac{1}{2}}\, t^{\frac{1}{2}}}\right)$$

$$\text{where erf } \emptyset = \frac{2}{\pi^{\frac{1}{2}}} \int_{0}^{\psi} \exp.\,(-Z^2)\,dZ$$

The error function is a finite integral having zero as the lower limit and has the form



that is erf $\emptyset \longrightarrow 1$ as $\emptyset \gg 2$

This solution to Fick's second law gives the concentration of A at all times and positions. Because the diffusing molecule A is electrolysed as soon as it reaches the electrode surface, the current flowing at time t is given by

$$i_t = nFAJ(o,t) = nFJ(o,t)$$

since the area of the electrode is equal to the area of the cross section of the diffusing layer

Now $\quad J(x,t) = D. \dfrac{\partial c(x,t)}{\partial x}$

But $\quad C(x,t) = C \operatorname{erf} \left(\dfrac{x}{2D^{\frac{1}{2}}t^{\frac{1}{2}}} \right)$

Therefore $\quad J(x,t) = \dfrac{2DC}{\pi^{\frac{1}{2}}} \left(\exp \left(\dfrac{-x}{2D^{\frac{1}{2}}t^{\frac{1}{2}}} \right)^2\right) \quad \dfrac{d \left(\dfrac{x}{2D^{\frac{1}{2}}t^{\frac{1}{2}}} \right)}{dx}$

$$= \frac{2DC}{\pi^{\frac{1}{2}}} \left(\exp \left(\frac{-x}{2D^{\frac{1}{2}}t^{\frac{1}{2}}} \right)^2\right). \quad \frac{1}{2D^{\frac{1}{2}}t^{\frac{1}{2}}}$$

Therefore $\quad J(o,t) = \left(\dfrac{D}{\pi t}\right)^{\frac{1}{2}} C$

and hence $\quad i_t = nFAC\left(\dfrac{D}{\pi t}\right)^{\frac{1}{2}} = nFAD^{\frac{1}{2}}C \dfrac{1}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}} \qquad \ldots\ldots\ 3$

This equation is known as the Cottrell Equation

(b) In this method the steady state or quasi-steady state was established in the apparatus. Quasi-steady state because it is not experimentally very feasible to establish really steady state conditions but a condition whereby the concentration gradient, $\frac{dc}{dx}$, changes only very slowly with time.

Almost the only really steady state results obtained are those of Clack[31], and presented in his article in 1924. Clack established his steady state by maintaining the concentration at the lower end of his diffusion column at saturation by means of a reservoir of solid salt while at the uppor end was maintained effectively at zero by means of a slow flow of water. While by using this method the diffusion coefficients could be directly calculated from Fick's steady state equation thus simplifying the mathematics the experimental difficulties of establishing and maintaining the steady state were too great. A quasi-steady state was reached in the present work by using the diaphragm-cell method for measuring diffusion coefficients.

The Diaphragm-Cell Method

The difficulty in measuring diffusional flows is that mass transfer in liquids across any plain of reference can take place not only by diffusion but also by convection currents or bulk flow. The fundamental idea of the diaphragm method is to eliminate these disturbing effects (often due to mechanical vibrations or small temperature fluctuations) by confining the diffusion process to the capillary pores of a sintered glass diaphragm. There are a number of factors which have to be considered in using the diaphragm-cell. The first is that an approximate steady state is established at all times during an experiment. This is accomplished by performing a "prediffusion" prior to an experimental run. This is a procedure in which material is allowed to diffuse for some length of time until a concentration gradient which does not change markedly with time is established before an actual diffusion run is timed. The establishment of a steady state can also be greatly helped if the volumes of liquid in contact with the sinter are large and separately uniform in composition.

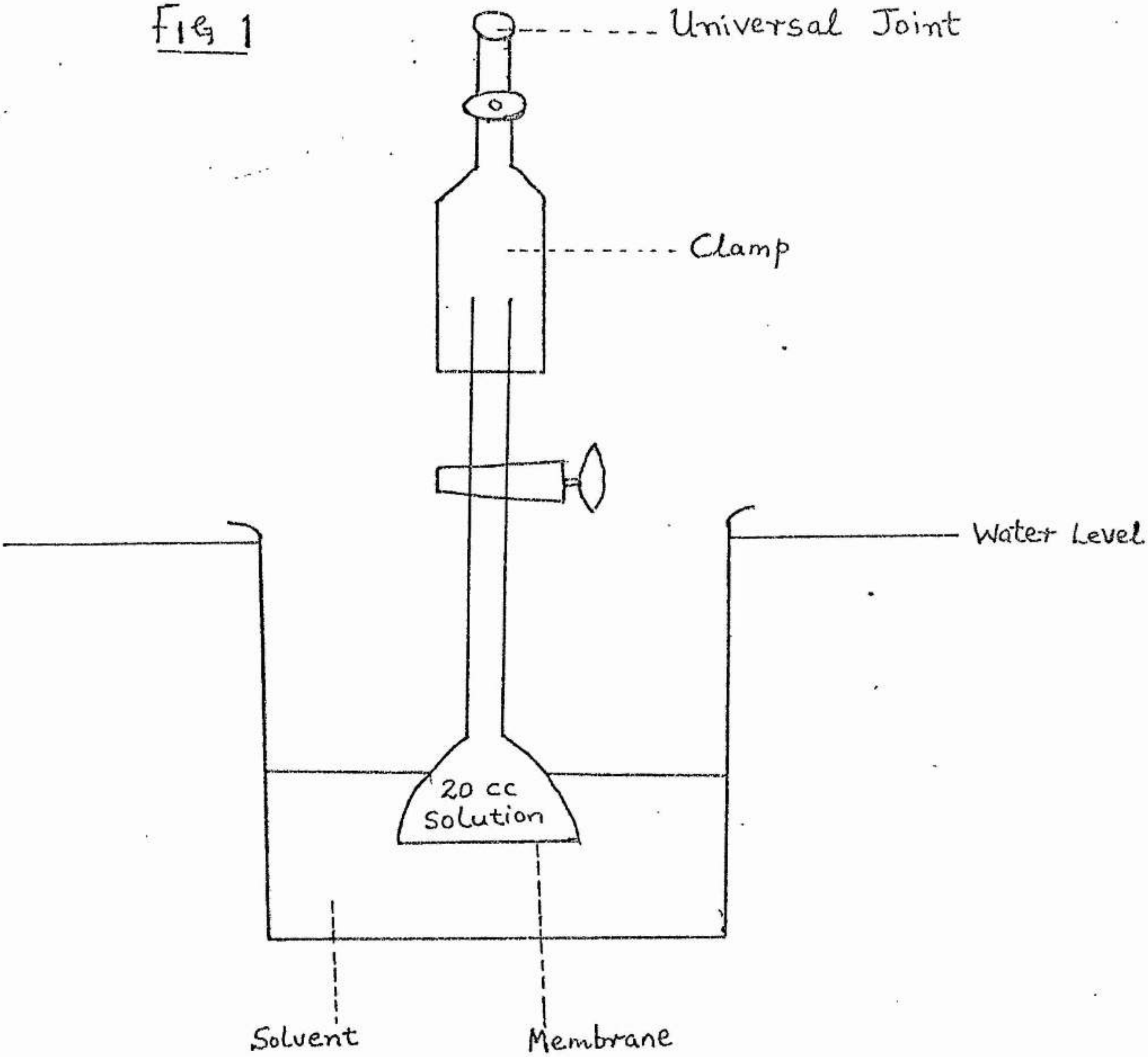
Secondly since the overall area and length of the diffusion path have to be known in order to measure the diffusion coefficients and these in a sinter cannot be measured directly the diaphragm-cell has to be standardized against absolute diffusion methods such as the conductimetric or the Goüy Interference method. Since the geometry of the sinter is constant this may be done by calibration with a system with known diffusion coefficients in order to obtain a cell constant.

A third problem is the existence of stagnant layers on the diaphragm. It is a paramount condition in accurate diffusion work that the diffusion process be confined entirely to the pores of the diaphragm. This condition is achieved by stirring the solution to maintain a uniform concentration in each compartment right up to the surface of the diaphragm. If relative rather than absolute diffusion coefficients are the aim of the diffusion experiments this condition can be relaxed if there is negligible density gradient between the solutions in the diaphragm cell. This situation is explained later on.

Finally it is important to choose pores of a diaphragm which are not too coarse to allow transport to occur by bulk streaming through the diaphragm as well as by diffusion; a condition which is more likely to occur if the denser liquid is above the diaphragm[32].

It was the desire to prevent convection currents which were inherent in the classical diffusion methods and to accelerate the diffusion process that first led Northrop and Anson[29], the originators of the diaphragm method, to confine diffusion across porous diaphragm. The diffusion apparatus which they assembled is shown in Figure I. The cell contained 20 cc of solution and the external solution would be 10 to 50 cc depending on rate of diffusion. The cell was calibrated with hydrochloric acid lactose or [illegible] salts whose diffusion coefficient were known. Stirring of the solution to maintain uniformity was done by putting the denser solution in the top part of the apparatus and thus inducing a density gradient streaming of the solution.

Fig 1



The experimental run was timed after a steady-state condition was reached. The existence of a steady state was proved by taking samples of the bottom solution and analysing them. A steady state was established when the amount of solute passing through the membrane per equal time interval was the same. With this apparatus Northrop and Anson were able to measure the diffusion coefficients of the haemoglobin molecule and use them to calculate its molecular weight.

In the following decade a number of workers suggested modifications to the Northrop and Anson cell and developed the diaphragm-cell as is known to-day with two glass compartments divided by a sintered glass diaphragm. In the middle 1930s McBain and Dawson[33] used a double-ended cell with two compartments of almost equal volumes separated by a sealed-in membrane of sintered glass to measure the diffusion coefficients of potassium chloride. This was an improvement in that after a preliminary diffusion, solutions on both sides of the diaphragm would be emptied without disturbing the established diffusion columns in the sinter and filled with fresh solutions of accurately known composition. They still used density stirring. But later, Mouquin and Cathcart[34] and Hartley and Runnicles[35] showed that density stirring was insufficient particularly when density differences between solutions are small and in their cells they used mechanical stirring. Mouquin and Cathcart[34] used balls which fell through the solutions as the cell was inverted end over end while Hartley and Runnicles[35] used glass balls which rolled on the diaphragm as it rotated in a slanting position.

With the use of diaphragm-cells it was no longer easy to sample the solutions to test whether a steady state had been established before timing the experiment as Northrop and Anson[29] had done. A rough but safe procedure was suggested by Gordon[36] using what is now known as the "Gordon inequality", $D\tau/\ell^2 > 1.2$, where D is the diffusion coefficient in $cm^2\ sec^{-1}$ and ℓ is the "apparent thickness" of the frit ($\ell \approx 1.6$ x actual thickness) and τ is the prediffusion time in seconds. For the usual type of frit $\ell \approx 0.4$ cm[37]. Although it has been shown lately that the Gordon inequality overestimates the time required to establish a linear concentration distribution[37,38] it still remains a useful guiding principle to a difficult problem.

But the most important contributions to the development of the diaphragm-cell as an accurate method of determining diffusion coefficients were those of Stokes[39]. After a thorough investigation of the diaphragm-cell Stokes made several recommendations and tabulated the guiding procedures which have now become standard. Stokes showed that neither density gradient stirring nor ball rolling was sufficient to remove stagnant layers off the diaphragm. He used a rotating magnet to rotate the stirrers both on top and bottom of the diaphragm. The stirrers were sealed glass tubes enclosing an iron wire. He also recommended diaphragm-cells of number 4 porosity. Stokes calibrated his cell with aqueous potassium chloride whose diffusion coefficient values had been carefully measured by the conductimetric absolute method by Harned and Nattall[40]. An authoritative review of the diaphragm-cell has been carried by Mills and and Woolf[38] who have also made important innovations. But generally the Stokes cell is now universally used.

However for all the advantages that the diaphragm-cell has over the classical methods, it has a serious limitation. It has been shown that the diaphragm-cell measurements on dilute electrolyte solutions below about 0.05 M, when compared with absolute measurements give higher results. The effect seems to arise through an enhancement of mobility in the electrical double layer on the pore walls. This has been confirmed by Mysels and McBain[41] by conductivity measurements in a cell in which a porous diaphragm was interposed between the electrodes. Although to a great extent in the present work the above limitation was not important since a non-electrolyte was used it became important in a mutual diffusion experiments of the non-electrolyte and the electrolyte.

Despite the experimental advantages of the diaphragm-cell it is not simple to derive the actual differential diffusion coefficient D from the diffusion measurements. What is easily derived mathematically from Fick's first law is a quantity $\bar{D}$, a complicated double average known as the diaphragm-cell integral coefficient. Robinson and Stokes[32] have given a mathematical procedure for deriving the diffusion coefficient, D, values in diffusing electrolytes. Let it be assumed that diffusion of the solute is from bottom of the diaphragm-cell to the top. Let the volume of the lower compartment of the diaphragm-cell be V_1, the volume of the upper compartment be V_2 and the volume of the diaphragm be V_3. The concentrations of the diffusing solute at the beginning and end of the experimental run should be denoted by C_1, C_2, C_3 and C_4 where C_1 is the initial concentration of the bottom compartment; C_2 is the initial concentration of the top compartment; C_3 is the final concentration of the bottom compartment after the run and C_4 is the final concentration of the top compartment. The total effective cross-section of the diaphragm pores should be written as A and their effective average length along the diffusion path as 1. The diaphragm is assumed to be in a steady state during the experiment. The flux J will however vary slowly with time, decreasing as the process of diffusion reduces the concentration-difference. To emphasize this the flux shall be written as J(t).

If the concentrations of the upper and lower compartments are denoted by c" and c' respectively, the rates of change of these concentrations are related to the flux J(t) by:

$$\frac{dc'}{dt} = - J(t)\,\frac{A}{V_1}$$

$$\frac{dc''}{dt} = J(t)\,\frac{A}{V_2}$$

Subtracting the top rate of change from the bottom rate of change of concentration with time gives

$$\frac{d(c' - c'')}{dt} = - J(t)\,A\left(\frac{1}{V_1} + \frac{1}{V_2}\right) \qquad \ldots\ldots 4$$

An average value of the diffusion coefficient D with respect to concentration over the concentration range c' to c" prevailing at the time considered is now introduced; this quantity D is also a function of time and is denoted as $\bar{D}(t)$:

$$\text{Then} \qquad \bar{D}(t) = \frac{1}{c' - c''}\int_{c''}^{c'} D\,dc = \frac{1}{c' - c''}\int_{x=0}^{1} D\left(\frac{c}{x}\right) dx$$

$$= \frac{1J(t)}{c' - c''} \qquad \ldots\ldots\ldots 5$$

Since $J(t) = - D\frac{\partial c}{\partial x}$ is a constant for all points within the diaphragm at time t, x being the distance of the plane considered from the lower surface of the diaphragm. Combining equations 4 and 5 gives

$$-\frac{d\ \ln\ (c' - c'')}{dt} = \frac{A}{l}\ (\frac{1}{V_1} + \frac{1}{V_2})\ \bar{D}(dt)$$

Intergrating between the initial and final concentration conditions give

$$\frac{\ln\ c_1 - c_2}{c_3 - c_4} = \frac{A}{l}\ (\frac{1}{V_1} + \frac{1}{V_2}) \int_{t=o}^{t=t} \bar{D}(t)\ dt$$

$\bar{D}$ is defined as the time-average of $\bar{D}(t)$ (which is itself already a concentration-average) that is

$$\bar{D} = \frac{1}{t} \int_{o}^{t} \bar{D}(t)$$

If $(A/l)\ (\frac{1}{V_1} + \frac{1}{V_2})$ the cell constant is denoted by β, then

$$\bar{D} = \frac{1}{\beta t}\ \ln \frac{c_1 - c_2}{c_3 - c_4} \qquad \ldots\ldots\ 6$$

The problem is now to convert $\bar{D}$, the diaphragm-cell integral coefficient into the required differential coefficient D. Gordon[36] has however demonstrated that a negligible error is introduced in all ordinary cases of $\bar{D}$ is related to D by:

$$\bar{D} = \frac{1}{cm' - cm''} \int_{cm''}^{cm'} D\ dc \qquad \ldots\ldots\ 7$$

where $cm' = c_1 + c_3$ and $cm'' = \frac{c_2 + c_4}{2}$

If the diffusing solute is an electrolyte and if its Nernst limiting value is known (i.e. that accurate limiting ionic conductivities are available) D at various values of c from a set of $\bar{D}$ values obtained in experiments using various concentrations can be obtained by a method of simple graphical approximations. On the other hand if the solute is non-electrolyte or an electrolyte whose Nernst limiting value is unknown a certain mathematical assumption has to be made. Stokes[39] and Stokes and Hammond[42] assumed a suitable analytical expression with arbitrary coefficients for D as a function of c and the coefficients determined so that equation 7 will fit the observed $\bar{D}$ values.

A quantity $\bar{D}^o(c)$ is defined as the average D with respect to concentration over the range o to c

$$\bar{D}^o(c) = \frac{1}{c} \int_o^c D \, dc$$

This quantity has been computed by Stokes[43] for potassium chloride at 25°C from D values of Harned and Nuttall[40] and of Gosting[44]

$$\bar{D} = [\bar{D}^o(cm') - \frac{cm''}{cm'} \bar{D}^o(cm'')]/(1 - \frac{cm''}{cm'}) \qquad \ldots\ldots 8$$

The cell constant (β) of the diaphragm-cell used in the present work was determined by a calibration with aqueous potassium chloride. The $\bar{D}^o(cm)$ values at various concentration, c, are tabulated by Stokes[43]. A graph of $\bar{D}^o(c)$ versus c was drawn and from it the $\bar{D}^o(cm)$ values at different concentrations at the end of the aqueous potassium chloride diffusion run were determined. Once the values of $\bar{D}^o(cm)$ were known equation 6 was used to calculate $\bar{D}$. $\bar{D}$ is related to (β) as shown in equation and the cell constant was determined by that equation.

Solution Theory - The Ion-Solvent Interaction

The study of ion-solvent interaction has come a long way since the days of Arrhenius who in 1887 made the then radical postulate that many solutes exist wholly or in part as ions when in solution. In 1920 Born formulated an approximate model for ion-solvent interactions. In the Born model, an ion is viewed as a rigid sphere (of radius r_i) bearing a charge $z i l_o$ (l_o is the electronic charge) and the solvent is taken to be a structureless continuum. The model thus suggests a simple method for calculating the free energy of ion-solvent interactions, that is the work of transfering an ion from vacuum into the solvent. In the 1920's Debye and Hückel put forward their ionic interaction theory in dilute solutions. The basic point of this theory is the idea of an "ion atmosphere", that is a cation has in its neighbourhood an excess distribution of anions while an anion is surrounded by an excess of cations. All ions are considered to be surrounded by solvent molecules and the extent of this solvation depends on the polarity (that is, in the main on dipole moment) of the molecules of the solvent. Thus ionization of the solute will be determined by this shielding effect on ions by solvent molecules. This prevents the ions of unlike charges of the solute from recombining to form neutral or uncharged entities.

The weakness of the Born model was to assume the structure of the solvent to be a continuum. The best way to look at the problem of ion-solvent interactions is to understand the structure of the solvent and how this structure affects the behaviour of ions and how in turn it is affected by the presence of different ionizing solutes. An acceptable way of looking at this for aqueous solutions was that presented by Frank and Wen[45] in 1957. Apart from the direct action of the ionic charge on water as a dielectric medium, they also considered how ions may exert an influence on the equilibrium between the ice-like and non-ice like forms which are present in room-temperature water. This provided a way of accounting for experimental results in a variety of areas, including diffusion, viscosity and ionic mobility. In this model a small ion is pictured as being surrounded by three different layers of solvent (water) molecules. Since water is a polar, structured solvent it is a forgone conclusion that its structure will be affected by the presence of ions due to ion-dipole interactions. If an individual ion is singled out in an aqueous medium it is easy to visualize that the ion-dipole interactions will be strongest nearest the ion and will diminish as the distance away from the ion is increased until a region where there will be no electrostatic interactions. It is generally agreed that in aqueous solutions of ions not larger than the caesium cation (Cs^+) and the iodide ion (I^-), the nearest neighbour water molecules are always essentially immobilized by direct ion-dipole interactions. These molecules can be said to be trapped and oriented in the field of the ion. This is the first layer. The second layer around the first one is an area where there is less but sufficient ion-dipole interaction to disrupt the normal structure of water. The structure of the solvent in this region will be a compromise structure between the tetrahedrally bonded networks characteristic of normal water and that of the first layer. The third layer is that where there are no or practically no ion-dipole interactions and will be just the ordinary structure of water.

The immobilized water molecules in the vicinity of the ion ceases to associate with other water molecules to form the network characteristic of water. If the ion moves, these immobilized water molecules move with it. Immobilization thus enhances the structure of the solvent in this region. In the intermediate region (that is, second layer) between the inner-most region and that of bulk water the structure is partly broken down.

From this picture an ionic solute can thus be described as a structure maker (that is, one which enhances the structure of the solvent) and a structure breaker depending upon its effects according to these three visualized layers or degree of solvation. Structure makers are those ions which manage to immobilize a lot of solvent molecules around them; that is in which the first layer is predominant over the second layer or stabilize the amount of structured solvent at a distance from the ion. Structure breakers are those ions which are incapable of immobilizing many solvent molecules around them but substantially disorganize the solvent structure. In this case the second region is predominant over the first. Certain solutes, particularly the hydrogen-bonding solutes or groups like $-NH_2$ or $-OH$, do not seem to alter the structure of water very much, if at all. This may be so because these solutes or groups are able to enter the water structure with only slight distortion, and to transmit both structure-forming and structure-disrupting tendencies. On the other hand small ions or highly charged ions which are strongly solvated, that is, they have immobilized many water molecules around them are known to be structure makers and large ions or ions of less charge are structure breakers. For example in water, cations smaller or more highly charged than potassium ion (K^+) are net structure makers or formers and become more strongly so the smaller and the more highly charged. K^+ is slightly structure breaking on balance and this tendency increases through rubidium ion (Rb^+) and caesium ion (Cs^+). The fluoride ion (F^-) is a structure-former and other halide anions are structure breakers increasing in tendency with size.

The structure of solid formamide has been determined by X-ray diffraction analysis[46] and it appears from this that the high dielectric constant 109.5 ± 0.2 at 25°C[1] in the liquid is probably due to the formation of "flickering" chain structures[3]. It is thus reasonable to consider extending the general theories developed for aqueous solutions to electrolytic solutions in formamide.

EXPERIMENTAL PROCEDURE

(a) Determination of Diffusion Coefficients by Electrochemical Semi-Infinite Linear Diffusion Technique - The Chronoamperometric Method.

Three modes of mass-transfer are normally encountered in electrode reactions. These are migration, convection and diffusion. Mass-transfer by migration is a result of the force exerted on charged particles by an electric field. Convection arises from thermal, mechanical or other disturbances of the solution. Diffusion exists whenever concentration differences are established as discussed in the Introduction under "Diffusion". During an electrode reaction a concentration gradient develops as soon as electrolysis starts. If migration of the electroactive species to the electrode is minimized to negligible proportions (in the case of ionic species by addition to the solution of excess background electrolyte) and the cell is free of mechanical and thermal disturbances; that is, migration and convection of the electroactive species are absent, one can restrict its mass-transfer to the electrode to diffusion alone. By in turn restricting diffusion to one direction only linear diffusion can be obtained. One can make the dimensions of the cell very large with respect to the electrode and fix the electrode firmly to the cell walls in such a way that diffusion is exactly in one direction without any peripheral contributions. In addition to that, if the concentration of the diffusing material is maintained at a value of practically zero at the electrode surface by maintaining a potential at the electrode such that the diffusing material is immediately oxidized or reduced upon reaching the electrode surface, a condition of semi-infinite linear diffusion can be established. Under these conditions the current is experimentally found to be proportional to the concentration (Co^b) of the diffusing substance in the bulk of the solution and proportional to the area (A) of the electrode. Also, the current decreases with time of electrolysis. A derivation which connects current and time is the Cottrell Equation; $i_t = \frac{nFAC_o^b D^{\frac{1}{2}}}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}}$ as outlined above in the Introduction which allows the diffusion coefficient to be determined.

If current during electrolysis can be followed with time at a constant potential, one then has a "chronoamperometric" method for the determination of diffusion coefficients of substances in solution. An experimental evaluation of linear diffusion is usually made by checking the constancy of the product $it^{\frac{1}{2}}$ with time. Precise studies of linear diffusion to solid electrodes were first made by Laitinen and Kolthoff[47,48] who showed that unless the direction of the diffusion is such that the less dense solution (either the diffusing material or the electrode reaction product) lies above the denser solution, convection currents due to density gradients cause greater supply of diffusing material to the electrode than by diffusion alone and consequently the measured current becomes abnormally high. Later on von Stackelberg et al[49] using the linear diffusion technique measured with great precision diffusion coefficients of a number of substances in a number of background electrolytes. Since the geometric area of the electrode is normally different from the electrochemical area, it is important that the latter be determined. It is recommended[50] that all electrochemical electrode area measurements be calculated from an $it^{\frac{1}{2}}$ determination on potassium ferrocyanide in aqueous 2M potassium chloride as supporting electrolyte using the diffusion coefficient results of von Stackelberg et al[49].

The linear diffusion technique was used in the present work to try to measure the diffusion coefficients of ferrocene in formamide at 25°C in a number of halide salts. The cell used was a three electrode assembly constructed from a block of Teflon, as shown in Figure 2 below. The three electrodes were a flat, polished platinum disc as test or working electrode; another platinum sheet as counter-electrode and a saturated calomel electrode as reference. Holes were bored through the body of the Teflon block through which water from a thermostated bath was circulated. This maintained the temperature of the cell and solutions at the 25°C working temperature. The potential was controlled by a Heath polarography module (Model EUA-19-2) and associated operational amplifiers. (Model EUA-19-4). The whole apparatus is shown below in Figure 3.

EXPERIMENTS

The Teflon cell was washed in Teepol in an ultrasonic bath and then with distilled water. The platinum electrodes were cleaned by dipping them in strong chromic acid for about two minutes and thoroughly rinsed with distilled water. This electrode cleaning procedure was done at least every day the electrodes were used[50]. The calomel electrode was periodically refilled with fresh, saturated potassium chloride aqueous solution.

The method of pretreatment of the test electrode as recommended by Adams[50] was tried but was not successful. This method demands that after washing the electrode as explained above a potential of about −0.2 V versus SCE (saturated calomel electrode)

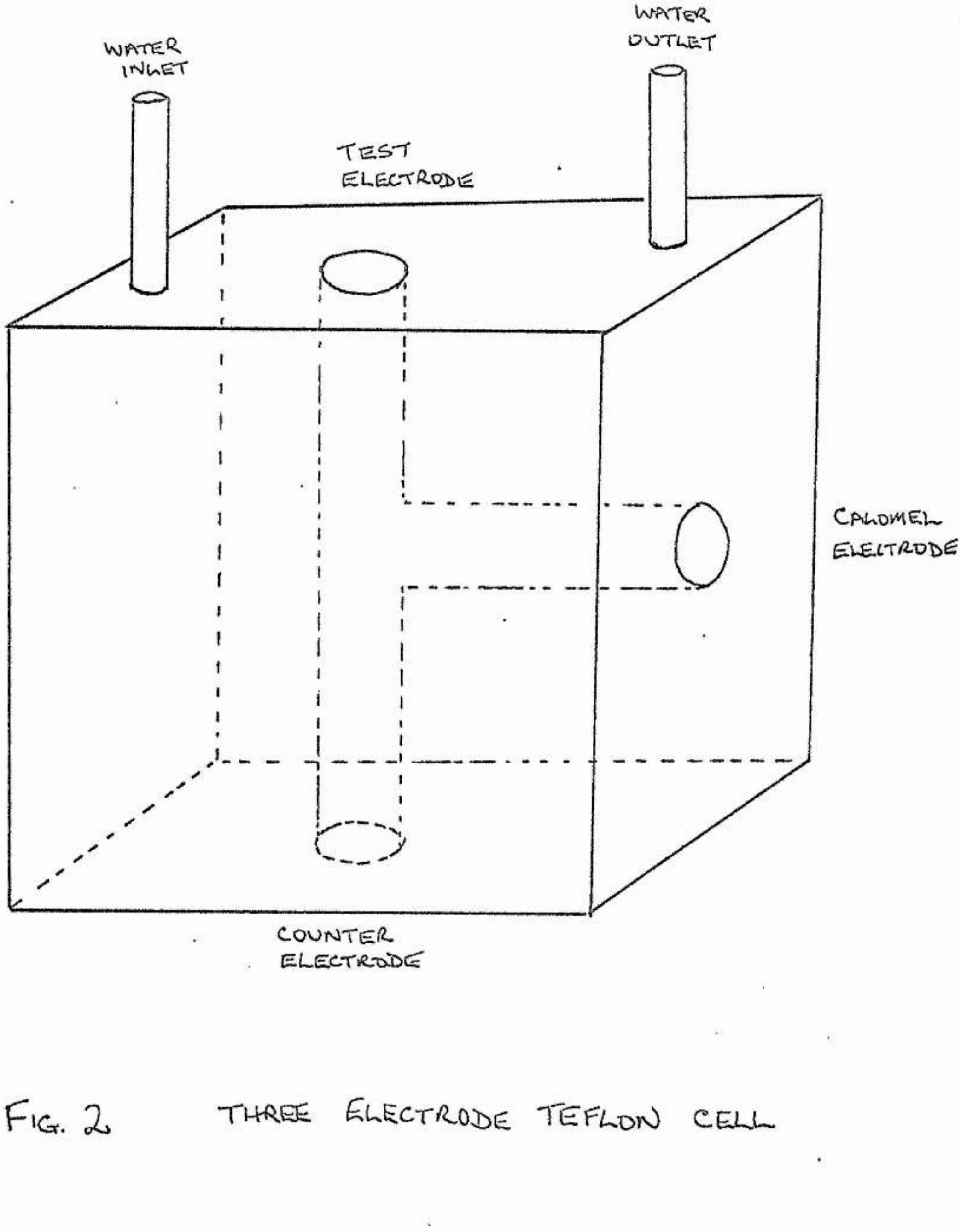


FIG. 2 THREE ELECTRODE TEFLON CELL

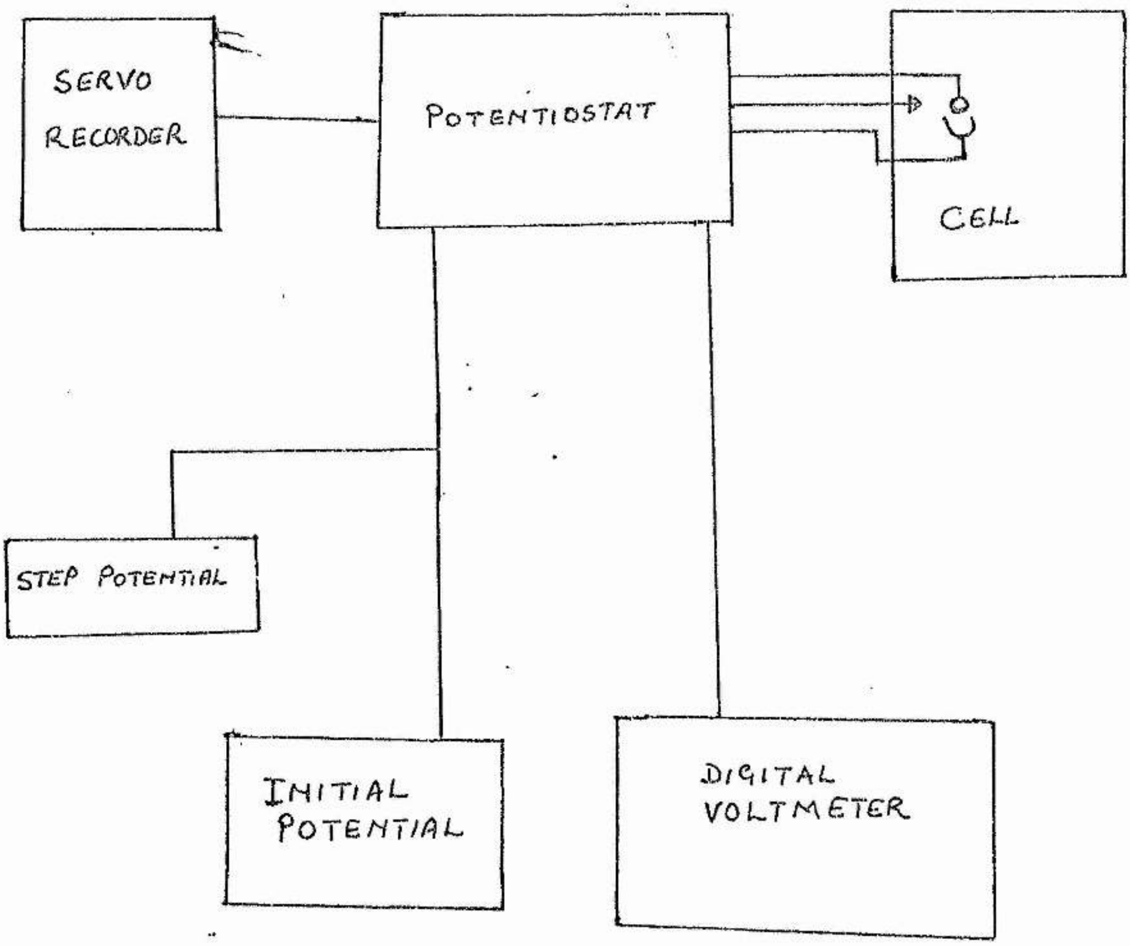


FIG 3 BLOCK DIAGRAM OF ELECTROCHEMICAL DIFFUSION APPARATUS

be applied to it to reduce its surface oxides until the cathodic current decays to zero. Then the potential is moved slightly anodic (about +0.05 V versus SCE) to reoxidize any sorbed hydrogen now on the electrode surface until the anodic current for hydrogen dissolution decays to close to zero. In the present work pretreatment was done by filling the cell with appropriate solution of the background electrolyte. The apparatus was then set at the working constant potential of the diffusing substance until current fell almost to zero. The effectiveness of this pretreatment method was checked by upward diffusion experiments on aqueous potassium ferrocyanide with potassium chloride as background electrolyte at 0.7 V constant potential. The graphs of $it^{\frac{1}{2}}$ versus time (t) gave straight lines as are required if the test electrode was in perfect working condition. In these and all subsequent experiments the background current caused by (a) charging current and (b) small impurity Faradaic currents, of each respective background electrolyte in appropriate solvent at constant potential of the diffusing material was noted for as long as the actual experiments would take and the results were subtracted from the actual experimental diffusion currents.

