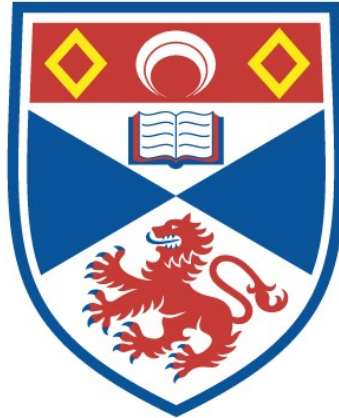


VISCOSITY STUDIES OF SOLUTION INTERACTIONS  
IN FORMAMIDE

Joseph McCartney McDowall

A Thesis Submitted for the Degree of PhD  
at the  
University of St Andrews



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A Thesis

presented for the degree of

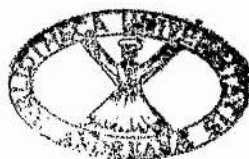
DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St. Andrews

by

Joseph McCartney McDowall



December 1973

United College of St. Salvator  
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DECLARATION

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

This 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 since 1st October 1970.

Joseph M. McDowall

(iii)

CERTIFICATE

I hereby certify that Joseph M. McDowall 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

ACKNOWLEDGEMENTS

I would like to thank Dr. C.A. Vincent for his unceasing enthusiasm and encouragement.

My thanks are also due to Mr. N.F. Jackson of The Plessey Company Limited, for the many useful discussions which we have had; and also to Mr. E. Hollands for looking after me during the time I spent working with the Company at Bathgate. I am also indebted to Professor D.S. Campbell of Loughborough University.

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SUMMARY

The effect of some simple salts on the viscosity of formamide has been studied at a number of temperatures and interpreted in terms of ion-solvent interactions using the equation suggested by Jones and Dole. Further evidence to support the various conclusions drawn has been provided by application of Eyring's reaction rate theory to the viscosity processes in solution.

The viscosities of binary mixtures of formamide and water, methanol or dimethylformamide have been investigated over the whole composition range and the ability of three semi-empirical models to describe these systems has been discussed. A new three parameter equation has been proposed.

Finally the effect of sodium chloride on the binary mixture formamide/water has been considered. It has been shown that, in general, for viscosity measurements to be a useful tool for investigating ion-solvent and solvent-solvent interactions, it is important that the measurements be made at more than one temperature.

CHAPTER ONE

## INTRODUCTION

1.1 A quantitative understanding of the interactions of species in solution is one of the problems still facing modern science. As early as the sixteenth century, at the time of Galileo, there was a common axion "ignorato motu, ignoratur natura". The experimental and theoretical study of transport phenomena in liquids has received a great deal of attention since the sixteenth century. Today the theoretical approach is dominated by physicists and mathematicians<sup>1-11</sup> whose investigations are limited to simple systems.

Chemists, on the other hand, when dealing with solutions, are normally concerned with systems which even in their simplest form, e.g. a monovalent salt dissolved in a pure solvent, may be very complex. Rigorous mathematical models for such systems have not yet proved possible and physical chemists dealing with electrolytic solutions are left with semi-empirical models such as those of Frank and Evans<sup>12</sup>, Frank and Wen<sup>13</sup>, Gurney<sup>14</sup> and Samoilov<sup>15</sup>. These models have been constructed from data obtained from aqueous systems. The investigation of ion-ion, ion-solvent, and solvent-solvent interactions in other solvents provides further experimental data which may be used to extend the validity of such models and lead to a better understanding of the micro environment of the individual ions in solution.

1.2 The study of the effect of solution composition and change in temperature on viscosity provides a useful means of investigating solution interactions.

The theory of liquid viscosity was developed from the concepts of hydrodynamics, the study of fluids in motion. The early development of this subject took place in the eighteenth

century and workers of this period (Bernoulli, d'Alembert, Euler and Legrance) were mainly concerned with so called "perfect fluids", which were considered to be characterised by the fact that they had no tangential component of stress. This led to the d'Alembert paradox which suggested that a solid sphere immersed in a stream would not be carried along by it. Previously in the seventeenth century, Newton had formulated a hypothesis regarding the magnitude of the force required to overcome viscous resistance. Newton's fundamental hypothesis was that if two laminae having an area of contact A, move with constant velocities,  $v_1$  and  $v_2$ , the force F required to maintain the constant difference of velocity is

$$F = \eta A \frac{(v_1 - v_2)}{(S_1 - S_2)} \quad (1.1)$$

Here  $S_1$  and  $S_2$  are distances measured in the direction perpendicular to the laminae and  $\eta$  is a constant. Since the velocity in the liquid changes continuously this can be rewritten

$$F = \eta A \frac{dv}{dS} \quad (1.2)$$

where  $\eta$  is called the coefficient of viscosity and is a characteristic constant for each liquid. Liquids for which  $\eta$  is independent of the velocity of the shearing motion (i.e. the rate of shear) are called Newtonian liquids. The main development of the theory of viscous fluids was made in the nineteenth century chiefly by Navier and Stokes. Navier<sup>16</sup> attempted to find a solution to the problem of motion in viscous liquids corresponding to the hydrodynamic equations already mentioned for "perfect fluids". Stokes<sup>17,18</sup> deduced the same equations as Navier by a different method.

For an incompressible fluid of viscosity  $\eta$  and density  $\rho$ , the motion of the fluid at the point P (x,y,z) was considered to be characterised by a velocity vector q having components u, v, w, in the direction of x, y, and z respectively. At the point P, the fluid was considered to be subject to an external force F per unit

mass, with components, X, Y, and Z. It was assumed that  $\eta$  was constant, i.e. the viscosity was independent of the direction and rate of shear as is the case for Newtonian liquids. The pressure at any point in the liquid is p.

Incompressible liquids satisfy the equation

$$\text{div } q \equiv \nabla \cdot q \equiv \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad (1.3)$$

From this relationship equations for the flow of an incompressible liquid at sufficiently low velocities were deduced to be

$$\rho X = \frac{\partial p}{\partial x} - \eta \nabla^2 u \quad (1.4)$$

$$\rho Y = \frac{\partial p}{\partial y} - \eta \nabla^2 v \quad (1.5)$$

$$\rho Z = \frac{\partial p}{\partial z} - \eta \nabla^2 w \quad (1.6)$$

and in the absence of the external force

$$\frac{\partial p}{\partial x} = \eta \nabla^2 u \quad (1.7)$$

$$\frac{\partial p}{\partial y} = \eta \nabla^2 v \quad (1.8)$$

$$\frac{\partial p}{\partial z} = \eta \nabla^2 w \quad (1.9)$$

The usual boundary condition employed to allow solutions to the above equations was that at any solid surface there would be no "slip", i.e. that the velocity of the liquid would vanish at a solid surface. In all cases where this has been experimentally checked it has been found to be correct.

The solution of these equations of importance in this study is that due to Hagenbach<sup>19</sup> (Chapter 2). For laminar flow of an incompressible liquid of viscosity  $\eta$  through a capillary tube of length  $l$ , and radius R where the pressure difference across the length of the tube is  $p_0 - p_1$ , the volume V, flowing through the tube in unit time t, is given by

$$\frac{V}{t} = \frac{\pi (p_0 - p_1) R^4}{8\eta l} \quad (1.10)$$

1.3           The viscosity of a liquid can be considered to be due to the interactions of the various solution species. In 1929 Jones and Dole<sup>20</sup> reported an empirical relationship between the concentration of solute and the viscosity of aqueous electrolytic solutions. From this relationship it was shown<sup>21</sup> that the first term corresponded to the "stiffening" of the solution due to ion-ion interactions. The second term was considered to be a measure of the solute-solvent interactions (see Chapter 3).

Modern theories of solution<sup>22</sup> stress the importance of evaluating not only the effects of the ions on the structure of the particular solvent but also the specific ion-solvent interactions involved. It is no longer acceptable to consider that a solvated ion is one which moves through the solution with a certain number of solvent molecules firmly bound to it and that an unsolvated ion is "bare" of solvent molecules. Instead we must now visualise a dynamic situation in which solvent molecules spend a certain average period of time as nearest neighbours to the solute particles.

The viscosities or fluidities of non-electrolyte binary mixtures are as a rule not linear with composition and can be theoretically predicted only in homologous non-associating mixtures where the components have about equal molar volumes<sup>23</sup>. It is therefore not to be expected that a clear molecular interaction mechanism could be inferred from the hydrodynamic properties as measured by viscosity. It is frequently possible however to discuss solution viscosities qualitatively in terms of solvation or of the formation of associated molecular species<sup>24-30</sup>.

1.4           The problem therefore is to obtain information which can be interpreted in terms of the interactions of the solvent molecules with each other and the effect of ions on these

interactions. The greatest advances in the theory of solvation have taken place for aqueous solutions. The models of Frank and Evans<sup>12</sup>, and Samoilov<sup>15</sup> were based on their understanding of the structure of water. The "structure breaking" or "negative hydration" effects mentioned by these authors have been reported in water, and a few other highly associated solvents such as ethylene glycol<sup>31</sup>, glycerol<sup>32</sup>, sulphuric acid<sup>33</sup> and the effect has been studied in mixed solvents such as water-alcohol mixtures<sup>34-36</sup>.

The electrochemistry of the simple amides has been reviewed comprehensively by Vincent<sup>37</sup>, where it was suggested that in order to understand the fundamentals of electrochemical transport processes it would be necessary to appreciate the nature of the ion-solvent interactions involved.

The simplest of these amides, formamide, is considered to be, like water, an associated solvent. It is a reasonably good solvent<sup>38</sup> and has a dielectric constant (approx. 109)<sup>39</sup> which is greater than that of water at room temperature. In this study the effect of simple electrolytes on the viscosity of formamide, the viscosity of binary mixtures containing formamide and methanol, dimethylformamide and water and the effect of a single electrolyte (sodium chloride) on the viscosity of the binary mixture formamide/water over the complete concentration range has been investigated.



**CHAPTER TWO**

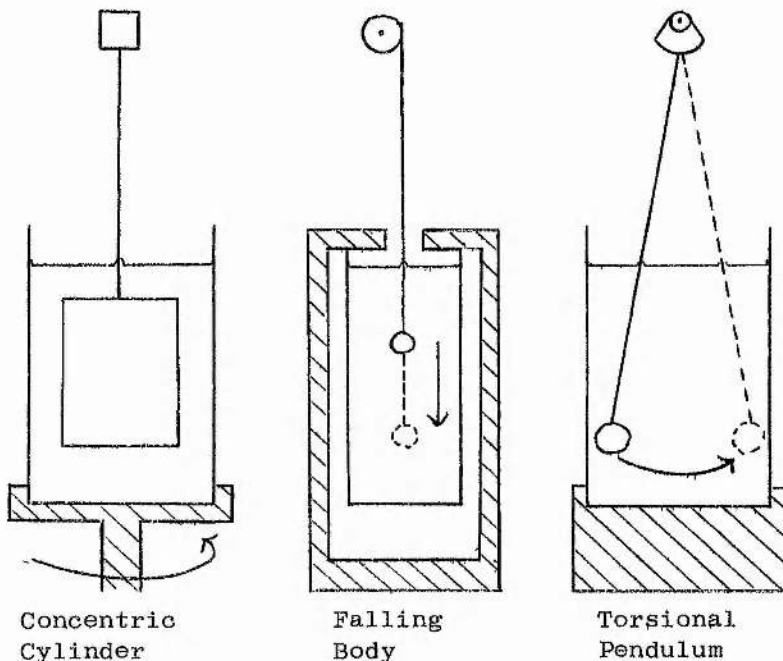
EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

The study of the flow of liquids through capillary tubes is still the most popular method employed by physical chemists to measure viscosity. Although this method is in principle that adopted by Poiseuille<sup>40</sup> in his classical researches of the mid-nineteenth century, modern technique has advanced a great deal with improved experimental design and the use of electronic data retrieval and analysis.

As well as capillary flow methods, other methods of measuring viscosity are available, such as the concentric cylinder system, the falling body system, and the torsional pendulum, see fig (2.1) but the first two of these have been shown by MacKenzie<sup>41</sup> to be accurate only to viscosities over  $0.001 \text{ J m}^{-3}\text{s}$ .

Fig. (2.1)



The torsional pendulum, or oscillating body method as it is generally called, is an accurate method of determining the absolute viscosities of molten salts where high temperatures and the use of furnaces make capillary flow techniques unsuitable. The maintenance of long zone constant temperatures and the change in diameter of capillaries due to slight etching and recrystallisation together with the difficulty of detecting capillary flow are further drawbacks associated with these measurements.

The problem of the oscillating sphere was studied by Verschaffelt<sup>42</sup> who set up a differential equation for the motion of the rigid spherical shells and derived an equation which gave the viscosity as a function of measurable quantities and although an exact mathematical solution is not possible, the problem lends itself to numerical solution by computer.

The viscometers used in the present work were of the capillary type because of the accuracy attainable and the ease with which they lend themselves to automation. Ease of cleaning and refilling was also very important because of the number of solutions required to be examined. Capillary viscometers are easily mounted in a water bath so that accurate temperature control ( $\pm 0.01$  K) is possible and equilibration to a new temperature is reasonably fast.

## 2.2 POISEUILLE'S LAW

Measurements with capillary viscometers depend for their interpretation on a relationship between the rate of flow of liquids under an applied pressure and the dimensions of the capillary tube through which the liquids are forced.

Poiseuille, who was interested in the flow of blood through the capillaries of the body, approached the problem by investigating

the flow of water through small bore glass capillaries and thus in contrast to his predecessors he had to deal with the problem of laminar flow. He proved that capillary flow in such tubes is a fundamentally simpler process than in the wide tubes which had previously been employed.

A long series of measurements was carried out, which showed that

(i) The quantity of liquid discharged in unit time is proportional to the pressure, provided the length of the tube exceeds a certain minimum, which increases with the radius.

(ii) The quantity of liquid discharged in unit time is inversely proportional to the length of the tube.

(iii) The quantity of liquid discharged in unit time is directly proportional to the fourth power of the radius.

This led in 1846 to the empirical expression:

$$Q = K \frac{PR^4}{\lambda} \quad (2.1)$$

where  $Q$  is the flux,  $P$  the applied pressure,  $R$  the radius of the tube, and  $\lambda$  the length of the tube and  $K$  is the constant of proportionality.

### 2.3 THEORETICAL DERIVATION OF POISEUILLE'S LAW

An important advantage of capillary viscometers is that the mathematical theory can be developed with perfect strictness and without approximations. Hagenbach<sup>19</sup> (1860) appears to have been the first to give the derivation in the present form.

Consider a portion  $AB$  of a horizontal cylindrical tube having a circular cross section of radius  $R$  fig. (2.2). The distance  $AB = \lambda$ , and a difference of pressure =  $\Delta P$  is maintained

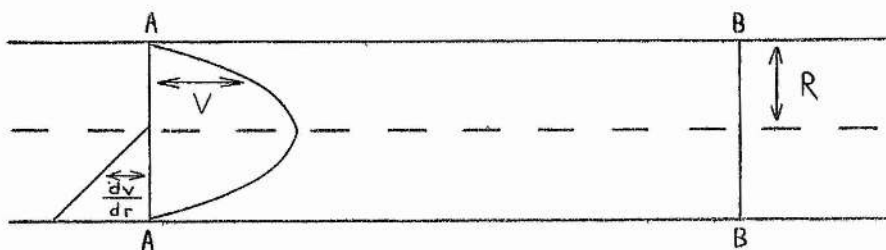


Fig. 2.2

between A and B, which causes the fluid to flow through the tube from left to right. The total effective pressure differential  $\Delta P$  is used up in doing various forms of work.

(i) Near the entrance to the capillary, the particles of the fluid undergo a rapid acceleration; the associated absorption of kinetic energy causes a fall in pressure amounting to  $p_K$ .

(ii) Within the capillary, there may be a finite movement of the fluid at the walls of the tube, due to slipping. Unless the external friction is zero or infinite, work will be done and there will be a fall of pressure  $p_S$ .

(iii) Unless the internal friction is zero, the layers of fluid nearer the walls of the tube will move more slowly than the layers nearer the axis of the tube, and an absorption of energy resulting in a pressure drop due to this internal friction will result.

Let this pressure drop be  $p_V$ .

(iv) If the path of the particles through the capillary is not perfectly linear, the additional distance travelled in the eddies will give rise to a further drop in the pressure amounting to  $p_e$ . This "turbulent flow" is certain to occur when the velocity of flow becomes sufficiently high.

(v) Even before the velocity becomes turbulent, it is possible that the stream lines at the extremities of the tube may be somewhat

distorted, in which case there must be a drop in pressure  $p_d$ .

(vi) Heat is produced due to the above energy dissipation processes as the fluid passes through the tube and therefore the temperature may be different at different points of the liquid, and since the temperature greatly affects the viscosity of most substances, this may affect the amount of work done in the passage through the tube. If the fluid is incompressible it will have the same mean velocity through each cross section of the capillary and the pressure must fall in a linear manner at least so long as the flow is linear. If, on the other hand, the substance is compressible, the velocity must increase as the fluid passes through the tube, because of the expansion which results from the decrease in pressure. With the expansion there is a decrease in temperature. Let the resultant effect of these changes in temperature upon the effective pressure be  $p_T$ . This can be either negative or positive.

The sum of these possible losses of effective pressure is then;

$$\Delta P = p_K + p_S + p_v + p_e + p_d + p_T \quad (2.2)$$

Consider in fig. (2.2) that the fluid is incompressible. This is a good approximation for most liquids where  $P = p_v$ . Further, assume that every particle of fluid moves parallel to the axis of the cylinder with a constant velocity  $v$ . For reasons of symmetry this velocity will be the same for all points lying on the same circle centred on the axis of the tube so that the liquid may be considered to be composed of cylindrical laminae moving with velocities which are functions of their radii.

The force exerted by the pressure  $P$  on a cylinder of radius  $r$  is

$$F_P = \pi r^2 P \quad (2.3)$$

while the resistance round the surface of the cylinder, caused by the viscosity of the liquid, will, according to the assumptions

above, be given by the product of area x viscosity coefficient x velocity gradient, i.e.

$$F_V = 2\pi r \lambda \eta \frac{dv}{dr} \quad (2.4)$$

If the velocity of the particles is to remain constant, the forces acting on the cylinder must be equal and opposite, and therefore

$$rP = -2\lambda\eta \frac{dv}{dr} \quad (2.5)$$

$$\therefore \frac{dv}{dr} = -\frac{rP}{2\lambda\eta} \quad (2.6)$$

$$\therefore \text{On integration} \quad v = -\frac{r^2 P}{4\lambda\eta} + C \quad (2.7)$$

If it is now assumed that no slipping occurs at the wall of the cylinder, i.e. when  $v = 0$ ,  $r = R$ , the constant of integration can be determined

$$C = \frac{R^2 P}{4\lambda\eta} \quad (2.8)$$

so that the velocity is given by

$$v = \frac{P}{4\lambda\eta} (R^2 - r^2) \quad (2.9)$$

Equation (2.9) shows that the velocity profile is parabolic, the velocity being zero at the walls of the tube and a maximum in the centre. Since  $v$  is the distance travelled in unit time, the particles of liquid which were on the plane AA at zero time will be on the surface of the parabola, after unit time; in other words the volume of this paraboloid is the volume of liquid  $Q$  which passes in unit time. The volume of this solid of revolution is

$$Q = 2\pi \int_0^R v r dr \quad (2.10)$$

$$\text{From (2.9)} \quad Q = \frac{\pi P}{2\lambda\eta} \int_0^R (R^2 - r^2) r dr \quad (2.11)$$

$$= \frac{\pi P R^4}{8\lambda\eta} \quad (2.12)$$

This formula corresponds to the Law of Poiseuille, equation (2.1).

If  $Q$  is the total volume of efflux in the time  $t$ , the formula

becomes:

$$Q = \frac{\pi R^4 t}{8\eta} \quad (2.13)$$

#### 2.4 CORRECTION FACTORS

It is important to restate here the conditions which must be adhered to if the above equation, (2.13), is to hold.

- (i) The flow everywhere must be parallel to the axis of the tube.
- (ii) The flow must be steady, initial disturbances due to accelerations from rest having been damped out.
- (iii) There must be no slip at the walls of the tube.
- (iv) The fluid must be incompressible.
- (v) The fluid must flow when subjected to the smallest shearing force, the viscous resistance being proportional to the velocity gradient.

These requirements influence the design of capillary viscometers and departures from them necessitate the introduction of correction factors.

Both Hagen<sup>43</sup> and Poiseuille<sup>40</sup> reported deviations from the linear relationship between discharge and pressure when the pressure was raised beyond a certain limit or the length of the tube reduced below a certain limit. Condition (i), the condition of laminar flow, was not being adhered to in these cases. It was soon shown by Reynolds<sup>44</sup> that with a given tube and liquid, there existed a critical velocity at which the flow changed abruptly from the laminar type, in which each particle moves with constant velocity parallel to the axis of the tube, to the turbulent type, in which the particles move in irregular paths. All things being equal, the



critical velocity is proportional, not to the viscosity, but to the viscosity divided by the density: i.e. to the kinematic viscosity. Reynolds further showed that the conditions of flow for any tube and liquid could be characterised by a non-dimensional quantity now known as the "Reynolds Number". The variables affecting the flow in a cylindrical tube can be combined to give the following non-dimensional expression:

$$R_N = \frac{vD\rho}{\eta} \quad (2.14)$$

where:

$R_N$  = Reynolds Number

$v/\text{ms}^{-1}$  = mean velocity of the liquid

$D/\text{m}$  = The diameter of the tube

$\rho/\text{Kgm}^{-3}$  = the density of the liquid

$\eta/\text{Jm}^{-3}\text{s}$  = viscosity of the liquid

Flow behaviour in different tubes with different liquids will be the same when the Reynolds Numbers are the same. More particularly there will be a change from laminar to turbulent flow when  $R_N$  reaches a certain value, which experiment has shown to be generally about 1400 to 2000 for capillaries.

#### THE KINETIC ENERGY CORRECTION

Viscometers for which condition (ii) is fulfilled are characterised by very long efflux times and usually inconveniently small capillary bores. Long efflux times (in some of Poiseuille's work one run lasting several hours) are obviously tedious and small bores inevitably result in difficulties due to dust particles lodging in the capillary and altering the characteristics of the viscometer. For most capillary viscometers therefore account must be taken of the work done in accelerating the liquid from rest, i.e. imparting

kinetic energy. Hagenbach (1860) was the first to attempt to make this correction. However in 1891 Wilberforce<sup>45</sup> showed that Hagenbach had made an error and that he should have arrived at the same result as that obtained by Couette<sup>46</sup> (1890) which also agreed with a result obtained independently by Neumann and Finkener<sup>47</sup>. The correction was deduced as follows:

From equation (2.10) the mass of fluid passing any cross section of the cylindrical tube per unit of time is given by

$$\int_0^R 2\pi v r dt \rho \quad (2.15)$$

The kinetic energy of this fluid is therefore

$$\int_0^R 2\pi v r dt \rho \frac{v^2}{2} \quad (2.16)$$

From equation (2.9)

$$v = \frac{P}{4\eta} (R^2 - r^2)$$

Substituting for v in (2.16)

$$\text{KINETIC ENERGY} = \frac{\pi P^3}{64\eta^3} \int_0^R r dt (R^2 - r^2)^3 \quad (2.17)$$

From Poiseuille's formula (2.13) the total efflux volume in time t, is given by

$$Q = \frac{\pi P R^4 t}{8\eta} \quad (2.18)$$

Therefore the mean velocity of the fluid (U) is given by

$$U = \frac{Q}{\pi R^2 t} = \frac{P R^2}{8\eta} \quad (2.19)$$

Substituting for U in equation (2.17) we get after integration

$$\pi P R^2 U^3 \quad (2.20)$$

This is the kinetic energy of the fluid passing any cross section of the tube in unit time. The volume of fluid passing any cross section in unit time is, from equation (2.19)

$$\pi R^2 U$$

and the energy supplied in producing this flow is

$$\pi R^2 U P \quad (2.21)$$

therefore the energy converted into heat within the tube is

$$\pi R^2 U (P - \rho U^2) \quad (2.22)$$

From equations (2.2) and (2.19)

$$p_K = \rho U^2 = \frac{\rho Q^2}{\pi^2 R^4 t^2} \quad (2.23)$$

Allowing for this in Poiseuille's equation (2.13) we have

$$\eta = \frac{\pi P R^4 t}{8 Q \lambda} - \frac{m Q \rho}{8 \pi \lambda t} \quad (2.24)$$

where  $m$  is a constant, in this case equal to unity. Boussinesq<sup>48</sup> proposed a value of  $m = 1.2$  and this has been used in a number of investigations.

A second correction factor arises from condition (i). Couette<sup>46</sup> suggested that the non-laminar flow at the ends of the capillary had to be considered. This takes the form of a nominal lengthening of the capillary whereby equation (2.24) becomes

$$\eta = \frac{\pi P R^4 t}{8 Q (\lambda + \lambda)} - \frac{m \rho Q}{8 \pi (\lambda + \lambda) t} \quad (2.25)$$

The value of  $\lambda$  cannot be deduced theoretically, but must be found by experiment and is usually of the order of a few diameters.

For viscosity measurements in kinematic instruments the pressure term  $P$  is replaced by the term  $h_m g$  called the hydrostatic pressure head

$$\eta = \frac{\pi R^4 h_m g t}{8 Q (\lambda + \lambda)} - \frac{m \rho Q}{8 \pi (\lambda + \lambda) t} \quad (2.26)$$

where  $h_m$  is the mean height of the liquid column and  $g$  is the acceleration due to gravity. Measurements with kinematic viscometers therefore are usually associated with accurate determinations of density.

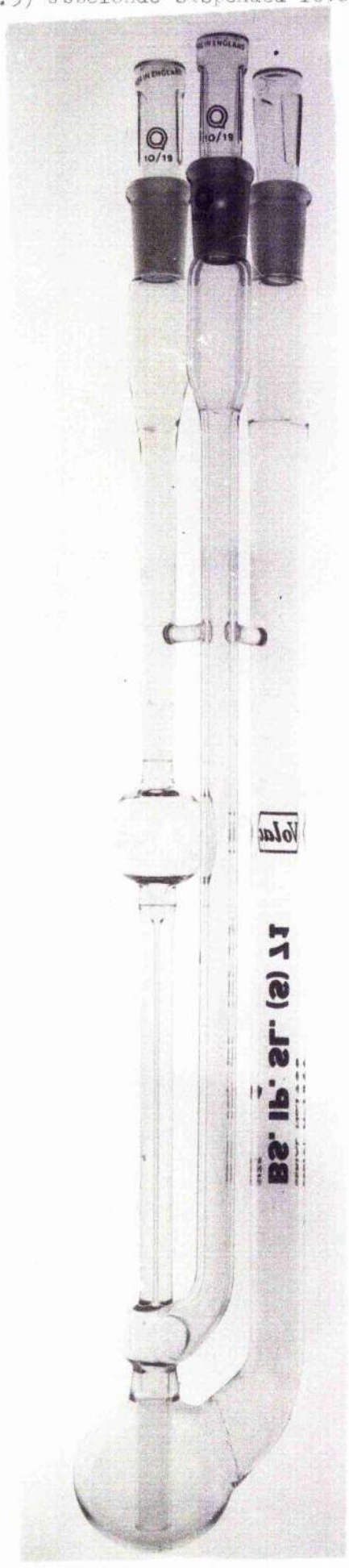
## 2.5 VISCOMETER DESIGN

For many of the original kinematic viscometers, which were often basically glass U-tubes, some difficulties arose in the determination of the exact mean hydrostatic pressure head ( $h_{m,gp}$ ). As flow progresses, the pressure changes continuously due to the drop in the height of the liquid column on one side and the increase in the column on the other. The Ostwald viscometer used for the determination of relative viscosity simplifies matters by using a fixed volume of liquid (delivered by means of a pipette) so that the mean height of the liquid column,  $h_m$ , is constant for each determination and can therefore be incorporated in a general viscometer constant.

Surface tension effects arising from the adhesion of liquid to the walls of the bulbs immediately above the capillary and in the exit reservoir can also alter the hydrostatic pressure head and create uncertainties in measurements, particularly when the surface tensions of the calibration liquid and the liquid under investigation are very different.

The Ubbelohde suspended level viscometer, as used in this investigation, is reputed to eliminate these effects by the provision of the 'suspended level' at the exit of the capillary. This 'suspended level', which is simply a bulb maintained at the same external pressure as that exerted on the liquid and of similar shape to the liquid reservoir, ensures that changes of the mean hydrostatic pressure head for different solutions are determined only by the density of the solution since the pressure is maintained constant. The total volume of liquid introduced into the viscometer does not need to be known accurately since that which falls to, or remains in, the lower reservoir contributes nothing to the mean hydrostatic pressure head. This is of particular advantage when measurements

Fig.(2.3) Ubbelohde suspended level viscometer



at more than one temperature are required since the actual volume under investigation is fixed by the marks on the upper reservoir and expansion of the liquid in the viscometer need not be taken into account. Surface tension effects were also minimised by the use of the Ubbelohde suspended level viscometers. At the curved surface of the bulb at the exit of the capillary a certain traction is developed which acts in the opposite direction to the surface tension of the liquid in the upper bulb of the viscometer.

It is important that the viscometer be mounted firmly in a level position to maintain a constant hydrostatic pressure head. For a change of angle  $A$  to  $A+dA$  in the alignment of the vertical capillary axis, the change in the liquid head is given by

$$1 - \cos(A + dA) / \cos A \quad 49$$

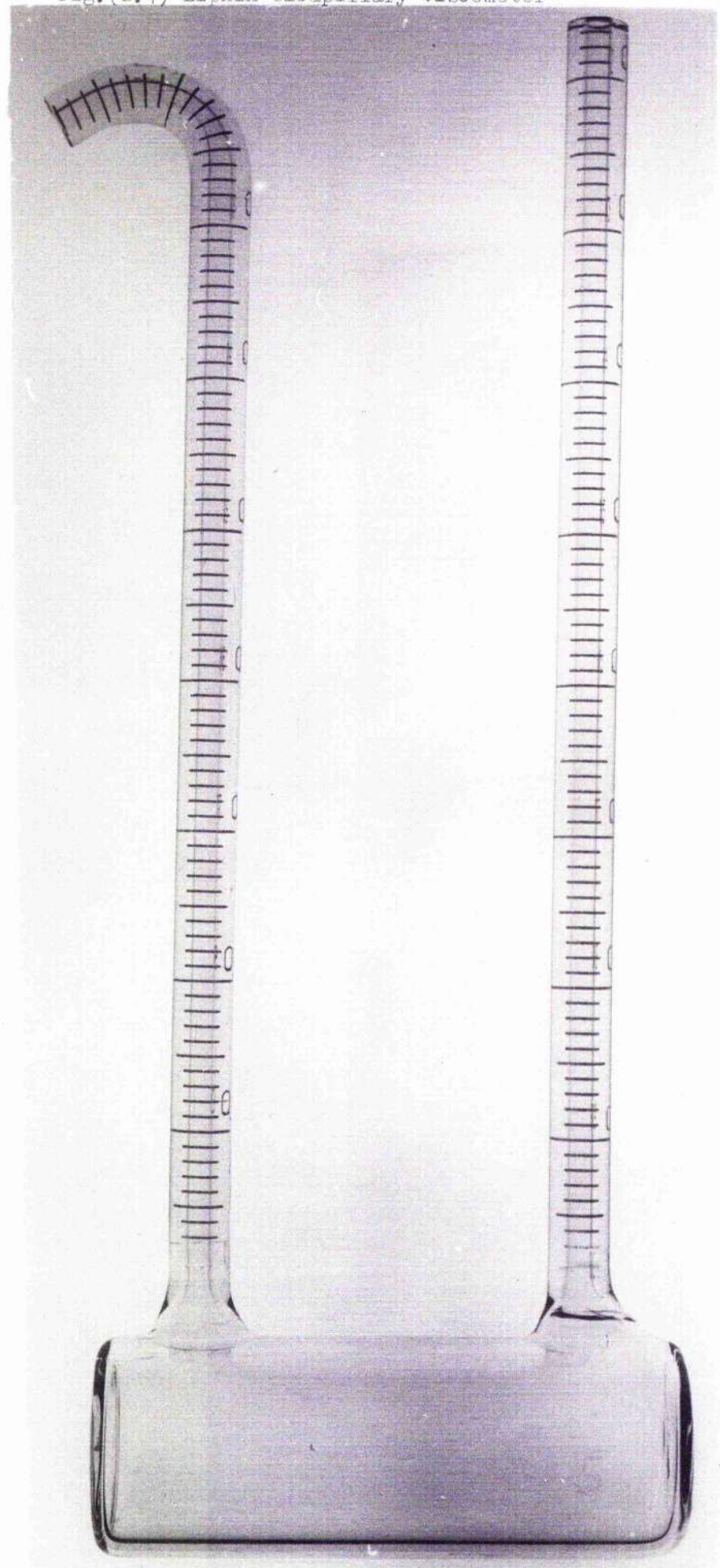
A deviation of 0.0436 radians will therefore produce an inaccuracy of 0.1% in the measured viscosity. Jones and Dole<sup>20</sup> noted that, despite their efforts to maintain a rigid reproduceable mounting for their viscometer, the efflux time changed by approximately 0.1%. The cause of this was attributed to the fact that their laboratory building was jacked up at one end to allow some repairs to be carried out on the foundations!

Accurate temperature control is necessary for accurate viscosity measurements. This is especially true for associated solvents which often have large temperature coefficients of viscosity.

## 2.6 APPARATUS

The viscometers used in the present work were Ubbelohde suspended level models conforming to British Standard BS.IP.SL(S)71 fig.(2.3).. The capillary sections were approximately 80 mm long and 1.00 mm in diameter and the quantity of solution required for each determination was about 10 to 15 ml. These were equipped

Fig.(2.4) Lipkin bicapillary <sup>pycnometer</sup> ~~viscosimeter~~



with ground glass sockets so that they could be stoppered firmly to the air.

In the early work size 4 of the viscometers were used. These had efflux times of about 30 s with water at 298K. Most of the later work was carried out with size 2 models which had efflux times of about 250 s, although a few measurements were made with a size 3 viscometer which had an efflux time of about 90 s.

The efflux times were measured by means of photo-cell lamp assemblies coupled to a Hewlett Packard auto-viscometer 5901 B in conjunction with a Hewlett Packard 5903 A Programmer. These instruments were designed to handle four separate viscometers at any one time.

The viscometers were mounted in a thermostatted water bath by means of special rigid metal clamps which could be individually levelled by means of a spirit level.

Density was measured by means of glass pycnometers of approximately 30 ml capacity, fig. (2.4).

## 2.7 THERMOSTAT BATH

This was a water filled bath supplied by Townson and Mercer Ltd, (model E.270 series III) of about 45 l capacity. The temperature was controlled by means of a thyristor and thermistor bridge arrangement and was considered to be accurate to at least  $\pm 0.01\text{K}$ , throughout the range. The water in the bath was circulated over a weir to which was attached a serpentine cooling coil through which water could be passed from an external cooling system. The cooling system consisted of a coiled copper tube encased in a subsidiary bath which could be packed with ice. The flow of the water through this cooling coil was controlled by means of a flow gauge (Rotameter series 1100).



Fig. (2.6) PHOTO-CELL DETECTOR AND LIGHT SOURCE ASSEMBLY

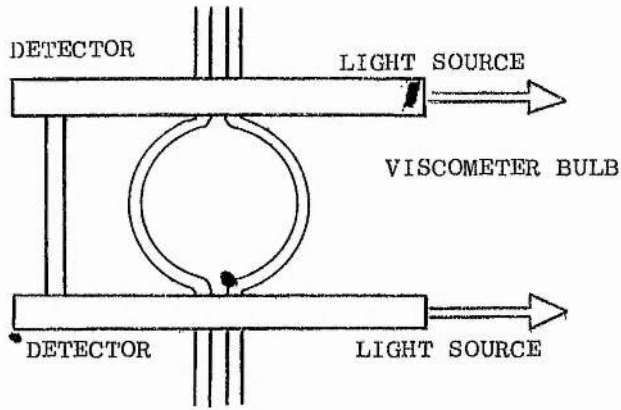
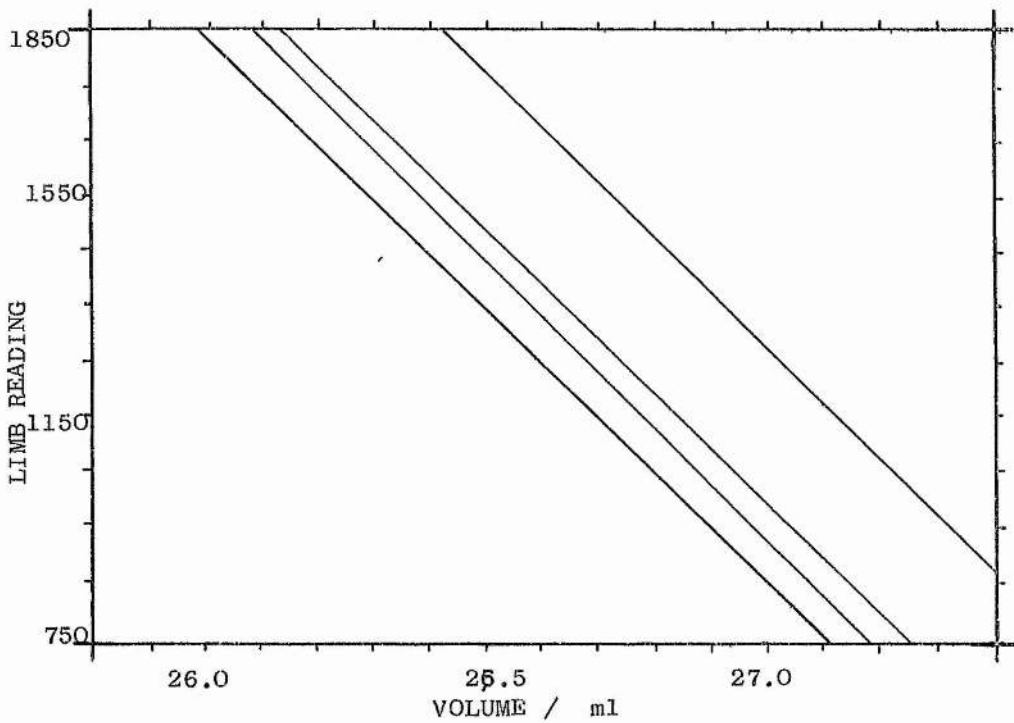


Fig. (2.5) CALIBRATION GRAPH FOR FOUR PYCNOMETERS



Two mercury filled, glass, precision thermometers were used to measure the temperature. These were total immersion thermometers supplied by Zeal Ltd. One covered the range 273.00 to 298.00K and the other from 298.00 to 323.00K with graduations every 0.05K and both were standardised at 273.00K at the ice point.

## 2.8 DENSITY MEASUREMENTS

The density of the solutions was measured with Lipkin type bicapillary pycnometers. These were constructed from 1.0 ml pipettes (Pyrex catalogue no. 3240/20) with graduations every 0.01 ml and had a capacity of about 30.00 ml fig.(2.4). The pycnometers were calibrated with distilled water at various temperatures at 2.5K intervals from 288.0K to 323.0K by filling with a known weight of water and noting the limb readings at the various temperatures. From the known density of water at these temperatures, a calibration graph of volume (abscissa) against limb readings (the sum of both the left and right limb readings) was constructed fig. (2.5). The densities of water used for this calibration are given in Appendix I. The left hand limb of each pycnometer was bent over to allow it to be filled by capillary action. The limb readings were observed by using a magnifying glass which permitted an accuracy of  $4.0 \cdot 10^{-6}$  l in  $30.0 \cdot 10^{-3}$  l. Since the weighing procedure was more accurate than this, the accuracy of the density measurements was therefore just better than 0.02%.

The procedure adopted for the measurement of densities was to wash the pycnometer out three times with distilled water and then three times with dry distilled acetone. The pycnometer was then flushed with a stream of dust free dry nitrogen and weighed. Care was taken when weighing the pycnometers to avoid contact with the skin so that errors due to the deposition of finger prints were eliminated.

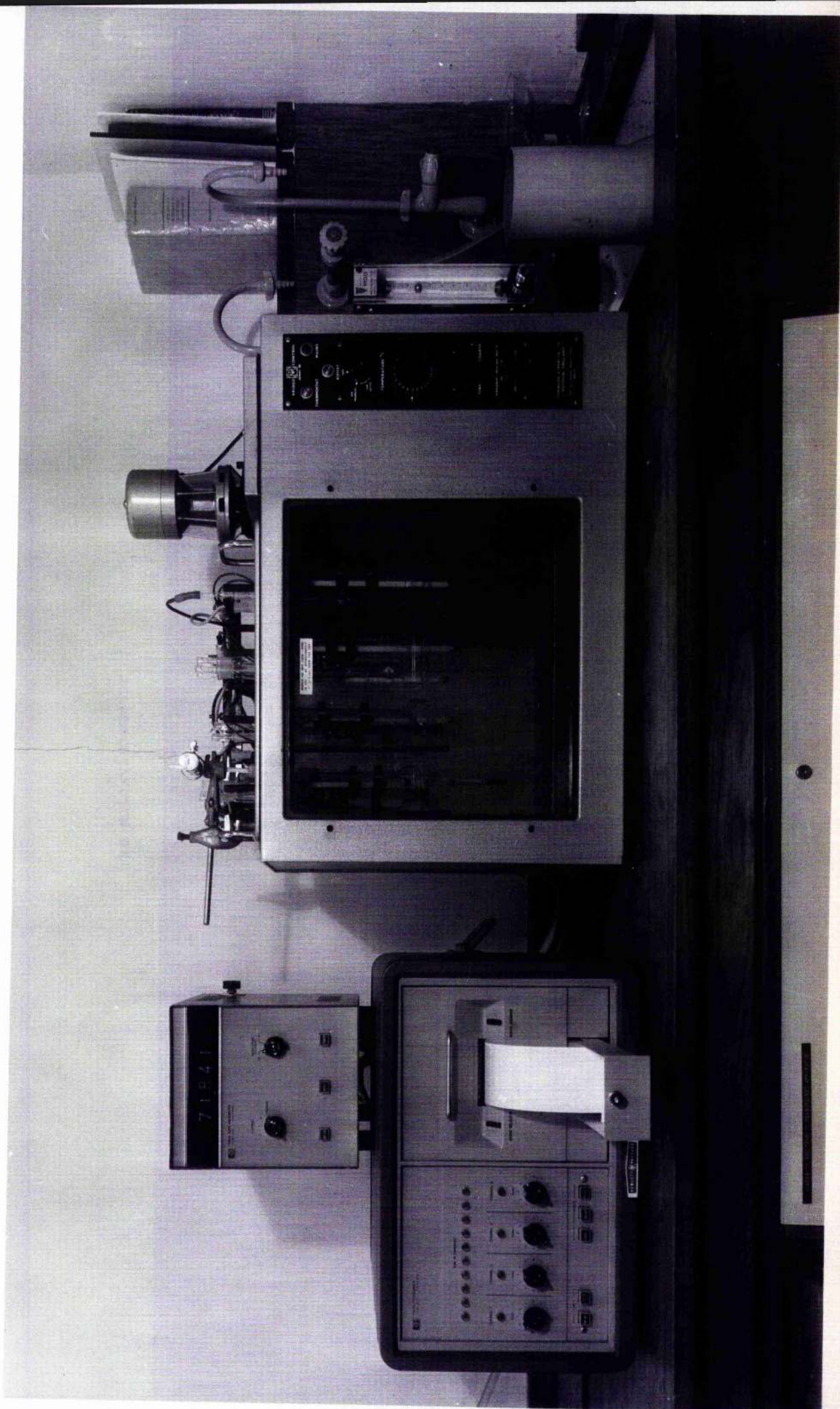
This was done mainly by handling with paper tissues. The pycnometer was then filled with the test solution by capillary action and any liquid which lodged in the top of the left hand limb was removed and the pycnometer reweighed. It was then clamped firmly in position in the water bath with the limbs vertical so that the latter could be observed through the glass front of the bath. Care was taken to ensure that the observer's eye was level with the level of the meniscus in the limbs since an error of about 0.05% could occur if the operator was too high or too low. In all cases where the temperature was changed the level of the meniscus was found to be steady after five minutes equilibration.

## 2.9 THE AUTO-VISCOMETER

The Hewlett Packard auto-viscometer model 5901 B measures efflux times in glass capillary viscometers and provides automatic influxing in preparation for the efflux measurement. Very accurate timing is realised, because the efflux time is measured with a transistorised electronic counter using a quartz-crystal oscillator as a time base reference. A neon display provides a digital read-out that can be held for observation until released by the operator.

Automatic influxing and timing eliminates errors between operators due to differences in technique and human fatigue. The accuracy of the timer is considered to be at least  $\pm 0.001$  s. The electronic counter measures efflux times automatically through the use of photocell detectors mounted above and below the upper bulb on the glass viscometer, fig. (2.6). The photocells actuate electronic circuits during liquid efflux. Time measurement for the meniscus to travel between the two detectors is displayed on the instrument register. The photocell detectors also control the limits of liquid transport during influx and the release of the

The auto-viscometer



liquid for the efflux measurement. Each detector consists of a miniature light-source and photocell moulded into a water-tight case. A constant pressure pneumatic pump provides the pressure required to force the liquid back into the upper bulb and is automatically shut off by a signal from the upper detector when the meniscus passes on the way up. When the meniscus again passes this detector on the way down, a signal is sent to start the timer which is only shut off when the liquid meniscus passes the lower detector. When incorporated with the programmer printer a permanent record of the efflux times is obtained.

The auto-viscometer is equipped with four sets of detectors and can therefore accommodate four viscometers.

#### 2.10 THE PROGRAMMER/PRINTER

The Hewlett Packard model 5903 A programmer/printer is a transistorised electromechanical device which programs the output of the 5901 B auto-viscometer and provides a printed record of the efflux time measurements. It can program the operation of the auto-viscometer so that the measurement at any channel is repeated, between 0 and 10 times with 25 second intervals between measurements. This sequence can be repeated indefinitely. The printer records the efflux time for each run to 0.001 or 0.01 seconds as selected on the auto-viscometer along with a coded identification of the programmed channel and the run number.

#### 2.11 VISCOSITY MEASUREMENTS

For accurate measurements of viscosity in capillary viscometers there are three practical areas of importance:

- (i) efflux time measurement;
- (ii) accurate temperature control;
- (iii) efficient cleaning of the viscometer and protection against

solid particles lodging in the capillary.

As has been mentioned, the human error in the measurement of efflux times with manually operated chronometers can now be eliminated by using electronic triggers. As early as 1933, Jones and Talley<sup>50</sup> used photo-electric cells to measure the efflux time automatically. One of the problems was found to be the difficulty of cleaning the viscometer without altering the position of the recording apparatus and thus changing the viscometer characteristics. An important advantage of the Hewlett Packard auto-viscometer is that the photo-cells are firmly attached to the viscometer, fig. (2.6), and need not be altered in order to remove the viscometer for cleaning. Eicher and Zwolinski<sup>51</sup> reported that they noted some heating effect leading to a change in efflux time due to the lamps in the detector unit and consequently they adapted their apparatus so that the lamps could be turned down when not in use. This effect was not observed in this investigation. Fig. (2.7) shows two sections of the print out from the programmer/printer. The section on the left shows the efflux times for three of the viscometers used in the earlier work, and the one on the right is for one of the later viscometers. The efflux times are for water at 298.15K. One covers a time span of about 15 minutes and the other about 150 minutes. It can be seen by inspection of these that there is no trend, and, apart from the spurious times caused by false triggering due to bubbles, the efflux times do not vary by more than 0.02%. After a viscometer had been cleaned and dried it was sometimes found that the first run would have a slightly longer efflux time than any of the subsequent runs. This was considered to be due to the initial wetting effect of the liquid on the walls of the capillary.

Bad triggering was usually associated with faulty mounting of the photocell lamp unit. The units were mounted firmly by their

Fig.(2.7)

Samples of print-out from the programmer-printer. Efflux times for water at 298.15K.

