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by

Bruce Edward Koel

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by Brua Edward Koel*

SECTION 1

INTRODUCTION

The system 1-propanol-H_2O-KI is one of a general class of electrolytes in mixed solvent systems. An understanding of the detailed nature of this ternary system requires first an understanding of the nature of the components of the solvent, water and 1-propanol, and the nature of the mixed solvent before the introduction of the electrolyte. A brief description of the types of systems mentioned will be given along with references which summarize much of the available information.

1.1 *Solvents*

Due to its ubiquitous nature, much is known about liquid water.[1] The polar nature of the water molecule and its ability to form hydrogen-bonds results in cooperative association into multimolecular aggregates. The structure of associated liquids has eluded investigators for many years. Water is the most complex example of an associated liquid since the water molecule is able to participate in three hydrogen-bonds at once and forms three-dimensional networks. The elucidation of the structure of water has been worked on for many years and a huge volume of literature is available but the exact structure of liquid water is still not known. Several sources are available that discuss the structure theories and the associated experimental evidence.[2-18]

One principal difference between an organic or nonaqueous solvent and water is the difference in their dielectric constants. Many early theories and some used currently consider this dif-

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*This study originated as a master's thesis under the direction of Dr. Charles M. Greenlief in the Division of Physical Sciences at Emporia State University. The author is currently a doctoral student in the Department of Chemistry at the University of Texas-Austin.

ference to be the only one affecting ions in solutions. The fact that many of the theoretical models worked well in predicting experimental results accounted for the failure to develop more physically meaningful models. Currently, researchers are steering away from modeling the bulk solvent as a continuum characterized by its dielectric constant, and all realize this to be a false, although simplifying, assumption.

The non-aqueous component of the mixed solvent used in this work is 1-propanol. Alcohols as a class are highly structured liquids due to hydrogen-bonding, although structured to a lesser extent than water. Each molecule can participate in a maximum of two hydrogen-bonds simultaneously and the two-dimensional rings or chains formed make alcohols much simpler liquids than water. Still, the exact structure of these liquids is not known absolutely.

The introduction of 1-propanol into water to create a mixed solvent causes several changes.[19-25] One effect is to reduce the dielectric constant of the solvent to a value between that of either pure component depending on composition. Table 1 lists the value of the dielectric constant for 1-propanol-water mixtures at 25°C. Another effect of adding 1-propanol to water is to modify

TABLE 1

DIELECTRIC CONSTANTS FOR WATER AND 1-PROPANOL MIXTURES AT 25°C[a]

Weight Percent Water	Dielectric Constant
100	78.5
90	71.8
80	64.9
70	57.7
60	50.3
50	43.0
40	36.4
30	30.7
20	26.1
10	22.7
0	20.1

[a] H.S. Harned and B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd ed., p. 161 (Reinhold, New York, 1958).

the water structure.[26, 27] This creates a mixed solvent with a structure that probably contains none of either of the pure component's structure (although this depends on the relative amount of each). Alcohol-water mixed solvents have been studied a great deal and much is known about their structure.[28-36]

The structure of alcohol-water solutions has been studied from several different approaches.[37] Alcohols in water can be thought of as solutes introducing hydrophobic groups into solution. The resulting new structure is due to the interactions between these groups and water.[38-42] Another approach would suggest that hydrogen-bonding between the alcohol and water molecules reduces the three-dimensional structure of pure water and accounts for a different structure.[43] The detailed nature of the interactions in the mixed solvent will not be considered in this manuscript. However, this investigation will yield some insight into the nature of the mixed solvent.

There are several methods available for investigating the structure of the 1-propanol-water mixed solvent. One method is to study the mixed solvent itself, observing the behavior of a physical property of the solvent as its composition is changed. Another method is to dissolve an electrolyte in the mixed solvent and use the ions as a probe of the structure of the solvent. The study of the electrolyte solution gives information about the mixed solvent in addition to that about the ions. This work seeks to use both of these techniques to obtain as yet qualitative information about the mixed solvent.

1.2 *Electrolytic Solutions*

The presence of an electrolyte profoundly alters the structure of the solvent.[44-51] Coulombic interaction energies between ions and diploar molecules cause solvation[52] of the ions. This energy is larger than the dipolar interaction energy between solvent molecules and also larger than hydrogen-bonding energies. According to one theory, the local perturbation of the solvent structure is called the solvation atmosphere of the ion and is itself complex, consisting of an inner, structure-enhanced region and an outer region of broken solvent structure.[53, 54] A given ion can have a net structure making or breaking effect depending on the relative sizes of the inner and outer regions. Another theory calls essentially the same region of oriented solvent dipoles around the ion the "cosphere" of the ion.[55] Due to the presence of the dielectric, the strength of the electrostatic field falls off (quickly in aqueous solutions) and has little effect on solvent molecules outside of the "cosphere".

Water is used extensively as a solvent for electrolytes due to the strong interactions between the water dipoles and the ionic solid that results in a high solubility and also in the existance of independent ions over a large concentration range. Correspondingly, most is known about aqueous electrolyte solutions. Much is uncertain about non-aqueous solvents, and especially non-aqueous mixed solvents, in regard to electrolyte solutions and there are consequently many models of solvent structure and ion solvation.[56, 57]

The amount of literature on ionic systems is quite staggering. Almost all reviews disclaim completeness. Several sources, however, can be used as a good introduction to the pertinent literature of these solutions.[58-60]Harned and Owen's[61] treatise on the physico-chemical aspects of electrolytic solutions still serves as an excellent reference for fundamental principles and as a source of the older literature. Robinson and Stokes[62] also discuss physicochemical aspects of electrolytic solutions. Covington [63] and Janz and Tomkins[64] systematized a large amount of data on the properties of electrolytes in organic solvents. A recent book by Gordon[65] reviews organic electrolyte systems, and deals with the influence of ions on reaction rates. Excellent bibliographies are given following the chapters on ion solvation and on ion association.

There are still not many general treatments of electrolytes in mixed organic-water solvents. A large amount of data is scattered about in the literature, but studies have mainly been done at one temperature, usually 25°C, and thus some important thermodynamic information is still missing.

The selective solvation of ions in mixed solvents may occur either over a limited range or over a large range of composition of the solvent.[66] Selective solvation implies that in the immediate environment of the ion one type of solvent molecule is preferred. In the system studied in this work, it is expected that the more polar water molecules would selectively solvate the charged ions due to a larger decrease in free energy, barring any specific interactions between 1-propanol and the ions (which is not expected). The details are not known, but there is an oscillatory effect observed in the relative solvation of ions in alcohol-water mixed solvents.[67] This is explained by the successive replacement of the water in the different solvation layers of the ions as the composition of the mixed-solvent is increased toward the pure alcohol limit.

An additional fact needs to be pointed out concerning solutions of electrolytes. The terms "strong" and "weak" as applied to electrolytes are not very useful concerning electrolytic solutions in non-aqueous or mixed solvents. In these solvents, electrolytes are better represented as associated and non-associated.[68] Association refers to any lasting "togetherness" of oppositely charged ions. Association of the ions complicates the solution due to the existence of several kinds of solute entities: solvated ions, unsolvated ions, and associated groups of ions. Association constants are discussed, as opposed to dissociation constants, so that there is the possibility of having a "weak" electrolyte without neutral molecules.

1.3 *Transport Properties and Viscosity*

After this brief introduction to the nature of the solutions studied in this work, it is in order to describe how to determine some of the properties of these solutions by which they can be characterized. There are two types of measurements that can be used to determine properties of electrolytic solutions: (1) those of systems in equilibrium and (2) those of systems in non-equilibrium or disturbed states. Those of the first type are such things as boiling point or freezing point depression and are treated by thermodynamics. Irreversible processes, transport processes, constitute the second group.[69, 70]

Transport properties are of interest since they are indicators of how solute and solvent species move about in solution. Thus, transport processes in solution are closely related to the structure of the solution and shed much light on the nature of these solutions. Of the several types of transport processes, *e.g.* dielectric relaxation, diffusion, viscosity and electrical conductivity, viscosity is the property chosen to be studied in this work.

Viscosity is a parameter which is especially sensitive to the structure of solutions. The viscosity of a liquid is related to its resistance to flow. Information about the nature of the solution is obtained since viscous flow involves the displacement of the molecules from equilibrium positions as adjacent layers of liquid move past one another. The fluid friction caused by the forces exerted by the molecular and ionic constituents is of major interest. The shear viscosity relative to a stationary surface is measured to obtain knowledge of the drag forces in the solution.

Horne[71] has expressed reservations about using shear viscosities with respect to a surface to measure internal fluid friction in the solution, however, the former viscosities appear to work and they represent results of the only methods available to determine solution viscosity.[72] This objection may have merit since it is known that the structure of water is considerably perturbed near an interface[73] and in an electrolyte solution the ions might even be excluded from this region.

Electrolytes can either increase or decrease the viscosity of the solution relative to that of the solvent and are termed either "structure makers" or "structure breakers".[74] Due to the inability of the solvated ion to fit into the existing solvent structure large ions tend to introduce more disorder into the system than the increased structure brought about by their solvation. This "breaking" of the structure is observed as a decrease in the viscosity of the solution. Small ions have the opposite effect due to the many solvent molecules present in the solvation sphere and thus increase the viscosity of the solution.

Information obtained from viscosity measurements is limited to a certain extent. The viscosity is a macroscopic quantity, *i.e.*, it is an average value arrived at from measurements on a large group of molecules. It also is a quantity averaged over a long period of time (several minutes). It tells nothing directly about the microscopic environment in the solution or about processes occurring on a much shorter time scale. One can make guesses as to what is occurring on a molecular level in order to account for the observed viscosity behavior of the solution.

The structure of the mixed solvent is complex and perhaps nothing definitive can be said about the structure of the solvent from viscosity measurements alone. Quite a bit of information can be gained about the relative amount of structure present in the solution as a function of the temperature, composition of solvent, and concentration of the electrolyte.[75] This investigation has as part of its goal the elucidation of such qualitative information.

Accurate viscosity measurements appear deceptively simple, but they are difficult to make. Several sources are available describing the accurate measurement of viscosity [76-79] and describing accurate viscometers.[80-83]

Almost universally in electrolyte studies, kinematic viscometers are used to make relative viscosity measurements in which the viscosity of the solution is determined by comparison with a standard of known viscosity. The kinematic viscosity, υ, of a solution is determined by measuring the time for a volume of solution to flow under the influence of its own hydrostatic head through a capillary.[84]

The dynamic viscosity, η, can be obtained by multiplying the measured kinematic viscosity by the density of the solution.[85] The dynamic viscosity, commonly called the viscosity of the liquid, is actually the coefficient of viscosity and is equal to the ratio between the applied shear stress and the rate of shear.

The viscometer used in this work is an Ubbelohde suspended level viscometer and is of the class described above.

1.4 *Reasons for Study*

1-propanol was chosen as a solvent since it forms part of a homologous series with water and other alcohols. Data on 1-propanol systems could be used to examine trends in this series. Also 1-propanol is relatively easy to work with, is obtainable in high purity, and is miscible in all proportions with water. Its vapor pressure is similar to that of water and it should have little tendency to selectively evaporate from solutions or to absorb moisture from the air compared to methanol and ethanol systems.

Almost no viscosity data exists for electrolytes in solutions containing 1-propanol and this work will fill a gap in the literature. 1-Propanol-water mixtures over most of the range of composition have a dielectric constant greater than that of methanol and should lend themselves to theoretical interpretations of the observed behavior. Data was taken on solutions with pure 1-propanol in order to determine whether ion association at reasonably dilute concentrations precludes analysis of the data according to theory. The validity of the Jones-Dole equation $\eta/\eta_0 = 1 + Ac^{1/2} + Bc$ was tested for solutions of KI in 1-propanol-water mixed solvents and for KI in pure 1-propanol (for discussion of this equation see Section 2.1).

KI was chosen as the electrolyte of study based on two physical considerations: solubility and purity. Table 2 gives the solubility of some salts in 1-propanol. KI has a reasonable solubility limit, considering viscosity studies, and is obtainable in high purity. It is not greatly hygroscopic and thus its handling is simplified. Electrolytes other than uni-univalent salts should not be used because of deviation in their viscosity behavior. Further, comparative data for KI in methanol and methanol-water mixtures exists in the literature. KI has also been studied in several other organic solvents.

Information on viscosity is important for many reasons. Viscosity effects partially control changes in specific conductance and ion mobilities. In addition to several other theromodynamic and solvation effects, the viscosity of the solution has an effect on

TABLE 2

SOLUBILITY OF SALTS IN 1-PROPANOL

Salt	Solubility m, moles (kg solvent)$^{-1}$	Temperature °C	Reference
$CaBr_2$	1.13	20	(a)
$CaCl_2$	1.422	20	(a)
NaCl	0.00212	20	(a)
$HgCl_2$	0.9451	20	(b)
$KClO_4$	0.0007	25	(c)
$Ca(NO_3)_2$	3.50	25	(a)
LiCl	3.823	25	(a)
KBr	0.00264	25	(a)
KCl	0.0005	25	(a)
KI	0.044	25	(a)
$CsNO_3$	0.00049[f]	25	(d)
$CeCl_3$	1.379, 1.06	25	(d), (e)
$PrCl_3$	1.907	25	(d)
$NdCl_3$	1.587	25	(d)
$ScCl_3$	2.333	25	(d)
$LnCl_3$	0.112	25	(e)

[a] G.J. Janz and R.P.T. Tomkins, Eds., *Nonaqueous Electrolytes Handbook*, Vol. I (Academic Press, New York, 1972).

[b] V.A. Mikhailov, J. Struct. Chem. *9*, 687(1968).

[c] H.H. Willard and G.F. Smith, J. Amer. Chem. Soc. *45*, 286(1923).

[d] A.K. Covington and T. Dickenson, Eds., *Physical Chemistry of Organic Solvent Systems* (Plenum, London, 1973).

[e] F.R. Hartley and A.W. Wylie, J. Chem. Soc., 679(1962).

[f] Molarity, moles/(liter solution).

reaction rates and mechanisms, especially in ion-ion reactions. The viscosity of the medium will presumably influence any rate process which is diffusion controlled. Independent results from viscosity measurements can be compared to, and also supplement, those from other types of measurements such as proton nuclear magnetic resonance[86-88] and infrared studies[89] to reinforce information on the nature of solutions.

SECTION 2

THEORETICAL INTERPRETATION OF VISCOSITY OF ELECTROLYTIC SOLUTIONS

2.1 *The Jones-Dole Equation*

An empirical equation that adequately represented the viscosity data of many solutions of electrolytes in water was found by Jones and Dole[90], and others[91, 92], and is given as

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \qquad (2\text{-}1)$$

where η is the viscosity of the solution, η_0 is the viscosity of the solvent, c is the concentration of the added solute as molarity, and A and B are constants. Equation (2-1) is the Jones-Dole (JD) equation and the constants A and B are the Jones-Dole coefficients. These investigators found that at high dilution, the viscosity of solutions of strong electrolytes varies linearly with the square root of the concentration. At high concentration the viscosity varies linearly with the concentration. Equation (2-1) has been found to be valid up to concentrations of a few tenths molar in aqueous solutions of strong electrolytes.[93-95]

The limiting law (at high dilution) for the viscosity of an electrolytic solution has been deduced by Falkenhagen[96] and was shown to be of the form

$$\eta/\eta_0 = 1 + Ac^{1/2} \qquad (2\text{-}2)$$

This result was obtained from mathematical treatment of the effect that electrical forces between ions in adjacent layers of solution will increase the viscosity. Falkenhagen's result verified Jones and Dole's experimental conclusions. The behavior of dilute electrolyte solutions according to Equation (2-2) is described in the older literature as the "Gruniensen effect".[97]

The JD equation, Equation (2-1), is valid for solutes other than electrolytes. For solutes such as the 1-propanol in water, the JD equation accurately represents the viscosity of the solution when the concentration of the 1-propanol is expressed in terms of molarity. However, for solutes of zero charge the A coefficient is zero.

The JD equation has been found to be valid for many solvents besides water.[98-102] The behavior of electrolytes in nonaqueous solvents is similar to that in water but Equation (2-1) might be expected to fail at a lower concentration upper limit than for water.[103]

Little work has been done on the viscosity of electrolyte solutions using 1-propanol-water mixed solvents or using 1-propanol as the pure solvent. Some work has been done on solutions using methanol and ethanol as pure solvents and also using the alcohol-water mixed solvent. In pure methanol the JD equation was found to be valid only up to 0.01 M.[104] The low dielectric constant of the solvent allows ion association at low concentrations and decreases the range of validity of the JD equation. Based on considerations of the dielectric constant, it is expected that the JD equation will be valid up to at least 0.01 M for solutions in most 1-propanol-water mixtures and to slightly less in pure 1-propanol.

Venkatasetty and Brown[105] have measured the viscosities of LiI, NH_4I and Bu_4NI in 1-butanol (dielectric constant = 17.1, at 25°C) at 0, 25, and 50°C and attempted to fit the data to the Jones-Dole equation. They were unable to obtain A and B coefficients due to deviations from linearity of plots used to evaluate these coefficients at all concentrations.

2.1.1 *Ion-Ion Interactions*

The A coefficient in the JD equation represents the viscosity increment due to long range electrostatic interactions. Coulomb interactions between the ions in one layer moving in shear past ions in adjacent layers retard the motion of these ions and increase the viscosity of the solution. Thus, the value of A gives information about ion-ion interactions in solution.

The A coefficient is a function of solvent properties, ionic charge and mobilities, and temperature. The interionic attraction theory behind the deduction of the theoretical equation for A, derived by Falkenhagen[106], is too lengthy to be given an adequate explanation here, but a detailed treatment is available.[107] For uni-univalent electrolytes, A is given by the equation[108]

$$A = \frac{1.45}{\eta_0 (2D_0 T)^{1/2}} \left[\frac{\lambda_+ + \lambda_-}{4\lambda_+\lambda_-} + \frac{(\lambda_+ - \lambda_-)^2}{(3 + 2^{1/2})\, \lambda_+\lambda_-(\lambda_+ + \lambda_-)} \right] \qquad (2\text{-}3)$$

where η_0 is the solvent viscosity, D_0 is the dielectric constant of the solvent, T is the temperature, and λ_+ and λ_- are the molal conductances of the different ionic species. The expression is much more complicated for higher valence type electroytes.