Measurement of the electrochemical area of the test electrode was undertaken with aqueous 5×10^{-4} M potassium ferrocyanide in aqueous 2 M potassium chloride. The $it^{\frac{1}{2}}$ obtained was then used to calculate the area using the appropriate von Stackelberg diffusion coefficient value. The area of the electrode so determined was confirmed by doing a number of upward diffusion experiments on different concentrations of potassium ferrocyanide with aqueous 0.1 M potassium chloride. Downward diffusion experiments were also done on silver nitrate with aqueous 0.1 M potassium nitrate as supporting electrolyte as a further check on the method. A straight line was drawn by Computer through the points of $it^{\frac{1}{2}}$ with time. The line was extrapolated to zero time and that $it^{\frac{1}{2}}$ was used to calculate diffusion coefficients from the Cottrell Equation. The diffusion coefficients so obtained were used to recalculate the currents at different times for each respective case. A perfect fitting curve through the points of currents versus time was a measure on the accuracy of the diffusion coefficient. This is shown by graphs Figures 4 and 5. The other results are also shown below.

RESULTS

1. The electrochemical area (A) of the test electrode was 0.7073 cm^2. This is compared with the geometric area of 0.535 cm^2 measured by a travelling microscope.

2. Diffusion coefficients of potassium ferrocyanide at different concentrations in aqueous 0.1 M potassium chloride at 0.7 V constant potential at 25°.

(a) 2×10^{-4} M potassium ferrocyanide diffusion coefficient was 0.629×10^{-5} cm^2 sec^{-1}. The experimental parameters are shown in Table 1.

TABLE 1

Time (t) in secs.	$t^{\frac{1}{2}}$	Background current in microamps.	Total current in microamps.	Faradaic current in microamps.	$it^{\frac{1}{2}}$ Faradaic current x time
12	3.46	1.4	6.8	5.4	18.68
16	4.0	1.3	6.2	4.9	19.6
20	4.47	1.2	5.5	4.3	19.2
24	4.90	1.1	5.2	4.1	20.0
28	4.29	1.05	4.8	3.75	19.8
32	5.65	1.0	4.5	3.4	19.2
36	6.0	1.0	4.3	3.3	19.8
40	6.32	0.95	4.1	3.15	19.9
44	6.63	0.8	3.9	3.1	20.5
48	6.93	0.8	3.7	2.9	20.1
52	7.14	0.8	3.5	2.7	19.3
56	7.48	0.8	3.45	2.55	19.1
60	7.74	0.75	3.3	2.55	19.7
64	8.0	0.75	3.2	2.45	19.6
68	8.24	0.75	3.1	2.35	19.4
72	8.48	0.75	3.0	2.25	19.1
76	8.72	0.75	2.85	2.1	18.3
80	8.94	0.75	2.8	2.05	18.3
84	9.16	0.65	2.75	2.1	19.2
88	9.38	0.65	2.7	2.05	19.2
92	9.59	0.65	2.6	1.95	18.7
96	9.8	0.65	2.5	1.85	18.1
100	10.0	0.6	2.5	1.9	19.0

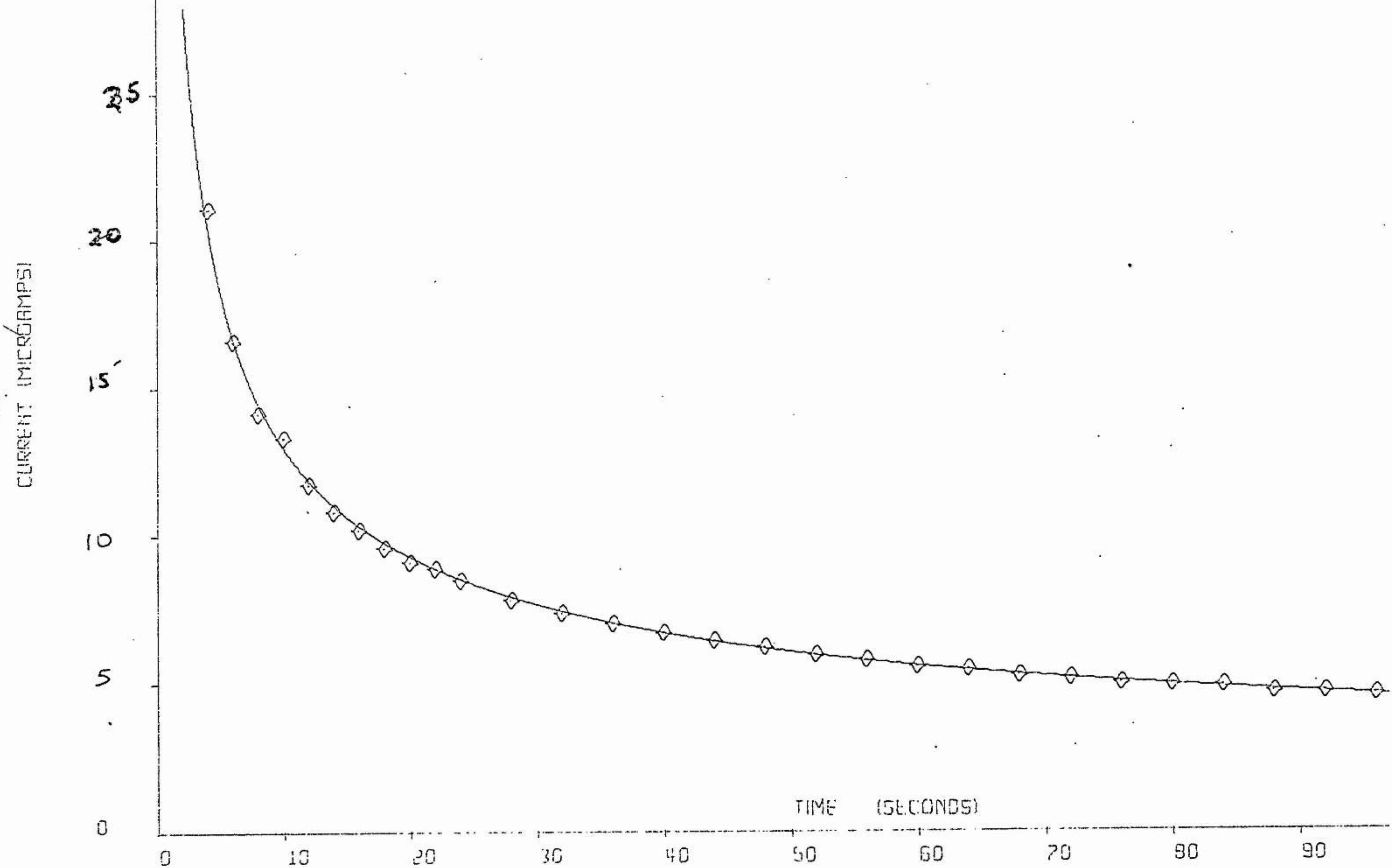


Fig. 4 5×10^{-4} M. Potassium Ferrocyanide in 10^{-1} M KCl (aq.)

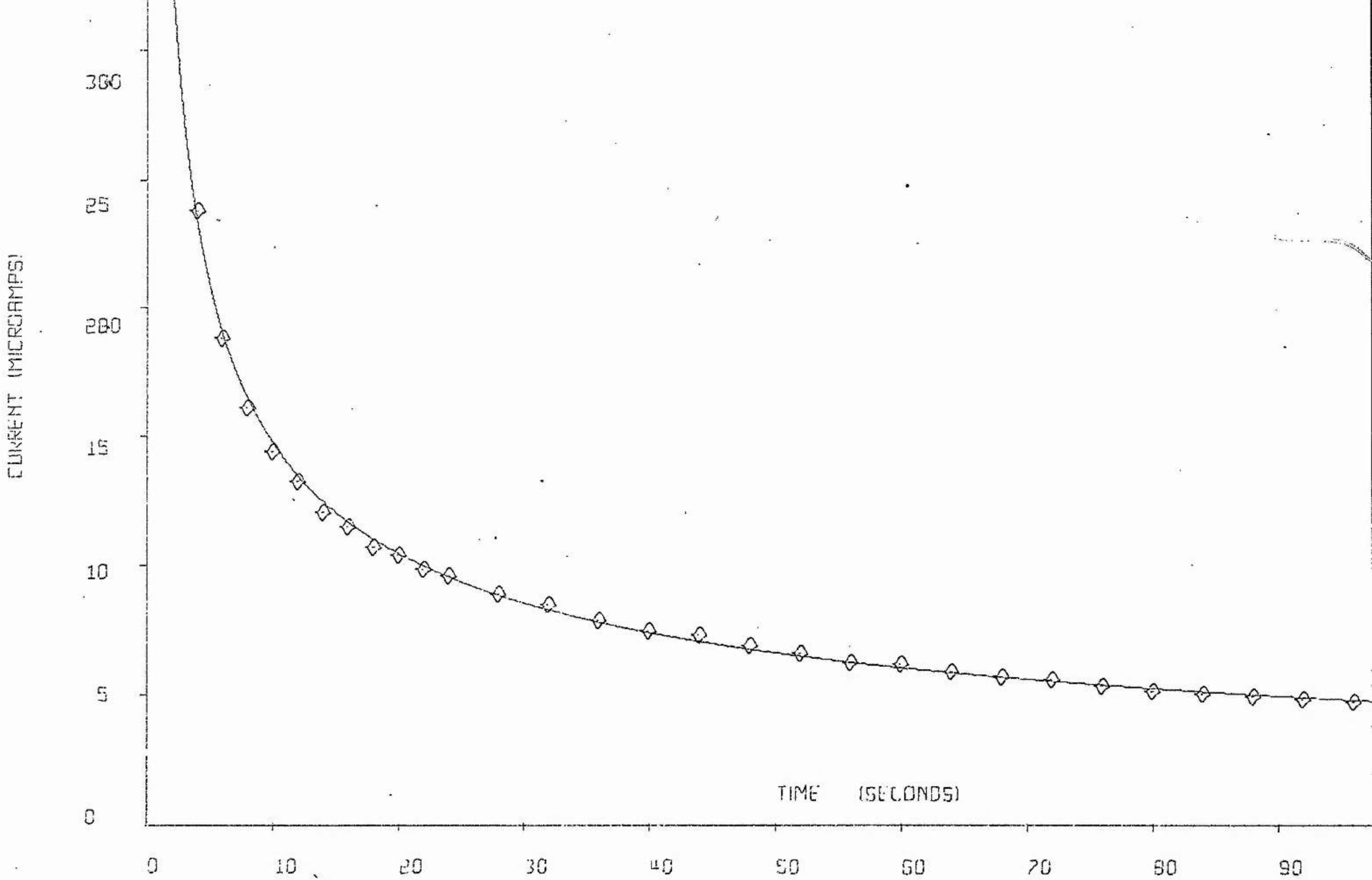


Fig. 5 5×10^{-4} M $AgNO_3$ in 10^{-1} M KNO_3 (aq)

(b) 5×10^{-4} M potassium ferrocyanide diffusion coefficient was 0.635×10^{-5} cm^2 sec^{-1}. The experimental measurements are shown below in Table 2.

TABLE 2

Time (t) in secs.	$t^{\frac{1}{2}}$	Background current in microamps.	Total current in microamps.	Faradaic current in microamps	$it^{\frac{1}{2}}$ Faradaic current x time
8	2.83	1.5	18.5	17.0	48.1
12	3.46	1.4	15.3	13.9	48.1
16	4.0	1.3	13.4	12.1	48.4
20	4.47	1.2	12.1	10.9	48.7
24	4.9	1.1	11.2	10.1	49.5
28	5.29	1.05	10.4	9.35	49.4
32	5.65	1.0	9.9	8.9	50.3
36	6.0	1.0	9.3	8.3	49.8
40	6.32	0.95	8.8	7.85	49.6
44	6.63	0.8	8.5	7.7	51.0
48	6.93	0.8	8.1	7.3	50.6
52	7.14	0.8	7.8	7.0	50.0
56	7.48	0.8	7.4	6.6	49.4
60	7.74	0.8	7.3	6.55	50.7
64	8.0	0.75	7.0	6.25	50.0
68	8.24	0.75	6.8	6.05	49.8
72	8.48	0.75	6.7	5.95	50.4
76	8.72	0.75	6.4	5.65	49.3
80	8.94	0.75	6.2	5.45	48.7
84	9.16	0.75	6.0	5.35	49.0
88	9.38	0.65	5.9	5.25	49.2
92	9.59	0.65	5.8	5.13	49.4
96	9.8	0.65	5.7	5.05	49.5
100	10.0	0.60	5.5	4.9	49.0

(c) 1×10^{-3} M potassium ferrocyanide diffusion coefficient was 0.619×10^{-5} cm^{2} sec^{-1}. The measured currents and time are shown in Table 3.

TABLE 3

Time (t) in secs.	$t^{\frac{1}{2}}$	Background current in microamps.	Total current in microamps.	Faradaic current in microamps.	$it^{\frac{1}{2}}$ Faradaic current x time
12	3.46	2.9	30.0	27.1	93.7
16	4.0	2.5	26.0	23.5	94.0
20	4.47	2.25	23.3	21.15	94.0
24	4.9	2.0	21.4	19.4	95.0
28	5.29	1.8	19.8	18.0	95.2
32	5.65	1.7	18.5	16.8	94.9
36	6.0	1.6	17.4	15.8	94.8
40	6.32	1.5	16.5	15.0	94.8
44	6.63	1.45	15.5	14.05	98.1
48	6.93	1.35	14.9	13.55	93.9
52	7.14	1.25	14.1	12.85	91.8
56	7.48	1.22	13.5	12.28	91.7
60	7.74	1.2	13.0	11.8	91.3
64	8.0	1.1	12.55	11.45	91.6
68	8.28	1.1	12.2	11.1	91.4
72	8.48	1.05	11.8	10.75	91.2
76	8.72	1.0	11.5	10.5	91.5
80	8.94	1.0	11.2	10.2	91.2
84	9.16	0.95	10.9	9.95	91.1
88	9.38	0.9	10.6	9.7	91.0
92	9.59	0.9	10.4	9.5	91.1
96	9.8	0.9	10.2	9.3	91.1
100	10.0	0.8	10.0	9.2	92.0
104	10.2	0.8	9.8	9.0	91.8
108	Lo.39	0.8	9.6	8.8	91.4
112	10.58	0.75	9.45	8.7	92.0
116	10.72	0.75	9.4	8.65	92.6
120	10.95	0.75	9.3	8.55	93.6

Von Stackelberg's diffusion coefficient value in aqueous 10^{-1} M potassium chloride at 4×10^{-3} M potassium ferrocyanide is 0.650×10^{-5} cm^{2} sec^{-1}. This gives an error of about 3% with the best of the results given above.

3. The Diffusion Coefficient of 5×10^{-4} M silver nitrate in aqueous 10^{-1} M potassium nitrate was 1.549×10^{-5} cm^{2} sec^{-1} at 25°C and 0.1 V constant potential. This gives an error of about 0.26% against that of von Stackelberg which is 1.55×10^{-5} cm^{2} sec^{-1}. The experimental results are given in Table 4 below.

TABLE 4

Time (t) in secs.	$t^{\frac{1}{2}}$	Background current in microamps.	Total current in microamps.	Faradaic current in microamps.	$it^{\frac{1}{2}}$
8	2.83	4.4	31.0	26.6	75.3
12	3.46	3.8	25.8	22.0	76.0
16	4.0	3.6	22.7	19.1	76.4
20	4.47	3.4	20.5	17.1	76.4
24	4.9	3.2	19.2	15.9	77.9
28	5.29	3.2	17.9	14.7	77.7
32	5.65	3.1	17.0	13.9	78.5
36	6.0	3.0	16.2	13.2	79.0
40	6.32	2.8	15.4	12.6	79.6
44	6.63	2.8	14.9	12.1	80.0
48	6.93	2.7	14.4	11.7	81.1
52	7.14	2.7	13.9	11.2	79.9
56	7.48	2.6	13.5	10.9	81.5
60	7.72	2.55	13.0	10.45	80.7
64	8.0	2.5	12.8	10.3	82.4
68	8.24	2.45	12.4	9.95	82.0
72	8.48	2.4	12.1	9.7	82.2
76	8.72	2.4	11.8	9.4	81.9
80	8.94	2.3	11.6	9.3	83.1
84	9.16	2.2	11.4	9.2	84.3
88	9.38	2.2	11.0	8.8	82.5

Upward Diffusion - Diffusion Coefficients of Ferrocene in Formamide at 25°C and 0.8 volts Constant Potential.

Formamide was refluxed over freshly ignited calcium oxide for three hours, followed by two successive distillation through a column under vacuum at a pressure of 0.8 mm of Mercury[7].
The distillation temperature was 69°C. The middle portion of the distilled formamide was used for the experiments below. Further explanation about the purification process is outlined later on under the "Diaphragm-Cell Method". Experiments were carried out using a rotating platinum wire electrode to establish the optimum potential at which ferrocene electrolysed. The value was 0.8 ±0.05V. The area of the electrode was measured regularly because it changes in value with use. Numerous diffusion experiments were carried out with ferrocene in formamide solution of halide salts.

Results

Bromide salts

The oxidation potential of Br^- ion in formamide was about 0.35 volts as against the optimum constant potential of ferrocene in formamide of 0.8 v. It was not therefore possible to obtain measurements in bromide salts solutions in formamide because of the difficulties experienced.

Chloride salts

The concentrations were 1×10^{-3} molal ferrocene in 10^{-1} molal salts solutions in formamide. The diffusion coefficients of ferrocene in different chloride salts solutions in formamide shown in Table 5 below were calculated from the Cottrell Equation by Computer using a test electrode area of 0.564 cm^2.

TABLE 5

No. of runs	Lithium Chloride	Sodium Chloride	Potassium Chloride	Caesium Chloride
	D x 10^{+5} cm^2 sec^{-1}	D x 10^{+5} cm^2 sec^{-1}	D x 10^{+5} cm^2 sec^{-1}	D x 10^{+5} cm^2 sec^{-}
1	0.870	1.377	1.080	0.843
2	0.753	1.070	0.912	0.651
3	0.721	0.980	0.876	0.603
4	0.755	0.987	1.114	0.564
5		0.992	1.054	0.558
6		1.148	1.060	
7		1.103		
8		1.029		

(b) METHODS OF ANALYSIS OF FERROCENE IN FORMAMIDE

Numerous experiments were undertaken to find out the most reliable method of analysing ferrocene in formamide. Both ferrocene and formamide were used unpurified in these experiments.

1. Redox Method

The fact that ferrocene is oxidized to ferricenium ion by certain oxidizing agents like ferric chloride and ceric sulphate in certain solvent medium was reported over twenty years ago[51,52]

$$(C_5H_5)_2Fe = [(C_5H_5)_2Fe]^+ + \bar{e}$$

(a) Direct Visual Titration

The first trial at redox method was a direct titration of ferrocene in formamide solvent medium against aqueous ceric sulphate. It was considered that since the ferrocene solution is yellow in formamide and the ferricenium ion is blue; a complete change from yellow to blue at the end point would be visually marked.

An ampoule of ceric sulphate was diluted to 500 mls with 1 Molar (aq) sulphuric acid to yield 0.05 Molar ceric sulphate solution. The acidic medium guarantees stability to the ceric sulphate. Some 0.05 M ceric sulphate solution was diluted to 0.025 M by 1 M (aq) sulphuric acid. It should be noted that all subsequent dilutions of the ceric sulphate solutions were done with 1 M (aq) sulphuric acid. 0.01 molal ferrocene in formamide was prepared. Some hard shaking and gentle warming were necessary in order to dissolve the ferrocene faster.

Two samples 6.76 grams and 7.25 grams of 0.01 molal ferrocene were weighed into a 250 ml conical flask and titrated against 0.025 M (aq) ceric sulphate. The end point was not sharp. Ceric sulphate was diluted to 0.0125 M and titrated against 20.20 g and 19.65 g of 0.01 m ferrocene. Again the end point was not clear. Further several titrations did not improve the result. The end point of the reaction $(C_5H_5)_2Fe + Ce^{+4} = [(C_5H_5)_2Fe]^{+} + Ce^{+3}$ could not be determined this way.

(b) The potentiometric titration method

0.05 M ceric sulphate (aq) was diluted eight times to 0.00625 M. A 32.89 g sample of 0.01 molal ferrocene was then potentiometrically titrated against the 0.00625 M ceric sulphate using a Roband digital voltmeter to follow the potential of a platinum electrode with respect to a saturated calomel electrode. The volumes of ceric sulphate added each time were plotted on a graph against the electrode potential. No clear inflection was noted near the calculated equivalence point. It was also found that some ferrocene recrystallized from solution due to the addition of water from the very dilute 0.0625 M ceric sulphate. A second attempt, titration of 0.01 m samples of ferrocene with 0.05 M ceric sulphate did not improve the result. A quick check on whether the voltmeter was working well was performed by titrating potentiometrically 25 mls of 0.0113 M potassium ferrocyanide (aq) solution with 0.05 M ceric sulphate. The graph of volume of titrant versus electrode potential (in volts) gave a very clear end point. The electrodes and the voltmeter were in good condition.

0.05 M potassium permanganate standardized against 0.1 M solution of potassium ferrocyanide was then used to titrate against ferrocene in formamide instead of 0.05 M ceric sulphate. The graphs of volume versus potential were even worse than those when ceric sulphate was the titrant.

Methanol was substituted for formamide as solvent. 0.01 Molar ferrocene in methanol was titrated against 0.05 M ceric sulphate. The graph of volume of titrant versus electrode potential (in volts) gave a sharper and clearer end point than in formamide. The trouble therefore was probable due to the formamide solvent under these conditions.

The graphs of electrode potential versus volumes of ceric sulphate titrated against ferrocene in formamide and ferrocene in methanol are shown in Figure 6, and the titration results in Tables 6 and 7.

TABLE 6

25 mls of 0.001 m ferrocene in formamide potentiometrically titrated with 0.05 M (aq) ceric sulphate.

0.05 M ceric sulphate volume increments in mls	Total volume of 0.05 M ceric sulphate added in mls	Electrode potentials (E) in volts
0.0	0.0	0.148
0.1	0.1	0.260
0.1	0.2	0.278
0.1	0.3	0.280
0.1	0.4	0.291
0.1	0.5	0.302
0.1	0.6	0.314
0.1	0.7	0.330
0.1	0.8	0.351
0.1	0.9	0.377

TABLE 7

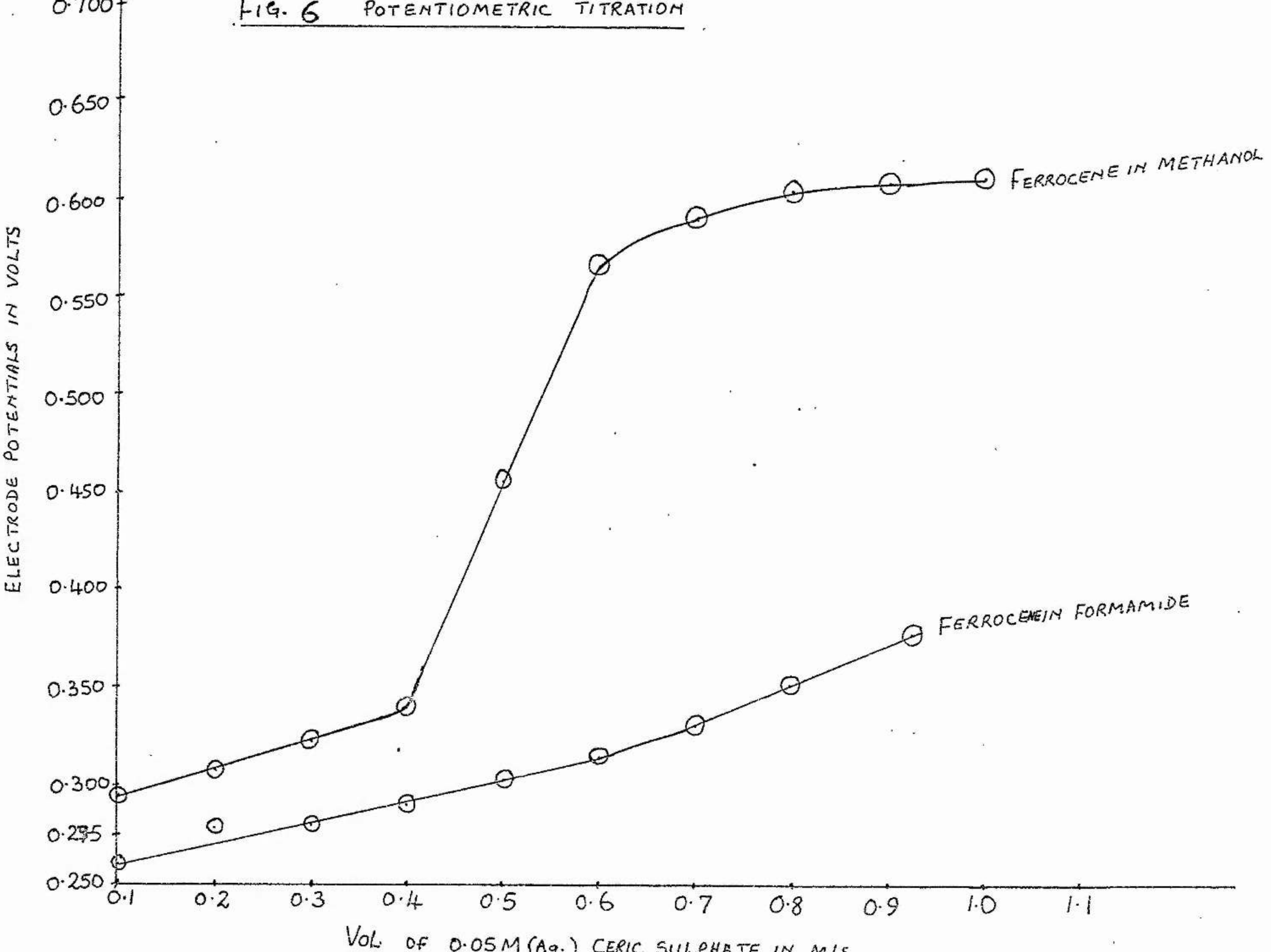
20.94 grams of 0.001 m ferrocene in methanol potentiometrically titrated with 0.05 M (aq) ceric sulphate.