4	9	2	8	.	9	9	7
4	8	2	8	.	9	9	7
4	7	2	8	.	9	9	6
4	6	2	8	.	9	9	6
4	5	2	8	.	9	9	5
4	4	2	8	.	9	9	4
4	3	2	8	.	9	9	6
4	2	2	8	.	9	9	7
4	1	2	8	.	9	9	8
2		2	9	.	2	4	4
2	9	2	9	.	2	4	5
2	8	2	9	.	2	4	3
2	7	2	9	.	2	4	4
2	6	2	9	.	2	4	1
2	5	2	9	.	2	4	3
2	4	2	9	.	2	4	2
2	3	2	9	.	2	4	4
2	2	2	9	.	2	4	7
2	1	2	9	.	2	4	8
1		3	3	.	1	2	8
1	9	3	3	.	1	2	9
1	8	3	3	.	1	3	1
1	7	3	3	.	1	3	1
1	6	3	3	.	1	3	0
1	5	3	3	.	1	2	9
1	4	3	3	.	1	3	0
1	3	3	3	.	1	3	0
1	2	3	3	.	1	3	1

(a) (b) (c)

(I)

4	2	2	5	0	.	2	0
4	1	2	5	0	.	3	0
4		3	4	0	.	3	0
<u>4</u>	<u>9</u>	<u>2</u>	<u>5</u>	<u>0</u>	.	<u>3</u>	<u>0</u>
4	8	2	5	0	.	2	0
4	7	3	4	5	.	4	0
<u>4</u>	<u>5</u>	<u>3</u>	<u>1</u>	<u>3</u>	.	<u>5</u>	<u>0</u>
4	5	2	5	0	.	3	0
4	4	2	5	0	.	3	5
4	3	3	4	0	.	0	4
4	2	2	5	0	.	0	6
<u>4</u>	<u>1</u>	<u>3</u>	<u>2</u>	<u>6</u>	.	<u>0</u>	<u>5</u>
4		2	5	0	.	3	6
4	9	2	5	0	.	3	7
4	8	2	5	0	.	3	5
4	7	2	5	0	.	3	3
4	6	2	5	0	.	3	8
4	5	2	5	1	.	3	1
<u>4</u>	<u>4</u>	<u>2</u>	<u>3</u>	<u>7</u>	.	<u>0</u>	<u>3</u>
<u>4</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>0</u>	.	<u>3</u>	<u>1</u>
4	2	2	5	0	.	3	1
4	1	3	3	0	.	2	7
4		0	0	0	.	5	0
4	9	2	5	0	.	3	7
4	8	2	5	0	.	3	2
4	7	0	0	0	.	0	0
<u>4</u>	<u>7</u>	<u>0</u>	<u>0</u>	<u>0</u>	.	<u>3</u>	<u>5</u>
4	6	2	5	0	.	3	0
4	5	2	5	0	.	3	7
4	4	2	5	0	.	3	5
4	3	2	5	0	.	3	3
4	2	2	5	0	.	3	3
4	1	2	5	0	.	3	0
4		2	5	0	.	3	0

(II)

- (a) Viscometer number.
- (b) Run number.
- (c) Efflux time in seconds.

Those times which are underlined in (II) are considered to be spurious because they were caused by false triggering.

securing screws, fig. (2.6), and sealed against interference from air bubbles in the water bath with a silicon sealant (supplied by Dow Corning). As an extra protection the whole unit was then painted with polyurethane varnish. Another cause of bad triggering was due to insufficient filling of the viscometer. If the quantity of liquid was too small air bubbles were forced into the top bulb of the viscometer, and the timer was activated prematurely.

In practice, the minor fluctuations in efflux time for the same solution in the same viscometer were due to variations in the bath temperature. Because it was general practice to measure viscosities at more than one temperature each day, the water bath rarely had a chance to settle itself completely. It was therefore necessary for the operator to maintain a steady temperature by careful manipulation of the coarse and fine temperature adjusters, careful control of the cooling water of the thermostatted bath, and a vigilant watch on the thermometer (with the aid of a telescope). This was sometimes a very demanding procedure.

The viscometers were cleaned by flushing three times with distilled water and then three times with analytical grade acetone (about 15 ml each time) and finally with a stream of dust free nitrogen, all of which were firstly passed through a number 2 glass filter in order to trap any solid particles. This procedure was followed before each viscometer was filled with a new solution. At convenient intervals (of about three months) the viscometers were completely filled with freshly prepared and filtered chromic acid and left to soak for a few days after which they were washed out with, and then filled with, distilled water and soaked for about a week to ensure that no traces of chromic acid remained.

## 2.12 CALIBRATION OF THE VISCOMETERS

The early viscometers (size 4) were initially calibrated



with water at various temperatures, by measuring the efflux times at these temperatures. Assuming that the dimensions of the viscometer capillary do not change by much over the temperature range under investigation, it can be seen that equation (2.26) can be rewritten

$$\eta = \rho (At - B/t) \quad (2.27)$$

$$\text{or} \quad \eta/\rho t = A - B/t^2 \quad (2.28)$$

A plot of  $1/t^2$  against  $\eta/\rho t$  should therefore give a straight line of gradient  $1/t^2$  and intercept  $\eta/\rho t$ . The second term represents the kinetic energy correction (section 2.4). The known values for the viscosity and the density of water and the measured values for the efflux times were therefore substituted into equation (2.28) and the values of the constants found for each viscometer. The values which were used for the viscosity and the density of water are given in Appendix I. Equation (2.28) was solved by a computer program incorporating a least squares calculation (see Appendix II).

The kinetic energy correction term for these early viscometers amounted to more than 15% of the total value when the viscosities were of the same magnitude as water. For more viscous liquids, of viscosity similar to formamide, this term still amounted to more than 1%. A check on the viscosity of aqueous potassium iodide solutions, and 30% by weight aqueous sucrose solution showed that these calibration constants gave a value which was respectively 1% high and 0.1% too low.

It was therefore decided to use viscometers with smaller bore capillaries in order to increase the efflux time and reduce the kinetic energy correction. The calibration results for these new viscometers can be seen in Appendix III. Water at four temperatures, and 30% aqueous sucrose solutions each at three temperatures were used for this calibration. The calibration graphs are shown in

figs. (2.8 - 2.11). For water at 323.15K the kinetic energy correction amounted to just over 1% and for formamide at the same temperature less than 0.1%. As can be seen from the calibration graphs a slight curvature is noticeable. Table (2.1) reflects the effect of this on the viscosity calculations. Columns one and two give the calibration constants (a) for calibration with only water (see Appendix III) and (b) for calibration with water, and 30% aqueous sugar solution.

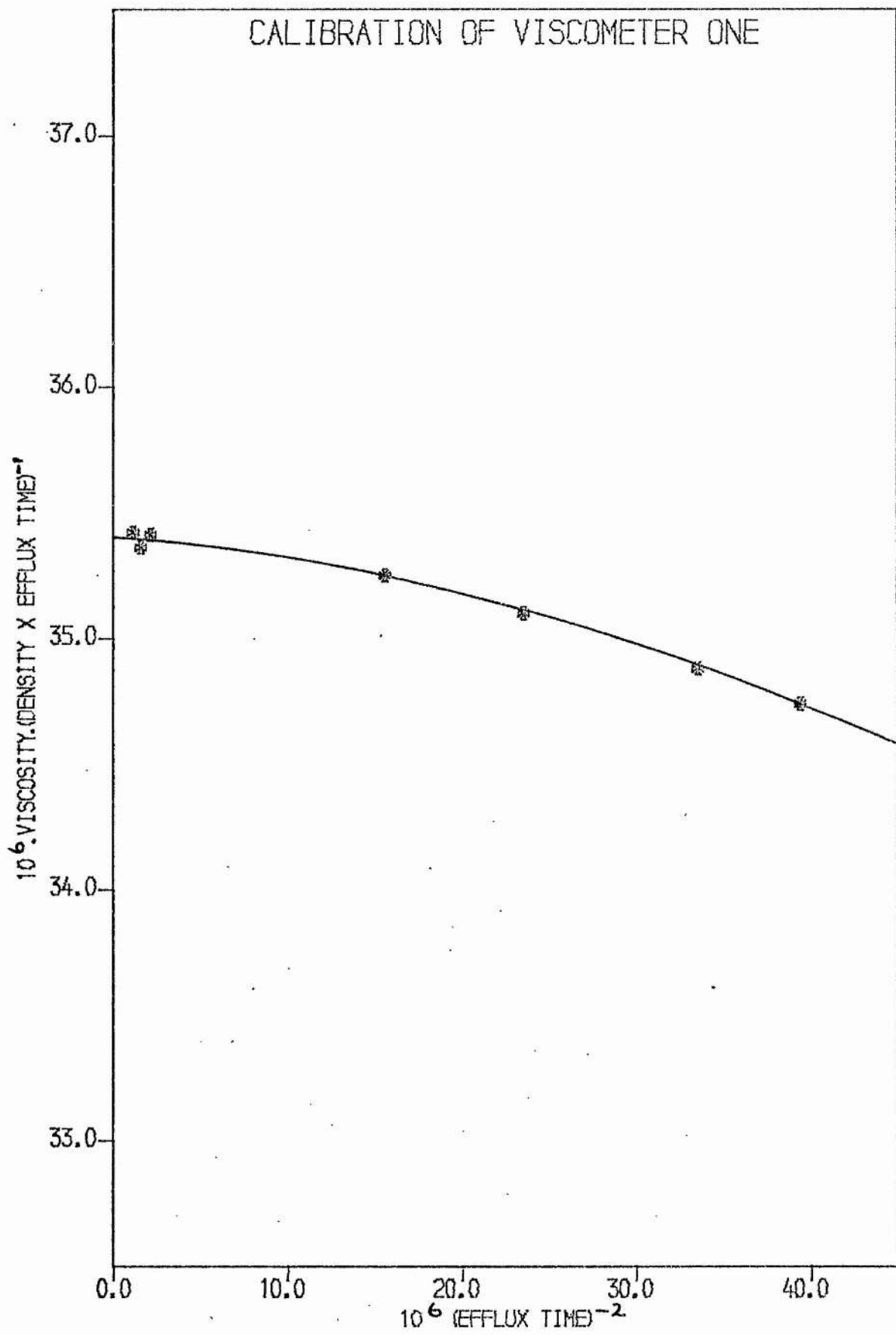
TABLE 2.1 VALUES FOR VISCOMETER 2

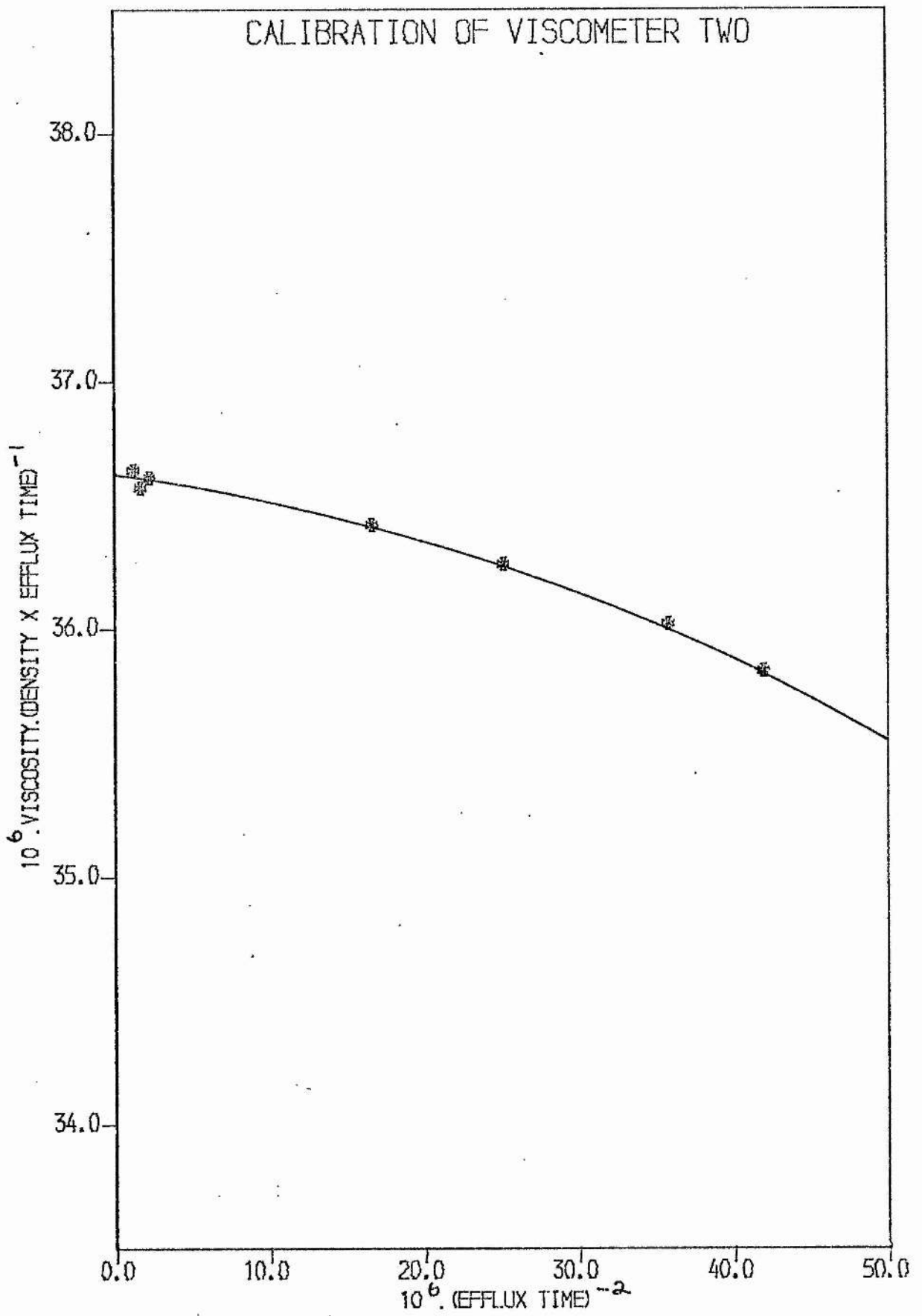
	A	B	Calculated Viscosity *	
			Water	Formamide
(a)	$.3682 \times 10^{-4}$	$-0.2305 \times 10^{-1}$	$.8906 \times 10^{-3}$	$3.334 \times 10^{-3}$
(b)	$.3666 \times 10^{-4}$	$-0.18177 \times 10^{-1}$	$.8886 \times 10^{-3}$	$3.3098 \times 10^{-3}$

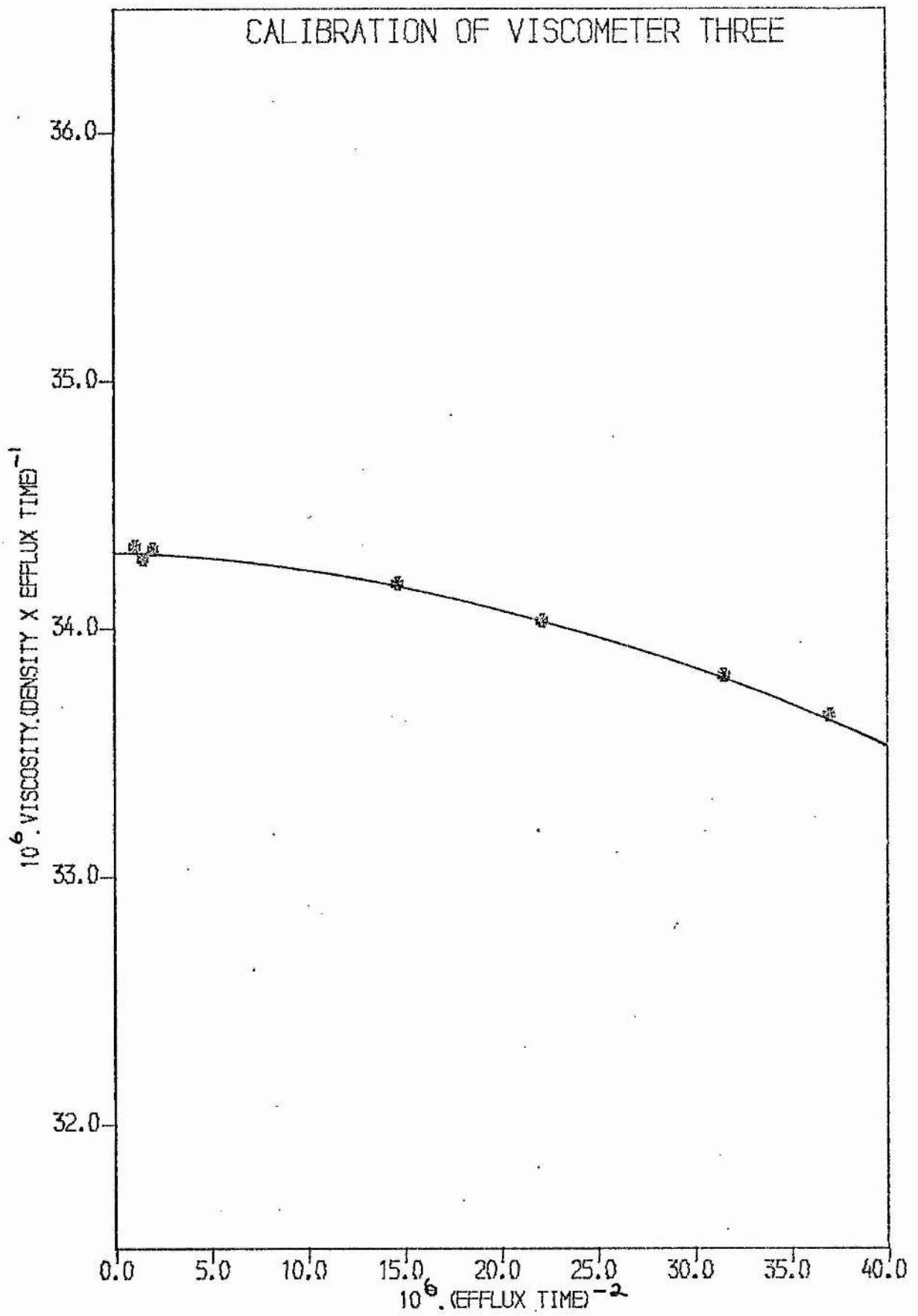
\* Units expressed in  $J m^{-3}s$

As is to be expected (a) gives a good value for the viscosity of water (better than 0.04% accurate). On the other hand, (b) gives a value which is 0.23% lower for water. However in view of the fact that the calibration graphs do show a definite curvature the calibration "constants" would both be expected to be lower and (b) therefore probably represents more accurately the viscosity of formamide. The scatter which appears for the 30% sucrose solution is to some extent false. The viscosities of the sucrose solution used for the calibration were accurate to less than 0.1% (see Appendix I) and therefore the 30% aqueous sucrose solution points on the calibration graph fall within this value. The actual values of the calibration constants used were therefore those calculated from the 30% aqueous sucrose solutions at 288.15K, 293.15K and 298.15K and water at 298.15K, 308.15K, 318.15K, and 323.15K [see Appendix III and (b) in table (2.1)].

### CALIBRATION OF VISCOMETER ONE







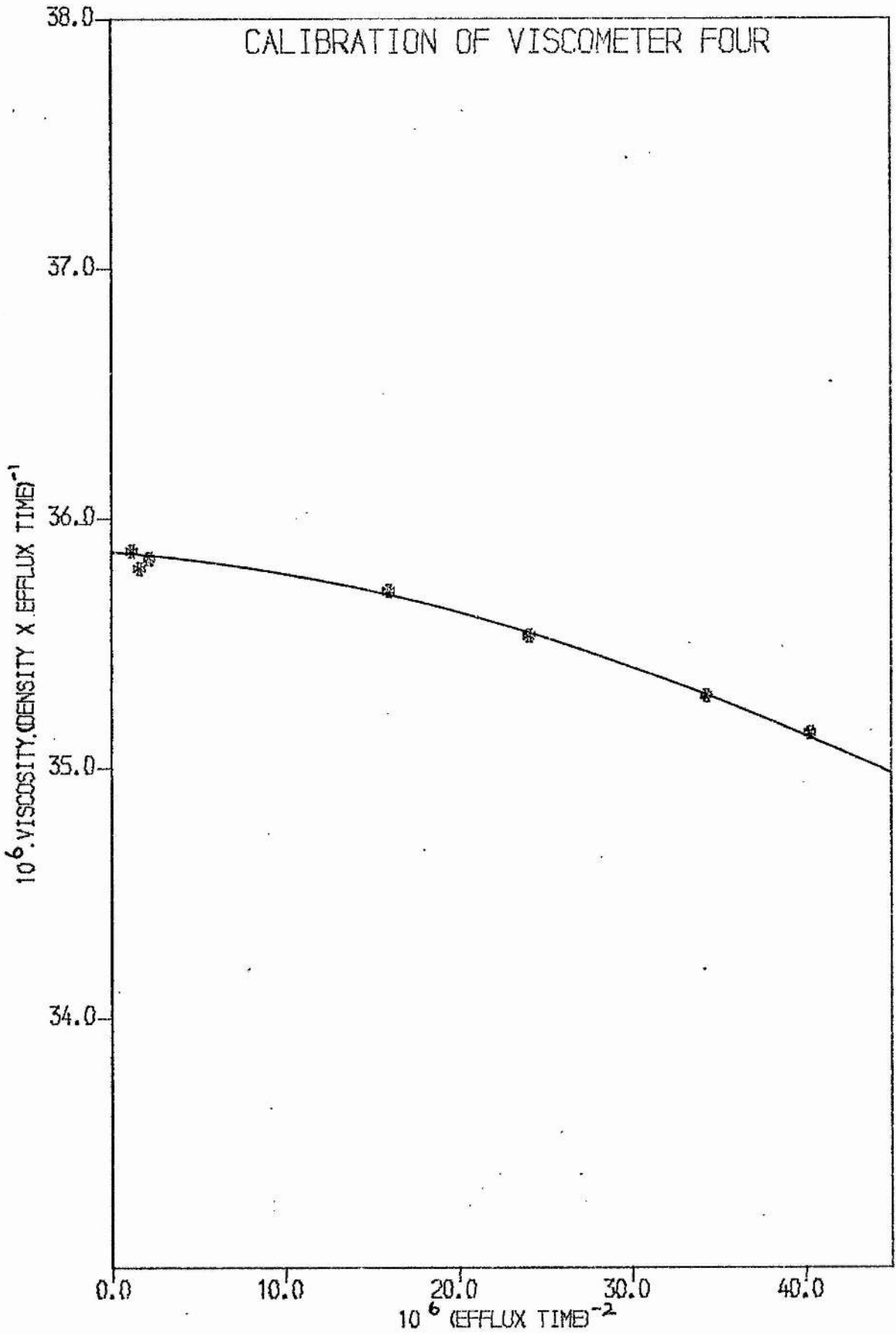


Table (2.2) gives the precision with which the efflux times used for the calibration were measured.

TABLE 2.2

Standard Deviation of Efflux Times (t) Used for Viscometer Calibration

t s	$(t-\bar{t})^2$	
826.77	0.04	$\bar{t} = \frac{\sum t}{n} = 826.56 \text{ s}$
826.78	0.05	
826.61	0.00	$\sigma = \frac{\sum (t-\bar{t})^2}{n-1} = 0.17 \text{ s}$
826.40	0.03	
826.50	0.01	
826.44	0.02	<u>Note</u> the efflux times quoted here
826.88	0.10	are for viscometer one containing
826.39	0.03	a liquid of viscosity approximately
826.60	0.00	$0.003 \text{ J m}^{-3} \text{ s}$
826.61	0.00	
826.38	0.03	$\sigma =$ standard deviation
826.40	0.03	

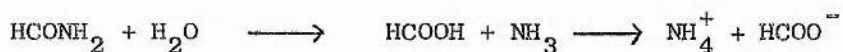
### 2.13 PURIFICATION OF FORMAMIDE

The most common method used for the purification of formamide is by fractional crystallisation<sup>52</sup>. This method however is very wasteful and not convenient for large quantities.

The most important impurities in commercial formamide are water and dissolved ions. Notley and Spiro<sup>53</sup> proposed a method of purification involving ion exchange resins and molecular sieves. This purification technique was tried but was not found to be practicable. The main problem was due to the use of molecular sieves as drying agent. It was found to be impossible to exclude the dust from these pellets even although care was taken not to disturb the sieve bed (the sieves were placed in a vertical column through which the formamide was eluted). Solvent treated in this way was then

filtered through a number 3 glass filter. Despite this the efflux times were continually found to be spurious and excessively long corresponding to impedance of flow in the capillary due to dust particles.

The method of purification adopted was to distil the formamide under reduced pressure. The still employed was equipped with ground glass joints throughout (it was necessary to wet these joints with formamide to ensure a good vacuum), and had a vertical fractionating column, 25 mm, broad and packed with glass helices (Fenske rings) to a height of 0.5 m. A pressure of less than  $100 \text{ Nm}^{-2}$  was obtained by using a rotary oil pump and a liquid nitrogen trap. In each case the first 100 ml of distillate was discarded. Crude formamide from the suppliers (Fisons) was found to be neutral and was therefore used directly for distillation, however if a bottle once opened was left without being properly sealed the formamide soon became acidic and smelled of ammonia. This was assumed to be due to the hydrolysis of the formamide by water



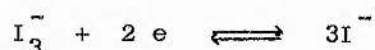
In this case the formamide was neutralised with dilute aqueous sodium hydroxide solution (bromothymol blue as indicator) and heated to 313K under reduced pressure. The neutralisation was repeated until the formamide remained neutral for more than five minutes when heated under reduced pressure. The formamide was then distilled in the usual way.

The formamide prepared in this way had a water content of 0.023%, that is 0.013 M. This water content could be further reduced to 0.0083 M by using molecular sieves, not however without the accompanying problems due to dust. The water content was estimated by the Karl Fischer method.



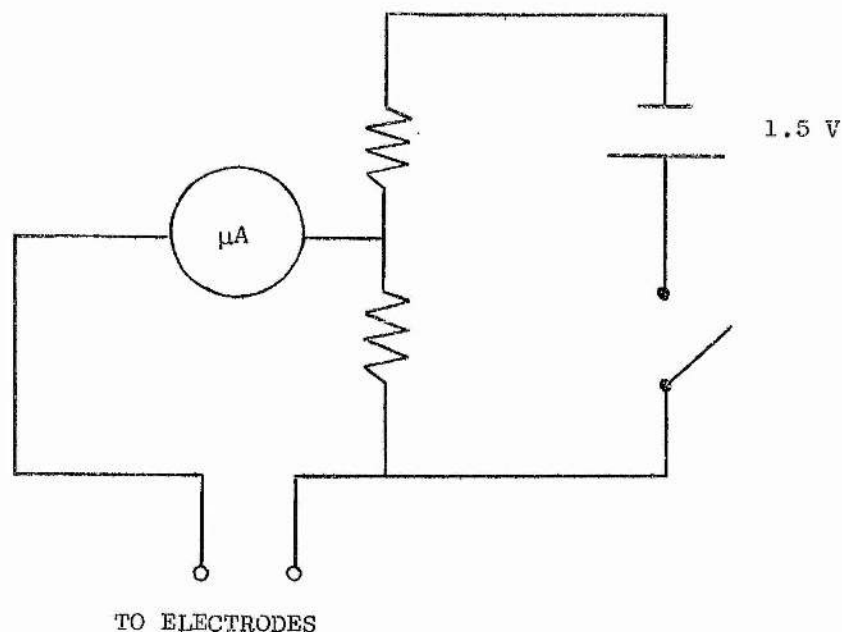
## 2.14 KARL FISCHER METHOD OF DETERMINING WATER CONTENT

The method employed for determining the water content of solutions was a direct titration with "Modified Karl Fischer Reagent"<sup>54</sup>, based on the method suggested by BDH Ltd<sup>55</sup>. The end point was determined electrometrically using a biamperometric or "dead stop" technique. In this method two small platinum wire electrodes are placed close together in the titration vessel and a potential of about 20 mV is impressed across them. With excess reagent present a current passes due to the reaction

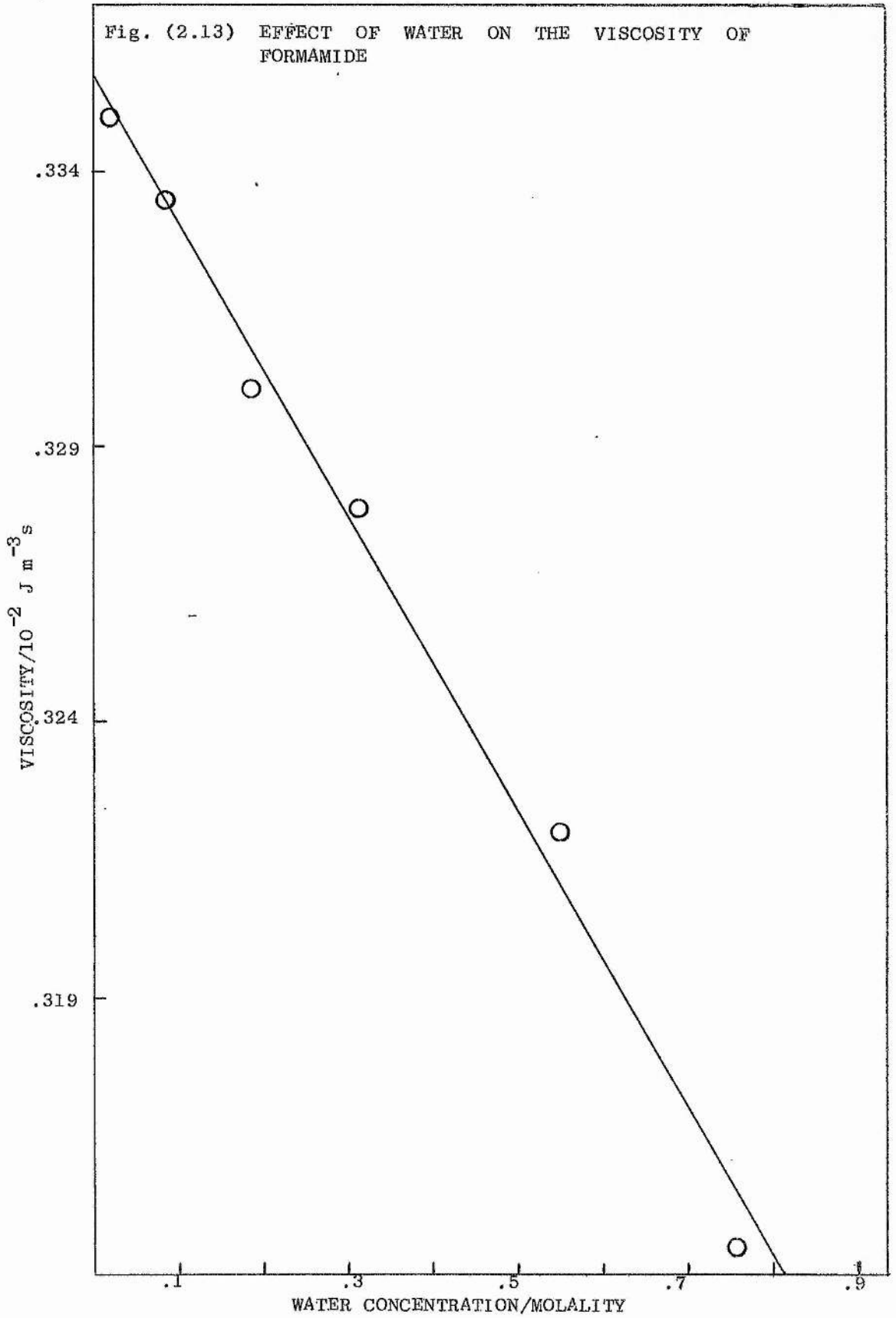


With excess water there is no current. In the present study the current was detected on a microammeter placed between the electrodes as in fig. (2.12).

Fig. (2.12) CIRCUIT DIAGRAM FOR KARL FISCHER APPARATUS



The system was calibrated using known quantities of water delivered from a micro-syringe (Agla Ltd).



The effect of water on the viscosity of formamide was studied by preparing solutions of traces of water in formamide and measuring the viscosity. The solutions were prepared by weight and then checked by means of a Karl Fischer titration. It can be seen from fig. (2.13) that even small traces of water lower the viscosity of formamide appreciably. Since in this work small changes in viscosity were sometimes under investigation (for the measurement of Jones-Dole B coefficients) it was desirable to protect the solutions as far as possible from the atmosphere. This was attempted by fixing calcium chloride tubes to the open ends of the viscometers, but was not successful due to a partial blocking of the drying-tubes which caused a partial back pressure which affected the hydrostatic head. The technique which was finally adopted was simply to stopper all three viscometer limbs when not in use. In this way the viscosity of formamide changes by less than 0.02% on standing overnight. Figs. (2.12-2.20) show sections of print-out which represent the efflux times ( $t$ ) for formamide at 298.15 K. Fig. (2.14) represents the efflux times for freshly prepared formamide. Fig. (2.15) represents the situation after the viscometer has been left standing overnight unstoppered. It can be seen that the viscosity has fallen by approximately 0.125%. On leaving the solution overnight the viscosity again fell by about 0.125%, fig. (2.16). The viscometer was then allowed to run automatically for 48 hours continuously during which time the viscosity steadily decreased so that at the end of two days it had fallen by more than 0.5% fig. (2.16).

Another sample of this same formamide which had been sealed in the stock bottle for the duration of the above run was transferred to the same viscometer after cleaning and drying the latter, as

Fig(2.14)

Fresh formamide.

4	8	8	1	6	.	1	3
4	7	8	1	6	.	1	7
4	6	8	1	6	.	1	6
4	5	8	1	6	.	2	4
4	4	8	1	6	.	2	7

Fig(2.15)

The same formamide  
the next day.

4	2	8	1	5	.	3	9
4	1	8	1	5	.	2	4
4		8	1	5	.	1	7
4	9	8	1	5	.	3	4
4	8	8	1	5	.	4	0
4	7	8	1	5	.	2	8
4	6	8	1	5	.	1	6
4	5	8	1	5	.	1	9
4	4	8	1	5	.	3	3
4	3	8	1	5	.	1	1
4	2	8	1	5	.	4	1
4	1	8	1	5	.	4	2

Fig(2.16)

4	9	8	1	3	.	0	1
4	8	8	1	3	.	9	0
4	7	8	1	3	.	2	0
4	6	8	1	3	.	1	0
4	5	8	1	3	.	1	7
4	4	8	1	3	.	1	1
4	4	8	1	3	.	1	9
4	3	8	1	3	.	1	0
4	2	8	1	3	.	1	7
4	1	8	1	3	.	3	0
4	9	8	1	3	.	2	8
4	8	8	1	3	.	2	5
4	7	8	1	3	.	4	1
4	6	8	1	3	.	3	6
4	5	8	1	3	.	4	1
4	4	8	1	3	.	3	5
4	3	8	1	3	.	2	9
4	2	8	1	3	.	5	7
4	1	8	1	3	.	4	2
0	0	0	0	0	.	0	0
4	9	8	1	3	.	6	7
4	8	8	1	3	.	9	2
4	7	8	1	4	.	0	9
4	6	8	1	4	.	1	0
4	5	8	1	4	.	0	2
4	4	8	1	4	.	0	7
4	4	8	1	4	.	0	2
4	3	8	1	4	.	0	7
4	4	8	1	4	.	0	2
4	3	8	1	4	.	0	7
4	2	8	1	4	.	0	0
4	1	8	1	4	.	0	2
4	2	8	1	4	.	0	1
4	1	8	1	4	.	0	2
4	9	8	1	4	.	1	0
4	8	8	1	4	.	0	8
4	7	8	1	4	.	1	7
4	6	8	1	4	.	2	9
4	5	8	1	4	.	2	6
4	4	8	1	4	.	1	2
4	3	8	1	4	.	1	0
4	2	8	1	4	.	2	6
4	1	8	1	4	.	3	3
4	9	8	1	4	.	0	6
4	8	8	1	3	.	9	1
4	7	8	1	4	.	2	3
4	6	8	1	4	.	2	4
4	5	8	1	4	.	2	3
4	4	8	1	4	.	3	0
4	3	8	1	4	.	2	7
4	2	8	1	4	.	2	4
4	1	8	1	4	.	2	5

Fig(2.17)

Original formamide from  
sealed container.

4	7	8	1	6	.	0	0
4	6	8	1	5	.	8	0
4	5	8	1	5	.	3	5
4	4	8	1	6	.	0	6
4	3	8	1	5	.	9	3
4	2	8	1	5	.	9	6
4	1	8	1	6	.	1	0

Fig(2.18)

The next day after  
standing in a sealed  
viscometer.

4	4	8	1	5	.	8	0
4	3	8	1	5	.	7	2
4	2	8	1	5	.	7	7
4	1	8	1	5	.	7	6

For an explanation of the various columns see Fig.2.7.

Fig(2.16) Continued.

4	2	8	1	1	.	9	4	4	8	8	0	9	8	0	9
4	1	8	1	1	.	8	5	4	8	8	0	8	8	0	8
0	0	0	0	0	.	0	1	0	7	8	1	7	8	0	8
4	1	8	1	8	.	7	0	1	0	0	0	6	8	0	8
4	8	8	2	8	.	0	1	2	1	8	1	4	8	0	8
4	6	8	2	9	.	5	4	4	5	8	1	1	8	0	8
4	5	8	1	0	.	3	6	9	3	8	1	9	8	0	8
4	4	8	1	2	.	1	0	4	0	0	0	0	8	0	8
4	3	8	1	2	.	2	5	4	2	8	1	1	8	0	8
4	2	8	1	2	.	1	3	4	2	8	1	1	8	0	8
4	1	8	1	2	.	2	3	2	3	8	1	1	8	0	8
4	9	8	1	2	.	3	2	6	0	8	1	1	8	0	8
4	8	8	1	2	.	2	1	0	6	8	1	1	8	0	8
4	7	8	1	2	.	1	3	0	2	8	1	1	8	0	8
4	6	8	4	7	.	3	2	0	6	8	1	1	8	0	8
4	5	8	1	2	.	2	6	8	2	8	1	1	8	0	8
4	4	8	1	2	.	2	2	7	7	8	1	1	8	0	8
4	3	8	1	2	.	1	1	3	6	8	1	1	8	0	8
4	2	8	1	2	.	1	5	0	4	8	1	1	8	0	8
4	1	8	3	4	.	4	4	9	4	8	1	1	8	0	8
4	9	8	1	2	.	4	4	4	5	8	1	1	8	0	8
4	8	8	1	2	.	5	5	4	5	8	1	1	8	0	8
4	7	8	4	1	.	5	4	4	4	8	1	1	8	0	8
4	6	8	1	3	.	5	5	5	2	8	1	1	8	0	8
4	5	8	1	2	.	4	4	8	4	8	1	1	8	0	8
4	4	8	1	2	.	4	4	4	4	8	1	1	8	0	8
4	3	8	1	2	.	4	4	1	0	8	1	1	8	0	8
4	2	8	1	2	.	6	6	0	1	8	1	1	8	0	8
4	1	8	3	2	.	6	7	4	0	8	1	1	8	0	8
4	9	8	1	2	.	7	3	3	7	8	1	1	8	0	8
4	8	8	1	2	.	7	7	8	4	8	1	1	8	0	8
4	7	8	1	2	.	6	6	4	4	8	1	1	8	0	8
4	6	8	1	2	.	6	6	4	4	8	1	1	8	0	8
4	5	8	1	2	.	6	6	0	3	8	1	1	8	0	8
4	4	8	1	2	.	3	3	3	4	8	1	1	8	0	8
4	3	8	1	2	.	7	6	2	8	8	1	1	8	0	8
4	2	8	1	2	.	6	6	8	9	8	1	1	8	0	8
4	1	8	1	2	.	7	7	9	4	8	1	1	8	0	8
4	9	8	1	2	.	7	7	5	1	8	1	1	8	0	8
4	8	8	1	2	.	8	6	6	4	8	1	1	8	0	8
4	7	8	1	2	.	6	7	7	3	8	1	1	8	0	8
4	6	8	1	2	.	7	7	3	2	8	1	1	8	0	8
4	5	8	1	2	.	8	7	3	2	8	1	1	8	0	8
4	4	8	1	2	.	7	8	4	1	8	1	1	8	0	8
4	3	8	1	2	.	6	7	3	8	8	1	1	8	0	8
4	2	8	1	2	.	7	8	4	3	8	1	1	8	0	8
4	1	8	3	4	.	8	2	5	2	8	1	1	8	0	8

previously described, and the efflux time measured, fig. (2.17). As can be seen from figs. (2.14 and 2.17) this formamide had only changed by 0.03%. The viscometer was then stoppered and left overnight and then run the following morning. The viscosity of the formamide had again only decreased marginally (less than 0.02%) as can be seen from fig. (2.18).

Protection from the atmosphere was therefore very important and viscometers were kept tightly stoppered unless in use. All solutions were kept in flasks with ground glass stoppers and joints and sealed with paraffin film.

As a further precaution, for each series of measurements, the stock solvent was run in each viscometer at each temperature before any measurements on the solutions under investigation were carried out. This solvent was again run in one viscometer at one temperature after the series of measurements was complete to check that no change had taken place.

#### 2.15 PREPARATION OF SALTS

Lithium chloride was recrystallised from anhydrous methanol and vacuum dried in a desiccator over phosphorus pentoxide. Analytical grade sucrose was used for the calibration solutions after drying for three days over phosphorus pentoxide.

All other salts which were also of analytical grade were used without further purification after drying at 393 K for three days.

#### 2.16 PREPARATION OF METHANOL

Analytical grade solvent was distilled under reduced

pressure (less than  $100 \text{ N m}^{-2}$ ) in a still, similar to that used for the formamide. The middle fraction which came over at 337.6K was collected.

#### 2.17 PREPARATION OF DIMETHYLFORMAMIDE

Laboratory reagent grade solvent (ex. Fisons) was left standing over anhydrous barium oxide for 48 hours and then distilled at 305.1-310.1K at  $500-800 \text{ N m}^{-2}$  in a still, similar to the above. The first 100 ml of the distillate was rejected.

CHAPTER THREE



### 3.1 Jones-Dole Formula

It has long been established that the viscosity of aqueous solutions of electrolytes is approximately a linear function of the concentration. This was pointed out by Sprung<sup>56</sup> who published measurements as early as 1876 on many salts over a range of temperatures. At high concentrations, however, this limiting law does not hold. Thus Arrhenius<sup>57</sup> showed that at concentrations higher than molal, the viscosity rose faster than the concentration. He proposed the relationship:

$$\eta = A^c \quad (3.1)$$

where  $\eta$  is the relative viscosity (  $\frac{\eta_{\text{SOLUTION}}}{\eta_{\text{SOLVENT}}}$  ), and A is a constant for a given salt and temperature. This relationship was tested by Reher<sup>58</sup> and Wagner<sup>59</sup> and found to hold within a few tenths of a percent between 0.125 and 0.5 molal and within approximately 1% up to one molal.

While most salts give solutions with viscosity greater than that of water at all concentrations, many can effect a marked decrease in the viscosity of water at certain concentrations. The latter effect cannot be described by the Arrhenius equation given above. It was suggested by Sutherland<sup>60</sup> that the depolymerisation of "triple water molecules" by the dissolved salts might cause this diminution in viscosity.

In 1906 Einstein<sup>61</sup> deduced from the principles of hydrodynamics that if the solute could be regarded as being made up of spherical incompressible uncharged particles which were large in comparison with the molecules of the solvent, the viscosity of the solution would be given by

$$\eta = 1 + 2.5 \phi \quad (3.2)$$

where  $\phi$  is the total volume of the solute particles per unit volume of solution. This treatment was extended by Finkelstein<sup>62</sup> to

solutions of binary electrolytes in polar solvents. He investigated mathematically the effect on the viscosity of the relaxation times of the solvent dipoles and concluded that the charge effect of the ions on the polar solvent would increase the viscosity proportionally to the concentration. Neither of these theories could account for the fact that some solutes diminish the viscosity of water.

Using an improved experimental technique, Grüneisen<sup>63</sup> extended viscosity measurements to greater dilution than those of his predecessors. Although he found that for sucrose the linear relationship was valid, he noted that for electrolytes, deviation from the linear law became more pronounced at low concentrations. Instead of remaining linear at low concentration the curve exhibited a negative curvature which he demonstrated by plotting  $\frac{\eta-1}{c}$  against  $c$  to give a curve rather than the expected straight line. The viscosity always increased initially with concentration. This "Grüneisen effect" was found to hold for all the salts investigated, whether they increased or decreased the viscosity of water, and was confirmed by later workers, especially Schneider, Appelby and Merton<sup>64</sup>. The idea that deviations from Stokes' Law for the conductance of any salt was due to incomplete dissociation was still widely held at this time and Grüneisen proposed the following equation to explain his viscosity results

$$\eta = 1 + Aic + B(1-i)c + Cc^2 \quad (3.3)$$

where  $i$  is the degree of dissociation as computed from the conductivity and  $A$ ,  $B$  and  $C$  are constants for any given salt and temperature.  $A$  was taken to represent the effect of the "friction" of the ions on the water,  $B$  that of the unionised molecules on the water and  $C$  that of the ions and molecules on each other.

In 1929 Grinnell Jones and Malcolm Dole<sup>20</sup>, who were interested in accurate viscosity data at low concentrations in connection with studies of electrolytic conductance, found that the Grüneisen effect

was magnified at even greater dilution, and at the same time demonstrated that the fluidity ( $\frac{1}{\eta}$ )/concentration curve has a simpler form than the viscosity/concentration curve. Although the principal effect of the dissolved salts on the viscosity was proportional to the concentration of the electrolyte, they suggested that another effect, relatively more important at low concentrations, would have to be present to account for the negative curvature. By considering the Debye-Hückel theory of interionic attraction which suggests that the electrical interactions between ions in solution tend to establish and maintain a preferred arrangement of the ions which resists distortion and therefore "stiffens" the solution with a consequent increase in the viscosity, they attempted to derive an equation which would account for the Grüneisen effect. Although they did not succeed, they inferred that the effect would be proportional to the square root of the concentration and suggested an empirical equation of the form

$$\phi = 1 + A\sqrt{c} + Bc \quad (3.4)$$

where  $\phi$  is the relative fluidity  $\frac{1}{\eta_{\text{SOLUTION}}/\eta_{\text{SOLVENT}}}$  and A was expected to be negative for all electrolytes and zero for non-electrolytes. Falkenhagen and Dole<sup>21</sup> then attacked the problem deductively and by considering a binary salt for which the anion and cation have the same mobility in solution, they obtained a partial solution which they regarded as a limiting law; this was

$$\eta = 1 + A\sqrt{c} \quad (3.5)$$

The A in this relationship is the same as the A in the Jones-Dole equation (3.4) with reversed sign and is considered to be a measure of the ion-ion interaction.

Falkenhagen<sup>65</sup> later derived an equation of the same form but with a more explicit evaluation of the constant A, applicable to any salt with ions of any valence and any mobility. In 1932

Onsager and Fuoss<sup>66</sup> published a comprehensive paper on the theory of irreversible processes in electrolyte solutions in which they developed a general equation to describe viscosity for a system containing more than two species of ions.

Jones and Talley<sup>50</sup> (1933) suggested that for salts which diminish the viscosity of water it was best to use the relationship

$$\eta = 1 + A \sqrt{c} \pm Bc \quad (3.7)$$

where A and B have the same value as in the fluidity equation except for reversed signs. This only holds for concentrations much less than molar and where the B coefficient is small and where the experimental error in B is relatively large. In the present measurements the minimum experimental error in B is about 1% and even although the B coefficients are much larger than those in water equation (3.7) is still considered to be valid. This can be seen by taking the reciprocal of both sides of equation (3.4) and considering the magnitude of the terms.

$$1/\phi = 1/(1+A\sqrt{c} + Bc) \quad (3.8)$$

also  $\eta = 1/\phi \quad (3.9)$

$$\begin{aligned} &= \frac{1 - A\sqrt{c} - Bc}{(1+A\sqrt{c} + Bc)(1 - A\sqrt{c} - Bc)} \\ &= \frac{1 - A\sqrt{c} - Bc}{1 - A^2c - 2ABc^{3/2} - B^2c^2} \end{aligned} \quad (3.10)$$

For sodium chloride at 298 K in formamide  $A = 0.0064$ , (by calculation) and  $B = 0.594$  (by experiment).

Consider the terms in the denominator of equation (3.10) for a maximum value of 0.1 molal concentration,

$$\begin{aligned} \text{(i)} \quad A^2c &= 0.0064^2 \times 0.1 \\ &= 4.0 \times 10^{-6} \end{aligned}$$

$$\text{(ii)} \quad 2ABc^{3/2} = 2 \times 0.0064 \times 0.594 \times 0.1^{3/2}$$

$$\begin{aligned} \text{(iii) } B^2 c^2 &= 0.594^2 \times 0.1^2 \\ &= 3.5 \times 10^{-3} \end{aligned}$$

ie the denominator is 0.42% too large in equation (3.7), but since the value of B is accurate to less than 1% the equation is quite valid.

### 3.2 THE JONES-DOLE B COEFFICIENT

Whereas the A coefficient of the Jones-Dole equation adequately describes the change in the viscosity of solutions of electrolytes up to concentrations of about 0.002 molal by considering only the ion-ion electrostatic interactions, this effect is rapidly swamped at high concentrations by the linear term which extends the fit of the Jones-Dole equation to concentrations greater than 0.1 molal for aqueous solutions and somewhat less than 0.1 molal in non-aqueous solutions.

Gurney<sup>14</sup> coined the term "ionic co-sphere" to refer to the spherical region of solvent which encloses the ion and which is somewhat modified by the presence of the ion. Each ion is enclosed in its own co-sphere while the remainder of the solvent between the ion does not differ in any way from ordinary pure solvent. He considered that the viscosity B coefficient represents the contributions of the co-spheres of the ions to the viscosity, and that in dilute solution the contributions from the positive and negative ions would be independent and therefore additive. The problem was therefore to determine the individual contributions of the ions (which he called the ionic B coefficients), from the values of the B coefficients obtained for each salt.