The agreement of observed and theoretical values of A in aqueous solutions is generally good and the validity of the theoretical equation for A at low concentrations can be regarded as established. The temperature influence on the value of A has been found to be in good accord with theory.[109, 110]

The coefficient A can be found if the data extends to high enough dilutions even if B is not constant over the entire range. For non-aqueous systems the agreement is fair but much more precise data is needed for adequate testing of these cases. The A coefficient has sometimes been found to be negative in non-aqueous solvents. The value of A, the theoretical limiting slope, is always positive due to the nature of the ion-ion interaction, and negative values are without physical significance.[111] One possible explanation for experimentally determined, negative values of A is that the experimental limiting slopes in non-aqueous solvent systems are subject to errors caused by the adsorption of moisture by the solvents. At high dilution, even a small percentage of water in the solvent becomes a large amount when compared on a mole ratio basis with the electrolyte.

It is evidently necessary to obtain precise measurements at very low concentrations to evaluate A in non-aqueous solvents.[112] As is the case with limiting equivalent conductances of weak electrolytes, it may be impossible to determine the value of A from direct extrapolation of the data to infinite dilution if association is extensive.

Theoretical values of A cannot be evaluated for many non-aqueous solvents and mixed solvents due to the lack of limiting ionic conductivity data in those solvents. Conductivity data is hard to obtain for solutions of electrolytes in non-aqueous solvents with dielectric constants lower than methanol because the data is so strongly influenced by ion association that the solute cannot be thought of as a strong electrolyte.

The electrostatic theory applies in aqueous electrolyte solutions up to about 0.002 M and the term containing A describes well the viscosity behavior of the system. In non-aqueous solvent systems the theory should fail at a lower concentration due to the increased ion association.

The size of the value of A is fairly small, *ca.* 0.01 to 0.001, in aqueous solutions. Ion association should decrease the size of A. Organic solvents with small dielectric constants should cause A to be larger since the value of A is inversely proportional to the dielectric constant of the solvent.

This parameter is of great theoretical utility but is not of much practical use since it is swamped out as most concentrations by the linear term in the JD equation. At high concentrations some authors neglect this term. In view of this, the theory of the Coulomb interations of ions in solutions has not been extended to higher concentrations and this theory as it applies to viscosity has not been developed further.

2.1.2 *Ion-Solvent Interactions*

The Jones-Dole B coefficient is a useful parameter for qualitatively interpretating ion-solvent interactions.[113-120] The linearity of the Bc term in concentration indicates that the value of B is a manifestation of ion-solvent interactions. There has been no completely satisfactory manner of calculating theoretical values of B. However, the B value is very useful even though there has been no satisfactory theoretical interpretation of this parameter. It correlates with many solution properties such as ionic entropies[121, 122] and the self diffusion coefficient of water,[123] and it describes ion solvation atmospheres.[124] The B coefficient has been related to the volume parameters of electrolytes.[125, 126] The value of B can be thought of as a qualitative measure of the order or disorder introduced by the ions into the solvent structure or as a qualitative measure of the structure altering properties of the ions.[127]

Much information on the viscosity of aqueous electrolyte solutions exists in which the B coefficients have been evaluated. Robinson and Stokes,[128] and Stokes and Mills[129] give values of B for aqueous salt solutions. The constant B is highly specific for the electrolyte and the temperature. It is approximately additive for the constituent ions.[130-132]

It is possible to talk of individual ionic values even though these quantities cannot be measured directly. Individual ionic values of B can be assigned, since B is an additive property of the ions, once reference ions have been chosen. The reference for aqueous solutions is $B(K^+, 25°C) = -0.007$ mole^{-1}l. Stokes and Mills[133] list some of these ionic B values. No division into ionic B values has been made for non-aqueous or mixed solvents (except for H_2SO_4) because no reference ion value has been chosen.

Less information is available for B values in non-aqueous or mixed solvents.[134] B values vary widely for different solvents and show progressive changes in mixed solvents.

The effect of introducing a solute into solution would be to increase the solution viscosity.[135] Negative B values are accounted for by the ability of the ions to disrupt the solvent structure in their vicinity. These two effects contribute to the observed behavior in all solutions.

Stokes and Mills[136] have treated viscosity changes based on competition of several effects. The viscosity of a dilute electrolyte solution η can be explained by the competition of five sources as

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D \qquad (2\text{-}4)$$

where η_0 is the viscosity of the solvent, η^* is a increment in viscosity caused by coulombic interactions, η^E is the viscosity increment arising from the shape and size of the ion, η^A is the increment due to the orientation of polar molecules by the ionic field, and η^D is the viscosity decrement associated with distortion of the solvent structure and accounts for a greater fluidity.

If Equation (2-4) is substituted in the JD equation, then

$$\eta^* + \eta^E + \eta^A + \eta^D = \eta_0(Ac^{1/2} + Bc). \qquad (2\text{-}5)$$

Eliminating the ionic interaction contributions from both sides yields

$$\eta^E + \eta^A + \eta^D = \eta_0 Bc. \qquad (2\text{-}6)$$

At a given concentration, B can be thought of as the result of competition between several specific viscosity effects in a given solvent at a given temperature.

Salts that have negative values of B are termed "structure breakers" since the result of adding the salt to the solvent is a decrease in the viscosity. Salts composed of large, relatively hydrated ions often have negative B values at low temperatures. In all cases known, the value of dB/dT has been found to be positive for aqueous solutions. At high temperatures all salts increase the viscosity of the solution, *i.e.*, have positive B values.

The increase in B with temperature is due to thermal destruction of the solvent leaving little structure to be "broken".

A "structure making" salt has a positive value of B. All salts have positive B values in the non-aqueous solvents studied so far.[137]

The B coefficient may not always be constant. Variations in B are caused by high charge type electrolytes and by ion association.

2.2 *Alternative Equations*

The JD equation is not the only equation used to describe the viscosity behavior of electrolytic solutions. Some of the other equations that are used are given below.

Einstein[138] derived an equation for the solution viscosity, η, of the form

$$\eta = \eta_0 (1 + 2.5\Phi), \qquad \Phi < 0.03, \qquad (2\text{-}7)$$

which described the viscous flow of non-interacting hard spherical particles, occupying a volume fraction Φ, moving in a continuous medium of viscosity η_0. This equation serves as a first approximation of the viscosity effects for both non-electrolytes and electrolytes.

Equation (2-7) has been extended to higher solute concentrations and the relative viscosity, η/η_0, can be represented by

$$\eta/\eta_0 = 1 + 2.5\Phi + C\,\Phi \qquad (2\text{-}8)$$

This equation can be related to the Jones-Dole equation by substituting the relation between c and Φ into Equation (2-8) and equating coefficients of c.

By refining Einstein's hydrodynamic treatment of streamline interference by large particles, Vand[140] obtained the following relationship for spherical particles:

$$\ln\left[\frac{\eta}{\eta_0}\right] = \frac{2.5\Phi}{1 - Q\Phi} \qquad (2\text{-}9)$$

where Φ is the volume fraction occupied by the particles and Q is an interaction coefficient. Padova[141] and Mooney[142] discuss this and other similar equations. This equation can be applied to electrolyte solutions if the ions have a large solvation radius. The Jones-Dole B coefficient can be related to Φ and the molal volume, V_i. Since $\Phi = cV_i$, then $2.5V_i = B$ for small volume fractions.

Breslau and Miller[143] have correlated viscosities of concentrated aqueous electrolytic solutions by the use of an equation developed by Thomas:[144]

$$\eta/\eta_0 = 1 + 2.5\Phi + 10.05\Phi^2 \qquad (2\text{-}10)$$

where Φ is the particle volume fraction and is less than 0.25. This equation is a truncated form of a power series regression. The Jones-Dole B coefficient can be related to Φ.

Herskovitz and Kelly[145] measured the viscosity of aqueous 1-propanol solutions at 25°C and determined the B_1 and C coefficients in the equation

$$\eta/\eta_0 = 1 + B_1m + Cm^2 \qquad (2\text{-}11)$$

where m is the molality of 1-propanol. B_1 is not numerically the same as the Jones-Dole B-coefficient but arises from the same effect since the term containing it is also linear in concentration. They found that B_1 was linearly correlated to the partial molal volumes of alcohols. They offer an equation for B_1 describing the viscosity behavior of ellipsoidal particles of approximately the same dimensions as the solute, and the water structure forming and structure breaking influence of the hydrophobic and hydrophilic groups in the molecules.

Suryanarayana and Venkatesen[146] proposed an empirical relation for concentrated aqueous electrolytes (1 M to saturation) that can be written as

$$\eta/\eta_0=\exp\,(BC_p) \qquad (2\text{-}12)$$

where B is a constant related to the solute and C_p is the ratio of the mole fraction of the solute to that at saturation. Its significance is not certain.

Onsager and Fuoss[147] have proposed a generalized expression describing the variation of solution properties as functions of the concentration which gives for viscosity the equation

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc\log c \qquad (2\text{-}13)$$

where A, B, and D are constants. Jones[148] found that this equation could extend the fit of the data to higher concentrations in studies using methanol.

To extend the usefulness of the Jones-Dole equation in fitting viscosity data to higher concentrations, the following extended form of Equation (2-1) has been suggested:

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2 \qquad (2\text{-}14)$$

where A, B, and D are constants. This equation was suggested by Kaminsky[149] and originally used for NMF solutions.[150]

Das, Das, and Patnaik[151] suggested a modified form of the

Jones-Dole equation:

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc^x \qquad (2\text{-}15)$$

where x is determined from the data. This equation has been tested for several salt and solvent pairs and has been found to satisfactorily represent viscosity data for 1-2 and 2-2 type electrolyte solutes.[152, 153]

When ion association occurs, the Jones-Dole equation can be written in the form[154]

$$\eta/\eta_0 = 1 + A(c\gamma)^{1/2} + Bc\gamma + B'c(1-\gamma) \qquad (2\text{-}16)$$

where B and B′ are the Jones-Dole coefficients for the free ions and the ion pair, and $1-\gamma$ is the associated fraction.

The Jones-Dole equation is often referred to as a semiempirical equation, but it has more theoretical foundation than many others presented here. It is the equation that should be used for the interpretation of viscosity behavior.

SECTION 3

PURITY OF MATERIALS

3.1 *Potassium Iodide*

Potassium iodide was Certified A.C.S. reagent grade from Fisher Scientific Company. Its purity was better than 99.9%. It was used as received after drying at 110°C. Lot analysis on the reagent bottle showed a loss on drying at 150°C of 0.06%.

3.2 *1-Propanol*

High purity 1-propanol is available, with the principal impurity often being 2-propen-1-ol.[155] The 1-propanol used was from a previously unopened can and was Mallinkrodt Analytical Reagent. The maximum limit of impurities are: acidity (as CH_3COOH) 0.015%, alkalinity (as NH_3) 0.002%, residue after evaporation 0.005%.

A simple distillation was done on a 100 ml sample of 1-propanol from the reagent can. The boiling point range was 97.14°C-97.31°C at 733.5 mm Hg for the 50 ml center cut. The boiling point corrected to 760 mm Hg is 98.1°C. The distillation rate was slightly less than 4 ml/min. The temperature after five drops of distillate was 97.09°C. Superheating of the vapor accounted for a final temperature of 101.2°C with less than 1 ml remaining undistilled. Stem corrections were applied to the thermometer readings. The results compare favorably with literature values given for the boiling point of 1-propanol at 760 mm Hg of 97.2 and 97.8°C. [156, 157] The 1-propanol is of high purity as evidenced by the small boiling point range. Discrepancy in the measured boiling point temperature with that described in the literature might be accounted for by a lack of calibration of the thermometer. The 1-propanol used in the preparation of the mixed aqueous solvents was not further purified.

Gas chromatography detected only water as an impurity in the 1-propanol that was used. The amount was determined to be 0.0005 volume fraction water. The instrument used was a Hewlett-Packard 5750 Gas Chromatograph. A Porapak S column was used. Only two peaks were present, water and 1-propanol, and the water peak was identified by analysis of a pure water sample. The following program gave good separation of the two peaks:

Flow rate = 30 ml He/minute
Initial temperature = 85°C; hold for 3 minutes
Rate of temperature increase = 30°C/minute
Final temperature = 190°C; hold for 0 minutes.

The attenuation was assumed to be linear and was changed between peaks. The proper baseline for each attenuation level was used. The peaks were symmetrical and peak heights were used for the analysis. The peak height fraction of water corresponded most closely to weight fraction water, but division of the peak height fraction by 1.62 gave the volume fraction water. The calibration factor was determined from measurements on mixtures of known composition.

Appropriate corrections in the solvent compositions of the solutions were made.

To obtain the anhydrous solvent for salt solutions in pure 1-propanol, Linde 4A Molecular Sieves were used to dry the alcohol. Forty grams of the sieves were used to dry two liters of 1-propanol, and the 1-propanol was allowed to remain in contact with the sieves for several days. Gas chromatography showed this sieve-dried 1-propanol to contain 0.0002 volume fraction water. The amount of water remaining may well be a practical limit, due to the necessity of maintaining the purity. Covington [158] points out that if rigorous precautions are not used in the drying of vessels used, water content can increase to 0.01% by desorption from the surfaces of the vessels. Also, these solutions under the experimental conditions were exposed to the atmosphere during their preparation and the measurement of their viscosity. The 1-propanol was not purified further, although several methods are available.[159, 160]

3.3 *Water*

Deionized water was obtained from a Barnstead Bantam Demineralizer by passing distilled water through the four bed system (two beds each of cation and anion exchange resins alternately arranged). These resins discharged H^+ and OH^- ions only. A direct reading conductivity meter calibrated in parts per million of ionized solids and specific resistance as ohms cm^{-3} gave a quality check on the effluent. Deionized water used in this work contained less than 2 ppm salts (as NaCl) and had a specific resistance greater than 200,000 ohms cm^{-3}.

The deionized water was suction filtered through a Millipore filter. The filter was type HA and had a pore size of 0.45 μm. The filtered, deionized water (hereafter referred to only as water) was stored in polyethylene containers. No provisions were made to remove organic contaminants or to exclude CO_2 from the water. In these and other respects the water used here does not conform to the rigorous standards of the best available "conductivity water." [161] However, care was taken to purify the water to an extent such that any impurities present would cause a negligible error in the experimental results.

SECTION 4

THE EXPERIMENTAL APPARATUS

4.1 *Constant Temperature Bath*

A circulating water bath was used to maintain temperature control. Figures 1 and 2 are diagrams of the bath. A Sargent Thermonitor Model S-W (Catalog no. S-82055) temperature controller regulated the temperature of the water bath. The Thermonitor is activated by a thermistor sensor immersed in the bath and comprising one arm of an A.C. Wheatstone bridge circuit.

The bath has a height of 25 cm, diameter of 40 cm, and a capacity of about 30 liters. The large volume of water presents considerable thermal inertia and helps to stabilize small temperature fluctuations. A central tower in the bath houses the heating rods and the impeller that rapidly circulates the water. About 12 ft of 0.25 inch copper tubing was coiled about the base of the central tower to provide a heat sink for temperature control at less than room temperature. A submersible pump placed in the reservoir of an ice bath was used to pump cold water through the cooling coils of copper at a rate determined by a pinch valve on a connecting hose. With some attention, the temperature of the bath was controlled to ±0.003°C over an interval as long as several hours and to better than ±0.01°C over an indefinite period of time. Variations in temperature with position in the bath was less than ±0.02°C.

The base of the tower was set on several rubber pads to minimize vibrations transmitted to the walls of the bath. Some vibration was still present but its effect on the viscosity determinations was considered negligible.

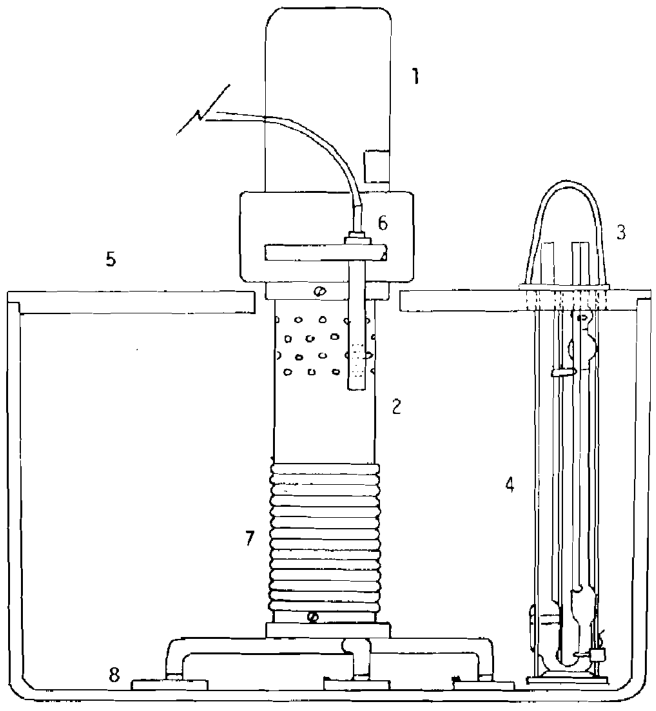

Figure 1. Side view of the water bath and the experimental arrangement. Numbered parts include: 1, stirring motor; 2, central tower; 3, viscometer holder; 4, viscometer; 5, lid; 6, thermistor; 7, cooling coils; 8, rubber pads.