0.05 M ceric sulphate volume increments in mls	Total volume of 0.05 M ceric sulphate added in mls	E in volts
0.1	0.1	0.293
0.1	0.2	0.307
0.1	0.3	0.323
0.1	0.4	0.341
0.1	0.5	0.455
0.1	0.6	0.565
0.1	0.7	0.591
0.1	0.8	0.604
0.1	0.9	0.607
0.1	1.0	0.610

(c) Amperometric Titrations

The techniques of amperometry and amperometric titrations have been reviewed by Lingane[53] and Stock[54]. In the present work a single polarizable electrode was used in conjunction with a non-polarizable reference electrode. A constant voltage was applied to the former so that a mass-transport limited current due to $(C_5H_5)_2Fe - e \longrightarrow [(C_5H_5)_2Fe]^+$ followed through the cell. The indicator or polarizable electrode was the rotated platinum microelectrode similar to that used by Laitinen and Kolthoff[55] with a constant speed of 600 r.p.m. The non-polarizable reference

FIG. 6 POTENTIOMETRIC TITRATION

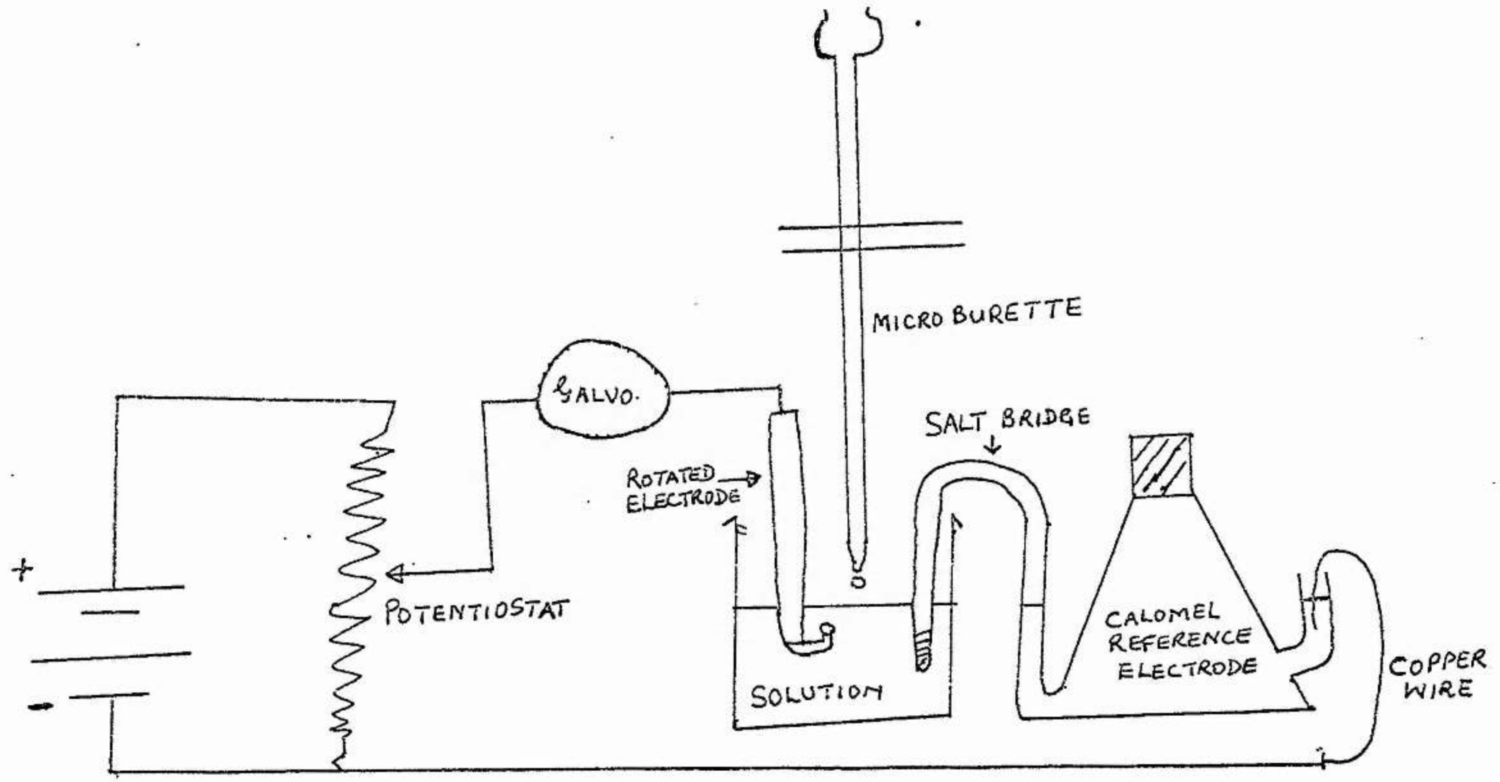


electrode was a large calomel electrode.

The large calomel electrode was made as follows:
The inside of the clean flask was smeared with Desicote to prevent water interfering with the mercury. The top of the mercury in the flask was covered with a thin layer of mercurous chloride (Hg_2Cl_2) skin. Saturated potassium chloride (aq) was filled up to the neck of the flask without disturbing the mercurous chloride layer. More pot. chloride crystals were added to the flask to maintain the saturation equilibrium. The head of the salt bridge was filled with jelly made up by boiling in the ratios, 3. g of potassium chloride; 0.3 g of agaragar and 10 mls of distilled water. The salt bridge was connected to the one arm of the flask with a clean plastic tube filled with saturated aqueous potassium chloride. When not in use the jelly head of the salt bridge was kept under saturated potassium chloride in a beaker.

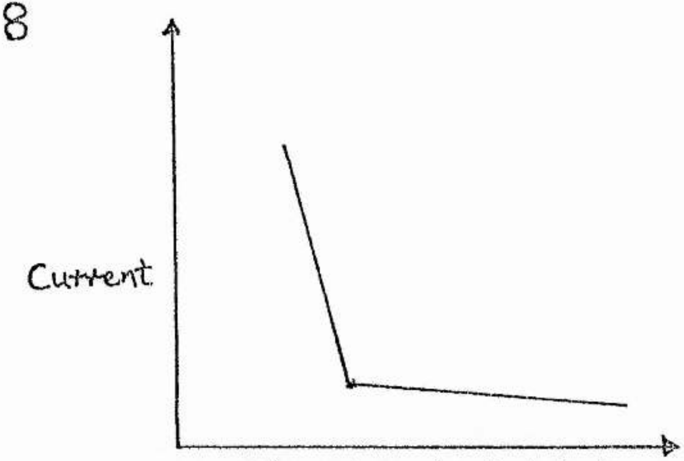
Once the colomel electrode and salt bridge were made and all the apparatus set (Figure 7) two calibration experiments were done. The first calibration was with ammonium ferrous sulphate and ammonium nitrate.

Fig. 7 THE AMPEROMETRIC TITRATION APPARATUS



To 200 mls of 0.1 M ammonium nitrate (aq) as supporting electrolyte in a 400 ml beaker were added volumetrically small increments of 0.1 M ammonium ferrous sulphate (aq) at 1.0 volt constant potentials and increase in current noted. The graph of ferrous mls. added versus current gave the expected result of a rising straight line. The second calibration was the titration of 0.1 M ammonium ferrous sulphate with 0.05 M ceric sulphate (aq) with 0.1 M ammonium nitrate as supporting electrolyte at 1.0 volt constant potential. The graph of current versus millilitres of ceric sulphate used gave the expected amperometric titration end-point for this system as shown in Figure 8. (In both experiments above the solution had nitrogen gas bubbled into them to remove oxygen.) The apparatus and the ceric sulphate were thus shown to be in good order.

FIG 8



Titration of Ferrocene in Formamide with Ceric Sulphate

In an article entitled "The Polarographic Chemistry of Ferrocene, Ruthenocene and the Metal Hydrocarbon Iron", Page and Wilkinson ^{52} reported of their experimental work to the effect that ferrocene-ferricenium ion was a thermodynamic reversible system in the alcoholic supporting electrolyte, with an oxidation-reduction potential of -0.59 volts [versus the Normal Hydrogen Electrode (NHE)]. The standard electrode potential (E^{o}) for ferrocene in formamide has been given as -0.93 volts[56] versus the NHE. Using the apparatus shown above (Figure 7) the constant potential for amperometrically titrating ferrocene with ceric sulphate was here determined volumetrically on 200 mls of 0.001 molal ferrocene in formamide. The voltage was varied and the current noted. The voltage at which current became constant was about 0.7 volts and the working constant potential in all the amperometric titration of ferrocene in formamide with ceric sulphate (aq) was taken as 0.8 volts against the calomel electrode (E^{o} = 0.2415 V versus NHE).

Once the constant potential was known and apparatus calibrated 0.025 M ceric sulphate (aq) was volumetrically titrated into 0.005 molal and 0.001 m ferrocene in formamide with 0.1 Molal poteassium chloride as supporting electrolyte. The graph of millilitres of ceric sulphate versus current gave the result as in Figure 8 but the experimental end-point was lower than the theoretical end-point. Then 0.025 M ceric sulphate was standardized amperometrically by volumetric titration with 0.1 M ammonium ferrous sulphate. The ceric sulphate was found to be 0.0253 M. 0.4 g of 0.01 m ferrocene solution with 80 mls of 0.1 M potassium chloride was titrated with 0.0253 M ceric sulphate. The experimental results were again lower of the order of 19 per cent to the calculated results. Using a weight burette for ceric sulphate instead of a volumetric burette did not improve the results.

The 0.05 M ceric sulphate was standardized with standard arsenious oxide (AS_2O_3) by both visual titration detection using ferroin indicator[57] and by the potentiometric titration. The ceric sulphate was also amperometrically standardized against standard 0.1 M ammonium ferrous sulphate (aq). The average concentration of 0.05 M ceric sulphate was found to be 0.0478 M.

The newly standardized ceric sulphate (0.0478 M) using a weight burette was titrated amperometrically into 0.004 molal ferrocene in formamide. This time a stream of nitrogen gas was slowly bubbled into the titration beaker (it was stopped when current reading was being taken not to disturb the equilibrium). The titrant concentration (ceric sulphate 0.047 M) was also just about twelve times more concentrated than the ferrocene concentration. Stock[54] recommended a titrant concentration ten times more than the concentration of the titrate in order to minimize the dilution effect on the inflection end point on the curve (Figure 8). Because although the indicator current is directly proportional to concentration it is not directly proportional to volume of added titrant solution because of the increasing volume of solution to which the titrant is added. A computer programme to locate the exact inflection end point was used. Under these conditions the end point result improved markedly with an average error of about 1.6%. The bottom half of the curve was not however exactly horizontal as theoretically it ought to be but sloped slightly downwards perhaps due to some small traces of oxidizable impurities in the solution. The use of iodine as titrant instead of ceric sulphate was also considered but the attempt was dropped when it was discovered that iodine attacks formamide[58] by the reaction

$$\text{H-CONH}_2 + \text{I}_2 = \text{H.CONHI} + \text{HI}$$

Several experiments were conducted to see the effect of acids in formamide.

Ferrocene in formamide was vigorously bubbled with dry nitrogen gas to remove oxygen. Concentrated hydrochloric acid and concentrated sulphuric acid were also bubbled with nitrogen. Two portions of the ferrocene solution were added each to the concentrated hydrochloric acid and concentrated sulphuric acid. The mixed solution were analysed spectrophotometrically for the ferricenium ion peak. There was none. When the ferrocene above solution above were not bubbled with nitrogen to remove the air, it reacted with the concentrated acids to give ferricenium ion. Ferrocene in ninety-five percent ethanol plus concentrated hydrochloric acid or concentrated sulphuric acid in air also gave ferricenium ion. This confirmed what Wilkinson et al[51] had observed. So since the ceric sulphate is made in an acid medium however dilute, it was essentially important to remove air which might facilitate the reaction between ferrocene and the acid.

A test was also carried out to see if there was any reaction between the ceric sulphate with the formamide used as solvent. To 30 mls of 0.05 M ceric sulphate was added 30 mls of formamide. Immediately the mixture was titrated with arsenious oxide with ferroin as indicator. The molarity of ceric sulphate was found to be 0.0507 M. Forty minutes later it was 0.0494 M and one-hundred and five minutes later it was 0.0485 M. 0.05 M ceric sulphate solution mixed with formamide and left over night formed a precipitate. Ceric sulphate in this medium reacted with either formamide or impurities in formamide but at a very slow rate to have appreciably affected the titrations.

Some of the problems of voltmetrically and amperometrically working with the cerium(IV)-cerium(III) couple in 1 M (aq) sulphuric acid have been discussed by Stock[54]. Stock has referred to the voltmetric studies of Kolthoff and Nightingale that showed that the cerium(IV)-cerium(III) couple in 1 M sulphuric acid is highly irreversible at a rotating platinum electrode.

RESULTS

Some results on the amperometric titration of ferrocene in formamide with ceric sulphate can be appreciated in Figures 9 and 10, and Tables 8 and 9 respectively. The observed end point for Figure 9 or Table 8 is 1.4% higher than the calculated one while for Figure 10 or Table 9 it is 1.87% higher. Both these titrations were done with a constant bubbling in of nitrogen gas to remove oxygen.

TABLE 8

6.646 g of 0.01 m ferrocene in formamide with 80 mls of 0.1 M KCl in formamide as supporting electrolyte, amperometrically titrated with 0.0478 M (aq) ceric sulphate at 0.8 volts constant potential.

Volume in mls of 0.0478 M ceric sulphate added	Units of current
0.2	420
0.4	370
0.5	330
0.7	260
0.9	185
1.1	110
1.2	87.5
1.3	55
1.5	5
1.6	5
1.7	5
1.8	4
2.0	4

FIG. 9. AMPEROMETRIC TITRATION OF FERROCENE IN FORMAMIDE

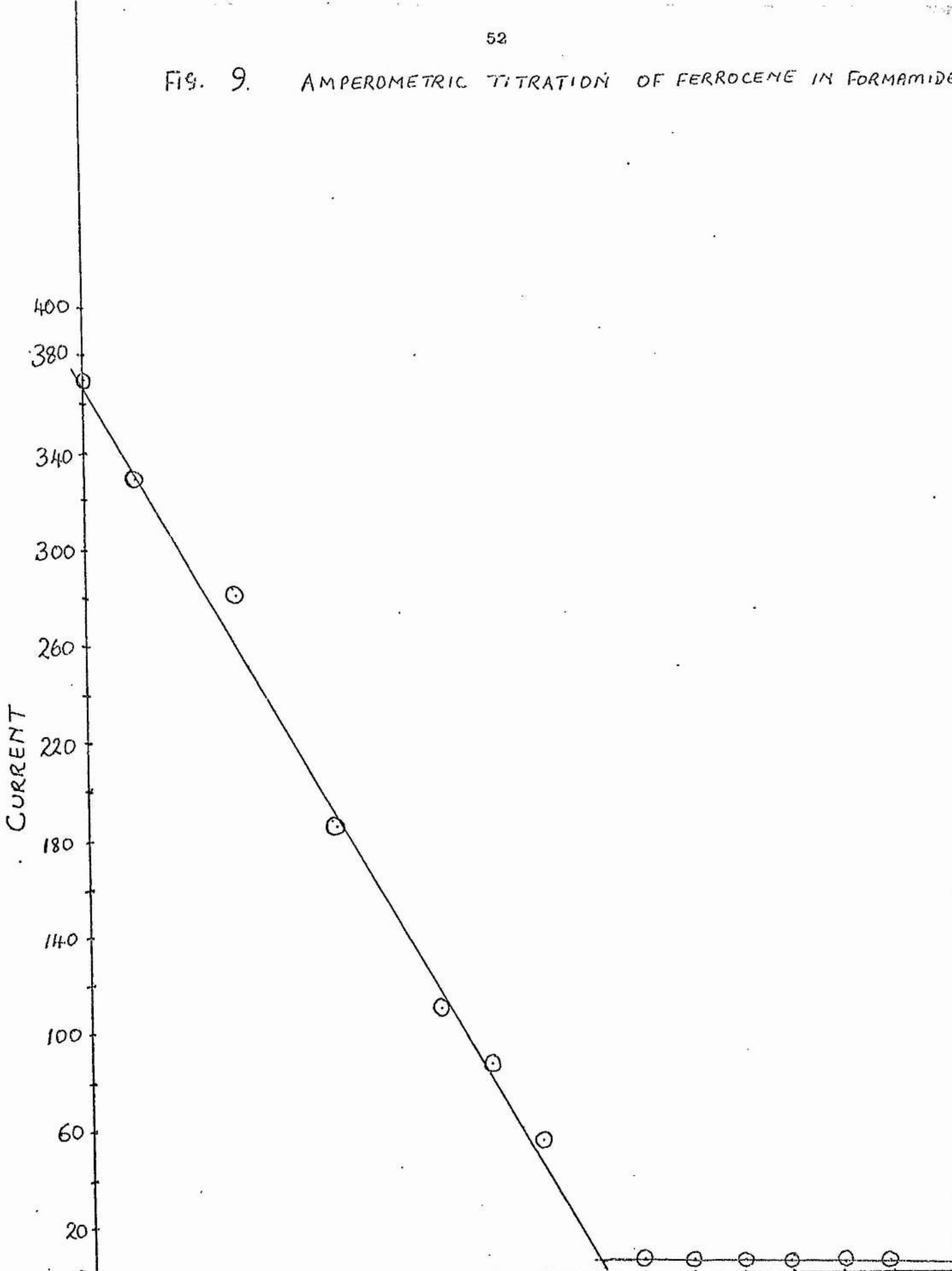


FIG. 10. AMPEROMETRIC TITRATION OF FERROCENE IN FORMAMIDE

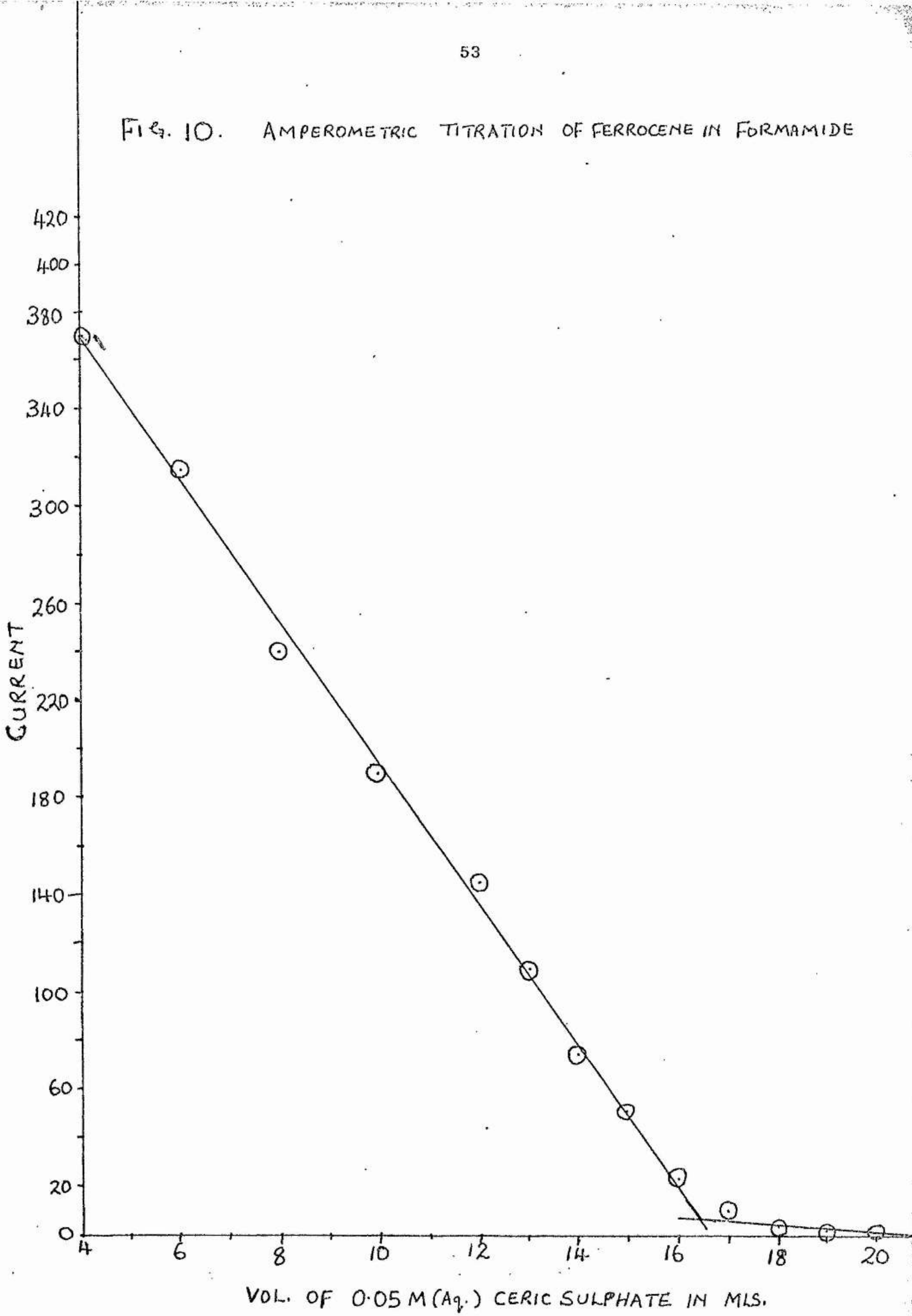


TABLE 9

7.6635 g of 0.01 m ferrocene in formamide with 80 mls of 0.1 M KCl in formamide as supporting electrolyte, amperometrically titrated with 0.0478 M (aq) ceric sulphate at 0.8 volts constant potential.

Volume in mls of 0.0478 M ceric sulphate added	Units of current
0.2	420
0.4	370
0.6	315
0.8	240
1.0	190
1.2	145
1.3	110
1.4	75
1.5	50
1.6	24
1.7	10
1.8	4
1.9	2
2.0	2

2. Spectrophotometry and Spectrophotometric Titration

Ferrocene has been reported to absorb in the ultraviolet and visible region at wavelengths 325 $m\mu$ and 440 $m\mu$[59] and ferricenium ion as ferricenium tetrafluoroborate at wavelengths 250 $m\mu$ and 617 $m\mu$. The ferricenium peak at 617 $m\mu$ is sharper than these of ferrocene. This sharp peak whose height should vary with concentration much more noticeably than the broader peaks of ferrocene might therefore prove the basis of another method of determining ferrocene concentration in formamide. Spectrophotometric titrations of ferrocene with ceric sulphate were therefore carried out.

First, a check was conducted to confirm the wavelengths reported by Rosenblum[59]. Three concentrations (0.01 molal; 0.001 m and 0.0001 m) of ferrocene in formamide were examined by Unicam SP800 Ultraviolet Spectrophotometer. The wavelength of the absorption maximum of the ferricenium ion in formamide was 622 mμ and not 617 mμ as reported by Rosenblum in aqueous solution for ferricenium tetrafluoroborate.

In each of eight flasks were placed 20 g of 0.01 molal ferrocene in formamide. To each flask were added amounts of 0.05 M ceric sulphate (aq) as shown in Table 10. The ferricenium ion absorbance was determined by the SP800 Ultraviolet Spectrophotometer, using 10 mm square silica cells with formamide as standard.

TABLE 10

Flask numbers	Concentration of ferrocene in molality	Volume of 0.05 M ceric sulphate added to each flask in mls	Calculated concentration of ferricenium ion in molality	Absorbance of ferricinium ion.
1	0.01 m	0.0	0.0	0.0
2	0.00975	0.1	0.000249 m	0.16
3	0.0095	0.2	0.000495	0.24
4	0.00854	0.5	0.00122	0.66
5	0.0077	0.8	0.00192	1.0
6	0.00714	1.0	0.00238	1.18
7	0.0058	1.5	0.00349	1.64
8	0.00454	2.0	0.00454	2.0

In a second experiment 0.1 molal ferrocene was diluted to 0.004 m to reduce the volume of 0.05 M ceric sulphate required. 20 g of 0.004 m ferrocene were then titrated to completion with 0.05 M ceric sulphate in the manner of Table 9 with addition of the titrant to each of nine flasks used. The absorbances of the ferricenium were recorded as in the previous experiment.

According to the Beer-Lambert law $A = \epsilon dc$ where A is absorbance; ϵ is a constant (extinction coefficient); d is distance of cell and c is concentration. For ferrocene and ferricenium tetrafluoroborate the wavelengths (η) in mμ and ϵ values in 95% ethanol for ferrocene and in water for the ferricenium ion are given as follows[59].

Ferrocene		Ferricenium tetrafluoroborate	
(max) in mμ	ϵ	(max) in mμ	ϵ
325 mμ ⟶	52	250 mμ ⟶	12,000
440 mμ ⟶	91	617 mμ ⟶	340

A graph of absorbance (A) versus c thus generally gives a straight line. The graphs of the two experiments above did not give a good straight line. There was too much scatter of points particularly at higher concentration of the ferricenium ion as more and more ceric sulphate were added.

Absorbance of Ferrocene

The other spectrophotometric method used was that of direct absorbance measurements of ferrocene in formamide. The sharper ferrocene absorbance peak at 325 mμ was used as opposed to the broader peak at 440 mμ. The wavelength was fixed at 325 mμ

and absorbance of ferrocene varied with concentration. 10 mm square silica cells were used in the SP500 Visible and Ultraviolet Spectrophotometer. Since ferrocene is not very soluble in formamide it was not going to be easy to use this method to measure the very small ferrocene concentrations in the actual experiments of ferrocene in formamide. To do so would require very large cells, which was not practical. But ferrocene is very soluble in toluene and toluene is immiscible with formamide. Ferrocene therefore should have a large distribution coefficient (from formamide to toluene) in these two phases.

The extraction of ferrocene from formamide to toluene was done by mixing a known volume of ferrocene in formamide with a known volume of toluene. The mixture was shaken for about one minute and allowed to stand and separate for over 20 minutes. The lower solution, that is formamide was drawn off into a flask, and the top solution collected.

A calibration was done of ferrocene in toluene in the concentration range of 0.473×10^{-3} Molar to 20×10^{-3} M. The graph of absorbance versus concentration was a straight line as expected from the equation $A = \epsilon dc$ already referred to above.

Three single extractions as described above of 0.0011 M ferrocene in formamide into toluene were done. The first was of 20 mls of ferrocene solution into 20 mls of toluene, the second was of 50 mls of ferrocene solution into 20 mls of toluene and the third was of 100 mls of ferrocene solution into 20 mls of toluene. The third extraction gave the smallest error of 10% below the original 0.0011 M ferrocene in formamide. If a second extraction was carried out on each 0.0011 M ferrocene sample this would not be easily detectable spectrophotometrically with type of cells used, since it would be too dilute. The problem of using this method for ferrocene analysis from experiments on ferrocene in formamide to be undertaken in this work were obvious. On the one hand large quantities of ferrocene in formamide would be extracted in smaller volumes of toluene in order to concentrate the ferrocene while on the other hand a second or third extraction on each sample would be too dilute to be accurately determinable.

3. The Radiometric Method

The radiometric method was the third in this series of trials to find a more reliable method of analysing ferrocene in formamide.

Radioactive Ferrocene

Santer et al.[60] reported on the protonation of ferrocene by strong acids. A little later on, Nesmeyanov et al[61] reported a successful deutrefication of ferrocene with deuterotrifluoroacetic acid. The mechanism under which protonation occurs is that of electrophilic substitution. The radioactive ferrocene in this work was made by tritiation of inactive ferrocene in trifluoroacetic acid. First attempts to use concentrated sulphuric acid instead of trifluoroacetic acid were abandoned because the product was very low in radioactivity. Although the acids do turn some of the ferrocene in ferricenium ion it has been shown by Nesmeyanov[61] et al that the ferricineum ion does not take part in the hydrogen exchange and that both the electrophilic substitution and oxidation reactions of ferrocene go hand in hand.

To 30 mls of trifluoroacetic acid in a 250 ml conical flask was added about 1.5 g of inactive ferrocene. The contents were stirred and the solution turned into a deep reddish blue colour (ferricenium ion). 2 mls of tritiated water with a radioactive concentration of $40\mu ci/ml$ was added. The flask and its contents were shaken and the tritiated water allowed to exchange its radioactive hydrogen (tritium) with the hydrogen of some of the ferrocene in the flask. Large quantities of distilled water were added to the flask to decompose the ferricenium ion back into ferrocene because ferricenium ion has been known to decompose rapidly to ferrocene in neutral aqueous solutions[51,59]. The radioactive ferrocene was filtered and washed with more distilled water. It was then dissolved by acetone to which was added more inactive ferrocene. The ferrocene was precipitated from acetone by addition of distilled water. After repeated washing with more distilled water under vacuum water pump the ferrocene was collected in a beaker and dried for four days in a vacuum dessicator containing silica gel.

Several attempts to reduce the radioactivity in the ferrocene were carried out as described above, that is by the addition of more inactive ferrocene into radioactive ferrocene dissolved in acetone until when 10 mls of about 5×10^{-4} molal radioactive ferrocene gave about 250,000 counts per minute in the Beckman LS-100 Liquid Scintillation machine radioactive counter.

Extraction of Ferrocene from Formamide by the Scintillator Solution

Since the scintillator solution was made in toluene; that is by dissolving 8.0 g of Butyl P.B.D. [2-(4'-tert-butylphenyl)-5-(4"-biphenyl)-1,3,4-oxadiazole] and 0.5 g of P.B.B.O. in one litre of Fisons scintillation grade toluene[62,38], the procedure for extracting ferrocene from formamide was as already described above under spectrophotometry. The only difference was that in this case water was added to the ferrocene-formamide-toluene mixture partly to wash out any formamide from toluene and partly to make ferrocene even more insoluble in the formamide-water phase. After first discarding the formamide-water portion, the ferrocene-toluene solution was washed by several additions of water and dried in a stoppered bottle containing anhydrous magnesium sulphate for over three hours. The reason for extracting ferrocene into the scintillator solution was however different from that under spectrophotometry. The reason this time, was that, because of its carbonyl function formamide gives a very high quench rate[63] (that is, it reduces the efficiency of radioactive counting) and is insoluble in toluene. Coloured or opaque[63] solutions also cause quenching. In the case of the yellow colouring of the ferrocene this problem was dealt with by keeping the concentration of ferrocene constant and as dilute as possible in all subsequent experiments using ferrocene in formamide. This meant that the quenching due to the yellow colour of ferrocene was as low and as constant as possible. Under this condition a quenching calibration curve was avoided.

Efficiency of Extraction

The efficiency of extraction of ferrocene from formamide into scintillator solution was tested in a series of extractions and countings explained below. In six stoppered conical flasks, each containing 200 grams of formamide were dissolved different amounts of radioactive ferrocene. Extractions were done in each case by taking 5 ml of the sample into a 100 ml separating funnel containing about 30 mls of distilled water. 15 mls of the scintillator solution were then added into the mixture. The extraction procedure has already been described above. All the water-formamide solution was collected and extracted with another 15 mls of the scintillator solution, so that there was double extraction for each sample. On each concentration two 5 ml aliquotes were extracted. After drying in anhydrous magnesium sulphate for over three hours 10 mls of each sample were counted at 0.2% error in the Beckman LS-100 scintillation instrument.

The results shown in Table 11 indicate that over 99% of ferrocene is extracted in the first extraction and that the more concentrated the ferrocene solution the greater the percentage amount extracted in the first extraction. The conclusion to be drawn from this evidence is that the extraction technique is very efficient and whether a second extraction on each sample is to be performed will depend on the degree of accuracy required.