### 3.3 IONIC B COEFFICIENTS

In 1934 these B coefficients were assigned individual ionic values. Cox and Wolfenden<sup>67</sup> argued that if the solvated ions

in solution behaved as rigid spheres (the radius being that of the ion plus its molecules of solvation) then the kinetic entities would be large enough to obey Stokes' Law even when the solute particle itself was as small as the lithium ion,  $\text{Li}^+$ . The ionic mobility of this ion in water is less than 3% smaller than the ionic mobility of the iodate ion,  $\text{IO}_3^-$ , and hence in accordance with Stokes' Law the radius of the hydrated  $\text{Li}^+$  ion must be less than 3% larger. If the hydrated ions are considered to be spherical then the volume of the hydrated  $\text{Li}^+$  ion would be nearly 10% greater than the volume of the hydrated  $\text{IO}_3^-$  ion. In support of this they cited the fact that the temperature coefficient of the mobilities of these two ions is not far from the value demanded by Stokes' Law, which, it was concluded, they therefore obeyed satisfactorily. Since the Einstein expression,

$$\eta = \eta_0 (1 + 2.5 \phi) \quad (3.11)$$

where  $\phi$  is the volume increase due to the dissolution of the solute particles in unit volume of solvent, is derived from Stokes' Law (and since it was assumed that these two ions obey Stokes' Law) the argument leads directly to the prediction that the B coefficient of  $\text{Li}^+$  must be nearly 10% greater than the B coefficient of  $\text{IO}_3^-$ . From these postulates Cox and Wolfenden assigned the values of  $0.14_6$  and  $0.13_6$  to  $\text{Li}^+$  and  $\text{IO}_3^-$  respectively for aqueous solutions at 291 K. The values for the other ions followed from this choice assuming the ionic B coefficients were additive.

Gurney<sup>14</sup> approached the problem of assigning different ionic B coefficient values from a slightly more fundamental point of view. The mobility of an ion and its temperature coefficient are almost the only quantities for which experimental values can be obtained separately for anions and cations. Gurney plotted the temperature coefficient of ionic mobility which he defined as  $C_{T_1}^{T_2} = \frac{u_2 \eta_2}{u_1 \eta_1}$

Fig. (3.1)

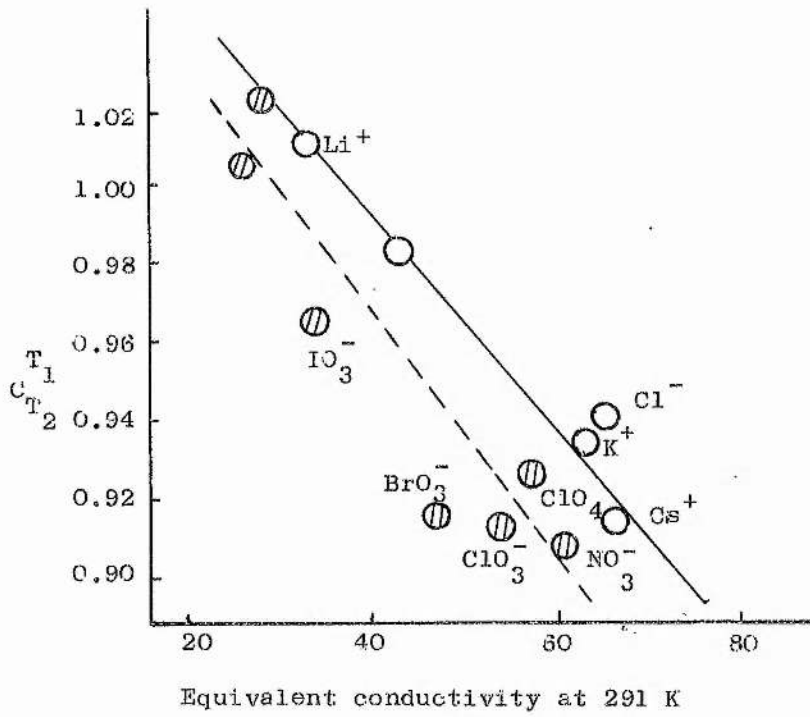
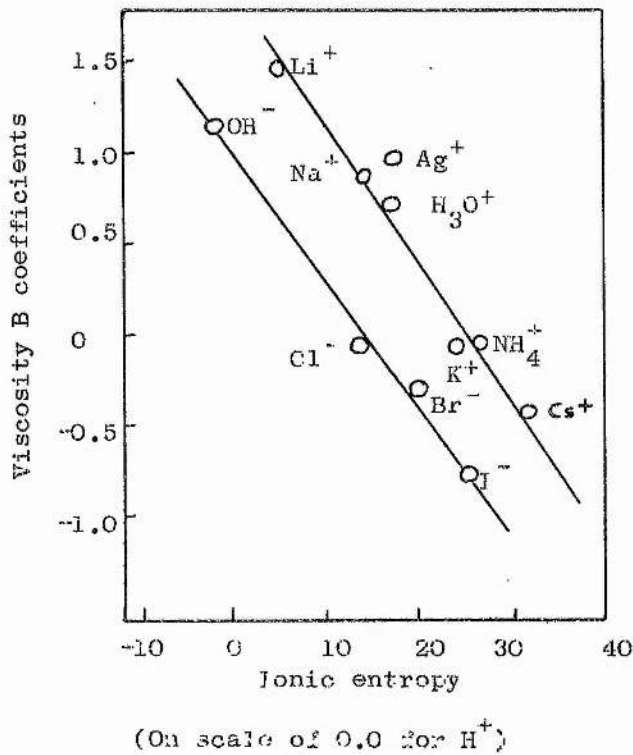


Fig. (3.2)



against the equivalent conductivity of the ions at  $T_2$ . His argument was that for any ions obeying Stokes' Law this ratio would be equal to unity. He obtained a graph of the form in fig. (3.1). For most species it was found that  $C_{T_2}^{T_1}$  was appreciably less than unity; with a rise in temperature the mobility increased somewhat less rapidly than expected from Stokes' Law. It can be seen that ions with an abnormally high mobility, have at the same time an abnormally low temperature coefficient of mobility, and that the atomic ions have values lying near to a straight line. This he explained in terms of the ions having a region, or co-sphere of water in which the local structure has been loosened, to increase the random motion of the ion due to the Brownian effect. This would also lead to an increase in its mobility under an applied electric field and would mean that with the rise in temperature the freedom of movement of the ion would be affected less than otherwise.

The important point to note from fig. (3.1), however, is that the points for  $K^+$  and  $Cl^-$  were found to lie very close together. This tended to rule out the possibility of the small value of B for KCl in water being due to  $K^+$  and  $Cl^-$  having large values but of opposite sign. Gurney therefore considered that the value of the B coefficient for KCl (-0.0140) could be split into two equal contributions of -0.007. The value obtained for the lithium ion ( $Li^+$ ) in water by this method is 0.147 which is in very close agreement with that obtained by Cox and Wolfenden, namely 0.146. Gurney explained negative B coefficients in terms of an increase in the fluidity in the co-spheres around the ion; conversely a positive B coefficient would indicate a decrease in the fluidity of the solvent in the co-sphere of the ion. He further considered the entropy changes which occur in the co-spheres of several ions in water and methanol to see if a relationship existed between the B coefficient and the degree of order or disorder about the ion.



Such a relationship is illustrated in fig. (3.2) and in both cases it is seen that the ions with the greatest ionic entropies are those with the most negative viscosity B coefficients.

On comparing the results obtained with those shown in fig. (3.1), Gurney concluded that the striking resemblance was due to the fact that all four of the ionic properties which are involved in these diagrams are largely dependent on the same factor, namely the degree of order or disorder in the ionic co-spheres.

Kaminsky<sup>68</sup> writing in 1957 commented that since the B coefficients used by Cox and Wolfenden were in some cases subject to an uncertainty of about 15% the exact additivity could not be regarded as having been established. In a similar way to Gurney he considered that since the ionic mobilities of the  $K^+$  and  $Cl^-$  ions differed by only 3% over the temperature range investigated (288°K to 315.5 K) then the ions might be considered to have the same effect on the viscosity and therefore the ionic B coefficient for  $K^+$  would equal that for  $Cl^-$ .

#### 3.4 TEMPERATURE DEPENDENCE OF THE JONES-DOLE B COEFFICIENT

Kaminsky found that the temperature coefficient of the viscosity B coefficient could be either positive or negative *ie*,  $\frac{dB}{dT} > 0$ . This was contrary to the general opinion<sup>69,70</sup> that  $\frac{dB}{dT}$  is always positive.

From his experimental evidence he proposed three rules to govern the behaviour of ionic B coefficients.

I. Within a group of the periodic table (alkali metals, alkaline earths, halogens) the ionic B coefficients would decrease as the crystal ionic radius increases.

II. Within a group of the periodic table the temperature coefficient of the ionic B coefficient should increase (from negative

or slightly positive values) as the crystal ionic radius increases.

III. Only cations exhibit negative temperature coefficients.

Kaminsky further suggested that for cations the influence of hydration on the ionic B coefficient is dominant (apart from certain effects due to structure disruption). The hydration effect increases as the ionic radius decreases and the surface charge density goes up and results in an increase in the viscosity because of the increased 'particle' size. At very high intensities of the ionic fields a long range ordering effect of the ion on the solvent molecules becomes noticeable. This effect again causes an increase in viscosity and applies the ions  $\text{Li}^+$ ,  $\text{Be}^{2+}$ , and  $\text{Mg}^{2+}$ .

The anions are considered to cause chiefly structure breaking of the solvent, an effect which gains in importance as the crystal ionic radius goes up, and this effect lowers the viscosity.

As the temperature of water is increased Kaminsky considered that the ice-like structure of the water breaks down and consequently the contribution which certain solute ions make to the disruption of the solvent structure decreases. The viscosity changes which are due to this effect of the ions diminish therefore in importance relative to those caused solely by the rise in temperature; the ionic B coefficients become less negative and  $\frac{dB}{dT}$  is therefore positive. He also suggested that the hydration effect may increase the viscosity more strongly at higher temperatures because the concentration of single water molecules is greater so that the condition of attachment of water molecules to the ion may be more favourable.

On the other hand, the long range ordering of the solvent which is important for strongly hydrated ions (eg  $\text{Li}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ) diminishes at higher temperatures because of increasing thermal agitation. For these ions  $\frac{dB}{dT}$  would be expected to be negative. It should be noted that over the temperature range which he examined

the so-called first hydration shell is largely temperature independent<sup>71</sup>.

For predominantly structure breaking ions (eg  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) a rise in temperature is accompanied by a less rapid decrease of the solution viscosity ( $\eta_s$ ) than that of the solvent viscosity ( $\eta_0$ ). This is because the introduction of the ions into the solution is considered to have already brought about a certain amount of structure disruption. The largest, positive, temperature coefficient of the ionic B coefficient which he found was therefore for the ions with the strongest structure breaking influence because the numerator in the ratio  $\frac{\eta_s}{\eta_0}$  can not decrease much further as the temperature increases but the denominator can.

If the structure breaking effect decreases and the hydration of the ions increases (eg for the alkali metals in the sequence  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ) then a stage is reached when the numerator and denominator (in  $\frac{\eta_s}{\eta_0}$ ) decrease in a comparable fashion (eg  $\text{Na}^+$ ), so that the large positive temperature coefficient at the beginning of the series grows smaller and ultimately approaches zero.

As already discussed for strongly hydrated ions  $\frac{dB}{dT}$  was expected to be negative because of the destruction of the long range ordering of the solvent due to the ionic field, by thermal motion.

Kaminsky then plotted B ion against temperature for certain ions and compared it with plots of apparent molal heat capacities and apparent molal volumes of the same ions against temperature. The three quantities showed a very similar temperature dependence. Eigen and Wicks<sup>72</sup> had already interpreted the temperature coefficient of the heat capacity and apparent molal volumes by a similar argument.

Negative B coefficients have only been found with solutes dissolved in solvents capable of associating in three dimensional

units.

Frank and Wen<sup>13</sup> (1957) proposed a simple model for small ions in water which can explain negative B coefficients. The first effect which a small ion can have is the immobilisation of the dipolar solvent molecules which are nearest neighbours to the ions themselves. The field strength about a spherical ion of radius 0.2-0.3 nm in a medium of dielectric constant 80, is in the order of  $10^8 \text{ V m}^{-1}$  and it seems to be generally agreed that in aqueous solutions of ions not larger than  $\text{Cs}^+$  and  $\text{I}^-$  the nearest neighbour water molecules are always essentially immobilised by direct ion-dipole interaction. This region, Frank and Wen called A, and considered that the increase in the viscosity of water caused by dissolved LiCl could be taken as experimental justification of the above effect.

However as discussed above, negative B coefficients mean that the viscosity of water will be decreased. To explain this and some "anomalous" entropy data<sup>12</sup> a second region, B, was proposed in which the water structure was suggested to be "loosened" or rather less ice-like.

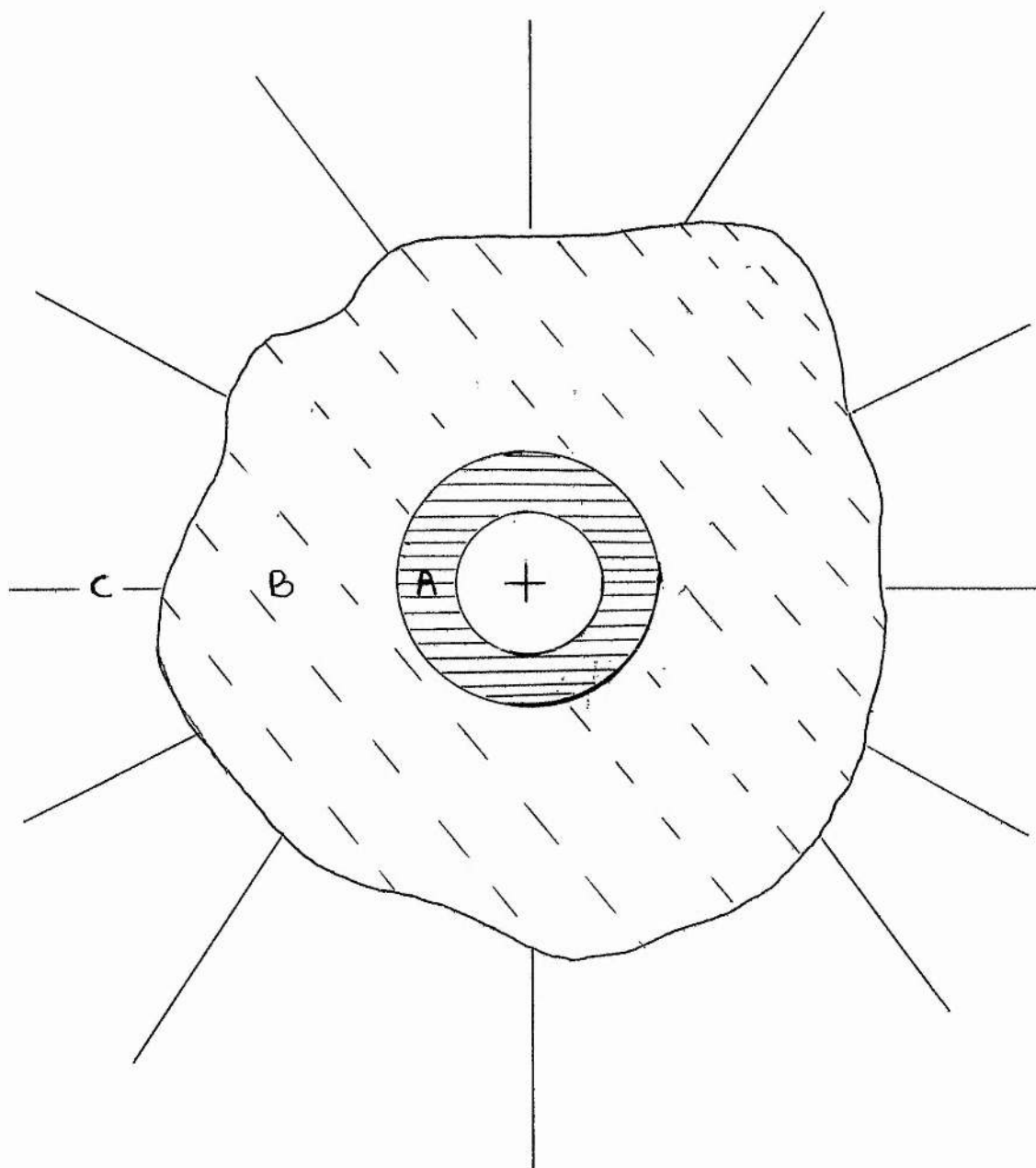
Lastly a third region, C, was considered in which the water structure was undisturbed by the ion (Fig. 3.3).

The cause of the structure breaking effect observed in region B was said to be due to the approximate balance between the two orientating influences which act on any given water molecule. One of these is the "normal" structure orientating influence of neighbouring water molecules; the other is the orientating influence upon the dipoles of the spherically symmetrical ionic field. The latter influence predominates in region A and the former in region C in which significantly more orientational disorder should be present than in either A or C.

Frank and Evans imagined that the region A composed of nearest

Fig. (3.3)

Frank and Wen's model for the structure modifications produced by a small ion in solution



A = region of immobilisation of solvent molecules

B = region of structure breaking

C = region of "normal" solvent structure

neighbour water molecules always existed, and that an ion which was small, or multiply charged, or both (eg  $\text{Li}^+$ ,  $\text{F}^-$ ,  $\text{Mg}^{2+}$ ) might induce additional structure (entropy loss) of some sort beyond the first water layer. It was considered that such an encroachment on region B might almost extinguish that region and would certainly tend towards a net structure making influence as is observed for these ions. They remarked that the outward orientation of like dipoles in all of region A should always produce at least some disorder in a region B but that large singly charged ions ( $\text{I}^-$ ,  $\text{Cs}^+$ ) exhibit more net structure breaking than this alone could account for.

An additional type of solute-water interaction was then considered. This was equivalent to the structure making influence of non polar solutes, or of non polar groups in solute molecules, inferred by Frank and Evans<sup>12</sup> from entropies of hydration and confirmed by various later workers<sup>73-76</sup> by various experimental means. Consider fig. (3.3) as the radius of the ion is gradually increased. As the radius is increased the surface charge density will decrease and eventually when this falls below a certain figure the region A will cease to exist. The next region to disappear will be B when the surface charge density becomes too small for it to compete with the "natural" structure of the water. But now a new effect is considered to become important which is observed when krypton<sup>12</sup> or ethane<sup>12</sup> or the hydrocarbon tail of amyl alcohol<sup>12</sup> is dissolved in water. The effect of these is that the water adjacent to the non-polar groups becomes more "ice-like" than normal, and the effect is roughly proportional to the volume of the non polar region.

Frank and Wen<sup>13</sup> explained this by postulating that the formation of hydrogen bonds in water is a co-operative phenomenon so that in most cases when one bond forms, several (perhaps many) will form and when one bond breaks, then, typically a whole cluster will "dissolve". This gave the now famous picture of "flickering

clusters" of various sizes and shapes" jumping to attention and then relaxing at ease."

In this picture the statistical degree of "ice-likeness" of the sample is proportional to the average size and to the average half life of the clusters. A cluster will come into existence when a volume element of suitable size and shape suffers an energy fluctuation of such magnitude as to outweigh the disruptive influences at the boundaries of the element, and will dissolve when these disruptive influences - torques and displacements - succeed in transmitting into the cluster the necessary energy of 'melting'. A nonpolar solute particle or group is considered to be relatively incapable of producing or of transmitting such disruptive influences on account of the relative feebleness of the electrostatic interactions into which it can enter. An ice-like patch should therefore be able to form more readily in a volume element bounded by a non-polar solute particle, and once formed should have a longer half-life than "normal" by reason of having half its boundary protected from attack. This would consequently produce extra "ice-likeness" in solution. A word of caution has been mentioned by Emerson and Holzer<sup>77</sup> against too literal interpretation of the above theory. These authors have successfully pointed out that qualitative arguments based on the flickering cluster concept are not unambiguous even in the simple, well established case of the reported increase in structure of  $D_2O$  compared with  $H_2O$ .

Stokes and Mills<sup>78</sup> (1965) reviewed the ionic B coefficients obtained by Kaminsky and others in both water and non-aqueous solvents. They considered that the important qualitative explanations which had been advanced in terms of ion-solvent interaction were more significant if considered for individual ionic coefficients. They restated the trends noted by Kaminsky,

adding that molecular ions such as tetraalkylammonium ions and the picrate ion had large positive B ion values and emphasising that observed viscosity changes take place as a result of competition between various effects occurring in the neighbourhood of the ion.

The viscosity of a dilute electrolyte solution was equated to that of the solvent plus contributions from four other sources in the following manner:-

$$\eta = \eta^{\circ} + \eta^{*} + \eta^{\text{E}} + \eta^{\text{A}} + \eta^{\text{D}} \quad (3.12)$$

where  $\eta^{\circ}$  represented the viscosity of the pure solvent,  $\eta^{*}$  represented the effect on the viscosity of the coulombic attraction between the ions,  $\eta^{\text{E}}$  represented the viscosity increment arising from shape and size effects (of the solute),  $\eta^{\text{A}}$  was the effect due to the alignment of polar molecules by the ionic field and  $\eta^{\text{D}}$  the viscosity change due to the disruption of the solvent structure.

Substitution into the Jones-Dole equation (3.7) gave

$$\eta^{*} + \eta^{\text{E}} + \eta^{\text{A}} + \eta^{\text{D}} = \eta^{\circ}(A\sqrt{c} + Bc) \quad (3.13)$$

and elimination of the ionic interaction from both sides led to

$$\eta^{\text{E}} + \eta^{\text{A}} + \eta^{\text{D}} = \eta^{\circ}Bc \quad (3.14)$$

At a given concentration the B coefficient could therefore be interpreted in terms of a competition between these specialised viscosity effects. Small and highly charged cations such as  $\text{Li}^{+}$  and  $\text{Mg}^{2+}$  were considered to strongly orientate water molecules to the extent that they are regarded as having a primary sheath of firmly attached molecules which move with them as a kinetic entity (see Nightingale<sup>79</sup>) and  $\eta^{\text{E}}$  was therefore considered to be large because the ion and its solvation sheath could be considered as a single particle. At room temperature for these ions it is possible that water molecules beyond the first layer would be orientated to some extent to give a positive  $\eta^{\text{A}}$ . It was suggested that the



sum of  $\eta^A$  and  $\eta^E$  would far outweigh the decrease due to  $\eta^D$  which for these ions was considered to be small because the fixed outward pointing hydrogen atoms which were considered to fit reasonably well into the tetrahedral water structure. For this class of ions therefore  $\eta^E + \eta^A \gg \eta^D$  and B would be fairly large and positive.

By a similar argument Stokes and Mills concluded that ionic B coefficients for the large ions in any group of the periodic table would be negative because for them both  $\eta^E$  (because of the relatively weak surface charge density these ions were considered to be "bare") and  $\eta^A$  would be smaller than for small highly charged ions while  $\eta^D$  would be great. For this class therefore it was probable that  $\eta^E + \eta^A < \eta^D$ .

Ions of intermediate size were considered to have small ionic B coefficients because  $\eta^E + \eta^A \approx \eta^D$  (eg  $K^+$ ) while large molecular ions such as tetraalkylammonium ions were expected to have large  $\eta^E$  because of their size.  $\eta^A$  and  $\eta^D$  were considered small and therefore  $\eta^E + \eta^A > \eta^D$  and again the ionic B coefficients would be positive and large.

These terms were then used to explain the temperature dependence of the ionic B coefficients. As discussed before, negative ionic B coefficients have, associated with them, fairly large  $\eta^D$ . As the temperature is raised  $\eta^D$  becomes smaller although  $\eta^E$  would remain constant and  $\eta^A$  might also fall. Eventually  $\eta^A + \eta^E$  might exceed  $\eta^D$  and B would become positive (as was found for  $K^+$  by Kaminsky<sup>68</sup>).

The negative temperature coefficient of B for small, highly charged ions, was also explained by associating a large  $\eta^A$  with orientation of solvent beyond the first layer. With increased thermal motion  $\eta^A$  was considered to decrease and therefore result in an ionic B coefficient still positive, but smaller.

### 3.5 RESULTS AND DISCUSSION

B coefficients have been measured in many non-aqueous solvents. With the exception of the highly associated solvents, glycerol, some dihydric alcohols, and sulphuric acid they have all been found to be positive. In other associated solvents such as the alcohols and N-methylamides the fact that only positive B coefficients have been detected has been attributed to the linear nature of the association of these molecules. In other words negative B coefficients have only been found in solvents which are capable of forming three dimensional aggregates by hydrogen bonding.

Formamide, which is known to be an associated solvent, has the ability to form three hydrogen bonds per molecule. It is a good electrolytic solvent (with a dielectric constant greater than water) and is thus a very interesting medium for the study of electrochemical processes<sup>37</sup>. Because of the possibility of association in three dimensions it would seem possible that important structure breaking effects might be present when salts are dissolved in formamide, and that these could lead to small or even negative values of the B coefficient.

The relative viscosities of solutions of LiCl, LiBr, NaCl, NaBr, KCl and KBr in formamide were measured at 298.15 K over the concentration range 0.005 to 0.1 molal. The relative viscosities of the latter four salts were also measured at 308.16, 318.15 and 323.15 K. From the Jones-Dole equation

$$\eta = 1 + A\sqrt{c} + Bc$$

$\frac{\eta-1}{\sqrt{c}}$  was plotted against  $\sqrt{c}$  to give the B coefficient. The B coefficients were calculated by computer using the method of least squares.  $\eta^{-1}$  is called the specific viscosity ["ETA SP." in figures (3.4-3.12)]. Fig. (3.4) shows the Jones-Dole plot for

LiCl and LiBr at 298.15 K, figs. (3.5-3.8) show similar plots for the other four salts at the temperatures 298.15, 308.15, 318.15 and 323.15 K respectively. In all the graphs and tables the temperature was Kelvin and the concentration in molality. The next set of graphs, figs. (3.9-3.12) shows the Jones-Dole plots for each salt at all temperatures.

Tables (3.1-3.10) list the data used to plot the above graphs where  $X = \frac{\eta - 1}{\sqrt{c}}$ ,  $Y = \sqrt{c}$ , Y CALC is the value of Y recalculated for the best straight line determined by the method of least squares and the DEVIATION is defined as (Y-Y CALC).

The first set of tables (3.1-3.6) combines all earlier measurements which were made at 298.15 K for each system. The second set, tables (3.7-3.10), shows the values used in figs. (3.5-3.12). Table (3.12) gives the calculated slopes and intercepts from figs. (3.4-3.8) and hence the Jones-Dole B coefficients. The B coefficients for 298.15 K were calculated by considering all the measurements made at this temperature, see table (3.13).

TABLE 3.13

Calculated B coefficients in formamide

	298.15 K	308.15 K	318.15 K	323.15 K
LiCl	0.54 <sub>7</sub>			
LiBr	0.60 <sub>4</sub>			
NaCl	0.59 <sub>4</sub>	0.539	0.497	0.487
NaBr	0.56 <sub>0</sub>	0.534	0.488	0.468
KCl	0.40 <sub>4</sub>	0.389	0.376	0.359
KBr	0.37 <sub>8</sub>	0.340	0.341	0.345

Table (3.11) brings together the gradients and intercepts calculated for all the salts from the data in tables (3.1-3.6).

Key to Figs. (3.4) to (3.12)

Fig. (3.4)	△	Represents lithium chloride.
	⊗	Represents lithium bromide .
Figs. (3.5-3.8)	⊗	Represents sodium chloride .
	□	Represents sodium bromide .
	△	Represents potassium chloride.
	⊗	Represents potassium bromide.
Figs. (3.9-3.12)	⊗	Represents 298.15 K .
	△	Represents 308.15 K .
	□	Represents 318.15 K .
	⊗	Represents 323.15 K .

Table 3.1	Early data	LiCl at 298.15 K .
Table 3.2	Early data	LiBr at 298.15 K .
Table 3.3	Early data	NaCl at 298.15 K .
Table 3.4	Early data	NaBr at 298.15 K .
Table 3.5	Early data	KCl at 298.15 K .
Table 3.6	Early data	KBr at 298.15 K .

DATA used for figs. (3.9) to (3.12)

Table 3.7	NaCl at four temperatures .
Table 3.8	NaBr at four temperatures .
Table 3.9	KCl at four temperatures .
Table 3.10	KBr at four temperatures .

Fig.(3.4)

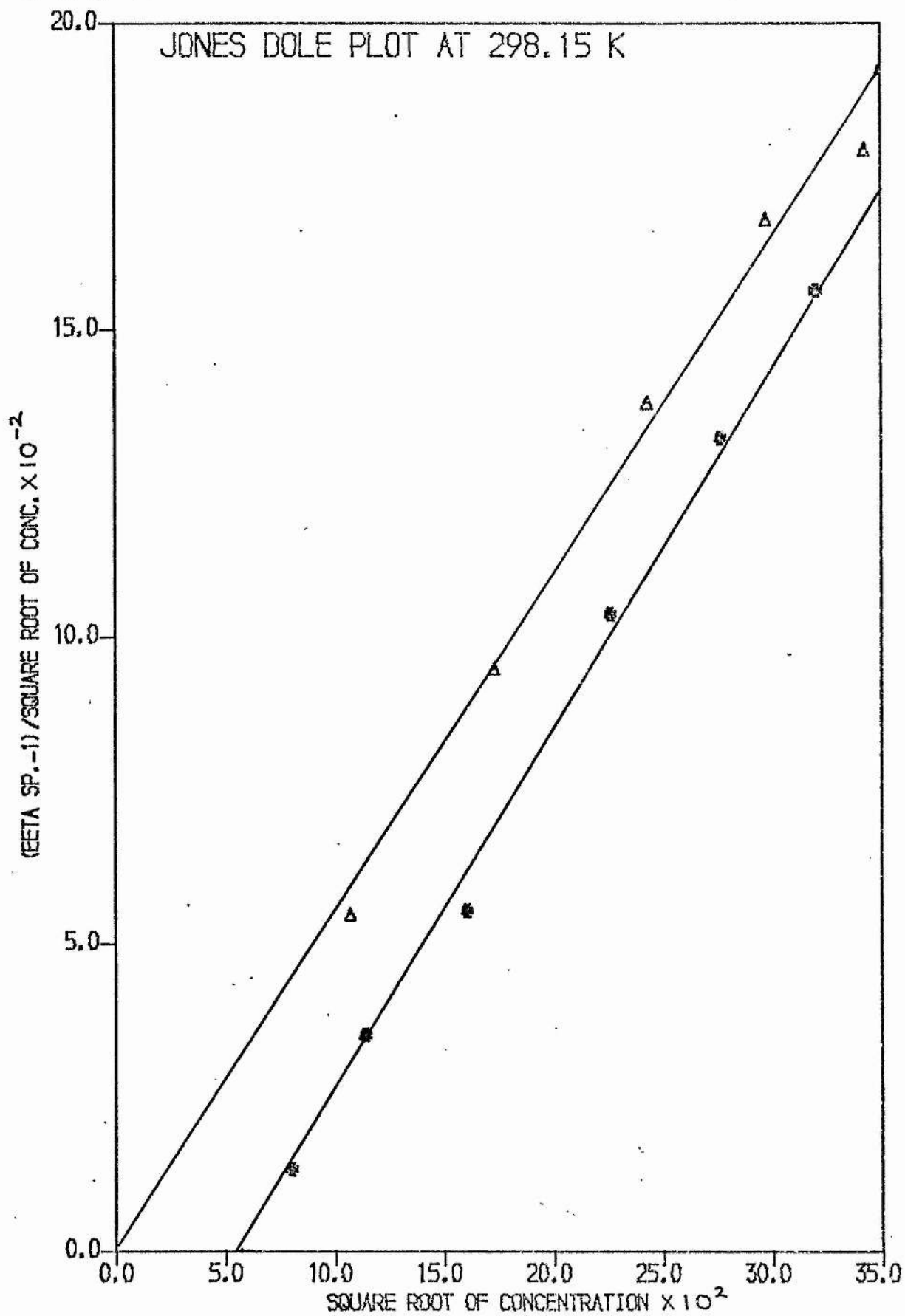


Fig.(3.5)

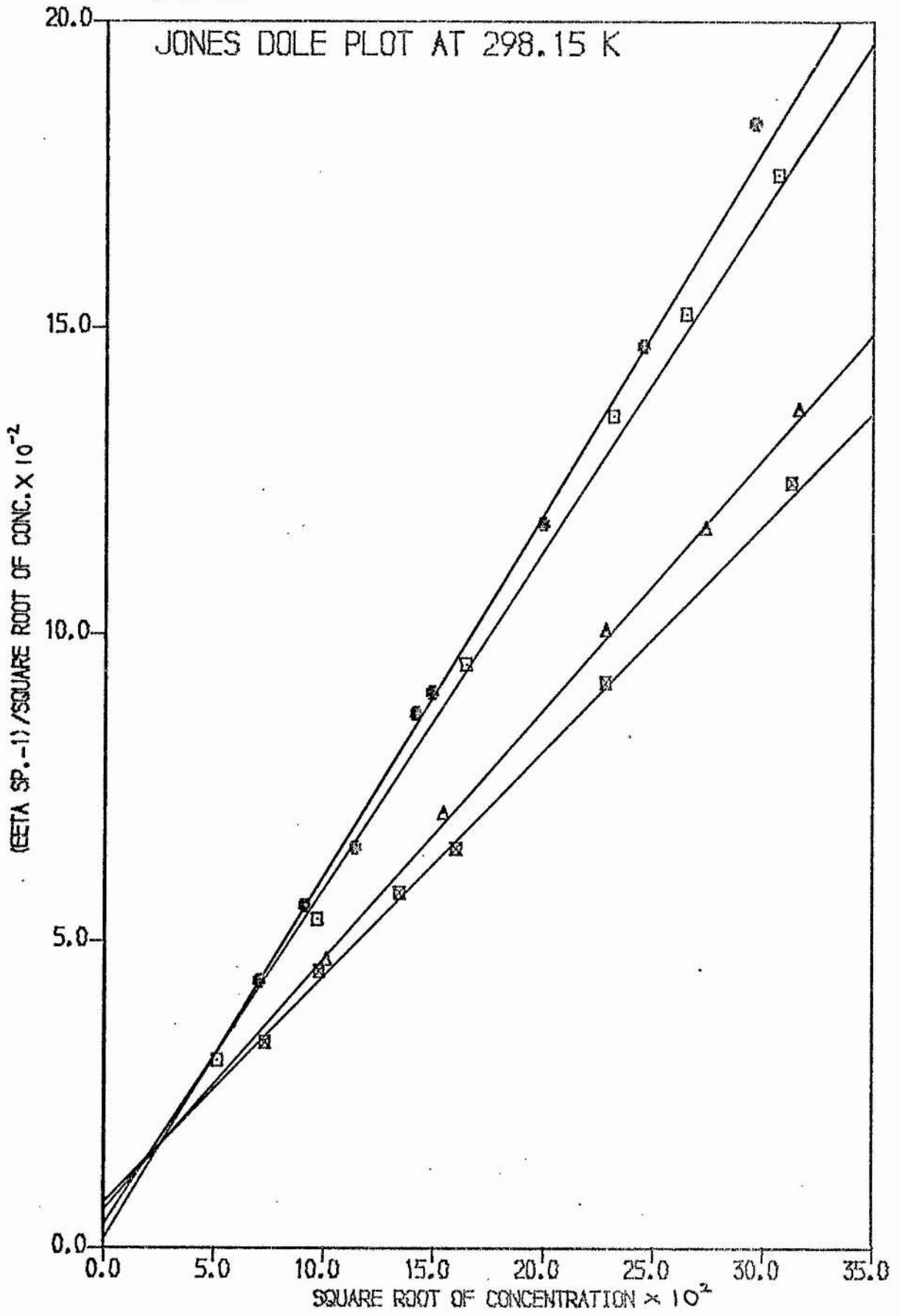


Fig.(3.6)

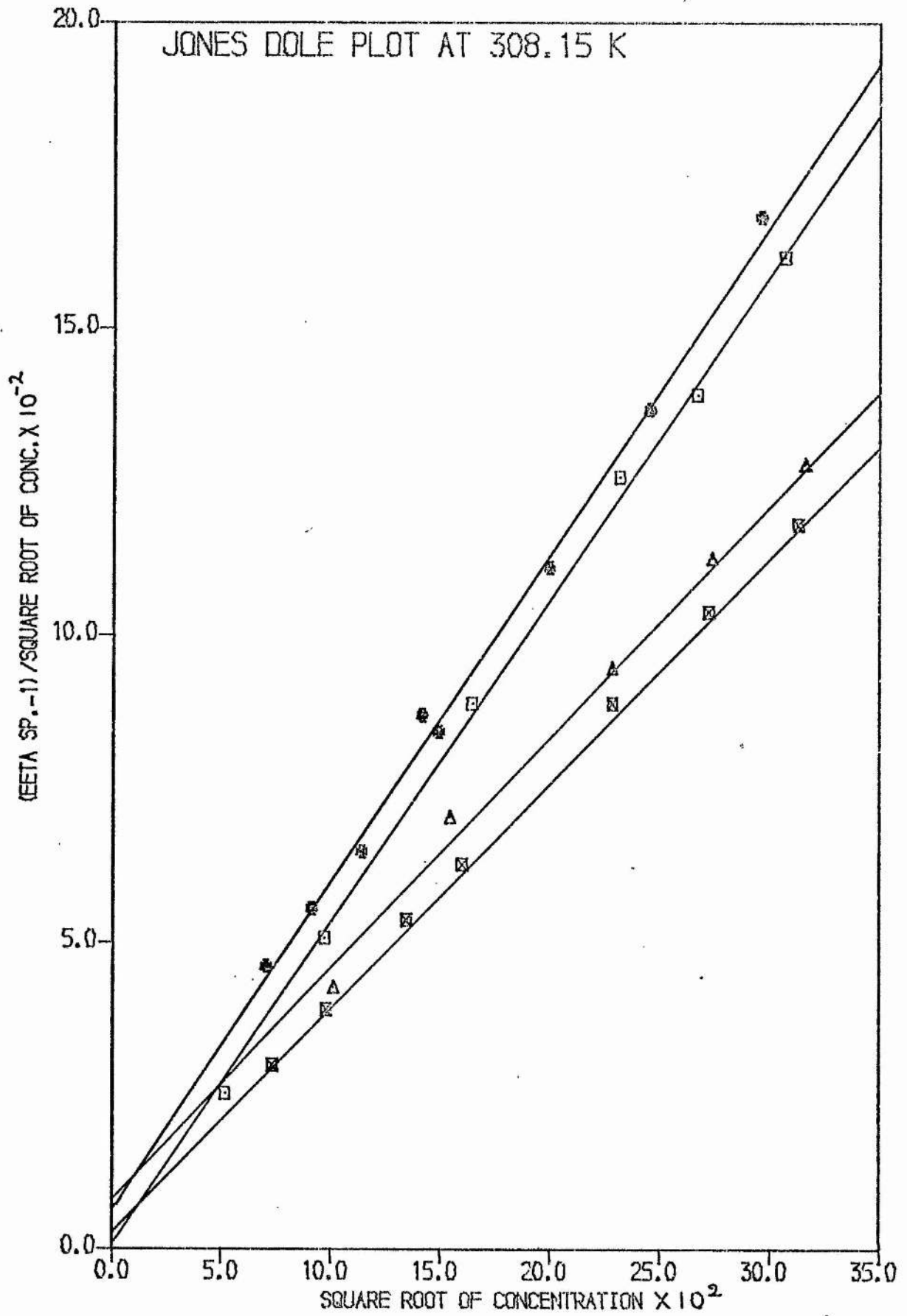


Fig.(3.7)

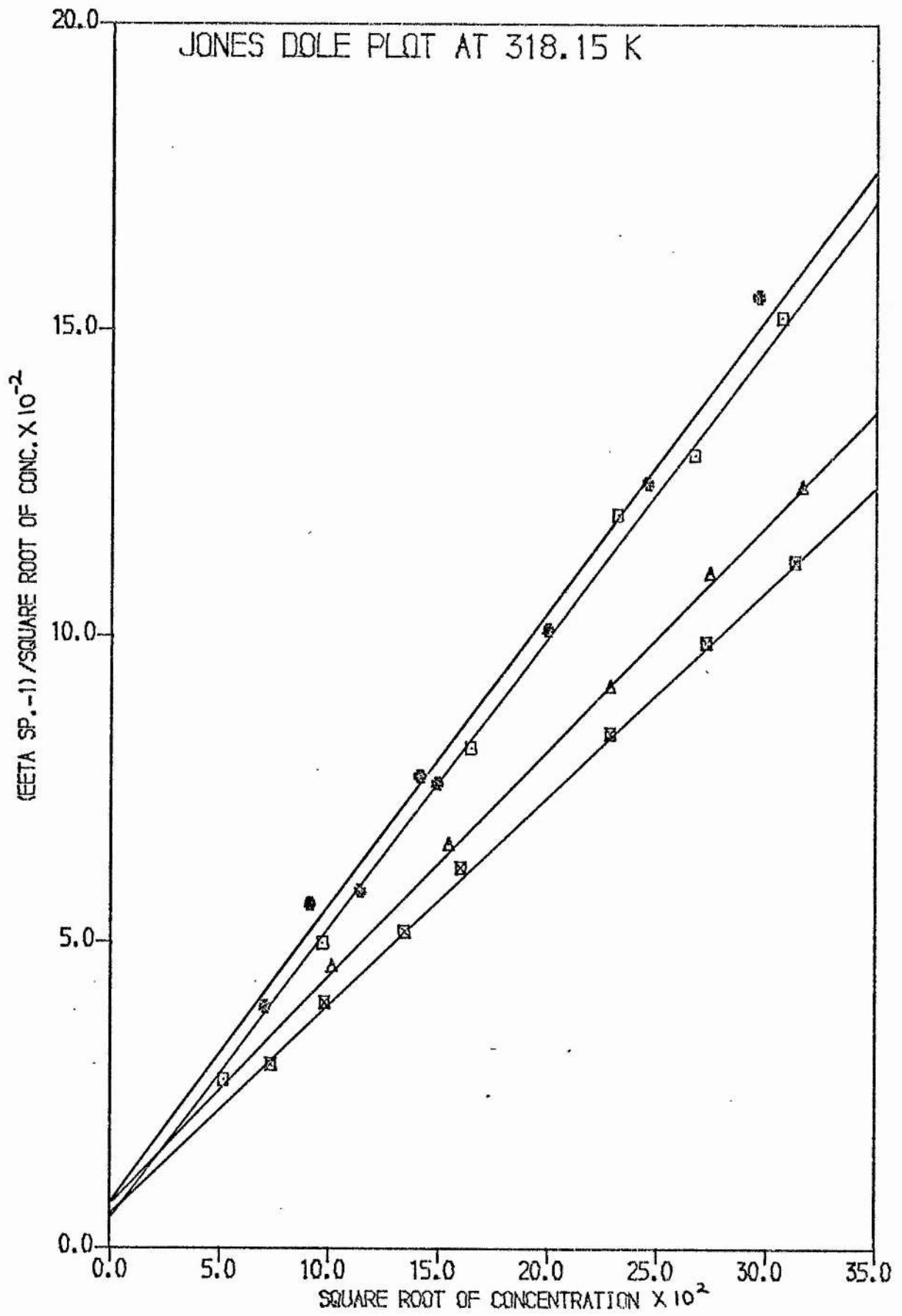




Fig.(3.8)

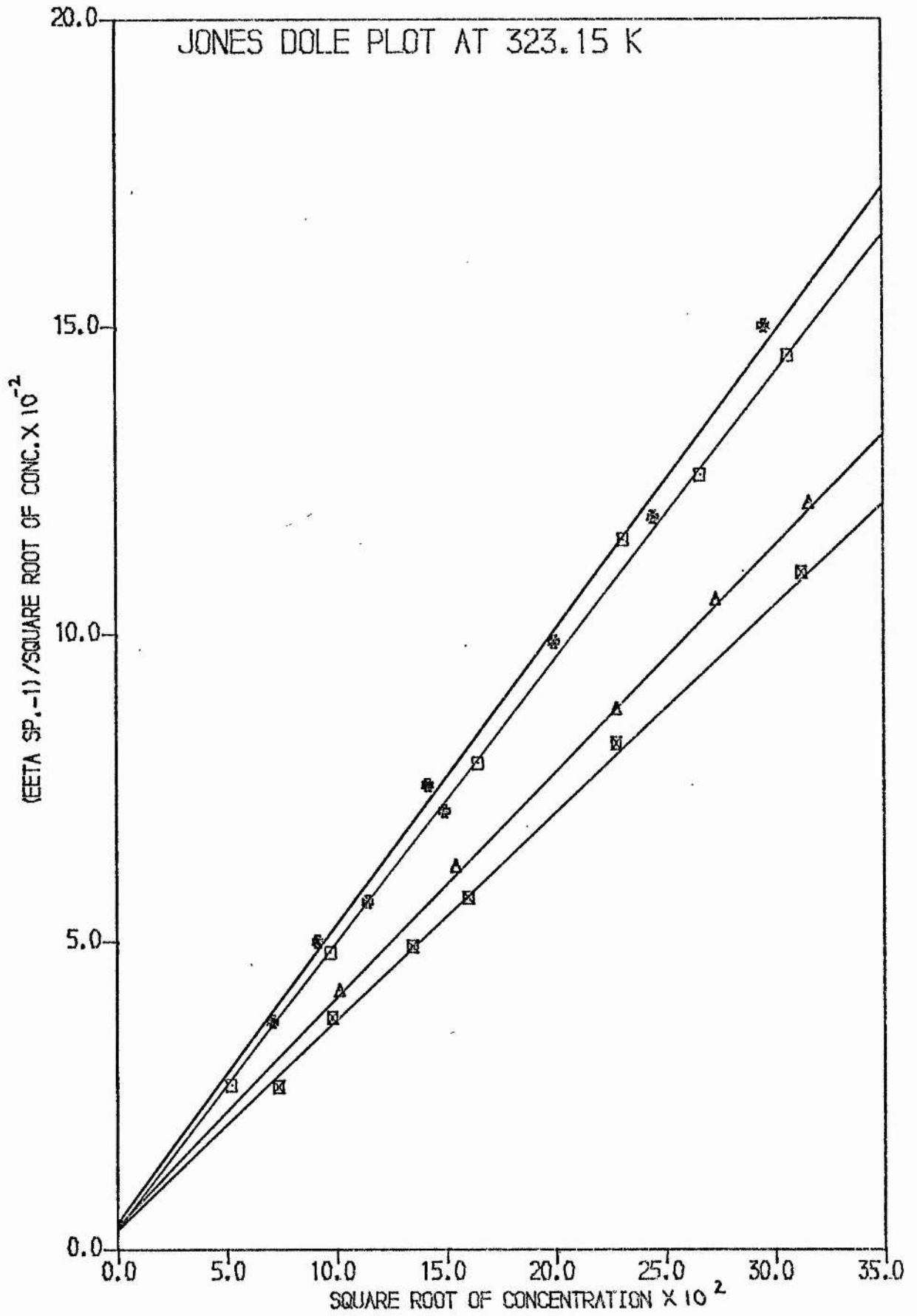


Fig.(3.9)