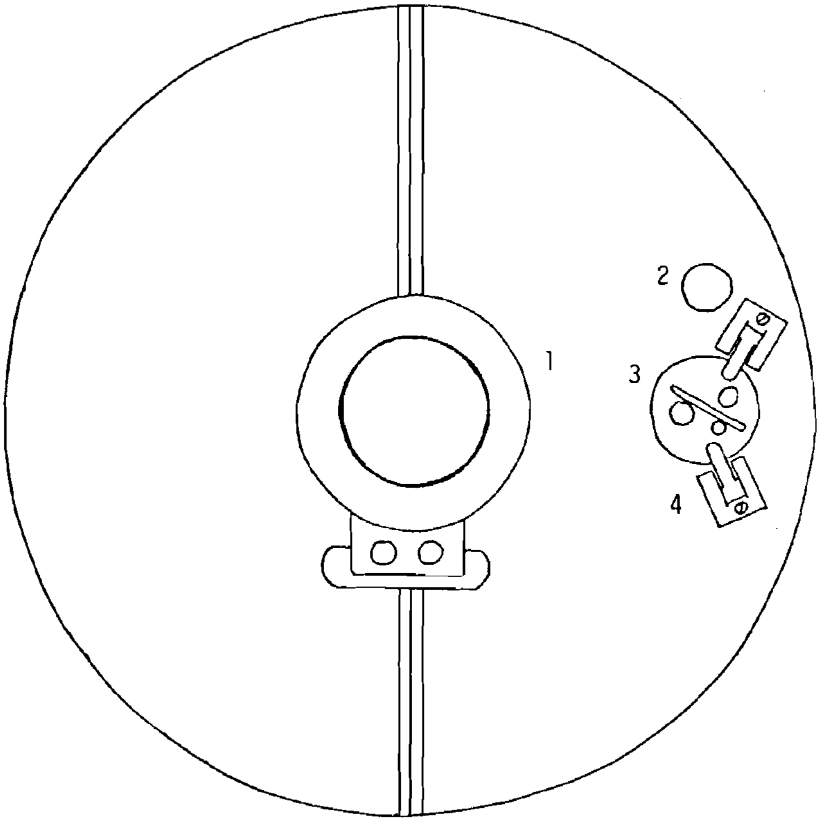

Figure 2. Top view of the water bath and the experimental arrangement. Numbered parts include: 1, central tower; 2, thermometer with rubber stopper; 3, viscometer holder; 4, spring clamps.

Two 0.25 inch sheets of plexiglas cut to the inside and outside diameter of the water bath respectively were glued together to form a 0.5 inch thich lid which fit snugly on top of the bath. The lid was cut in half for easy use and holes were cut out for the central tower and the thermister. A notch was cut along the edge for the cooling coils to enter the bath.

The purpose of constructing the lid was to provide a solid, reproducible mount for the viscometer. The viscometer could then be suspended in the same position for measurements of solutions as when it was calibrated. Holes were drilled for the viscometer and a thermometer about half-way from the center to the edge of the bath. A viscometer holder from Sargent Welch Scientific Co. (Catalog no. S-67438) actually held the viscometer and the upper lip on this holder fit over the hole in the lid. Heavy-duty spring clamps were screwed into the lid adjacent to the viscometer hole. These clamps locked tightly down on the upper lip of the viscometer holder to hold it sturdily in place and snapped back to allow the viscometer holder to be easily removed. The viscometer was left in the holder throughout the measurements. Figures 1 and 2 illustrate the experimental arrangement.

The viscometer was aligned using a cathetometer and subsequently checked daily with a small leveling bubble. The viscometer capillary was aligned to within ±1° of vertical. During the course of the measurements the Plexiglas lid warped and in order to maintain alignment the entire bath was tilted by raising one edge of the base.

One-half of the lid was removed to allow the pycnometers to be placed in the water bath to make the density measurements.

4.2 *Capillary Viscometer*

One viscometer was used in all the viscosity measurements and is shown in Figure 3. It is a kinematic viscometer of the Ubbelohde suspended level type and was obtained from Matheson Scientific. It was made of borosilicate glass with capillaries and bulbs designed to produce times of efflux in exact proportions to kinematic viscosity in centistokes. The following catalog information describes this viscometer:

ASTM size no.	Nominal viscometer constant	Kinematic viscosity range	Catalog no.
1	0.01 cS s^{-1}	2 to 10 cS	55210-05

4.3 *Pycnometers*

Weld type pycnometers of 25 ml capacity was used in the density determinations. A cap with a ground glass joint prevented evaporation of solution from each pycnometer. The pycnometers were made of Pyrex glass.

4.4 *Additional Equipment for Viscosity Measurements*

The efflux time in viscosity measurements was measured by a Faehr electronic-timer (no. S-100 S, 66, J102) with a precision of ±0.01 sec. This timer was calibrated against a precision Huer stopwatch and a Seiko Quartz watch. Timing intervals for calibration were sufficiently long to render error in starting the watches simultaneously to be negligible. No correction was necessary when the timer was left plugged into its A.C. adapter when tested over intervals as long as 55 minutes.[162] The Faehr timer can be considered to give accurate time measurement within 0.3 seconds for a timed interval of 55 minutes. The viscosity measurements usually were performed over a 15 hour period and hence the timer was always used with the A.C. adapter connected.

A Sargent G 41409 thermometer was used to measure the temperature for viscosity and density measurements. It was placed adjacent to the capillary of the viscometer or adjacent to the pycnometers to obtain accurate temperature readings. The scale was 18 to 38°C in 0.01°C. With a reading lens, the temperature was readable to ±0.002°C.

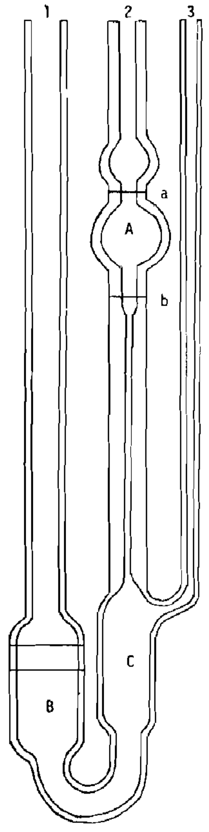

Figure 3. Ubbelohde suspended level viscometer.

This thermometer was calibrated by comparison with a liquid in glass thermometer certified by the National Bureau of Standards. The calibrated thermometer is marked Max Kaehler & Martini NBS No. 31203 and has a scale of 17 to 34°C in 0.05°C. The corrections for this thermometer were only given to 0.01°C and so the absolute accuracy of the temperature is only ±0.005°C.

However, due to the scale of the Sargent G thermometer variations in the temperature of ±0.002°C can be measured.

The calibration of the Sargent G thermometer was carried out by placing it and the NBS thermometer side by side in the water bath. Stem corrections were applied to each reading due to the different levels of immersion necessary to keep the mercury bulbs adjacent. Non-uniformity of the bore necessitates calibration at several temperatures and a calibration curve of the temperature correction versus the thermometer reading was made for the NBS thermometer and for the Sargent G thermometer. The corrections to the Sargent G thermometer at 20, 25, and 30°C were determined from these graphs and are:

Temperature of measurement	Correction to reading
20.0°C	—0.007°C
25.0	—0.030
30.0	—0.019

The NBS test record showed calibration in 1949. If this thermometer has not been checked since, the calibration data could well be in error. Unfortunately, this was the only calibrated thermometer available.

SECTION 5

METHOD

5.1 *Measurement of Viscosity*

The measurement of the kinematic viscosities of the solutions was made according to standard methods.[163-165] The suggested techniques of measurements and for calibrating the viscometer were adhered to except for the differences noted in section 6.3. These guidelines are for Newtonian liquids which undergo laminar flow and are appropriate for the solutions studied.

Measurement of the viscosity with a capillary type viscometer depends on the relationship between the rate of flow of the liquid under an applied pressure and the dimensions of the capillary tube through which it is forced. This relationship can be described taking into account the design of the instrument, and after solving for the dynamic viscosity, η, one obtains

$$\eta = \frac{\pi h g \rho r^4 t}{8V(l+nr)} - \frac{m \rho V}{8\pi(l+nr)t} \tag{5-1}$$

where

h = mean height of the liquid column
g = acceleration due to gravity
ρ = density of the liquid
r = radius of the tube
t = time of efflux of the liquid
V = volume of the liquid
l = length of the tube
n = coefficient of the Couette correction
m = coefficient of the Hagenbach correction.

For practical purposes, Equation (5-1) can be written in the form

$$\upsilon = C_\upsilon t - mB_\upsilon/t \tag{5-2}$$

Where υ is the kinematic viscosity, $C_\upsilon = \pi r^4 hg/[8V(l+nr)]$ and $B_\upsilon = V/[8\pi(l+nr)]$. The coefficients C_υ and mB_υ are regarded as instrumental constants.[166] The kinematic viscosity of a solution is simply related by the instrument constants to the measured time of efflux.[167]

Often the kinematic viscosity is simply proportional to the flow time. In this work the additional term in t^{-1} is not negligible and amounted to several percent of the kinematic viscosity of the solutions with the shortest flow times (*ca.* 100 s)

5.1.1 *Calibration of the Viscometer*

The instrument constants can be determined by using two or more liquids whose kinematic viscosities are well known. This calibration was carried out by measuring the efflux time of pure water, which has been studied extensively, at several temperatures. Tables 3 and 4 list the values of the viscosity and density of water used in the calibration.

A graph of υt vs. t^2 gives C_υ as the slope and $-mB_\upsilon$ as the intercept. The results of the calibration are:

$C_\upsilon = 0.008328 \pm 0.000002\ (1\sigma)$ cSt s^{-1}
$mB_\upsilon = 1.20 \pm 0.03\ (1\sigma)$ cSt s.

Primarily, one is concerned with relative viscosities among the measured solutions and so this precision in calibration is adequate. The calibration constants are independent of temperature.

TABLE 3

VISCOSITY OF WATER[a]

Temperature t, °C	Viscosity η, cP	References
10	1.3069, 1.3061, 1.306	(a), (a), (c)
15	1.1382, 1.1381, 1.138	(a), (a), (c)
18	1.053	(b)
20	1.0020, 1.002	(a), (b)
25	0.8903	(a)
30	0.7975, 0.7976	(a), (a)
35	0.7195, 0.7194	(a), (c)
38	0.6783	(c)
40	0.6532, 0.6531	(a), (a)
	0.6526, 0.6527	(a), (a)

[a] L. Korson, J. Phys. Chem. 73, 34(1969). Korson gives an equation of the form

$$\log_{10} \frac{\eta_t}{\eta_{20}} = \frac{A(20 - t) - B(t - 20)^2}{t + C}$$

where $A = 1.1709$
$B = 0.001827$
$C = 89.93$

and t is the temperature. This equation fits the experimental data to within experimental error over the range $10 < t < 70$.

[b] R.H. Stokes and R. Mills, *Viscosity of Electrolytes and Related Properties* (Pergamon Press, New York, 1965).

[c] R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*, 2nd ed. (Butterworths, London, 1965).

Some concern has been expressed over the use of water as a calibrating liquid with a surface tension much different from the solutions to be measured. Oil standards are available for use in calibration over a range of viscosities, but these were unavailable for this work. Surface tensions of aqueous solutions of electrolytes change very little with concentration. But, for mixed solvents and pure organic solvents there can be a large difference from water in surface tension. At 20°C for the liquid-gas interface the surface tension of water is 72.75 dyne cm^{-1} while that for 1-propanol is 23.8 dyne cm^{-1}.[168] The Ubbelohde viscometer is supposed to be relatively insensitive to surface tension effects, but this claim has been questioned. Peter and Wagner[169] computed an error of 0.17% for an Ubbelohde viscometer when using water and 1-propanol as the calibrating and test liquid. Surface tension effects are assumed to be negligible for the viscometer

TABLE 4

DENSITY OF WATER[a, b]

Temperature t, °C	Density ρ, g/ml
15	0.999129
16	0.998972
17	0.998804
18	0.998625
19	0.998435
20	0.998234
21	0.998022
22	0.997801
23	0.997569
24	0.997327
25	0.997075
26	0.996814
27	0.996544
28	0.996264
29	0.995976
30	0.995678
31	0.995372
32	0.995057

[a] G.S. Kell, J. Chem. Eng. Data 12, 67 (1967).

[b] A Least squares analysis of the data using an equation of the form

$\rho(H_2 0) = A + Bt + Ct^2$

where $A = 1.000374$

$B = -8.67867 \times 10^{-6}$

$C = -4.92765 \times 10^{-6}$

and t is the temperature, fits the data within experimental error over the range $15 < t < 35$ °C.

used based on the good agreement of the measured viscosity with literature values. Calculation of surface tension effects are tedious. An empirical correction has been applied in some work.[170]

5.1.2 *Viscosities of Solutions*

To determine the kinematic viscosity of a solution the time is measured in seconds for a fixed volume of solution to flow through the capillary of the calibrated viscometer at a closely controlled temperature. The use of the Ubbelohde suspended level type viscometer allows for a reproducible driving head that is independent of the total amount of solution in the viscometer. The addition of tube 2, in Figure 3, creating a suspended liquid level at the junction of the capillary and bulb C eliminates loading error and also surface tension effects. The kinematic viscosity is obtained from substitution of the measured efflux time into Equation (5-2).

The density, ρ, of the sample was determined at the same temperature as the flow time and used in the calculation to obtain the dynamic viscosity. The cgs unit of density should be used and is one gram per cubic centimeter (g cm^{-3}). For these calculations, the density determined as g ml^{-1} is taken to be numerically equivalent to that given in g cm^{-3}.

5.2 *Determination of Density*

The densities of solutions were measured with the aid of pycnometers in the constant temperature bath. The use of the pycnometers to determine densities requires a prior calibration with a suitable reference liquid of known density.

5.2.1 *Calibration of Pycnometers*

The volumes of the three pycnometers used were determined by calibration with water at 25°C. The pycnometers were filled at 25°C and weighed. The volumes were determined by a knowledge of the density of water. Values of the density of water were taken from Table 4.

The volumes were corrected for thermal effects for use at 20 and 30°C. The volume expansion of Pyrex is about 0.9×10^{-5} deg^{-1}. The results of the calibration are:

Pycnometer Number	Volume, ml 20°C	25°C	30°C
1	25.6101	25.6113 ± 0.0010	25.6125
2	25.7305	25.7317 ± 0.0009	25.7329
3	25.4690	25.4702 ± 0.0004	25.4714

Errors listed are those for a 90% confidence limit.

5.2.2 *Densities of Solutions*

Solution densities are obtained by weighing the pycnometer which contains the mass of solution necessary to fill it at the temperature of measurement and dividing this weight by the volume of the pycnometer as determined by calibration.

SECTION 6

PROCEDURE

6.1 *Preparation of 1-Propanol-Water Mixtures*

Solutions for four concentrations of 1-propanol in water were prepared by adding known volumes of the 1-propanol and water and converting these volumes into weights using densities. Density of water was taken from Table 4 and the density of 1-propanol was taken from Table 5. The temperature of preparation was 19.8 ± 0.5°C and the densities used were:

$\rho(H_2O) = 0.998274$ g/ml

ρ(l-propanol) = 0.80378 g/ml.

The composition of the four solutions corrected for 0.0005 volume fraction of water in the 1-propanol is given in Table 6. Composition of the mixed solvent expressed in weight percent 1-propanol is temperature independent.

These solutions were prepared volumetrically and not directly by weight since there were no balances available that could handle the large masses needed. About two liters of solution was prepared at one time. Volumetric flasks calibrated "to contain" were used "to deliver" for the large volumes needed. When used in this manner the flasks were allowed to drain at least 1.5 minutes. Even so, the accuracy is not as high as when used "to contain." Class A glassware was used. The glassware was calibrated for use at 20°C and correction for thermal effects was neglected.

6.2 *Preparation of Potassium Iodide Solutions*

The amount of KI needed to prepare 250 ml of a concentrated stock solution in each of the six solvent systems studied was dried at 110°C. The drying time for these samples was changed during the course of the investigation.

A twenty gram sample was dried for three days at 110°C before coming to constant weight due to the large sample size and the drying configuration. The weight loss was 0.007%. The stock solutions in the 21 and 42 weight percent 1-propanol solvent prepared from potassium iodide dried for this long period of time showed a yellow discoloration due to the presence of iodine from the oxidation of potassium iodide. The potassium iodide used in the preparation of other stock solutions was dried for a shorter period of time not exceeding four hours for the largest sample of

TABLE 5

DENSITY OF 1-PROPANOL

Temperature t,°C	Density ρ, g/ml	References
0	0.81920, 0.81926, 0.81923	(a), (b), (b)
	0.8193	(c)
10	0.8116	(c)
15	0.80749, 0.80733	(a), (a)
17	0.8061	(b)
19.75	0.8039	(d)
20	0.8035, 0.80357, 0.80358	(b), (b), (b)
	0.80375	(c)
24.81	0.7999	(d)
25	0.8008[e], 0.7998, 0.79968	(a), (a), (b)
	0.79985, 0.7999, 0.79975	(b), (b), (c)
29.84	0.7959	(d)
30	0.79567, 0.7960, 0.7957	(a), (b), (c)
34.77	0.7920	(d)
35	0.7914	(a)
39.80	0.7880	(d)
40	0.7875	(b)

[a] G.J. Janz and R.P.T. Tomkins, Eds., *Nonaqueous Electrolytes Handbook*, Vol. 1 (Academic, New York, 1972).

[b] J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* (Elsevier, New York, *1950)*.

[c] R.C. Wilhoit and B.J. Zwolinski, J. Phys. Chem. Ref. Data *2*, (1), 1(1973).

[d] M. Kikuchi and E. Oikawa, J. Chem. Soc. Japan *88*, 1259(1967).

TABLE 6

COMPOSITION OF THE 1-PROPANOL-WATER MIXED SOLVENTS

Solvent System	Weight Percent	1-Propanol Mole Percent	Molarity 20°C	30°C
I	0	0	0	0
II	21.15	7.443	3.406	3.385
III	42.24	17.98	6.502	6.451
IV	58.95	30.10	8.738	8.661
V	80.06	54.62	11.29	11.18
VI	100.	100.	13.38	13.24

thirty grams. These samples were then assumed to be dry. A three gram sample was dried to constant weight after drying for one hour at 110°C. It showed a weight loss of 0.0036%. Even with these shorter drying times discoloration was still present in solutions containing up to 59 weight percent 1-propanol. Some solutions not used in the viscosity measurements were prepared from undried potassium iodide and in all cases were clear.

The effect of the decomposition of the potassium iodide was considered to be negligible based on colorimetric analysis of the amount of iodine present in these solutions. It was found that the most discolored stock solution contained 5 x 10^{-6} M I_2. The more dilute solutions contained proportionately less.

The next to the most concentrated KI solution in the 0, 21, 42, and 59 weight percent 1-propanol solvents was taken as the stock solution. The most concentrated KI solution in the 80 and 100 weight percent 1-propanol solvents was taken as the stock solution. Stock solutions in 0, 80, and 100 weight percent 1-propanol solvent were suction filtered through a Millipore filter. Dilutions of the stock solution to 100 ml with the appropriate solvent produced the remaining more dilute solutions. The solutions more concentrated than the stock solution were prepared by weighing out the amount of KI needed for 100 ml of solution and preparing it directly. Class A glassware was used.