TABLE 11

No.s of sample flasks	No. of aliquotes of sample taken	1st Extractions Counts/minute	2nd Extraction Counts/minute	Total Counts/min	% of 1st Extraction $(\frac{1st \times 100}{1st + 2nd})$
1	1	14820.70	98.52	14919.22	99.3
	2	14963.98	89.27	15053.25	99.4
2	1	72660.49	174.17	72834.66	99.8
	2	72674.14	154.65	72828.79	99.9
3	1	17138.18	142.68	17282.86	99.2
	2	17082.96	191.91	17274.87	99.1
4	1	69176.69	333.54	69510.23	99.5
	2	69200.27	300.27	69500.54	99.6
5	1	14043.35	89.35	14132.70	99.4
	2	14067.61	70.09	14137.70	99.5
6	1	70385.45	343.97	70729.4	99.5
	2	70238.90	355.19	70594.09	99.5

Stability of Radioactivity in Ferrocene in Formamide

The half-life of 12.26 years[64] for tritium was long enough for experiments undertaken in this work. It has been reported in the Radiochemical Manual[64] that tritium in a benzoid structure may show no detectable loss whatsoever. Although ferrocene has some aromatic characteristics like benzene an experiment to check the degree of loss of radioactivity from the ferrocene structure was carried on. Two 5 ml samples of 5 c 10^{-4} m solution of ferrocene in formamide were each extracted into 15 ml of the scintillator solution and counted on the first day. The ferrocene solution was left at 25°C in a constant temperature bath. The extraction and counting were repeated on the second day and over a period of ten days. The results shown below show that there was no appreciably detectable decline in the count rates to have affected the accuracy of the results of the experiments undertaken. Ferrocene did not lose its tritium to formamide.

Average counts on first day = 123071.83 counts/min

Average counts on second day = 123103.24 counts/min

Average counts on tenth day = 122996.92 counts/min

Conclusion on Methods of Analysis of Ferrocene in Formamide

The radiometric method for ferrocene analysis in formamide was considered to be the most reliable method and was the one used in the analysis of ferrocene in the experiments to follow.

(c) MEASUREMENTS OF DIFFUSION COEFFICIENTS OF FERROCENE IN PLAIN FORMAMIDE AND IN SELECTED HALIDE SALTS SOLUTIONS IN FORMAMIDE USING THE DIAPHRAGM-CELL METHOD.

The Diaphragm-Cell Method with Rotated Magnetic Stirrers

The type of diaphragm-cell used for diffusion measurements described in the following pages was that used and recommended by R.H. Stokes[39], a pyrex glass cell with a sintered glass diaphragm of number 4 porosity. Since the primary use of the daphragm is to reduce mechanical bulk flow in diffusion experiments to a minimum diaphragms of coarser pores than those of number 4 are considered unsatisfactory because they might allow transport of material by both bulk streaming and diffusion[32]. On the other hand diaphragms with pore diammeters smaller than those of number 4 (which have pore diameters normally in the range 2μ to 10μ[38]) may give unnecessarity long diffusion times.

The final form of the cell as it was used for diffusion experiments is shown in Figure 11 B and T are the bottom and top compartments respectively. Both the sinking and floating stirrers were made of thin glass tubes containing powdered ferrite in beeswax which enabled the stirrers to rotate under the influence of a rotating magnet. The stirrers were made in such a way that

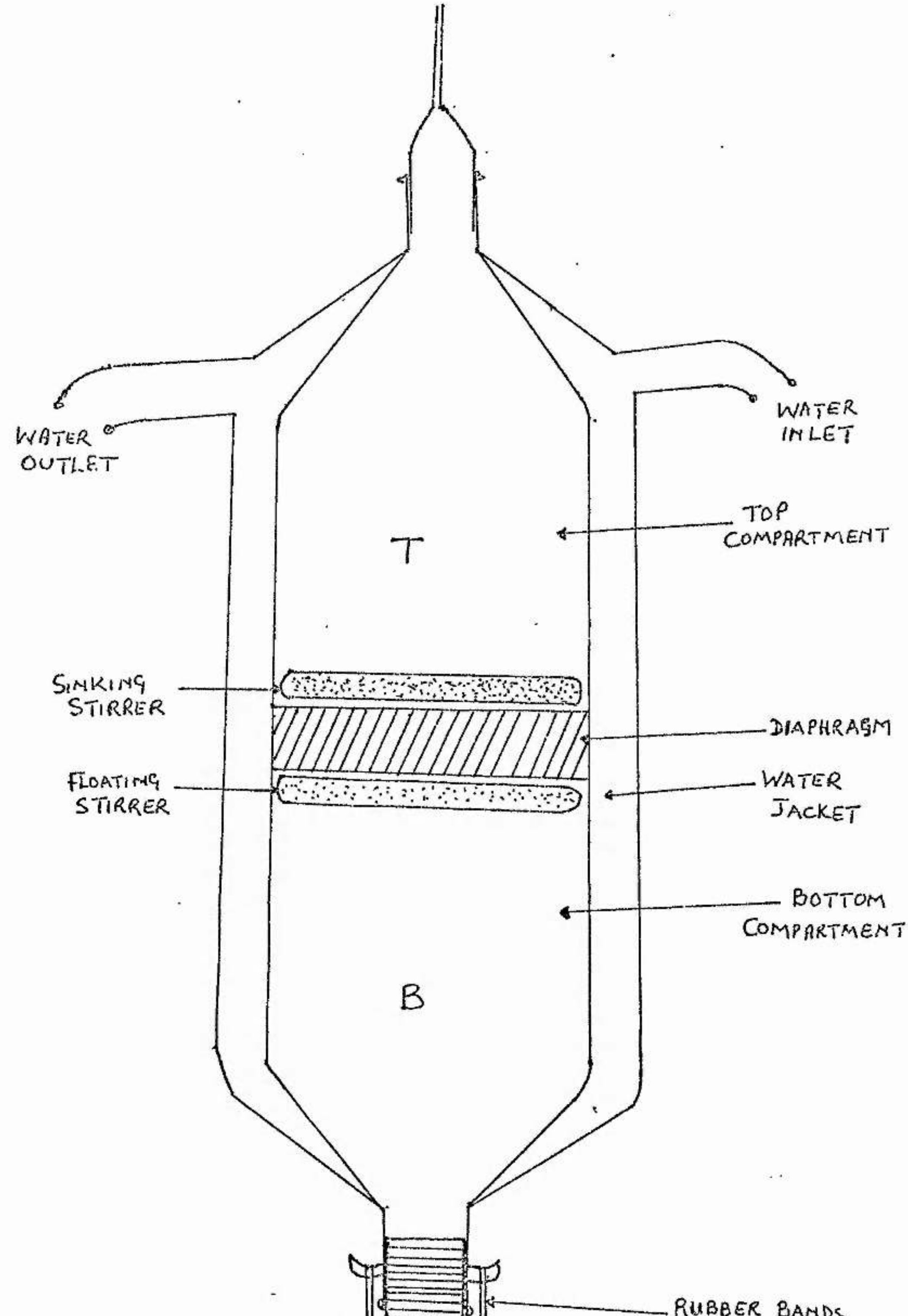


FIG. 11. THE DIAPHRAGM-CELL WITH ROTATED MAGNETIC STIRRERS

one floated and the other sank. This was accomplished by putting in more ferrite in the sinking stirrer than the floating one. Both stirrers were just shorter than the diaphragm diameter to enable them to rotate without getting stuck on the sides of the cell on the one hand and to enable them to sweep around over the entire diaphragm surfaces on the other.

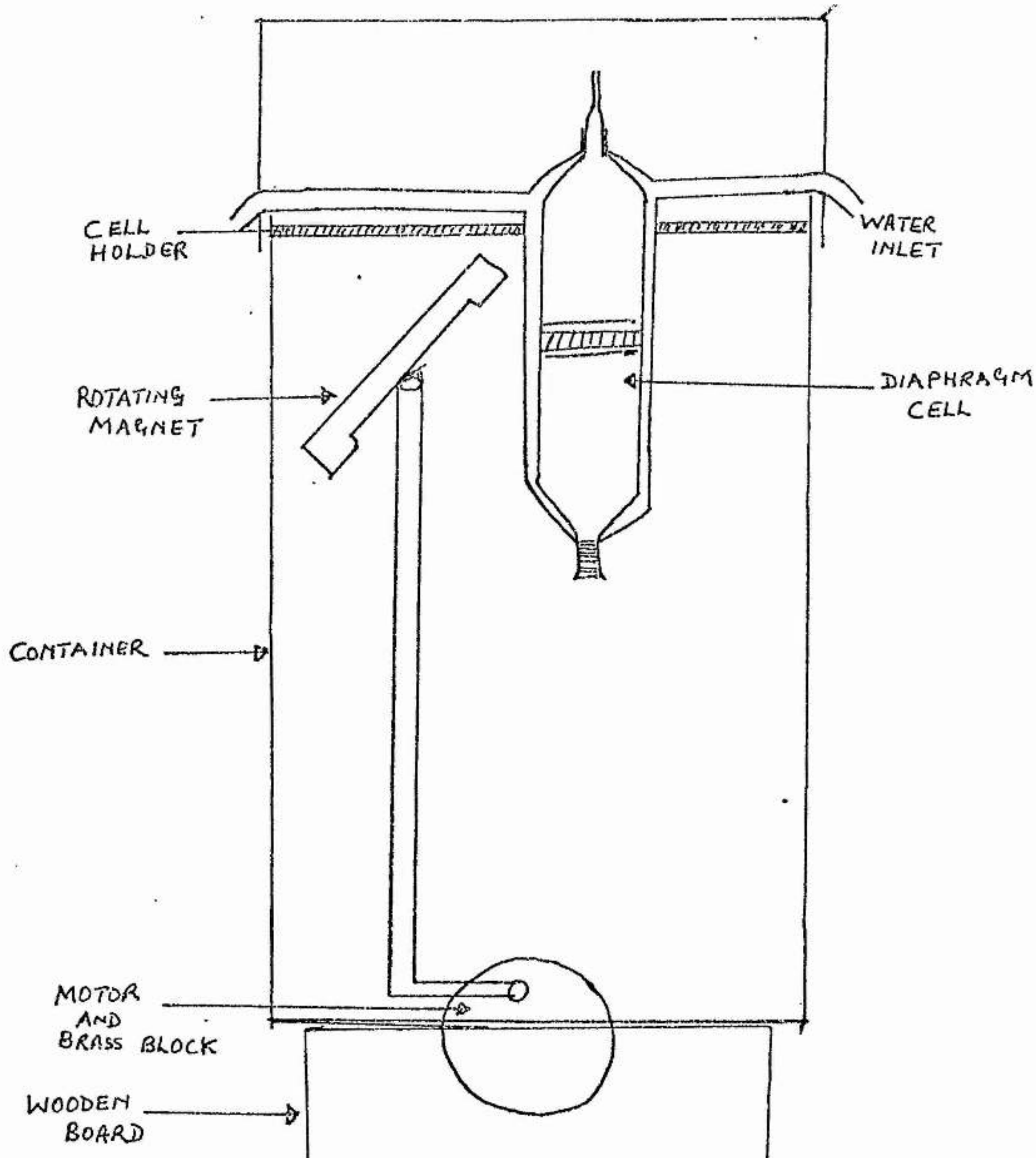
In many previous work by other workers the whole apparatus, that is, the diaphragm-cell and the rotating magnet were immersed in the constant temperature bath. It was considered here that a less clumsy and better way of doing it was to put the whole apparatus outside the bath but running through it equilibrated water from the bath. This was done by constructing the cell with a glass jacket around it, and a water inlet and outlet (Figure 11). A pump fixed to the bath drove the thermostated water through a plastic tube connected to it and the cell into the glass jacket around the cell and out again through the outlet and plastic tube back into the bath. This ensured that the temperature of the diaphragm-cell and solutions were kept constant to 0.05°C as required during the experiments. The bottom glass stopper was fitted with a teflon sleeve to prevent any leakage of solution from B and was held firmly into the cell by means of two rubber bands on both sides as shown ini Figure 11. The top stopper had a capillary to allow for any expansion of the solution which sometimes occurs during diffusion experiments[39].

The apparatus as shown in Figure 11 was mounted in a huge clear plastic tube-like container inside of which was fixed the rotating magnet. The magnet was driven around by means of an electric motor which was in turn fixed to a flat brass block acting as a heat sink for the motor and a flat wooden base. The speed of the rotating magnet was 60 r.p.m. This speed was chosen because it is one of the speeds at which the cell constant (β) does not change with speed of rotation of the stirrers. According to Stokes[39] the cell constant does not change with speed between about 25 r.p.m. to 80 r.p.m. Mills[38,65] has however extended this range to 129 r.p.m. The cell as shown in Figure 12 was firmly and vertically held so that there were no experimental errors arising from a departure of the cell from a vertical position[39]. The heavy brass block and wooden board at the base of the whole apparatus (Figure 12) ensured of a firm base which did not vibrate while the magnet was rotating.

Measurement of Volumes of Cell Compartments and Diaphragm

When the cell was being constructed care was taken not to make the volumes of the two compartments significantly different from each other. This was so because the majority of the equations developed to calculate the diffusion coefficient values from diaphragm-cell measurements are based on the condition that $V_B = V_T$[38]. However if the differences between the two volumes are small as in the case with the cell used in this work the equations can be used without any significant error. In the same way, due to the nature of the equations for calculating diffusion

FIG. 12 DIAPHRAGM-CELL DIFFUSION APPARATUS



coefficients the volumes of the two compartments were made very much larger than the volume of the diaphragm. Many workers generally use or have used compartment volumes of about 50 mls each and diaphragm volume of about 1 ml. The volumes of the diaphragm-cell used here were of the order of 100 mls for each compartment to about 1.6 mls for the diaphragm. These volumes were determined by the following method. First the cell was cleaned by filling with freshly made chromic acid and let to stand for sometime. It was then thoroughly washed with distilled water. By means of a water pump large quantities of distilled water were sucked through the diaphragm to remove any chromic acid that might have been trapped there. The cell was dried in an oven. When it was dry and cool it was weighed. The two cell compartments and the diaphragm were filled with distilled water by means of a water pump and reweighed[66]. The cell was emptied and dried with distilled acetone. One compartment and the diaphragm were then filled with water and weighed. The volume of the other compartment was computed by substraction. This procedure was reversed for the other compartment. The process was repeated several times and the average volume of each of the compartments and diaphragm were thus determined. This method is sufficient to determine the volume of the diaphragm, after all it is much smaller than the compartments. Because of their delicacy in handling the stirrers had the volumes occupied by them determined separately by the method of water displacement. A clean dry 10 ml graduated cylinder was weighed each time with one of the two stirrers in it. The cylinder was then filled with distilled water to the 10 ml mark and reweighed. One stirrer was dropped in and the displaced water removed by a pipette down to the 10 ml mark of the cylinder. The cylinder with water and stirrer were weighed. The process was repeated for the other stirrer. But since the floating stirrer could not sink into the water, a thin piece of wire was tied around it and while holding the wire the stirrer was forced to sink and the displaced water removed with a pipette to the 10 ml mark of the cylinder. The volume occupied by the wire was considered negligible. Thus the volume of water displaced by each stirrer was equal to the volume occupied by that stirrer. The volume of the sinking stirrer was then subtracted from the volume of the top compartment of the cell and that of the floating stirrer from that of the bottom compartment. In each of all these measurement procedures described above the temperature of the water was carefully noted so as to use a correct density for the calculation of the volumes from weight measurements of the water.

Calibration of the Diaphragm

Since the diaphragm-cell method is a relative one the cell had to be calibrated in relation to the absolute methods of diffusion measurements. The recommended calibration standard solution is potassium chloride in water whose diffusion coefficient values have been measured by the absolute conductance method by H.S. Harned and R. Nuttall[27]. 0.5 M aqueous potassium chloride was used here as the calibrating solution. The potassium chloride was of Analar grade dissolved up in boiled out distilled water. The solution was rid off of dissolved gases by applying a vacuum to it. The solution was then ready for filling into the cell. The top part of the diaphragm-cell was connected to a water pump and the bottom to the solution. The solution was then sucked into the cell through the diaphragm to fill part of the top compartment. The reason for sucking so much of the solution through diaphragm was in order to drive any air trapped in its pores. The cell was inverted and filled with more potassium chloride solution and the stopper fixed leaving no air bubble in the bottom compartment. The solution and the cell were then thermostated to equilibrate by passing through the glass jacket around the cell, the 25°C bath water for about fifteen minutes. After this time the upper part of the cell was rinsed three times with 25°C distilled water; the rinsing water being removed from the compartment by sucking with a pipette making sure not to suck the liquid out of the diaphragm. The top part was then filled with the 25°C solvent water and the prediffusion to establish a steady state in the diaphragm as described above in the Introduction proceeded for three hours. After three hours the top compartment was emptied, rinsed three times and then filled with the 25°C solvent water. The experiment was timed as soon as the filling of the top compartment commenced and the diffusion was allowed to continue for about four days. Within this time a constant check was carried on the experiment to see that the equilibrated bath was running through around the cell; that the stirrers were rotating and that the temperature in the bath was constant. Observation revealed that if the bath water was kept at 25.3°C ± 0.05 the temperature of the solutions in the cell was 25°C ± 0.05.

At the end of the run on the fourth day the circulating water and the rotating magnet were switched off and the cell immediately removed from the case container. The two compartments were emptied; first by quickly draining the bottom solution into a flask, and having allowed the top solution to drop through the diaphragm for some five minutes to remove the solution from it, the cell was inverted and the top solution collected. The process of emptying was done swiftly so that there was no chance for the solution from one compartment leaking into the other. A duplicate potassium chloride diffusion run was performed.

The potassium chloride solutions were analysed by both the gravimetric method as described by Vogel[57] and by potentiometric titration with standard 0.1 N silver nitrate (aq). For each analytical method on each potassium chloride solution of each diffusion run, duplicate determinations were done. The potentiometric method gave more consistent results than the gravimetric method which was perhaps subject to handling errors. The potentiometric method, potassium chloride concentrations results, were therefore used for calculating the cell constant (β). Once the cell constant was known the cell was ready for experiments on the diffusion of ferrocene in formamide.

Diffusion of Ferrocene in Formamide and in Formamide Salt Solutions

Formamide: Formamide was purified by fractionation under reduced pressure in a vacuum distillator at about 1 mm of mercury and around 68^{o}C. The middle portion of the distilled formamide was collected for use after discarding the first few hundred millilitres of the distillate and the substantial quantities of formamide left over in the distillation flask. During distillation a stream of air bubbles was allowed into the boiling formamide via a thin drawn out glass tube to prevent formamide bumping. The problem of getting a really purified formamide under whatever purification method, and conditions has been acknowledged by many workers[1,4,7,67,68]. However the degree of purity is governed by the type of experiments being performed. In the case of the work undertaken here the formamide as was distilled was considered adequately pure with a viscosity of 3.29 centipoise as opposed to the accepted value of 3.30 centipoise. But in order to avoid any excessive decomposition into ammonia and carbon monoxide to which formamide is so prone, it was used immediately after purification. The time of purification to the time of the end of the ferrocene diffusion runs in formamide and its analysis were all within two weeks. The purified formamide was kept in sealed bottles to avoid water absorption.

Diffusion Experiments

All the diffusion experiments in this work were upward diffusions. This was largely because with the way the cell was constructed, it was not easy to fill the bottom compartment after a prediffusion without introducing serious errors. This was so because to fill the bottom part after prediffusion would have required inverting the cell with the attendant result that some solution in the top compartment would have leaked out through the capillary. Also the top compartment was not completely filled, but up to a calibrated level in the capillary, so inverting the cell would mean there would be an empty space between the diaphragm and the solution in the top compartment with the consequent leaking of the solution from the diaphragm to the solution. The other but trivial reason for performing the diffusion upwards was in order to avoid errors which may arise out due to density differences due to gravity if the diffusion are downwards[39]. This reason was trivial in this case because the concentration of ferrocene was very dilute to have much density difference effects.

A trial diffusion run was carried out with 1×10^{-3} molal ferrocene in formamide to determine the approximate period for sufficient ferrocene to diffuse through the diaphragm into the top cell compartment. The ferrocene was used without any purification as obtained from BDH Ltd. The experiment was allowed to proceed for a matter of five days. The ferrocene concentrations were determined spectrophotometrically with toluene as standard medium. About 16% of the ferrocene had transfered within the five days. This was considered an adequate length of time and so all diffusion experiments of ferrocene in formamide under this rotated stirrer diaphragm-cell had a length of about five days.

The first three successive experiments were those of radioactive ferrocene diffusing in plain formamide; the concentration of ferrocene solutions in the bottom part of the cell being kept constant at 5×10^{-4} molal in all experiments. The top part was filled with plain distilled formamide. The filling of the cell and all other related procedures were as described in the case of calibration experiments. At all times however it was remembered to remove the air from the solution and solvent by subjecting them to a vacuum prior to the diffusion experiments. The duration of each experimental diffusion run was five days with a prediffusion of three hours. The prediffusion time τ was arrived at by all the considerations of the Gordon inequality $D\tau/l^2 > 1.2$[36] (where D is the diffusion coefficient in cm^2/sec; l is the "apparent thickness" of the frit which is usually ≈ 0.4 cm); the experimental work of Pikal[37] and the recommendations of Mills and Woolf[38]. The later authors have recommended that the solution filled method (the one used for filling cells in this work) need not require a prediffusion time since the concentration in the lower compartment is equal to that in the diaphragm. However a prediffusion time of three hours was considered necessary to establish a steady state in the diaphragm as has been done in earlier work with the diaphragm-cell method by other workers.

After those first three experiments were done, successive runs were performed of diffusion of the radioactive ferrocene in different concentrations of potassium chloride and potassium bromide solutions in formamide. The salt concentration in each experiment was strictly the same in all the three parts of the cell; so that there was no net diffusion of the salt due to concentration gradient. In all, five experiments were done in potassium chloride solutions in formamide (0.01 molal; 0.05 m; 0.1 m; 0.2 m and 0.4m) and another five were done in potassium bromide solutions in formamide (0.01 m; 0.04 m; 0.1 m; 0.4 m; and 1.0 m); the potassium bromide being more easily dissolved in formamide than potassium chloride. Both salts were of Analar grade and were used without purification. The concentrations of the radioactive ferrocene were determined radiometrically in the Beckman Ls-100 Liquid Scintillation instrument.

Problems with the Diaphragm-Cell Apparatus

Stokes[39] has reported a wearing off of the diaphragm due to the stirrers; that is, an increase in the cell constant of between

0.5 - 1.0% per 1000 hours use of the cell. After almost ten weeks of use of the cell it became visibly clear that the diaphragm was wearing off very rapidly. An immediate recalibration of the diaphragm with the 0.5 M potassium chloride (aq) proved the observation correct. The cell constant had almost doubled from 0.286 to 0.598. Earlier attempts to make better stirrers had not been very successful. The results therefore obtained from all the experiments done were not considered reliable. While fresh attempts would have been made to construct another cell with better stirrers it was considered that there was not sufficient time left to accumulate enough data for this research work using this type of apparatus. But since the primary aim of measuring the diffusion coefficients was to determine from them the effects of the different salts and different concentrations on the formamide structure that is relative rather than absolute measurement of diffusion coefficients it was decided that this might be done equally well in diaphragm-cells without stirrers. Craven and co-workers[69] have measured the diffusion coefficients of somee azo dyes in water in stirred and unstirred diaphragm-cells and have found that although the diffusion coefficients are lower in unstirred cells particularly at lower temperatures, they are very consistent. Stokes[39] and Mills and Woolf[38] have also reported of reproducibility of diffusion coefficient results in some cases of diaphragm-cell measurements, that is that stagnant layers on the surfaces of the diaphragm in unstirred cells are in some cases reproducible. Also it should be noted that bulk flow of material in the unstirred diffusion experiments, (due; to density differences) done here could be experimentally insignificant because of the negligible density gradient of the very dilute ferrocene solutions used.

Diaphragm-Cells without stirrers

Seven diaphragm-cells were constructed as previously shown, with the exception that there was no need of a glass jacket since the cells were directly immersed in the constant temperature bath (Figure 13). When in use the cells were supported firmly vertically, by a brass plate with holes through which the cells were held. Around the holes on thin edges were fitted rubber clamps. These rubber clamps worked on the simple principle that the cell would be pushed into the hole or taken out without difficulty. During experiments these rubber clamps held the cells by their bodies, firmly and vertically. The brass plate was fixed to the edges of the thermostat bath thoroughly immersed in bath water so that during experiments the cells were well under the bath water.

Volume measurements of the cell compartments and diaphragm were done as before and calibration experiment with 0.5 M aqueous potassium chloride proceeded for a matter of five days instead of four

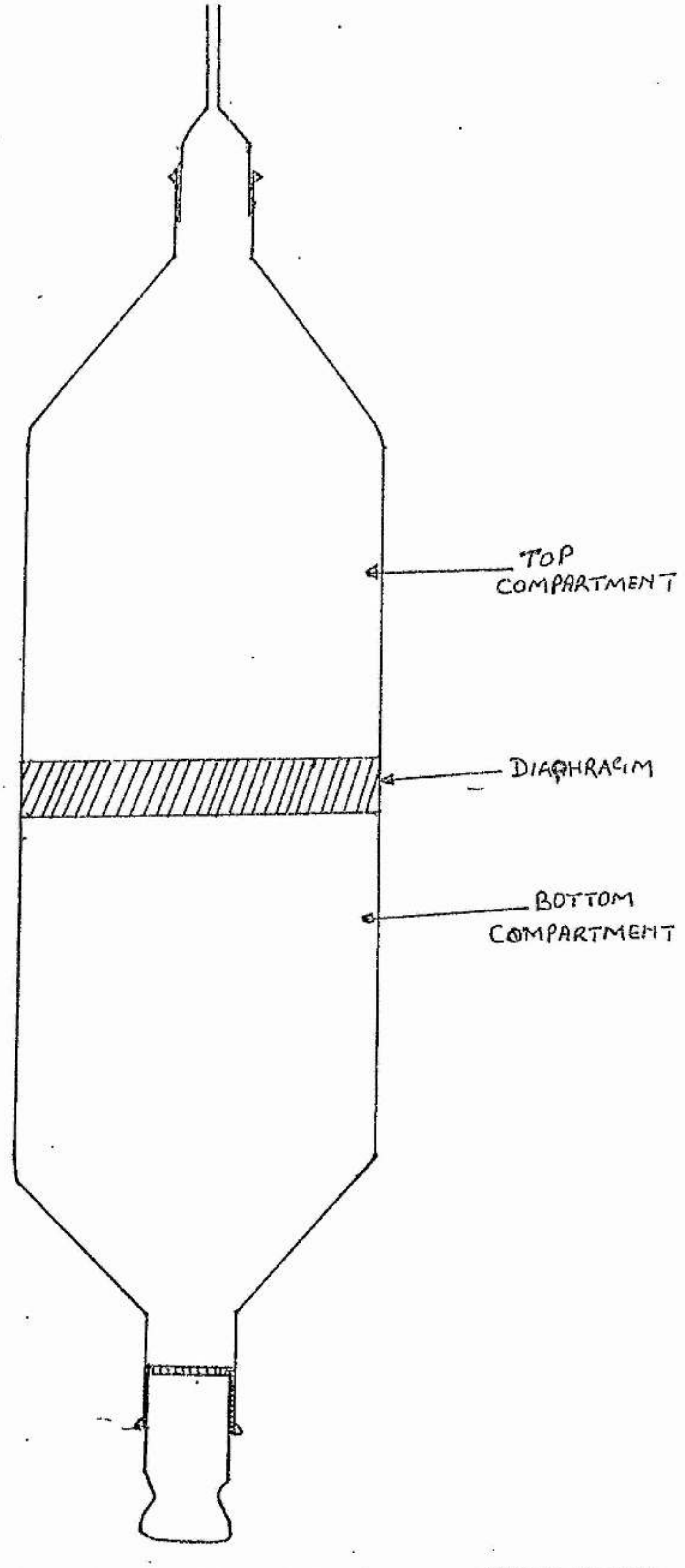


FIG. 13. DIAPHRAGM-CELL WITHOUT STIRRERS

previously. The cells were numbered 0 to 6 but in each diffusion experiment run only six were in use, with one in reserve.

Diffusion Experiments.

Two types of diffusion experiment measurements were done:-

(a) Upward Diffusion of Radioactive Ferrocene in Formamide and Salt Solutions of Formamide

In this set of experiments five salts were used; potassium fluoride, potassium chloride, potassium bromide, ammonium bromide and tetraethylammonium bromide. Tetraethylammonium bromide was purified[70,71] by recrystallizing once from absolute alcohol and then two times precipitated from absolute alcohol with solvent ether. The product was washed repeatedly with ether and vigorously sucking dry with a water pump. It was finally dried in a vacuum desiccator. The other salts except potassium fluoride were of Analar grade and were used without purification. The concentration ranges of each salt in formamide depended partly upon its solubility and partly on the amount of information to be gained. Potassium fluoride the least soluble of them all had its concentration in the ranges from 0.02 molal to 0.2 molal; potassium chloride, from 0.01 m to 0.4 m; potassium bromide 0.02 m to 1.0 m; ammonium bromide 0.02 m to 0.4 m and tetraethylammonium bromide 0.02 m to 0.45 m. The concentration of ferrocene was kept constant at approximately 5×10^{-4} molal.

Formamide was purified as before and all concentrations of the salts and ferrocene were in moles per 1,000 grams of formamide. The solutions were purged of air by vacuum before filling into the cells which was done as in the case of cell with stirrers.

The diffusion run was six days with a prediffusion of three hours.

The first set of experiments were on an accurate determination of diffusion coefficient of ferrocene in plain formamide. In each of all the later set of experimental runs one of the six cells was for the diffusion of ferrocene in plain formamide. This permitted a normalisation of the other experimental results in each run in relation to the accurately determined diffusion coefficient of ferrocene in plain formamide. This was to allow for small variations in results which may arise from experimental run to another due to say small differences in the formamide batches. During the runs the concentration of the salt in each cell were stricktly uniform so that there was no net diffusion in that salt.

(b) Simultaneous Diffusion of both Ferrocene and Salt in Formamide

Only one salt potassium bromide was used in this set of experiments:

1. Upward diffusion of ferrocene and potassium bromide

The concentration of ferrocene in formamide at 5×10^{-4} m was just as in (a), but that of potassium bromide varied in the range 0.04 m to 1.0 m. The solution of potassium bromide and ferrocene were put at the bottom part of the cell and plain formamide at the top. The runs were for six days with a prediffusion of three hours. In each set of experiments one cell had ferrocene diffusing in plain formamide.

2. Upward diffusion of potassium bromide and downward diffusion of ferrocene in formamide

Ferrocene was allowed to diffuse downwards while potassium bromide diffused upwards. Since the concentration of ferrocene was very small 5×10^{-4} molal as opposed to that of potassium bromide which ranged from 4×10^{-2} m to 3×10^{-1} molal, it was put in the top cell compartment. This was to prevent bulk flow due to gravity which occur when denser solutions are put in the top compartment[39]. All other experimental conditions were as in (b)1 except that there was no prediffusion this time, because it was not possible to empty both compartments and refilling them without at the same time emptying the diaphragm. However a prediffusion is not a requirement with the solution filled method used here as Mills and Woolf have discovered[38]. One cell in each run had ferrocene diffusing but downwards in plain formamide.

