RESEARCH ARTICLES

Determination of Extent of Hydration of Water-Miscible Organic Liquids in Aqueous Solution from Viscosity Data

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Abstract □ Three viscometric methods for estimating the extent of association in binary liquid mixtures were employed to determine the maximum hydration of acetone, dimethyl sulfoxide, dioxane, 1-propanol, and 2-pyrrolidinone in aqueous solution. Two of the methods are based on the increase in viscosity or the decrease in fluidity of binary aqueous solutions caused by association between water and the second component, *i.e.*, by hydration of the second component. The composition of maximum hydration is that at which the deviation of experimental viscosities or fluidities from additive viscosities or fluidities reaches a maximum. Additive values are calculated by interpolation between the viscosities or fluidities of water and the second liquid component. Additivity would be observed in ideal solutions, *i.e.*, in the absence of hydration. The first method of interpolation uses the Kendall equation, $\phi_{12calc} = \phi_1^{x_1}\phi_2^{x_2}$, to calculate the fluidities, ϕ, of the mixtures (subscript 12) from the fluidities and mole fractions, x, of water (subscript 1) and the second liquid (subscript 2). The Kendall equation has a theoretical basis and is applicable where the viscosities, η, of water and the second liquid are of the same order of magnitude, differing by less than a factor of five. The maximum number of bound water molecules per molecule of the second component was 3 for acetone and dimethyl sulfoxide, 4 for dioxane, and 5.7 for propanol. The second method of interpolation is based on the empirical Kendall–Monroe equation, $\eta_{12calc}^{1/3} = x_1\eta_1^{1/3} + x_2\eta_2^{1/3}$, which is applicable to mixtures where the viscosities of the two pure components differ by a factor of 10 or more. The resultant hydration ratio of one water molecule per molecule of pyrrolidinone is confirmed by the separation of the solid monohydrate at lower temperatures. A novel and universal method determines the maximum hydration as the composition at which the activation energy for viscous flow of the mixtures, indicative of the size of the flow units, goes through a maximum. This method requires viscosity data of higher accuracy and at more than one temperature. Its hydration results agreed with those of the other two methods where the latter were applicable. The change in the activation energy of water with temperature was used to obtain a relative measure of the degree of self-association in liquid water as a function of temperature.

Keyphrases □ Hydration—water-miscible organic liquids in aqueous solution, determination using three viscometric methods □ Binary liquid mixtures—extent of hydration, three viscometric methods □ Viscosity—determination of extent of hydration of water-miscible organic liquids in aqueous solution □ Organic solvents—extent of hydration in aqueous solution, viscosity data

The extent of hydration of water-miscible organic liquids is of interest because it affords estimates of the number of water molecules associated with the organic functional groups present in the molecules of these liquids as well as in other compounds containing the same functional groups, including drugs, polymers, and constituents of biological membranes and cells.

For example, a knowledge of the maximum number of water molecules associated with an ether group, obtained from studies of binary liquid systems comprising water and model ethers (1), was essential to understanding the hydration of micelles of nonionic polyoxyethylated surfactants, making it possible to distinguish between water molecules bound to ether groups by hydrogen bonding and those mechanically trapped in the coiled and interpenetrating chains of the polyoxyethylene moieties of the surfactants (2). Information concerning the maximum hydration of hydroxyl groups (3) may lead to a better understanding of the transport properties of aqueous solutions of natural or synthetic polyhydroxylated polymers and of the water vapor permeability of their films (4).

Finally, the composition of maximum hydration of solvents such as dimethyl sulfoxide (5) is important in connection with their use as vehicles for drugs and as reaction media.

THEORETICAL

Association in a binary liquid system usually can be detected by the deviation of the experimental values of an intensive property of the solutions from the additive values of the property. Additive values are calculated by linear interpolation between the two values of that property belonging to the two pure components as a function of composition. Additive values are observed experimentally in the absence of association between molecules of the two liquids in their binary mixtures. Association leads to deviations from additivity. Such deviations frequently reach maximum values at a stoichiometric composition corresponding to the complex formed between the two components or at the composition of maximum hydration when water is one of the two liquid components.

Among the properties tested as suitable indicators are density and partial molar volume, refractive index and molar refraction, dielectric

constant, magnetic susceptibility, IR and UV absorption spectra, and heat of mixing (6). Fluidity, ϕ, or its reciprocal, viscosity, η, is a reliable and sensitive property for detecting association between strongly (7) and weakly (1, 3, 5, 8, 9) interacting components.