The temperature of preparation ranged from 17 to 20°C. Thermal expansion of the glassware at the temperature of preparation was negligible, however the concentrations in terms of molarity were corrected due to thermal effects on the solution volumes. The solvent value of the temperature coefficient of the density, $d\rho/dT$, was used for all concentrations of solutions, except the most concentrated, to calculate the density of the solutions at the temperature of preparation from the measured density at 20°C. Values of $d\rho/dT$ at 20°C used for each of the solvent systems are listed in Table 7. The value of $d\rho/dT$ is taken to be constant for each solvent system over the range 17 to 20°C. The molarity at the temperature of preparation can be used with the densities at the temperature of preparation, 20°C, and 30°C, to correct the molarity to the proper value at 20 and 30°C.

A better approximation of $d\rho/dT$ for the most concentrated solutions was obtained by predicting a value of $d\rho/dT$ at 20°C based on the value of $\Delta\rho/\Delta T$ over the range 20 to 30°C which was obtained from measurements.

The concentrations of KI solutions listed in Appendix I have uncertainty in the last digit given. The standard deviation was calculated for the preparation of the solutions to determine the uncertainty in the concentrations. The corrections for the molarity to the proper value at 20 and 30°C introduced negligible error.

It may be better in the future to prepare these solutions by weight, since molality is temperature independent. However, the molarity of the solutions is the concentration term used in the analysis of viscosity results and thus the densities of the solutions are still needed to make the conversion.

Perhaps the best method would be to prepare the solutions by volume, but at the temperature of the viscosity measurements. This would involve more time in preparing the solutions, but would eliminate the previous calculations and result in more accurate values of the concentrations.

6.3 *Viscosity Measurements*

The operation of the Ubbelohde viscometer, shown in Figure 3, is quite simple. The viscometer is charged by pouring the sample into tube 1 to a level between the two lines on bulb B. To operate, tube 3 is closed with a finger and pressure is applied to tube 1 using a pipet bulb attached by Tygon tubing.[171] The liquid is forced into bulbs C and A and to half fill the small bulb above A. The pressure is released and tube 3 is opened. The time for the passage of the miniscus between the two etched marks a and b is observed and reported as the time of efflux or flow time.

The viscometer was originally cleaned with chromic acid cleaning solution (H_2SO_4 and $Na_2Cr_2O_7$). Several investigators have noted that the use of this agent seems to affect the calibration of their viscometers,[172] and so this cleaning solution was not used further. The viscometer was then cleaned using Micro™ cleaning solution in an ultrasonic bath. The viscometer was cleaned after each day's measureiments by filling with concentrated nitric acid and allowing it to set overnight at room temperature. The pycnometers and other glassware were cleaned in the same manner.

The flow time of water through the viscometer was determined at the beginning and end of each day's measurements. Obtaining reproducible results within experimental error for this flow time served as a check on the cleanliness of the viscometer.

timer accuracy, technique, and maintenance of calibration of the viscometer.

The viscosity of each of the solutions of KI in a particular solvent was measured. One sample from each solution was used at each temperature and six trials were made on each sample. The average flow time of these six trials was considered to be the flow time for the solution.

Between measurements of different solutions, the viscometer was rinsed with one ten ml portion of the pure solvent which was made to flow through the entire viscometer. Then, two ten ml portions of the new solution were introduced into the viscometer and each portion made to flow through the viscometer. Between rinses the viscometer was shaken to remove most of the rinse solution. The new sample was then placed in the viscometer.

Each sample was allowed to equilibrate with the bath water for 15 minutes at 30°C and 10 minutes at 20°C. The time of this equilibration was decided upon by measuring the temperature of a sample directly with a thermometer inside the viscometer. Thermal equilibrium was achieved in less than 15 minutes at 30°C. The sample was made to flow through the viscometer in the bath before the first measurement to give added assurance that each solution was at the bath temperature. Tight fitting foil caps were placed on the viscometer to eliminate solvent evaporation during equilibration.

The temperature control of the bath was such that over the length of the viscometer and between the viscometer and thermometer positions the temperature varied by less than 0.01°C.

The thermometer used was calibrated for total immersion and emergent stem corrections were applied to all thermometer readings in density and viscosity measurements. The stem correction to be added to the thermometer reading is given by [173]

$$\text{stem correction} = Kn(T\text{-}t) \qquad (6\text{-}1)$$

where K=differential expansion coefficient of mercury, may be taken as 0.00016 for centigrade thermometers
n=number of degrees emergent from the bath
T=temperature of the bath
t=average temperature of the emergent stem.

For viscosity measurements the Sargent G thermometer was immersed to 18°C and for density measurements it was immersed to 16°C. The value of t was determined by another thermometer adjacent to the stem to the nearest 0.5°C. For room temperature values, commonly 20 to 24°C, the stem corrections used for viscosity and density measurements ranged from -0.002°C to 0.019°C.

Using a Q_{crit} value of 0.56 for a 90% confidence level for six measurements, about 30 flow times out of almost 1000 measured were not used. The main cause of the erroneous values was small paper fibers that could sometimes be seen in the solution in the viscometer. A foil shroud was kept over the top of the viscometer at all times to reduce particulate contamination and solvent evaporation.

The flow times measured in this work ranged from 75 s to 425s. It is suggested that the flow time not be less than 200 s. This suggestion is made so the investigator can avoid the necessity of making a correction using the mB/t term in Equation (5-2). If the correction is made, which is easy to do, the results for flow times less than 200 s are as accurate as those determined for longer flow times. Also, it was desired to use the same viscometer throughout the investigation. A viscometer flow time of 200 s for water would have produced exceedingly long flow times for the other solutions.

A good approximation to the true standard deviation in the flow times through the viscometer was obtained by using data from a large number of trials on the same sample. The standard deviation for a flow time of about 100 seconds was found to be 0.05 seconds. If six trials are ran on each solution giving a mean flow time of about 100 seconds, then this mean has a 90% confidence limit of being within ±0.04 seconds of the true mean. All of the flow times measured were equal to or greater than 100 seconds and thus 0.04% error is an upper limit for timing errors. The relative error in the timing decreases as the flow time increases, but not as much as anticipated. The standard deviation of determining the flow time also increases with increasing flow time due to the slower passage of the meniscus past the calibration marks of the viscometer. The following error values represent 90% confidence limits for the mean of six trials on one sample:

Time of efflux, seconds

100 ± 0.04

200 ± 0.06

300 ± 0.08

400 ± 0.10

Many corrections to be applied to the determined value of the viscosity are suggested for the most exacting work.[174] No other corrections were applied to values obtained in the manner described herein. It is estimated that neglecting these corrections would introduce an error of 0.01% or less in the viscosity.

The precision of the reported viscosities is 0.01 to 0.05% relative error. After considering the error in the viscosity resulting from neglected corrections (0.01%), and errors in solvent composition (<0.02%), solution concentration (<0.1%), calibration constants (0.05%), temperature (<0.02%), vertical alignment of the viscometer (0.02%), density of solutions (0.004%), and determining the efflux times (<0.04%), viscosities reported in this work are believed to have an absolute accuracy which does not exceed 0.1% error.

6.4 *Density Measurements*

The pycnometer bulbs were filled with a solution at a temperature lower than that at measurement. Room temperature sufficed for determination at 30°C and an ice bath was used briefly to cool the pycnometers for those at 20°C. The capillary tip was then seated firmly in the neck of the bulb and the cap placed over the tip. An easily removable holder made of copper wire was placed around the neck of the bulb and the pycnometer was placed inside the bath along the edge with the holder bent over the edge for support. The sample was allowed 15 minutes to reach thermal equalibrium with the bath. This time was sufficient as verified once by a thermometer placed inside the pycnometer. Due to the position of the pycnometers along the edge of the bath and to the extent the pycnometers extended above the bath water, the temperature of measurement is only known to within ±0.01°C.

The pycnometers were removed from the bath, dried carefully, and allowed to set for several minutes before weighing in order to insure that the outer surfaces were dry.

The weight of the pycnometer corrected for buoyancy was divided by the volume as determined by calibration to give the solution density.

Buoyancy corrections were applied to the weighing of liquids in the density determinations. The correction of the weight in air to that in vacuum is accomplished by the formula

$$W_v = W_a \left[\frac{1 - (\rho/8.4)}{1 - (\rho/d_0)} \right] \tag{6-2}$$

where d_0 is the density of the liquid weighed, ρ is the density of air, and 8.4 g cm^{-3} is the density of the brass weights. The density of air has been found to be 0.0012 g cm^{-3} under most common conditions.[175] This correction is very important. For example, the correction needed to be applied to 25.6 g water at 25°C was 0.03 g or 0.11%. The error introduced by the neglect of this correction would be very much larger than any other incurred in the measurement. The density of the weighed solution, d_0, is needed to only two significant figures due to the precision in the values used for the density of the weights and of air. The uncorrected weight of the solution divided by the approximate pycnometer volume gave a good approximation to the solution density to be used in Equation (6-2).

The precision of the technique enables the density to be reported to six significant figures with uncertainty in the last digit. The accuracy of the pycnometer volumes, the weighing of solution, and the technique allows for the reported densities to have a relative standard deviation less than 0.005%.

SECTION 7

EXPERIMENTAL RESULTS

7.1 *Density of Solutions*

The results of the density measurements for the salt solutions are expressed as functions of the concentration of the salt, c, in the form suggested by Root[176]

$$\rho = \rho_0 + ac + bc^{3/2} \tag{7-1}$$

where ρ is the solution density, ρ_0 is the density of the solvent, and a and b are constants. Tables 12 and 13 in Appendix I give the measured densities of the 1-propanol-H_2O-KI solutions at 20 and 30°C and the coefficients for Equation (7-1). A computer program was used to obtain the best fit curve according to the method of non-linear least-squares.

The density values used in the Root equation were corrected for a small temperature difference between that of measurement and either 20 or 30°C. The value of $d\rho/dT$ of the pure solvent at either 20 or 30°C was used as the temperature correction for all of the measurements. Values of $d\rho/dT$ are given in Table 7. The error in the assumption of the same value of $d\rho/dT$ at all concentrations is negligible considering the size of the correction in the densities.

The Root equation fit the data over the entire concentration range in the solvent systems studied, with a standard deviation between the observed values and those computed of 0.005%. The deviations were caused by errors in the technique of measurement and do not indicate failure of the Root equation to fit the data.

TABLE 7

TEMPERATURE COEFFICIENTS OF THE DENSITY AND VISCOSITY OF 1-PROPANOL-WATER MIXTURES AT 20 and 30°C[a]

20°C

Weight Percent 1-Propanol x_2	$d\eta/dT$, cP deg^{-1}	$d\rho/dT$, g ml^{-1} deg^{-1}
0	—0.0248[b]	—0.000206[c]
21.15	—0.103	—0.00038
42.24	—0.132	—0.00059
58.95	—0.115	—0.00073
80.06	—0.090	—0.00085
100.	—0.056	—0.00079

30°C

x_2	$d\eta/dT$, cP deg^{-1}	$d\rho/dT$, g ml^{-1} deg^{-1}
0	—0.0171[b]	—0.000302[c]
21.15	—0.046	—0.00063
42.24	—0.067	—0.00071
58.95	—0.070	—0.00071
80.06	—0.061	—0.00083
100.	—0.037	—0.00079

[a] All values, except where noted, were determined graphically from M. Kikuchi and E. Oikawa, J. Chem. Soc. Japan *88*, 1259(1967).

[b] L. K son, J. Phys. Chem. *73*, 34(1969).

[c] G.S. Kell, J. Chem. Eng. Data *12*, 67(1967).

The measured densities of the 1-propanol-water mixed solvents compare well with literature values.[177-179] The measured density of these mixtures is compared to some literature values in Table 9.

7.2 *Solution Viscosities*

Smoothed values of the densities of the solutions at either 20 or 30°C were obtained from the appropriate Root equation. These values were converted to the temperature of the viscosity measurements for use in Equation (5-2). Again, $d\rho/dT$ of the pure solvent was used in the correction for all concentrations, and this results in negligible error.

Using the flow times and the density in Equation (5-2), the dynamic viscosity of the solution can be determined. A correction was applied for a small temperature difference between that of measurement and either 20 or 30°C. The value of $d\eta/dT$ of the pure solvent at either 20 or 30°C was used for all the measurements. Table 7 gives values for $d\eta/dT$. Considering the size of the correction in the viscosity (about 0.002 cP in the most extreme case) the error in the assumption of the same value of $d\eta/dT$ at all concentrations is negligible at concentrations less than 0.1 M and at least small at higher concentrations. At high concentrations the error in this correction may be of the same order of magnitude as the experimental error in making the measurement.

The measured values of the viscosity of the 1-propanol-H_2O-KI solutions at 20 and 30°C are listed in Tables 14 and 15 in Appendix I and are used to evaluate the Jones-Dole coefficients. The measured viscosities of the pure solvents compare well with accepted values.[180, 181]

Table 8 lists literature values for the viscosity of pure 1-propanol. Experimental and literature values for the viscosity of the 1-propanol-water mixed solvents are compared in Table 9. The reported precision of the viscosity data from this study in Table 9 is 0.1 to 0.01% relative error. The accuracy of the data is about 0.1% relative error.

One possible explanation of the poorer agreement between measured viscosities and densities and accepted values at high fractions of 1-propanol in the mixed solvent is contamination of the solvent by excess water.

The measured viscosities of KI in water can be compared to literature values[182-184] and are in good agreement.

TABLE 8

VISCOSITY OF 1-PROPANOL

Temperature t, °C	Viscosity η,cP	References
0	3.8827	(a)
10.	2.877	(b)
15.	2.522	(c)
19.75	2.239	(d)
20.	2.19, 2.2563, 2.230	(e), (a), (b)
24.81	2.976	(d)
25.	1.952, 1.971, 1.93	(f), (g), (h)
	1.944	(e)
29.84	1.754	(d)
30.	1.722, 1.74, 1.742	(c), (i), (e)
	1.756	(b)
34.77	1.566	(d)
39.80	1.396	(d)
40.	1.4050, 1.389	(a), (b)
44.77	1.246	(d)
49.80	1.129	(d)
50.	1.125	(b)
60.	0.901	(d)

[a] J.A. Dean, Ed., *Lange's Handbook of Chemistry*, 11th ed. (McGraw-Hill, New York, 1973).

[b] E.W. Washburn, Ed., *International Critical Tables*, Vol. 5 (McGraw-Hill, 1929), p. 215.

[c] J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, (Elsevier, New York, 1950).

[d] M. Kikuchi and E. Oikawa, J. Chem. Soc. Japan *88*, 1259(1967).

[e] E.W. Washburn, Ed., *International Critical Tables*, Vol. V, p. 23.

[f] J.F. Coetzee and C.D. Ritchie, Eds., *Solute-Solvent Interaction*, Vol. 2 (Marcel Dekker, New York).

[g] R.J. Raridon and K.A. Kraus, U.S. Office Saline Water Res. Develop. Progr. Rep. No. 302(U.S. Dept. of Int., Washington, D.C., 1968).

[h] T.A. Gover and P.G. Sears, J. Phys. Chem. *60*, 330(1956).

[i] P.L. Indovina, Atti. Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat., Rend. *42*, 53(1967).

TABLE 9

DENSITY AND VISCOSITY OF 1-PROPANOL-WATER MIXTURES AT 20 and 30°C

		20°C		
	ρ, g/ml		η, cP	
Weight Percent 1-Propanol	Present Study[a]	Lit. values	Present Study[b]	Lit. values
0	0.99824	0.9982[c]0.998234[d]	1.0019±0.0004	1.004[c], 1.0020[g]
21.15	0.96764	0.9665[c]	2.2541±0.0007	2.278[c]
42.24	0.92502	0.9249[c]	3.0362±0.0006	3.040[c]
58.95	0.89060	0.8902[c]	3.1631±0.0004	3.173[c]
80.06	0.84752	0.8473[c]	2.7995±0.0004	2.821[c]
100	0.80385	0.8037[c], 0.803551[e] 0.80375[f], 0.8035[f]	2.1898±0.0003	2.224[c], 2.19[h] 2.2563[h], 2.230[h]
		30°C		
0	0.99567	0.9956[c], 0.995678[d]	0.79718±0.0002	0.802[c], 0.7975[g]
21.15	0.96186	0.9610[c]	1.5883±0.0004	1.606[c]
42.24	0.91778	0.9182[c]	2.1385±0.0002	2.149[c]
58.95	0.88283	0.8825[c]	2.2630±0.0005	2.275[c]
80.06	0.83930	0.8390[c]	2.0715±0.0004	2.086[c]
100	0.79580	0.7957[c], 0.79567[f] 0.7960[f], 0.7957[f]	1.7223±0.0003	1.748[c], 1.722[h] 1.74[h], 1.742[h], 1.756[h]

[a] Values from Root equations. [b] Values from Jones-Dole equations. Error limits are those for 1 σ.

[c] Determined graphically from M. Kikuchi and E. Oikawa, J. Chem. Soc. Japan *88*, 1259(1967). The values should not be considered more accurate than ±0.0005 g/ml for the densities and ±0.003 cP for the viscosities due to graphing inaccuracies.

[d] Table 4. [e] M.E. Friedman and H.A. Scheraga, J. Phys. Chem. *69*, 3795(1965). [f] Table 5. [g] Table 3.

[h] Table 8.

SECTION 8

ANALYSIS OF THE DATA

8.6 *Methods for Obtaining the Jones-Dole Coefficients*

The usual method of obtaining the coefficients in the Jones-Dole (JD) equation is to make a plot of a linearized form of the JD equation. By rearrangement, Equation (2-1) can be expressed as

$$(\eta/\eta_0 - 1)/c^{1/2} = A + Bc^{1/2} \tag{8-1}$$

A plot of $(\eta/\eta_0 - 1)/c^{1/2}$ vs. $c^{1/2}$ gives B as the slope and A as the intercept. A computer program was used to obtain the best fit of the data according to Equation (8-1) by the method of linear least squares.

At low concentrations η/η_0 is close to unity and the term $(\eta/\eta_0 - 1)$ may have a large error associated with it even though η and η_0 are known to a good degree of precision. The error in the data at low concentrations is magnified unduly. Also, this method relies heavily on the accuracy of the determined value of η_0.

Stairs[185] suggested that an alternative method for fitting the JD equation to the data was to use the form

$$\eta = \eta_0 + ac^{1/2} + bc \tag{8-2}$$

in which η_0, $a(= \eta_0 A)$, and $b(= \eta_0 B)$ are all treated as adjustable parameters in a non-linear least squares procedure. This method was applied and a computer program was used to obtain the best fit according to the method of non-linear least squares.