In both experimental conditions (a) and (b) the ferrocene concentrations in formamide were determined by radioactive counting in the Beckman LS-100 Liquid Scintillation machine at 0.2% error for 100 minutes. Two 5 ml aliquotes on each sample were used for both top and bottom ferrocene solution in the diaphragm-cell, into 15 mls of the scintillator solution plus about 30 mls of distilled water. Only one extraction on each 5 ml ferrocene solutions sample was done. This was justified on the grounds that over 99% as already shown above the ferrocene was contained in the first extraction. The error therefore introduced by performing only one extraction was considered acceptable. On the other hand the error was reasonably kept constant by doing only one extraction in all other samples in all experiments. This meant that the comparisons and interpretations of the diffusion results in the different salts and concentrations in formamide would be negligibly affected.

The concentrations of potassium bromide salts in (b) (that is, when potassium bromide was also diffusing) were determined by the conductance method, from a calibration curve at 25°C constant water bath. The conductance bridge used was the Wyne-Kerr Universal Bridge B 221, and the platinum electrodes of the cell used were coated with platinum black to reduce electrode processes by the solutions and methods recommended by Jones and Bollinger[72].

RESULTS

Calculation of Diffusion Coefficients

The diffusion coefficients of both ferrocene and potassium bromide were calculated by the equation

$$D = \frac{1}{\beta t} \ln \frac{1 + f\frac{u}{l}}{1 - \frac{u}{l}} \quad [37] \qquad \ldots\ldots \quad 1$$

where

β is the cell constant determined by calibration with 0.5 M (aq) potassium chloride

t is time of diffusion experimental run in seconds

u and l are concentrations of species in upper and lower compartments of the diaphragm-cell respectively.

f is defined as

$$f = \frac{V_T + \frac{1}{2} V_D}{V_B + \frac{1}{2} V_D}$$

V_T and V_B are volumes of top and bottom compartments respectively and

V_D is the volume of the diaphragm.

For ferrocene the counting rates in counts per minute determined from the Scintillation machine were directly substituted for u and l in the above equation since the counts per minute are directly proportional to the concentration. Whether the diffusion was upwards or downwards the cell constant (β) was the same. This is so because β is actually $A/l \; \frac{1}{V_T} + \frac{1}{V_B}$ [32] where A is area and l is length of the diaphragm none of which changes whether diffusion is upwards or downwards. V_T and V_B are also constant.

For potassium bromide the concentration in moles per litre of formamide were computed from the conductance calibration curve. The diffusion coefficient of potassium bromide in formamide at infinite dilution (D^o) was calculated from the Nerst equation as given by Robinson and Stokes [37].

$$D_o = RT \; \frac{V_1 + V_2}{F^2 \; V_1 \; |Z_1|} \; \frac{\eta_1^o \, \eta_2^o}{\eta_1^o + \eta_2^o} \quad \ldots\ldots\ldots\ldots 2$$

where V_1 are cations of valency Z_1

V_2 are anions of valency Z_2

η_1^o is the limiting conductance of cations

and η_2^o is the limiting conductance of anions

At 25°C the equation 2 becomes

$$D^o/(\text{cm}^2\ \text{sec}^{-1}) = 2.661 \times 10^{-7} \; \frac{Z_1 + Z_2}{Z_1 Z_2} \; \frac{\eta_1^o \, \eta_2^o}{\eta_1^o + \eta_2^o} \quad \text{Int. Ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$$

For potassium bromide in formamide

[3] Br^- (η_2^o) = 17.2 cm^2 int. ohm^{-1} $equiv^{-1}$

K^+ (η_1^o) = 12.7 cm^2 int. ohm^{-1} $equiv^{-1}$

and $Z_1 = 1 = Z_2$

Diaphragm-Cell with magnetic stirrers

The volumes of the two compartments and the diaphragm of the diaphragm-cell with magnetic stirrers after subtraction of the volumes occupied by the stirrers were as follows:-

Volume of upper compartment = 106.40 mls ± 0.01

Volume of lower compartment = 103.24 mls ± 0.01

Volume of the diaphragm = 1.58 mls ± 0.01

The volume of water displaced by the stirrers were;

Volume of water displaced by floating stirrer = 0.94 mls

and the Volume of water displaced by sinking stirrer = 1.02 mls

The cell constant (β) was 0.286. After it was noticed that the diaphragm was wearing off at such a rapid rate a recalibration of the cell with 0.5 M (aq) potassium chloride gave β to be 0.598.

Diaphragm-Cells without stirrers

The volumes of the cell compartments and diaphragm and cell constants are given below in Table 12.

TABLE 12

Cell no.s	Volume of upper compartments in mls	Volume of lower compartments in mls	Volume of diaphragms in mls	Cell Constants (β)	$f = \frac{V_T+\frac{1}{2}V_D}{V_B+\frac{1}{2}V_D}$
0	115.85	118.87	1.40	0.064	0.9747
1	118.75	117.93	1.33	0.051	1.0061
2	121.58	120.26	1.35	0.052	1.0109
3	119.41	118.50	1.38	0.056	1.0076
4	120.02	122.32	1.41	0.056	0.9893
5	118.91	116.37	1.56	0.053	1.0216
6	115.50	115.20	1.45	0.053	1.0026

Diffusion Coefficients on Ferrocene and Potassium Bromide in Formamide in Diaphragm-Cells without Stirrers

The diffusion coefficient of 5×10^{-4} m ferrocene in plain formamide was 0.758×10^{-5} cm^2 sec^{-1}.

(A) Diffusion Coefficients of Ferrocene in Salt Formamide Solutions with only Ferrocene Diffusing.

(a) Table 13 - Diffusion coefficients of ferrocene in different concentrations of potassium, fluoride in formamide.

(b) Table 14 - Diffusion coefficients of ferrocene in different concentrations of potassium chloride in formamide.

(c) Table 15 - Diffusion coefficients of ferrocene in different concentrations of potassium bromide in formamide.

(d) Table 16 - Diffusion coefficients of ferrocene in different concentrations of ammonium bromide (NH_4Br).

(e) Table 17 - Diffusion coefficients of ferrocene in different concentrations of tetraethylammonium bromide $[(C_2H_5)_4NB_r]$.

The graphs of diffusion coefficients of ferrocene versus the different concentrations of salt reveal a maximum hump at about 0.085 m for potassium chloride and potassium bromide and at about 0.175 m for ammonium bromide and tetraethylammonium bromide. The effect in potassium fluoride is remarkably small.

TABLE 13

No. of cells	Potassium fluoride (kF) concentration in molality	Top Cell Compartments				Bottom Cell Compartments				Diffusion Coefficients D x 10^{+5} cm^2 sec^{-1}
		Sample 1 Extraction		Sample 2 Extraction		Sample 1 Extraction		Sample 2 Extraction		
		Counts/min	average Counts/min	Counts/min	average Counts/min	Counts/min	average Counts/min	Counts/min	average Counts/min	
0	0.02	10128.21	10128.79	10145.52	10112.73	76766.00	76781.92	76743.55	76803.90	0.789
		10129.38		10079.95		76797.85		76864.25		
3	0.05	7693.07	7673.46	7701.61	7700.80	68549.69	68498.73	68624.82	68595.96	0.777
		7653.85		7700.00		68447.77		68567.10		
4	0.10	9307.25	9301.39	9301.39	9297.11	80288.76	80231.31	81067.26	80972.02	0.796
		9308.29		9292.84		80173.84		80876.79		
5	0.15	7864.80	7860.98	7828.39	7831.81	73405.86	73367.04	72885.43	72871.30	0.790
		7857.17		7835.24		73328.22		72857.17		
6	0.20	7562.46	7558.48	7526.03	7516.70	72628.90	72686.81	72802.91	72774.36	0.754
		7554.51		7507.39		72744.72		72745.81		

TABLE 14

No. of cells	Concentration of Pot. Chloride in molality	Top Compartments Sample 1 Counts/min	Top Compartments Extraction average Counts/min	Top Compartments Sample 2 Counts/min	Top Compartments Extraction average Counts/min	Bottom Compartments Sample 1 Counts/min	Bottom Compartments Extraction average Counts/min	Bottom Compartments Sample 2 Counts/min	Bottom Compartments Extraction average Counts/min	D x 10^{+5} cm^2 sec^{-1}
2	0.01 m	8676.17 8650.07	8663.12	8653.55 8649.29	8651.42	74144.92 94052.70	74098.81	74255.03	74255.03	0.888
4	0.07	11270.13 11305.40	11287.76	11330.15 11327.29	11328.72	81487.29 81708.98	81598.13	81596.65 81763.39	81680.02	0.977
4	0.10	10999.92 10951.87	10975.89	10947.52 10921.09	10934.30	74560.28 73953.95	74257.11	74873.57 74383.19	74628.38	0.968
5	0.20	10564.27 10481.56	10522.91	10460.86 10509.51	10485.18	80158.57 80043.44	80101.00	79769.05 79508.82	79638.93	0.858
6	0.30	7786.39 7816.10	7801.24	7748.15 7765.25	7756.70	76951.00 77043.45	76997.22	76657.93 76966.92	76812.42	0.754
6	0.40	9098.46 9136.40	9117.43	9052.32 9108.29	9080.30	78344.47 78080.56	78080.56	78020.90 77898.05	77959.47	0.753

TABLE 15

No. of cells	Concentration of Pot. bromide in molality	Top Compartments				Bottom Compartments				D x 10^{+5} cm^2 sec^{-1}
		Sample 1 Counts/min	Extraction average Counts/min	Sample 2 Counts/min	Extraction average Counts/min	Sample 1 Counts/min	Extraction average Counts/min	Sample 2 Counts/min	Extraction average Counts/min	
2	0.02 m	8376.87	88376.87	8214.81	8214.81	77095.37	77095.37	76741.02	76741.02	0.806
1	0.04	8698.56 8697.08	8697.82	8837.32 8838.26	8837.79	75802.04 75969.55	75885.79	75344.72 75416.59	75380.65	0.908
2	0.075	9474.04 9552.30	9513.17	9538.30 9584.65	9561.47	74303.26 74512.50	74407.88	74830.96 74746.33	74788.64	0.957
5	0.12	8172.84 8191.00	8181.92	8219.94 8221.98	8220.96	73044.52 73281.96	73163.06	72674.41 72617.05	72645.73	0.954
5	0.15	8327.45 8331.66	8329.55	8277.01 8242.67	8259.84	67474.71 67683.76	67579.23	67706.29 67915.47	67810.88	0.903
4	0.20	9019.31	9019.31	8987.85	8987.85	77473.66	77473.66	76813.13	76813.13	0.804
4	0.30	9032.93	9032.93	8994.71	8994.71	74156.18	74156.18	74605.44	74605.44	0.704
5	0.50	8115.01	8115.01	8181.11	8181.11	76096.19	76096.19	75927.01	75927.01	0.668
6	0.85	8330.16 8330.68	8330.42	8269.50 8250.13	8260.13	84691.19	84691.19	84711.17	84711.17	0.622
6	1.00	7709.69	7709.69	7712.83	7712.83	79967.54	79967.54	79704.70	79704.70	0.599

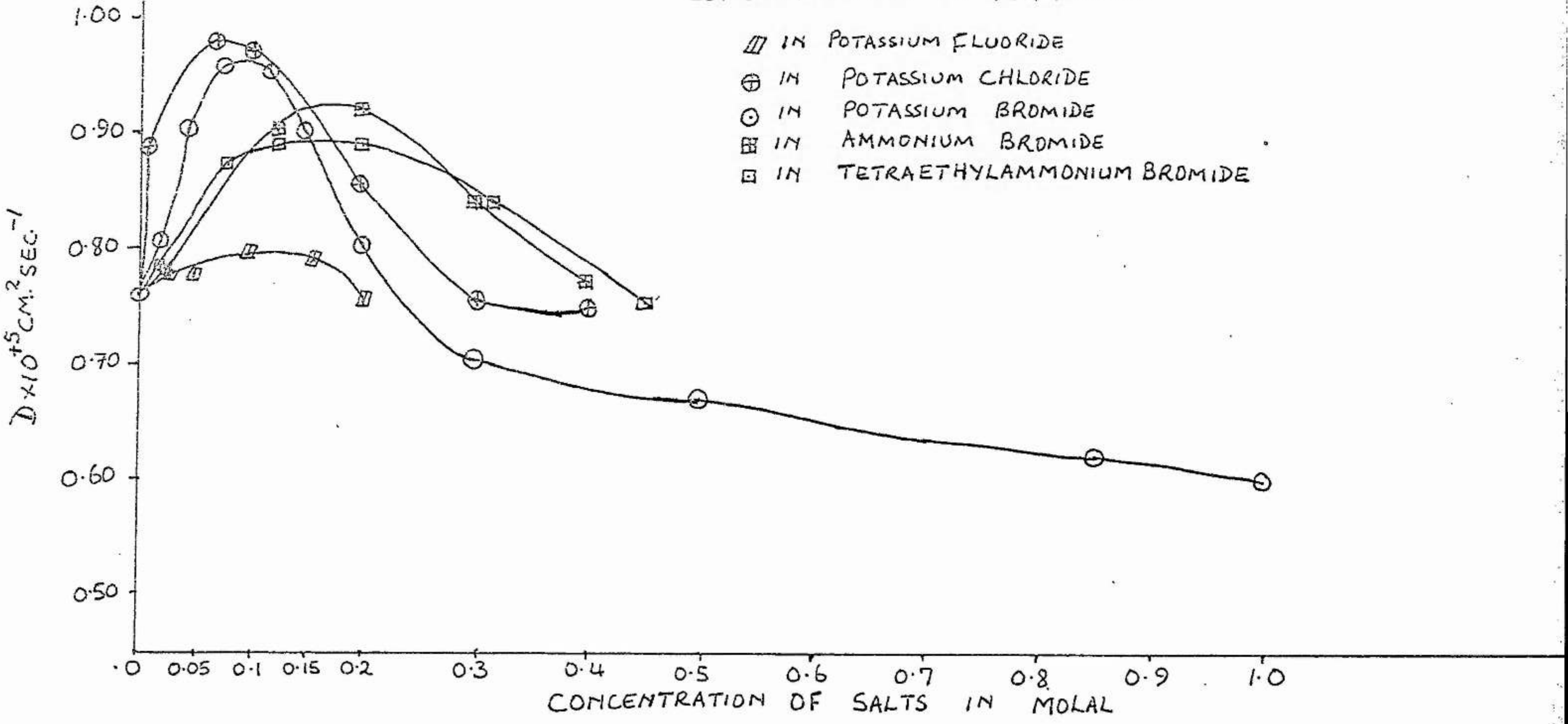
TABLE 16

No. of cells	Concentration of ammonium bromide in molality	Top Compartments				Bottom Compartments				$D \times 10^{+5}$ cm^2 sec^{-1}
		Sample 1 Counts/min	Extraction average Counts/min	Sample 2 Counts/min	Extraction average Counts/min	Sample 1 Counts/min	Extraction average Counts/min	Sample 2 Counts/min	Extraction average Counts/min	
0	0.02 m	9399.52 9377.03	9388.27	9363.67 9350.89	9357.28	72654.39 72579.60	72616.99	72860.37 72896.35	72878.36	0.780
4	0.125	9307.17 9307.70	9307.43	9260.31 9269.68	9264.99	71878.66 71991.43	71935.04	72196.60 71635.95	71916.27	0.901
5	0.20	10660.51 10666.01	10660.26	10621.34 10651.67	10636.50	86430.59 86063.25	86246.92	86454.62 86682.40	86568.51	0.919
6	0.30	8863.39 8885.96	8874.67	8884.56 8863.81	8874.18	77493.64 77484.27	77488.95	77218.44 77002.92	77110.68	0.840
5	0.40	8681.45 8672.31	8676.88	8691.68 8722.02	8706.85	83071.51 83277.68	83174.59	83130.92 83114.86	83.22189	0.770

TABLE 17

No. of cells	Concentrations of Tetraethyl-ammonium bromide in molality	Top Compartments				Bottom Compartments				$D \times 10^{+5}$ cm^2 sec^{-1}
		Sample 1	Extraction	Sample 2	Extraction	Sample 1	Extraction	Sample 2	Extraction	
		Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	
0	0.02 m	9643.06 9698.83	9670.94	9640.02 9673.02	9656.52	74727.93 74411.23	74569.58	75327.10 75157.02	75242.06	0.781
2	0.08	8423.92 8470.75	8447.33	8433.37 8465.96	8449.66	71909.92 72015.47	71962.69	72574.60 72824.74	72699.67	0.874
4	0.125	9133.71 9054.86	9094.28	9260.10 9210.19	9235.14	71932.92 71922.57	71927.74	71464.57 71437.35	71450.96	0.892
5	0.20	9458.87 9430.58	9444.72	9516.60 9462.17	9489.38	79444.32 79168.19	79306.25	78881.62 79302.85	79092.23	0.891
6	0.315	8881.20 8891.03	886.11	8858.82 8881.39	8870.10	78051.95 78113.34	78082.64	77999.14 78320.20	78159.67	0.841
6	0.45	9075.49 9110.14	9092.81	9185.13 9188.19	9186.66	88461.36 8882.94	88672.15	88881.34 88713.20	88797.27	0.753

FIG. 14 DIFFUSION COEFFICIENTS OF FERROCENE IN DIFFERENT SALTS CONCENTRATIONS IN FORMAMIDE



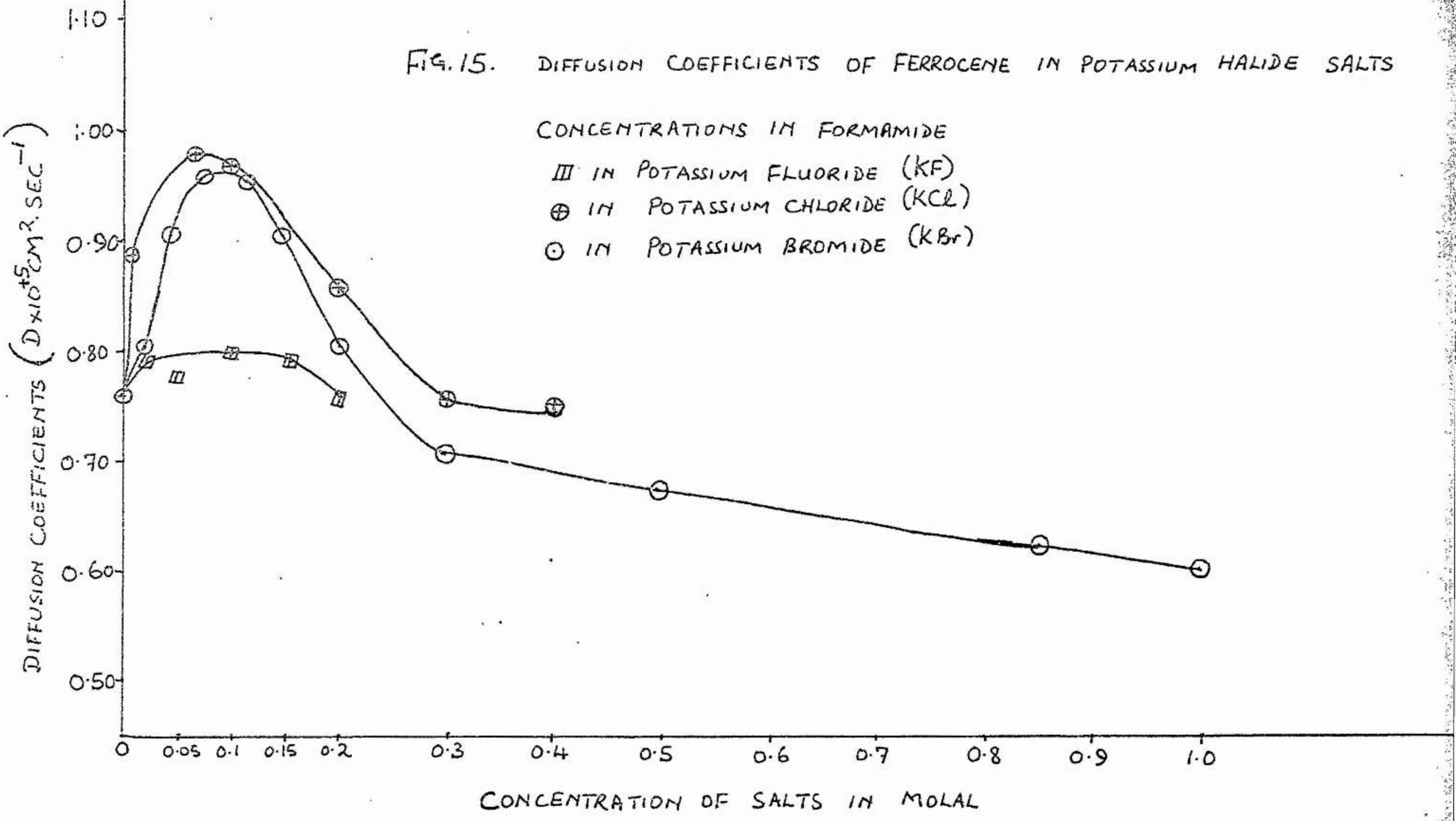


FIG. 15. DIFFUSION COEFFICIENTS OF FERROCENE IN POTASSIUM HALIDE SALTS

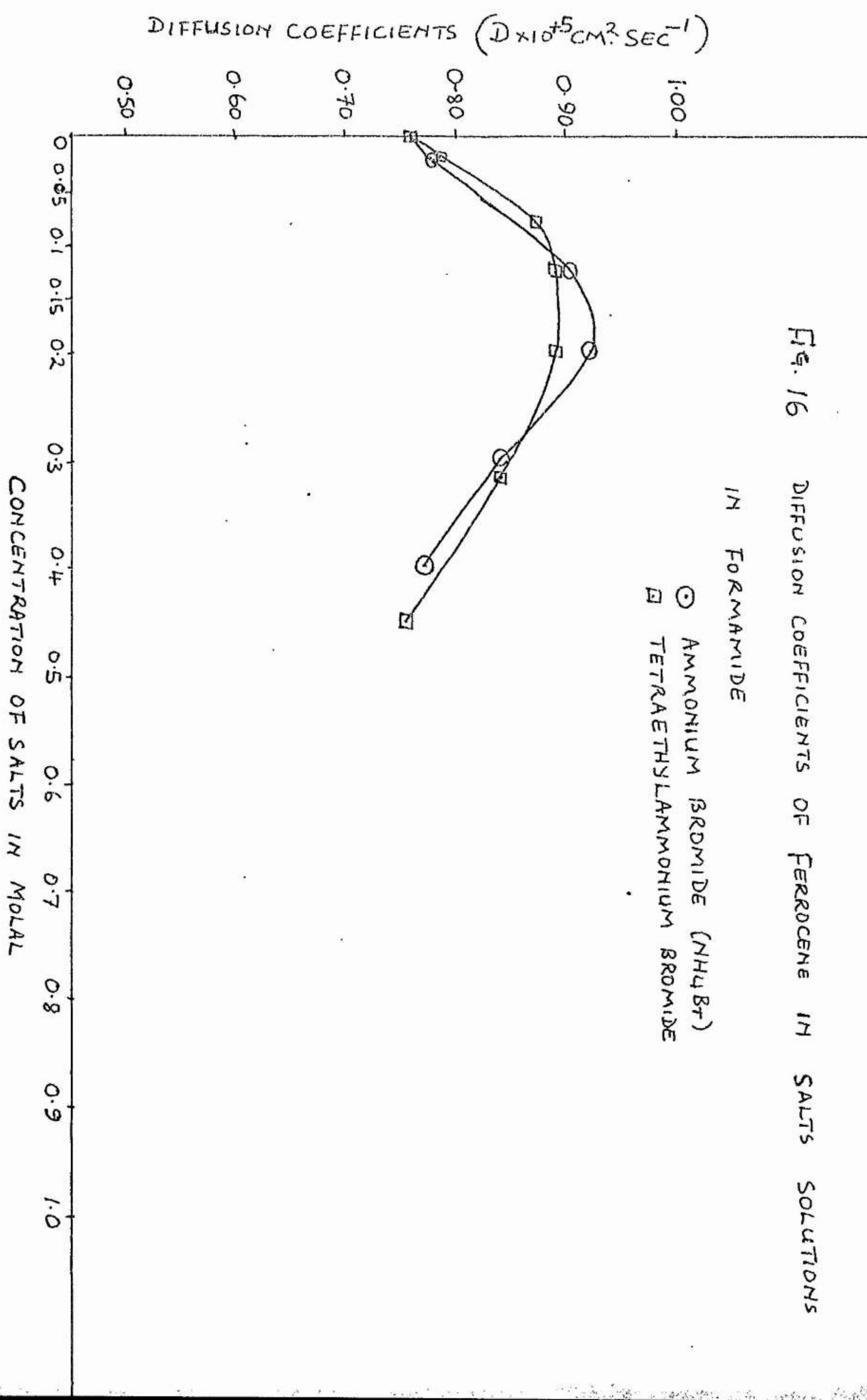


Fig. 16 DIFFUSION COEFFICIENTS OF FERROCENE IN SALTS SOLUTIONS IN FORMAMIDE

(B) Diffusion Coefficients of Ferrocene in Simultaneous Diffusion of both Ferrocene and Potassium Bromide in Formamide.

(a) Diffusion Coefficients of Ferrocene in Upward Diffusion of both Ferrocene and Potassium Bromide in Formamide are shown in Table 18.

(b) Diffusion Coefficients of Ferrocene in Downward Diffusion of Ferrocene and Upward Diffusion of Potassium Bromide in Formamide are shown in Table 19.

In (a) and (b) above the graphs of diffusion coefficients versus concentrations of pot. bromide also show a maximum hump at about the same value as that for ferrocene inneutral potassium bromide solutions. But, both (a) and (b) have lower values of diffusion coefficients than those in neutral potassium bromide solutions. In turn the values of (b) are lower than the values in (a).

(C) Diffusion Coefficients of Potassium Bromide in Simultaneous Diffusion of both Ferrocene and Pot. Bromide in Formamide.

(a) Table 20 shows Diffusion Coefficients of Pot. Bromide in upward Diffusion of both Ferrocene and Pot. Bromide.

(b) Table 21 shows Diffusion Coefficients of Pot. Bromide in Downward Diffusion of Ferrocene and upward Diffusion of Pot. Bromide.