Kendall and Kendall–Monroe Equations—The first equation used to calculate the fluidities of binary aqueous mixtures by interpolation between the fluidity of water and that of the second liquid component was the Kendall equation (10):

$$\log \phi_{12 \text{ calc}} = x_1 \log \phi_1 + x_2 \log \phi_2 \qquad \text{(Eq. 1)}$$

where x represents mole fraction and subscripts 1, 2, and 12 refer to water, the second liquid component, and their mixtures, respectively. This equation is obeyed by ideal or nearly ideal solutions (11).

Association between the two components causes the observed fluidity of their mixtures to be smaller than that calculated by Eq. 1. The composition corresponding to the greatest deviation of the experimental fluidity from that calculated by Eq. 1 is the composition at which the association between the two liquids is most extensive. Deviations in fluidity are defined as:

$$\Delta\phi = \phi_{12 \text{ calc}} - \phi_{12 \text{ exp}} \qquad \text{(Eq. 2)}$$

while percent relative deviations in fluidity are calculated as:

$$\text{relative deviation } \phi = 100\Delta\phi/\phi_{12 \text{ exp}} \qquad \text{(Eq. 3)}$$

The Kendall equation is easily derived from Eyring's theory of the viscosity of liquids (12) for the case where the molar volumes and, hence, the viscosities of the two pure liquid components are of comparable orders of magnitude. Molar volume refers to the volume of 1 mole of the kinetic or flow unit. If the liquid is self-associated, e.g., a dimer, the molar volume to be used is twice the ratio of the monomeric molecular weight to density. Molar volume is then related to the size of the holes or vacant sites which, according to the relaxation theory of transport phenomena, exist in liquids and determine their transport properties (13).

The Kendall equation is applicable to pairs of miscible liquids whose viscosities do not differ by too much, e.g., by less than a factor of 5. In that case, the fluidities of the mixtures calculated by means of Eq. 1 are correct in the absence of association between the two components. Therefore, where association does occur, the composition of maximum interaction is that corresponding to the maximum difference, $\Delta\phi$, between calculated and observed fluidities.

When the fluidities of the two liquid components differ appreciably, Kendall and Monroe (14) proposed the following empirical equation to calculate the viscosities of binary mixtures by interpolation between the viscosities of the pure components:

$$\eta_{12 \text{ calc}}^{1/3} = x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3} \qquad \text{(Eq. 4)}$$

Equation 4 correctly predicts the viscosity of binary mixtures of non-associated liquids when there is an appreciable difference between the viscosities and, hence, the molar volumes of the two liquids (7, 14). Deviations of the observed viscosities of aqueous solutions from the viscosities calculated by means of Eq. 4 can be used to determine the composition corresponding to maximum hydration only if the second liquid is considerably more viscous than water, having a viscosity at room temperature of at least 10 or 15 cps. Deviations in viscosity are defined as:

$$\Delta\eta = \eta_{12 \text{ exp}} - \eta_{12 \text{ calc}} \qquad \text{(Eq. 5)}$$

while percent relative deviations in viscosity are calculated as:

$$\text{relative deviation } \eta = 100 \, \Delta\eta/\eta_{12 \text{ exp}} \qquad \text{(Eq. 6)}$$

Neither Eq. 1 nor 4 is universally applicable. They are mutually exclusive; furthermore, Eq. 4 lacks a theoretical basis. Therefore, there is a need for a general method of determining the composition of most extensive hydration of binary systems. Such a method, while still based on rheology because of the large relative deviations observed, does not employ deviations from viscosities calculated by interpolation.

Activation Energy for Viscous Flow as a Measure of Association—The activation energy for viscous flow, ΔE, is defined by the Arrhenius–Gusman–Andrade equation (11):

$$\eta = A \exp(\Delta E/RT) \qquad \text{(Eq. 7)}$$

or:

$$\frac{d \log \eta}{d(1/T)} = \frac{\Delta E}{2.3026R} \qquad \text{(Eq. 8)}$$

where T is the absolute temperature; R is the gas constant, 1.98717 cal/mole/degree; A is another constant; and ΔE is expressed in calories per mole.