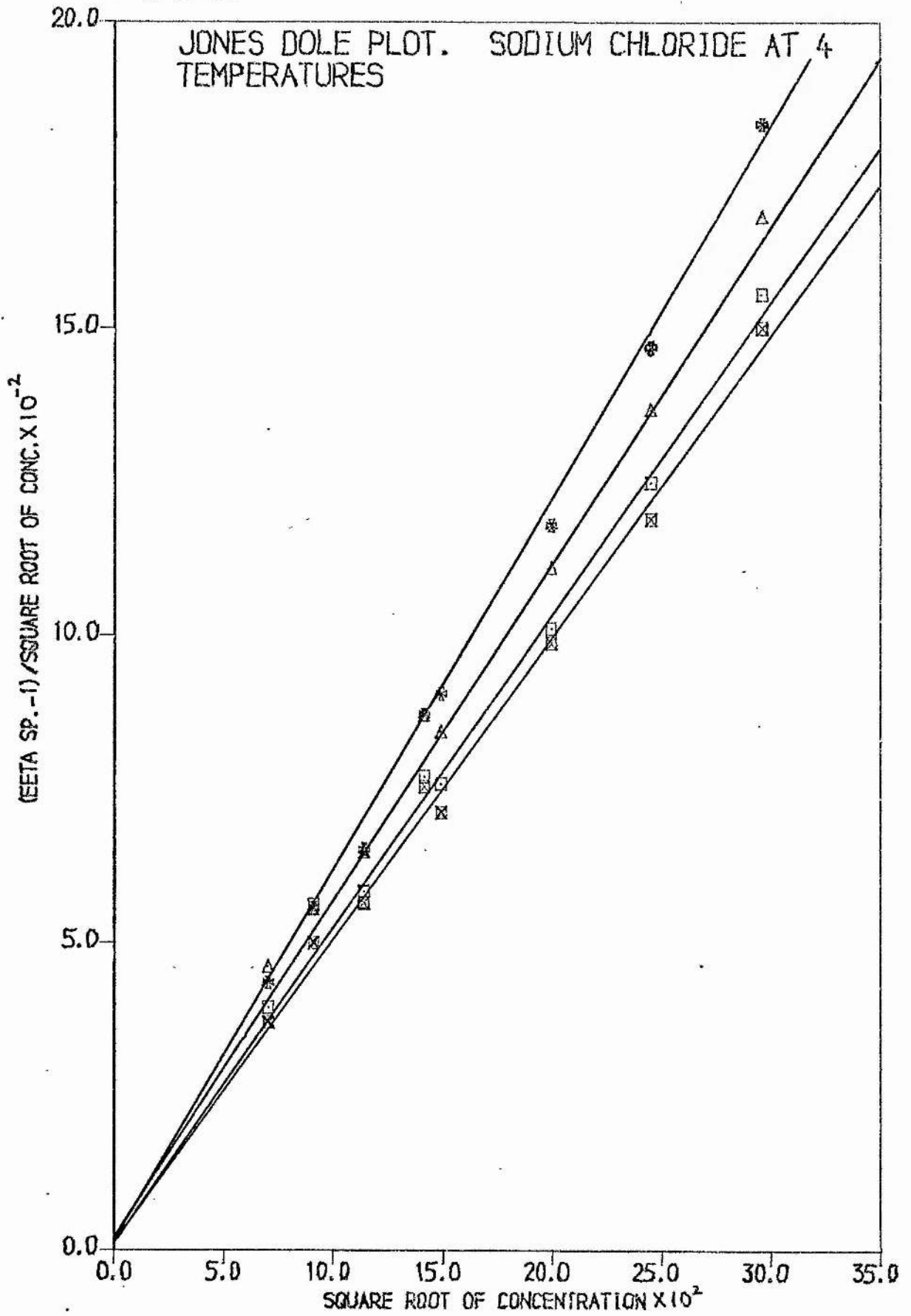


Fig.(3.10)

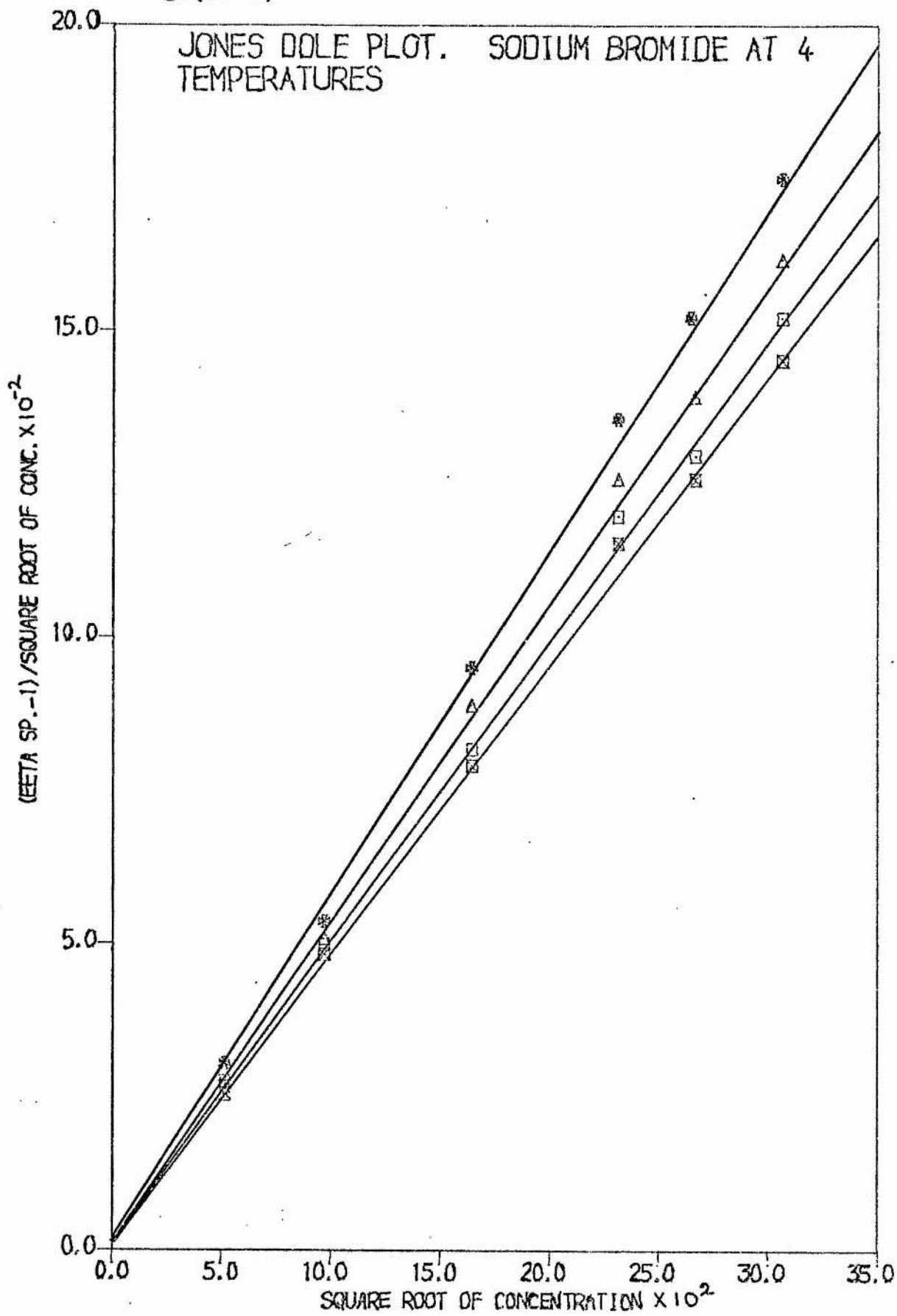
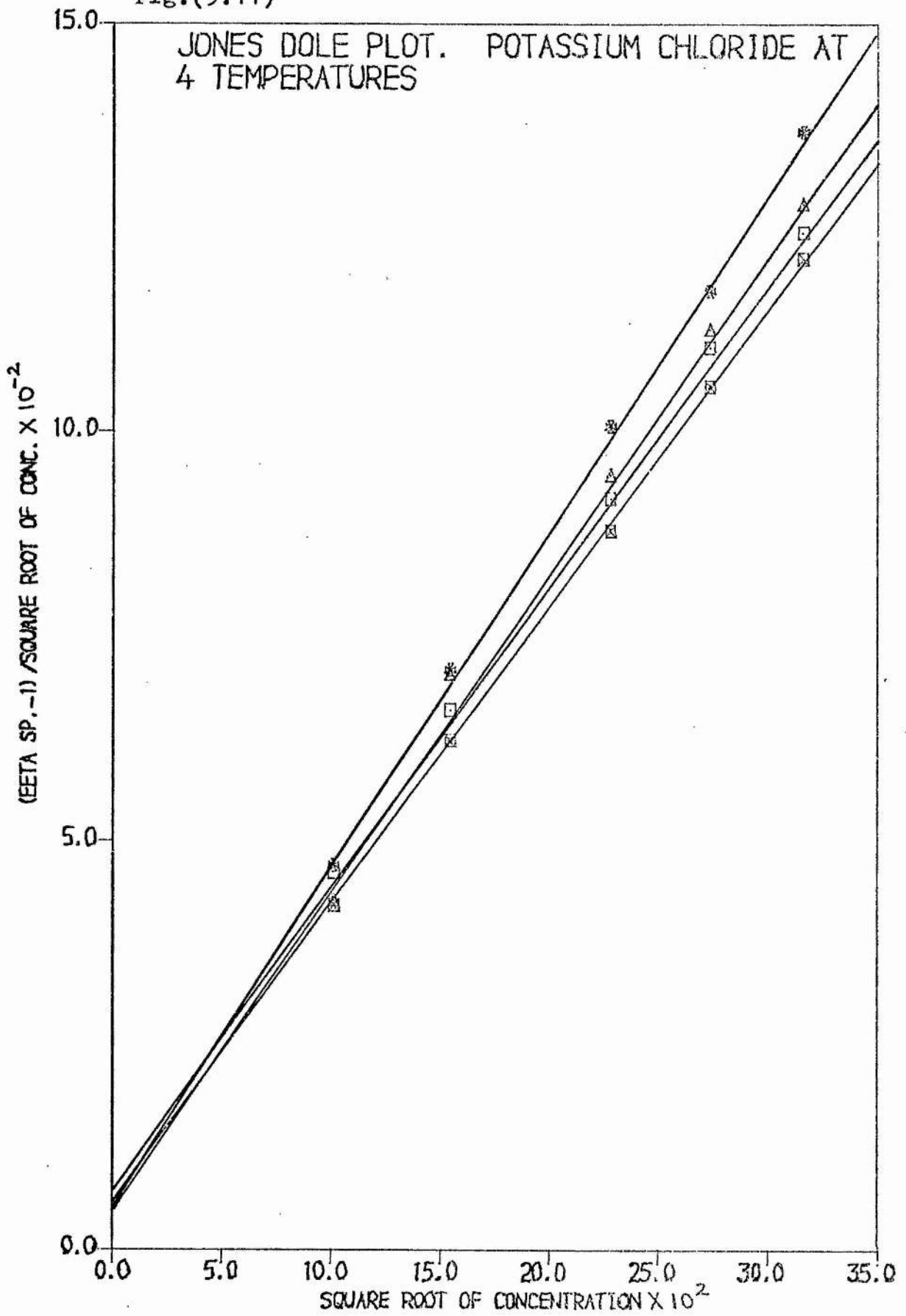


Fig.(3.11)



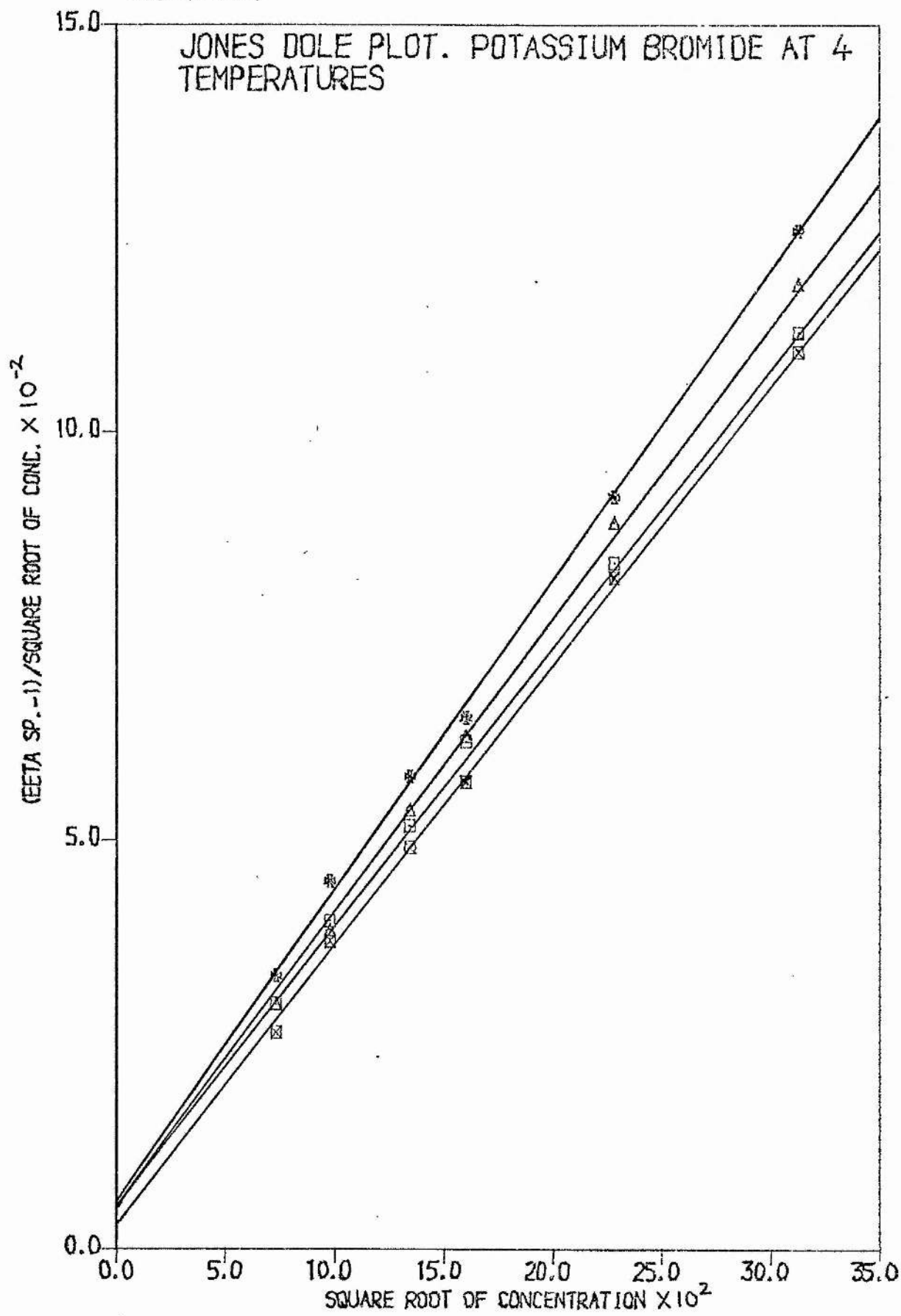


Table 3.1

X	Y	YCALC	DEVIATION
.342100E 00	.179420E 00	.187158E 00	-0.7738E-02
.297100E 00	.168100E 00	.162537E 00	0.5563E-02
.242800E 00	.138200E 00	.132828E 00	0.5372E-02
.172670E 00	.949500E-01	.944572E-01	0.4928E-03
.107100E 00	.548900E-01	.585818E-01	-0.3692E-02

Table 3.2

.320070E 00	.156400E 00	.157712E 00	-0.1312E-02
.276100E 00	.132440E 00	.131132E 00	0.1308E-02
.225900E 00	.103850E 00	.100786E 00	0.3064E-02
.160400E 00	.554800E-01	.611908E-01	-0.5711E-02
.113930E 00	.351800E-01	.330994E-01	0.2081E-02
.803000E-01	.133400E-01	.127699E-01	0.5701E-03

Table 3.3

.295700E 00	.183340E 00	.177880E 00	0.5459E-02
.245000E 00	.147040E 00	.147780E 00	-0.7397E-03
.199400E 00	.118020E 00	.120707E 00	-0.2687E-02
.149000E 00	.905700E-01	.907840E-01	-0.2140E-03
.141400E 00	.871600E-01	.862718E-01	0.8882E-03
.114000E 00	.652100E-01	.700043E-01	-0.4794E-02
.911000E-01	.557800E-01	.564085E-01	-0.6285E-03
.705000E-01	.435100E-01	.441782E-01	-0.6682E-03
.986500E-01	.595100E-01	.608910E-01	-0.1381E-02
.876999E-01	.513000E-01	.543899E-01	-0.3090E-02
.318800E-01	.212300E-01	.212493E-01	-0.1932E-04
.209000E-01	.156100E-01	.147304E-01	0.8796E-03
.153000E-01	.171400E-01	.114057E-01	0.5734E-02
.102000E-01	.122500E-01	.837779E-02	0.3872E-02
.274000E-01	.175000E-01	.185895E-01	-0.1090E-02
.315000E-01	.195000E-01	.210237E-01	-0.1524E-02

Table 3.4

.335900E 00	.192100E 00	.192048E 00	0.5180E-04
.287700E 00	.163600E 00	.165079E 00	-0.1479E-02
.235500E 00	.135800E 00	.135871E 00	-0.7099E-04
.173100E 00	.102000E 00	.100956E 00	0.1044E-02
.102400E 00	.649300E-01	.613969E-01	0.3533E-02
.301200E 00	.174400E 00	.172632E 00	0.1768E-02
.245200E 00	.138210E 00	.141298E 00	-0.3088E-02
.191000E 00	.113100E 00	.110972E 00	0.2128E-02
.146000E 00	.836000E-01	.857926E-01	-0.2193E-02
.911000E-01	.590900E-01	.550742E-01	0.4016E-02
.739999E-01	.462700E-01	.455061E-01	0.7639E-03
.306500E 00	.174900E 00	.175598E 00	-0.6979E-03
.264400E 00	.152260E 00	.152041E 00	0.2185E-03
.231400E 00	.135670E 00	.133577E 00	0.2093E-02
.164200E 00	.951200E-01	.959761E-01	-0.8562E-03
.969400E-01	.536000E-01	.583418E-01	-0.4742E-02
.516700E-01	.305300E-01	.330117E-01	-0.2482E-02

Table 3.5

X	Y	YCALC	DEVIATION
.316000E 00	.136800E 00	.135583E 00	0.1217E-02
.273400E 00	.117410E 00	.118229E 00	-0.8186E-03
.228100E 00	.100780E 00	.997738E-01	0.1006E-02
.154240E 00	.709700E-01	.696841E-01	0.1286E-02
.101180E 00	.470600E-01	.480681E-01	-0.1008E-02
.309780E 00	.132350E 00	.133049E 00	-0.6994E-03
.269070E 00	.111970E 00	.116465E 00	-0.4495E-02
.219750E 00	.902600E-01	.963721E-01	-0.6112E-02
.152640E 00	.669600E-01	.690323E-01	-0.2072E-02
.968300E-01	.493200E-01	.462960E-01	0.3024E-02
.720000E-01	.314200E-01	.361805E-01	-0.4761E-02
.481500E-01	.278900E-01	.264643E-01	0.1426E-02
.299000E 00	.132660E 00	.128658E 00	0.4002E-02
.261800E 00	.115340E 00	.113503E 00	0.1837E-02
.214400E 00	.944500E-01	.941926E-01	0.2574E-03
.175000E 00	.825100E-01	.781415E-01	0.4368E-02
.128100E 00	.607300E-01	.590350E-01	0.1695E-02
.993000E-01	.429700E-01	.473022E-01	-0.4332E-02
.709000E-01	.399100E-01	.357324E-01	0.4178E-02

Table 3.6

.331000E 00	.131810E 00	.131385E 00	0.4253E-03
.290000E 00	.114110E 00	.115902E 00	-0.1792E-02
.235800E 00	.976599E-01	.954352E-01	0.2225E-02
.166800E 00	.682400E-01	.693794E-01	-0.1139E-02
.119900E 00	.517300E-01	.516692E-01	0.6082E-04
.804999E-01	.365800E-01	.367910E-01	-0.2110E-03
.312600E 00	.124740E 00	.124436E 00	0.3036E-03
.271700E 00	.109310E 00	.108992E 00	0.3182E-03
.228100E 00	.921600E-01	.925276E-01	-0.3676E-03
.159700E 00	.650400E-01	.666984E-01	-0.1658E-02
.134300E 00	.578500E-01	.571069E-01	0.7431E-03
.979000E-01	.450600E-01	.433616E-01	0.1698E-02
.732300E-01	.334400E-01	.340457E-01	-0.6057E-03

Table 3.7 298.15K

X	Y	YGALC	DEVIATION
.295700E 00	.183340E 00	.180242E 00	0.3098E-02
.245000E 00	.147040E 00	.149075E 00	-0.2035E-02
.199400E 00	.118020E 00	.121044E 00	-0.3024E-02
.149000E 00	.905700E-01	.900611E-01	0.5089E-03
.141400E 00	.871600E-01	.853891E-01	0.1771E-02
.114000E 00	.652100E-01	.685455E-01	-0.3335E-02
.911000E-01	.557800E-01	.544681E-01	0.1312E-02
.705000E-01	.435100E-01	.418046E-01	0.1705E-02

308.15K

.295700E 00	.168280E 00	.165750E 00	0.2530E-02
.245000E 00	.136940E 00	.138401E 00	-0.1461E-02
.199400E 00	.111130E 00	.113802E 00	-0.2672E-02
.149000E 00	.843900E-01	.866147E-01	-0.2225E-02
.141400E 00	.870799E-01	.825150E-01	0.4565E-02
.114000E 00	.649000E-01	.677344E-01	-0.2834E-02
.911000E-01	.556000E-01	.553812E-01	0.2188E-03
.705000E-01	.461500E-01	.442688E-01	0.1881E-02

318.15K

.295700E 00	.155550E 00	.151989E 00	0.3560E-02
.245000E 00	.125080E 00	.126776E 00	-0.1696E-02
.199400E 00	.101170E 00	.104099E 00	-0.2929E-02
.149000E 00	.759100E-01	.790342E-01	-0.3124E-02
.141400E 00	.771300E-01	.752547E-01	0.1875E-02
.114000E 00	.584000E-01	.616285E-01	-0.3228E-02
.911000E-01	.563000E-01	.502401E-01	0.6060E-02
.705000E-01	.394800E-01	.399955E-01	-0.5155E-03

323.15K

.295700E 00	.150100E 00	.146829E 00	0.3271E-02
.245000E 00	.119070E 00	.122118E 00	-0.3048E-02
.199400E 00	.987900E-01	.998923E-01	-0.1102E-02
.149000E 00	.712399E-01	.753273E-01	-0.4087E-02
.141400E 00	.755100E-01	.716230E-01	0.3887E-02
.114000E 00	.565000E-01	.582683E-01	-0.1768E-02
.911000E-01	.500000E-01	.471068E-01	0.2893E-02
.705000E-01	.370200E-01	.370663E-01	-0.4629E-04



Table 3.8 298.15K

X	Y	YCALC	DEVIATION
.301200E 00	.174400E 00	.172199E 00	0.2200E-02
.245200E 00	.138210E 00	.141308E 00	-0.3098E-02
.191000E 00	.113100E 00	.111409E 00	0.1691E-02
.146000E 00	.836000E-01	.865851E-01	-0.2985E-02
.911000E-01	.590900E-01	.563002E-01	0.2790E-02
.739999E-01	.462700E-01	.468672E-01	-0.5972E-03

308.15K

.306500E 00	.161700E 00	.162887E 00	-0.1187E-02
.266400E 00	.139300E 00	.141486E 00	-0.2186E-02
.231400E 00	.125900E 00	.122807E 00	0.3093E-02
.164200E 00	.889800E-01	.869436E-01	0.2036E-02
.969400E-01	.507600E-01	.510481E-01	-0.2881E-03
.516700E-01	.254200E-01	.268882E-01	-0.1468E-02

318.15K

.306500E 00	.152120E 00	.152211E 00	-0.9072E-04
.266400E 00	.129650E 00	.132629E 00	-0.2979E-02
.231400E 00	.119860E 00	.115537E 00	0.4323E-02
.164200E 00	.817400E-01	.827207E-01	-0.9807E-03
.969400E-01	.497900E-01	.498754E-01	-0.8538E-04
.516700E-01	.275800E-01	.277685E-01	-0.1885E-03

323.15K

.306500E 00	.145190E 00	.146337E 00	-0.1147E-02
.266400E 00	.125870E 00	.127584E 00	-0.1714E-02
.231400E 00	.115380E 00	.111216E 00	0.4164E-02
.164200E 00	.790600E-01	.797885E-01	-0.7285E-03
.969400E-01	.482000E-01	.483334E-01	-0.1334E-03
.516700E-01	.267200E-01	.271623E-01	-0.4423E-03

Table 3.9 298.15K

X	Y	YCALC	DEVIATION
.316000E 00	.136800E 00	.136338E 00	0.4619E-03
.273400E 00	.117410E 00	.118808E 00	-0.1398E-02
.228100E 00	.100780E 00	.100166E 00	0.6139E-03
.154240E 00	.709700E-01	.697718E-01	0.1198E-02
.101180E 00	.470600E-01	.479371E-01	-0.8771E-03

308.15K

.316000E 00	.128000E 00	.129094E 00	-0.1094E-02
.273400E 00	.112670E 00	.112527E 00	0.1427E-03
.228100E 00	.948099E-01	.949109E-01	-0.1010E-03
.154240E 00	.704899E-01	.661882E-01	0.4302E-02
.101180E 00	.427700E-01	.455541E-01	-0.2784E-02
.998800E-01	.444700E-01	.450485E-01	-0.5785E-03
.489400E-01	.253500E-01	.252389E-01	0.1111E-03

318.15K

.316000E 00	.124500E 00	.125595E 00	-0.1095E-02
.273400E 00	.110410E 00	.109572E 00	0.8380E-03
.228100E 00	.919400E-01	.925338E-01	-0.5938E-03
.154240E 00	.660599E-01	.647538E-01	0.1306E-02
.101180E 00	.462000E-01	.447970E-01	0.1403E-02
.489400E-01	.232900E-01	.251486E-01	-0.1859E-02

323.15K

.316000E 00	.121300E 00	.120545E 00	0.7550E-03
.273400E 00	.105650E 00	.105245E 00	0.4048E-03
.228100E 00	.879599E-01	.889756E-01	-0.1016E-02
.154240E 00	.623700E-01	.624487E-01	-0.7869E-04
.101180E 00	.421500E-01	.433921E-01	-0.1242E-02
.998800E-01	.421900E-01	.429252E-01	-0.7352E-03
.489400E-01	.265400E-01	.246300E-01	0.1910E-02

Table 3.10 298.15K

X	Y	YCALC	DEVIATION
.312600E 00	.124740E 00	.124433E 00	0.3074E-03
.271700E 00	.109310E 00	.109008E 00	0.3015E-03
.228100E 00	.921600E-01	.925662E-01	-0.4062E-03
.159700E 00	.650400E-01	.667714E-01	-0.1731E-02
.134300E 00	.578500E-01	.571926E-01	0.6574E-03
.979000E-01	.450600E-01	.434655E-01	0.1594E-02
.732300E-01	.334400E-01	.341620E-01	-0.7220E-03

308.15K

.312600E 00	.118200E 00	.119102E 00	-0.9018E-03
.271700E 00	.103900E 00	.103966E 00	-0.6640E-04
.228100E 00	.890000E-01	.878317E-01	0.1168E-02
.159700E 00	.628000E-01	.625197E-01	0.2803E-03
.134300E 00	.537400E-01	.531202E-01	0.6198E-03
.979000E-01	.390900E-01	.396500E-01	-0.5600E-03
.732300E-01	.299800E-01	.305206E-01	-0.5406E-03

318.15K

.312600E 00	.112250E 00	.112860E 00	-0.6099E-03
.271700E 00	.990400E-01	.989156E-01	0.1244E-03
.228100E 00	.840800E-01	.840507E-01	0.2927E-04
.159700E 00	.621500E-01	.607307E-01	0.1419E-02
.134300E 00	.517600E-01	.520709E-01	-0.3109E-03
.979000E-01	.402000E-01	.396608E-01	0.5392E-03
.732300E-01	.300600E-01	.312499E-01	-0.1190E-02

323.15K

.312600E 00	.109900E 00	.110511E 00	-0.6105E-03
.228100E 00	.822500E-01	.813226E-01	0.9274E-03
.159700E 00	.571700E-01	.576961E-01	-0.5261E-03
.134300E 00	.491900E-01	.489224E-01	0.2676E-03
.979000E-01	.376400E-01	.363492E-01	0.1291E-02
.732300E-01	.264800E-01	.278277E-01	-0.1348E-02

TABLE 3.11

Gradients and intercepts obtained from a least squares plot of Jones-Dole data [tables (3.1-3.6)] at 298.15 K.

SALT	GRADIENT	INTERCEPT	RMS DEVIATION
NaCl	0.594	0.0023	0.0024
KCl	0.404	0.0065	0.0025
NaBr	0.560	0.0041	0.0020
KBr	0.378	0.0064	0.0011
LiCl	0.547	0.0000	0.0045
LiBr	0.605	-0.0358	0.0025

TABLE 3.12

Gradients and intercepts obtained from a least squares plot of the Jones-Dole data, tables (3.7-3.10).

SALT	TEMPERATURE	GRADIENT	INTERCEPT	RMS DEVIATION
NaCl	298.15	0.615	-0.0015	0.0019
	308.15	0.539	0.0062	0.0023
	318.15	0.497	0.0049	0.0029
	323.15	0.487	0.0027	0.0027
KCl	298.15	0.412	0.0063	0.0009
	308.15	0.389	0.0062	0.0019
	318.15	0.376	0.0067	0.0012
	323.15	0.359	0.0071	0.0010
NaBr	298.15	0.575	0.0000	0.0013
	308.15	0.534	-0.0007	0.0017
	318.15	0.488	0.0025	0.0020
	323.15	0.468	0.0030	0.0017
KBr	298.15	0.377	0.0065	0.0009
	308.15	0.370	0.0034	0.0006
	318.15	0.341	0.0063	0.0007
	323.15	0.345	0.0025	0.0008

Table (3.14) compares the B coefficients at 298.15 K with those obtained by Notley and Spiro<sup>80</sup> from viscosity measurements at concentrations of approximately 0.1 and 0.25 molal performed in 1915 by Davis et al.<sup>81</sup>.

TABLE 3.14

B coefficients in formamide

SALT	B this work	B ref. 80
LiCl	0.54 <sub>7</sub>	0.54
LiBr	0.60 <sub>5</sub>	0.49
NaCl	0.59 <sub>4</sub>	0.56
NaBr	0.56 <sub>0</sub>	0.51
KCl	0.40 <sub>4</sub>	0.38
KBr	0.37 <sub>8</sub>	0.33

Apart from the fact that they had only two experimental measurements for each salt, the concentrations were rather high for valid application of the Jones-Dole equation and the viscosity of the pure solvent in Davis' measurements was found to vary from 0.003194 to 0.003388 kg m<sup>-1</sup> s<sup>-1</sup>. The accuracy of these results is not therefore considered to be very high. In spite of this, Notley and Spiro attempted to divide the B coefficient into separate ionic contributions. Although they do not state how this division was made, it would appear that they considered the contributions of the Cs<sup>+</sup> and Cl<sup>-</sup> ions to the B coefficient to be almost identical, as had been suggested by Nightingale<sup>79</sup> for aqueous solution. Thus from the B coefficient for CsCl of 0.41 they attributed ionic B coefficients of 0.21 and 0.20 to the Cs<sup>+</sup> and Cl<sup>-</sup> ions respectively. Table (3.15) gives their ionic B coefficients of interest to the present work.

There are two basic ways of approaching the division into ionic B coefficients, the theoretical approach and the experimental approach. The method used by Cox and Wolfenden<sup>67</sup>, based on the theory of

TABLE 3.15

Ionic B coefficients calculated by Nightingale<sup>79</sup> from the measurements of Davis et al<sup>81</sup>

ion	B
Li <sup>+</sup>	0.34
Na <sup>+</sup>	0.36
K <sup>+</sup>	0.18
Cl <sup>-</sup>	0.20
Br <sup>-</sup>	0.15

Stokes' Law and the Stokes-Einstein relationship was discussed on page 47. On the other hand the method of Gurney<sup>14</sup> for aqueous solutions was based on experimental evidence which was already available for the individual ions. He considered that the plot of the temperature variation of ionic mobilities against equivalent conductivities provided evidence to suggest that the effects of K<sup>+</sup> and Cl<sup>-</sup> ions in aqueous solution were very similar and that the B coefficient for KCl could therefore be equally divided between the two ions. It should be noted that ionic B coefficients calculated by each of the above methods for aqueous solutions were identical within experimental error.

Since information on transport numbers in formamide is only available at one temperature<sup>80</sup> the approach to the splitting of the B coefficients followed here was that of Cox and Wolfenden. The ratio of the ionic mobilities of Na<sup>+</sup> and Cl<sup>-</sup> ions in solution in formamide is 10.1:17.1<sup>80</sup>. From Stokes' Law, therefore, the radius of the solvated sodium ion is therefore 70% greater than that of the solvated Cl<sup>-</sup> ion. This gives a volume ratio for the two solvated ions Na<sup>+</sup>:Cl<sup>-</sup> of 4.28:1. From this result the B coefficient of NaCl was split into two ionic contributions,

$$\begin{aligned}
 B \text{ NaCl} &= 0.594 \\
 \therefore B \text{ Na}^+ &= 0.594 \times \frac{4.82}{1.00 + 4.82} \\
 &= 0.492 \\
 B \text{ Cl}^- &= 0.594 \times \frac{1.00}{1.00 + 4.82} \\
 &= 0.102
 \end{aligned}$$

and from these values the others were readily obtained. Table (3.16) compares the values obtained in this study with those obtained by Notley and Spiro in formamide at 298.15 K and those for the same ions in water at the same temperature<sup>68</sup>.

As was mentioned earlier there is no information on transference numbers in formamide at temperatures other than 298.15 K. A splitting of the B coefficients obtained at other temperatures therefore becomes rather arbitrary.

TABLE 3.16

Ionic B coefficients in formamide and water

Ion	Formamide <sup>80</sup>	Formamide (this work)	Water <sup>68</sup>
Na <sup>+</sup>	0.36	0.49 <sub>2</sub>	0.0863
K <sup>+</sup>	0.18	0.30 <sub>2</sub>	-0.007
Cl <sup>-</sup>	0.20	0.10 <sub>2</sub>	-0.007
Br <sup>-</sup>	0.15	0.06 <sub>8</sub>	-0.032

It can be seen by inspection of table (3.16) that all of the ions investigated here have positive B coefficients for all measurements. For the Cl<sup>-</sup> ion the value at 298.15 K is quite large compared with the value in water. This might indicate that for the Cl<sup>-</sup> ion in formamide the structure making influences are relatively greater than the structure breaking influences. In water Cl<sup>-</sup> ion is considered to be a net structure breaker. This is because (i) at

certain temperatures the ionic B coefficient is negative and (ii) the temperature coefficient of the ionic B coefficient,  $\frac{dB}{dT}$ , is positive<sup>68</sup>, table (3.17).

TABLE 3.17

Ionic B coefficients of chloride ion in water

Cl <sup>-</sup> 68	288 K	298 K	308 K	315.5 K
	-0.0200	-0.0070	+0.0049	+0.0121

Kaminsky pointed out that anions do not exhibit negative temperature dependence of the ionic B coefficient in water and it is assumed that this is also true for formamide. In water the decrease in B for Cl<sup>-</sup> over the temperature range 288.0 - 315.5 K is very small, ie less than 0.04. Since for the Cl<sup>-</sup> ion in formamide the structure breaking effects are relatively less important than the structure making effects (compared with the situation for the Cl<sup>-</sup> ion in water), it is proposed that the ionic B coefficient for Cl<sup>-</sup> in formamide must drop by less than 0.04 over the temperature range 298-323 K. This would make any real drop in B for Cl<sup>-</sup> undetectable because the accuracy of the measurements is not greater than  $\pm 0.01$ . In spite of some evidence (see later) which confirms that the Cl<sup>-</sup> ion in formamide has some structure breaking influence,  $\frac{dB}{dT}$  is taken as zero for Cl<sup>-</sup> ion in formamide. From this, the other ionic B coefficients are readily available see table (3.18).

TABLE 3.18

Ionic B coefficients in formamide

	298.15 K	308.15 K	318.15 K	323.15 K
Na <sup>+</sup>	0.49 <sub>2</sub>	0.43 <sub>7</sub>	0.39 <sub>5</sub>	0.38 <sub>5</sub>
K <sup>+</sup>	0.30 <sub>2</sub>	0.28 <sub>7</sub>	0.27 <sub>4</sub>	0.25 <sub>7</sub>
Cl <sup>-</sup>	0.10 <sub>2</sub>	0.10 <sub>2</sub>	0.10 <sub>2</sub>	0.10 <sub>2</sub>
Br <sup>-</sup>	0.06 <sub>8</sub>	0.09 <sub>7</sub>	0.09 <sub>3</sub>	0.08 <sub>3</sub>



The fact that the  $\text{Br}^-$  ion has a smaller ionic B coefficient than the  $\text{Cl}^-$  ion at 298.15 K indicates that for  $\text{Br}^-$  in formamide more "structure breaking" of the solvent takes place than for the  $\text{Cl}^-$  ion. As the temperature is increased the ionic B coefficient of  $\text{Br}^-$  increases and then remains almost constant. This supports the suggestion that  $\text{Br}^-$  is to some extent a structure breaking ion.

It has been suggested by Neng-Ping Yao and Bennion<sup>82</sup> that the viscosity B coefficients are approximately related to the Einstein volume fraction according to the equation

$$B = 2.5 \frac{\phi}{c} = 2.5 \frac{4}{3} \pi \frac{r_+^3}{1000} N \quad (3.15)$$

where B is the ionic B coefficient,  $\phi$  is the volume fraction of the solute particles in cubic centimeters of solute/cubic centimeters of solution,  $r_+$  is the effective radius for a spherical ion, and N is Avogadro's number, and these authors used the above relationship to calculate the effective radii of a number of ions in dimethylsulphoxide from the ionic B coefficients. Nightingale<sup>79</sup> showed that there was indeed a relationship between the ionic B coefficients and the ionic hydrated radii but he stressed that the relationship was not to be confused with the Einstein relation which is only applicable for ions whose radii are large compared with that of the solvent molecules. Bearing in mind that Stokes' Law is also subject to such a fundamental criticism it was decided to calculate the solvated radius of the  $\text{Cl}^-$  ion from the ionic B coefficient using equation (3.15).

$$\therefore B = \frac{2.5 \times r^3 \times N \times 4 \times \pi}{3 \times 1000}$$

$$\therefore 0.102 = \frac{r^3 \times 2.5 \times 4 \times \pi \times 6.023 \times 10^{23}}{1000 \times 3}$$

$$\therefore r^3 = \frac{0.102 \times 3 \times 10^{-20}}{2.5 \times 4 \times \pi \times 5.023}$$

$$\therefore r = 0.25 \text{ nm}$$

This value of 0.25 nm compared with one of 0.181 nm for the ionic crystal radius of  $\text{Cl}^-$  ion<sup>83</sup> and 0.332 nm for the hydrated radius of the  $\text{Cl}^-$  ion as obtained by the corrected method of Nightingale<sup>79</sup>. It would seem therefore that the calculated solvated radius of the  $\text{Cl}^-$  ion in formamide (as calculated from the ionic B coefficient) is smaller than the hydrated radius of the  $\text{Cl}^-$  ion in water (as calculated from Stokes' Law). Since the volume occupied by a formamide molecule in solution is nearly three times that occupied by a water molecule and since (in water at least) simple monatomic ions are considered to be solvated to a minimal extent<sup>79</sup> the relative sizes of the calculated solvated radii for the  $\text{Cl}^-$  ion in formamide and water might indicate either

(i) in formamide the  $\text{Cl}^-$  ion is solvated to a lesser extent than in water

or  
(ii) in formamide the  $\text{Cl}^-$  ion is to some extent a structure breaking ion, and therefore the value of the hydrated radius obtained from the ionic B coefficient is too small because the ionic B coefficient contains a negative term due to the structure breaking effect of the  $\text{Cl}^-$  ion.

Bare and Skinner<sup>84</sup> have shown that for a homologous series of monohydric alcohols the viscosity B coefficients of NaI increased with increasing alkyl chain length, and attributed this to the fact that as the solvent molecule increased in size the volume of the solvodynamic unit would increase. It therefore would seem that the  $\text{Cl}^-$  ion is to some extent a structure breaking ion in formamide solution.

From the  $\frac{dB}{dT}$  values for the  $\text{Na}^+$  and  $\text{K}^+$  ions it is very probable that in formamide these are net structure makers,  $\text{K}^+$  to a lesser extent than  $\text{Na}^+$ . This is what would be expected on the basis of the surface charge densities of these ions. Potassium ion has a smaller surface charge density than the sodium ion and will therefore orientate the solvent dipoles beyond the first solvation sphere to a lesser

extent than sodium.

Without resorting to any arbitrary splitting into ionic B coefficients it is instructive to examine the mean difference  $B_{Na^+} - B_{K^+}$ . This can be done simply by subtracting the B coefficients of two salts with a common ion, eg, in formamide,

$$B_{Na^+} - B_{K^+} = 0.186$$

This difference can be taken as the difference of the effect of the  $Na^+$  ion and the  $K^+$  ion on the solution viscosity, and would be expected to be due to differences in the ability of the ions to promote or destroy structure in the solvent. It is therefore of interest to compare this difference for various solvents.

TABLE 3.19

Solvent	Group	$B_{Na^+} - B_{K^+}$
N-methylformamide <sup>85</sup>	I	-0.016
methanol <sup>86</sup>	I	-0.023
water <sup>68</sup>	II	0.093
formamide	II	0.186
1,3-propanediol <sup>84</sup>	II	0.362
1,2-propanediol <sup>84</sup>	II	0.406

For N-methylformamide and methanol  $B_{Na^+} - B_{K^+}$  is much less than for any of the other solvents in table (3.19). These solvents, which shall be called group I, although highly associated, tend to associate into dimers or chains rather than into three dimensional groupings. The other solvents in table (3.19) called group II, all have the ability to form associated aggregates in three dimensions. For all of these solvents  $B_{Na^+} - B_{K^+}$  is found to be positive.

It has been suggested<sup>85</sup> that the structure making contribution to B for the alkali metal ions in water decreases rather slowly and that the structure breaking contribution increases relatively rapidly

with increase in ionic radius. For group I solvents where the structure breaking contribution is probably negligible the ionic B values will therefore not change by much down the group. Evidence from other salts in other systems of this type is available to support this, ie LiCl, KI and KCl in N-methylpropionamide have values of 1.25, 1.30 and 1.37<sup>87</sup>.

The same analysis can be carried out for the anions in formamide.

TABLE 3.20

Solvent	$B_{Cl^-} - B_{Br^-}$
water <sup>68</sup>	0.034
methanol <sup>86,88</sup>	0.024
formamide	0.030
N-methyl formamide <sup>85</sup>	0.030

For the anions the difference is not very large and since it is the same for both solvent groups I and II it is unlikely to be a result of different structure breaking abilities of the anions.

If these results are considered in terms of the Stokes and Mills treatment, see page 56, then, for the cations in formamide it appears that although  $\eta^D$  (the structure breaking contribution) is important, the overall effect of the cations is to increase the viscosity due to  $\eta^E$  (size and shape contribution) and  $\eta^A$  (the ordering of the solvent ions in the immediate vicinity of the ion). The fact that  $\frac{dB}{dT}$  for each of the salts in formamide is negative indicates that  $\eta^A$  makes a large contribution to the overall effect.

For the anions the most important contribution is probably  $\eta^E$ . However as suggested above  $\eta^A$  may decrease with increasing ion size and this explains to some extent why the bromide ion contributes less than the chloride ion to the viscosity. It should be noted however that from the calculation of the solvated radii and

consideration of the size of the solvodynamic unit, it would seem that some contribution is also made by  $\eta^D$ .

Associated solvents have been divided into two groups, I and II. Group I are solvents which have linear or polymeric association in two directions such as N-methylformamide, N-methylpropionamide, N-methylacetamide and the monohydric alcohols. No structure breaking effects of ions would be expected in these solvents. Group II solvents on the other hand can form three dimensional aggregates and when certain ions are dissolved in them a degree of structure breaking takes place. Examples of group II solvents are water, formamide, and polyhydric alcohols.

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### 3.6 VISCOSITY AS A RATE PROCESS

Since the flow of liquid is a rate process in so far as it takes place with a definite velocity under given conditions, Eyring<sup>89</sup> considered that the theory of absolute reaction rates could be applied to the problem of viscosity.

He considered as his model two parallel layers of molecules of a fluid, one of which, under the influence of an applied force, moved with a velocity  $\Delta u$  greater than the other. This movement was envisaged as involving the passage of molecules from one equilibrium position to another in the same layer. Since energy would be required to produce a suitable site into which the molecule could "jump" it was suggested that the process could be represented by the potential energy diagram in fig. (3.13). It was assumed that the potential energy barrier was symmetrical.

Eyring calculated that the force acting on a single molecule in the direction of motion would be

$$Fx_1x_2 \quad (3.16)$$

where  $F$  is the force per unit area acting on the molecule,  $x_1$  is the distance between neighbouring molecules in the moving layer in the direction at right angles to the direction of the applied force and  $x_2$  is the mean distance between adjacent molecules in the moving layer in the same direction ( $x_1x_2$  is therefore the effective area per molecule).

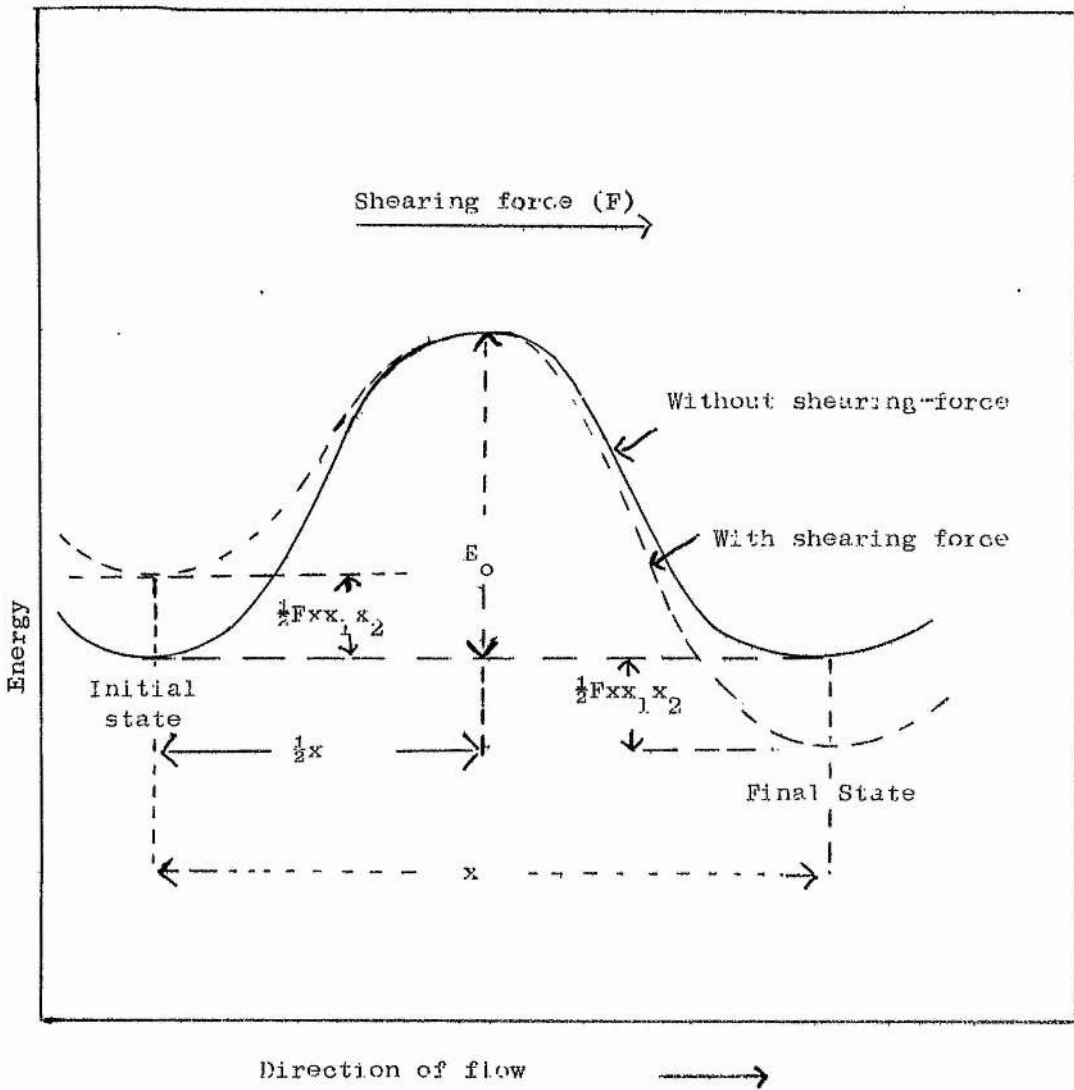
The distance between equilibrium positions was at  $x$ , and the energy acquired by a moving molecule when it has reached the top of the potential energy barrier is

$$F \frac{xx_1x_2}{2} \quad (3.17)$$

The effect of the force is therefore to reduce the height of the potential energy barrier by  $\frac{1}{2}Fx_1x_2$  in the direction of flow. In the opposite direction the barrier was increased by this amount.