TABLE 18

No. of cells	Initial concentration of potassium bromide in molality	TOP				BOTTOM				$D \times 10^{+5}$ cm^2 sec^{-1}
		Sample 1	Extraction	Sample 2	Extraction	Sample 1	Extraction	Sample 2	Extraction	
		Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	Counts/min	
1	0.02 m	4120.29 4133.35	4126.82	4181.08 4160.63	4170.85	72023.90 71469.42	71746.66	71726.23 71423.34	71574.78	0.436
1	0.04	5800.23	5800.23	5736.37	5736.37	76731.51	76731.51	76757.86	76757.86	0.514
2	0.06	5420.29 5444.59	5432.44	5439.76 5442.21	5440.98	69721.04 69928.51	69824.77	69670.89 70071.07	69870.98	0.644
2	0.075	6495.94	6495.94	6557.26	6557.94	74826.55	74826.55	76048.44	76048.44	0.650
5	0.15	5790.90 5834.04	5812.47	5754.25 5774.19	5764.22	72766.98 72964.33	72865.65	72759.70 73148.68	72954.19	0.647
6	0.20	5976.05 6011.51	5993.78	6063.76 6103.23	6083.49	75538.36 75932.56	75735.46	74904.04 75401.43	75152.73	0.647
6	0.30	6269.72	6269.72	6120.50	6120.50	75803.78	75803.78	76151.36	76151.36	0.564
2	0.45	4957.78 4968.52	4963.15	4948.43 4952.78	4950.60	76732.51 76664.38	76698.44	75809.77 76091.93	75950.85	0.463
6	1.00	3215.58 3233.09	3224.33	3253.81 3258.25	3256.03	66902.80 66958.83	66930.81	66534.19 66419.25	66476.72	0.342

TABLE 19

No. of cells	Initial concentration of Pot. bromide in molality.	Top		Bottom		$D \times 10^{+5}$ cm^2 sec^{-1}
		Sample 1 Counts/min	Sample 2 Counts/min	Sample 1 Counts/min	Sample 2 Counts/min	
1	0.04 m	3889.05	3881.96	73317.81	73103.28	0.373
2	0.075	4262.44	4275.75	73066.83	73665.24	0.449
5	0.020	3816.07	3862.13	69966.43	69781.79	0.417
6	0.30	3952.84	3860.84	69662.46	69432.89	0.424

TABLE 20

No. of cells	Initial concentration of potassium bromide in molality	Final molar concentration in top cell compartment	Final molar concentration in bottom compartment	D x 10^{+5} cm^2 sec^{-1}
1	0.04 molal	0.0023 Molar	0.0405 Molar	0.431
2	0.075 m	0.0057 M	0.08 M	0.530
4	0.14	0.0117	0.140	0.633
6	0.30	0.027	0.308	0.640
1	0.30	0.0272	0.32	0.646
2	0.45	0.0324	0.48	0.518
6	1.00	0.0575	0.965	0.435

TABLE 21

No. of cells	Initial concentration of potassium bromide in molality	Final molar concentration in top compartment	Final molar concentration in bottom compartment	D x 10^{+5} cm^2 sec^{-1}
1	0.04 molal	0.0019 Molar	0.0405 Molar	0.366
2	0.075 m	0.0059 M	0.077 M	0.575
4	0.14	0.0125	0.140	0.676
5	0.20	0.020	0.200	0.736
6	0.30	0.0295	0.305	0.706

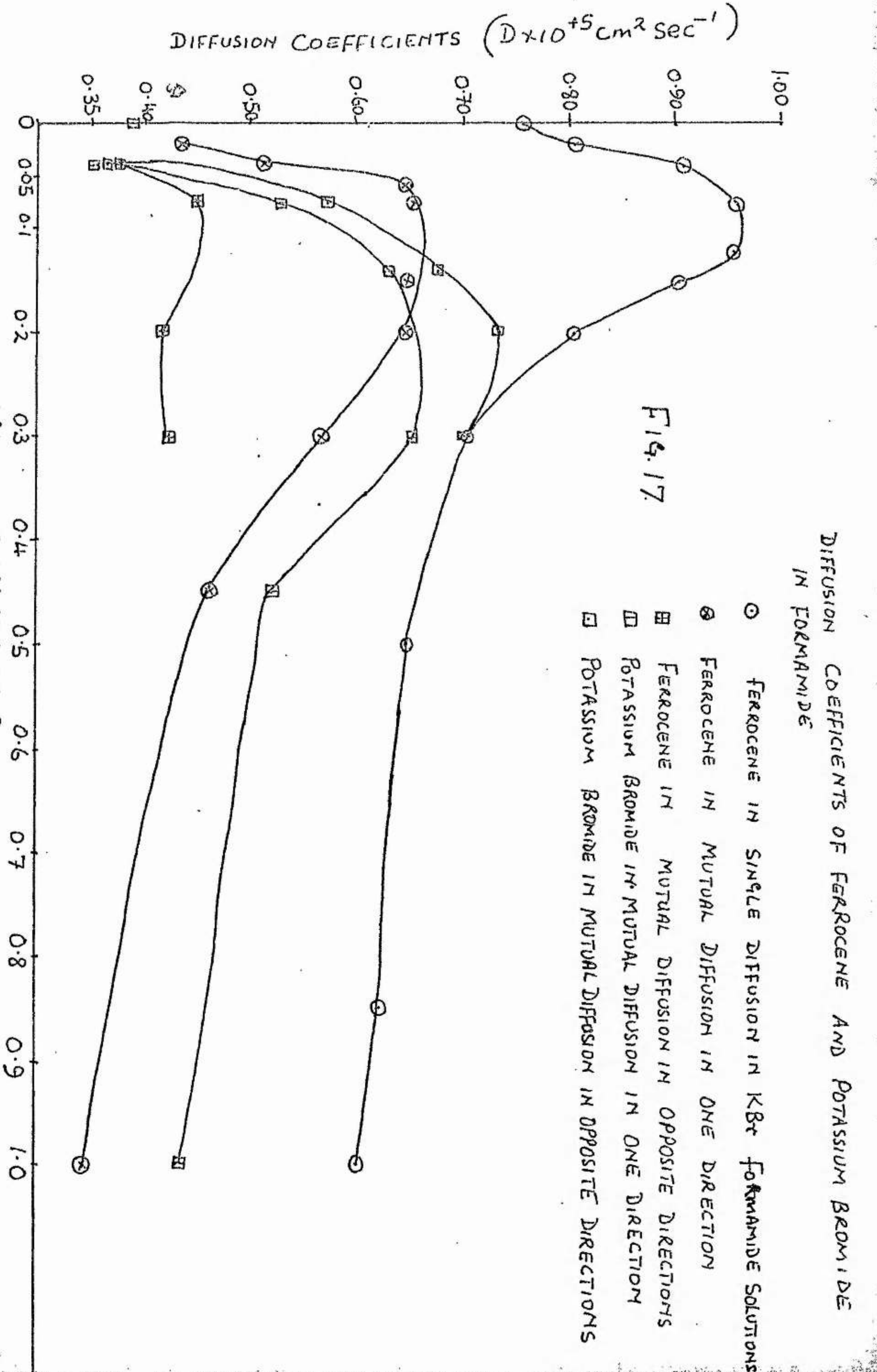


FIG. 17

DIFFUSION COEFFICIENTS OF FERROCENE AND POTASSIUM BROMIDE IN FORMAMIDE

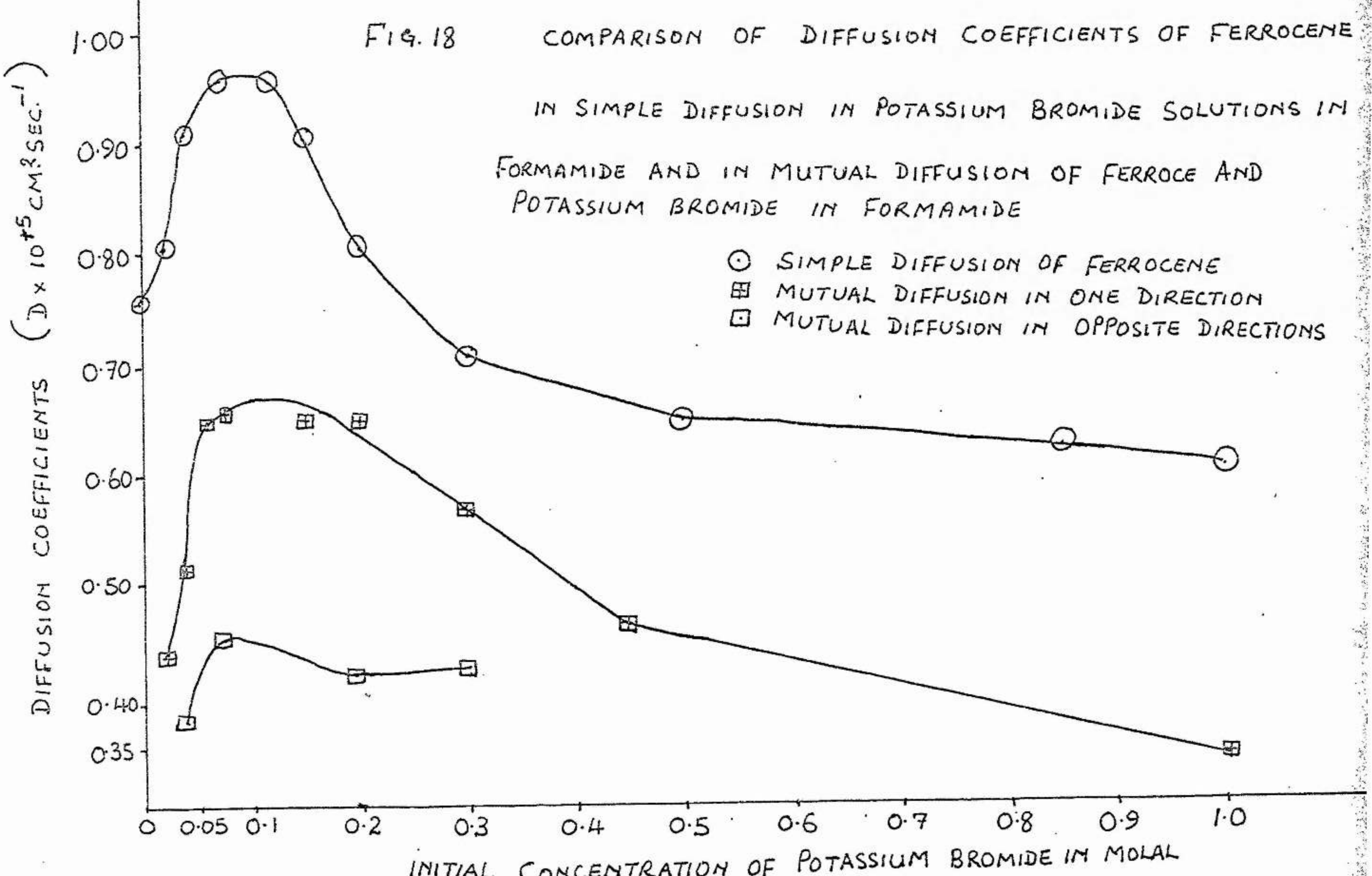


FIG. 18 COMPARISON OF DIFFUSION COEFFICIENTS OF FERROCENE IN SIMPLE DIFFUSION IN POTASSIUM BROMIDE SOLUTIONS IN FORMAMIDE AND IN MUTUAL DIFFUSION OF FERROCE AND POTASSIUM BROMIDE IN FORMAMIDE

Fig. 19 MUTUAL DIFFUSION OF FERROCENE AND POTASSIUM BROMIDE IN ONE DIRECTION IN FORMAMIDE

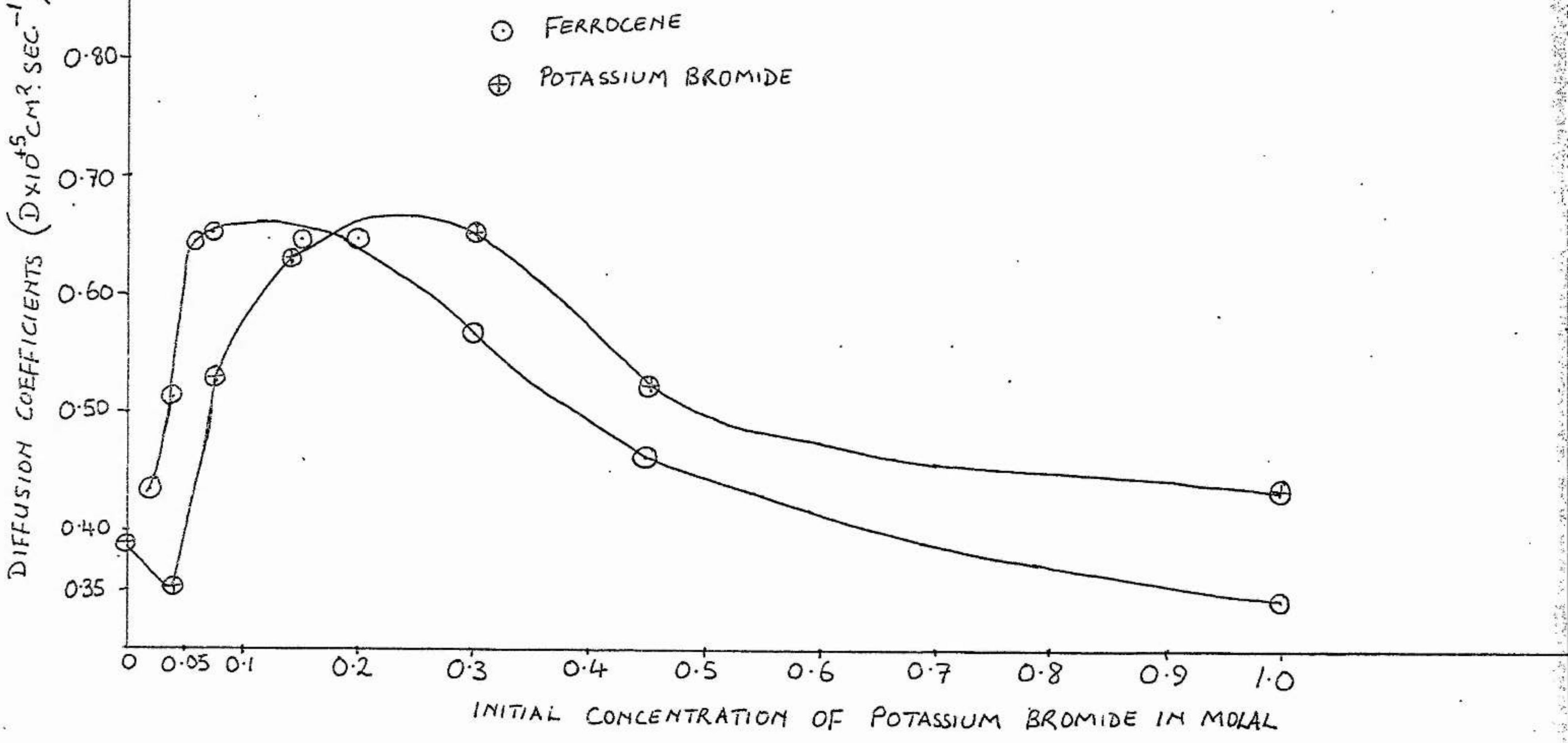
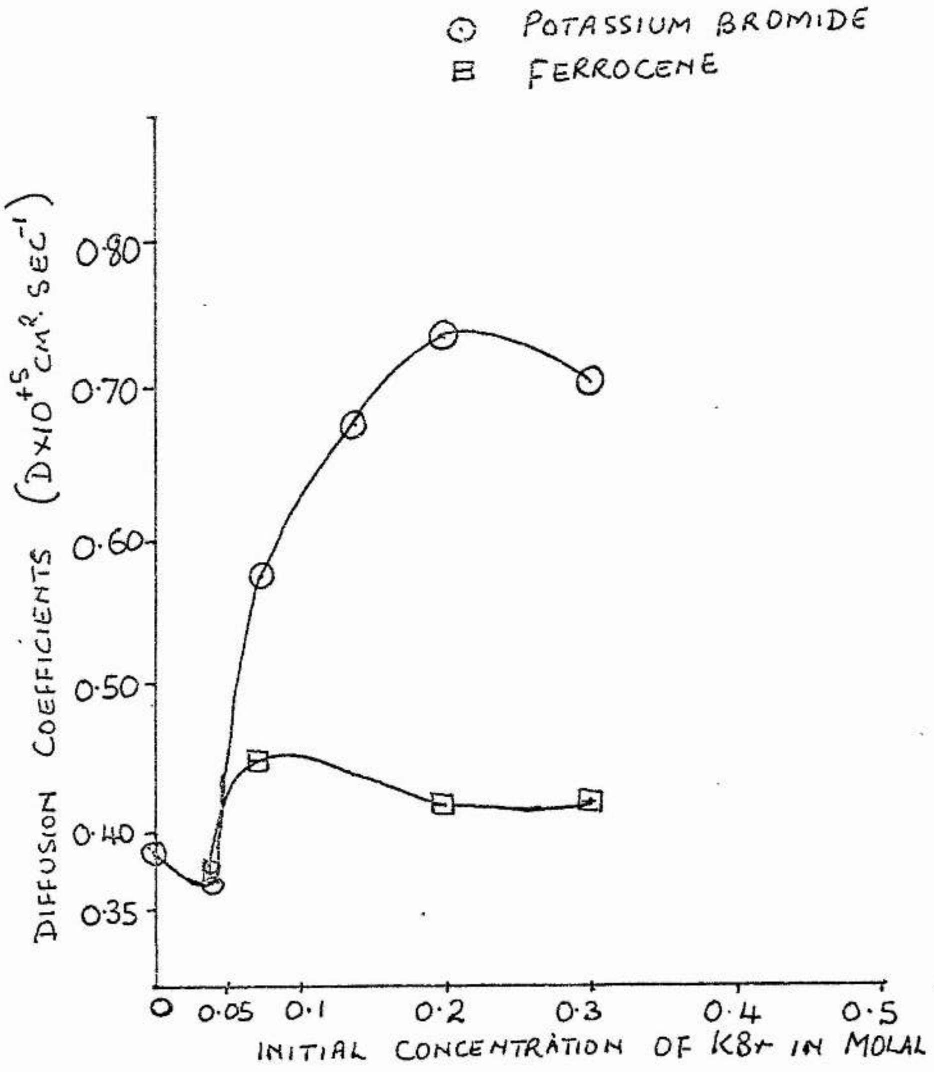


Fig. 20 DIFFUSION COEFFICIENTS OF POTASSIUM BROMIDE AND FERROCENE IN MUTUAL DIFFUSION IN OPPOSITE DIRECTIONS



DISCUSSION

1. Simple Diffusion of Ferrocene in Electrolyte Solutions in Formamide.

The technique of using a neutral molecule, ferrocene to diffuse through electrolyte solutions in formamide is a new method of examining solvent-solute interactions. By using a molecule as a diffusing species complicating factors which arise when ions diffuse in liquids, (that is electrophoretic and relaxation effects) were avoided. Secondly by keeping the concentration of ferrocene constant in all the experiments effects which might arise due to variation of ferrocene concentration were eliminated. Further the concentration of ferrocene in formamide at 5×10^{-4} molal was very dilute in relation to the concentrations of the salts. For example the most dilute salt concentration used was 1×10^{-2} molal concentration. Since the "measuring molecule" concentration was so low it might be considered to have had no gross effects on the solvent structure. The previous work done similar to the present work was that of Craven and co-workers[69] who measured the diffusion coefficients of four azo-dyes in several concentrations of potassium chloride in water using both stirred and unstirred diaphragm cells. They found out that though the diffusion coefficient results in unstirred cells were lower than those of stirred cells they were quite reproducible. The other nearest comparable type of measurements were the determinations of self-diffusion coefficients of water in different aqueous concentrations of different salts by Wang[73], Weiss and Nothnagel[23] and Monk et al[74]. Wang[75] also measured the tracer-diffusion of radioactive sodium ion in different aqueous concentrations of potassium chloride. Some of Wang's[75] results have been discussed by Samoilov[76].

The first attempt to measure diffusion coefficients of ferrocene in different electrolyte solutions in formamide was by the electrochemical method as described under "Experimental Procedure". This method was abandoned because the diffusion coefficient results were not reproducible enough due to the high background currents which disturbed the diffusion layers. The results discussed in this section are therefore those obtained by the diaphragm-cell method.

The Stoke's-Einstein equation $D = \frac{kT}{6\pi r \eta}$ gives the diffusion coefficient D to be inversely proportional to the "macroscopic" viscosity η, where k is the Boltzmann constant, T is the absolute temperature and r is the radius of the diffusion particle. According to this simple relationship of the diffusion coefficient to the viscosity it would be expected that the Walden Product $D\eta$ or $\lambda^{o}\eta$ should be a constant where λ^{o} is the mobility of the diffusing ionic particle; that is that the diffusion coefficient D should fall as the macroscopic viscosity of the electrolyte solution increases. McDowall[77] has measured the macroscopic viscosities of potassium chloride and potassium bromide solutions in formamide and has found that the viscosities increase with increasing salt concentrations over the whole concentration range here investigated. These viscosity results versus concentrations are shown on the graphs in Figures 21 AND 22. From this it would be expected that the diffusion coefficients of ferrocene in potassium chloride and potassium bromide formamide solutions should decrease with increasing concentration of the electrolytes and that the results of the observed ferrocene diffusion coefficients in

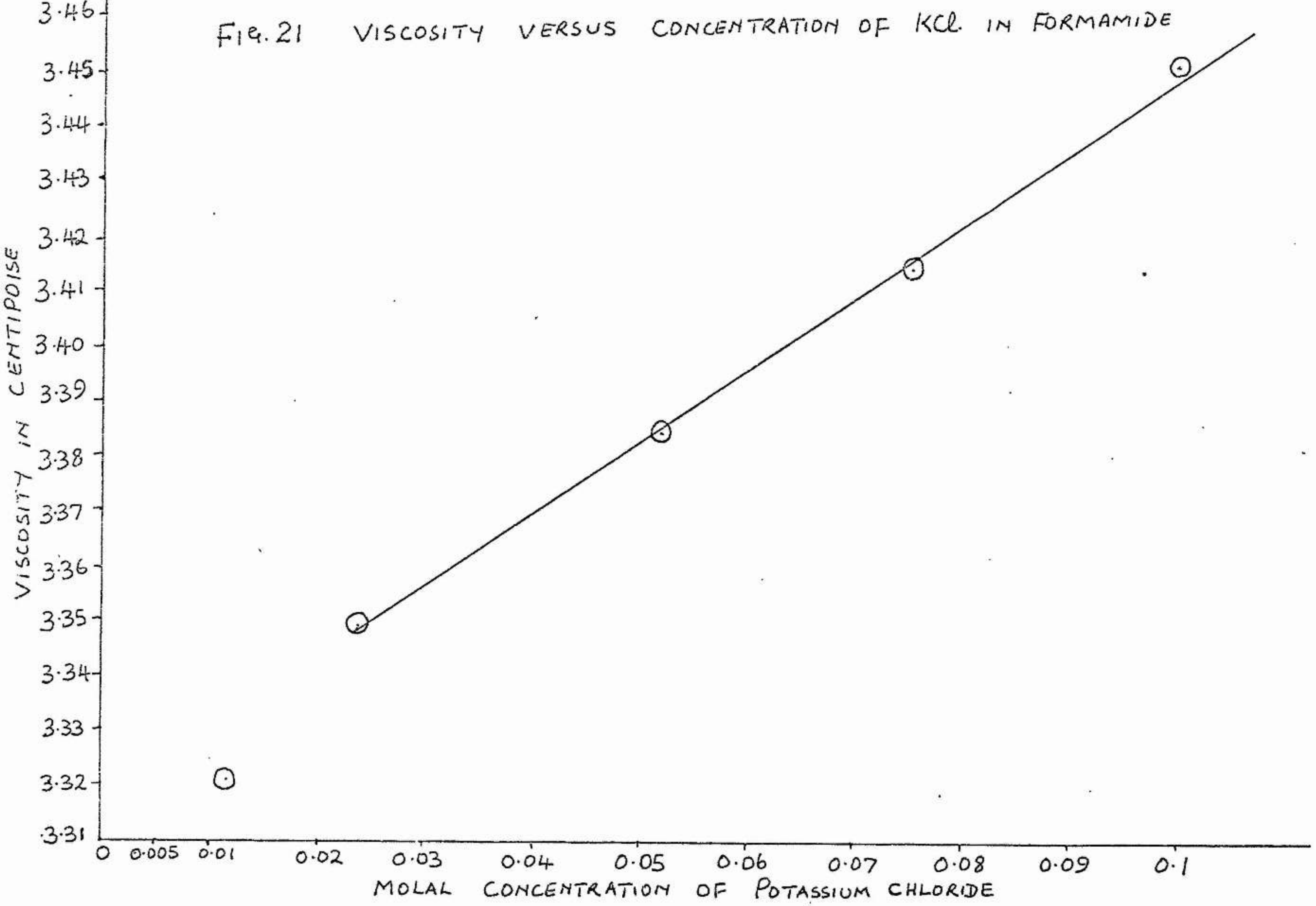


Fig. 21 VISCOSITY VERSUS CONCENTRATION OF KCl IN FORMAMIDE

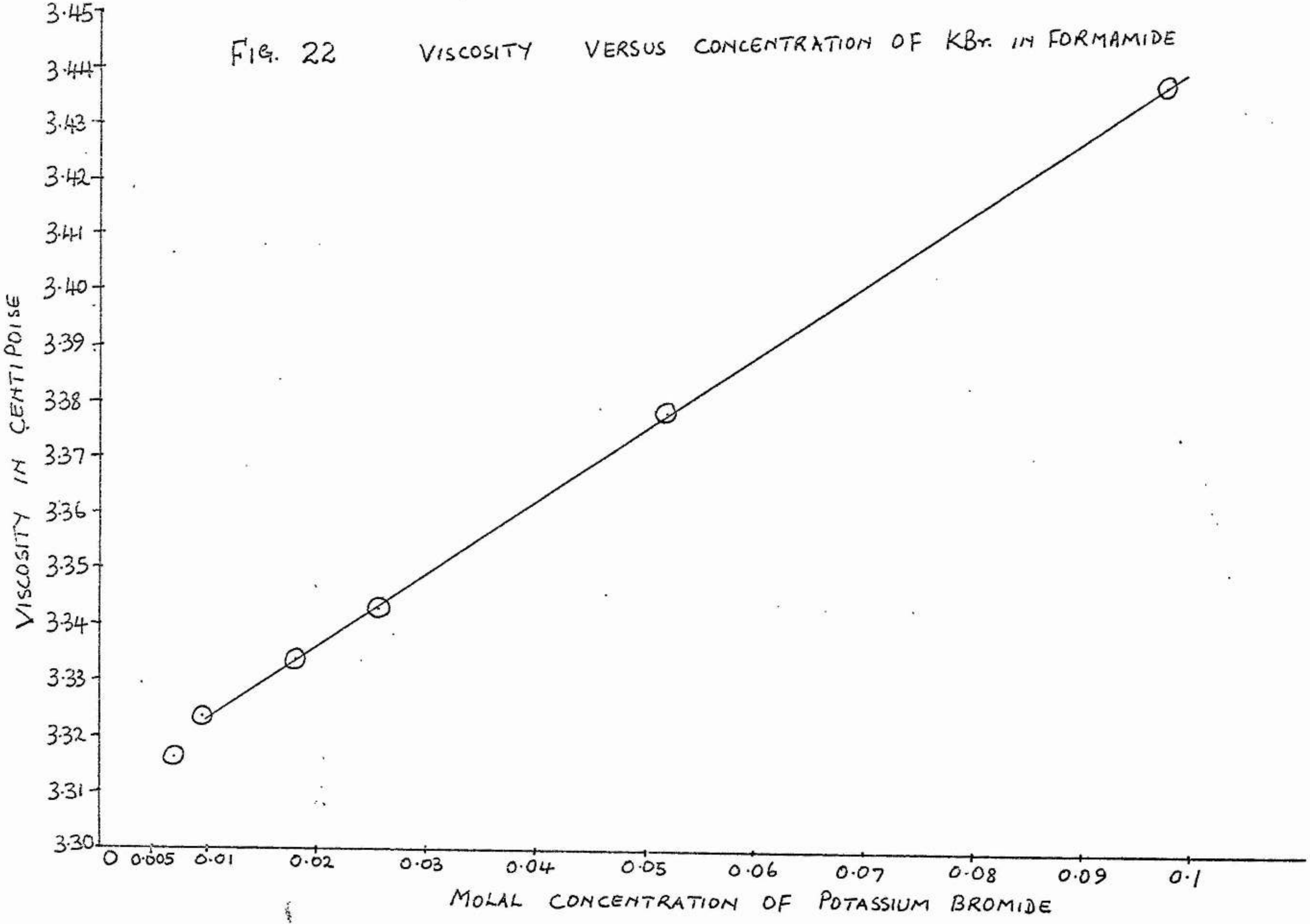


FIG. 22 VISCOSITY VERSUS CONCENTRATION OF KBr. IN FORMAMIDE

pure formamide times the viscosities of these electrolyte solutions in formamide $(\eta)(D^{o}\ )$ versus concentrations of the electrolytes should decline. Monk et al[74] found out that the self-diffusion coefficients of water declined with increasing aqueous concentrations of magnesium chloride, calcium chloride or barium chloride. Craven et al[69] have also shown that the diffusion coefficients of four azo dyes in three aqueous concentrations of pot chloride (0.001 m, 0.01 M and 0.03 M) declined with increasing salt concentration but not much reliance can be put on these results since only 3 dilute concentrations were observed.

A quick inspection of the graphs of diffusion coefficients of ferrocene in formamide and formamide salt solutions versus the concentrations of the salts reveals the general characteristic of a maximum in the curves. The maxima in the diffusion coefficients of ferrocene occur at about 0.09 molality concentration of alkali halides, potassium chloride and potassium bromide and at about 0.175 molality for ammonium bromide and tetraethylammonium bromide. The diffusion coefficient-concentration curve for potassium fluoride show a very small maximum. The curve for the potassium bromide is lower than that for potassium chloride. Thus the diffusion coefficients of ferrocene are greater in potassium chloride at any one concentration than in potassium bromide and potassium fluoride at the same concentration; $(D_{ferrocene})$ KCl $>$ $(D_{ferrocene})$ KBr $>$ $(D_{ferrocene})$ KF. The maximum values in the diffusion coefficients in ammonium bromide and tetraethylammonium bromide are not so high as in potassium chloride or potassium bromide-formamide solutions, but the maxima occur over a wider concentration range than for the alkali halides. The rise in the ferrocene diffusion coefficient values with increasing concentrations of potassium chloride and potassium bromide is sharp and the fall in the diffusion coefficients is sharp too up to a salt concentration of about 0.3 molal. Thereafter the decline in the diffusion coefficients is slow over a wide concentration range as can be seen for potassium bromide up to a concentration of 1.0 molal. (Figure 14). On the other hand the diffusion coefficients-concentration curves for ammonium bromide and tetraethylammonium bromide rise slowly with increasing salt concentrations up to a maximum at about 0.175 molal salt concentration and then fall off gently. In summary the approximate maximum diffusion coefficients of ferrocene in different salt solutions of formamide are shown below in Table 22. These values can be compared with the diffusion coefficient of ferrocene in pure formamide which was 0.758×10^{-5} cm^{2} sec^{-1}. The concentrations of salts at which the diffusion coefficients of ferrocene fell below that in pure formamide are also shown in the Table 22. The validity of the results just described was checked by using different diaphragm-cells to measure the diffusion coefficients at different concentrations. The cells were exchanged in different combinations at different salt concentrations to prove the reproducibility of the results. It is hoped that a general interpretation of these results in terms of a number of types of solvent-solute interaction will be given. The change in the diffusion behaviour of ferrocene in the alkali halides may be attributed to the effect of the halide ion (anion) since the cation was potassium ion in all these salts. It is instructive to compare the behaviour of the ions F^-, Cl^-, Br^-, NH_4^+ and the tetraethylammonium ion in formamide with their behaviour in water.

TABLE 22

Name of salts	Maximum diffusion coefficients of ferrocene in formamide	Concentration of salt at which maximum occurs	Approximate concentration of salt at which diffusion coefficient of ferrocene falls below 0.758×10^{-5} cm^2 sec^{-1}
Potassium Fluoride	0.795×10^{-5} cm^2 sec^{-1}	0.09 molal	0.2 molal
Potassium Chloride	0.985×10^{-5}	0.09 molal	0.3 molal
Potassium Bromide	0.96×10^{-5}	0.09 molal	0.25 molal
Ammonium Bromide	0.925×10^{-5}	0.175 molal	
Tetraethyl-ammonium Bromide	0.895×10^{-5}	0.175 molal	0.45 molal

An attempt was made to find a mathematical equation which would fit the curves of the diffusion coefficients versus concentrations of the salts. The different parameters of the equation which fitted the curves might then be related to the different physical properties which are operative during the diffusion process. The different mathematical relations which were tried are given below:

$$D_{calc} = D^{o} + Ac^{\frac{1}{2}} + Bc \qquad \text{(i)}$$

$$D_{calc} = D^{o} + Ac^{\frac{1}{2}} + Bc^{2} \qquad \text{(ii)}$$

$$D_{calc} = D^{o} + Ac^{\frac{1}{4}} + Bc^{\frac{1}{2}} \qquad \text{(iii)}$$

$$D_{calc} = (D^{o} + Ac)e^{Bc} \qquad \text{(iv)}$$

$$D_{calc} = D^{o} + Ac + Bc^{P}(1 + c)^{Q} \qquad \text{(v)}$$

Where D_{calc} is the calculated diffusion coefficient, D^{o} is the observed diffusion coefficient of ferrocene in pure formamide and A, B, P and Q are constants. The curves of the calculated diffusion coefficient values for the best computer fit to these equations versus the concentrations are shown together with the curve of the experimental diffusion coefficients of potassium bromide in Figures 23 AND 24. Only equation (v) fits the observed curve of potassium bromide within one per-cent of the error (± 1.0%). But the interpretation of this curve in accordance, with any observable physical parameters of the diffusion process or any chemical phenomenon of solvent-solute interactions were in no way obvious. The diffusion curves will therefore be interpreted in qualitative terms only.