Mixtures of simple liquids generally exhibit Newtonian flow behavior, so that η and, hence, ΔE are independent of shear stress. Plots of log η versus $1/T$ are sometimes very slightly convex toward the reciprocal temperature axis, especially over temperature ranges broader than $\sim30°$. The ΔE values used in the present study were calculated from viscosity data taken within temperature ranges of $\leq20°$. The Arrhenius equation was obeyed over these narrow ranges, and ΔE was calculated by the method of least squares.

When viscosity data at only two temperatures, T_1 and T_2, were considered, ΔE was calculated from the integrated form of Eq. 8:

$$\Delta E = \frac{(2.3026)(1.98717)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \log \frac{(\eta_{12 \text{ exp}})_{T_2}}{(\eta_{12 \text{ exp}})_{T_1}} \qquad \text{(Eq. 9)}$$

The energy of activation for viscous flow of a single liquid is related to its latent heat of vaporization. Liquids are mobile because of the presence of holes or vacant sites. According to Eyring's theory for viscous flow, the flow of liquids in shear consists of molecules squeezing past their neighbors to occupy such vacant sites. The activation energy for viscous flow is used mostly to form new holes (11–13). The size of the holes and, hence, the magnitude of the activation energy must increase as the flow unit increases. For binary aqueous mixtures, more extensive hydration of the second liquid increases the size of the flow unit and should increase the activation energy. Accordingly, the activation energy should go through a maximum at the composition at which the association is most extensive, i.e., at which the greatest number of water molecules are associated with each molecule of the second liquid. The composition corresponding to the highest activation energy is the composition of maximum hydration.

EXPERIMENTAL

Materials—Purification methods and properties of dimethyl sulfoxide (5), 1,4-dioxane (1, 15), and 1-propanol (3) were described previously; 2-pyrrolidinone[1] (also called 2-pyrrolidone or γ-butyrolactam) was purified by fractional distillation and repeated crystallization by freezing until the freezing point could not be increased further. The final value of 25.64° is in good agreement with the published values of 25.57° (16) and 25.67° (17). Because solid pyrrolidinone monohydrate separates at room temperature over a wide range of compositions (16), measurements for the water–pyrrolidinone system were made at temperatures above its melting point of 30.4°.

Acetone[2] was dried with anhydrous sodium sulfate and distilled twice from a 4-Å molecular sieve. Its normal boiling point, refractive index, and density at 25° (Table I) are in good agreement with published values (18, 19).

Water was double distilled. Water–solvent mixtures were prepared in batches of ~100 g by weighing the two liquids to the nearest milligram. Selected properties of the six purified liquids are listed in Table I.

Methods—The temperatures during the measurements were maintained constant within $\pm0.01°$. Viscosities were measured with Cannon–Fenske glass capillary viscometers for which the flow times exceeded 250 sec. The kinetic energy correction was thus too small to be considered. Duplicate measurements, made on fresh portions of the solutions, agreed within 0.2 sec. Densities were determined with a Sprengel–Ostwald pycnometer of 25-ml capacity. Duplicate measurements were identical within ±0.00003 g/ml or better.

RESULTS

Evaluation of Three Methods—The three viscometric methods for determining the composition at which binary mixtures of miscible liquids are most extensively associated were applied to aqueous solutions of acetone, dimethyl sulfoxide, dioxane, propanol, and pyrrolidinone. The data are plotted in Figs. 1–9 and summarized in Table II.

The activation energies for viscous flow for the various aqueous solvent systems were computed as follows. For acetone, new viscosity data at 20 and 25° were obtained because the ΔE values calculated from Ref. 19 as a function of x_2 were too irregular. While ΔE went through a maximum at $x_2 = 0.24$, $\Delta\phi$ went through maxima at $x_2 = 0.26$ for 20° and at $x_2 =$

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[1] Practical grade, Eastman Organic Chemicals.
[2] ACS reagent, spectro grade, Eastman Organic Chemicals.

Table I—Some Properties of Purified Materials

Solvent	Normal Boiling Point	Viscosity, cps, at 20.00°	Viscosity, cps, at 25.00°	Density at 25°, g/ml	Refractive Index at 25°[a]
Water	100.0°	1.0020	0.8903	0.9971	1.3325
Acetone	56.15°	0.3175	0.3028	0.7845	1.3563
Dimethyl sulfoxide	18.53°[b]	2.207	2.000	1.0957	1.4768
1,4-Dioxane	101.4° 11.81°[b]	1.310	1.196	1.0280	1.4198
1-Propanol	97.2°	2.193	1.938	0.7997	1.3833
2-Pyrrolidinone	25.64°[c]	9.109[d]	7.693[e]	1.0996[d] 1.0958[e]	—

[a] Sodium D line. [b] Melting point. [c] Freezing point. [d] At 35.00°. [e] At 40.00°.