Fig. (3.13)

Eyring's potential energy diagram for viscous flow



Statistical mechanical arguments lead to the expression for the frequency of an activated complex crossing a potential energy barrier being given by

$$k = \frac{KT}{h} \frac{f^*}{f} e^{-E_0/KT} \quad (3.18)$$

where  $k$  is the frequency,  $K$  the Boltzmann constant,  $h$  is the Planck's constant,  $f^*$  and  $f$  are the partition functions for unit volume of the molecule in the activated and initial state respectively,  $T$  is the absolute temperature,  $R$  the gas constant and  $E_0$  the activation energy <sup>PER MOLECULE</sup>. From this the rate of flow in the direction of the applied force was found to be

$$\begin{aligned} k_A &= \frac{KT}{h} \frac{f^*}{f} e^{-(E_0 - \frac{1}{2}Fx_1x_2)/KT} \\ &= k e^{(\frac{1}{2}Fx_1x_2)/KT} \end{aligned} \quad (3.19)$$

The rate of flow in the opposite direction was therefore

$$k_B = k e^{-(\frac{1}{2}Fx_1x_2)/KT} \quad (3.20)$$

From the net rate of flow Eyring obtained the difference in velocity between the layers

$$\Delta u = xk [e^{(\frac{1}{2}Fx_1x_2)/KT} - e^{-(\frac{1}{2}Fx_1x_2)/KT}] \quad (3.21)$$

and from the definition of viscosity

$$\eta = \frac{Fx_3}{\Delta u}$$

where  $x_3$  is the distance between the layers; and making the following assumptions:-

(i)  $2KT \gg Fx_1x_2x$

which is reasonable because  $F$  is the order  $10^{-3} \text{ kg m s}^{-2}$  and  $x_1, x_2$ , and  $x$  are each of the order  $10^{-1} \text{ nm}$

(ii)  $x_1 \approx x$

although they are not the same they are of the same order

(iii)  $x_1x_2x$  is the approximate volume inhabited by a single molecule in the liquid state,

and finally inserting for the frequency factor  $k$  from equation (3.18),



Eyring obtained the expression

$$\eta = \frac{hN}{V} \cdot \frac{f}{f^*} e^{E_0/KT} \quad (3.22)$$

where N is Avagadro's number and V is the molar volume of the liquid.

From his theory of absolute reaction rates the equilibrium constant

$k_e$  is related to the partition coefficients by

$$k_e = \frac{f^*}{f} e^{-E_0/KT}$$

Thermodynamic considerations, however, give

$$k_e = e^{-\Delta G^*/RT}$$

therefore

$$\eta = \frac{hN}{V} e^{\Delta G^*/RT} \quad (3.23)$$

and since  $\Delta G = \Delta H - T\Delta S$  equation (3.23) becomes

$$\eta = \frac{hN}{V} e^{-\Delta S^*/R} e^{\Delta H^*/RT} \quad (3.24)$$

Assuming  $\Delta S^*$  is constant over the temperature range and that the

molar volume of the liquid does not change by very much, then equation

(3.24) can be represented as

$$\eta = A e^{\Delta H^*/RT} \quad (3.25)$$

This is similar to the empirical relationship suggested by Arrhenius<sup>90</sup> in 1916.

Rewriting equation (3.25) gives

$$\Delta H^* = R \frac{d \ln \eta}{d(\frac{1}{T})} \quad (3.26)$$

In 1959 Nightingale and Benck<sup>91</sup> suggested that the effect of a strong

electrolyte on the viscosity of a solvent could also be treated as

a rate process. They substituted the Jones-Dole equation for the

viscosity of a dilute electrolyte solution into equation (3.26) to

give

$$\Delta H^* = R \frac{d \ln[\eta_0 (1 + A \sqrt{c} + Bc)]}{d(\frac{1}{T})} \quad (3.27)$$

For dilute solutions of electrolytes where B is not too small (which

is the case for most non-aqueous solvents at least) the influence of

the interionic attractions on the viscosity of the solution can be considered negligible, therefore

$$\Delta H^* \approx R \cdot \frac{d \ln \eta_o (1+Bc)}{d(\frac{1}{T})}$$

from equation (3.26)

$$\begin{aligned} R \frac{d \ln \eta}{d(\frac{1}{T})} &= \frac{R}{\eta_o (1+Bc)} \cdot \frac{d[\eta_o (1+Bc)]}{d(\frac{1}{T})} \\ &= \frac{R}{\eta_o (1+Bc)} \cdot \eta_o \frac{d(1+Bc)}{d(\frac{1}{T})} + (1+Bc) \frac{d\eta_o}{d(\frac{1}{T})} \\ &= \frac{R}{(1+Bc)} \cdot \frac{d(1+Bc)}{d(\frac{1}{T})} + \frac{R}{\eta_o} \frac{d\eta_o}{d(\frac{1}{T})} \end{aligned}$$

$$R \frac{d \ln \eta}{d(\frac{1}{T})} = R \cdot \frac{d \ln \eta_o}{d(\frac{1}{T})} + \frac{R}{(1+Bc)} \cdot \frac{d(1+Bc)}{d(\frac{1}{T})} \quad (3.28)$$

In equation (3.28)  $R \frac{d \ln \eta}{d(\frac{1}{T})}$  and  $R \frac{d \ln \eta_o}{d(\frac{1}{T})}$  can be identified as the activation enthalpies for solution,  $\Delta H^*_{\eta}$ , and solvent  $\Delta H^*_{\eta_o}$  respectively. Equation (3.28) can therefore be represented by

$$\Delta H^*_{\eta} = \Delta H^*_{\eta_o} + \Delta H^*_{\eta_s} \quad (3.29)$$

where  $\Delta H^*_{\eta_s}$  the second term on the right side of equation (3.28) may be considered to represent the increase or decrease of the activation enthalpy of the pure solvent due to the presence of the ions of the solute. Since it is considered to represent the effect due to the sum of the ionic effects, equation (3.29) can be rewritten

$$\Delta H^*_{\eta} - \Delta H^*_{\eta_o} = v^+ \Delta H^*_{+} + v^- \Delta H^*_{-}$$

where  $\Delta H^*_{+}$  and  $\Delta H^*_{-}$  represent the effect on the activation enthalpy due to each individual cation and anion and  $v^+$  and  $v^-$  are the number of cations and anions per molecule of solute.

3.7 RESULTS AND DISCUSSION (II)

Figs. (3.14-3.16) show the change that takes place in  $\Delta G^*$ ,  $\Delta H^*$ , and  $\Delta S^*$  for formamide when the salts NaCl, KCl, NaBr and KBr are added. The increases are very small and are dependent on the concentration of the salt. For a 0.1 molal solution of sodium chloride in formamide the increase in  $\Delta H^*$  amounts to only 2%. The maximum increase observed for  $\Delta G^*$  was much less (0.3% for a 0.1 molal solution). This can be attributed to the fact that the salts which cause the largest increase in  $\Delta H^*$  are also associated with less negative changes in the entropy of activation ( $\Delta S^*$ ). The maximum salt concentration used in these investigations was 0.1 molal.

Table (3.21) gives the values of  $\Delta G^*$ ,  $\Delta H^*$ , and  $\Delta S^*$  for the pure formamide used in this work and also the changes in them brought about by adding salts to form 0.1 molal solutions.

TABLE 3.21

	$\Delta G^*$ kJ/mole	$\Delta H^*$ kJ/mole	$\Delta S^*$ JK <sup>-1</sup> /mole
FORMAMIDE	48.58	17.17	-105.40
Increase for			
0.1 molal NaCl	0.14	0.36	0.72
0.1 molal NaBr	0.14	0.27	0.54
0.1 molal KCl	0.10	0.13	0.14
0.1 molal KBr	0.09	0.14	0.14

No satisfactory ionic partitioning of these values was possible due to the scatter and lack of accuracy for the small changes involved. However two important points emerge from an investigation of the results.

(i) For each of the salts containing the sodium ion the increase in the activation enthalpy ( $\Delta H^*$ ) for the 0.1 molal solutions was more than twice that caused by the corresponding potassium salts.

Fig.(3.14)

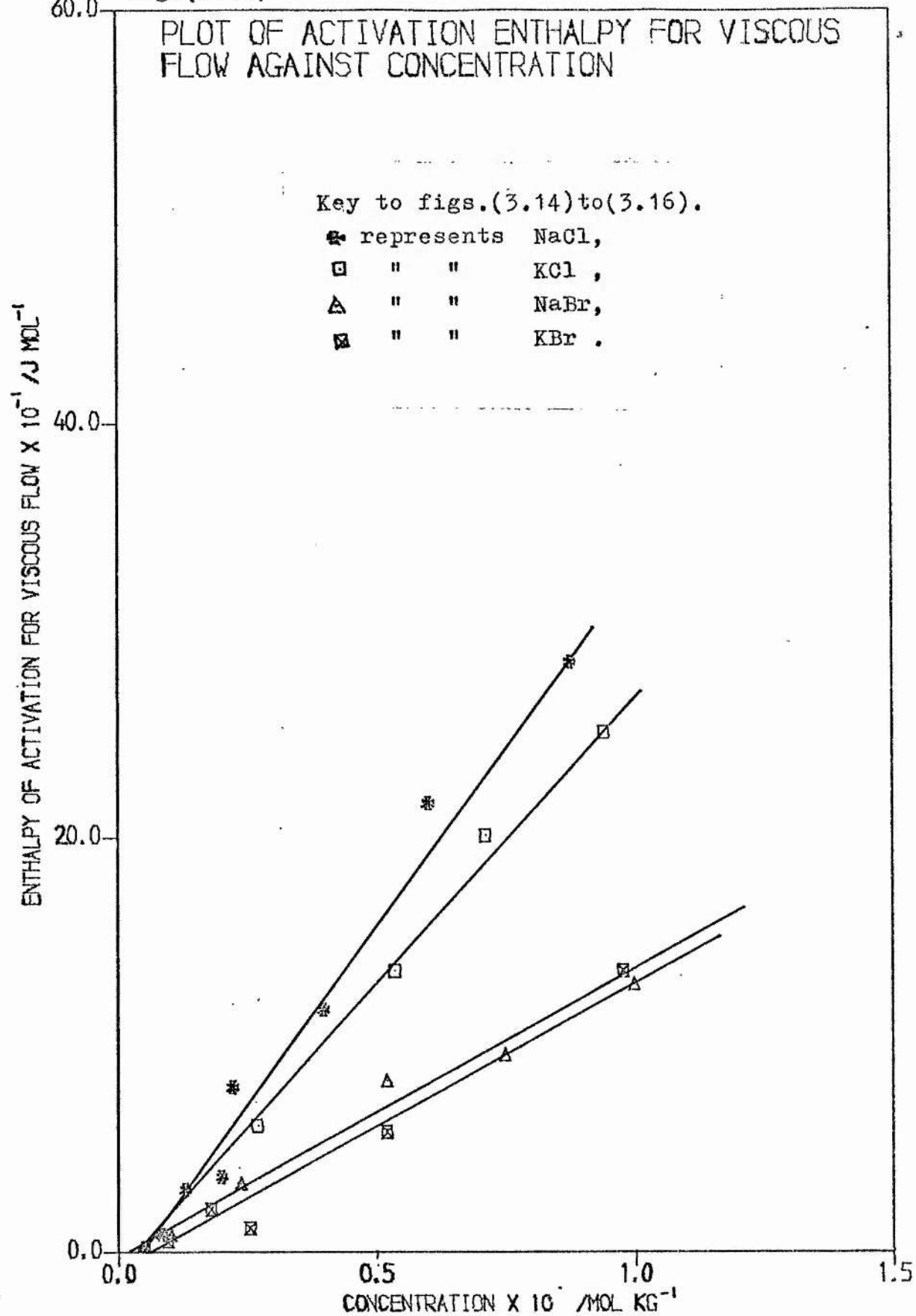


Fig.(3.15)

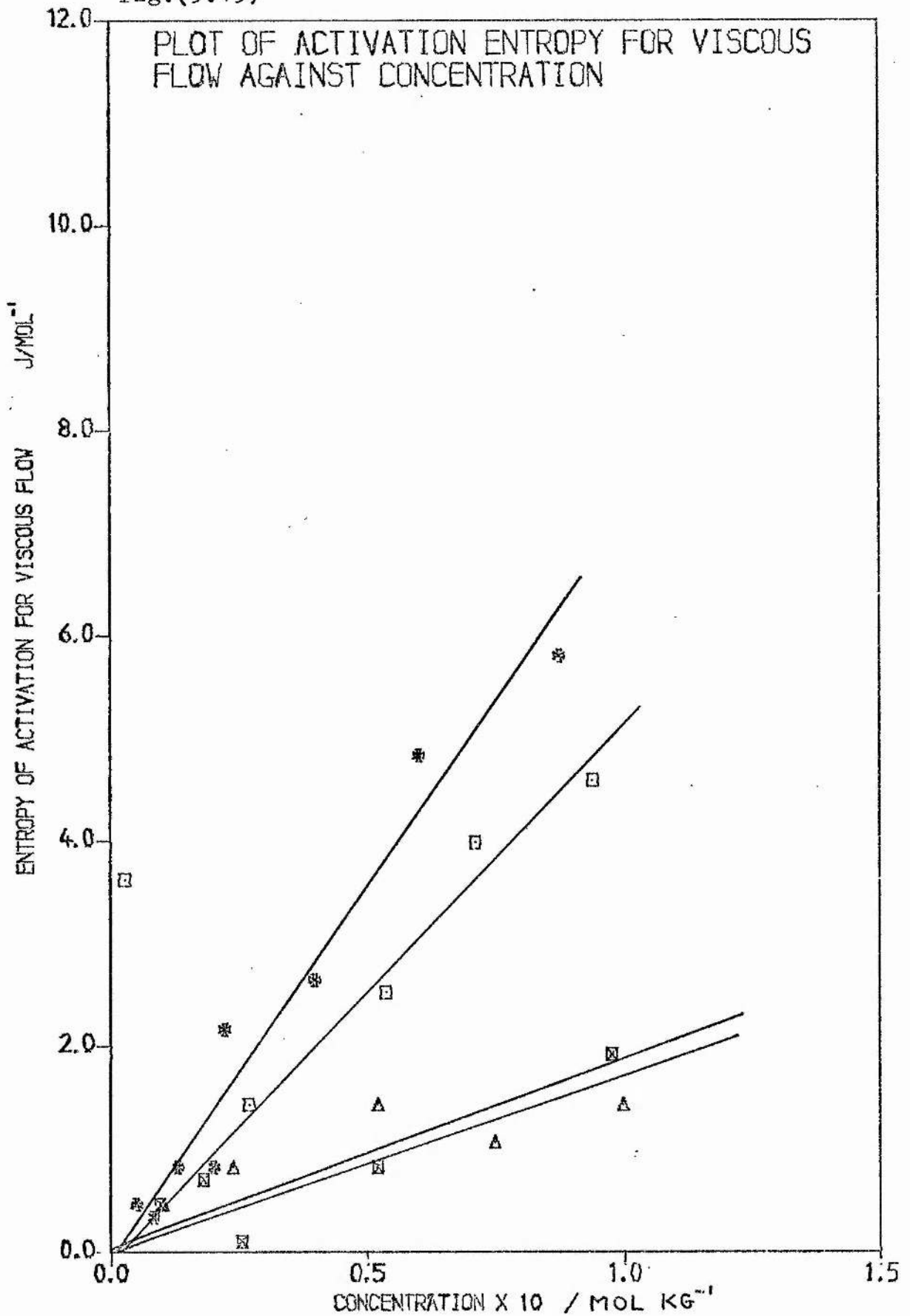
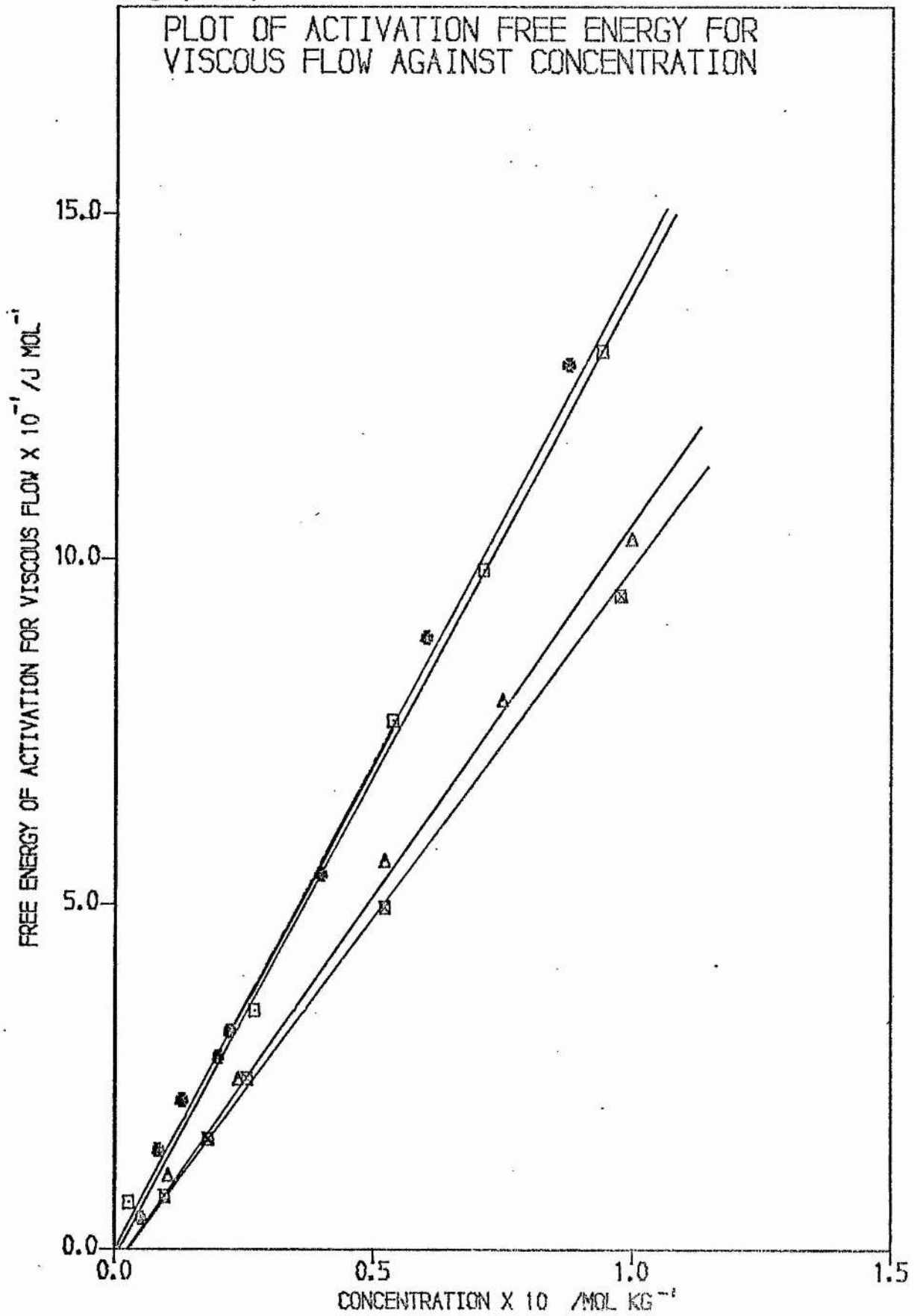


Fig. (3.16)



(ii) The activation entropy change ( $\Delta S^*$ ) brought about by the presence of the sodium salts resulted in a significantly less negative entropy change than that caused by the potassium ions.

Both these facts support one another, and the previous evidence, that  $\text{Na}^+$  ions are more order making than  $\text{K}^+$  ions. Because of the relatively strong ordering influence of the sodium ion on the formamide molecules, more energy will be required for a solvent molecule in the neighbourhood of a sodium ion to move into the next equilibrium position and hence  $\Delta H^*$  is greater for the movement of such an ion. If the transition state for such a movement of one solvent molecule from one equilibrium position to another is considered to be "crowded", or to put it another way, if the transition state is one in which a high degree of order exists, then  $\Delta S^*$  for the transition will be negative. However if the molecule is moving from a relatively ordered site around a sodium ion then the decrease in entropy will be less and  $\Delta S^*$  will therefore not be quite so negative.

By such reasoning, these results confirm that which was pointed out in section 3.5, namely that sodium ions are better structure making ions than potassium ions in formamide as was also found by Kaminsky<sup>68</sup> for these ions in water.

### 3.8 THE FALKENHAGEN-VERNON A COEFFICIENT

From the Jones-Dole equation and the plots shown in figs. (3.4-3.12) it should be possible to measure the long range electrostatic interaction of the ions in formamide solution. The A coefficient discussed in section 3.1 was considered to be a measure of this and should be given for each of the salts investigated here by the intercepts on figs. (3.4-3.12). These intercepts are listed in tables (3.11) and (3.12). It can be seen by inspection of these

tables that the intercepts were found to be negative in some cases. These results are considered to be spurious and it is not considered possible to determine A-coefficients with any precision with the experimental procedure used here. However it is possible to calculate A theoretically from equation (3.29) which was proposed in 1931 by Falkenhagen and Vernon<sup>65</sup> for a uni-univalent salt:-

$$A = \frac{1.45}{\eta \sqrt{2\epsilon_0 T}} \left[ \frac{\lambda_1^{\circ} + \lambda_2^{\circ}}{4\lambda_1^{\circ} \lambda_2^{\circ}} - \frac{(\lambda_1^{\circ} + \lambda_2^{\circ})^2}{(3 + \sqrt{2}) \lambda_1^{\circ} \lambda_2^{\circ} (\lambda_1^{\circ} + \lambda_2^{\circ})} \right] \quad (3.29)$$

The A coefficient is therefore a very complicated function of the valency type of the salt and the ionic mobilities of the ions. The units used in the equation as it is represented here are  $\eta$  = viscosity in poise, T = absolute temperature in Kelvin,  $\lambda_1^{\circ}$  and  $\lambda_2^{\circ}$  the equivalent conductances of the ions at infinite dilution in  $\text{cm}^2 \text{ int. } \Omega \text{ equiv.}^{-1}$

For the salts NaCl, KCl, NaBr, and KBr the A coefficients were calculated at 298.15K using the data of Notley and Spiro<sup>80</sup> for the limiting equivalent conductances of the various ions in formamide and the value of 109 for the dielectric constant due to Bass et al.<sup>92</sup>. The viscosity of formamide at 298.15 K was taken as 0.03292 poise as measured in this work. Table (3.22) gives the values obtained using equation (3.29) and compares them with the intercepts obtained experimentally. All the values are for solutions at 298.15 K. The experimental values of the A coefficient were calculated by computer by applying the method of least squares to the values shown in figs. (3.4-3.12). The root mean square deviation for these points is given as an indication of the precision.

TABLE 3.22

Salt	A <sub>theor</sub>	A <sub>expt</sub>
NaCl	0.0064	0.0023 ± 0.0023
NaBr	0.0064	0.0041 ± 0.0020
KCl	0.0058	0.0065 ± 0.0025
KBr	0.0058	0.0064 ± 0.0011



A computer program was then employed which enabled the theoretical value of A to be inserted into an equation of the same form as the Jones-Dole equation and a new value for the B coefficient was then calculated by a method of least squares. This produced no significant change in the B coefficients as reported in table (3.13).

### 3.9 CONCLUSIONS

All of the salts investigated here increase the viscosity of formamide and with the exception of the lithium salts it has been shown that they all have a net structure making effect on the solvent. (Both the lithium salts were only investigated at 298.15 K.) There is some evidence, however, to suggest that the anions do exhibit a certain amount of structure breaking influence on formamide, despite the fact that their overall effect is to increase the viscosity. The sodium ion is shown to have a greater ordering influence on formamide than that of the potassium ion, and both of these ions have a much greater ordering influence than either of the anions as is the case in aqueous solutions.

This idea of structure making and structure breaking is simply a concise way of discussing a situation which exists around an ion which is very complex and may be contributed to by many factors. In the words of Emerson and Holzer<sup>77</sup>, "Hydrodynamic problems are notoriously refractory to intuitive analysis".

CHAPTER FOUR

BINARY MIXTURES4.1 INTRODUCTION

Few have attempted to deduce the absolute value of the viscosity of a particular liquid from known molecular constants, with the notable exceptions of Andrade<sup>93</sup>, Kirkwood<sup>94</sup> and Stiel and Thodos<sup>95</sup>. Viscosities of binary liquid mixtures have been studied as a method of investigating the variation in type and degree of the interactions of unlike molecules. Most of this work has been directed towards predicting the viscosity of a mixture from the viscosities of the pure components<sup>96-101</sup> or discussing observed maxima or minima in the measured viscosity of various compositions of a binary mixture, in terms of complex species formed or interactions between the individual components<sup>102-104</sup>.

For ideal liquids Arrhenius<sup>96</sup> proposed the empirical equation for the viscosity of a binary mixture

$$\ln \eta = \phi_A \ln \eta_A + \phi_B \ln \eta_B \quad (4.1)$$

where  $\phi_A$  and  $\phi_B$  are the volume fractions and  $\eta_A$  and  $\eta_B$  are the viscosity coefficients of the pure components A and B respectively.

Dolezalek<sup>100</sup> and later on Hind et al<sup>105</sup> suggested the relationship

$$\eta = x_A^2 \eta_A + x_B^2 \eta_B + x_A x_B \eta_{AB} \quad (4.2)$$

which introduced a term specifically taking into account the molecular interactions A.....B.  $\eta_{AB}$  was called the "mutual viscosity coefficient". In 1960 an equation of the above form was derived from statistical mechanics by Bearman and Jones<sup>106</sup>, who considered as their basic assumptions that the mean frictional forces acting on the molecules of a binary system were related, on the one hand to the gradients of the local thermodynamic properties and on the other hand to the relative mean velocities of the components. They

found that the viscosity coefficient could be represented by the sum of three integrals representing respectively the interactions of like and unlike pairs of molecules.

From the statistical mechanical theory of Frenkel<sup>1</sup> and the rate theory of Eyring<sup>89</sup>, Tamura and Kurata<sup>98</sup> derived a semi-empirical relationship which was very similar to equation (4.2).

#### 4.2 TAMURA-KURATA EQUATION

The viscosity of a pure liquid A is given by

$$\eta_A = \frac{KT}{v_A} \tau_A \quad (4.3)$$

where  $\tau_A$  is the relaxation time of flow and is given by

$$\tau_A = \frac{h}{KT} e^{\Delta G_A^*/KT} \quad (4.4)$$

where K is the Boltzmann constant, T the absolute temperature,  $v_A$  the volume occupied by one mole of A and h is the Planck constant. Similar equations can be written for a pure liquid B. Tamura and Kurata considered that the same procedure might be used to describe a mixture of liquids A and B, ie

$$\eta = \frac{KT}{v} \tau \quad (4.5)$$

$$\text{and } \tau = \frac{h}{KT} e^{\Delta G^*/KT} \quad (4.6)$$

where the parameters with no subscript refer to the mixture. The term "mutual activation free energy of viscous flow",  $\Delta G_{AB}^*$ , relating only to A.....B contacts of molecules in the same way as the  $\Delta G_A^*$  and  $\Delta G_B^*$  relate to A.....A and B.....B contacts was then introduced such that  $\tau_{AB}$  was defined by

$$\tau_{AB} = \frac{h}{KT} e^{\Delta G_{AB}^*/KT} \quad (4.7)$$

$\tau_{AB}$  was taken to be the relaxation time of flow of a molecule A in liquid B.  $x_A$  and  $x_B$  were the mole fractions of A and B and the probabilities of the molecular contacts A.....A, B.....B and A.....B were supposed to be given by  $x_A^2$ ,  $x_B^2$  and  $2x_A x_B$  respectively.  $\tau$  was then assumed to be given by the weighted mean of the individual

relaxation times,

$$\tau = x_A^2 \tau_a + x_B^2 \tau_B + 2x_A x_B \tau_{AB} \quad (4.8)$$

The next step was to define a "mutual viscosity coefficient"  $\eta_{AB}$  by

$$\eta_{AB} = \frac{KT}{(v_A v_B)^2} \tau_{AB} \quad (4.9)$$

From equations (4.5) and (4.8)

$$\eta = \frac{KT}{v} (x_A^2 \tau_A + x_B^2 \tau_B + 2x_A x_B \tau_{AB}) \quad (4.10)$$

and from equations (4.3) and (4.9)

$$\eta = \frac{KT}{v} \left( x_A^2 \frac{\eta_A v_A}{KT} + x_B^2 \frac{\eta_B v_B}{KT} + 2x_A x_B \frac{v_A^{1/2} v_B^{1/2}}{KT} \eta_{AB} \right) \quad (4.11)$$

$$= x_A^2 \frac{v_A}{v} \eta_A + x_B^2 \frac{v_B}{v} \eta_B + 2x_A x_B \left( \frac{v_A v_B}{v^2} \right)^{1/2} \eta_{AB} \quad (4.12)$$

Further  $\frac{x_A v_A}{v} = \frac{w_A \rho}{\rho_A} = \phi_A$  where  $w_A$  = weight fraction and  $\phi_A$  = volume fraction of Z.

$$\therefore \eta = x_A \phi_A \eta_A + x_B \phi_B \eta_B + 2(x_A x_B \phi_A \phi_B)^{1/2} \eta_{AB} \quad (4.13)$$

This equation is similar to the Dolezalek equation (4.2) but introduces a degree of dependence of the viscosity on the volume.

It was shown by Tamura and Kurata<sup>98</sup> that the agreement between their equation and experimental results for a number of systems was considerably better than that of equation (4.2).

### 4.3 MATO-HERNANDEZ EQUATION

Mato and Hernandez<sup>101</sup> pursued a similar argument but considered that the probability of the molecular interactions (A.....A, B.....B, and A.....B) would be given by the product of the mole fraction and the volume fraction of the particular species, ie  
 Probability of A.....A interactions  $\propto x_A \phi_A$  where  $\phi_A = \frac{x_A v_A}{v}$  as before  
 Probability of B.....B interactions  $\propto x_B \phi_B$   
 Probability of A.....B interactions  $\propto 2(x_A x_B \phi_A \phi_B)^{1/2}$

This led to the expression

$$\tau = x_A \phi_A \tau_A + x_B \phi_B \tau_B + 2(x_A x_B \phi_A \phi_B)^{\frac{1}{2}} \tau_{AB} \quad (4.14)$$

which gives by a similar argument as before

$$\eta = \phi_A^2 \eta_A + \phi_B^2 \eta_B + \phi_A \phi_B \eta_{AB} \quad (4.15)$$

This is still of the same form as the Dolezalek equation (4.2) but now the volume fraction completely replaces the mole fraction.

These equations for the viscosity of a binary mixture (4.2), (4.13) and (4.15), are derived from Eyring's activation state theory<sup>89</sup>, which has been criticised and considered unsatisfactory by Rice et al<sup>107</sup>, who suggested that it is simply a parametric representation rather than a molecular theory because the parameters obtained from Eyring's theory cannot be related to the intermolecular potential or the radial distribution function. These authors admit, however, "it can not be denied that the model is easily visualised and formalised with simple mathematics. Moreover if the resulting formulae are considered to be parametric representations, then adjustment of the parameters often leads to useful representations of experimental data". Stephen Brush in his comprehensive review<sup>108</sup> comments "As this review does not, like some others, accord the place of honour to the rate theory of viscosity, it should be noted to its credit that the rate theory can be applied to non-Newtonian flow without introducing any additional hypothesis. Such applications will give a better indication of the validity of this theory than the controversies about whether the energy of viscosity should vary with temperature".

#### 4.4 THE McALLISTER EQUATION

One important limitation of equations (4.2), (4.3) and (4.15) is that they represent only two-body interactions. McAllister<sup>109</sup>

extended the Eyring approach to take into account three-body interactions. For a binary mixture of pure A and pure B the three-body interactions involving molecules of A and B can be represented as A.....A.....A, B.....B.....B, A.....B.....A, B.....A.....B, A.....A.....B, and B.....B.....A. McAllister assumed that for each of these interactions there was an associated activation free energy for viscous flow and he assumed that

$$\begin{aligned} \Delta G_{AAB}^* &= \Delta G_{ABA}^* = \Delta G_{AB}^* \\ \text{and} \quad \Delta G_{BBA}^* &= \Delta G_{BAB}^* = \Delta G_{BA}^* \end{aligned} \quad (4.16)$$

This led to the equation

$$\begin{aligned} \ln \eta &= x_A^3 k_1 \ln \eta_A + 3x_A^2 x_B k_2 \ln \eta_{AB} + 3x_B^2 x_A k_3 \ln \eta_{BA} \\ &\quad + x_B^3 k_4 \ln \eta_B + R^0 \end{aligned} \quad (4.17)$$

$$\begin{aligned} \text{where } R^0 &= x_B^3 \ln(M_B/M_A) + 3x_A x_B^2 \ln[(1+2M_B/M_A)/3] \\ &\quad + 3x_A^2 x_B \ln[(2+M_B/M_A)/3] - \ln(x_A + x_B M_B/M_A) \end{aligned}$$

where  $\eta$  is the viscosity of the mixture,  $M_A$  is the molecular weight of A and  $M_B$  the molecular weight of B.

Thus in contrast to the equations discussed above McAllister considered that the viscosity coefficient for the interactions on a molecule A in a solvent B ( $\eta_{BA}$ ) was not the same as that for a molecule B in a pure solvent A ( $\eta_{AB}$ ). Hence equation (4.17) contains two undetermined parameters  $\eta_{AB}$  and  $\eta_{BA}$  which are assumed to be independent of composition, and vary with temperature according to Eyring's theory.

In the present work a three parameter model was set up and used which was simply an extension of the one parameter models described above ie equations (4.2), (4.13), and (4.15).

#### 4.5 THE THREE PARAMETER EQUATION

In all of the one parameter models the presence of B

molecules is assumed to have no effect on the A.....A interactions and vice versa. The three parameter equation used in this investigation is an extension of the existing one parameter models to take such interactions into account. For the Dolezalek model the equation is

$$\eta = x_A^2 \eta_A^{(1+x_B k_1)} + x_B^2 \eta_B^{(1+x_A k_2)} + 2x_A x_B \eta_{AB} \quad (4.18)$$

where  $\eta_A$  represents the A.....A interactions,  $\eta_B$  the B.....B interactions and  $\eta_{AB}$  the A.....B interactions. The term  $(1+x_B k_1)$  introduces a dependence of the A.....A interactions on the presence of B molecules. When the concentration of B is very small, the A.....A interactions are hardly influenced at all (as we would expect, since when  $x_B$  vanishes to zero,  $\eta_A$  would represent the interaction A.....A for pure A) and the term  $(1+x_A k_2)$  would have a great effect on the B.....B interactions (since  $x_A = 1-x_B$ ).

#### 4.6 RESULTS AND DISCUSSION

Equations (4.2), (4.13) and (4.15) were solved by computer by means of polynomial regression analyses. Table (4.1) gives a list of the sums of the squares of the errors obtained for each equation and each system. The smaller the value of this, the better the ability of the equation to describe the experimental results. The three parameter versions of the above equations were analysed by a double variable polynomial regression analysis technique developed by Sinclair and Vincent<sup>110</sup>. Tables (4.2-4.10) give lists of the experimental and calculated viscosity data for each system and each equation.

For all three one parameter models, the viscosity of the binary mixtures was predicted to within 10% and usually to within 2%, tables (4.2-4.8). Although there was some variation in the extent to which each of the models described the systems there was no single model which described all three systems better than the others.



TABLE 4.1

The sums of the squares of the errors for each system and each model

	I formamide/water	II formamide/methanol	III formamide/dimethyl- formamide
318.15 K			
DOLEZ.	$0.4826 \times 10^{-6}$	$0.3660 \times 10^{-6}$	$0.3881 \times 10^{-5}$
TAM.-KUR.	$0.1950 \times 10^{-5}$	$0.4134 \times 10^{-6}$	$0.3842 \times 10^{-5}$
MAT.-HER.	$0.9475 \times 10^{-5}$	$0.4613 \times 10^{-6}$	$0.1591 \times 10^{-5}$
308.15 K			
DOLEZ.	$0.6189 \times 10^{-6}$	$0.6301 \times 10^{-6}$	$0.8150 \times 10^{-5}$
TAM.-KUR.	$0.3046 \times 10^{-5}$	$0.7087 \times 10^{-6}$	$0.7603 \times 10^{-5}$
MAT.-HER.	$0.1538 \times 10^{-4}$	$0.7881 \times 10^{-6}$	$0.3170 \times 10^{-5}$
298.15 K			
DOLEZ.	$0.1890 \times 10^{-5}$	$0.1550 \times 10^{-5}$	$0.1430 \times 10^{-4}$
TAM.-KUR.	$0.7839 \times 10^{-5}$	$0.1678 \times 10^{-5}$	$0.1609 \times 10^{-4}$
MAT.-HER.	$0.3307 \times 10^{-4}$	$0.1809 \times 10^{-5}$	$0.9017 \times 10^{-5}$
288.15 K			
DOLEZ.	$0.4455 \times 10^{-5}$	-	$0.3004 \times 10^{-4}$
TAM.-KUR.	$0.1848 \times 10^{-4}$	-	$0.3614 \times 10^{-4}$
MAT.-HER.	$0.7191 \times 10^{-4}$	-	$0.2349 \times 10^{-4}$

Key to tables (4.2) to (4.10)

X = mole fraction of component other than formamide (ie water, methanol or dimethylformamide)

Y(XPER) = experimentally measured viscosity in  $10^2 \text{ Jm}^{-3} \text{ s}$

Y(DOLEZ) = viscosity calculated using the Dolezalek model

Y(VINC 1) = viscosity calculated using the corresponding three parameter model

Y(A-A+B-B) = viscosity due to the A·····A, and B·····B interactions only (as calculated from the one parameter model)

eg for the Dolezalek model  $Y(A-A+B-B) = x_A^2 \eta_A + x_B^2 \eta_B$

A-B FACTOR = Y(DOLEZ) - Y(A-A+B-B)

(MAT.-HER.) = Mato-Hernandez Model

(TAM.-KUR.) = Tamura-Kurata Model

Table 4.2 Formamide/Water System(I) Temperature 318.15 K

X	Y (XPER)	Y (A-A + B-B)	Y (DOLEZ. )	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.175950D-01	0.157829D-01	0.179585D-01	0.176716D-01	0.217562D-02
0.202520D 00	0.162580D-01	0.136604D-01	0.166116D-01	0.162876D-01	0.295113D-02
0.354130D 00	0.135340D-01	0.954755D-02	0.137269D-01	0.134858D-01	0.417934D-02
0.500120D 00	0.113050D-01	0.676268D-02	0.113308D-01	0.112963D-01	0.456815D-02
0.600020D 00	0.100800D-01	0.552169D-02	0.990704D-02	0.100244D-01	0.438535D-02
0.725140D 00	0.861000D-02	0.472920D-02	0.837115D-02	0.862510D-02	0.364195D-02
0.801210D 00	0.784000D-02	0.466149D-02	0.757182D-02	0.785079D-02	0.291032D-02
0.900020D 00	0.682900D-02	0.504111D-02	0.668535D-02	0.689876D-02	0.164424D-02
0.950820D 00	0.638700D-02	0.544192D-02	0.629637D-02	0.642218D-02	0.854451D-03

Temperature 308.15 K

X	Y (XPER)	Y (A-A + B-B)	Y (DOLEZ. )	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.217440D-01	0.193955D-01	0.219049D-01	0.215897D-01	0.250941D-02
0.202520D 00	0.196660D-01	0.167840D-01	0.201879D-01	0.198320D-01	0.340389D-02
0.354130D 00	0.162720D-01	0.117176D-01	0.165381D-01	0.162733D-01	0.482054D-02
0.500120D 00	0.135220D-01	0.827800D-02	0.135470D-01	0.135092D-01	0.526900D-02
0.600020D 00	0.119710D-01	0.673792D-02	0.117961D-01	0.119252D-01	0.505816D-02
0.725140D 00	0.102230D-01	0.574154D-02	0.994224D-02	0.102214D-01	0.420070D-02
0.801210D 00	0.931500D-02	0.564267D-02	0.899950D-02	0.930615D-02	0.335683D-02
0.900020D 00	0.815600D-02	0.608657D-02	0.798307D-02	0.821764D-02	0.189650D-02
0.950820D 00	0.765500D-02	0.656651D-02	0.755205D-02	0.769033D-02	0.985542D-03

Temperature 298.15K

X	Y (XPER)	Y (A-A + B-B)	Y (DOLEZ. )	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.266890D-01	0.246090D-01	0.274434D-01	0.268859D-01	0.283431D-02
0.202520D 00	0.243860D-01	0.212900D-01	0.251346D-01	0.245054D-01	0.384461D-02
0.354130D 00	0.199510D-01	0.148415D-01	0.202862D-01	0.198187D-01	0.544468D-02
0.500120D 00	0.164170D-01	0.104484D-01	0.163996D-01	0.163344D-01	0.595120D-02
0.600020D 00	0.145290D-01	0.846909D-02	0.141821D-01	0.144125D-01	0.571306D-02
0.725140D 00	0.123780D-01	0.716713D-02	0.119117D-01	0.124076D-01	0.474458D-02
0.801210D 00	0.112820D-01	0.701537D-02	0.108068D-01	0.113511D-01	0.379145D-02
0.900020D 00	0.994000D-02	0.754064D-02	0.968269D-02	0.100988D-01	0.214205D-02
0.950820D 00	0.938100D-02	0.812841D-02	0.924156D-02	0.948681D-02	0.111314D-02

Temperature 288.15K

X	Y (XPER)	Y (A-A + B-B)	Y (DOLEZ. )	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.346040D-01	0.324726D-01	0.356857D-01	0.348276D-01	0.321308D-02
0.202520D 00	0.312890D-01	0.280839D-01	0.324423D-01	0.314739D-01	0.435839D-02
0.354130D 00	0.250760D-01	0.195418D-01	0.257141D-01	0.249950D-01	0.617229D-02
0.500120D 00	0.205290D-01	0.136974D-01	0.204439D-01	0.203446D-01	0.674650D-02
0.600020D 00	0.180840D-01	0.110444D-01	0.175209D-01	0.178766D-01	0.647653D-02
0.725140D 00	0.153820D-01	0.926460D-02	0.146432D-01	0.154078D-01	0.537863D-02
0.801210D 00	0.140310D-01	0.902129D-02	0.133194D-01	0.141583D-01	0.429813D-02
0.900020D 00	0.124630D-01	0.965229D-02	0.120806D-01	0.127218D-01	0.242831D-02
0.950820D 00	0.118350D-01	0.103932D-01	0.116551D-01	0.120330D-01	0.126190D-02

Table 4.3 formamide/water System(I) Temperature 318.15K

X	Y (XPER)	Y (A-A + B-B)	Y (TAM-KUR)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.175950D-01	0.170276D-01	0.182550D-01	0.177433D-01	0.156553D-01
0.202520D 00	0.162580D-01	0.152381D-01	0.169698D-01	0.163518D-01	0.220866E-01
0.354130D 00	0.135340D-01	0.113745D-01	0.140848D-01	0.135012D-01	0.345681D-01
0.500120D 00	0.113050D-01	0.819695D-02	0.114796D-01	0.112200D-01	0.418679E-01
0.600020D 00	0.100800D-01	0.651046D-02	0.993735D-02	0.998579D-02	0.437075D-01
0.725140D 00	0.861000D-02	0.502187D-02	0.819462D-02	0.860994D-02	0.404661D-01
0.801210D 00	0.784000D-02	0.459413D-02	0.732140D-02	0.787202D-02	0.347843D-01
0.900020D 00	0.682900D-02	0.473633D-02	0.643982D-02	0.694084D-02	0.217268E-01
0.950820D 00	0.638700D-02	0.520423D-02	0.614073D-02	0.646056D-02	0.119443D-01

Temperature 308.15K

X	Y (XPER)	Y (A-A + B-B)	Y (TAM-KUR)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.217440D-01	0.209212D-01	0.223035D-01	0.216630D-01	0.163818E-01
0.202520D 00	0.196660D-01	0.187196D-01	0.206696E-01	0.198963D-01	0.231097D-01
0.354130D 00	0.162720D-01	0.139702D-01	0.170226D-01	0.162925D-01	0.361762E-01
0.500120D 00	0.135220D-01	0.100498D-01	0.137444E-01	0.134203D-01	0.437864D-01
0.600020D 00	0.119710E-01	0.795367D-02	0.118178D-01	0.118792D-01	0.456767E-01
0.725140D 00	0.102230D-01	0.612113D-02	0.968955E-02	0.102097D-01	0.422908D-01
0.801210D 00	0.931500D-02	0.558226D-02	0.864914D-02	0.933827D-02	0.363467E-01
0.900020D 00	0.815600D-02	0.573035D-02	0.764436E-02	0.827071D-02	0.226837D-01
0.950820D 00	0.765500E-02	0.628615D-02	0.733770D-02	0.773724D-02	0.124623D-01

Temperature 298.15K

X	Y (XPER)	Y (A-A + B-B)	Y (TAM-KUR)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.266890D-01	0.265563D-01	0.280506D-01	0.270306D-01	0.166109D-01
0.202520D 00	0.243860D-01	0.237583D-01	0.258662D-01	0.246348D-01	0.234317D-01
0.354130D 00	0.199510D-01	0.177139D-01	0.210126D-01	0.198506D-01	0.366678D-01
0.500120D 00	0.164170D-01	0.127313D-01	0.167264D-01	0.162112D-01	0.444104D-01
0.600020D 00	0.145290D-01	0.100562D-01	0.142200E-01	0.143192D-01	0.462843D-01
0.725140D 00	0.123780D-01	0.768751D-02	0.115415D-01	0.123708D-01	0.428411E-01
0.801210D 00	0.112820D-01	0.697455D-02	0.102840E-01	0.113812D-01	0.367883D-01
0.900020D 00	0.994000D-02	0.711766D-02	0.918146D-02	0.101776D-01	0.229414E-01
0.950820D 00	0.938100D-02	0.779107D-02	0.892411D-02	0.955901D-02	0.125949D-01

Temperature 288.15K

X	Y (XPER)	Y (A-A + B-B)	Y (TAM-KUR)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.346040D-01	0.350332D-01	0.366116D-01	0.350444D-01	0.178853E-01
0.202520D 00	0.312890D-01	0.313373D-01	0.335637E-01	0.316721D-01	0.252288D-01
0.354130D 00	0.250760D-01	0.233447D-01	0.268283D-01	0.250447D-01	0.394745E-01
0.500120D 00	0.205290D-01	0.167402D-01	0.209580E-01	0.201697D-01	0.477935D-01
0.600020D 00	0.180840D-01	0.131805D-01	0.175745D-01	0.177307D-01	0.497901E-01
0.725140D 00	0.153820D-01	0.100069D-01	0.140722D-01	0.153495D-01	0.460659D-01
0.801210D 00	0.140310D-01	0.902647D-02	0.125161D-01	0.142037D-01	0.395434E-01
0.900020D 00	0.124630D-01	0.914010D-02	0.113134D-01	0.128426D-01	0.246266D-01
0.950820D 00	0.118350D-01	0.997635D-02	0.111683D-01	0.121419D-01	0.135069D-01

Table 4.4 formamide/water System(I) Temperature 318.15K

X	Y (XPER)	Y (A-A + B-B)	Y (MAT-HER)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.175950D-01	0.184074D-01	0.188375D-01	0.178784D-01	0.430096D-03
0.202520D 00	0.162580D-01	0.170872D-01	0.177183D-01	0.169343D-01	0.631094D-03
0.354130D 00	0.135340D-01	0.138725D-01	0.149641D-01	0.161490D-01	0.109161D-02
0.500120D 00	0.113050D-01	0.106047D-01	0.120697D-01	0.169429D-01	0.146503D-02
0.600020D 00	0.100800D-01	0.857063D-02	0.102338D-01	0.183166D-01	0.166315D-02
0.725140D 00	0.861000D-02	0.622829D-02	0.794491D-02	0.195848D-01	0.171662D-02
0.801210D 00	0.784000D-02	0.519928D-02	0.678654D-02	0.194029D-01	0.158727D-02
0.900020D 00	0.682900D-02	0.469223D-02	0.578833D-02	0.161635D-01	0.109610D-02
0.950820D 00	0.638700D-02	0.504475D-02	0.568222D-02	0.122133D-01	0.637468D-03

Temperature 308.15K

X	Y (XPER)	Y (A-A + B-B)	Y (MAT-HER)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.217440D-01	0.226151D-01	0.230556D-01	0.220151D-01	0.440493D-03
0.202520D 00	0.196660D-01	0.209893D-01	0.216355D-01	0.208758D-01	0.646245D-03
0.354130D 00	0.162720D-01	0.170445D-01	0.181627D-01	0.199749D-01	0.111824D-02
0.500120D 00	0.135220D-01	0.130069D-01	0.145057D-01	0.209689D-01	0.149877D-02
0.600020D 00	0.119710D-01	0.104901D-01	0.121891D-01	0.226453D-01	0.169896D-02
0.725140D 00	0.102230D-01	0.760996D-02	0.936367D-02	0.242031D-01	0.175370D-02
0.801210D 00	0.931500D-02	0.633731D-02	0.795832D-02	0.239488D-01	0.162101D-02
0.900020D 00	0.815600D-02	0.568902D-02	0.680655D-02	0.198669D-01	0.111753D-02
0.950820D 00	0.765500D-02	0.609986D-02	0.674895D-02	0.149427D-01	0.649092D-03

Temperature 298.15K

X	Y (XPER)	Y (A-A + B-B)	Y (MAT-HER)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.266890D-01	0.287169D-01	0.290973D-01	0.275335D-01	0.380428D-03
0.202520D 00	0.243860D-01	0.266490D-01	0.272071D-01	0.259130D-01	0.558073D-03
0.354130D 00	0.199510D-01	0.216210D-01	0.225860D-01	0.244240D-01	0.965012D-03
0.500120D 00	0.164170D-01	0.165105D-01	0.178056D-01	0.255379D-01	0.129509D-02
0.600020D 00	0.145290D-01	0.132776D-01	0.147429D-01	0.275689D-01	0.146533D-02
0.725140D 00	0.123780D-01	0.959888D-02	0.111106D-01	0.296105D-01	0.151167D-02
0.801210D 00	0.112820D-01	0.795330D-02	0.934822D-02	0.293748D-01	0.139492D-02
0.900020D 00	0.994000D-02	0.708689D-02	0.804705D-02	0.244747D-01	0.960159D-03
0.950820D 00	0.938100D-02	0.757042D-02	0.812732D-02	0.184433D-01	0.556896D-03

Temperature 288.15K

X	Y (XPER)	Y (A-A + B-B)	Y (MAT-HER)	Y (VINC 1)	A-B FACTOR
0.138150D 00	0.346040D-01	0.378706D-01	0.381028D-01	0.360488D-01	0.232215D-03
0.202520D 00	0.312890D-01	0.351400D-01	0.354807D-01	0.338025D-01	0.340630D-03
0.354130D 00	0.250760D-01	0.284946D-01	0.290834D-01	0.316210D-01	0.588850D-03
0.500120D 00	0.205290D-01	0.217285D-01	0.225183D-01	0.329433D-01	0.789727D-03
0.600020D 00	0.180840D-01	0.174387D-01	0.183315D-01	0.355501D-01	0.892815D-03
0.725140D 00	0.153820D-01	0.125526D-01	0.134728D-01	0.382339D-01	0.920247D-03
0.801210D 00	0.140310D-01	0.103513D-01	0.111998D-01	0.379641D-01	0.848568D-03
0.900020D 00	0.124630D-01	0.913341D-02	0.971595D-02	0.315959D-01	0.582538D-03
0.950820D 00	0.118350D-01	0.970983D-02	0.100470D-01	0.237561D-01	0.337214D-03



Table 4.5 methanol/formamide System (II) Temperature 318.15K

X	Y (XPER)	Y (A-A + B-B)	Y (DOLEZ.)	Y (VINC 1)	A-B FACTOR
0.893000	00	0.667504D-02	0.626330D-02	0.669797D-02	0.155967D-02
0.815000	00	0.764525D-02	0.719319D-02	0.774557D-02	0.246109D-02
0.692000	00	0.963139E-02	0.920552D-02	0.968878D-02	0.347901D-02
0.551000	00	0.125670D-01	0.123344D-01	0.124993D-01	0.403828D-02
0.509000	00	0.135697D-01	0.134361D-01	0.134836D-01	0.407941D-02
0.404000	00	0.163585E-01	0.165313D-01	0.162900D-01	0.393030D-02
0.291000	00	0.199372D-01	0.204063D-01	0.199349D-01	0.336773D-02
0.190000	00	0.237066D-01	0.243471D-01	0.238190D-01	0.251210D-02
0.112000	00	0.271851E-01	0.276988D-01	0.272695D-01	0.162342D-02
Temperature 308.15K					
0.893000	00	0.564339D-02	0.549101D-02	0.576178D-02	0.141062D-02
0.815000	00	0.654841D-02	0.626687D-02	0.661081D-02	0.222589D-02
0.692000	00	0.817851D-02	0.788577D-02	0.818627D-02	0.314652D-02
0.551000	00	0.105090D-01	0.103370D-01	0.104387D-01	0.365234D-02
0.509000	00	0.112907E-01	0.111901D-01	0.112185D-01	0.368955D-02
0.404000	00	0.134504D-01	0.135697D-01	0.134179D-01	0.355469D-02
0.291000	00	0.162387D-01	0.165246D-01	0.162294D-01	0.304588D-02
0.190000	00	0.190960D-01	0.195114D-01	0.191811D-01	0.227202D-02
0.112000	00	0.216750D-01	0.220414D-01	0.217730D-01	0.146827D-02
Temperature 298.15K					
0.893000	00	0.504519D-02	0.484080D-02	0.504905D-02	0.126649D-02
0.815000	00	0.566191D-02	0.549759D-02	0.576209D-02	0.199847D-02
0.692000	00	0.704359D-02	0.683162D-02	0.706257E-02	0.282504D-02
0.551000	00	0.892783D-02	0.880999D-02	0.888785D-02	0.327918D-02
0.509000	00	0.956373D-02	0.949204D-02	0.951350D-02	0.331258D-02
0.404000	00	0.112943D-01	0.113834D-01	0.112662D-01	0.319150D-02
0.291000	00	0.135039D-01	0.137160D-01	0.134885D-01	0.273468D-02
0.190000	00	0.157474D-01	0.160618D-01	0.158073D-01	0.203989D-02
0.112000	00	0.177684D-01	0.180418D-01	0.178350D-01	0.131825D-02

Table 4.6 formamide/methanol System(II) Temperature 318.15K.