As indicated in the Introduction there are two general theories which have been useful in the physical interpretation of the process of diffusion. These are the hydrodynamic or Stokes theory and the Eyring transition state theory. The Stoke's-Einstein equation, $D = \frac{kT}{6\pi r\eta}$ connects the macroscopic viscosity η of the solvent medium in which the particle is diffusing and the diffusion coefficient, D. This equation has been shown to be fairly valid for describing the diffusion of large spherical colloid particles or large spherical molecules[78,79]. The hydrodynamic theory regards the solvent as a continuum, that is a structureless medium. More surprisingly this theory has been applied with a great deal of success in order to account for the change in ionic mobility with viscosity, where the particles under consideration are of the same order of magnitude as the solvent molecules. The equation which connects ionic mobility (λ^o) and, viscosity (η) is the Walden Product relationship ($\lambda^o\eta$ = constant)

FIG. 23 OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS

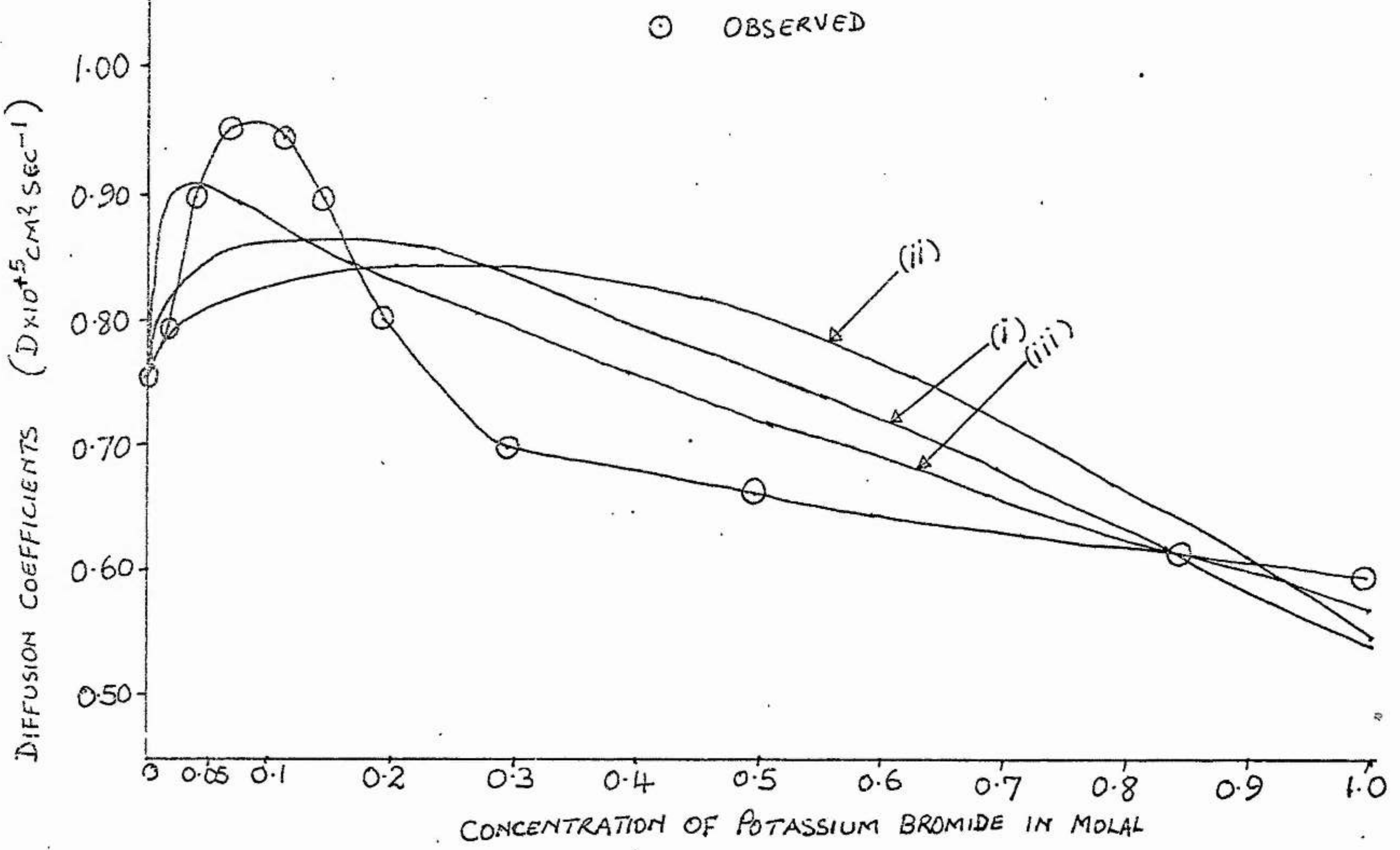
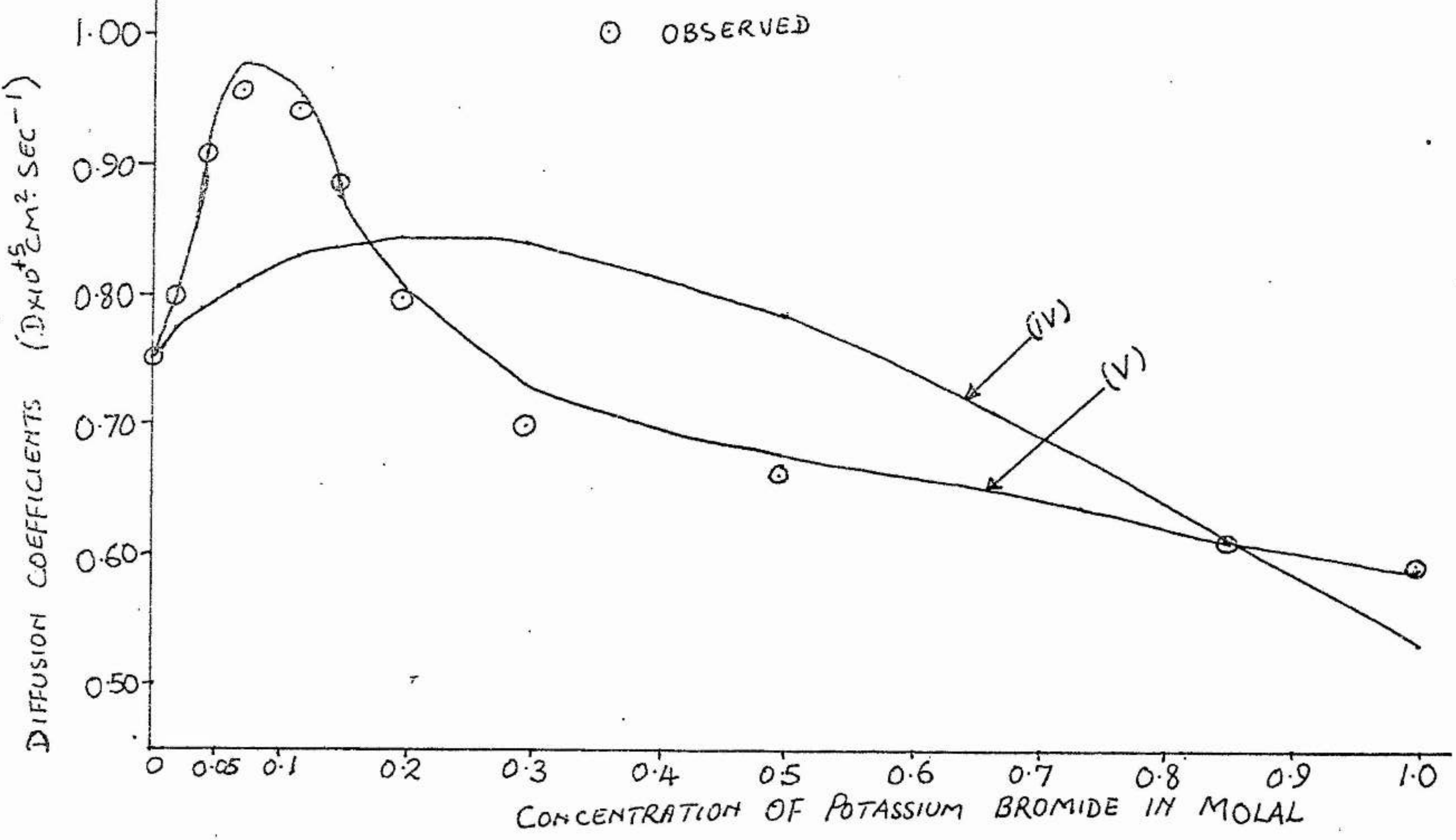


Fig. 24 OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS



already referred to above.

The Eyring[10] transition state theory as already referred to in the Introduction tries to explain the process of diffusion on the basis of a simple model for the liquid state. It is assumed in this theory that there is some unimolecular rate process in terms of which the diffusion process can be described and it is further assumed that in this process there is some configuration that can be identified as the activated state. In reality the liquid has a structure, that is, ions and molecules has definite arrangements at any one instant of time. This arrangement in a liquid (unlike that in the solid) is local in extent, transitory in time and mobile in space. The diffusing particle is considered to jump from one site into an empty site or "hole" and what determines diffusion in one direction is the frequency of these "jumps" in that direction. For a particle to jump from one site into another it must surmount an energy barrier, that is, it requires a minimum energy to move from one site into another. If due to ion-solvent interactions a salt, can lower this energy barrier, that is "weaken" the structure of that solvent it will facilitate rapid diffusion of a particle in that solvent. It is argued in the present work that if the halide salts dissolved in formamide at low concentration did weaken the structure of the formamide on a microscopic scale it would enable more diffusion of the ferrocene molecule than in a structure where there were no salts.

According to the model of Frank and Wen[45] already discussed in the Introduction ions in an aqueous medium can be classified as structure-breakers or structure-makers of the water system.

This effect arises from ion-solvent interactions where structure making ions are those ions which orient a lot of solvent molecules around them and stabilise transient hydrogen bonded "clusters" and structure breakers are those ions which do not orient many water molecules around them and in addition sufficiently dislocate the structure of the solvent within their environments. Thus in the latter case there are additional regions in the solution which might provide easier access for a diffusing particle than other regions. Samoilov[76] speaks of the time water molecules spend around a solute ion. If water molecules spend a long time around an ion the phenomenon is referred to as positive hydration. On the other hand if solvent molecules spend a shorter time around an ion the phenomenon is referred to as negative hydration. The situation has been investigated experimentally by the study of self-diffusion of water in different aqueous salt solutions. Wang[73] experimentally studied the self-diffusion of water in aqueous solutions of sodium chloride, potassium chloride and potassium iodide at 10°C and 25°C using H_2O^{18} as indicator. He showed that the self-diffusion coefficient of water in solutions of potassium chloride and potassium iodide, that is electrolytes consisting only of ions with negative hydrogation is greater than in pure water. On the other hand in sodium chloride solutions the self-diffusion coefficient of water was lower than in pure water. More recently Weiss and Nothnagel[23] have showed that the self-diffusion coefficients of water in lithium chloride-water system are lower than in pure water. In general therefore for water as solvents, lithium ion (Li^+), fluoride ion (F^-), tetraethylammonium ion are known to be structure-makers and ammonium ion (NH_4^+), potassium ion (K^+), chloride ion (Cl^-) and bromide ion (Br^-) are known to be structure-breakers[23,45,76,80].

Returning to the diffusion coefficients of ferrocene in formamide and formamide salt solutions; since the general shapes of the curves are almost identical for all the salts (with the possible exception of potassium fluoride) only one explanation of the general shape is required. But the magnitude of each curve indicates the degree of effect of each salt on the formamide structure. The fact that at low electrolyte concentration the diffusion coefficients rise with increasing addition of the salts would indicate that it is becoming increasingly easy up to a certain salt concentration for the ferrocene to diffuse. This points to the fact that the added salts initially loosen the microscopic structure of formamide. Vincent and Reid[3] have suggested the structure of liquid formamide to be predominantly one of chains of molecules due to hydrogen bonding. Thus due to the strong ion-solvent interactions it would appear that some of the weak hydrogen bonds would break up. If this happened there would be some regions in the formamide salt solutions which would offer easier diffusion than in pure formamide. But McDowall[77] has found out that the "macroscopic" viscosities of potassium chloride and potassium bromide do not decrease with increasing salt concentrations but increase over the whole concentration range. This anomaly has to be explained. Since the viscosity referred to above is macroscopic one would try to differentiate between results of this kind and the microscopic viscosity effects active in molecular diffusion. It is quite possible for ions to affect the structure of a solvent within their immediate environment without these effects showing themselves in the bulk of the solution on a macroscopic scale. Ordinarily this has been one of the weaknesses of the Stoke's-Einstein equation in that the viscosity parameter is macroscopic one and therefore not able to predict the effect on a molecular scale. Ferrocene being a symmetrical molecule it is assumed that it will not be affected by dipole or charge attraction. If it is true that the structure of formamide was weakened around the ion cospheres it is quite reasonable to argue that the diffusing ferrocene molecule (being in such dilute concentrations) would choose a path of least resistance or minimum energy barrier. The point is that the ferrocene molecules would jump into the microscopically loosened zones of the formamide where there are many empty holes. Since the concentrations of ferrocene was very small compared to that of the salts one can argue that the majority of the ferrocene molecules diffused through loosened regions of formamide structure although macroscopically these loosened regions were not significant enough to show themselves in terms of viscosity.

In the measurement of tracer-diffusion coefficients of radioactive sodium ion in different concentrations of potassium chloride in water Wang[75] found a maximum in the curve of tracer-diffusion coefficients versus concentration of potassium chloride although the macroscopic viscosity of aqueous potassium chloride is nearly constant[32]. Wang explained the increase in the tracer-diffusion coefficients due to the "distortion" in the structure of water in the immediate vicinity of the hydrated ion. This is so because, when the concentration of solution increases beyond a certain range, about 0.1 Molar, the mean distance between the ions and hence the number of "solvent" water molecules situated between the nearest oppositely charge ions continue to decrease. Thus it becomes increasingly difficult for the decreasing number of "solvent" water molecules to orient themselves to maintain the most stable semi-crystalline structure that exists in the solvent water in the immediate vicinity of the hydrated ions at infinite dilution. Consequently a greater degree of distortion would be present in the structure of immediately surrounding "solvent" water for solutions of concentration above the Debye-Hückel range. This greater distortion would cause the tracer-diffusion coefficient to increase with increasing salt concentration. From a macroscopic point of view, the above described distortion effect corresponds to a decrease in dielectric constant of the solvent medium. Hückel explained the increase in activity coefficients of ions by this saturation effect which tends to decrease the dielectric constant of the solvent medium and hence increase the self-energy of the ions. Although a molecule (ferrocene) was used in the present work as the diffusion species rather than an ion the explanation given by Wang[75] above for the increase in the diffusion coefficient would be to a great extent be the same for the increase in diffusion coefficient of ferrocene; that is that this is due to loosening of the solvent structure in certain regions with increasing salt concentration up to a certain concentration point.

The downward slope of the diffusion curve at higher concentrations may be explained in terms of the increasing macroscopic viscosity of the salt solutions of formamide. The increase in viscosity is explained in terms of overall stabilization of large regions of hydrogen-bonded structure. The success of Walden arguments for example for different temperatures for infinite dilution conductance is due to the fact that there are no special regions of ion induced structure breaking. It must be remembered that the macroscopic viscosity of a solution for example an aqueous electrolyte solution is an average of the viscosity of water near the ion and the viscosity of water far from the ion, that is in the bulk of the solution. The general stabilization of the solution with so many ions put in is at the expense of regions of local low viscosity through which diffusion may be channelled.

Onsager and Fuoss first recognized the effect of viscosity on diffusion of ions and molecules and Gordon[81] introduced the viscosity parameter in his empirical equation for the calculation of the diffusion coefficients. For the calcium chloride aqueous solutions Wang pointed out that the ratios of the self-diffusion coefficients at infinite dilution to those at 5.36 molar are 13 and 8 for the chloride ion and calcium ion respectively, while the ratio of the macroscopic viscosity of a 5.36 Molar calcium chloride solution to that of pure water is eleven. Many workers[13,14,15,16,17] have explained the fall in the diffusion coefficients versus concentration of the solutes or diffusing species in terms of increasing viscosity.

The diffusion coefficients of ferrocene in formamide salt solutions of potassium chloride are higher than those in potassium bromide and in turn higher than those in potassium fluoride solution. These results can be compared with the standard enthalpies of solution of potassium chloride, potassium bromide and potassium fluoride in formamide. Somsen and Weeda[82] and Visser and Somsen[83] have reported enthalpies of solutions of alkali halide salts and tetra-alkylammonium bromides in formamide. The standard enthalpies of solution in formamide of potassium fluoride, potassium chloride and potassium bromide are compared with the diffusion coefficients of ferrocene in formamide at the maximum point of the curves in Table 23 below. Both measurements were done at 25°C. The positive enthalpies of solution of potassium chloride and potassium bromide indicate that the net effect of solution is bond breaking and that this is a greater effect for potassium chloride than potassium bromide. This is in line with the diffusion coefficients of ferrocene which are higher in potassium chloride-formamide solution than in potassium bromide formamide solution. Potassium fluoride has negative enthalpy of solution in formamide and much low diffusion coefficients of ferrocene in formamide solution of this salt are observed.

TABLE 23

Name of salt	Maximum diffusion coefficients $D \times 10^{-5}$ cm^2 sec^{-1}	Standard enthalpies of solution of salts in formamide in K J/mole
Potassium fluoride	0.795	-13.3
Potassium chloride	0.985	+3.4
Potassium bromide	0.96	+1.0

2. Mutual Diffusion of Ferrocene and Potassium Bromide in Formamide

In the mutual diffusion experiments only potassium bromide salt was used. Two types of mutual diffusions were done. One was the "unidirectional" mutual diffusion of both ferrocene and potassium bromide, that is both diffusing species were allowed to diffuse together upwards in the diaphragm-cells. The other was the "opposed" mutual diffusion where ferrocene was allowed to diffuse downwards the diaphragm-cells and potassium bromide was allowed to diffuse upwards. For both opposed and unidirectional flows the curves of the diffusion coefficients of ferrocene versus the initial concentrations of potassium bromide salt again showed a maximum at about the same potassium bromide concentration (0.09 molal) as in the case of simple ferrocene diffusion. The curve of ferrocene diffusion coefficients versus initial concentrations of potassium bromide when both ferrocene and potassium bromide are diffusing in the same direction is higher than that when ferrocene and pot bromide diffuse in opposite directions. In turn both curves are much lower than the curves when only ferrocene is diffusing, and all the diffusing coefficients of ferrocene in mutual diffusions are lower than the diffusion coefficient of ferrocene in pure formamide. The curves of the diffusion coefficients of potassium bromide versus the initial potassium bromide concentrations also show maximum values but not at the same concentration as the maximum diffusion coefficient value of ferrocene. The maximum diffusion coefficient values of potassium bromide occur at the potassium bromide concentration of 0.23 molal (as opposed to 0.09 molal for ferrocene diffusion coefficients) for both mutual diffusion in one direction and in opposite directions. An interesting point to note here is that while the maximum diffusion coefficients of ferrocene and potassium bromide in mutual diffusion in one direction occur at different potassium bromide concentrations the maximum-diffusion coefficient values are almost of the same magnitude.

The diffusion coefficient (D^o) of Pot. bromide in formamide at infinite dilution calculated from the

Nernst equation as given by Robinson and Stokes[32] was 0.389×10^{-5} cm^2 sec^{-1}. This result can be compared to the maximum diffusion coefficient of potassium bromide in formamide experimentally determined here of 0.665×10^{-5} cm^2 sec^{-1} in the unidirectional mutual diffusion of ferrocene and potassium bromide.

Comparison of the maximum diffusion coefficients of ferrocene in all the diffusion conditions described above are remarkable. The maximum diffusion coefficient value for simple ferrocene diffusion is 0.96×10^{-5} cm^2 sec^{-1} while that for mutual diffusion of ferrocene and potassium bromide in one direction is 0.66×10^{-5} cm^2 sec^{-1} and that for mutual diffusion of ferrocene and pot bromide in opposite directions is 0.45×10^{-5} cm^2 sec^{-1}.

The diffusion coefficient results of the mutual diffusion of ferrocene and potassium bromide can be interpreted in terms of non-equilibrium thermodynamics. Because the diffusional flow depends on the forces (for example the gradient of chemical potential, gradμ) one can relate the flow J directly to the force and write: $J \propto X\alpha - \text{grad}\mu$ or $J = LX = -L\ \text{grad}\mu$. This is the equation in the case of a simple diffusion of a single particle in a solution. L is normally referred to as a phenomenological coefficient. X is the driving force which in diffusion is related to the chemical potential, μ . The phenomenological coefficient however becomes more important in systems with coupling of flows and forces like in mutual diffusion of two or more species in a solution, because the movement of one species may be affected by the movement of another species. Thus the diffusion of one substance may be enhanced or hindered by the diffusion of another substance in the same medium. The linear dependence of all mechanical flows on all mechanical forces operating in a system had earlier been studied by Rayleigh on his theory of sound. It was Onsager[84] in 1931 who extended the coupling of flows and forces concept to include all thermodynamic flows and forces. For example in the case of mutual diffusion of two species 1 and 2 in a solution their diffusional flows can be connected to their forces by a set of equations known as the "phenomenological equations" as follows:

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \qquad 1$$

These equations show simply that the force which drives substance 1 may also contribute to flow of substance 2 and vice-versa. The coefficients L_{12} and L_{21} have been shown to be equal[85]. The equations above can also be written as:

$$\begin{aligned} J_1 &= -L_{11} \text{ grad } \mu_1^c - L_{12} \text{ grad } \mu_2^c \\ J_2 &= -L_{21} \text{ grad } \mu_1^c - L_{22} \text{ grad } \mu_2^c \end{aligned} \qquad 2$$

The dependence of chemical potential on position is due to the local changes of the solute concentrations c_1 and c_2 so that

$$\begin{aligned} \text{grad } \mu_1^c &= \frac{\partial \mu_1^c}{\partial c_2} \text{ grad } c_1 + \frac{\partial \mu_1^c}{\partial c_2} \text{ grad } c_2 \\ &= \mu_{11} \text{ grad } c_1 + \mu_{12} \text{ grad } c_2 \end{aligned}$$

$$\text{and grad } \mu_2^c = \frac{\partial \mu_2^c}{\partial c_1} \text{ grad } c_1 + \frac{\partial \mu_2^c}{\partial c_2} \text{ grad } c_2$$

$$\text{in which } \mu_{ij} = \frac{\partial \mu_i^c}{\partial c_j}$$

Rearranging all the equation above one can write J_1 and J_2 as

$$J_1 = -(L_{11}\mu_{11} + L_{12}\mu_{21}) \text{ grad } c_1 - (L_{11}\mu_{12} + L_{12}\mu_{22}) \text{ grad } c_2$$
$$J_2 = -(L_{21}\mu_{11} + L_{22}\mu_{21}) \text{ grad } c_1 - (L_{21}\mu_{12} + L_{22}\mu_{22}) \text{ grad } c_2 \qquad 3$$

In terms of diffusion coefficients

$$J_1 = -D_{11} \text{ grad } c_1 - D_{12} \text{ grad } c_2$$
$$J_2 = -D_{21} \text{ grad } c_1 - D_{22} \text{ grad } c_2 \qquad 4$$

The flows are related to the gradients of concentration of both solutes and four diffusion coefficients, two straight coefficients D_{11} and D_{22}, and two cross-coefficients, D_{12} and D_{21}. The above equations 3 and.4 for J_1 and J_2 indicate that

$$D_{11} = L_{11}\mu_{11} + L_{12}\mu_{21} \qquad D_{12} = L_{11}\mu_{12} + L_{12}\mu_{22}$$
$$D_{21} = L_{21}\mu_{11} + L_{22}\mu_{21} \qquad D_{22} = L_{21}\mu_{12} + L_{22}\mu_{22}$$

Careful determinations of the four diffusion coefficients above have been carried out by Gosting and his co-workers[86,87] for several three-component systems and it has been shown that for the system sodium chloride-potassium chloride-water the cross coefficients L_{12} and L_{21} are appreciable and cannot be neglected relative to the straight coefficients L_{11} and L_{22}. If the coefficients L_{12} and L_{21} are negative then the diffusion coefficients D_{11} and D_{22} of the two substances 1 and 2 shall be smaller where there is mutual diffusion than when there is single diffusion of either substance 1 or 2. In the mutual diffusion of ferrocene and potassium bromide in the present work the diffusion coefficients of ferrocene were found much lower than the diffusion coefficients in simple ferrocene diffusion. Since there could be no charge attraction between potassium bromide ions and ferrocene, the latter being a neutral molecule the drag effect exerted by the moving potassium bromide on the ferrocene might be due to the fact that the ferrocene diffusion path was being blocked by the moving potassium bromide ions. This could be the explanation for mutual diffusion of ferrocene and potassium bromide in one direction. The reduction in the diffusion coefficients of ferrocene in mutual diffusion of ferrocene and potassium bromide in opposite directions was simply that the upward diffusing potassium bromide opposed the downward diffusing ferrocene molecules.

Our preconceived ideas on mutual diffusion in the one direction led us to believe that the diffusion coefficient of the ferrocene might only be enhanced by the co-diffusion of the salt. Thus over an initial concentration range of 0.04 - 0.25 molal potassium bromide it was considered that ferrocene at any cross-section of diffusion path and at any time during diffusion period would be in a region of salt concentration where in the absence of salt motion one would expect a higher diffusion coefficient than in pure formamide. It was further expected that drag of the moving solvated ions would if anything increase the mean velocity of the ferrocene molecule still more.

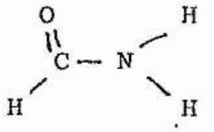
(B) THERMODYNAMICS SECTION

MEASUREMENTS OF VAPOUR PRESSURES OF THE SYSTEMS: FORMAMIDE-WATER, N-METHYLFORMAMIDE-WATER AND DIMETHYLFORMAMIDE-WATER BINARY MIXTURES.

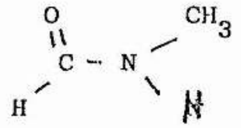
INTRODUCTION

The three amides considered in this study are:

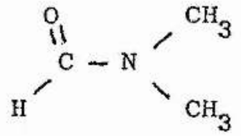
Formamide ⟶



N-Methylformamide ⟶



and Dimethylformamide ⟶



Formamide has two hydrogen atoms situated on the nitrogen, available for hydrogen bonding. N-Methylformamide has only one and Dimethylformamide has none. Due to their relatively high dielectric constants all these substances are important in their own right as solvents for electrolytes. The binary mixtures of each of these substances with water are, however of increasing technical importance since they provide solvent systems which are both less expensive and have superior physical properties for a number of applications than the pure solvents. There is eventually considerable interest in the use of such binary mixtures as solvent systems in electrochemical power sources and electrolytic capacitors.

Vapour pressures for different compositions of binary solutions at any one temperature show characteristic features which can be interpreted analytically in terms of their molecular interactions. If a graph of vapour pressures versus mole fractions of either of the components gives a straight line the binary mixture is said to obey Raoult's law or to behave ideally. The linear relation of partial pressure to liquid composition is expressed as $p_A = p_A^o \; x_A$ and $p_B = p_B^o \; x_B$ where p_A and p_B are the partial pressures of A and B respectively above their solution and p_A^o and p_B^o are the vapour pressures of the pure liquids A and B; x_A and x_B are the mole fractions in the binary mixtures. Solutions which obey Raoult's law are usually two liquids composed of molecules of similar size and related constitution, for example benzene-toluene binary mixtures. These solutions are those in which A......A, B......B and A......B interactions are all similar.

Deviations from Raoult's law which may be negative (that is where the vapour pressure curve falls below that for an ideal solution) or positive (that is, where the vapour pressure curve lies above that for an ideal solution) therefore may reveal particular types of interaction between the different molecules. Thus, measurements of vapour pressures yield important information about the molecular behaviour of such liquids. It is important to note that the majority of binary liquids show marked deviations from Raoult's law. Positive deviations like that of the carbon disulphide-acetone system occur mainly if the forces of attraction between unlike molecules contribute less to stability of the solution than do those between like molecules. This may be the case if one or other of the species is "associated"; that is, its molecules have strong specific interactions such as hydrogen bonding. Positive deviations can also be expected if the molecules are greatly dissimilar in size and shape. Negative deviations on the other hand may occur if the molecules composing the two liquids have particularly great affinities for one another. Negative deviations usually are accompanied by negative enthalpies of mixing which indicate great interactions of the molecules which may even result in compound formation.

Vapour pressures may also be used to determine certain important thermodynamic properties of mixtures such as enthalpies of vapourization. The equation which connects vapour pressure (p) and the enthalpy of vaporization (ΔHv) is the Clausius-Clapeyron equation $\ln P = -\frac{\Delta Hv}{RT} + \text{constant}$ where R is the universal gas constant and T is absolute temperature.

In the present work total vapour pressures of Formamide-Water, N-methylformamide-Water and Dimethylformamide-Water systems and the partial pressures of the water vapour in these systems were determined with a view to furthering the understanding of intermolecular behaviour between the amides and water. Enthalpies of vapourizations of the water in the systems were calculated using the Clausius-Clapeyron equation at different compositions over a range of temperatures.

EXPERIMENTS

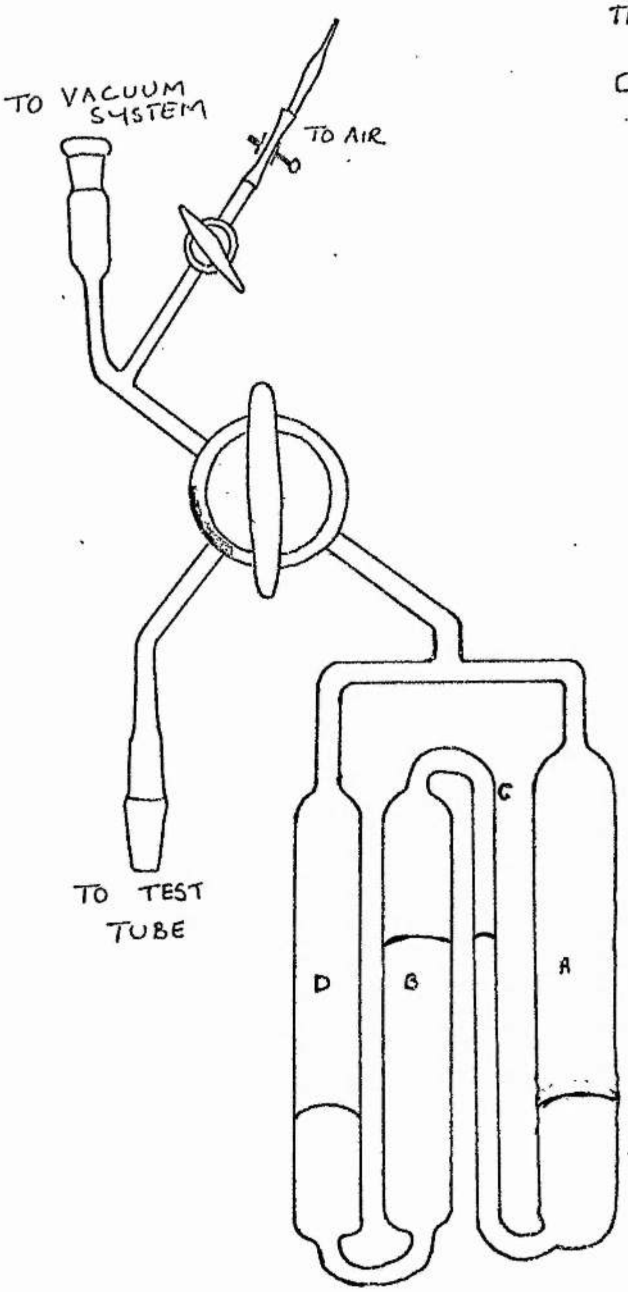
Total vapour pressures of the systems, Formamide-Water; N-Methylformamide-Water and Dimethylformamide-Water at a number of mole fractions at several temperatures were measured with a Zimmerli manometric gauge[88] as shown in Figure X . The manometer and the flask containing the solution were connected to a vacuum system consisting of oil and mercury diffusion pumps to remove air. The solution was degassed by sequentially, gently warming with a hot air drier to remove gases and freezing with liquid nitrogen and pumping out. The process was repeated until no air bubbles were noticeable when warming the solution. Care was taken not to alter the concentration of the solution. When this was done the apparatus was closed to the air pumped down and removed from the vacuum system. It was then immersed in a constant temperature bath. The total vapour pressure of the solution at each temperature required was then measured using a Griffin and George Cathetometer. The efficiency of this procedure was tested by measuring the vapour pressures of distilled water at several temperatures. The results are shown in Table 24 below.