0.25 for 25° (Figs. 1 and 3). These three values of x_2 are identical within the precision of the methods.

The ΔE values for water–dimethyl sulfoxide mixtures (Fig. 3) are based on viscosity data of Ref. 20 at 25 , 35, and 45°; of Ref. 21 at 25 and 45°; and on new data at 20° combined with published data at 25° (5). The three sets of data agree well with one another. The ΔE values for water–dioxane mixtures (Fig. 6) are based on data of Ref. 22 at 20, 25, and 30° plus new data at 20° combined with published data at 25° (1, 23).

The viscosity data of Refs. 3 and 24 for water–propanol mixtures are in good agreement. The ΔE values are based on data of both references at 25 and 30°. The melting points of solid pyrrolidinone and its monohydrate, 25.6 and 30.4°, respectively (16, 17), require higher working temperatures. Published viscosity data at 31, 35, 40, 45, and 50° (17) were supplemented by new data at 37 and 45°, especially for determining ΔE (Fig. 8).

The disparity between the viscosities of the second liquid and water is relatively small for acetone (1:3 ratio; seventh column of Table II), dimethyl sulfoxide and propanol (2:1 ratio), and dioxane (approximately equal). Therefore, the Kendall equation (Eq. 1) should provide the correct fluidity or viscosity in the absence of association. Consequently, the composition of maximum deviation, $\Delta\phi$, defined by Eq. 2 should be the composition corresponding to the highest hydration.

The applicability of the method based on the Kendall equation is corroborated by the excellent agreement between the composition of maximum hydration, x_2, obtained from $\Delta\phi$ and ΔE for the first four liquids in Table II (compare the x_2 values in the second and sixth columns). The x_2 values calculated by the Kendall–Monroe equation (Eq. 4) and $\Delta\eta$ (Eq. 5), shown in the fourth column, disagree with the x_2 values determined by the other two methods.

The following additional point confirms the use of $\Delta\phi$ rather than $\Delta\eta$ for the first four systems. The maximum deviation in $\Delta\phi$ and ΔE for water–dioxane mixtures occurred at $x_2 = 0.20$ and 0.19, corresponding to a maximum hydration ratio of four water molecules per dioxane molecule or two water molecules per ether group. This hydration ratio of two is to be expected because each ether oxygen has two lone or unshared electron pairs. The same ratio also was found experimentally for linear polyfunctional ethers (1, 8). The x_2 value corresponding to a maximum in $\Delta\eta$, 0.23, would result in a hydration ratio of 3.35 or only 1.67 water molecules per ether group.

The viscosity of pyrrolidinone is 12–13 times higher than that of water at comparable temperatures, indicating that the Kendall–Monroe equation and $\Delta\eta$ rather than the Kendall equation and $\Delta\phi$ should provide the composition corresponding to maximum hydration. Both ΔE and $\Delta\eta$ result in $x_2 = 0.51$ for maximum hydration, compared to $x_2 = 0.15$
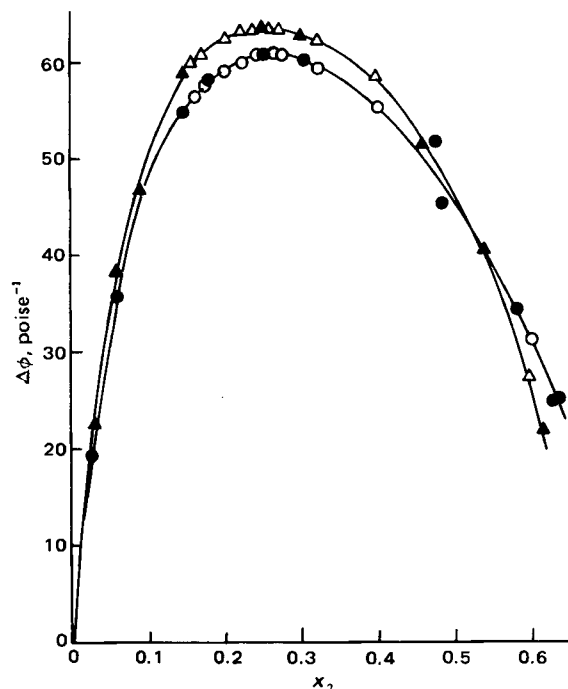