Y(XPER)	Y(A-A + B-B)	Y(TAM-KUR)	Y(VINC 1)	A-B FACTOR
0.893000D 00	0.504519D-02	0.360633D-02	0.483530D-02	0.190284D 00
0.815000D 00	0.568191D-02	0.353593D-02	0.548720D-02	0.302120D 00
0.692000D 00	0.704359D-02	0.403975D-02	0.681528D-02	0.429741D 00
0.551000D 00	0.892783D-02	0.553915D-02	0.878372D-02	0.502362D 00
0.509000D 00	0.956373D-02	0.621432D-02	0.949280D-02	0.507613D 00
0.404000D 00	0.112943D-01	0.822954D-02	0.113948D-01	0.490081D 00
0.291000D 00	0.135039D-01	0.110179D-01	0.137296D-01	0.419865D 00
0.190000D 00	0.157474D-01	0.140516D-01	0.160766D-01	0.313524D 00
0.112000D 00	0.177684D-01	0.167525D-01	0.180585D-01	0.202207D 00

Temperature 308.15K

0.893000D 00	0.564339D-02	0.411438D-02	0.548354D-02	0.190552D 00
0.815000D 00	0.654841D-02	0.408183D-02	0.625531D-02	0.302491D 00
0.692000D 00	0.817851D-02	0.477619D-02	0.786457D-02	0.429822D 00
0.551000D 00	0.105090D-01	0.670043D-02	0.103114D-01	0.502549D 00
0.509000D 00	0.112907D-01	0.754613D-02	0.111910D-01	0.507275D 00
0.404000D 00	0.134504D-01	0.100606D-01	0.135761D-01	0.489254D 00
0.291000D 00	0.162387D-01	0.135309D-01	0.165434D-01	0.419264D 00
0.190000D 00	0.190960D-01	0.172857D-01	0.195350D-01	0.313039D 00
0.112000D 00	0.216750D-01	0.206104D-01	0.220603D-01	0.201786D 00

Temperature 298.15K

0.893000D 00	0.667504D-02	0.473990D-02	0.625637D-02	0.190835D 00
0.815000D 00	0.764525D-02	0.477636D-02	0.718227D-02	0.302763D 00
0.692000D 00	0.963139D-02	0.576883D-02	0.918518D-02	0.429919D 00
0.551000D 00	0.125670D-01	0.830897D-02	0.122972D-01	0.501879D 00
0.509000D 00	0.135697D-01	0.941824D-02	0.134464D-01	0.506911D 00
0.404000D 00	0.163585D-01	0.126713D-01	0.165563D-01	0.488896D 00
0.291000D 00	0.199372D-01	0.170824D-01	0.204029D-01	0.417857D 00
0.190000D 00	0.237066D-01	0.218935D-01	0.243756D-01	0.312351D 00
0.112000D 00	0.271851D-01	0.261312D-01	0.277316D-01	0.201400D 00

Table 4.7 formamide/methanol System(II) Temperature 318.15K

X	Y(XPERJ)	Y(A-A + B-B)	Y(MAT-HER)	Y(VINC 1)	A-B FACTCR
0.893000D 00	0.504519D-02	0.363884D-02	0.483116D-02	0.666752D-02	0.119232D-02
0.815000D 00	0.568191D-02	0.357359D-02	0.547840D-02	0.708034D-02	0.190481D-02
0.692000D 00	0.704359D-02	0.407450D-02	0.680083D-02	0.618477D-02	0.272634D-02
0.551000D 00	0.892783D-02	0.555016D-02	0.875982D-02	0.423170D-02	0.320965D-02
0.509000D 00	0.956373D-02	0.625023D-02	0.949429D-02	0.341199D-02	0.324406D-02
0.404000D 00	0.112943D-01	0.826800D-02	0.114066D-01	0.260207D-02	0.313856D-02
0.291000D 00	0.135039D-01	0.110549D-01	0.137433D-01	0.348615D-02	0.268846D-02
0.190000D 00	0.157474D-01	0.140816D-01	0.160913D-01	0.665271D-02	0.200968D-02
0.112000D 00	0.177684D-01	0.167816D-01	0.180751D-01	0.110775D-01	0.129355D-02
Temperature 308.15K					
0.893000D 00	0.564339D-02	0.414883D-02	0.547734D-02	0.777934D-02	0.132852D-02
0.815000D 00	0.654841D-02	0.412352D-02	0.624516D-02	0.824617D-02	0.212164D-02
0.692000D 00	0.817851D-02	0.481461D-02	0.784498D-02	0.705136D-02	0.303037D-02
0.551000D 00	0.105090D-01	0.671884D-02	0.102877D-01	0.457751D-02	0.356890D-02
0.509000D 00	0.112907D-01	0.759274D-02	0.111924D-01	0.354618D-02	0.359967D-02
0.404000D 00	0.134504D-01	0.101070D-01	0.135825D-01	0.254826D-02	0.347549D-02
0.291000D 00	0.162387D-01	0.135836D-01	0.165622D-01	0.370791D-02	0.297859D-02
0.190000D 00	0.190960D-01	0.173323D-01	0.195584D-01	0.773613D-02	0.222605D-02
0.112000D 00	0.216750D-01	0.206479D-01	0.220792D-01	0.133251D-01	0.143129D-02
Temperature 298.15K					
0.893000D 00	0.667504D-02	0.477662D-02	0.674928D-02	0.939713D-02	0.147266D-02
0.815000D 00	0.764525D-02	0.482140D-02	0.717049D-02	0.100172D-01	0.234909D-02
0.692000D 00	0.963139D-02	0.581250D-02	0.916323D-02	0.849023D-02	0.335073D-02
0.551000D 00	0.125670D-01	0.832432D-02	0.122582D-01	0.529703D-02	0.393390D-02
0.509000D 00	0.135697D-01	0.946076D-02	0.134535D-01	0.398254D-02	0.397272D-02
0.404000D 00	0.163585D-01	0.127424D-01	0.165779D-01	0.270941D-02	0.383555D-02
0.291000D 00	0.199372D-01	0.171265D-01	0.203965D-01	0.420039D-02	0.326993D-02
0.190000D 00	0.237066D-01	0.219523D-01	0.244018D-01	0.941145D-02	0.244946D-02
0.112000D 00	0.271851D-01	0.261872D-01	0.277630D-01	0.166314D-01	0.157583D-02

Temperature 298.15K

X	Y(XPER)	Y(A-A + B-B)	Y(DOLEZ.)	Y(VINC 1)	A-B FACTOR
0.901000D 00	0.735554C-02	0.539656D-02	0.783813D-02	0.719872D-02	0.244158D-02
0.752000D 00	0.866275D-02	0.493380D-02	0.944299D-02	0.857814D-02	0.450919D-02
0.690000D 00	0.101681D-01	0.509895D-02	0.109539D-01	0.102149C-01	0.585491D-02
0.598000D 00	0.117960D-01	0.574399D-02	0.123242D-01	0.118829D-01	0.658017C-02
0.473000D 00	0.143630D-01	0.737433D-02	0.141974D-01	0.142883D-01	0.682310D-02
0.367000D 00	0.161000D-01	0.943743D-02	0.157963D-01	0.163144C-01	0.635886D-02
0.281000D 00	0.178525C-01	0.115702D-01	0.171005D-01	0.178569D-01	0.553025D-02
0.181300D 00	0.196084D-01	0.145573C-01	0.186202D-01	0.194364D-01	0.406286D-02
0.888600D-01	0.207312D-01	0.178206D-01	0.200368D-01	0.206137C-01	0.221616D-02

Temperature 288.15K

X	Y(XPER)	Y(A-A + B-B)	Y(DOLEZ.)	Y(VINC 1)	A-B FACTOR
0.901000D 00	0.829766D-02	0.603991D-02	0.886763D-02	0.795438D-02	0.282773C-02
0.792000D 00	0.991841C-02	0.561017D-02	0.108325D-01	0.959708D-02	0.522234D-02
0.650000D 00	0.113479D-01	0.593006D-02	0.127110D-01	0.116551D-01	0.678090D-02
0.598000D 00	0.138492D-01	0.681737D-02	0.144382D-01	0.138073C-01	0.762086D-02
0.473000D 00	0.166823D-01	0.893298D-02	0.168352D-01	0.169635D-01	0.790221D-02
0.367000D 00	0.195518D-01	0.115485D-01	0.189131D-01	0.196518D-01	0.736456D-02
0.281000D 00	0.217563D-01	0.142245D-01	0.206294D-01	0.217084D-01	0.640490D-02
0.181300D 00	0.240961C-01	0.179479D-01	0.226533D-01	0.238179D-01	0.470543C-02
0.888600D-01	0.255647D-01	0.219960D-01	0.245627D-01	0.253860D-01	0.256666D-02

Table 4.8 formamide/dimethylformamide System(III)Temperature 318.15K

X	Y(XPER)	Y(A-A + B-B)	Y(DOLEZ.)	Y(VINC 1)	A-B FACTOR
0.901000D 00	0.948272D-02	0.683963D-02	0.102521D-01	0.905014D-02	0.341246D-02
0.792000D 00	0.114742D-01	0.648101D-02	0.127833D-01	0.111575D-01	0.630226D-02
0.650000D 00	0.138604D-01	0.703933D-02	0.152224D-01	0.138233D-01	0.818311D-02
0.598000D 00	0.165412D-01	0.828422D-02	0.174810D-01	0.166514D-01	0.919676D-02
0.473000D 00	0.202743D-01	0.111023D-01	0.206386D-01	0.208092D-01	0.953629D-02
0.367000D 00	0.241014D-01	0.145090D-01	0.233965D-01	0.243702D-01	0.888746D-02
0.281000D 00	0.272041D-01	0.179588D-01	0.256881D-01	0.271098D-01	0.772935D-02
0.181300D 00	0.304399D-01	0.227271D-01	0.284055D-01	0.299396D-01	0.567846D-02
0.888600D-01	0.324667D-01	0.278859D-01	0.309833D-01	0.320677D-01	0.309741D-02

Temperature 308.15K

X	Y(XPER)	Y(A-A + B-B)	Y(DOLEZ.)	Y(VINC 1)	A-B FACTOR
0.901000D 00	0.109739D-01	0.784147D-02	0.119868D-01	0.102634D-01	0.414532D-02
0.792000D 00	0.134920D-01	0.763293D-02	0.152887D-01	0.129580D-01	0.765573D-02
0.690000D 00	0.165838D-01	0.858333D-02	0.185238D-01	0.165330D-01	0.994052D-02
0.598000D 00	0.201456D-01	0.103905D-01	0.215624D-01	0.203744D-01	0.111719D-01
0.473000D 00	0.252559D-01	0.142898D-01	0.258741D-01	0.261209D-01	0.115843D-01
0.367000D 00	0.306831D-01	0.188996D-01	0.256958D-01	0.310943D-01	0.107961D-01
0.281000D 00	0.350932D-01	0.235186D-01	0.329079D-01	0.349488D-01	0.938930D-02
0.181300D 00	0.398168D-01	0.298588D-01	0.367568D-01	0.389584D-01	0.689796D-02
0.888600D-01	0.425818D-01	0.366827D-01	0.404454D-01	0.420014D-01	0.376261D-02

Table 4.9 formamide/dimethylformamide System(III) Temperature 318.15K

X	Y(XPER)	Y(A-A + B-B)	Y(TAM-KUR)	Y(VINC 1)	A-B FACTOR
0.9010000 00	0.7355540-02	0.5573370-02	0.7866300-02	0.7308100-02	0.1343630 00
0.7920000 00	0.8662750-02	0.5006500-02	0.9501480-02	0.8668790-02	0.2634000 00
0.6900000 00	0.1016810-01	0.4847110-02	0.1103270-01	0.1022410-01	0.3624700 00
0.5980000 00	0.1179600-01	0.5080530-02	0.1243560-01	0.1183530-01	0.4309970 00
0.4730000 00	0.1436300-01	0.6056590-02	0.1429830-01	0.1417290-01	0.4829520 00
0.3670000 00	0.1610000-01	0.7643450-02	0.1589910-01	0.1623990-01	0.4837710 00
0.2810000 00	0.1785250-01	0.9558770-02	0.1720170-01	0.1786750-01	0.4478680 00
0.1813000 00	0.1960840-01	0.1264610-01	0.1870840-01	0.1955980-01	0.3552430 00
0.8886000-01	0.2073120-01	0.1650210-01	0.2006590-01	0.2074190-01	0.2088350 00

Temperature 308.15K

X	Y(XPER)	Y(A-A + B-B)	Y(TAM-KUR)	Y(VINC 1)	A-B FACTOR
0.9010000 00	0.8297660-02	0.6225170-02	0.8963780-02	0.8167210-02	0.1343930 00
0.7920000 00	0.9918410-02	0.5647300-02	0.1101940-01	0.9829010-02	0.2636270 00
0.6900000 00	0.1134790-01	0.5343830-02	0.1243370-01	0.1133970-01	0.3489070 00
0.5980000 00	0.1384920-01	0.5923690-02	0.1469830-01	0.1383650-01	0.4306010 00
0.4730000 00	0.1668230-01	0.7236720-02	0.1706530-01	0.1687690-01	0.4823240 00
0.3670000 00	0.1955180-01	0.9274640-02	0.1911020-01	0.1959160-01	0.4830600 00
0.2810000 00	0.2175630-01	0.1168850-01	0.2079790-01	0.2173280-01	0.4470290 00
0.1813000 00	0.2409610-01	0.1554570-01	0.2277090-01	0.2397120-01	0.3545680 00
0.8886000-01	0.2556470-01	0.2032190-01	0.2456770-01	0.2552200-01	0.2083560 00

Temperature 298.15K

X	Y(XPER)	Y(A-A + B-B)	Y(TAM-KUR)	Y(VINC 1)	A-B FACTOR
0.901000D 00	0.948272D-02	0.704222D-02	0.103919D-01	0.924646D-02	0.134773D 00
0.792000D 00	0.114742D-01	0.644346D-02	0.129920D-01	0.112886D-01	0.263476D 00
0.690000D 00	0.138604D-01	0.646876D-02	0.154788D-01	0.138259D-01	0.362512D 00
0.598000D 00	0.165412D-01	0.706227D-02	0.177673D-01	0.165428D-01	0.430708D 00
0.473000D 00	0.202743D-01	0.887305D-02	0.208553D-01	0.206036D-01	0.482097D 00
0.367000D 00	0.241014D-01	0.115472D-01	0.235243D-01	0.242242D-01	0.481888D 00
0.281000D 00	0.272041D-01	0.147070D-01	0.258105D-01	0.271748D-01	0.446740D 00
0.181300D 00	0.304399D-01	0.196638D-01	0.284674D-01	0.302094D-01	0.354206D 00
0.888600D-01	0.324667D-01	0.257642D-01	0.309374D-01	0.323194D-01	0.208140D 00

Temperature 288.15K

X	Y(XPER)	Y(A-A + B-B)	Y(TAM-KUR)	Y(VINC 1)	A-B FACTOR
0.901000D 00	0.109739D-01	0.805818D-02	0.122486D-01	0.105378D-01	0.135153D 00
0.792000D 00	0.134920D-01	0.747827D-02	0.156528D-01	0.131146D-01	0.263650D 00
0.690000D 00	0.165838D-01	0.770891D-02	0.189528D-01	0.164912D-01	0.362646D 00
0.598000D 00	0.201456D-01	0.865695D-02	0.220119D-01	0.201899D-01	0.430733D 00
0.473000D 00	0.252559D-01	0.112541D-01	0.262040D-01	0.258318D-01	0.482172D 00
0.367000D 00	0.306831D-01	0.149560D-01	0.299220D-01	0.309697D-01	0.482695D 00
0.281000D 00	0.350932D-01	0.191883D-01	0.330308D-01	0.350652D-01	0.446459D 00
0.181300D 00	0.398168D-01	0.258043D-01	0.367761D-01	0.393716D-01	0.353871D 00
0.888600D-01	0.425818D-01	0.337564D-01	0.401778D-01	0.422281D-01	0.207106D 00

Table 4.10 formamide/dimethylformamide System(III) Temperature 308.15K

X	Y(XPER)	Y(A-A + B-B)	Y(MAT-HER)	Y(VINC I)	A-B FACTOR
0.901000 00	0.829766D-02	0.648151D-02	0.880004D-02	0.899517D-02	0.231853D-02
0.792000 00	0.991841D-02	0.595490D-02	0.107856D-01	0.998262D-02	0.483068D-02
0.690000 00	0.113479D-01	0.526167D-02	0.117784D-01	0.916530D-02	0.651668D-02
0.598000 00	0.138492D-01	0.573724D-02	0.145689D-01	0.916372D-02	0.883162D-02
0.473000 00	0.166823D-01	0.643061D-02	0.171168D-01	0.754246D-02	0.106862D-01
0.367000 00	0.195518D-01	0.788933D-02	0.193907D-01	0.629779D-02	0.115014D-01
0.281000 00	0.217563D-01	0.991134D-02	0.212368D-01	0.611776D-02	0.113254D-01
0.181300 00	0.240961D-01	0.136172D-01	0.233155D-01	0.814301D-02	0.969826D-02
0.888600D-01	0.255647D-01	0.188181D-01	0.249577D-01	0.140552D-01	0.613959D-02

Temperature 318.15 K

X	Y(XPER)	Y(A-A + B-B)	Y(MAT-HER)	Y(VINC I)	A-B FACTOR
0.901000 00	0.735554D-02	0.580923D-02	0.771324D-02	0.779660D-02	0.190402D-02
0.792000 00	0.866275D-02	0.530354D-02	0.926554D-02	0.851995D-02	0.396200D-02
0.690000 00	0.101681D-01	0.501530D-02	0.107937D-01	0.844946D-02	0.577837D-02
0.598000 00	0.117900D-01	0.500445D-02	0.122738D-01	0.790316D-02	0.725930D-02
0.473000 00	0.143630D-01	0.547652D-02	0.142790D-01	0.667064D-02	0.880251D-02
0.367000 00	0.161000D-01	0.658431D-02	0.160615D-01	0.574116D-02	0.947723D-02
0.281000 00	0.178525D-01	0.817245D-02	0.175122D-01	0.564032D-02	0.933975D-02
0.181300 00	0.196084D-01	0.111230D-01	0.191213D-01	0.725351D-02	0.799832D-02
0.888600D-01	0.207312D-01	0.153198D-01	0.203872D-01	0.118760D-01	0.506740D-02



Temperature 298.15K

X	Y(XPER)	Y(A-A + B-R)	Y(MAT-HER)	Y(VINC I)	A-B FACTOR
0.901000D 00	0.948272D-02	0.733307D-02	0.102075D-01	0.103669D-01	0.287444C-02
0.792000D 00	0.114742D-01	0.673705D-02	0.126855D-01	0.114761D-01	0.594843D-02
0.650000D 00	0.138604D-01	0.651909D-02	0.151915D-01	0.113241D-01	0.867246D-02
0.598000D 00	0.165412D-01	0.670873D-02	0.176017D-01	0.103672D-01	0.108930D-01
0.473000D 00	0.202743D-01	0.773822D-02	0.208997D-01	0.829473D-02	0.131615D-01
0.367000D 00	0.241014D-01	0.968461D-02	0.237948D-01	0.674501D-02	0.141102D-01
0.281000D 00	0.272041D-01	0.123876D-01	0.263315D-01	0.664901C-02	0.139439D-01
0.181300D 00	0.304399D-01	0.171833D-01	0.291149D-01	0.944087D-02	0.119315C-01
0.888600D-01	0.324667D-01	0.238517D-01	0.314049D-01	0.173002D-01	0.755316D-02

Temperature 288.15K

X	Y(XPER)	Y(A-A + B-B)	Y(MAT-HER)	Y(VINC I)	A-B FACTOR
0.901000D 00	0.109739D-01	0.838805D-02	0.120576D-01	0.122767D-01	0.366956D-02
0.792000D 00	0.134920D-01	0.774468D-02	0.153058D-01	0.136812D-01	0.756114C-02
0.650000D 00	0.165838C-01	0.762412D-02	0.186414D-01	0.134376D-01	0.110173D-01
0.558000D 00	0.201456D-01	0.802767D-02	0.218573D-01	0.121232D-01	0.138296D-01
0.473000D 00	0.252559D-01	0.961005D-02	0.263230D-01	0.935308C-02	0.167129C-01
0.367000D 00	0.306831D-01	0.124011D-01	0.303731D-01	0.734548D-02	0.179720D-01
0.281000D 00	0.350932D-01	0.160445D-01	0.337231D-01	0.725917D-02	0.176786D-01
0.181300D 00	0.398168D-01	0.224920D-01	0.376098D-01	0.111717C-01	0.151178D-01
0.888600D-01	0.425818C-01	0.311170D-01	0.406102D-01	0.218077D-01	0.949319D-02

Ghai and Dullien<sup>111</sup> investigated the Tamura Kurata equation for eleven binary mixtures. They found that for the ideal solutions, ie solutions for which there was no possibility of hydrogen bonding or complex formation (such as m-bromotoluene/toluene, and benzene/toluene), the fit was very good (better than 1%) but that for other systems (especially the n-propanol/toluene system) a much poorer fit was obtained. They also pointed out that the McAllister equation did much better than the Tamura Kurata in only one case, that of the n-propanol/toluene system.

Reynaud<sup>112</sup>, on the other hand, investigated the ability of equations (4.2), (4.13) and (4.15) to describe the viscosity of the binary mixtures N-ethylacetamide/water and N-methylacetamide/water. The experimental measurements on these systems were made by Assarsson and Eirich<sup>113</sup> who concluded that the maxima which they obtained in the viscosity/concentration graphs was indicative of complex hydrogen bonding between the two components of the mixtures. For these systems, Reynaud suggested that both the Tamura-Kurata, and the Dolezalek equations were reasonably good representations and that the Tamura-Kurata equation was especially good at high concentrations of amide.

Tamura and Kurata<sup>98</sup> did point out that their equation was less applicable to mixtures where  $\eta_A$  and  $\eta_B$  were very different (eg water and glycerol).

From table (4.1) which gives a list of the sums of the squares of the errors obtained in applying each model to all three systems at the various temperatures it can be seen that

(i) for the formamide/water mixtures, System (I), the Dolezalek model, equation (4.2), provides the best comparison with the experimental results,

(ii) for the formamide/methanol mixtures, System (II), all three

models are equally good; and

(iii) for the formamide/dimethylformamide mixtures, System (III), the Mato-Hernandez model, equation (4.15), is the best.

#### 4.7 ACTIVATION PARAMETERS

According to the Eyring rate theory, the activation enthalpy of viscous flow for a simple liquid is given by equation (3.24), Chapter 3, and is independent of temperature. A plot of  $\ln \eta$  against  $\frac{1}{T}$  should give a straight line (assuming  $V$  and  $\Delta S^*$  are constant) from which  $\Delta H^*$  can be calculated. For associated liquids however it has been proposed that  $\Delta H^*$  is not independent of temperature<sup>89,114</sup>. Tyuzyo<sup>114</sup> used this fact to classify associated solvents into two groups. Associated liquids of the first kind he considered would have an activation enthalpy of viscous flow which would be independent of temperature. However he considered that formamide and methanol would both belong to this group. This classification of formamide is not supported in the present work.

Figs. (4.1) and (4.2) show such plots for the solvents used in the above investigations. It can be seen that the viscosity of both methanol and dimethylformamide change very little with increasing temperature, fig. (4.2). The behaviour of formamide however is similar to that of water, fig. (4.1). The temperature coefficient of the viscosity is large and for both these solvents a marked curvature can be seen in fig. (4.1). This behaviour is that normally attributed to solvents which have a high degree of association.

Similar plots can be seen, fig. (4.3), for the mutual viscosity coefficients,  $\eta_{AB}$ , obtained for the various models for the three systems.

Fig. (4.1)

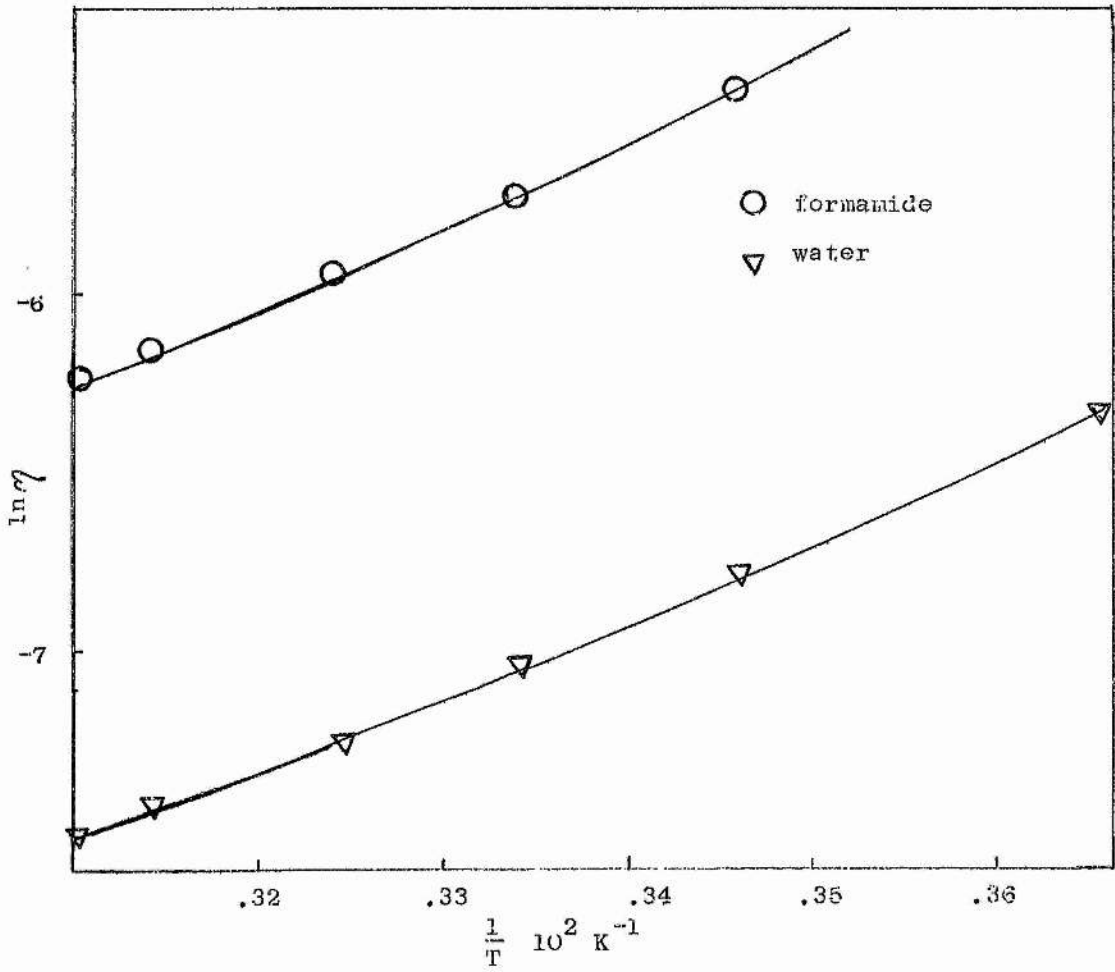
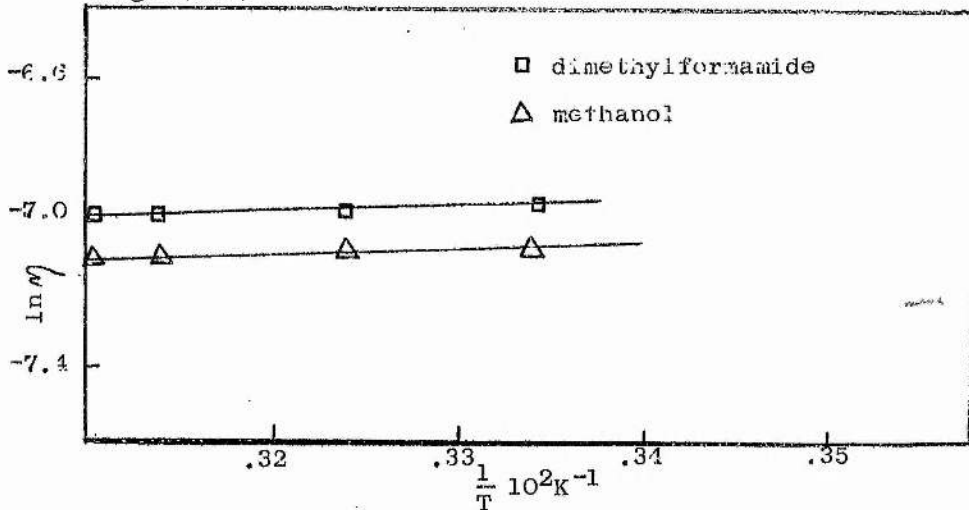


Fig. (4.2)



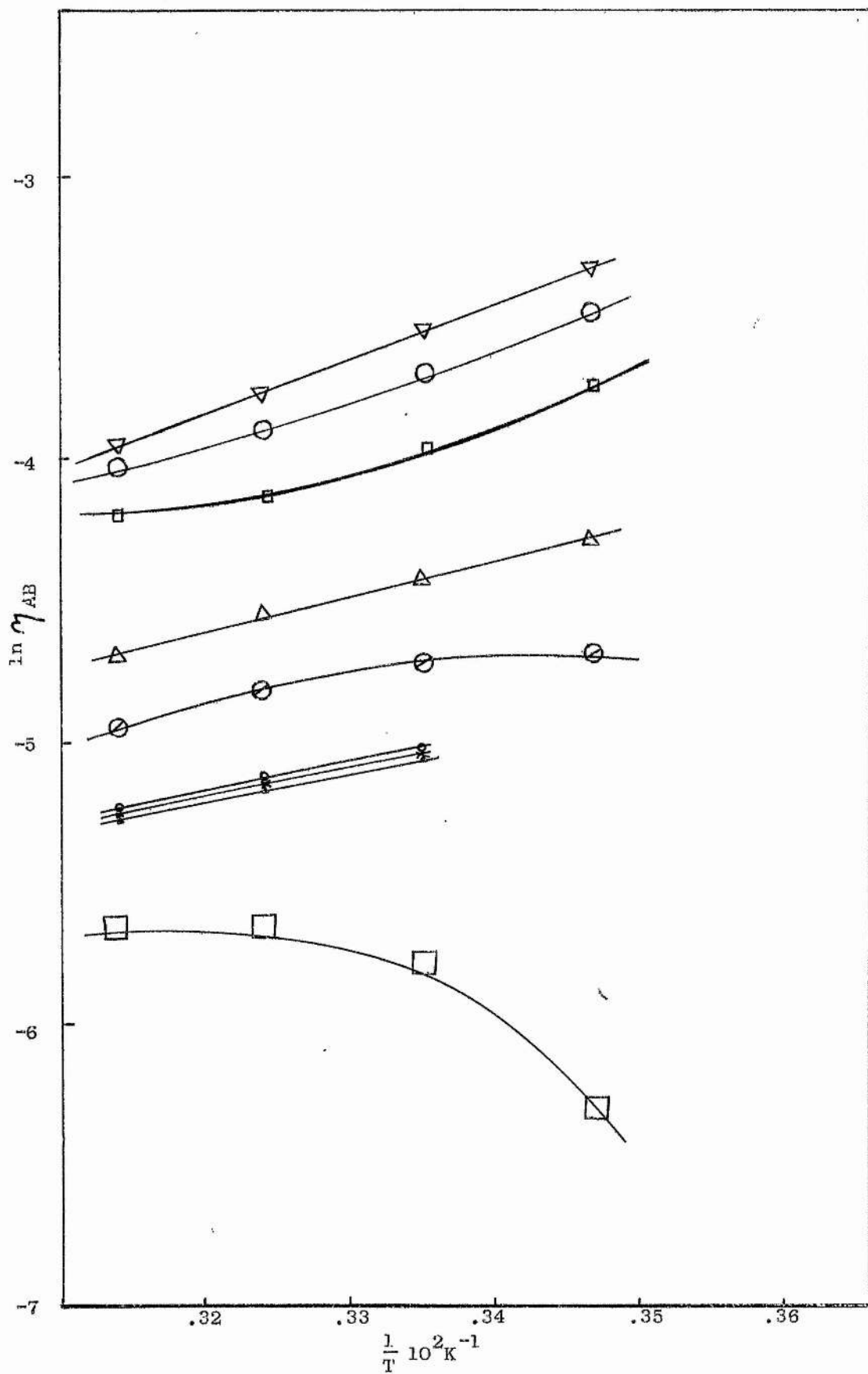
Key to fig. (4.3)

- ▽ Represents  $\eta_{AB}$  for System III (formamide/dimethylformamide) calculated by the Mato-Hernandez model (equation 4.15)
- Represents  $\eta_{AB}$  for System III calculated by the Tamura-Kurata model (equation 4.13)
- ◻ Represents  $\eta_{AB}$  for System III calculated by the Dolezalek model (equation 4.2)
- △ Represents  $\eta_{AB}$  for System I (formamide/water) calculated from equation (4.2)
- ⊙ Represents  $\eta_{AB}$  for System I calculated from equation (4.13)
- Represents  $\eta_{AB}$  for System I calculated from equation (4.15)

NOTE For clarity the plots of  $\ln \eta_{AB}$  for system II (formamide/methanol) were all reduced by 0.2 on the  $\ln \eta_{AB}$  scale

- Represents  $\eta_{AB}$  for System II calculated from equation (4.2)
- × Represents  $\eta_{AB}$  for System II calculated from equation (4.13)
- ▲ Represents  $\eta_{AB}$  for System II calculated from equation (4.15)

Fig. (4.3)



4.8 SYSTEM II, formamide/methanol

As noted earlier, all three models describe this system equally well. This can probably be attributed to the fact that the molar volumes of formamide and methanol are very similar (39.84 and 40.75 ml respectively at 298.15 K) and therefore for each model approximately the same dependence is put on each pure component irrespective of whether the volume fractions or the mole fractions are considered. The plots of  $\ln \eta_{AB}$  against  $\frac{1}{T}$  for the mutual viscosity coefficients,  $\eta_{AB}$ , for all three one parameter models for this system gave straight lines, fig. (4.3) which were almost parallel. The values of  $\Delta G_{AB}^*$ ,  $\Delta H_{AB}^*$  and  $\Delta S_{AB}^*$  as calculated by computer program are given in table (4.11).

TABLE 4.11

Activation parameters for  $\eta_{AB}$  from each model for System II

Model	$\Delta G_{AB}^*$ KJ/Mol	$\Delta H_{AB}^*$ KJ/Mol	$\Delta S_{AB}^*$ KJ <sup>-1</sup> /Mol
(1) Dolezalek	50.87	7.45	-145.7
(2) Tamura-Kurata	50.80	7.30	-145.7
(3) Mato-Hernandez	50.73	7.30	-145.7
	$\Delta G^*$	$\Delta H^*$	$\Delta S^*$
formamide	54.29	15.92	-125.4
methanol	49.89	9.37	-136.0

Agreement is good for the three models.  $\Delta H_{AB}^*$  is smaller than for either solvent but because  $\Delta S_{AB}^*$  is also smaller,  $\Delta G_{AB}^*$  lies between the value obtained for formamide and methanol. This could imply that the association between unlike molecules in this system is less than that between like molecules.

Because  $\Delta H_{AB}^*$  is less than  $\Delta H^*$  for either solvent, this suggests that fewer bonds are required to be broken for a molecule A

in the neighbourhood of a molecule B moving to the next equilibrium position than are required to be broken for a molecule B moving from a similar position, and vice versa.

The fact that  $\Delta S^*$  for  $\eta_{AB}$  is more negative than for either  $\eta_A$  or  $\eta_B$  can indicate one of two things, (a) that the entropy loss is greater for  $\eta_{AB}$  due to the ordered situation of B around A or vice versa being less than that of A around A or B around B, or that (b) the extent of ordering in the transition states (for  $\eta_{AB}$ ,  $\eta_A$  and  $\eta_B$ ) is not the same.

The results obtained in this work for the viscosity of formamide/methanol mixtures are in agreement with those measured by Kozlowski<sup>115</sup> at 298.15 K.

#### 4.9 SYSTEM III, formamide/dimethylformamide

This system is best described by the Mato-Hernandez model. The molar volume of dimethylformamide at 298.15 K is 77.44 ml compared with that of formamide at the same temperature, 39.84 ml. Since the Mato-Hernandez model lays the most stress on volume fractions, this model therefore emphasises the contribution to  $\eta$  from the dimethylformamide.

Plots of  $\ln \eta_{AB}$  against  $\frac{1}{T}$  for this system can be seen in fig. (4.3). For the Mato-Hernandez equation the plot of  $\ln \eta_{AB}$  against  $\frac{1}{T}$  is almost linear. Table (4.12) gives  $\Delta G_{AB}^*$ ,  $\Delta H_{AB}^*$  and  $\Delta S_{AB}^*$  for  $\eta_{AB}$  and the pure solvents.

Both  $\Delta H_{AB}^*$  and  $\Delta S_{AB}^*$  are greater for  $\eta_{AB}$  than for pure dimethylformamide which suggests that the dimethylformamide solvent molecules associate to a greater extent with formamide than with each other.



TABLE 4.12

Activation parameters for  $\eta_{AB}$  and System III

MODEL	$\Delta G_{AB}^*$ KJ/Mol	$\Delta H_{AB}^*$ KJ/Mol	$\Delta S_{AB}^*$ JK <sup>-1</sup> /Mol
(2) Tamura-Kurata	54.58	14.45	-134.6
(3) Mato-Hernandez	54.90	15.62	-131.8
formamide	54.38	17.74	-122.9
dimethylformamide	52.43	8.27	-148.2

4.10 SYSTEM I, formamide/water

The Dolezalek equation (4.2), describes this system more accurately than the others. Fig. (4.3) gives the plot of  $\ln \eta_{AB}$  against  $\frac{1}{T}$  for this system. Again it can be seen that this is nearest to a straight line for the Dolezalek model. The molar volume of water is 18.07 ml compared with 39.84 ml for formamide, thus the other models, which emphasise molar volumes and hence further increase the formamide contribution to  $\eta$ , do not describe this system so well. Table (4.13), gives the values of  $\Delta G_{AB}^*$ ,  $\Delta H_{AB}^*$  and  $\Delta S_{AB}^*$  for  $\eta_{AB}$  and the pure solvents.

TABLE 4.13

Activation parameters for  $\eta_{AB}$  and System I.

MODEL	$\Delta G_{AB}^*$ KJ/Mol	$\Delta H_{AB}^*$ KJ/Mol	$\Delta S_{AB}^*$ JK <sup>-1</sup> /Mol
(1) Dolezalek	50.94	9.34	-139.6
(2) Tamura-Kurata	50.13	5.48	-149.8
formamide	54.33	17.78	-122.7
water	50.13	5.48	-149.8

Using an argument similar to that used in section 4.8 it would appear that unlike molecules in this system associate to a lesser extent than like molecules.

Although for the Dolezalek model a plot of  $\ln \eta_{AB}$  against  $\frac{1}{T}$ ,

fig. (4.3), is almost rectilinear, on close inspection it is seen to have a slight degree of curvature. This curvature indicates that as the temperature is increased,  $\Delta H_{AB}^*$  increases. This is considered to be due to a structure breaking influence of either solvent on the other, ie the A.....A and B.....B interactions were weakened by the present of B or A respectively. Accompanying this a decrease in  $\Delta H^*$  for  $\eta_A$  (for the A.....A interactions) and  $\eta_B$  would be expected.

The term  $\eta_{AB}$  is calculated by taking weighted averages of the viscosities of the pure components  $\eta_A$  and  $\eta_B$ . Any decrease in  $\Delta H^*$  for  $\eta_A$  and  $\eta_B$ , due to an effect like the one proposed above, will therefore have an overall effect on  $\eta$ , the viscosity of the mixture. In equations (4.2), (4.13) and (4.15) the values used for  $\eta_A$  and  $\eta_B$  are those obtained from the pure components (ie due to A.....A interactions not under the influence of B etc). At lower temperatures where the structure breaking effect would be expected to be most pronounced, the overall effect on  $\eta$  is reflected in  $\eta_{AB}$  since  $\eta_A$  and  $\eta_B$  are fixed.

As the temperature is raised, the structure breaking effect might be expected to decrease in importance (due to increased thermal motion) and therefore  $\Delta H^*$  for  $\eta_{AB}$  could be seen to increase.

In all cases it was found that the particular model which described the viscosity of each binary mixture most closely also gave an  $\eta_{AB}$  the activation enthalpy of which was most independent of temperature.

#### 4.11 THE THREE PARAMETER EQUATION

For each model, the respective three parameter equation as described in section (4.5), was investigated for each system. In all cases, as would be expected, the three parameter

extension gave a better fit to the experimental data, tables (4.2-4.10). However for the Mato-Hernandez model the three parameter equation did not converge for any of the systems. Table (4.14) gives a list of the parameters,  $\eta_{AB}$ ,  $k_1$  and  $k_2$  for the 3 parameter equation and compares them with the  $\eta_{AB}$  from the one parameter models.

Fig. (4.4), gives a plot of  $\ln \eta_{AB}$  against  $\frac{1}{T}$  for these new values of  $\eta_{AB}$  for systems I and III and models (1) and (2). It can be seen that compared with the same graph for the one parameter models, fig. (4.3), there is no apparent curvature. Table (4.15) gives  $\Delta G_{AB}^*$ ,  $\Delta H_{AB}^*$  and  $\Delta S_{AB}^*$  obtained for these values of  $\eta_{AB}$ . A comparison with those obtained for the one parameter models, tables (4.11-4.13), shows that no gross change takes place. For System I however the values obtained by the three parameter models are much closer together, especially for  $\Delta H_{AB}^*$  and  $\Delta S_{AB}^*$ .

Examination of table (4.14) indicates that for the formamide/water system (I),  $\eta_{AB}$  for the three parameter models is found to be greater than for the one parameter models. By taking into account the effect of A on B.....B interactions, etc,  $\eta_{AB}$  appears to increase. This supports the interpretation given in section (4.10) where it was suggested that for this system the introduction of either solvent into the other caused a degree of structure loosening of the main solvent and hence a decrease in  $\eta_A$  and or  $\eta_B$ .