TABLE 24

Temperature in ^{o}C	Observed vapour pressures of water	Accepted vapour[89] pressures of water
25	23.81	23.756
30	31.83	31.824
35	42.29	42.175
40	55.27	55.324
45	72.17	71.88
50	92.77	92.51

FIG X ZIMMERLI GAUGE

B AND D are the columns of the U-tube; C is a capillary tube, A is the mercury reservoir



Once the total vapour pressures of the solutions were measured the partial vapour pressures of water and the amides were then determined by the following procedure. Firstly, the refractive indexes of the water-amide solutions at different mole fractions were determined in a Refractometer and standard calibration curves of mole fractions versus refractive indexes were drawn. Secondly, the liquified vapour of the water-amide solutions at each concentration where the total vapour pressure was measured was collected at each appropriate temperature by a transpiration technique described below. Pre-dried nitrogen gas passing from the nitrogen tank was allowed to equilibrate by passing it through a four-meter glass spiral in the thermostat. The gas was then passed through a sinter fixed in a glass tube containing the water-amide solution to form bubbles. The equilibrated vapour of the two components was then driven by the nitrogen gas into a test tube immersed in liquid nitrogen to freeze out all the vapour as immediately as it came in. Care was taken not to allow vaporization to continue to an extent which would alter the solution composition noticeably. The collected solution had its refractive index measured and its concentration was determined from the standard calibration curves.

RESULTS

1. Formamide-Water

Since the vapour pressure of formamide below 100°C is so small(about 0.15 mm of Hg at 50°C calculated from[90]) it was not necessary to measure its vapour pressure in this work. Consequently for this system the calibration curve was not determined. The total vapour pressures of the solution at the experimental temperatures, 40°C, 45°C and 50°C, were assumed therefore to be primarily that of water. The graphs of mole fractions of water versus observed vapour pressures are shown in Figure 25 . Using these graphs the estimated vapour pressures were calculated by computer and the enthalpies of vaporizations were calculated from the Clapeyron equation

$$\ln P = - \frac{\Delta H_v}{R} \frac{1}{T} + \text{constant}$$

where P is in this case the vapour pressure of formamide-water mixtures; ΔH_v is the enthalpy of vaporization, R the gas constant is 8.315 kJ mol^{-1} and T is temperature on absolute scale. The slope of the plot of log P against $\frac{1}{T}$ is $\Delta H_v/2.303$ R (the factor 2.303 to convert from ln to log) and the enthalpy of vaporization can be calculated. Table 25 shows the mole fractions of water, the slopes ($\Delta H_v/2.303$ R) and the enthalpies of vaporization, ΔH_v. The plot of mole fractions of water versus the enthalpies of vaporization is shown in Figure 26 .

TABLE 25

Mole fractions of water	Slopes ($\Delta H_v/2.303$ R)	ΔH_v of water in kJ mol^{-1}
1.0000	-2291.67	43.87
0.9401	-2256.41	43.21
0.8713	-2241.57	42.93
0.8066	-2250.00	43.09
0.7143	-2177.21	41.69
0.6324	-2158.95	41.34
0.5855	-2162.16	41.40
0.4078	-2212.12	42.36
0.3361	-2333.33	44.68
0.2187	-2526.31	48.38
0.0998	-2707.69	51.85

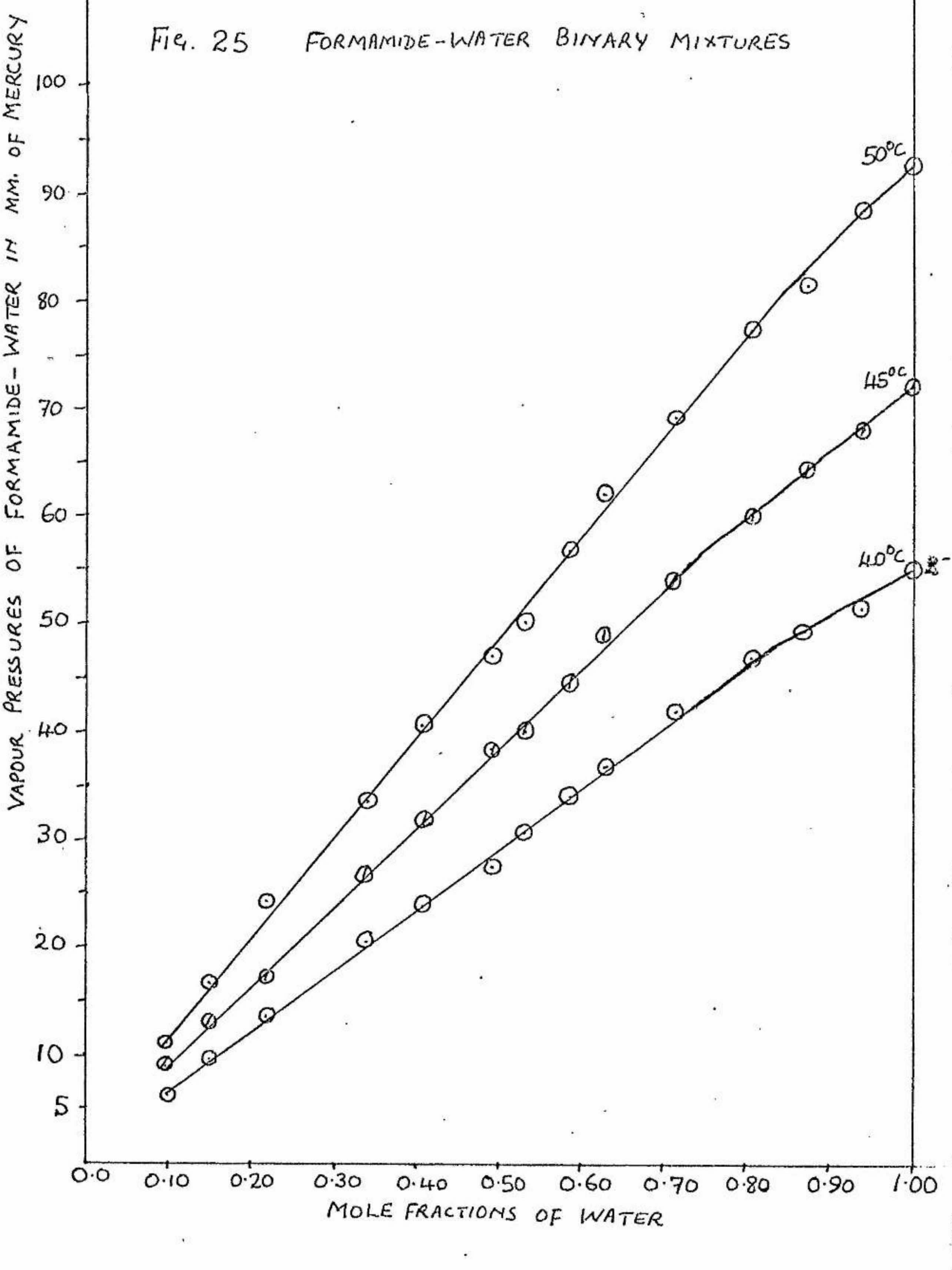
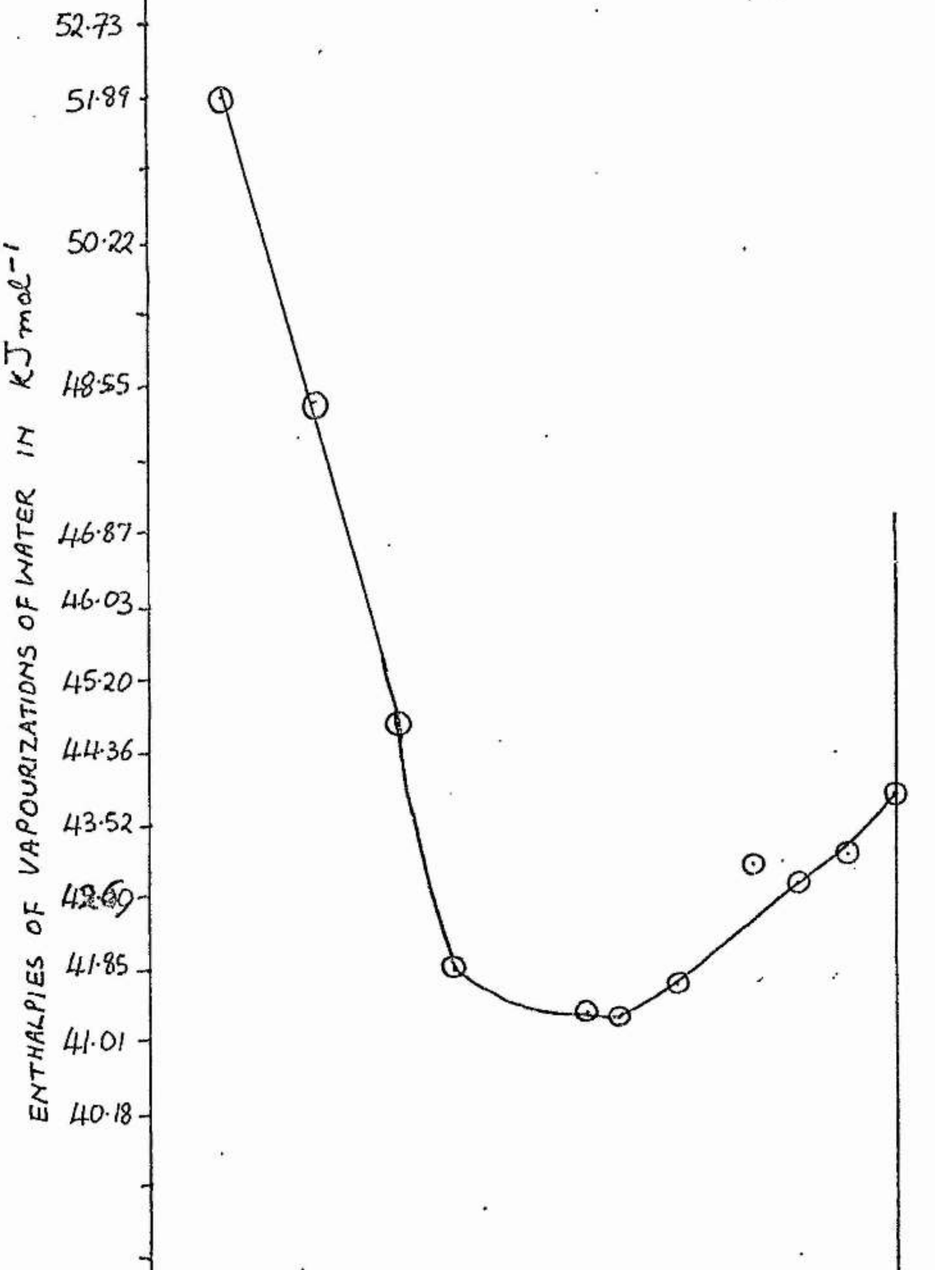


FIG. 25 FORMAMIDE-WATER BINARY MIXTURES

FIG. 26 FORMAMIDE—WATER BINARY MIXTURES



ΔH_v of pure formamide at 25°C is 64.99 kJ mol^{-1} and that of pure water is 43.04 kJ mol^{-1}

2. N-Methylformamide-Water

Experiments were carried out at 25°, 30°, 35°, 40° and 45°C and the partial vapour pressures of water (determined from calibration curve of refractive indexes versus mole fractions of water) against mole fractions of water are shown in Figure 27. The vapour pressures of pure N-methylformamide in mm of Hg at 44°C, 47°C and 55°C are 0.4, 0.6 and 1.5 respectively as given by Riddick and Bunger [68]. As in the case of formamide-water enthalpies of vaporizations (ΔH_v) were calculated from the Clapyron equation. The enthalpies of vaporizations of water in the N-methylformamide-water mixtures are given in Table 26 and the results of ΔH_v against mole fractions of water are plotted as shown in Figure 28.

TABLE 26

Mole fractions of water	Slopes = $\frac{-\Delta H}{2.303\ R}$	ΔH_v of water in kJ mol^{-1}
1.0000	-2291.67	43.87
0.8941	-2288.33	43.73
0.8006	-2266.67	43.41
0.7074	-2266.67	43.41
0.5962	-2266.66	43.41
0.5008	-2235.78	42.82
0.4006	-2233.33	42.78
0.3104	-2250.00	43.09
0.2569	-2266.67	43.41
0.2001	-2400.00	45.86
0.1014	-2666.67	51.08

FIG. 27 N-METHYLFORMAMIDE— WATER BINARY MIXTURES

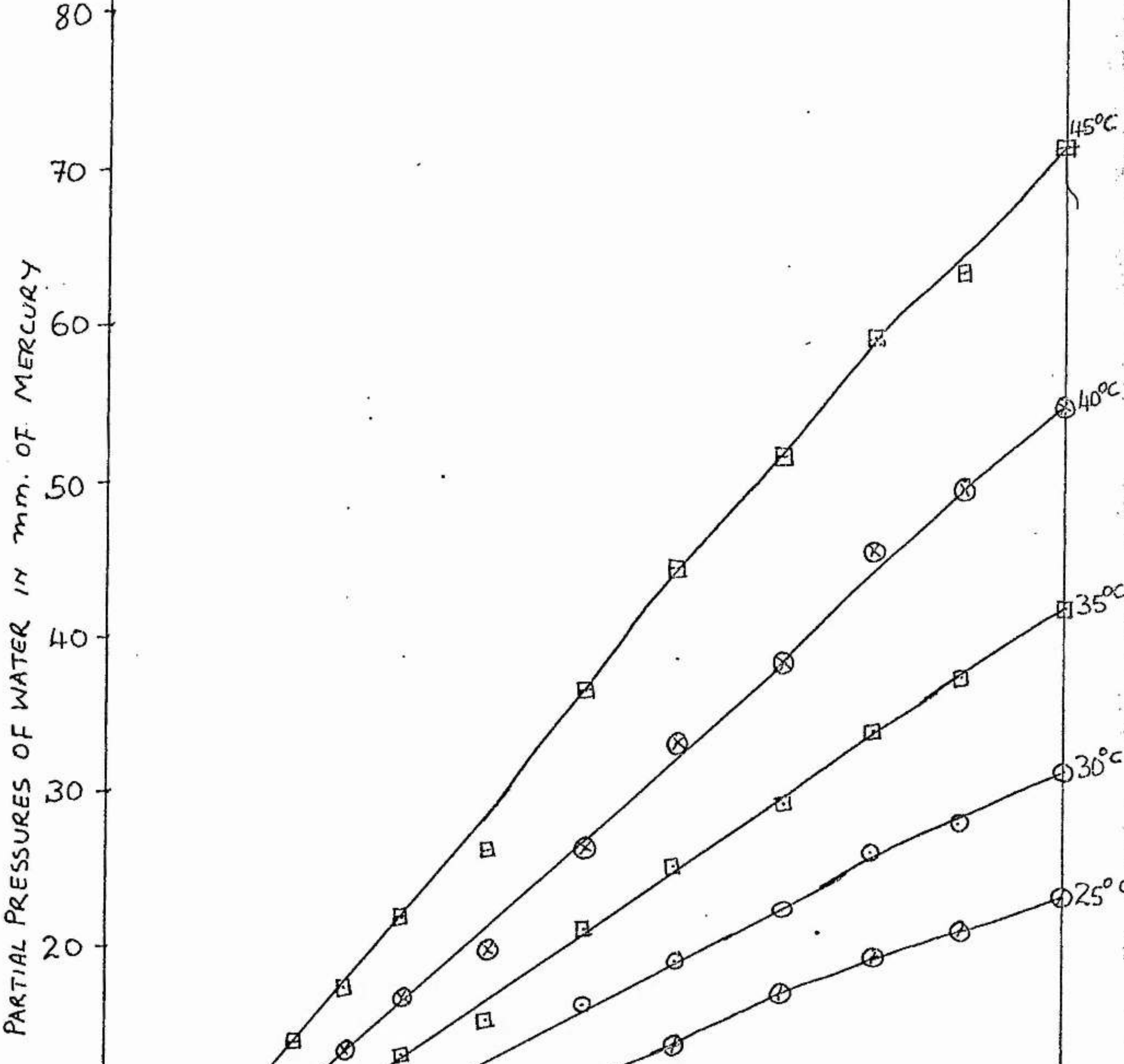
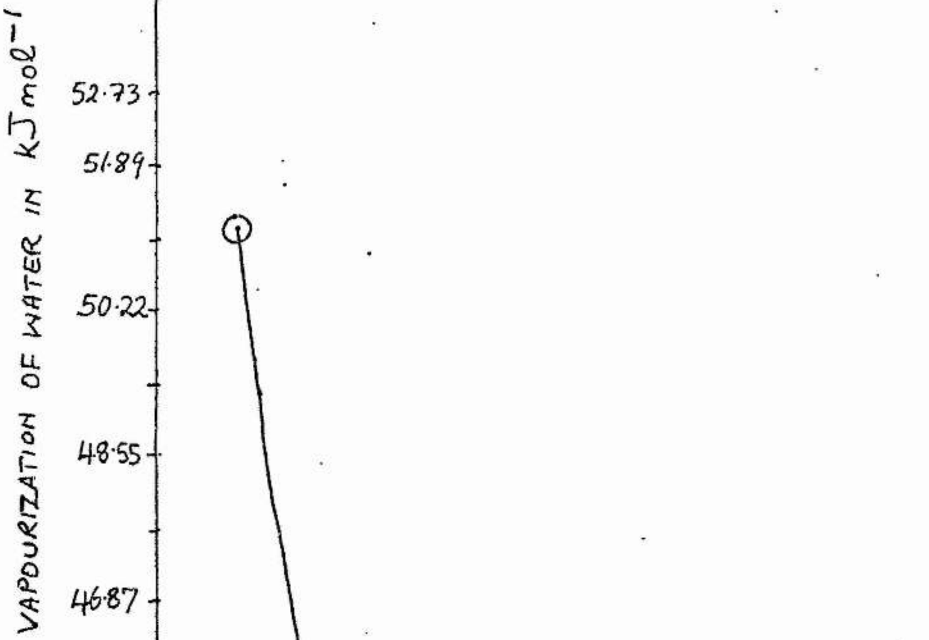


Fig. 28 N-METHYLFORMAMIDE–WATER BINARY MIXTURES



3. Dimethylformamide-Water

Measurements were performed over the same temperature range as for N-methylformamide-water (25°, 30°, 35°, 40° and 45°C) and the partial pressures of water versus mole fractions of water at the different temperatures are shown in Figure 29. Table 27 shows the mole fractions of water and the heats of vaporizations of water in the Dimethylformamide-Water mixtures. The results of ΔH_v versus mole fractions of water are given in Figure 30. The ΔH_v of pure Dimethylformamide observed at the above temperature range was 44.49 kJ mol^{-1} which may be compared with the result given by Geller[91] of 47.59 kJ mol^{-1}

TABLE 27

Mole fractions of water	Slopes ($\Delta H_v/2.303\ R$)	ΔH_v of water in kJ mol^{-1}
1.0000	-2291.67	43.87
0.9378	-2270.27	43.48
0.8087	-2266.67	43.41
0.7052	-2250.00	43.09
0.5986	-2275.00	43.57
0.5260	-2354.00	45.10
0.3276	-2375.00	45.49
0.2541	-2411.76	46.19

FIG. 29 DIMETHYLFORMAMIDE-WATER BINARY MIXTURES

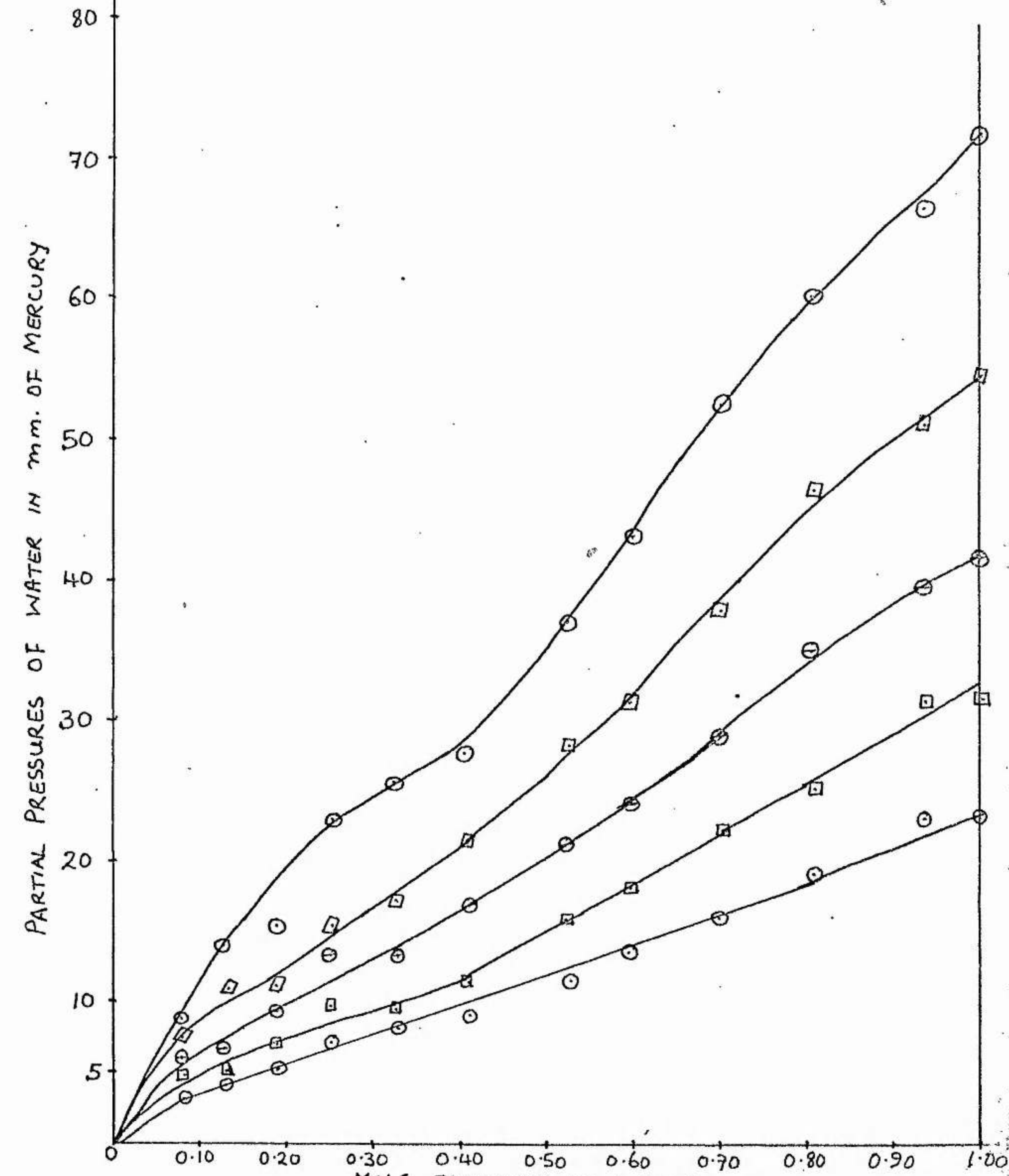


Fig. 30 DIMETHYLFORMAMIDE—WATER BINARY MIXTURES

DISCUSSION

Within experimental errors all the systems, formamide-water, N-methylformamide-water and dimethylformamide-water, obey Raoult's law with the latter system showing very slight positive deviation at low concentrations of water. Ivanova and Geller[91] reported that the system dimethylformamide-water obeyed Raoult's law at temperatures 414.7-365.6 K they worked on. These results on the water-amides systems can be contrasted with the water-alcohols systems where the considerable positive deviations from Raoult's law increase with the increasing size of the alcohols [$CH_3OH < C_2H_5OH < C_3H_7OH < C_4H_9OH$][92].

Since the amides and water molecules are not of the same size the interpretations of the results above can be attempted in terms of hydrogen bonding between the amide and water molecules. Johansson and Kollman[93] found out that(1) the amide-amide (N-H......O=C) bond energy is considerably stronger than either amide-water bonds (O-H......O=C and N-H......O) and(2) that the amide N-H group appeared to be a 3.0 kcal mol^{-1} better proton donor than H_2O and the formamide C=O a 2.0 kcal mol^{-1} better proton acceptor than water in formamide H bonding. From the first point it would seem that since the N-H......O=C bond is stronger than either amide-water bonds there would be little tendency for the amide hydrogen (N-H) to attach itself to the water oxygen atom. The second point shows that there would be greater interactions between the formamide molecules than between formamide and water molecules. This means that the overall structure of the two liquids might be affected to a very small extent in the presence of each other. This might explain why the systems conformed to Raoult's law. Further evidence for this comes from a comparison of formamide-formamide, formamide-water and water-water H bond energies or energies of dimerization. The energies in kcal mol^{-1} are 9.4^{93} $(9)^{94}$ for formamide-formamide (N-H......O=C); 6.4^{93} for formamide-water ($H_2NC(H) = O$ HOH); 7.4^{93} formamide-water (CHO-HNH OH_2) and 6.53^{93} $(6.65)^{95}$ for water-water $(H_2O)_2$. The energy results for $H_2NC(H) = O$......HOH and $(H_2O)_2$ are almost equal and point to a similarity of the water-amide and water-water interactions. Thus from the partial vapour pressures of water versus mole fractions of water alone the amides in the binary mixtures seem neither to increase nor to decrease the overall stability of the water.

The enthalpies of vaporization (ΔHv) of water in the amide-water systems versus mole fractions of water all show a minimum in the curves. The minima troughs decrease in the order, formamide-water, N-methylformamide-water and dimethylformamide-water. It must be emphasized that in all the systems the minima are only very small. These results can be compared with the enthalpies of activation of viscous flow of the system formamide-water observed by Vincent[96] (Table 28 and Figure 31) which also show a minimum value versus mole fractions of water. In view of the fact that the systems soundly confirmed to Raoult's law rigorous analysis of the ΔHv results should be deferred until the enthalpies and entropies of mixing of the amide-water systems are known.

TABLE 28

Mole fractions of water	Enthalpies of activation of viscous flow (ΔH v.f.) in kJ mol^{-1}
0.000	18.330
0.138	17.020
0.202	16.610
0.354	15.650
0.500	15.110
0.600	14.830
0.725	14.720
0.801	14.760
0.900	15.250
0.951	15.650
1.000	16.400

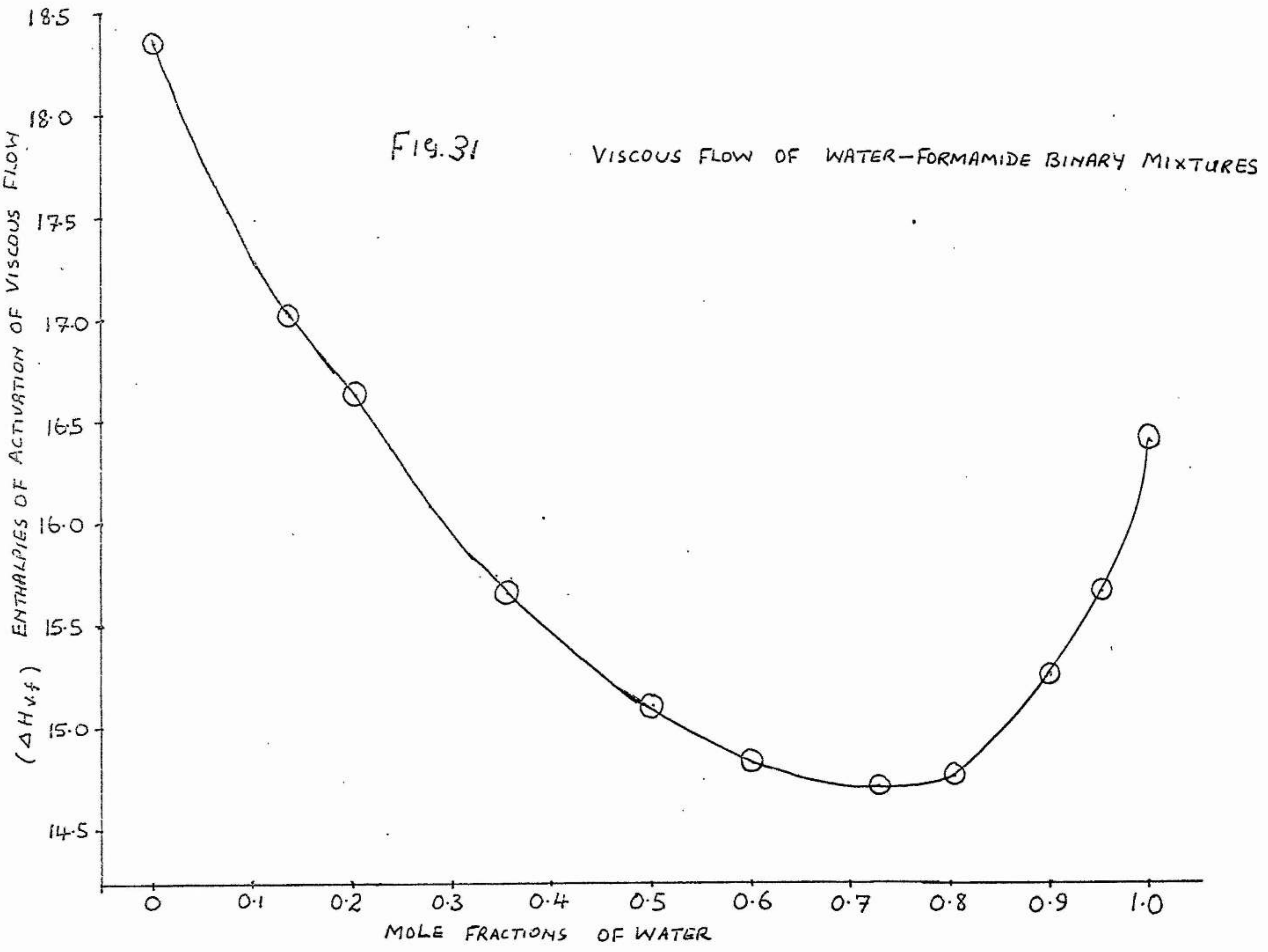


Fig. 31 VISCOUS FLOW OF WATER—FORMAMIDE BINARY MIXTURES

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