Figure 1—*Difference between calculated and experimental fluidities of water–acetone mixtures as a function of the mole fraction, x_2, of acetone. Key: ●, Ref. 19 at 20°; ○, present work at 20°; ▲, Ref. 19 at 25°; and △, present work at 25°.*

from $\Delta\phi$. The following is direct evidence for the correctness of the unit hydration ratio in liquid water–pyrrolidinone mixtures and of the methods for determining this ratio. The solid monohydrate has a congruent melting point at 30.4°. The maximum in the water–pyrrolidinone phase diagram corresponding to this compound is relatively sharp rather than flat (16). These facts indicate that the monohydrate is stable in the liquid state above the melting point as well as in the solid state below it and that dissociation in the melt at temperatures close to the melting point is not extensive (25). Hence, the monohydrate largely persists over the 31–45° range in which the viscosity measurements were conducted.

Precision of Three Methods—The points of most plots of $\Delta\phi$ and $\Delta\eta$ versus x_2 fell right on the curves because the usual experimental errors have only moderate effects on $\Delta\phi$ and $\Delta\eta$. Compositions of maximum deviation can be located with a precision of 0.005. Extensive sets of viscosity data by different investigators agreed within 0.01 of the x_2 value corresponding to maximum hydration.

The viscosities of water and the other five pure solvents were determined by five or more measurements each and were practically identical with the literature values reported for the carefully purified liquids at comparable temperatures. If the viscosities of the pure components are assumed to be free of experimental error, the standard deviation of $\Delta\eta$ is the same as that of $\eta_{12\ exp}$ according to Eq. 5. Since fluidity is the reciprocal of viscosity, the standard deviation of $\phi_{12\ exp}$ and $\Delta\phi$ is equal to the standard deviation of $\eta_{12\ exp}$ divided by the square of that viscosity (26).

Table II—Maximum Hydration of Organic Solvents According to the Three Viscometric Methods

Second Component	Compositions of Maximum Δ as Mole Fraction x_2 and Relative Deviations According to					Ratio (η_2/η_{H_2O}) at 25°	Hydration Ratio[f] (Molecules Water / Molecule Second Component)
	$\Delta\phi$[a]	Relative Deviation ϕ[b], %	$\Delta\eta$[c]	Relative Deviation η[d], %	ΔE[e]		
Acetone	0.25	78	0.17	—	0.24	0.34	3.0
Dimethyl sulfoxide	0.23	208	0.32	—	0.26	2.25	3.2
Dioxane	0.20	107	0.23	—	0.19	1.34	4.1
Propanol	0.15	142	0.24	—	0.15	2.18	5.7
Pyrrolidinone	0.15	—	0.51	49	0.51	12.7[g]	1.0

[a] Calculated with Eq. 2 at 25° except for pyrrolidinone. [b] Calculated with Eq. 3. [c] Calculated with Eq. 5 at 25° except for pyrrolidinone. [d] Calculated with Eq. 6. [e] Calculated with Eq. 8 or 9. [f] Based on weighted average of x_2 from $\Delta\phi$ (first four systems) or $\Delta\eta$ (last system) and ΔE. [g] At 35°.
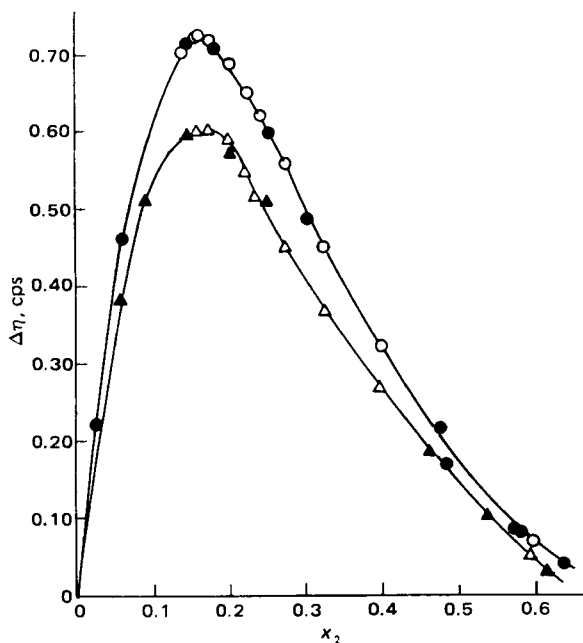
Figure 2—*Difference between experimental and calculated viscosities of water–acetone mixtures as a function of the mole fraction, x_2, of acetone. Key:* ●, *Ref. 19 at 20°;* ○, *present work at 20°;* ▲, *Ref. 19 at 25°; and* △, *present work at 25°.*

Experimental errors in the viscosity and temperature measurements greatly affect the activation energy values. Points of ΔE versus x_2 plots were more widely scattered about the curves than those of the other two methods, and some published sets of η versus x_2 values at different temperatures could not be used due to lack of precision in the viscosity measurements.