For the formamide/dimethylformamide system (III), on the other hand,  $\eta_{AB}$  for the one parameter equations is greater than for the three parameter versions. It would seem, therefore, that when the effects of A on the B.....B interactions and vice versa are taken into account the A.....A and B.....B interactions are considered to contribute more to the total viscosity  $\eta$  and hence  $\eta_{AB}$  is relatively smaller. Reference to fig. (4.5), and section (4.12) supports this view as evidence there pointed to a degree of complex

TABLE 4.14

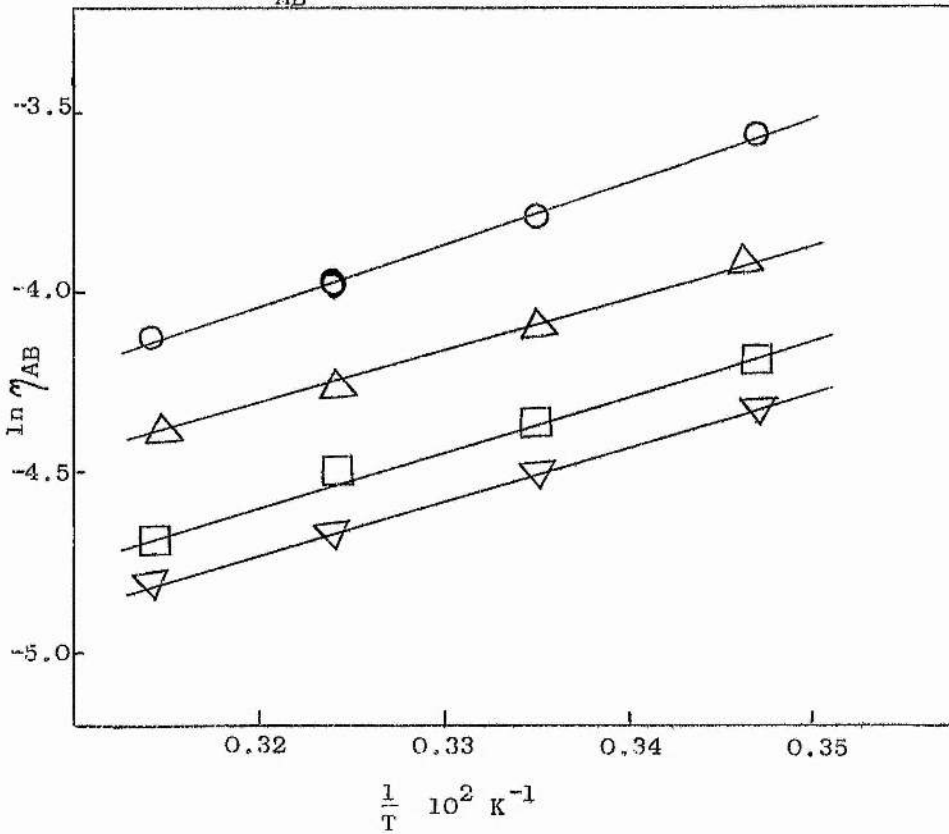
All parameters for each equation and each system

SYSTEM I	318.15 K			308.15 K		
	$\gamma_{AB}$ $J_m^{-3} s$	$k_1$	$k_2$	$\gamma_{AB}$ $J_m^{-3} s$	$k_1$	$k_2$
Model						
<u>ONE PARAMETER</u>						
TAM. -KUR.	0.007100			0.007981		
DOLEZ.	0.009136			0.01054		
<u>THREE PARAMETER</u>						
TAM. -KUR.	0.008326	0.7878	-0.3210	0.009572	0.8049	-0.3283
DOLEZ.	0.009602	0.6983	-0.3840	0.0112	0.7506	-0.3492
SYSTEM II						
<u>ONE PARAMETER</u>						
TAM. -KUR.	0.006459			0.007185		
DOLEZ.	0.006627			0.007382		
MAT. -HER.	0.006293			0.006992		
<u>THREE PARAMETER</u>						
TAM. -KUR.	0.006963	0.4860	-0.1762	0.007716	0.5526	-0.1860
DOLEZ.	0.007020	0.4687	-0.1652	0.007952	0.5339	-0.1749
SYSTEM III						
<u>ONE PARAMETER</u>						
TAM. -KUR.	0.01706			0.02038		
DOLEZ.	0.01369			0.01585		
<u>THREE PARAMETER</u>						
TAM. -KUR.	0.01599	-0.8912	0.6682	0.01885	-1.1422	0.7664
DOLEZ.	0.01251	-1.0282	0.5154	0.01417	-1.316	0.5961

Table 4.14 (cont)

	298.15 K			288.15 K		
SYSTEM I	$\eta_{AB}^{AB}$ $J_m^{-3} s$	$k_1$	$k_2$	$\eta_{AB}^{AB}$ $J_m^{-3} s$	$k_1$	$k_2$
Model						
<u>ONE PARAMETER</u>						
TAM. -KUR.	0.008607			0.009070		
DOLEZ.	0.01190			0.01349		
<u>THREE PARAMETER</u>						
TAM. -KUR.	0.01120	0.9739	-0.4192	0.01332	1.0800	-0.4989
DOLEZ.	0.01284	0.9060	-0.4768	0.01499	0.9972	-0.5326
SYSTEM II						
<u>ONE PARAMETER</u>						
TAM. -KUR.	0.007947					
DOLEZ.	0.008162					
MAT. -HER.	0.007728					
<u>THREE PARAMETER</u>						
TAM. -KUR.	0.008926	0.7462	-0.2325			
DOLEZ.	0.009032	0.7352	-0.2232			
SYSTEM III						
<u>ONE PARAMETER</u>						
TAM. -KUR.	0.02485			0.03101		
DOLEZ.	0.01913			0.02323		
<u>THREE PARAMETER</u>						
TAM. -KUR.	0.0226	-1.4537	0.8739	0.02770	-1.9042	0.9892
DOLEZ.	0.0169	-1.5378	0.6191	0.02001	-1.9375	0.6755

Fig. (4.4)  $\ln \gamma_{AB}$  from the three parameter models



- System III, TAM.-KUR. MODEL
- △ System III, DOLEZ. MOLEL
- System I, DOLEZ. MODEL
- ▽ System I, TAM.-KUR. MODEL

TABLE 4.15

SYSTEM I	$\Delta G_{AB}^*$ KJ/Mol	$\Delta G_{AB}^*$ KJ/Mol	$\Delta S_{AB}^*$ JK <sup>-1</sup> /Mol
3 parameter T/K	50.84	11.50	-132.0
3 parameter D/Z	51.18	10.8	-125.7
SYSTEM II			
3 parameter T/K	54.31	13.22	-137.8
3 parameter D/Z	53.59	11.43	-141.5

formation between the formamide and dimethylformamide molecules.

#### 4.12 ACTIVATION PARAMETERS AS A FUNCTION OF COMPOSITION

$\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  for viscous flow can be considered as a function of composition of the mixture: Janelli<sup>29</sup> considered that for an ideal binary mixture the activation enthalpy of viscous flow was an additive function of composition. He plotted the excess functions  $\Delta H_E^*$ ,  $\Delta S_E^*$  and  $\Delta G_E^*$  (where the excess enthalpy of activation was defined as  $\Delta H^*$  experimental -  $\Delta H^*$  theoretical, from the above considerations) for the system benzene/sulpholane and concluded that the minima in  $\Delta G_E^*$  and  $\Delta H_E^*$  for the system were due to structural effects.

The  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  for Systems I, II, and III were plotted as a function of composition. From the graph of the activation free energy of viscous flow for formamide/water and formamide/methanol fig. (4.5) it can be seen that  $\Delta G^*$  is an additive function of the mole fraction. This suggests that no stable compound formation takes place. Kozlowski<sup>115</sup>, from measurements of the viscosity of formamide/water, and formamide/methanol at 298.15 K also concluded that these systems could be considered to be "perfect" mixtures. For formamide/dimethylformamide on the other hand there is a maximum in  $\Delta G^*$  at about 0.18 mole fraction dimethylformamide. It has been reported elsewhere that dimethylformamide forms a complex with water<sup>116</sup>. The hydrate has been given the formula dimethylformamide,  $3H_2O$ . Vasenko and Dubrovsky<sup>117</sup> carried out investigations on water/diethylformamide and formamide/diethylformamide and in both cases they obtained a maximum for viscosity as a function of composition. It was therefore assumed that dimethylformamide and diethylformamide would show a similar type of interaction with water and formamide molecules and they suggested that formamide

and dimethylformamide would form a complex similar to that of water and dimethylformamide.

As pointed out above, formamide can be considered to be an associated solvent. It has a high viscosity due to intermolecular hydrogen bonding. On the addition of water or methanol there occurs merely an interchange of hydrogen bonds between donor/acceptor molecules, fig. (4.8).

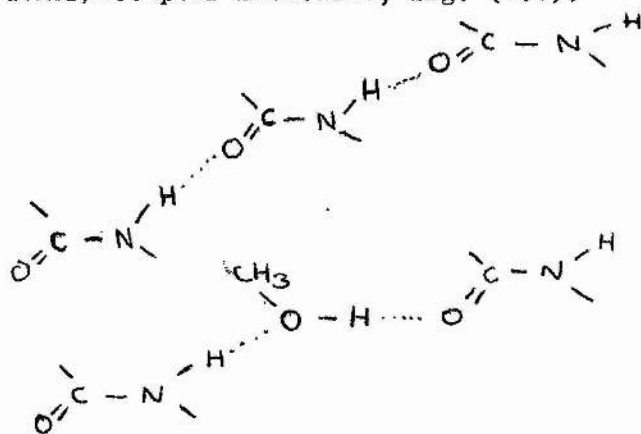


Fig. (4.8)

However with dimethylformamide the maximum in  $\Delta G^*$  indicates relatively strong associations with formamide molecules in excess of the weak associations in the pure dimethylformamide. The maximum in the viscosity of this system is much smaller than that for the dimethylformamide/water system and therefore the complex which is formed appears to be much greater. The position of the maximum corresponds to a complex of molecular formula formamide  $\cdot 4$  dimethylformamide. Because of the pre-exponential volume term in equation (3.24), no direct comparison can be made between the values for  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  for the three systems.

Fig. (4.7) is a plot of the entropy of activation of viscous flow ( $\Delta S^*$ ) against composition. This term is associated with the entropy change occurring when a molecule in a position of minimum free energy in a solution frees itself, perhaps by severing some



Fig.4.5

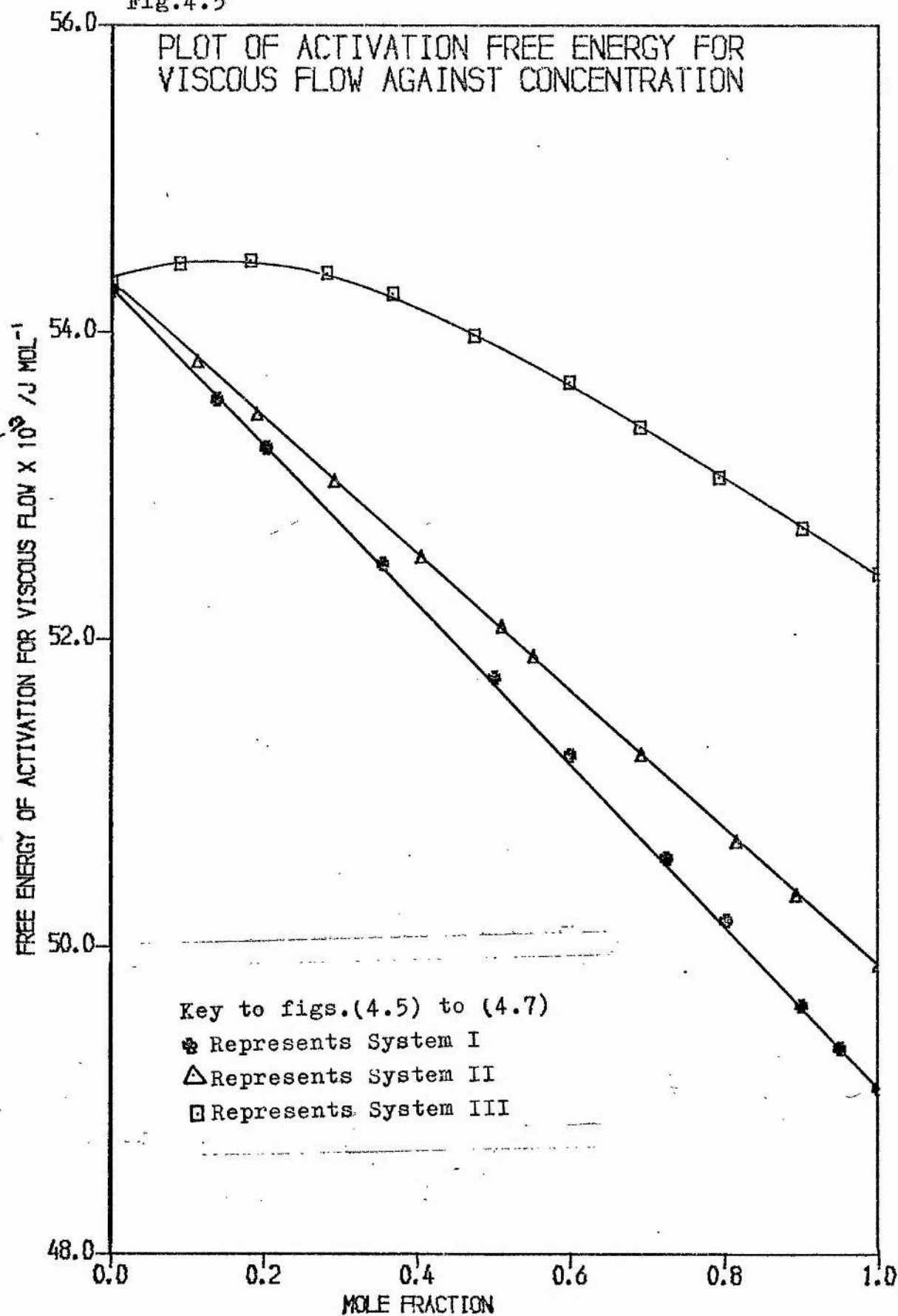


Fig.4.6

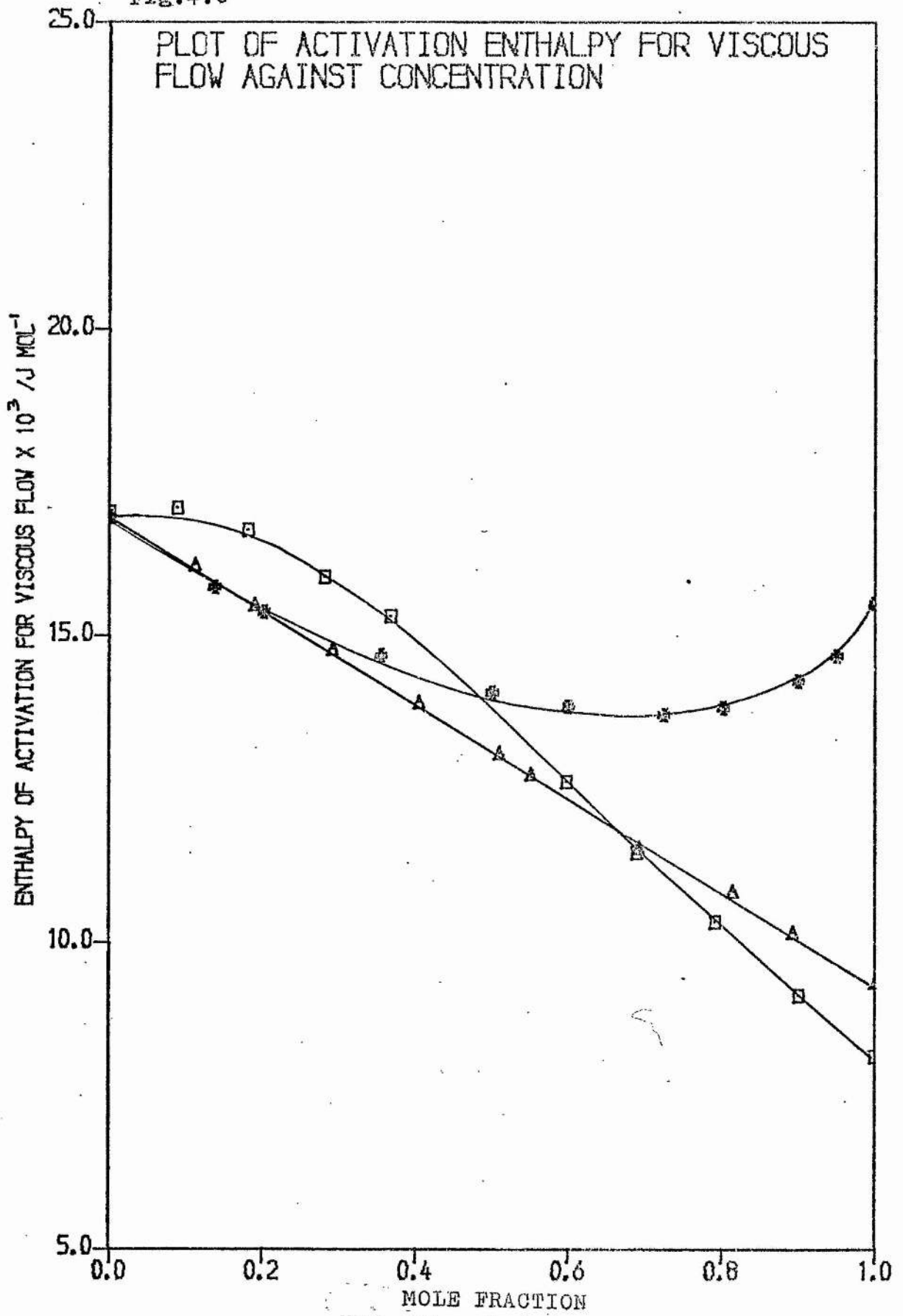
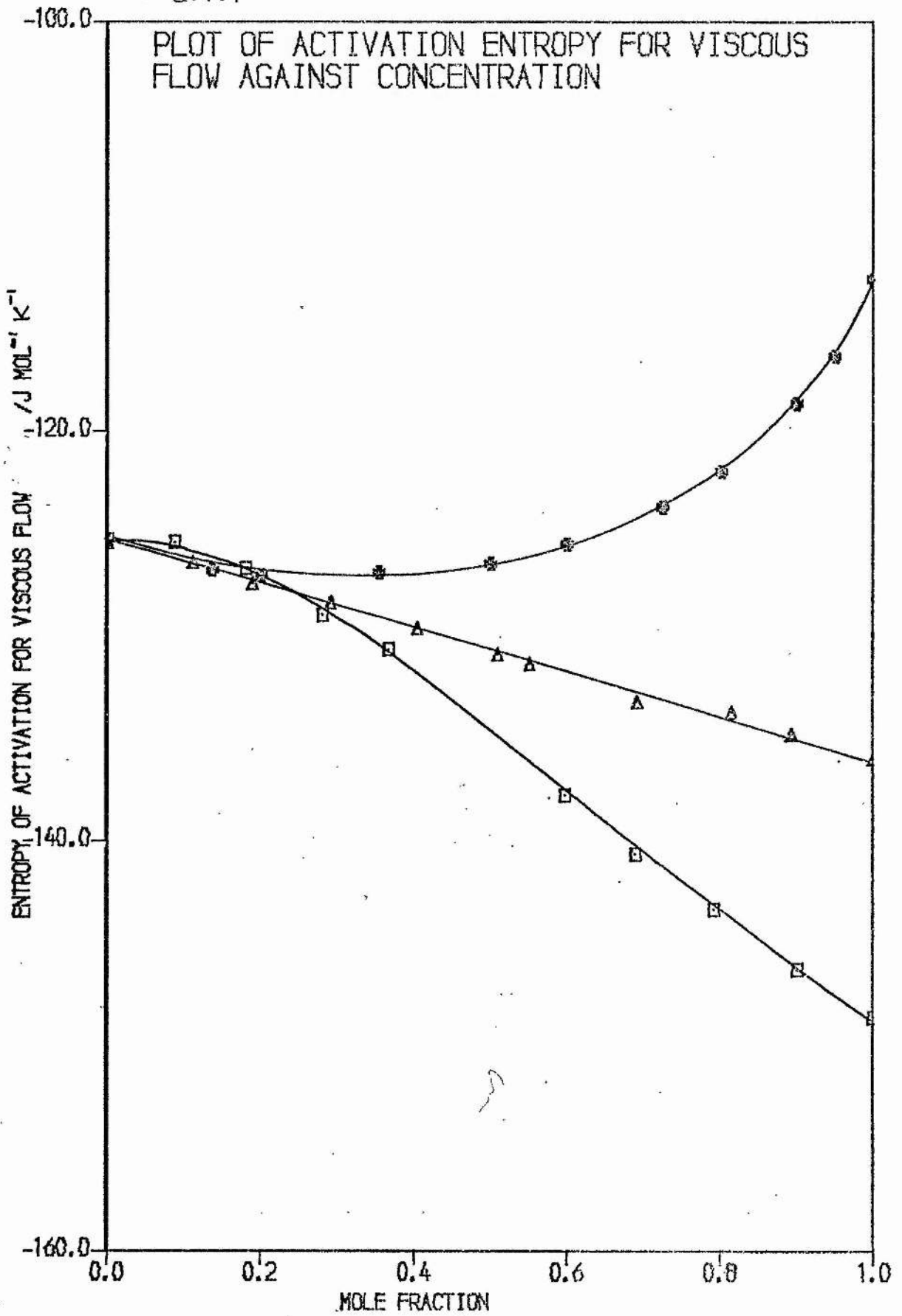


Fig.4.7



hydrogen bonds, in order to be activated to the transition state for viscous flow. The more the liquid is associated, the more bonds have to be broken, and the greater is the increase in entropy associated with the attainment of the activated state. For the addition of formamide to water or vice versa there is a decrease in  $\Delta S^*$  which might suggest that the structure of either solvent is broken down by the addition of the other. For the other systems no such decrease is detected.

From fig. (4.6) the enthalpy of activation for viscous flow for the formamide/water system again shows a minimum. This is interpreted as a "loosening" of the hydrogen bonds which make these systems associated, when one solvent is added to the other.

From measurements of the dielectric constant of binary mixtures of water and a number of amides Rhodewald and Moldner<sup>118</sup> concluded that the mixing of unalkylated amides with water led to a loose liquid structure, whereas with mono and dialkylated amide solutions a more dense structure was obtained. The latter is supported in this work by the maximum exhibited in  $\Delta H^*$  by the formamide/dimethylformamide system, fig. (4.6), which is another indication of the formation of a more tightly bonded complex.

It was considered that the unalkylated amides were built-in via hydrogen bonding into the water structure and vice versa. The increase in the dielectric constant for such mixtures was considered to be due to the more parallel ordering of the individual dipoles.

Fig. (4.9) shows the plot of  $\Delta \epsilon$  against composition for formamide/water where  $\Delta \epsilon = \epsilon_{\text{observed}} - \epsilon_{\text{id.}}$  and  $\epsilon_{\text{id.}} = \epsilon_1 x_1 + \epsilon_2 x_2$ , where  $x$  is the mole fraction and  $\epsilon$  the dielectric constant. Fig. (4.10), on the other hand gives a plot of viscosity based on similar reasoning ie a plot of  $\Delta \eta = \eta_{\text{observed}} - \eta_{\text{id.}}$  against concentration for formamide/water. The shape of the curves in

Fig. (4.9)

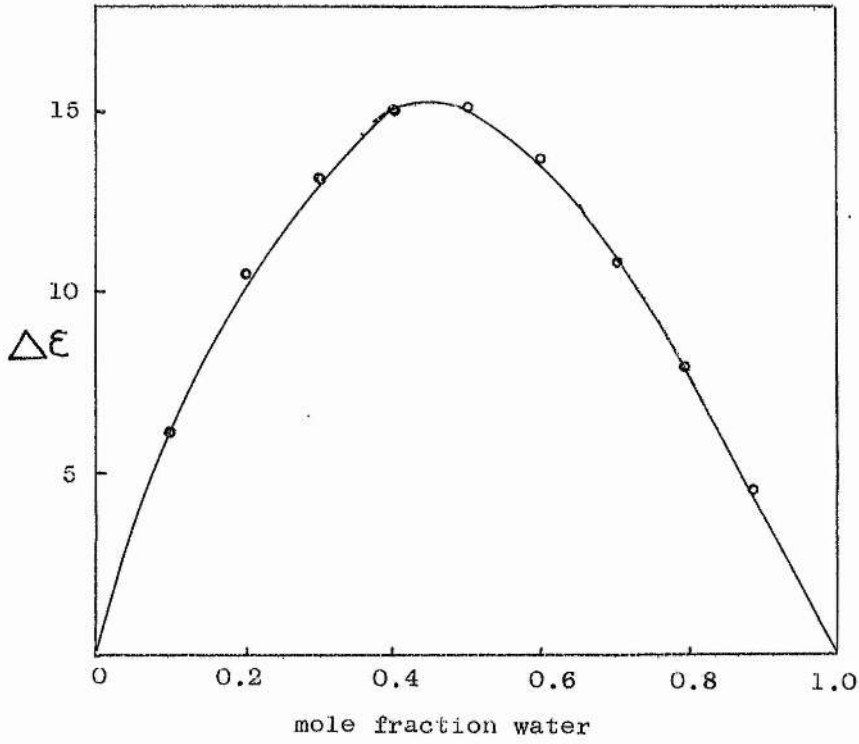
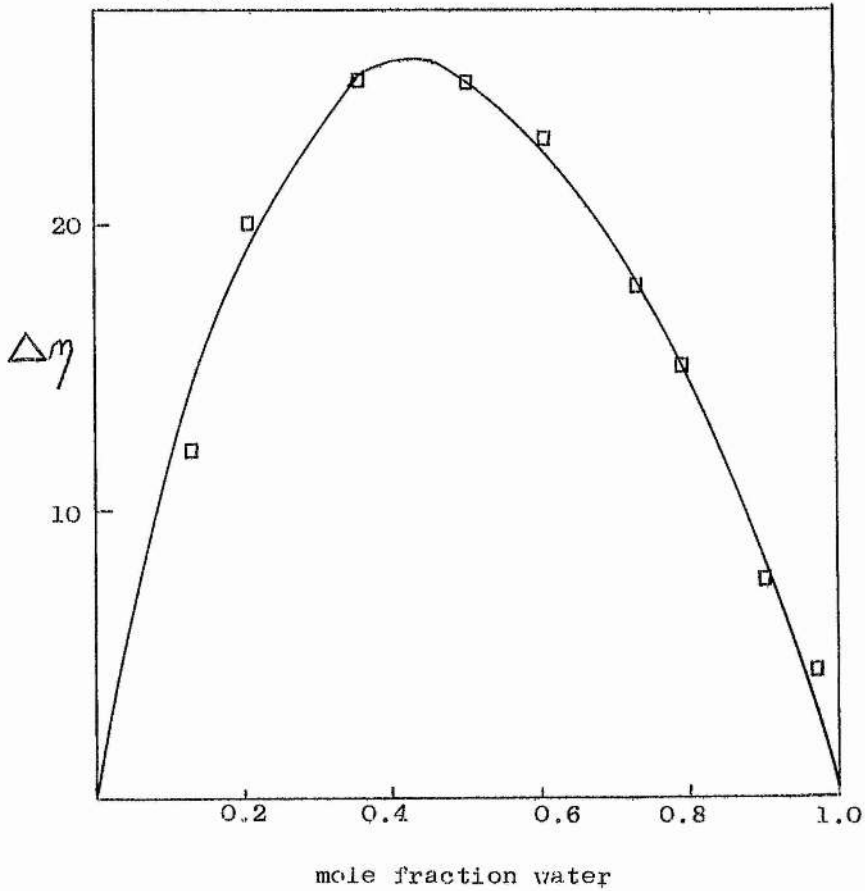


Fig. (4.10)



figs. (4.9) and (4.10) are very similar.

The reason why the dialkylated amide/water system exhibits a maximum in the viscosity/concentration curve and a minimum in the dielectric constant/concentration curve was suggested<sup>118</sup> to be due to interstitial packing of the water around the alkyl groups of the amides causing a decrease in volume of the mixture and hence a more dense structure. From this reasoning it can be suggested that the reason for the formamide/dimethylformamide system exhibiting a much smaller maximum in the viscosity/concentration curve than that of water/dimethylformamide could be due to the poorer ability of the formamide to participate in such an interstitial structure.

#### 4.13 CONCLUSIONS

It is universally recognised that the full knowledge of the structural behaviour of the components of liquid mixtures other than the very simplest (eg argon and helium) is very much beyond present day investigatory techniques and the complex solvent interactions which are present can not as yet be determined or explained by any rigorous theory.

However from the investigations carried out in the present work using several models, the following conclusions can be drawn.

(i) For the system formamide/water, like molecules appeared to be more strongly associated than unlike molecules. The structure of each solvent, however, was 'loosened' on mixing with the other.

(ii) For the system formamide/methanol, the strength of the molecules of each solvent was in the same order as in (i) above, but in this case the structure of each solvent was not disrupted by the presence of molecules of the other solvent. A simple interchange of hydrogen bonds between molecules of both solvents

is considered to take place.

(iii) Dimethylformamide has no capacity for forming hydrogen bonds. In mixtures of this solvent with formamide the unlike solvent molecules appear to form stronger association with each other than do the like molecules. Further evidence suggested that there was in fact a certain complex formation between the two solvents which had the formula 1 formamide : 4 dimethylformamide.

(iv) Because of the different nature of the solvents involved, eg three-dimensionally hydrogen bonded, two-dimensionally hydrogen bonded and non-hydrogen bonded, no single empirical model was able to describe all three systems better than the others. Evidence was provided in Chapter Three which indicated that the solvent structure of methanol was essentially different from that of water and formamide.

CHAPTER FIVE



JONES-DOLE IN BINARY MIXTURES

5.1 INTRODUCTION

It has been suggested that ions may be used as "internal indicators" for the investigation of the structural effects which influence the electrochemical properties of mixed solvent systems<sup>119</sup>. In Chapter Three it was shown that information on the effect of ions on the viscosity of a solvent could be directly related to the changes in the solvent structure which took place in the immediate environment of the ion (Gurney's co-sphere, Frank and Wen's A, B and C regions). This led to the suggestion that solvents could be classified by considering the difference in the ionic B coefficient for two simple ions ( $\text{Na}^+$  and  $\text{K}^+$ ). In Chapter Four the idea that the structures of the components of binary liquid mixtures are often influenced in specific ways by each other was developed by means of semi-empirical models and the use of Eyring's theory of absolute reaction rates as applied to viscosity. From the information gained from these two investigations it was considered that valuable information might be obtained for the formamide/water system by using NaCl as an "internal indicator" of solvent structure.

Apart from the simple systems such as liquid helium, argon and krypton, perhaps the most extensively studied liquid binary mixture is that of methanol/water<sup>34,88,120</sup>. Feakins et al<sup>34</sup> measured the viscosity B coefficients of some simple salts in methanol/water mixtures and obtained further evidence to support the proposals which Frank and Ives<sup>121</sup> put forward in their extensive review, for the structural changes which take place in alcohol/water mixtures.

Investigations of viscosity B coefficients in other mixed solvent systems are relatively few and there are almost no published

investigations on the temperature dependence of the viscosity B coefficient,  $\frac{dB}{dT}$  in such systems. As was pointed out by Kaminsky and shown also in Chapter Three,  $\frac{dB}{dT}$  can often yield more information than the B coefficients alone, on the effect of the solute on the solvent structure. Measurements of  $\frac{dB}{dT}$  were therefore considered to be of great importance.

Feakins et al<sup>34</sup> in 1968 investigated the viscosity B coefficients of NaCl, KCl, RbCl and CsCl in several methanol/water mixtures at various temperatures. They found that the B coefficients of all of these salts became more negative in the 20% methanol/water solutions than in pure water. As the methanol content was further increased to 40% the B coefficients became more positive. This result supported the thesis of Frank and Ives<sup>121</sup> that in the region of 20% alcohol, in this particular case, ethanol, the alcohol exerted a co-operative effect on the structure of water, stabilising the "icebergs", resulting in a decrease in the excess heat capacity at constant volume with increase in temperature. This enhanced structure would be expected to be particularly sensitive to the structure breaking effects of ions which result in negative B coefficients. The values of the B coefficients would therefore be expected to be less in such a mixture than in pure water because of the increase in  $\eta^D$ . This behaviour was in fact found. These results were later confirmed by Singh and Yadav<sup>120</sup> for KI and by Werblan et al<sup>88</sup> for  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and NaCl.

Experiments on the viscosity of the formamide/water system (Chapter Four) and on partial molar volumes in this system<sup>122</sup> showed the absence of complex formation or anomalous behaviour for mixtures throughout the whole composition range. It was therefore decided to investigate the viscosity B coefficient of sodium chloride in various solvent mixtures of formamide/water at

298.15 K to 323.15 K. There are no previously reported B coefficients for any solvent mixtures containing formamide.

## 5.2 EXPERIMENTAL AND RESULTS

Formamide was prepared as described in Chapter Two. Deionised water was fractionally distilled from alkaline permanganate. Four batches of solvent were prepared by mixing the above solvents by weight in proportions giving solutions of 0.2, 0.4, 0.6 and 0.8 mole fraction of water. Eight sodium chloride solutions were then made up for each "solvent" in concentrations varying from 0.005 to 0.100 molal. The relative viscosities of the sodium chloride solutions were measured by first measuring the efflux time of the bulk solvent in each viscometer at each temperature and then repeating with the various sodium chloride solutions. The densities of all solutions were measured as described in Chapter Two.

From the efflux times ( $t_0$ ) of the "solvent" and the efflux times of the solution ( $t$ ) the relative viscosities were calculated by 
$$\eta = \frac{t \rho}{t_0 \rho_0}$$
 where  $\rho$  and  $\rho_0$  are the densities of the solution and solvent respectively. The kinetic energy correction factor was neglected in this case because of the small difference in the viscosities of the "solvent" and the solutions.

The values were then used as described in Chapter Three to give Jones-Dole plots by graphing  $\frac{\eta-1}{\sqrt{c}}$  against  $\sqrt{c}$  where  $c$  is the concentration (molality). Figs. (5.1-5.4) give these Jones-Dole plots at 298.15, 308.15, 318.15 and 323.15 K respectively for the sodium chloride solutions in formamide, 0.2, 0.4, 0.6, 0.8 and 1.0 mole fraction of water. Table (5.1) gives the values of the viscosity B coefficients for sodium chloride in each solvent system at each temperature. Figs. (5.5-5.10) show the variation in the Jones-Dole plot with temperature for each solvent system.

Key to figs. (5.1) to (5.11)

In figs. (5.1) to (5.10) the concentration is in molality.  $\eta_{sp}$  represents the relative viscosity  $\eta/\eta_0$ , where  $\eta$  represents the viscosity of the solution and  $\eta_0$  the viscosity of the solvent.

In figs. (5.1) to (5.4)

- ⊗ represents NaCl in formamide
- △ represents NaCl in 0.2 mole fraction water
- ◻ represents NaCl in 0.4 mole fraction water
- ⊠ represents NaCl in 0.6 mole fraction water
- ◻ represents NaCl in 0.8 mole fraction water
- represents NaCl in water

In figs. (5.5) to (5.10)

- ⊗ represents 298.15 K
- △ represents 308.15 K
- ◻ represents 318.15 K
- ⊠ represents 323.15 K

Fig. (5.5) gives the Jones-Dole plot for NaCl in formamide

Fig. (5.6) gives the Jones-Dole plot for NaCl in 0.2 mole fraction water

Fig. (5.7) gives the Jones-Dole plot for NaCl in 0.4 mole fraction water

Fig. (5.8) gives the Jones-Dole plot for NaCl in 0.6 mole fraction water

Fig. (5.9) gives the Jones-Dole plot for NaCl in 0.8 mole fraction water

Fig. (5.10) gives the Jones-Dole plot for NaCl in water

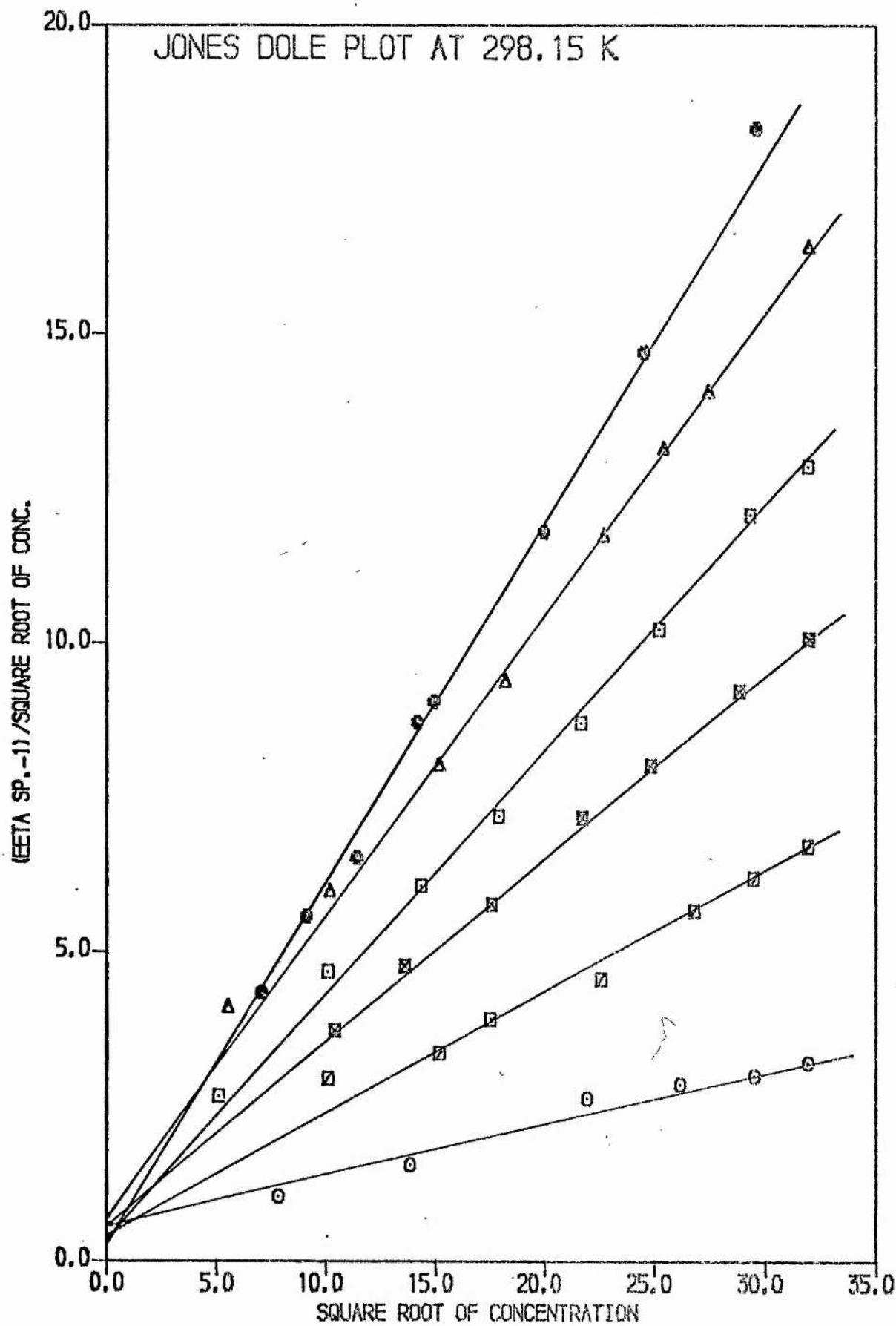


Fig.(5.2)

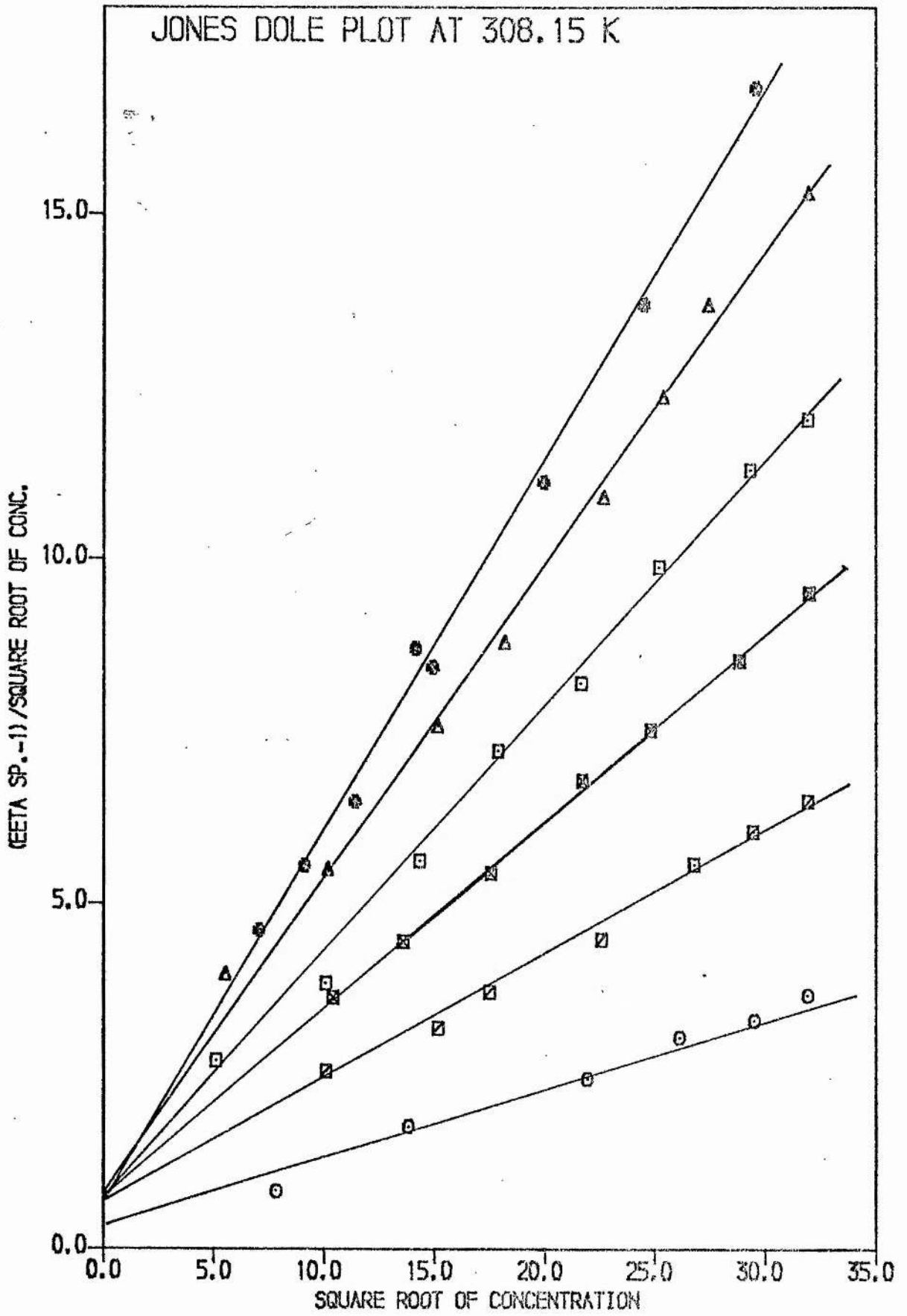
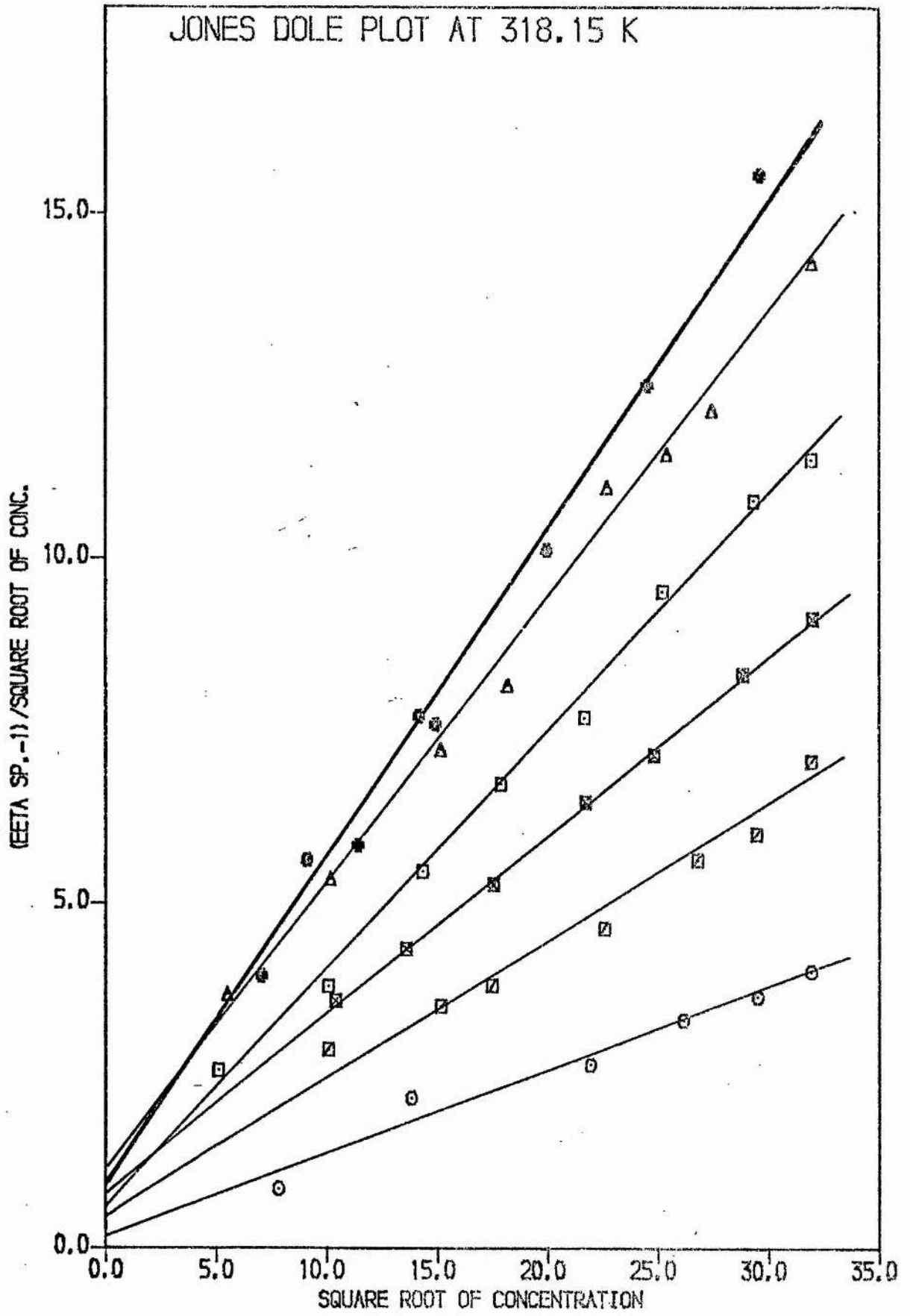


Fig. (5.3)



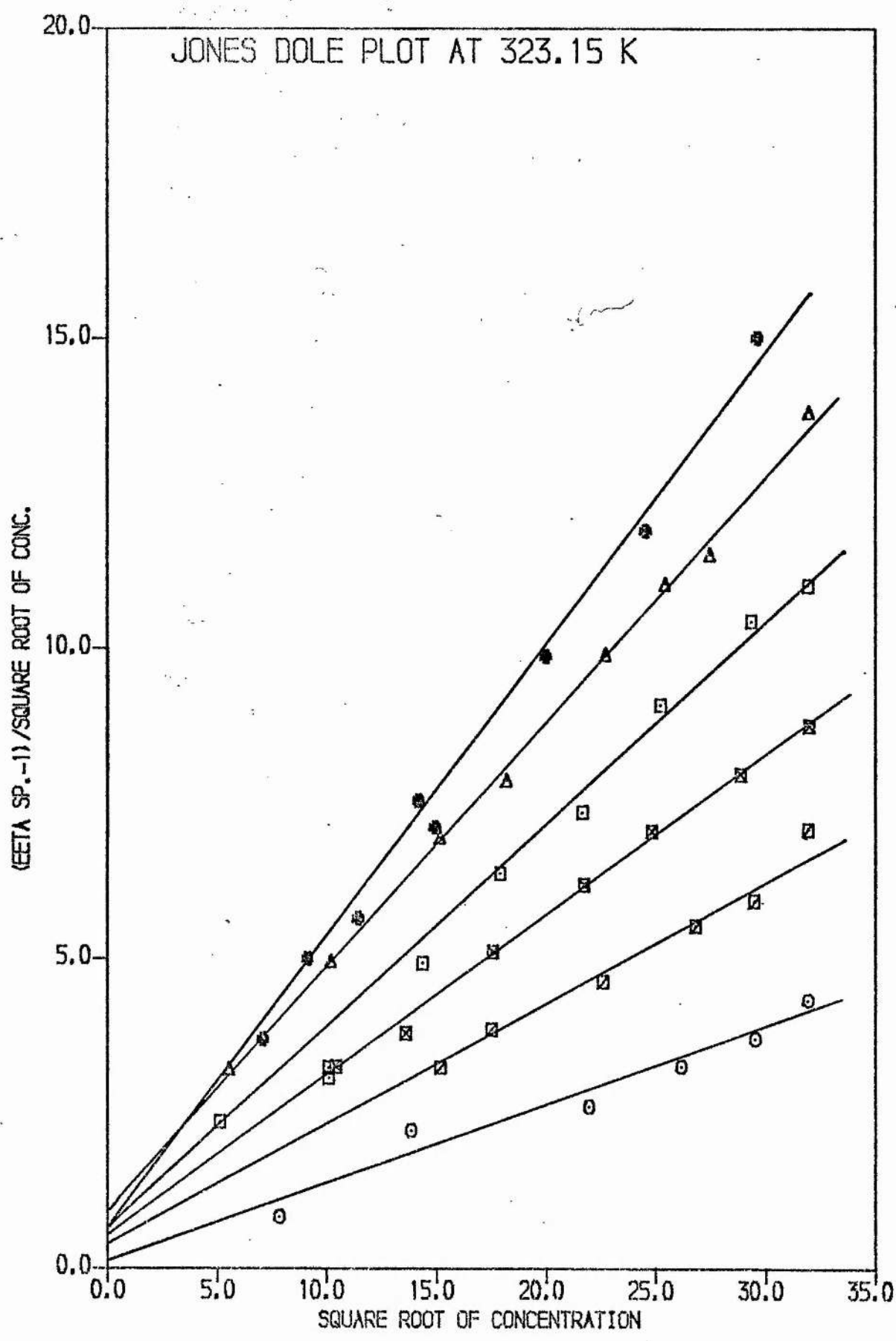




Fig.(5.5)