Another method of fitting the JD equation to the data without being influenced by the inflated errors at low concentration is to make a weighted fit. The linearized form of the JD equation is used but a weighted linear least squares analysis of the data is performed which counts those points with less certainty less heavily. The best fit straight line is more accurate since large variations near $c = 0$ does not unduly affect the parameters of the line. A computer program for this analysis was also used.

The programs for the three methods of analysis described above also contain steps to evaluate the precision of the Jones-Dole coefficients after they have been determined. The methods can be compared in one respect by the precision with which they determine the Jones-Dole coefficients. The results of each method, used for data at 20°C, are shown in Table 10. The same range of concentration was used in each analysis to facilitate

TABLE 10

COMPARISON OF THE RESULTS OF METHODS USED TO EVALUATE THE JONES-DOLE COEFFICIENTS AT 20°C

Weight Percent 1-propanol	Jones-Dole Coefficients[a]					
	A, (mole/liter)$^{-1/2}$			B, *(mole/liter)*$^{-1}$		
x_2	Method[b]: I	II	III	I	II	III
0	−0.009±0.004	−0.0009±0.002	−0.003±0.002	−0.091±0.008	−0.091±0.006	−0.084±0.008
21.15	−0.006±0.003	−0.006±0.002	−0.008±0.002	−0.181±0.004	−0.181±0.003	−0.178±0.005
42.24	0.008±0.002	−0.008±0.001	0.006±0.002	−0.170±0.005	−0.170±0.004	−0.163±0.01
58.95	0.014±0.003	0.013±0.001	0.011±0.001	−0.08±0.01	−0.084±0.008	−0.07±0.01
80.06	0.024±0.005	0.024±0.003	0.021±0.002	0.15±0.04	0.15±0.03	0.18±0.03
100	0.029±0.009	0.029±0.007	0.026±0.004	1.1±0.1	1.1±0.1	1.2±0.09

[a] Error limits are those for the standard deviation, 1σ.

[b] Method I: Non-linear least squares treatment of $\eta = \eta_0 + ac^{1/2} + bc$.

Method II: Weighted linear least squares analysis of linearized form of JD equation.

Method III: Linear least squares analysis of linearized form of JD equation.

comparisons. Also, the value of η_0 determined from the nonlinear least square analysis was used as the value of η_0 for the linearized treatments.

Table 10 bears out the expectations that either the non-linear least squares analysis or the weighted linear least squares analysis is acceptable as a method of determining the A and B coefficients. The unweighted linear least squares analysis is unacceptable for obtaining accurate values for the coefficients. It may be possible to use an unweighted fitting technique only if the data covers a very small concentration range where the viscosity changes only slightly and the weights of the points are essentially the same.

The non-linear least squares technique has some definite advantages as the better method of analysis. One would expect a better fit of the data by this technique since there are three adjustable parameters in this method instead of two. A much better value of η_0 is obtained from this method than is obtained with the use of one or two experimentally measured values. More measurements can be incorporated in determining the value of η_0 since data from higher concentrations can be used. Even if the weighted linear least squares technique was to be used, it might be advantageous to determine the value of η_0 from the non-linear analysis of the lower concentration data.

One drawback of the non-linear technique is the possibility that the endpoints of a small data set are unduly weighted in a technique with three adjustable parameters.

The use of the weighted linear least squares technique requires extra work to determine the weight of each data point and may adversely affect the results if the assigned weights are inappropriate. However, no serious error should result since the relationship of the weights relative to each other is important and not their absolute value in the method used herein.

It may be concluded that either the non-linear least squares method or the weighted linear least squares method may be used to analyze the data, but the former is the more expedient method.

8.2 *Results for the Jones-Dole Coefficients*

There are several difficulties in evaluating the A and B coefficients from the data. It is known that the JD equation cannot describe the behavior of solutions over a large range of concentrations. Deviation from a curve describing dilute solution behavior must occur at some higher concentration. The departure from the limiting dilute behavior must be experimentally determined from a graphical analysis of the data and this task is difficult unless a large amount of highly precise data is available. When working with a limited data set the choice of the points to be included in the determination of A and B is a difficult one. It must be decided whether a point slightly displaced from a possible curve shows deviation in the behavior of the solution or only shows experimental error.

The type of graph commonly seen in the literature for the determination of the A and B coefficients is a linear plot according to Equation (8-1). Figures 9 to 20 in Appendix II are graphs of $(\eta/\eta_0 - 1)/c^{1/2}$ vs. $c^{1/2}$ for each system studied. The values of $(\eta/\eta_0 - 1)/c^{1/2}$ used in these graphs are given in Tables 14 and 15. The quantity $(\eta/\eta_0 - 1)$ is an extremely sensitive parameter and illustrates the precision of the data necessary to evaluate reliable A coefficients.

The length of the vertical bars on the data points in the figures in Appendix II corresponds to a 90% confidence limit, calculated according to the method of weighted least squares.

The plot of the data according to the linearized Jones-Dole equation facilitates observing the concentration of KI at which deviation from dilute solution behavior occurs. Tables 14 and 15 also list the range of validity of the Jones-Dole equation.

The JD equation was found to be valid for KI in 1-propanol-water mixtures and for KI in pure 1-propanol up to a certain concentration of KI. The curvature in plots of $(\eta/\eta_0 - 1)/c^{1/2}$ vs. $c^{1/2}$ observed for several salts at low concentrations in 1-butanol[186] was not observed for KI in 1-propanol. Data on the viscosity for solutions of KI in 1-propanol was extended to more dilute concentrations than those studied in 1-butanol and no curvature at these concentrations was observed.

Some investigators have found that at higher concentrations the JD equation fits the data, but that this equation has a different value of B than does the equation describing the dilute solution behavior. In other words, a plot of $(\eta/\eta_0 - 1)/c^{1/2}$ vs. $c^{1/2}$ changes slope at some point at high concentration. This effect was not investigated in this work, but some of the graphs in Appendix II tend to support this conclusion.

Figures 21 and 22 are graphs of the Jones-Dole equation as analyzed by the non-linear least squares analysis. The precision of the data is such that in this type of plot the visconsities form a single smooth curve as a function of concentration of KI. This type of plot gives a more obvious indication of the effect of KI on the viscosity of the solution.

The values of A and B obtained from a least squares analysis of the data were observed to change continuously as the number of data points used in the analysis was changed from the full concentration range to only the last few most dilute solution measurements. A method was devised, using the non-linear least squares technique for fitting the data, to evaluate the A and B values reported in the results.

Possible values of A and B were determined from the data by gradually decreasing the number of points used in the analysis starting from high concentrations and proceeding toward lower concentrations. Use was made of several guidelines in determining the best value of A and B from the several possible values. First, the standard deviation of fit of the data to the calculated curve gives an indication of the accuracy with which the curve represents the data and can be used as a guideline when choosing A and B. Second, the computed value of η_0 must agree to a good degree with the measured value if one has faith in the measurements. Third, from theory A is known to be either zero or positive. A reasonable value of A may be chosen in this manner. Further, it is known that B should be a smooth function of the composition of the solvent. Some insight into the value of B along an isotherm may be gained by a graph of possible B values versus composition of the mixed solvent. Using these guidelines, best values of A and B were chosen for each system studied.

The results for the A and B coefficients are listed in Table 11. These values are compared to both theoretical and experimental values from the literature. The error limits given in Table 11 are the standard deviations as evaluated by the least squares analysis. The A values determined in this work seem reasonable based on a comparison of our experimental values with theory and literature values for the two pure solvents. Two possibilities exist to explain the negative, experimentally determined values of A. Either the data is not sufficiently precise or else the extrapolation to infinite dilution is made from too high of a concentration.

Figures 4, 5, and 6 illustrate the behavior of the experimentally determined values of η_0, B, and A as a function of concentration of 1-propanol in the mixed solvent system.

The conductance data of Gover and Sears[187] was analyzed by Evans[188] and Kay[189] to yield limiting single ion conductances, λ_i, for potassium iodide in 1-propanol. Provisional values for λ_i can be determined by assuming that for a reference electrolyte, λ_+ of the cation and λ_- of the anion are equal. Ideally, transport numbers are used to determine limiting ionic conductances, but these are not available for KI in 1-propanol.

The use of the single ion conductances in Equation (2-3) gave theoretical values of A for KI in 1-propanol equal to 0.0350 and 0.0355 (moles/liter)$^{-1/2}$ at 20 and 30°C respectively. It was assumed in the calculation that $d\lambda_i/dT$ for our system was the same as for KI in methanol.

The theoretical values of A for KI in aqueous solution at 20

TABLE 11

JONES-DOLE COEFFICIENTS FOR 1-PROPANOL-H_2O-KI SOLUTIONS AT 20 AND 30°C[a]

20°C			
Weight Percent 1-Propanol	A, (moles/liter)$^{-1/2}$ Experimental	Theoretical	B, (moles/liter)$^{-1}$ Experimental
0	—0.0009 ± 0.004	0.0048[b]	—0.091± 0.008
	0.0045[b]		—0.0920[b]
21.15	—0.006 ± 0.003		—0.181 ± 0.004
42.24	0.008 ± 0.002		—0.17 ± 0.05
58.95	0.014 ± 0.003		—0.08 ± 0.01
80.06	0.024 ± 0.005		0.15± 0.04
100.	0.029 ± 0.009	0.0350[c]	1.1 ± 0.1

30°C			
Weight Percent 1-Propanol	A, (moles/liter)$^{-1/2}$ Experimental	Theoretical	B, (moles/liter)$^{-1}$ Experimental
0	—0.005 ±0.002	0.0051[c]	—0.054 ± 0.002
	0.0052[b]		—0.0604[b]
21.15	—0.005 ± 0.003		—0.141 ± 0.005
42.24	0.013 ± 0.001		—0.105 ± 0.003
58.95	0.014 ± 0.005		—0.005 ± 0.02
80.06	0.021 ± 0.005		0.21 ± 0.03
100.	0.047 ± 0.009	0.0355[c]	0.8 ± 0.1

[a] Error limits are values of 1σ.

[b] M. Kaminsky, Z. Phys. Chem. 5, 154(1955).

[c] Calculated in this study.

and 30°C have been determined by Kaminsky[190] and are given in Table 11.

Lack of conductivity data precludes calculation of theoretical values of A in the mixed solvent systems.

The values of the B coefficient determined in this study can be compared to literature values only in one case, for KI in aqueous solutions. Table 11 lists both experimental values and the agreement is good. The fact that B is a smooth function of solvent composition in Figure 5 lends credibility to our B values.

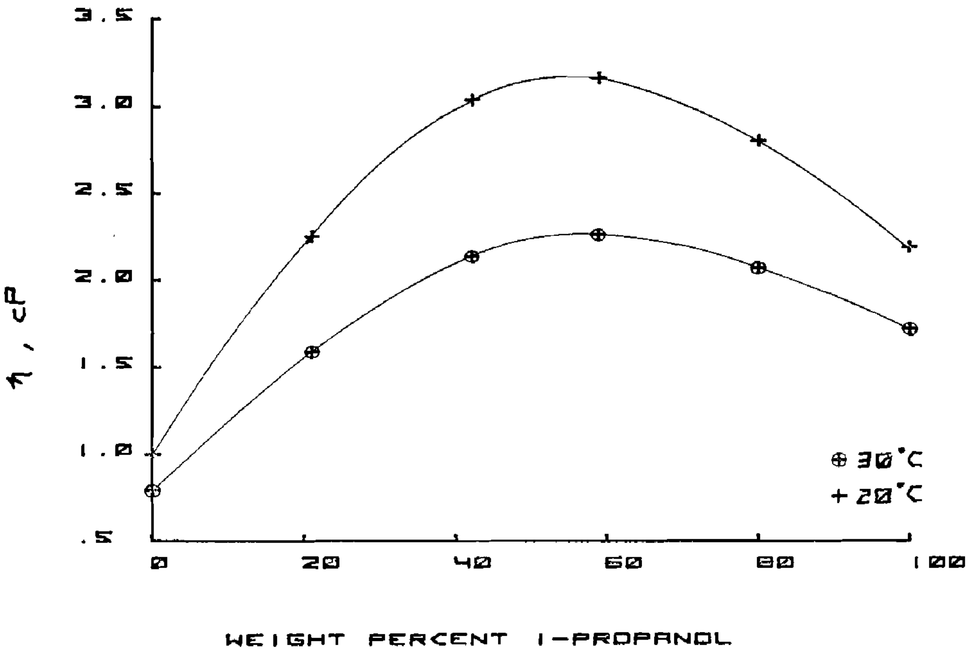

Figure 4. Viscosity of 1-Propanol-Water Mixtures at 20 and 30°C.

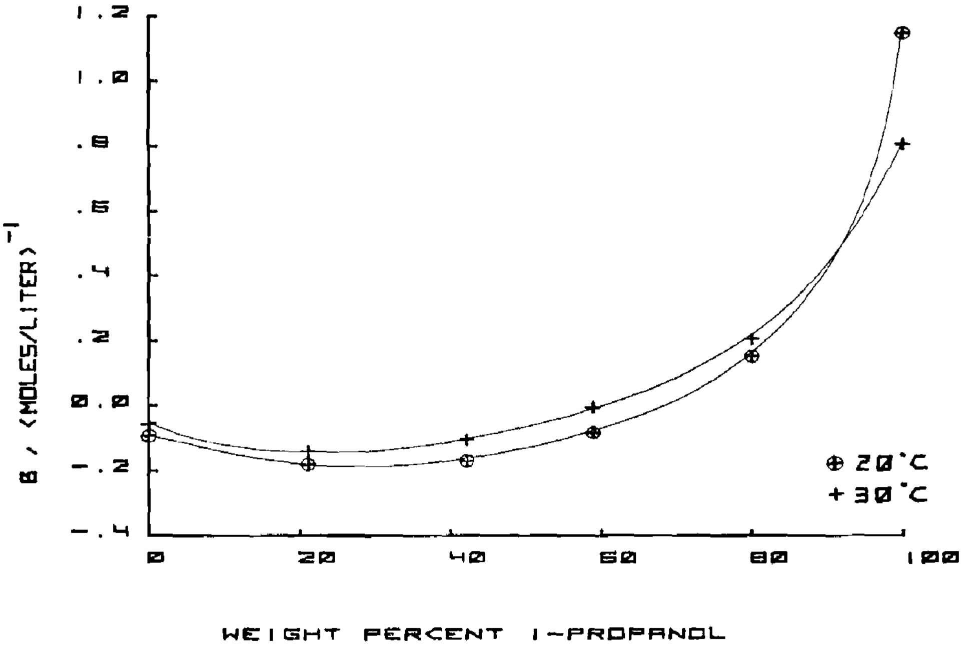

Figure 5. Plot of the B-coefficient as a function of the composition of the solvent.

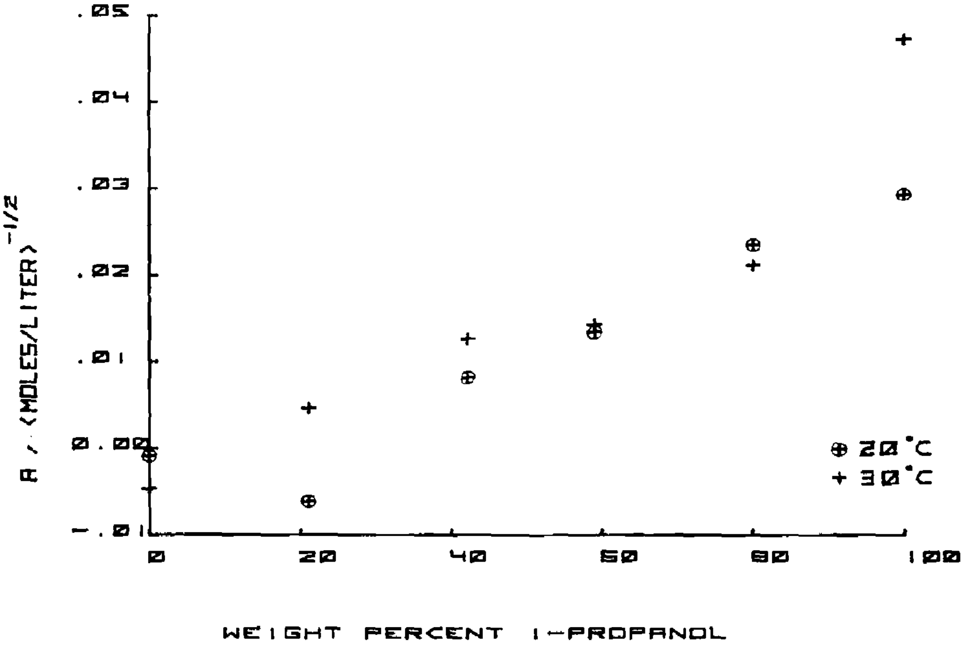

Figure 6. Plot of the A-coefficient as a function of the composition of the solvent.

SECTION 9

DISCUSSION OF THE RESULTS

9.1 *1-Propanol-Water Mixtures*

The Jones-Dole B coefficient for 1-propanol in water was not evaluated from the experimental data due to the small number of values measured. Rupley [191] found that B was equal to 0.320 (moles/liter)$^{-1}$ for 1-propanol at infinite dilution at 25°C. Figure 4 shows that our measured viscosities agree qualitatively.

Upon initial addition of 1-propanol to water, the viscosity of the solution increases. Two effects are responsible for this behavior. First, the "obstruction effect" causes the viscosity to rise in all solutions containing a solute whose effective volume disrupts streamlines in the flow of the liquid. Second, an increase in viscosity results from increased ordering of the solvent. The filling of the interstices in the three-dimensional water structure by 1-propanol molecules stabilizes the structure.

With continued addition of 1-propanol, a maximum in the viscosity of the solution is reached. The reason for the existence of the maximum and of the ensuing decrease in the viscosity with further additions of 1-propanol is that beyond a certain concentration the 1-propanol can no longer be accommodated into the voids or interstices of the water structure. The water structure becomes disrupted as the 1-propanol starts to aggregate and induce its own structure. The two types of structures are in competition and the fluidity of the solution increases as the previous stable structure is destroyed.