The experimental errors in maintaining and measuring temperatures were small compared to those incurred in measuring viscosities. Since ΔE and T are exponential terms in Eq. 7 or, alternatively, since viscosity appears as a logarithmic term in Eqs. 8 and 9, the experimental errors in η affect ΔE less than would comparable errors in T (26). However, two
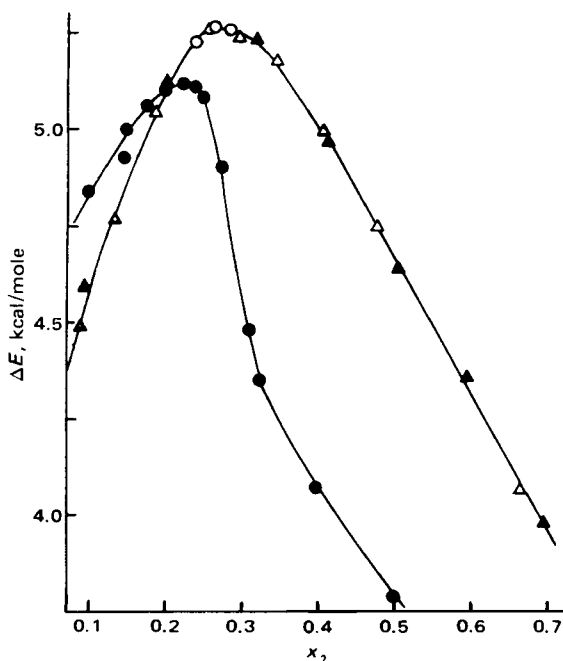

Figure 3—*Activation energies for viscous flow of water–acetone and water–dimethyl sulfoxide mixtures as a function of the mole fraction, x_2, of the organic liquids. Key:* ▲, *dimethyl sulfoxide, Ref. 20;* △, *dimethyl sulfoxide, Ref. 21;* ○, *dimethyl sulfoxide, present work; and* ●, *acetone, present work.*
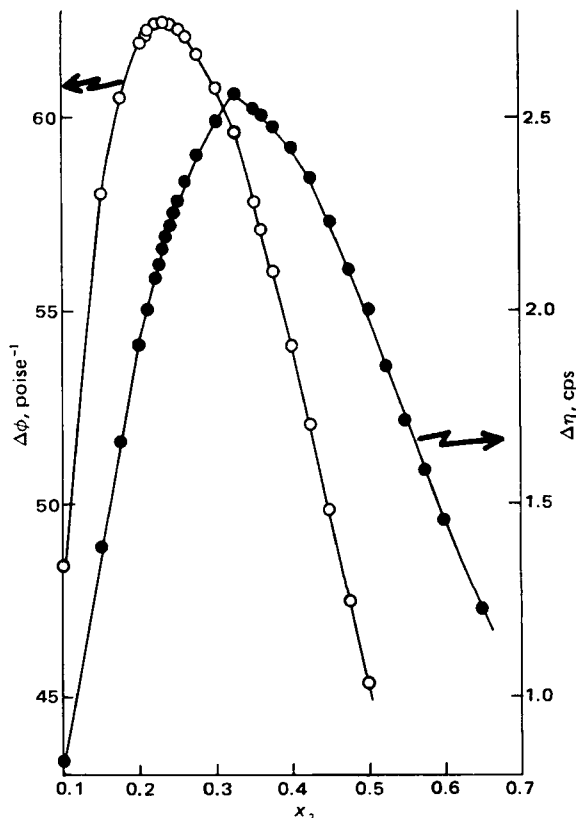

Figure 4—*Differences between calculated and experimental fluidities and viscosities of water–dimethyl sulfoxide mixtures as a function of the mole fraction, x_2, of dimethyl sulfoxide at 25°. Key:* ○, $\Delta\phi$; and ●, $\Delta\eta$.

or more pairs of η, T measurements are required to determine each value of the dependent variable ΔE to eliminate the unknown preexponential factor A, which varies with composition. This requirement raises the standard deviation of ΔE substantially, increasing it above the standard deviations of $\Delta\phi$ and $\Delta\eta$.