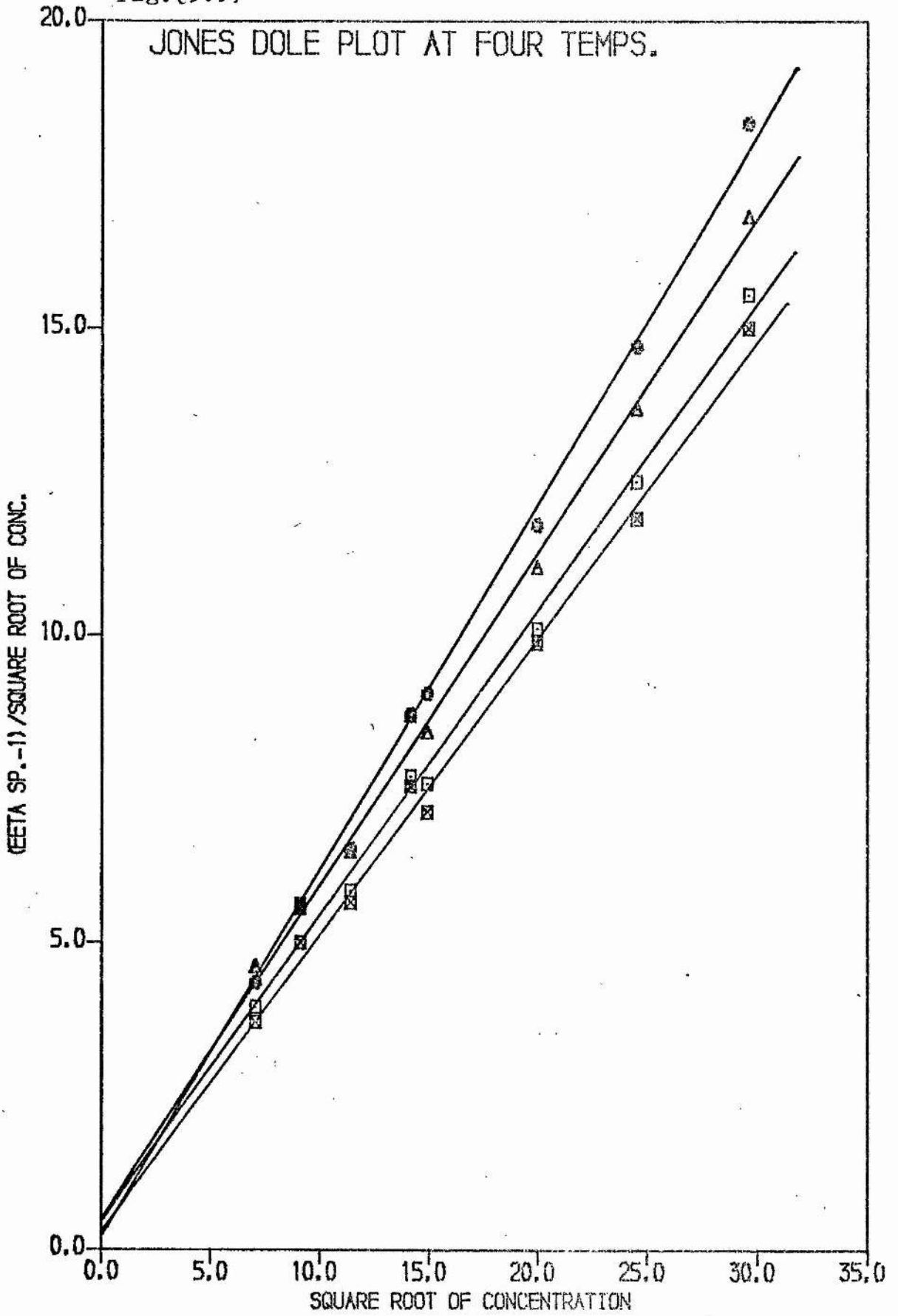


Fig.(5.6)

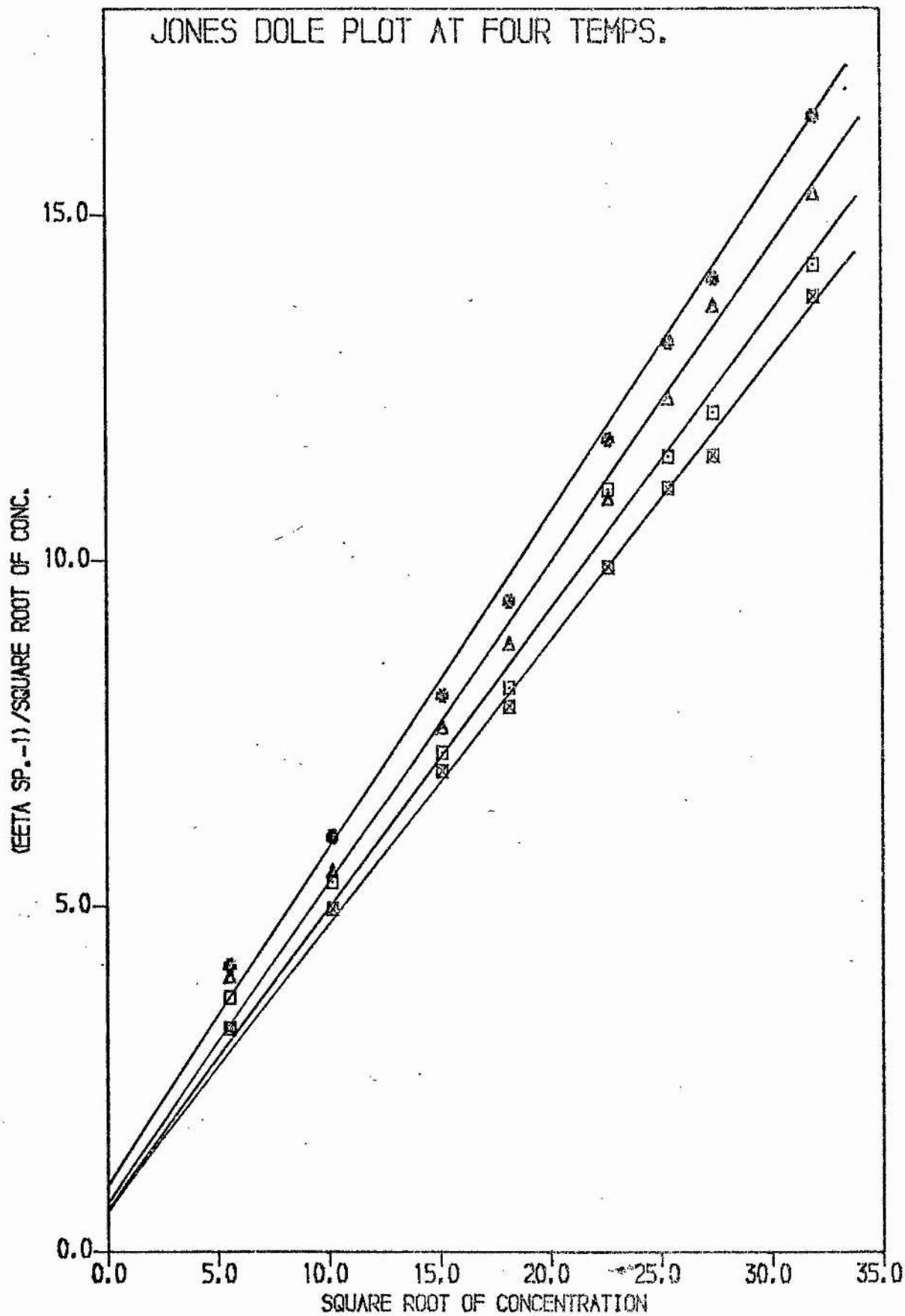


Fig.(5.7)

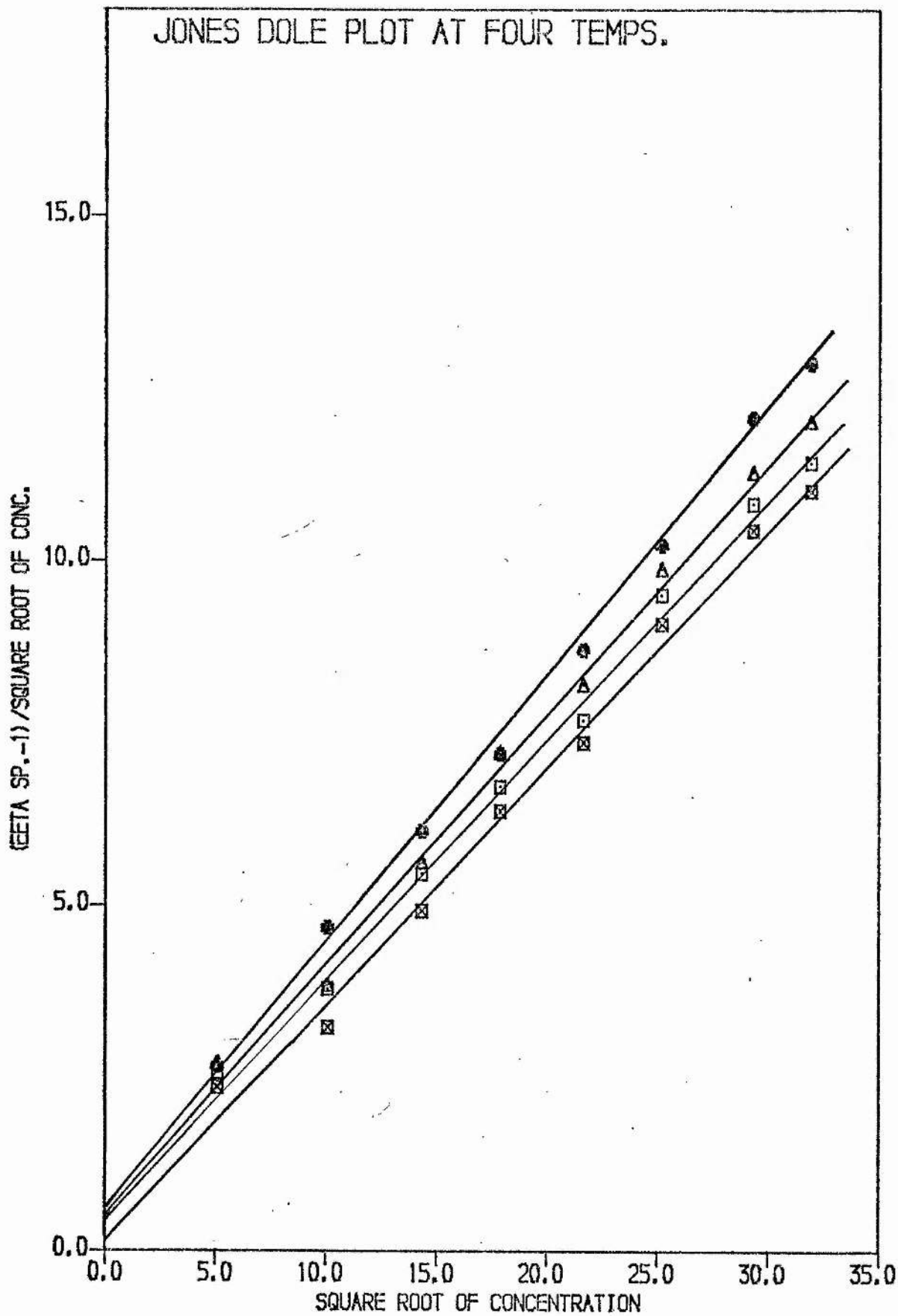


Fig.(5.8)

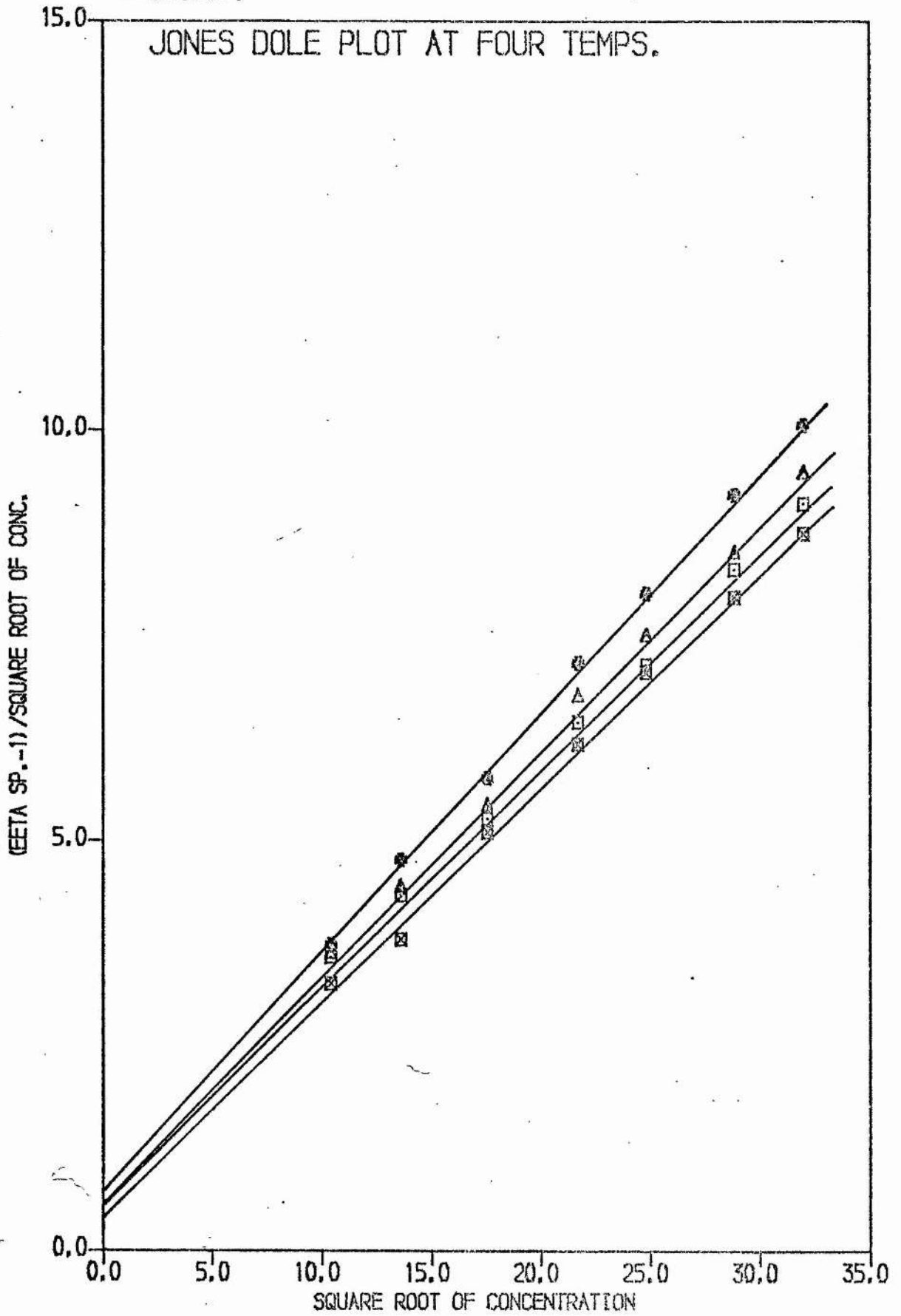


Fig.(5.9)

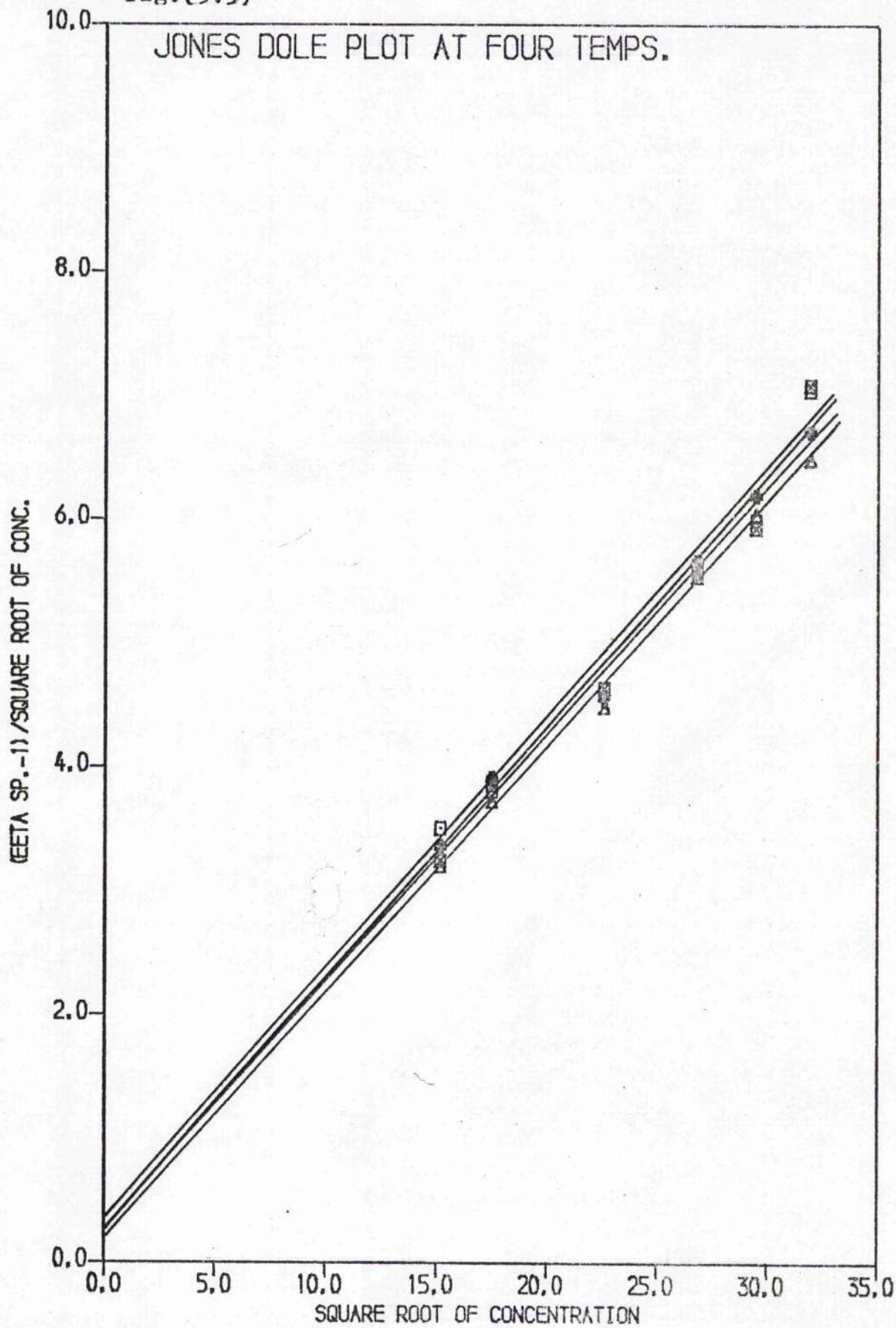
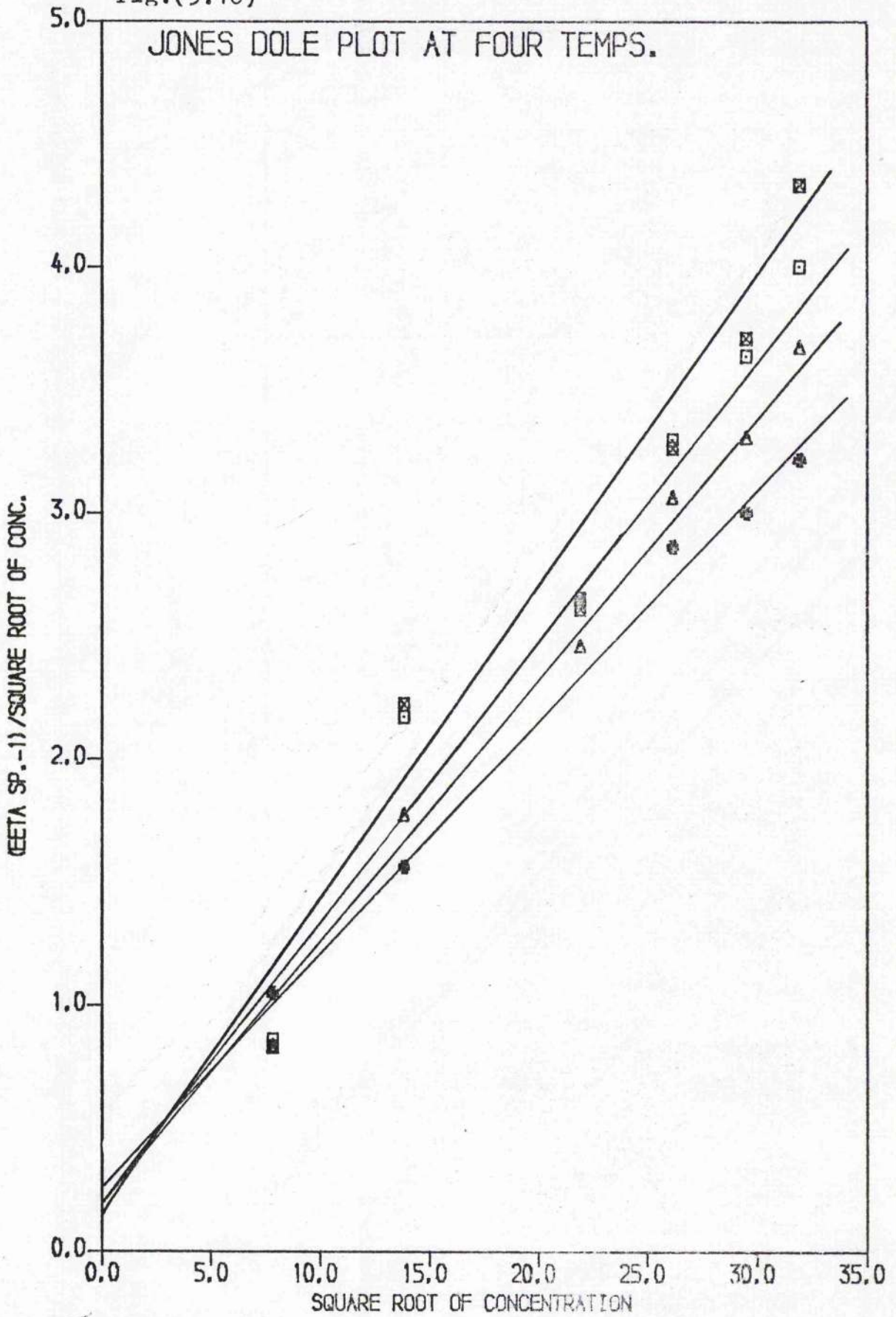


Fig.(5.10)



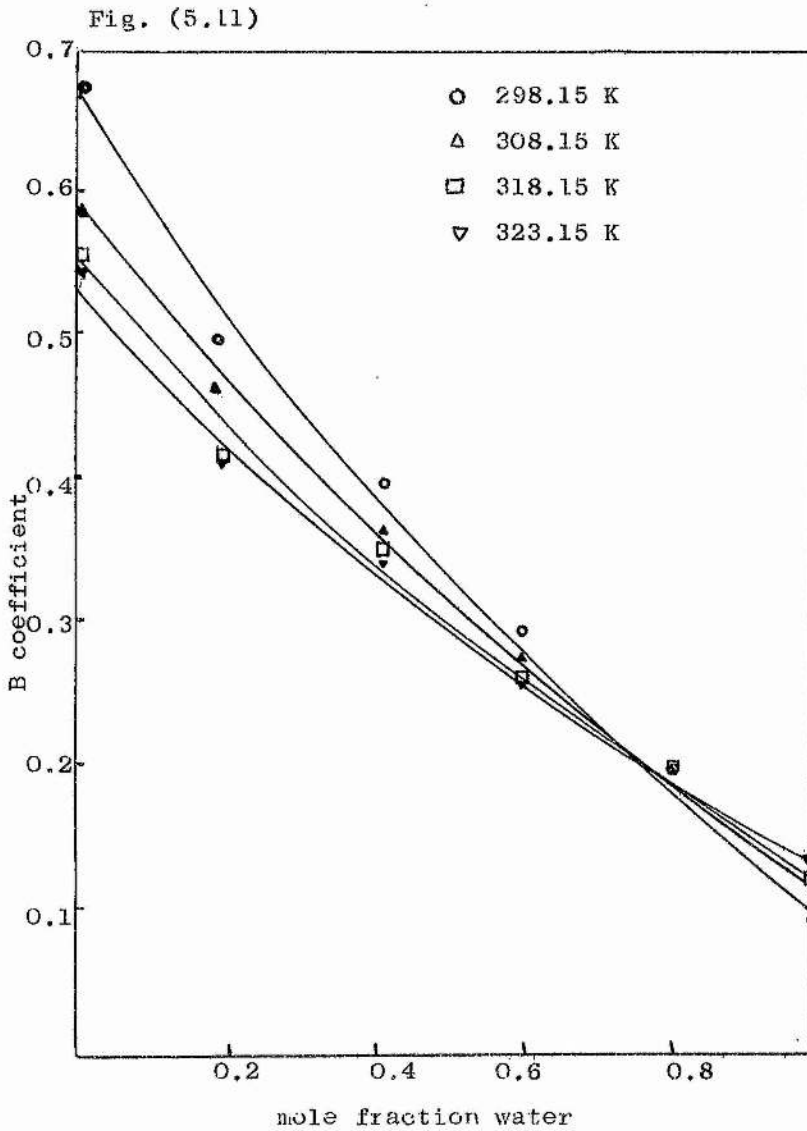


TABLE 5.1

Viscosity B coefficients for NaCl in formamide/water mixtures

MOLE FRACTION OF WATER	B Coefficient			
	298.15K	308.15K	318.15K	323.15K
0.0000	0.67 <sub>3</sub>	0.58 <sub>2</sub>	0.55 <sub>0</sub>	0.54 <sub>5</sub>
0.1970	0.49 <sub>2</sub>	0.46 <sub>4</sub>	0.41 <sub>1</sub>	0.40 <sub>9</sub>
0.4136	0.39 <sub>4</sub>	0.36 <sub>4</sub>	0.34 <sub>8</sub>	0.35 <sub>0</sub>
0.6035	0.29 <sub>3</sub>	0.27 <sub>2</sub>	0.26 <sub>1</sub>	0.25 <sub>8</sub>
0.8003	0.19 <sub>4</sub>	0.19 <sub>4</sub>	0.20 <sub>4</sub>	0.20 <sub>6</sub>
1.0000	0.08 <sub>2</sub>	0.11 <sub>1</sub>	0.11 <sub>7</sub>	0.13 <sub>5</sub>

Fig. (5.11) is a plot of the B coefficients at different temperatures for all the solvent compositions. Two points immediately arise from fig. (5.11).

(i) The B coefficient for NaCl at any temperature in formamide is greater than the B coefficient for NaCl in water at the same temperature. The reasons for this were discussed in Chapter Three.

(ii) The temperature coefficient of B for NaCl in formamide,  $\frac{dB}{dT}$ , is negative, whereas that of B in water is positive.

### 5.3 DISCUSSION

In Chapter Three the fact that the ionic B coefficients were all positive was attributed to the relative importance of the structure making effects ( $\gamma^E + \gamma^A$ ). As indicated by Feakins and Lawrence<sup>85</sup> and Feakins et al<sup>34</sup> there is evidence to suggest that B coefficients increase with increasing molar volume of the solvent. This increase would be associated with an increase in  $\gamma^E$ , and would explain why the B coefficients in formamide were so much larger than in water. It was however pointed out that for  $Cl^-$  at least, there was some evidence for structure breaking ( $\gamma^D$ ). Kaminsky suggested that in water  $Cl^-$  is a net structure breaking ion and that  $\frac{dB}{dT}$  for  $Cl^-$  ion in water is positive due to the fact that as the temperature is increased and the bulk structure of the solvent is broken down due to increased thermal motion, then  $\gamma^D$  becomes smaller with respect to  $\gamma^E$  and  $\gamma^A$ . Hence the B coefficient increases. For  $Na^+$  in water,  $\frac{dB}{dT}$  is almost zero indicating that any change in  $\gamma^D$  is offset by a change in  $\gamma^A$  and  $\gamma^E$ .

As the temperature is increased the B coefficient for NaCl in formamide decreases quite significantly. This can be explained by considering that  $\gamma^A + \gamma^E$  which for NaCl in formamide is greater

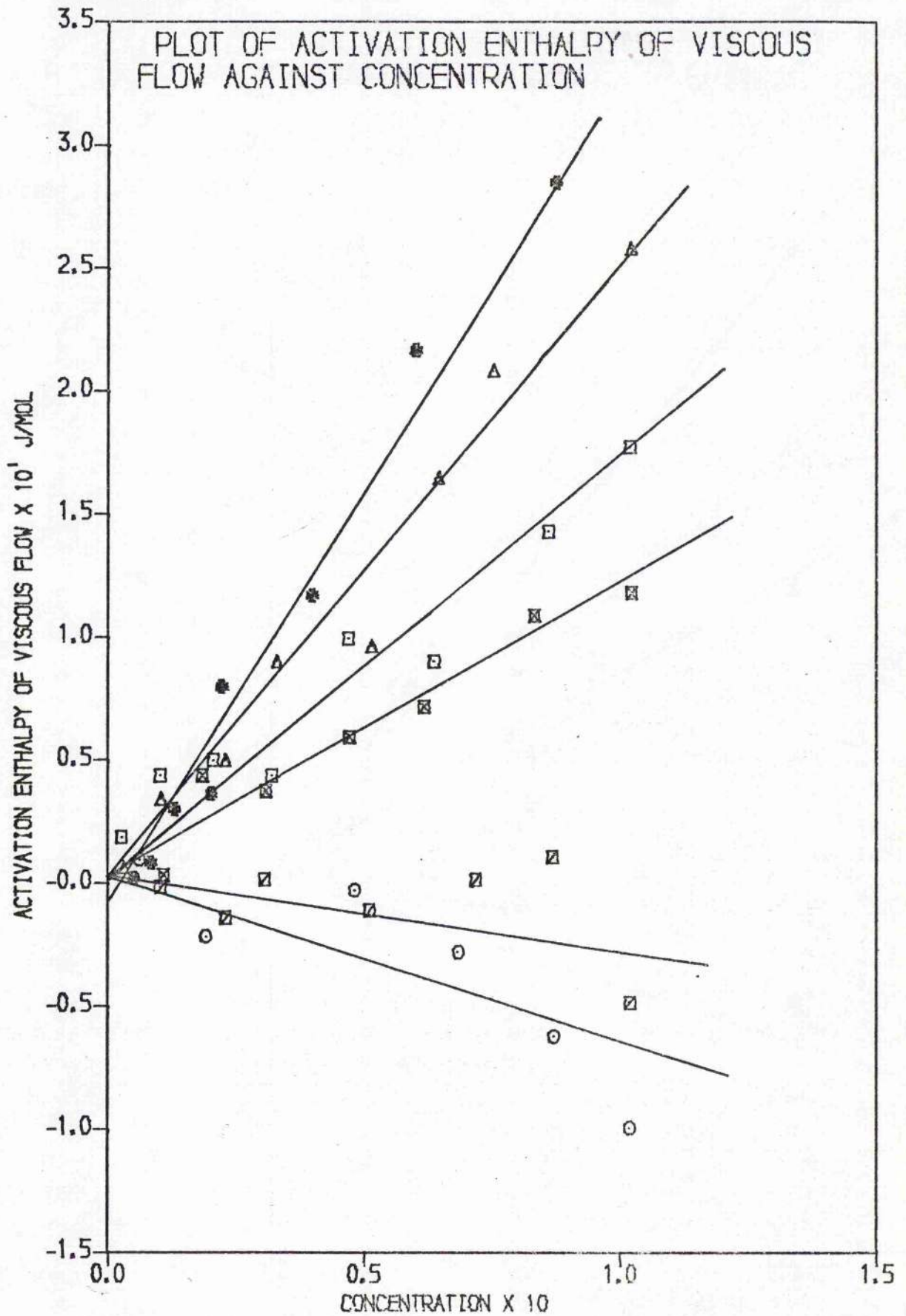


than  $\eta^D$ , becomes smaller as the temperature is increased. Fig. (5.11) shows that as the solvent mixture becomes increasingly rich in water,  $\frac{dB}{dT}$  for NaCl becomes progressively less negative until at a solvent composition of about 0.8 mole fraction of water B does not change significantly with temperature. As the water content is further increased,  $\frac{dB}{dT}$  then becomes increasingly positive.

Such an effect has not been reported before. For the water/methanol system, although a decrease in B with solvent composition was observed,  $\frac{dB}{dT}$  was found to be positive throughout the whole composition range<sup>85</sup>, being most positive for the particular composition where the B coefficients were most negative. This was taken as a further indication of the importance of the "structure breaking" effects of the ions. In the formamide/water system investigated here, not only did the B coefficient of NaCl decrease as the solvent mixture increased in water content, but the net structure making effect as determined by  $\frac{dB}{dT}$  became less important until at about 0.8 mole fraction of water the structure breaking influences were sufficiently important to cause  $\frac{dB}{dT}$  to be negative.

Fig. (5.12) gives a plot of the activation enthalpy of viscous flow ( $\Delta H^*$ ) for NaCl in the formamide/water mixtures. For high concentrations of formamide,  $\Delta H^*$  is positive and decreases with increase in water content. Thus it would seem that as the water content of the solvent mixture increases, the  $\text{Na}^+$  and  $\text{Cl}^-$  ions have less effect on the transition of solvent molecules from equilibrium positions to the activated complex. The increase in  $\Delta H^*$  for formamide under the influence of the  $\text{Na}^+$  ions was considered in Chapter Three to be due to the order making influence of these ions. Nightingale<sup>91</sup> suggested that an increase in  $\Delta H^*$  for the solvent on addition of a salt was due to certain ions orientating the solvent molecules sufficiently to cause them to be held more firmly than

Fig.(5.12)



in the bulk solvent. Although it is not possible to partition the increase in  $\Delta H^*$  between the individual ions, it would seem, from the observations discussed in Chapter Three, that the sodium ion is responsible for most of the increase in  $\Delta H^*$  for formamide. Conversely, since it has been suggested that  $\text{Na}^+$  in water has little effect on  $\Delta H^*$ <sup>68</sup>, most of the decrease in  $\Delta H^*$  as seen from fig. (5.12) is due to the  $\text{Cl}^-$  ion.

#### 5.4 CONCLUSIONS

Although ionic B coefficients are considered to characterise the ion species as a kinetic entity, they may mask important properties of the ion due to the fact that they can be considered to be made up of several contributions i.e.  $\eta^A$ ,  $\eta^E$  and  $\eta^D$  as discussed previously, which may to some extent cancel one another.

The results of this part of the work confirm Nightingale's ideas on the specificity of electrolyte solvation, and further indicate that not only is the action of different ions on the same solvent very specific but also the action of identical ions on different solvents can be very different. Thus the net effect of NaCl on formamide is a structure ordering one (from the  $\Delta H^*$  and  $\frac{dB}{dT}$  data), but the effect of NaCl on water is structure disordering.

It can be seen from the above that when the mixture of ion-solvent interactions is being investigated by means of viscosity measurements it is important to measure the viscosity changes at more than one temperature to enable information to be obtained from  $\frac{dB}{dT}$  and  $\Delta H^*$ .

APPENDIX I

VISCOSITY AND DENSITY OF CALIBRATION LIQUIDS

LIQUID	TEMPERATURE K	VISCOSITY $10^{-3} \text{ Jm}^{-3} \text{ s}$	DENSITY $10^3 \text{ kg m}^{-3}$
Water <sup>123</sup>	288.15	0.01138	0.99913
	298.15	0.008903	0.99707
	308.15	0.007194	0.99406
	318.15	0.005963	0.99024
	323.15	0.005467	0.98807
30% aqueous <sup>124</sup> sucrose solution	288.15	0.03757	1.12863
	293.15	0.03187	1.12698
	298.15	0.02735	1.12517

APPENDIX II

```
PROGRAMME CV10 FOR CALIBRATING VISCOMETERS
DIMENSION TEMP(20),TIM(20),T(20),DENS(20),VISC(20),EETA(20),RO(20),
1,X(20),Y(20),Z(20),XCALC(2000),YCALC(2000),YCOR(20),DEV(20)
5 READ(5,10)NRUN
10 FORMAT(I4)
   IF(NRUN)900,900,20
20 READ(5,30)N
30 FORMAT(I2)
   READ(5,40)(TEMP(J),TIM(J),J=1,N)
40 FORMAT(2F10.0)
   T(1)=15.0
   T(2)=17.5
   T(3)=20.0
   T(4)=298.0
   T(5)=288.15
   T(6)=293.15
   T(7)=298.15
   T(8)=25.0
   T(9)=35.0
   T(10)=37.5
   T(11)=40.0
   T(12)=42.5
   T(13)=45.0
   T(14)=50.0
   DENS(1)=1.12863
   DENS(2)=0.99871
   DENS(3)=1.12698
   DENS(4)=1.12517
   DENS(5)=1.08233
   DENS(6)=1.08096
   DENS(7)=1.07940
   DENS(8)=0.99707
   DENS(9)=0.99406
   DENS(10)=0.99318
   DENS(11)=0.99224
   DENS(12)=0.99127
   DENS(13)=0.99025
   DENS(14)=0.98807
   VISC(1)=0.03757
   VISC(2)=0.010739
   VISC(3)=0.03187
   VISC(4)=0.02735
   VISC(5)=0.02254
   VISC(6)=0.01945
   VISC(7)=0.01695
   VISC(8)=0.008903
   VISC(9)=0.007194
   VISC(10)=0.006858
   VISC(11)=0.006531
   VISC(12)=0.006241
   VISC(13)=0.005963
   VISC(14)=0.005467
   DO 130 K=1,14
   DO 125 J=1,N
       IF(T(K)-TEMP(J)) 120,110,120
110 EETA(J)=VISC(K)
       RO(J)=DENS(K)
120 CONTINUE
125 CCNTINUE
130 CONTINUE
       DO150 J=1,N
       X(J)=1/((TIM(J))**2)
150 Y(J)=EETA(J)/(RO(J)*TIM(J))
       SUMX=0.0
       SUMY=0.0
       SUMXX=0.0
       SUMXY=0.0
       SUMZ=0.0
       DO 200 J=1,N
       SUMX=SUMX+X(J)
       SUMXX=SUMXX+X(J)**2
       SUMY=SUMY+Y(J)
200 SUMXY=SUMXY+X(J)*Y(J)
       G=N
       DENOM=SUMX**2-G*SUMXX
       GRAD=(SUMX*SUMY-G*SUMXY)/DENOM
```

APPENDIX II(cont.)

```
CONST=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
DO 222 J=1,N
220 Z(J)=((GRAD*X(J)-Y(J)+CONST)/(SQRT(GRAD**2+1.0)))**2
222 SUMZ=SUMZ+Z(J)
RMS=SQRT((SUMZ)/G)
DO 230 J=1,N
YCOR(J)=GRAD*X(J)+CONST
230 DEV(J)=Y(J)-YCOR(J)
WRITE(6,700)
700 FORMAT(52H1 CALIBRATION OF VISCOMETERS//)
WRITE(6,710)NRUN
710 FORMAT(28X,18H EXPERIMENT NUMBER,I5)
WRITE(6,720)
720 FORMAT(1H0)
WRITE(6,730)CONST
730 FORMAT(22X,22H THE A-PARAMETER IS ,F12.8/)
WRITE(6,740)GRAD
740 FORMAT(22X,22H THE MB-PARAMETER IS ,F12.8/)
WRITE(6,750)RMS
750 FORMAT(22X,22H THE RMS DEVIATION IS ,F12.8//)
WRITE(6,751)
751 FORMAT(72HOTEMPERATURE TIME VISCCSITY DENSITY
1 Y/)
WRITE(6,760)(TEMP(J),TIM(J),EETA(J),RO(J),X(J),Y(J),J=1,N)
760 FORMAT(2X,F6.2,4X,F8.3,4X,F9.6,4X,F8.5,4X,F11.8,4X,F11.8)
WRITE(6,765)
765 FORMAT(53HOTEMPERATURE Y YCALC DEVIATION/)
WRITE(6,770)(TEMP(J),Y(J),YCCR(J),DEV(J),J=1,N)
770 FORMAT(2X,F6.2,4X,F11.8,4X,F11.8,4X,F11.8)
GOTO 5
900 CONTINUE
WRITE(6,920)
920 FORMAT(1H1)
CALL EXIT
END
```

APPENDIX III

CALIBRATION OF VISCOMETERS

Experiment number indicates viscometer number ie 1010 refers to viscometer 1.

Temperatures 25.0, 35.0, 45.0 and 50.0 refer to calibration with water at 298.15, 308.15, 318.15 and 323.15 K.

Temperatures 15.0, 20.0 and 298.0 refer to calibration with 30% aqueous sucrose solution at 288.15, 293.15 and 298.15 K.

The terms X, Y, Y CALC and DEVIATION are explained in Appendix II.

CALIBRATION OF VISCOMETERS

EXPERIMENT NUMBER 1010

THE A-PARAMETER IS 0.00003559

THE MB-PARAMETER IS -0.02137094

THE RMS DEVIATION IS 0.00000001

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
25.00	253.313	0.008903	0.99707	0.00001558	0.00003525
35.00	206.191	0.007194	0.99406	0.00002352	0.00003510
45.00	172.640	0.005963	0.99025	0.00003355	0.00003488
50.00	159.267	0.005467	0.98807	0.00003942	0.00003474

TEMPERATURE	Y	YCALC	DEVIATION
25.00	0.00003525	0.00003526	-0.00000001
35.00	0.00003510	0.00003509	0.00000001
45.00	0.00003488	0.00003487	0.00000001
50.00	0.00003474	0.00003475	-0.00000001



CALIBRATION OF VISCOMETERS

EXPERIMENT NUMBER 2010

THE A-PARAMETER IS 0.00003682

THE MB-PARAMETER IS -0.02304789

THE RMS DEVIATION IS 0.00000002

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
25.00	245.140	0.008903	0.99707	0.00001664	0.00003642
35.00	199.606	0.007194	0.99406	0.00002510	0.00003626
45.00	167.166	0.005963	0.99025	0.00003579	0.00003602
50.00	154.410	0.005467	0.98807	0.00004194	0.00003583

TEMPERATURE	Y	YCALC	DEVIATION
25.00	0.00003642	0.00003644	-0.00000001
35.00	0.00003626	0.00003624	0.00000001
45.00	0.00003602	0.00003600	0.00000002
50.00	0.00003583	0.00003586	-0.00000002

CALIBRATION OF VISCOMETERS

EXPERIMENT NUMBER 3010

THE A-PARAMETER IS 0.00003453

THE MB-PARAMETER IS -0.02341985

THE RMS DEVIATION IS 0.00000001

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
25.00	261.241	0.008903	0.99707	0.0001465	0.00003418
35.00	212.666	0.007194	0.99406	0.00002211	0.00003403
45.00	178.102	0.005963	0.99025	0.00003153	0.00003381
50.00	164.410	0.005467	0.98807	0.00003700	0.00003365

TEMPERATURE	Y	YCALC	DEVIATION
25.00	0.00003418	0.00003419	-0.00000001
35.00	0.00003403	0.00003402	0.00000001
45.00	0.00003381	0.00003380	0.00000001
50.00	0.00003365	0.00003367	-0.00000001

CALIBRATION OF VISCOMETERS

EXPERIMENT NUMBER 4010

THE A-PARAMETER IS 0.00003609

THE MB-PARAMETER IS -0.02349257

THE RMS DEVIATION IS 0.00000001

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
25.00	250.030	0.008903	0.99707	0.00001600	0.00003571
35.00	203.675	0.007194	0.99406	0.00002411	0.00003553
45.00	170.628	0.005963	0.99025	0.00003435	0.00003529
50.00	157.457	0.005467	0.98807	0.00004033	0.00003514

TEMPERATURE	Y	YCALC	DEVIATION
25.00	0.00003571	0.00003572	-0.00000000
35.00	0.00003553	0.00003553	0.00000001
45.00	0.00003529	0.00003529	0.00000001
50.00	0.00003514	0.00003515	-0.00000001

CALIBRATION OF VISCOMETERS

EXPERIMENT NUMBER 1010

THE A-PARAMETER IS 0.00003544  
 THE MB-PARAMETER IS -0.01660516  
 THE RMS DEVIATION IS 0.00000004

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
15.00	939.880	0.037570	1.12863	0.00000113	0.00003542
20.00	799.760	0.031870	1.12698	0.00000156	0.00003536
298.00	686.460	0.027350	1.12517	0.00000212	0.00003541
25.00	253.313	0.008903	0.99707	0.0001558	0.00003525
35.00	206.191	0.007194	0.99406	0.0002352	0.00003510
45.00	172.640	0.005563	0.99025	0.00003355	0.00003488
50.00	159.267	0.005467	0.98807	0.00003942	0.00003474

TEMPERATURE	Y	YCALC	DEVIATION
15.00	0.00003542	0.00003542	-0.00000001
20.00	0.00003536	0.00003542	-0.00000006
298.00	0.00003541	0.00003541	0.00000000
25.00	0.00003525	0.00003518	0.00000007
35.00	0.00003510	0.00003505	0.00000005
45.00	0.00003488	0.00003489	-0.00000001
50.00	0.00003474	0.00003479	-0.00000005

CALIBRATION OF VISCOMETERS

EXPERIMENT NUMBER 2010

THE A-PARAMETER IS 0.00003666  
 THE MB-PARAMETER IS -0.01817724  
 THE RMS DEVIATION IS 0.00000005

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
15.00	908.410	0.037570	1.12863	0.00000121	0.00003664
20.00	773.320	0.031870	1.12698	0.00000167	0.00003657
298.00	663.560	0.027350	1.12517	0.00000227	0.00003661
25.00	245.140	0.008503	0.99707	0.00001664	0.00003642
35.00	199.606	0.007194	0.99406	0.00002510	0.00003626
45.00	167.166	0.005563	0.99025	0.00003579	0.00003602
50.00	154.410	0.005467	0.98807	0.00004194	0.00003583

TEMPERATURE	Y	YCALC	DEVIATION
15.00	0.00003664	0.00003664	0.00000000
20.00	0.00003657	0.00003663	-0.00000006
298.00	0.00003661	0.00003662	-0.00000001
25.00	0.00003642	0.00003636	0.00000007
35.00	0.00003626	0.00003620	0.00000005
45.00	0.00003602	0.00003601	0.00000001
50.00	0.00003583	0.00003590	-0.00000006

CALIBRATION OF VISCOMETERS

EXPERIMENT NUMBER 3010

THE A-PARAMETER IS 0.00003436

THE MB-PARAMETER IS -0.01748816

THE RMS DEVIATION IS 0.00000005

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
15.00	969.560	0.037570	1.12863	0.00000106	0.00003433
20.00	824.950	0.031870	1.12698	0.00000147	0.00003428
298.00	708.240	0.027350	1.12517	0.00000199	0.00003432
25.00	261.241	0.008503	0.99707	0.00001465	0.00003418
35.00	212.666	0.007194	0.99406	0.00002211	0.00003403
45.00	178.102	0.005963	0.99025	0.00003153	0.00003381
50.00	164.410	0.005467	0.98807	0.00003700	0.00003365

TEMPERATURE	Y	YCALC	DEVIATION
15.00	0.00003423	0.00003434	-0.00000011
20.00	0.00003428	0.00003434	-0.00000006
298.00	0.00003432	0.00003433	-0.00000001
25.00	0.00003418	0.00003410	0.00000007
35.00	0.00003403	0.00003397	0.00000006
45.00	0.00003381	0.00003381	0.00000000
50.00	0.00003365	0.00003371	-0.00000006

CALIBRATION OF VISCCMETERS

EXPERIMENT NUMBER 4010

THE A-PARAMETER IS 0.00003589

THE MB-PARAMETER IS -0.01707746

THE RMS DEVIATION IS 0.00000005

TEMPERATURE	TIME	VISCOSITY	DENSITY	X	Y
15.00	928.150	0.037570	1.12863	0.00000116	0.00003587
20.00	790.010	0.031870	1.12698	0.00000160	0.00003580
298.00	678.290	0.027350	1.12517	0.00000217	0.00003584
25.00	250.030	0.008903	0.99707	0.00001600	0.00003571
35.00	203.675	0.007194	0.99406	0.00002411	0.00003553
45.00	170.628	0.005963	0.99025	0.00003435	0.00003529
50.00	157.457	0.005467	0.98807	0.00004033	0.00003514

TEMPERATURE	Y	YCALC	DEVIATION
15.00	0.00003587	0.00003587	-0.00000000
20.00	0.00003580	0.00003586	-0.00000006
298.00	0.00003584	0.00003585	-0.00000001
25.00	0.00003571	0.00003561	0.00000010
35.00	0.00003553	0.00003548	0.00000006
45.00	0.00003529	0.00003530	-0.00000001
50.00	0.00003514	0.00003520	-0.00000006

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