9.2 *Potassium Iodide Solutions*

The introduction of potassium iodide into a 1-propanol-water mixed solvent causes a change in the viscosity of the solution. Figures 7 and 8 illustrate the effects of KI on the viscosity of the solutions. It is interesting to note that there are several instances where the addition of definite amount of KI causes no change in solvent viscosity.

Kaminsky's [192] results indicate that potassium iodide is a weak "structure breaker" in water at 25°C (B = —0.0755). In methanol, potassium iodide is a strong "structure maker" indicated by a large positive B (B = 0.67 at 25°C). In 1-propanol, as in methanol, the large B coefficients indicate that the solvent contained little structure initially. It is commonly thought, and experimental evidence exists, that the alcohols are associated through hydrogen-bonding. One interpretation of the B coefficient is that the alcohols are similar to unstructured solvents such as DMF and DMSO in which alkali halide B values are 0.6 to 0.7.

The existence of a minimum in B as a function of the solvent composition in Figure 5 should correlate well with the composition of the maximum viscosity in Figure 4. It has been pointed out that most properties of the mixed solvent correlate with the maximum in the first derivative rather than the maximum in the viscosity curve.[193] This correlation is attributed to a maximum structural effect at low compositions of the organic component. These correlations illustrate the utility of B for indicating structure of the solvent. B becomes less positive and tends toward negative values as the solvent becomes more structured. Negative B values are common only to water, ethylene glycol, and glycerol, all of which are extensively structured in three-dimensions.

The value of B in 20 to 30 weight percent 1-propanol is more negative than in water. This may be interpreted as evidence for an increase in the three-dimensional order in this mixture over that in water. A more positive value of B as the 1-propanol fraction in the solution is increased may be accounted for by the increase in the size of the solvated ion in the presence of 1-propanol, or to a greater ordering of water in the solvation sphere, or both. Several possible explanations can be proposed to explain the observed behavior of B.[194, 195]

Information about the solvent structure can be obtained by analyzing the value of the B coefficient as a function of the composition of the mixed solvent. This analysis is facilitated by adopting the rationale of Equation (2-6). B is seen as the result of competition between differentiated viscosity contributions.

The potassium ion, K^+, is intermediate in size and might be expected to have a close balance of viscous forces near the ion, *i.e.*, $\eta^E + \eta^A = \eta^D$, and B due to K^+ may be close to zero. Iodide ion has a large radius and a small charge density. It has only a weak orienting effect on a few water molecules in the first hydration layer. η^E is about the same as for the bare ion and very small and η^A is also small. The water structure is considerably disrupted around the ion due to the ionic field competing with the bulk aqueous structure, and thus η^D should be large. The total effect on

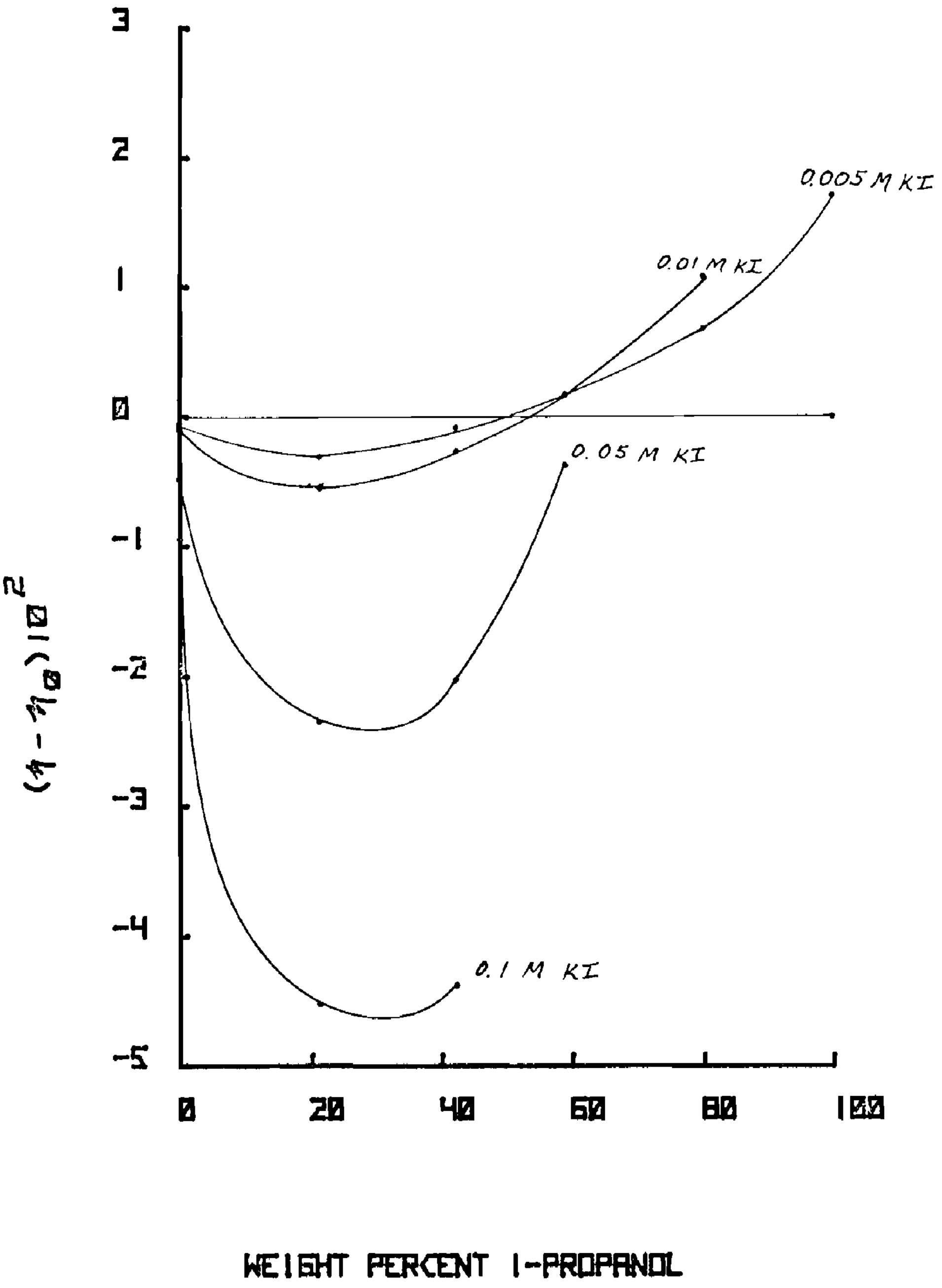

Figure 7. The effect of KI on the viscosity of 1-propanol-water mixtures at 20°C.

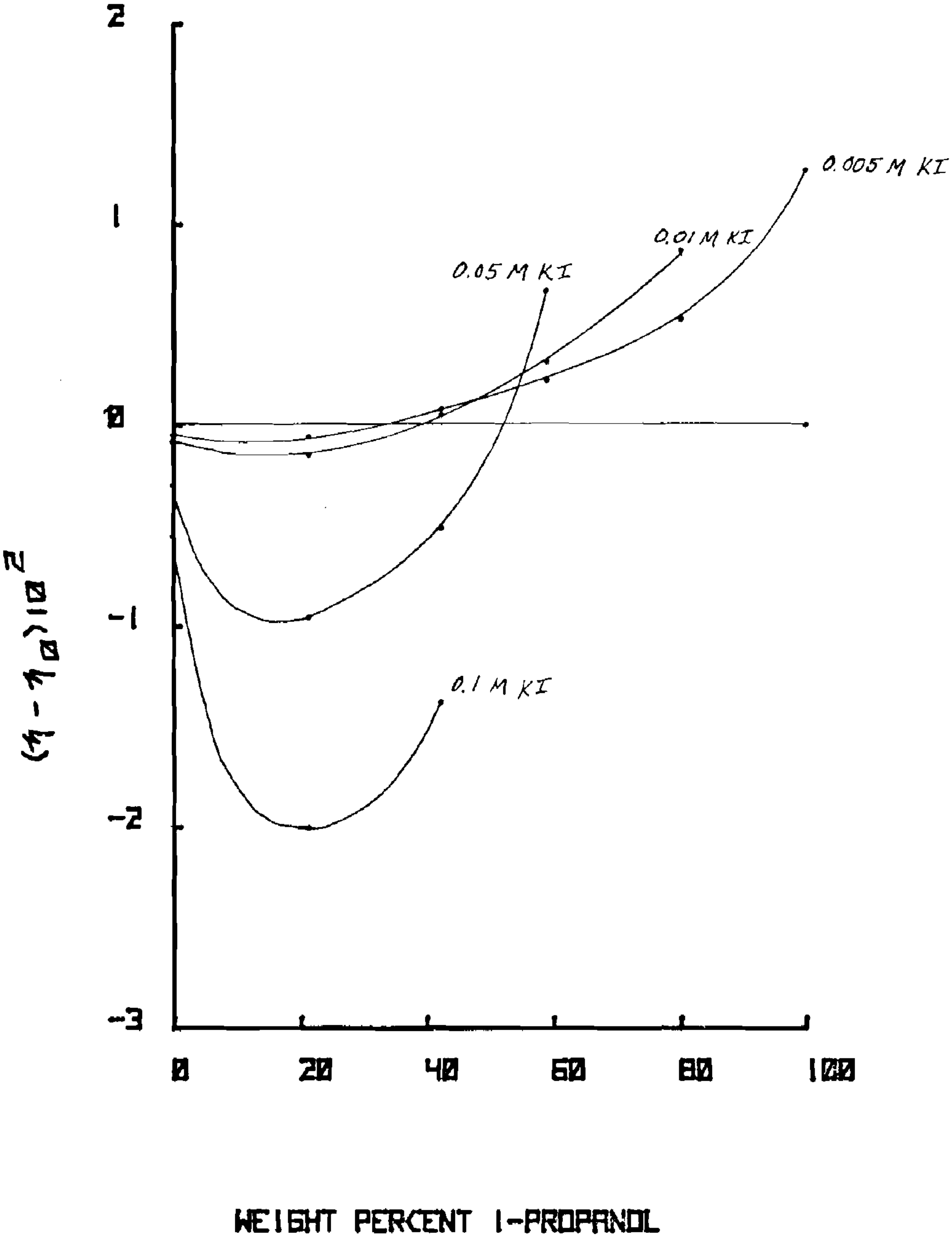

Figure 8. The effect of KI on the viscosity of 1-propanol-water mixtures at 30°C.

the solution viscosity is due to the effects of both ions. For aqueous solutions, since B is negative, overall $\eta^E + \eta^A < \eta^D$.

The results in Figure 5 show that the B coefficient initially decreases with increasing amounts of 1-propanol. B reaches a minimum and then increases until it becomes positive. Increasing the amount of 1-propanol further causes a continual increase in B.

η^D is thought to be relatively small for aqueous solutions because the tetrahedral water configuration easily accepts the outward pointing hydrogen atoms which results from solvation of the potassium ion. The addition of small amounts of 1-propanol enhances the solvent structure and increases the value of η^D due to the competition between forces in the bulk solvent and the ionic field. In these solutions $\eta^E + \eta^A << \eta^D$ and B is increasingly negative with further small additions of 1-propanol.

The ions are selectively solvated by water molecules in 1-propanol-water mixtures. As the amount of 1-propanol increases, the ions begin to strongly orient those closest water molecules and move through the solution with the solvent shell as a kinetic entity. Thus, η^E and η^A increases. Also further addition of 1-propanol disrupts the solvent structure and η^D decreases. B is equal to zero when $\eta^E + \eta^A = \eta^D$. With additional increases in 1-propanol, $\eta^E + \eta^A << \eta^D$ and B becomes positive and gradually increases.

The large value of B in pure 1-propanol can be attributed in part to the larger size of the solvent molecules. This would cause a large η^E value for the solvated ions and also a large η^A effect can be visualized.

The results obtained in this investigation are consistent with results for KI in methanol-water mixtures.[196]

The calculation of parameters related to the determined B values constitute further studies.

SECTION 10

SUMMARY

10.1 *Conclusion*

Density and viscosity measurements covering a large range of concentrations were made for solutions of KI in 1-propanol-water mixtures. The viscosity data was analyzed in terms of the Jones-Dole equation. This equation adequately represented the viscosity of solutions at 20 and 30°C from zero concentration to 0.5 M KI in water and to 0.007 M KI in 1-propanol. The range of validity of the Jones-Dole equation varies between these values as the composition of the mixed solvent is changed.

The A coefficient determined experimentally for solutions of KI in 1-propanol is in agreement with the approximate theoretical value and supports a conclusion that the theoretical equation for A is valid in non-aqueous solvents. A was found to increase roughly linearly with addition of 1-propanol to the mixed solvent.

Values of the B coefficient ranged from -0.054 to 0.8 $(\text{mole/liter})^{-1}$ at 20°C and -0.091 to 1.1 $(\text{mole/liter})^{-1}$ at 30°C for KI in 1-propanol-water mixtures. A minimum occured at 30 weight percent 1-propanol at 20°C and at 25 weight percent 1-propanol at 30°C in a graph of B vs. composition of the mixed solvent. Although KI causes a decrease in viscosity when dissolved in water, the effect was opposite in 1-propanol.

It was determined that an accurate and expedient method to calculate the Jones-Dole coefficients was to perform a non-linear least squares analysis on the Jones-Dole equation and solve for η_0, A, and B of best fit.

The behavior of solutions of KI in 1-propanol-water mixed solvents is similar to that of KI and similar electrolytes in lower monohydric alcohol-water mixed solvents previously studied in the literature.

One interesting result of this investigation is the negative value of $\Delta B/\Delta T$ for KI in 1-propanol.

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APPENDIX I

Experimental Data

TABLE 12

Density of 1-Propanol-H_2O-KI Solutions at 20°C

Weight Percent 1-Propanol	Concentration	Density
x_2	c, M	ρ_4^{20}
0	0	0.998234
	0.002452	0.998636
	0.00981	0.999336
	0.04906	1.00421
	0.49058	1.05740
	2.0019	1.23675

Root equation: $\rho_4^{20} = 0.998239 + 0.122000c - 0.002021c^{3/2}$

x_2	c, M	ρ_4^{20}
21.15	0	0.967614
	0.01004	0.968901
	0.02511	0.970605
	0.12556	0.982721
	0.2511	0.997591
	1.5128	1.14654

Root equation: $\rho_4^{20} = 0.967644 + 0.120164c - 0.001553c^{3/2}$

x_2	c, M	ρ_4^{20}
42.24	0	0.925052
	0.008030	0.925952
	0.02007	0.927412
	0.10037	0.937418
	0.20074	0.949406
	0.6005	0.997361

Root equation: $\rho_4^{20} = 0.925017 + 0.123674c - 0.004140c^{3/2}$

x_2	c, M	ρ_4^{20}
58.95	0	0.890597
	0.000612	0.890689
	0.002041	0.890883
	0.008164	0.891500
	0.02041	0.893230
	0.20408	0.915848
	0.4021	0.940213

Root equation: $\rho_4^{20} = 0.890601 + 0.124738c - 0.002151c^{3/2}$

x_2	c, M	ρ_4^{20}
80.06	0	0.847498
	0.003985	0.848147
	0.009962	0.848782
	0.02490	0.850794
	0.04981	0.853944

Root equation: $\rho_4^{20} = 0.847519 + 0.136273c - 0.032596c^{3/2}$

x_2	c, M	ρ_4^{20}
100.	0	0.803805
	0.0002021	0.803863
	0.002527	0.804243
	0.005054	0.804574
	0.007581	0.804960
	0.010107	0.805724

Root equation: $\rho_4^{20} = 0.803848 + 0.057547c + 1.20865c^{3/2}$

[a] G.S. Kell, J. Chem. Eng. Data *12*, 67(1967).

TABLE 13

Density of 1-Propanol-H_2O-KI Solutions at 30°C

Weight Percent 1-Propanol	Concentration	Density
x_2	c, M	ρ_4^{30}
0	0	0.995678[a]
	0.00489	0.996268
	0.02446	0.998572
	0.12231	1.01038
	0.2446	1.024927
	1.9934	1.231505

Root equation: $\rho_4^{30} = 0.995671 + 0.120441c - 0.001512c^{3/2}$

x_2	c, M	ρ_4^{30}
21.15	0	0.961860
	0.0009981	0.962006
	0.00500	0.962436
	0.01997	0.964246
	0.04992	0.967780
	0.49917	1.02110
	1.5040	1.13986

Root equation: $\rho_4^{30} = 0.961860 + 0.119104c - 0.000615c^{3/2}$

x_2	c, M	ρ_4^{30}
42.24	0	0.917790
	0.000797	0.917882
	0.003983	0.918251
	0.01593	0.919693
	0.03983	0.922703
	0.39868	0.966160
	0.5960	0.989892

Root equation: $\rho_4^{30} = 0.917778 + 0.123131c - 0.002775c^{3/2}$

x_2	c, M	ρ_4^{30}
58.95	0	0.882843
	0.004046	0.883341
	0.010115	0.884059
	0.05057	0.889143
	0.10115	0.895445
	0.3986	0.931942

Root equation: $\rho_4^{30} = 0.882827 + 0.126061c - 0.004499c^{3/2}$

x_2	c, M	ρ_4^{30}
80.06	0	0.839298
	0.000986	0.839338
	0.001973	0.839683
	0.004932	0.839803
	0.01479	0.841101
	0.09868	0.851885

Root equation: $\rho_4^{30} = 0.839300 + 0.116419c + 0.035376c^{3/2}$

x_2	c, M	ρ_4^{30}
100.	0	0.795810
	0.001001	0.795910
	0.003502	0.796227
	0.006003	0.796651
	0.010003	0.797306

Root equation: $\rho_4^{30} = 0.795803 + 0.091522c + 0.593415c^{3/2}$

[a] G.S. Kell, J. Chem. Eng. Data *12*, 67(1967).