Use of the activation energy for viscous flow to determine the composition of maximum association between two liquids thus requires a larger number of more accurate viscosity measurements than does use of the maximum deviation in fluidity or viscosity. The present values for x_2 of maximum hydration obtained from maxima in activation energies are only good to ±0.015. The greatest uncertainty is in the water–dimethyl sulfoxide and water–pyrrolidinone systems, where the curves have flat peaks.

STRUCTURAL CONSIDERATIONS

Possible structures for the most extensively hydrated species prevalent in the water–solvent systems are discussed here. The 3:1 hydration ratio found in the acetone and dimethyl sulfoxide systems is probably represented (5) by Structure I, where two water molecules are hydrogen bonded to the carbonyl or sulfoxide oxygen while a third water molecule is associated with the organic molecule by attraction between the negative end of its dipole and the positive end of the carbonyl or sulfoxide dipole.

IR studies (27) showed that carbonyl groups can bind two water molecules through their two lone electron pairs. Hydrogen bonding increases
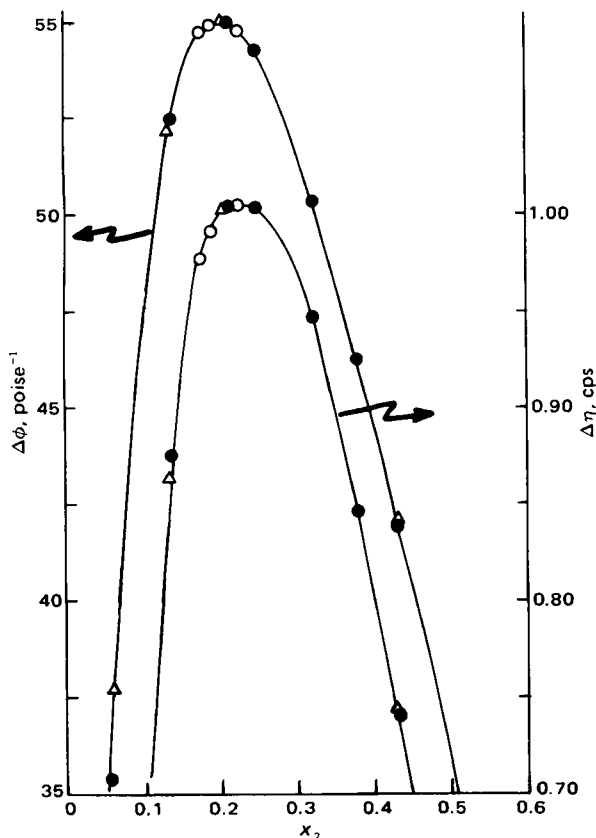

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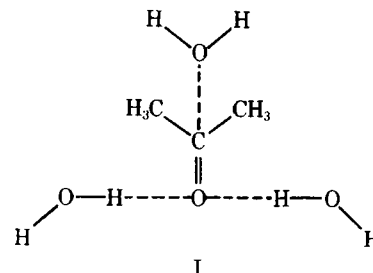
Figure 5—Differences between calculated and experimental fluidities and viscosities of water-dioxane mixtures as a function of the mole fraction, x_2, of dioxane at 25°. Key: O, Ref. 1; ●, Ref. 22; and △, Ref. 23.
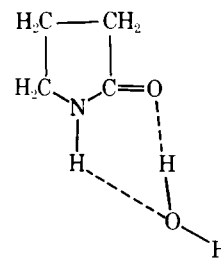
II

the dipole moment of the carbonyl group, enhancing its binding of a third water molecule by dipole–dipole attraction.

The three aprotic solvents acetone, dimethyl sulfoxide, and dioxane can only act as proton acceptors in hydrogen bonding with water. The simple and integer hydration ratios of 3:1 for the carbonyl and sulfoxide groups and 2:1 for the ether group may be due to this fact. The high and fractional hydration ratio of propanol probably results because this solvent acts as a proton donor as well as acceptor, forming hydrogen-bonded clusters consisting, on the average, of 5.67 water molecules for each propanol molecule. Hydrophobic interaction (28) probably plays a role in forming such clusters—viz., the structure of the water molecules surrounding the normal propyl chain is enhanced or tightened. Accordingly, such clusters may consist of water molecules hydrogen bonded to the hydroxyl group of propanol and other water molecules bunched around its hydrocarbon chain and hydrogen bonded to each other.