TABLE 14

Viscosity of 1-Propanol-H_2O-KI Solutions at 20°C

Weight Percent 1-Propanol	Concentration	Viscosity	
x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2/c^{1/2}$
0	0	1.0020[a]	
	0.002452	1.0013	—1.11
	0.00491	1.0011	—1.07
	0.00981	1.0011	—0.79
	0.02452	0.99947	—1.53
	0.04906	0.99791	—1.79
	0.12263	0.98970	—3.47
	0.2453	0.97931	—4.55
	0.49058	0.95978	—6.00
	2.0019	0.88700	—8.10

Jones-Dole equation: $\eta = 1.00187 - 0.000872c^{1/2} - 0.09106c$ (0<c<0.25)

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2/c^{1/2}$
21.15	0	2.2546	
	0.001004	2.2528	—1.71
	0.00503	2.2500	—2.53
	0.01004	2.2494	—2.07
	0.02009	2.2449	—2.87
	0.02511	2.2414	—3.54
	0.05022	2.2306	—4.65
	0.12556	2.1962	—7.25
	0.2511	2.1462	—9.55
	0.50226	2.0387	—13.48
	1.5128	1.7589	—17.86

Jones-Dole equation: $\eta = 2.25410 - 0.0137c^{1/2} - 0.4087c$ (0<c<0.5)

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2/c^{1/2}$
42.24	0	3.0361	
	0.000803	3.0357	—0.60
	0.004015	3.0354	—0.41
	0.008030	3.0354	—0.28
	0.01606	3.0319	—1.12
	0.02007	3.0294	—1.59
	0.04015	3.0201	—2.65
	0.10037	2.9913	—4.66
	0.20074	2.9440	—6.77
	0.40150	2.8499	—9.68
	0.6005	2.7669	—11.45

Jones-Dole equation: $\eta = 3.03619 + 0.0249c^{1/2} - 0.5166c$ $(0<c<0.2)$

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2/c^{1/2}$
58.95	0	3.1636	
	0.000612	3.1638	0.89
	0.002041	3.1640	0.59
	0.004081	3.1644	0.63
	0.008164	3.1656	0.88
	0.010204	3.1646	0.48
	0.02041	3.1639	0.16
	0.05102	3.1592	−0.55
	0.10205	3.1488	−1.42
	0.20408	3.1213	−2.92
	0.4021	3.0691	−4.69

Jones-Dole equation: $\eta = 3.16312 + 0.0426c^{1/2} - 0.2642c$ $(0<c<0.05)$

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2/c^{1/2}$
80.06	0	2.7997	
	0.000996	2.8018	2.65
	0.001992	2.8030	2.82
	0.003985	2.8050	3.10
	0.004981	2.8069	3.72
	0.009962	2.8106	3.96
	0.01494	2.8137	4.14
	0.02490	2.8192	4.46
	0.04981	2.8293	4.77
	0.09962	2.8456	5.22

Jones-Dole equation: $\eta = 2.79950 + 0.0658c^{1/2} + 0.4239c$ $(0<c<0.015)$

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2/c^{1/2}$
100.	0	2.1898	
	0.0002021	2.1910	3.86
	0.0005054	2.1926	5.73
	0.001011	2.1942	6.29
	0.002527	2.1999	9.23
	0.003538	2.2020	9.38
	0.005054	2.2071	11.11
	0.006064	2.2087	11.12
	0.007581	2.2143	12.88
	0.010107	2.2196	13.54

Jones-Dole equation: $\eta = 2.18977 + 0.0642c^{1/2} + 2.507c$ $(0<c<0.005)$

[a] L. Korson, W. Drost-Hansen, and F.J. Millero, J. Phys. Chem. *73*, 34(1969).

TABLE 15

Viscosity of 1-Propanol-H_2O-KI Solutions at 30°C

Weight Percent 1-Propanol	Concentration	Viscosity	
x_2	c, M	η, cP	$(\eta/\eta_0-1)10^2/c^{1/2}$
0	0	0.79747[a]	
	0.002446	0.79690	—0.71
	0.00489	0.79640	—1.41
	0.00979	0.79609	—1.38
	0.02446	0.79571	—1.18
	0.04893	0.79442	—1.56
	0.12231	0.79063	—2.35
	0.2446	0.78472	—3.16
	0.48892	0.77347	—4.25
	1.9934	0.73907	—5.16

Jones-Dole equation: $\eta = 0.797182 - 0.00372c^{1/2} - 0.04318c$ $(0<c<0.49)$

x_2	c, M	η, cP	$(\eta/\eta_0-1)10^2/c^{1/2}$
21.15	0	1.5888	
	0.0009981	1.5880	—0.70
	0.00500	1.5876	—0.62
	0.009981	1.5863	—1.30
	0.01997	1.5848	—1.57
	0.02496	1.5845	—1.53
	0.04992	1.5794	—2.52
	0.12479	1.5624	—4.62
	0.2496	1.5362	—6.57
	0.49917	1.4893	—8.82
	1.5040	1.3530	—12.08

Jones-Dole equation: $\eta = 1.58835 + 0.00756c^{1/2} - 0.2247c$ $(0<c<0.25)$

x_2	c, M	η, cP	$(\eta/\eta_0-1)10^2/c^{1/2}$
42.24	0	2.1387	
	0.000797	2.1391	—6.52
	0.003983	2.1388	—5.25
	0.007967	2.1387	—3.42
	0.01593	2.1387	—1.99
	0.01992	2.1377	—0.82
	0.03983	2.1350	—0.25
	0.099584	2.1250	0.10
	0.19920	2.1058	0.12
	0.39868	2.0676	0.23
	0.5960	2.0308	1.04

Jones-Dole equation: $\eta = 2.13846 + 0.0271c^{1/2} — 0.2237c$ $(0<c<0.2)$

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2/c^{1/2}$
58.95	0	2.2634	
	0.000607	2.2636	1.02
	0.002023	2.2634	0.34
	0.004046	2.2659	2.03
	0.008092	2.2658	1.35
	0.010115	2.2661	1.36
	0.02023	2.2676	1.42
	0.05057	2.2696	1.30
	0.10115	2.2690	0.84
	0.20236	2.2644	0.13
	0.3986	2.2507	—0.86

Jones-Dole equation: $\eta = 2.26301 + 0.0324c^{1/2} — 0.01132c$ $(0<c<0.05)$

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2c^{1/2}$
80.06	0	2.0718	
	0.000986	2.0728	1.89
	0.001973	2.0741	2.79
	0.003946	2.0766	3.88
	0.004932	2.0767	3.57
	0.009864	2.0800	4.13
	0.01479	2.0831	4.60
	0.02465	2.0889	5.34
	0.04931	2.0986	5.89
	0.09868	2.1161	6.85

Jones-Dole equation: $\eta = 2.07154 + 0.0438c^{1/2} + 0.4265c$ $(0<c<0.025)$

x_2	c, M	η, cP	$(\eta/\eta_0\text{-}1)10^2c^{1/2}$
100.	0	1.7223	
	0.0002001	1.7235	4.93
	0.0005004	1.7249	6.75
	0.001001	1.7263	7.38
	0.002501	1.7297	8.63
	0.003502	1.7320	9.58
	0.005003	1.7346	10.08
	0.006003	1.7376	11.45
	0.007503	1.7394	11.50
	0.010003	1.7440	12.57

Jones-Dole equation: $\eta = 1.72229 + 0.0813c^{1/2} + 1.386c$ $(0<c<0.0075)$

[a] L. Korson, W. Drost-Hansen, and F.J. Millero, J. Phys. Chem. 73, 34(1969).

APPENDIX II

Graphs for the Jones-Dole Equation

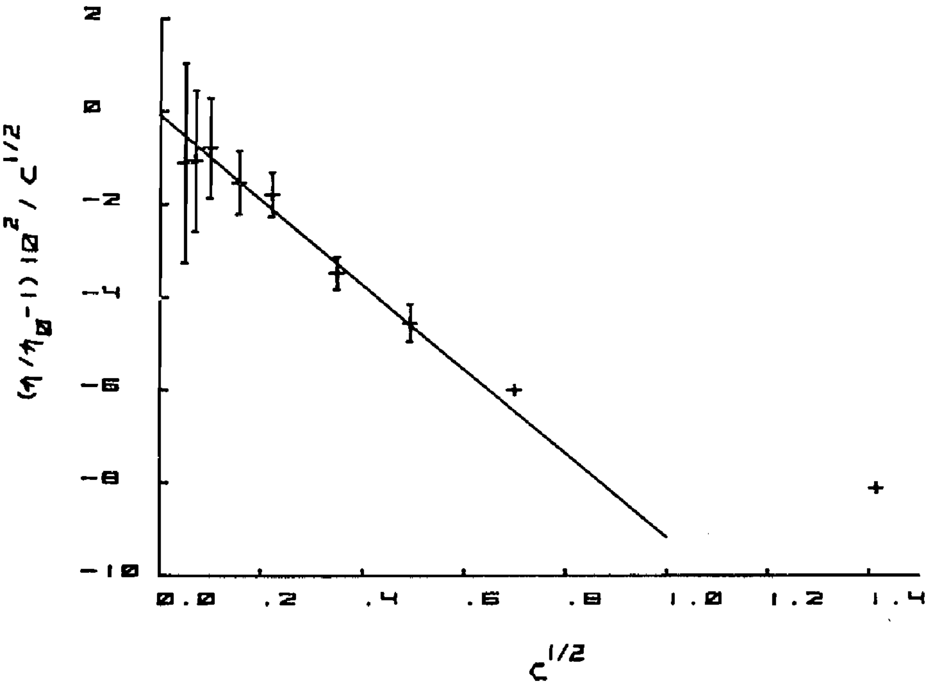

Figure 9. Plot of the linearized Jones-Dole equation for KI in water at 20°C.

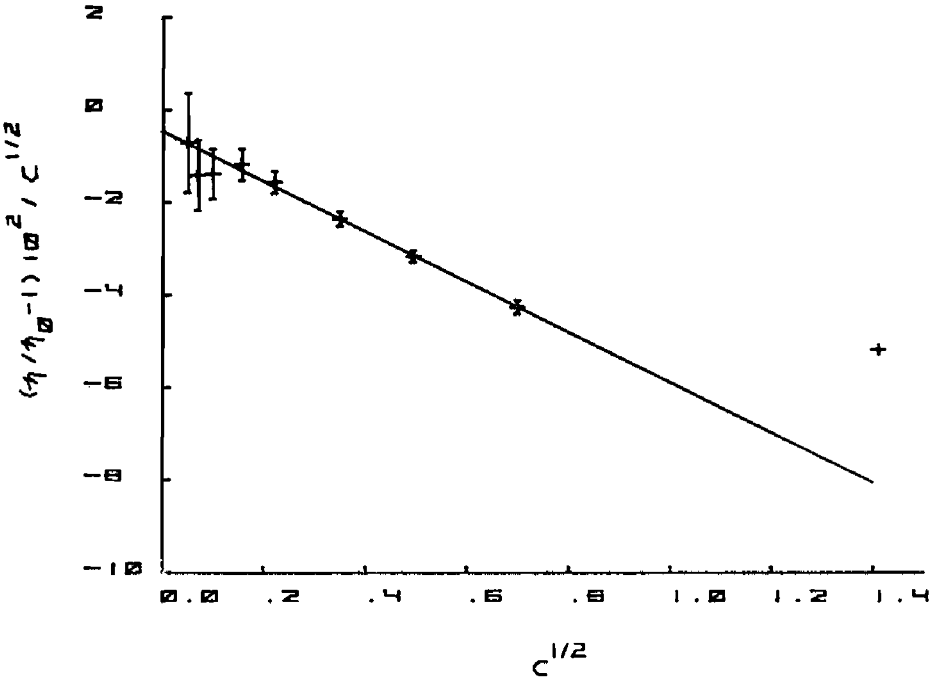

Figure 10. Plot of the linearized Jones-Dole equation for KI in water at 30°C.

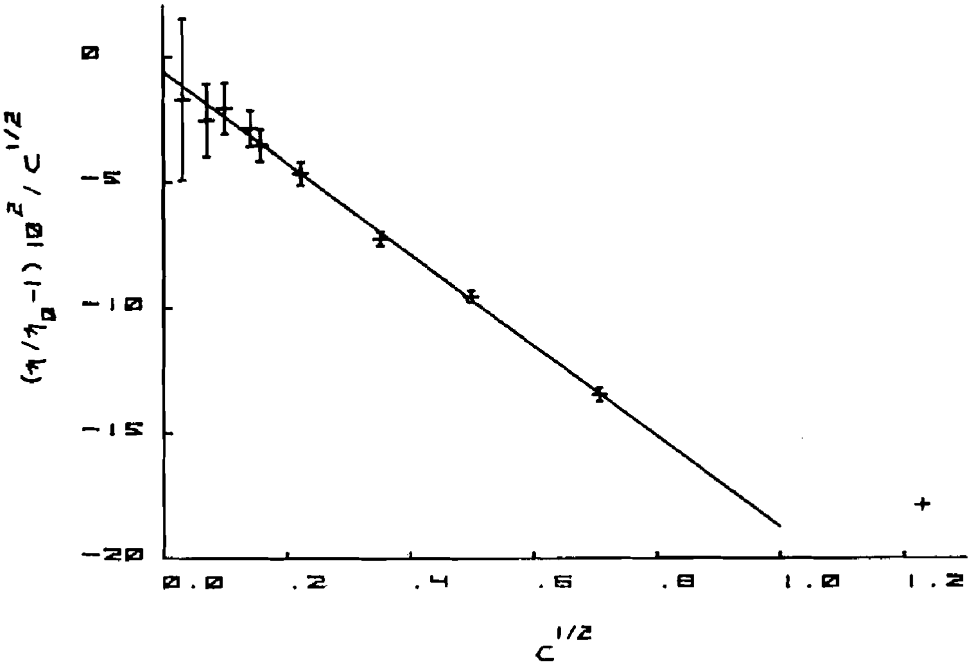

Figure 11. Plot of the linearized Jones-Dole equation for KI in 21.15 weight percent 1-propanol at 20°C.

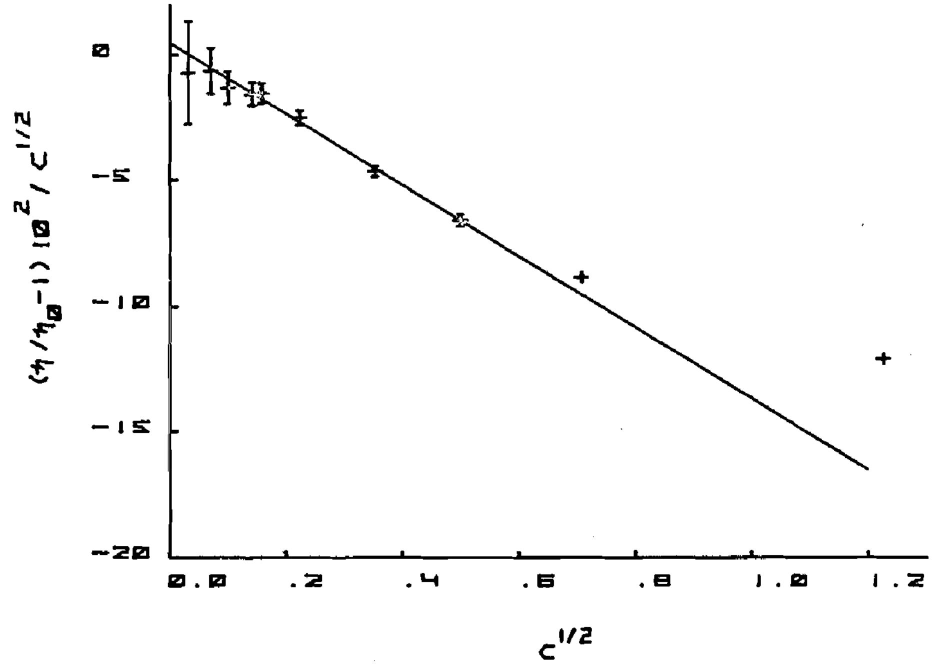

Figure 12. Plot of the linearized Jones-Dole equation for KI in 21.15 weight percent 1-propanol at 30°C.

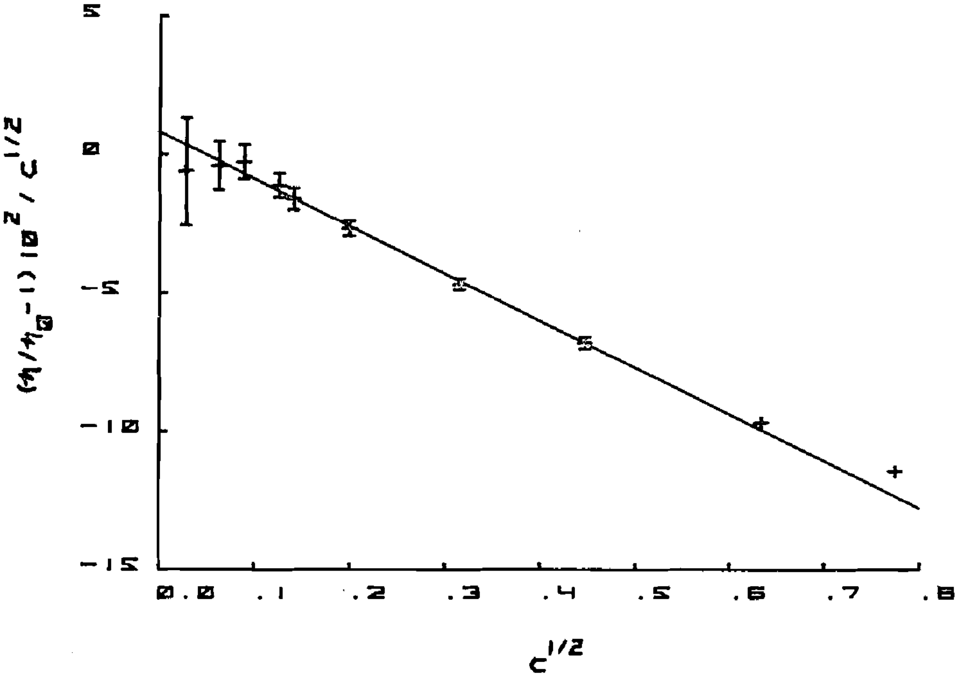

Figure 13. Plot of the linearized Jones-Dole equation for KI in 42.24 weight percent 1-propanol at 20°C.

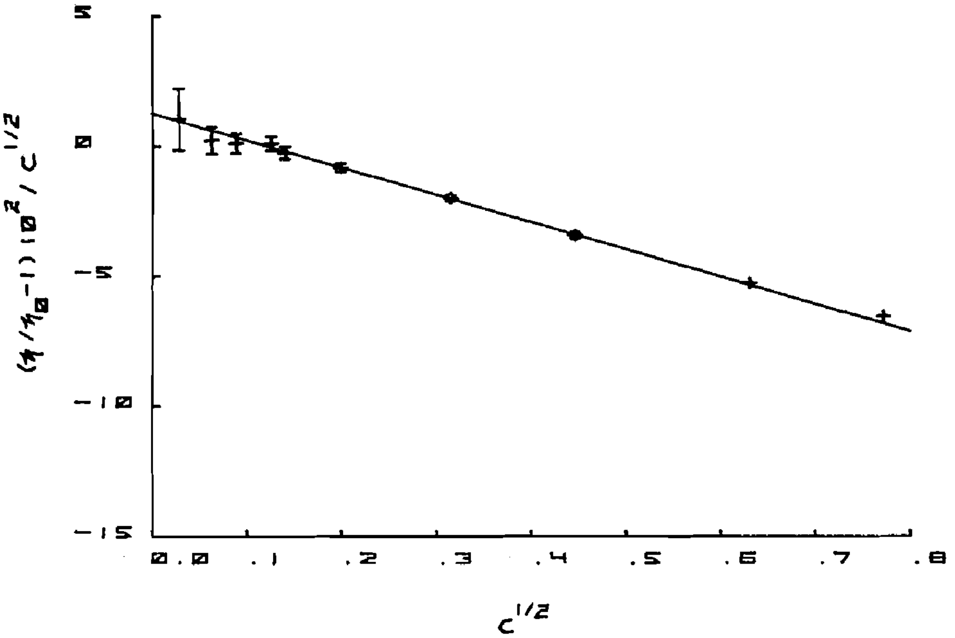

Figure 14. Plot of the linearized Jones-Dole equation for KI in 42.24 weight percent 1-propanol at 30°C.

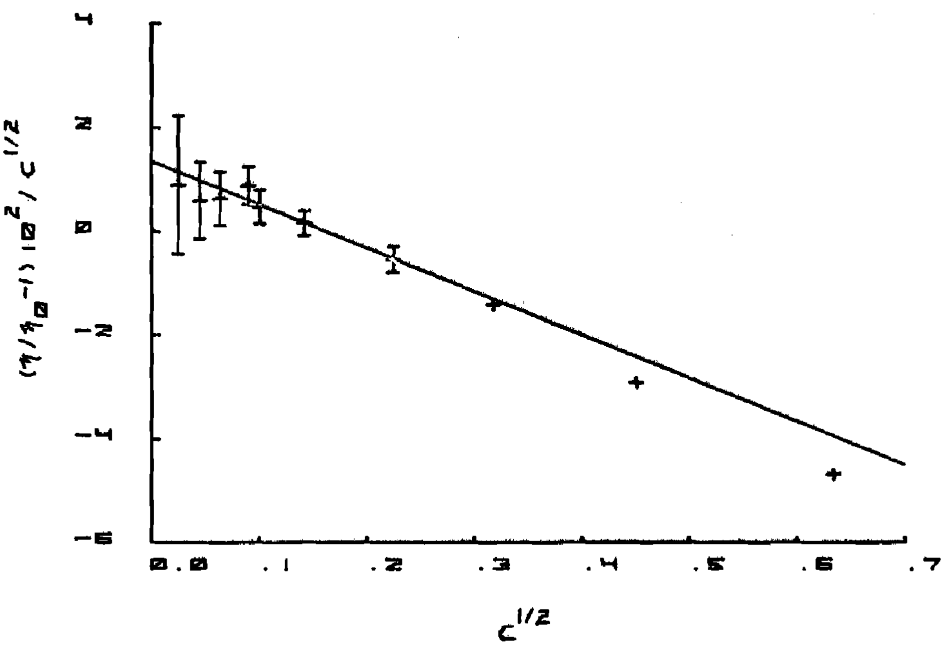

Figure 15. Plot of the linearized Jones-Dole equation for KI in 58.95 weight percent 1-propanol at 20°C.

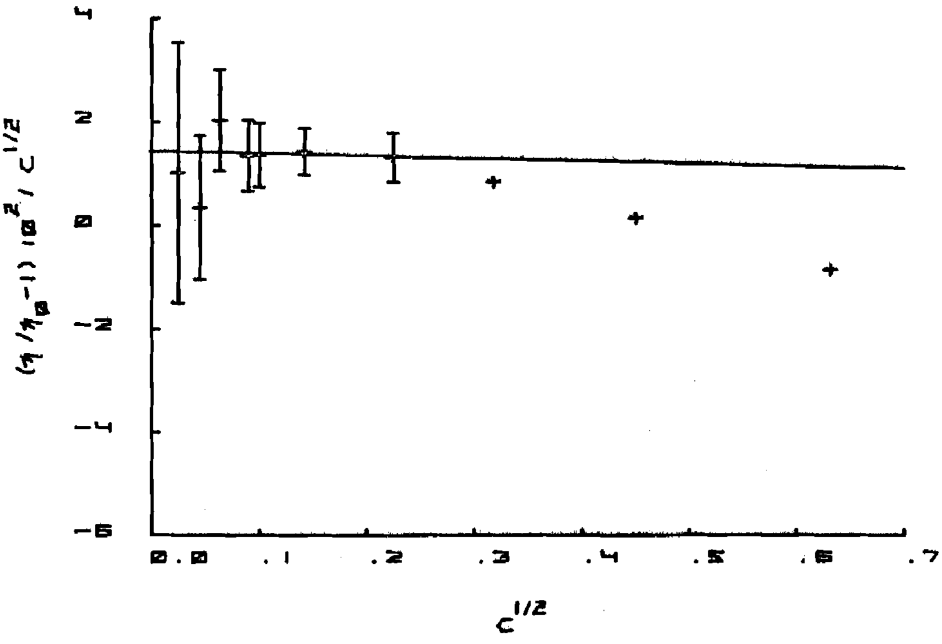

Figure 16. Plot of the linearized Jones-Dole equation for KI in 58.95 weight percent 1-propanol at 30°C.

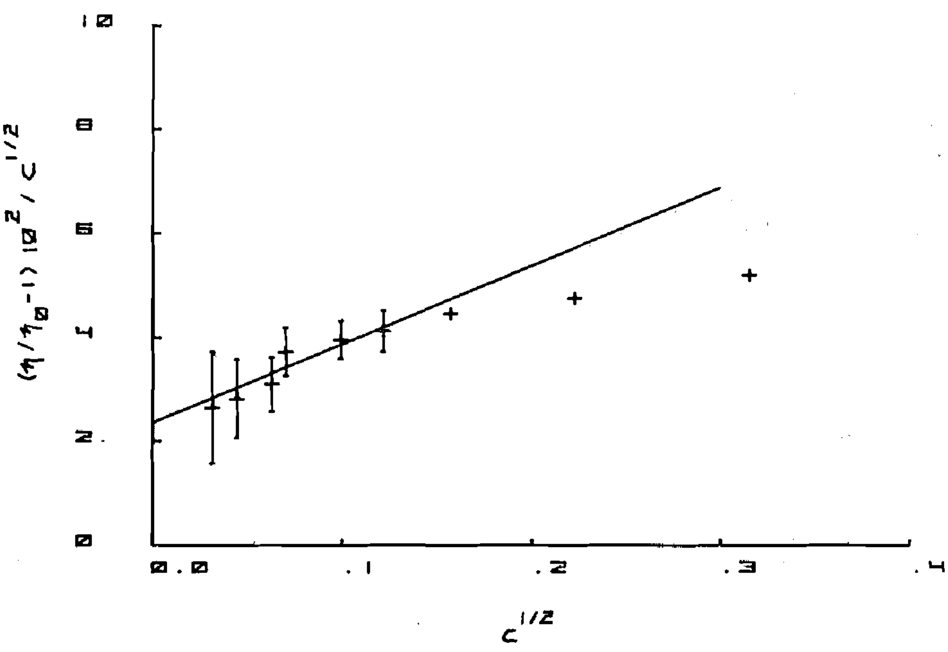

Figure 17. Plot of the linearized Jones-Dole equation for KI in 80.01 weight percent 1-propanol at 20°C.

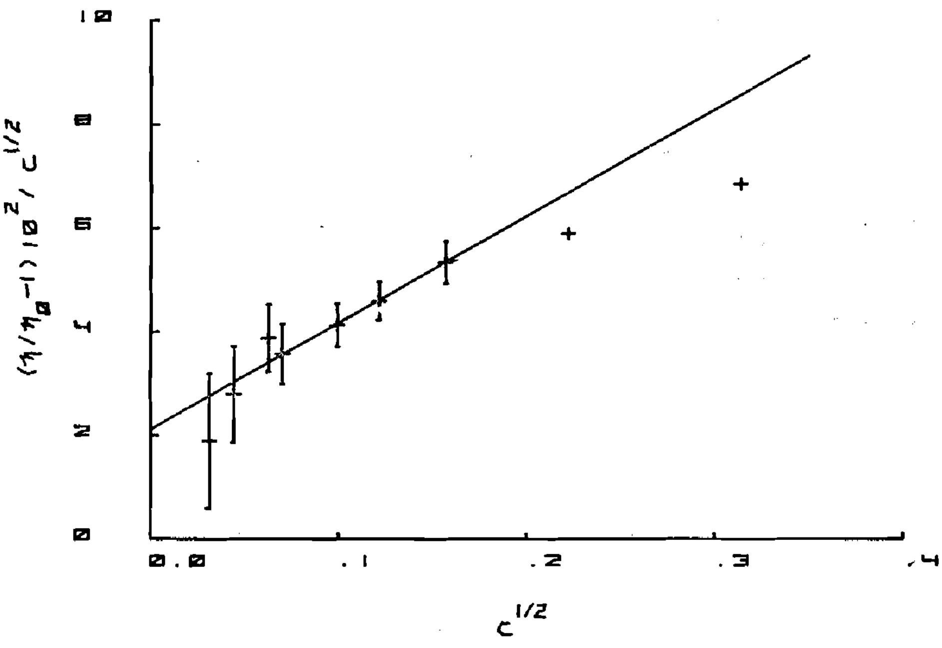

Figure 18. Plot of the linearized Jones-Dole equation for KI in 80.01 weight percent 1-propanol at 30°C.

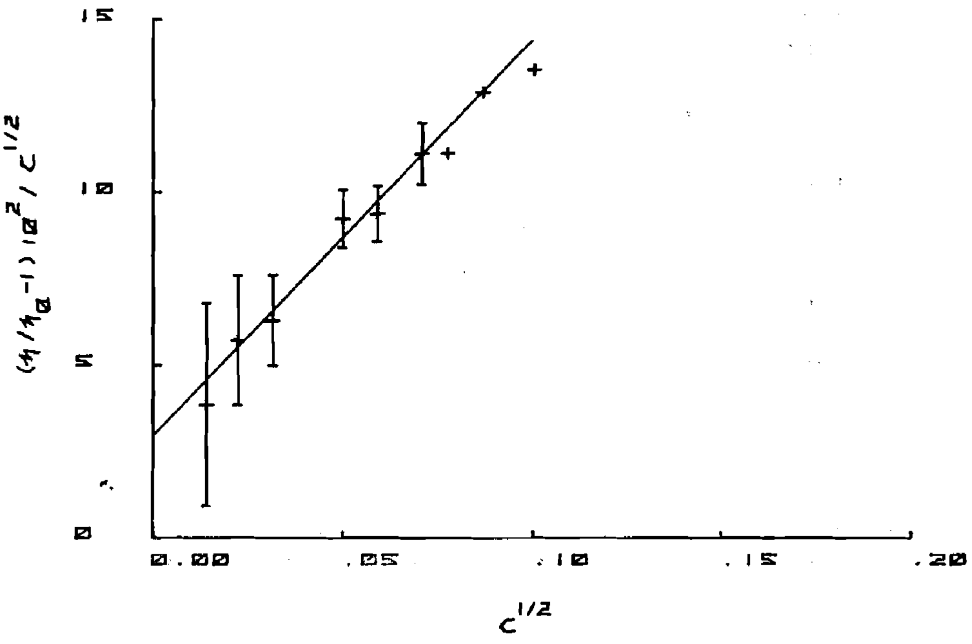

Figure 19. Plot of the linearized Jones-Dole equation for KI in 1-propanol at 20°C.

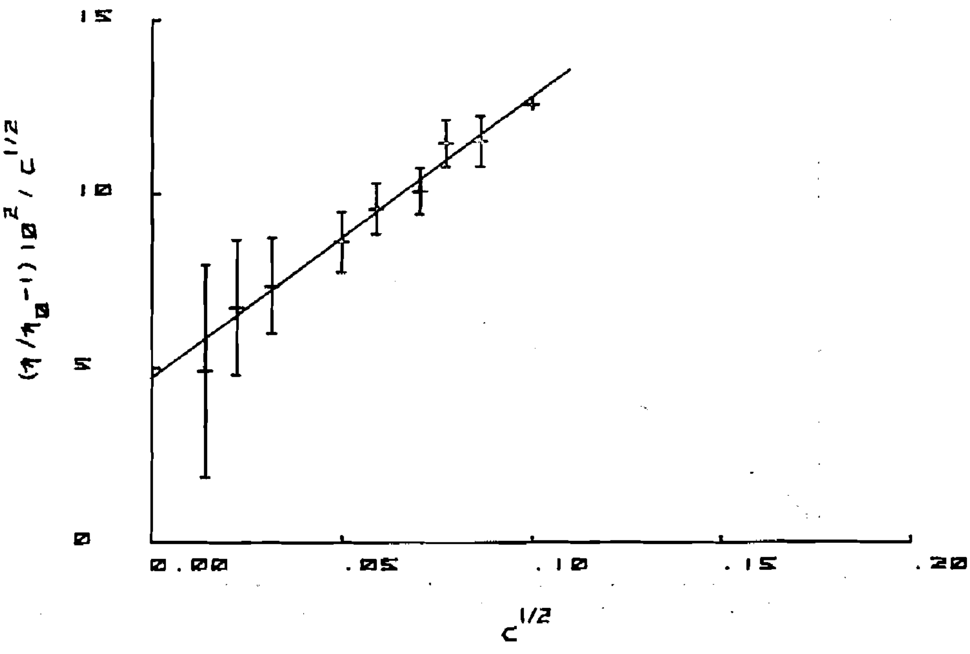

Figure 20. Plot of the linearized Jones-Dole equation for KI in 1-propanol at 30°C.

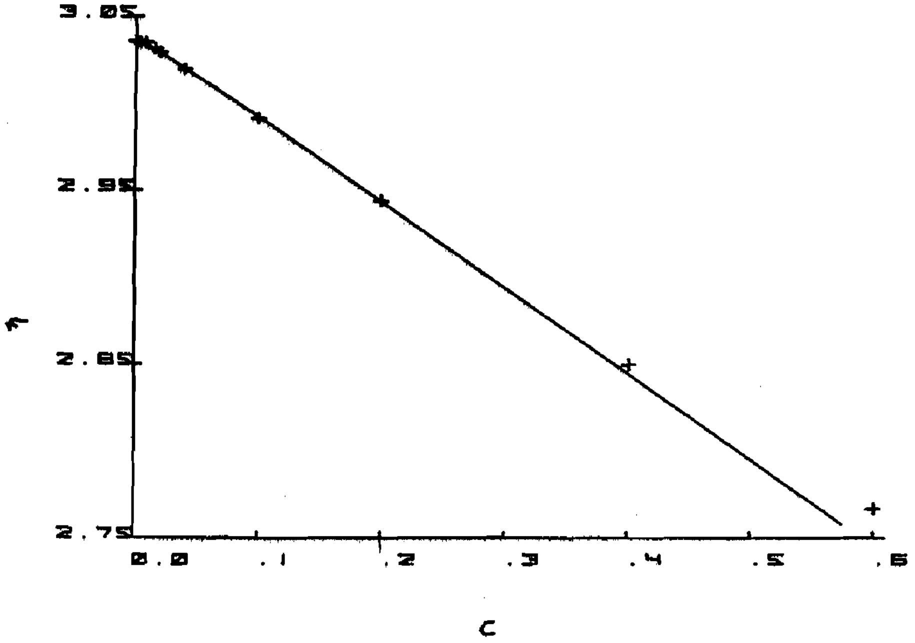

Figure 21. Plot of the Jones-Dole equation for KI in 42.24 weight percent 1-propanol at 20°C.

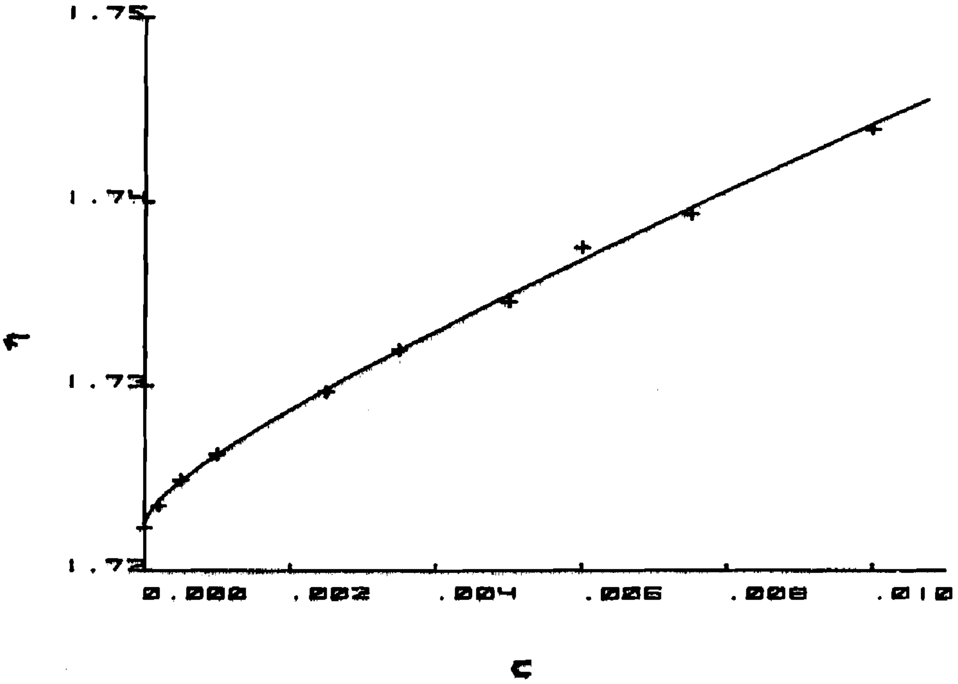

Figure 22. Plot of the Jones-Dole equation for KI in 1-propanol at 30°C.