The following two experimental observations are consistent with the existence of such clusters and with the enhancement of the water structure around the propyl chain (3). In the homologous series of lower alcohols, the hydration ratio at 25° decreases with the hydrocarbon chain length of the alcohol, from 5.7 for 1-propanol to 4.0 for ethanol and 1.4 for methanol. For propanol, the hydration ratio or cluster size decreases with increasing temperature, being 5.7, 5.3, 4.9, and 4.6 at 25, 30, 40, and 50°, respectively. The hydration ratio of ethanol decreases merely from 4.0 to 3.7 while that of methanol remains practically constant, increasing from 1.4 to 1.5 between 25 and 50° (3). The effect of alkyl chain length on the hydration of monofunctional alcohols and aprotic solvents is under investigation.

The monohydrate of pyrrolidinone is probably represented chiefly by Structure II, where the hydrogen-bonded water molecule participates in a six-membered ring.

COMPARISON WITH OTHER METHODS

Other Viscometric Methods—Viscosity maxima for binary liquid mixtures have frequently been reported. For instance, the compilation of Raridon and Kraus (29) covered 39 aqueous mixtures of organic sol-
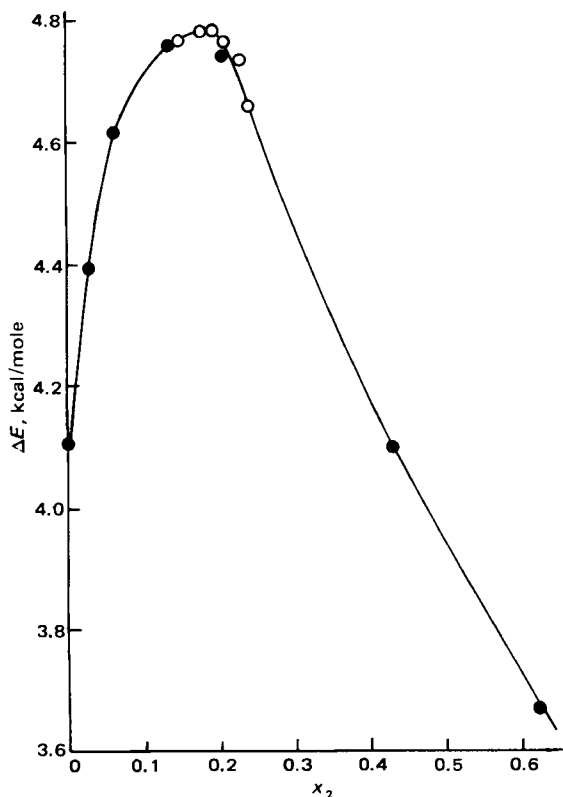

Figure 6—Activation energy for viscous flow of water-dioxane mixtures as a function of the mole fraction, x_2, of dioxane. Key: ●, Ref. 22; and O, present work.
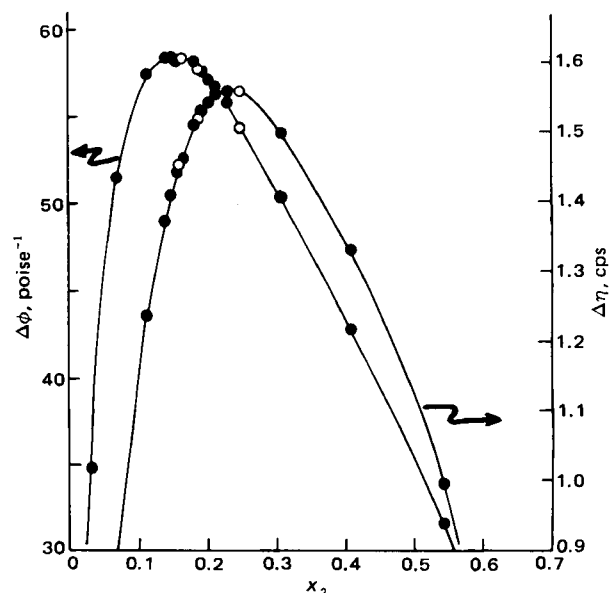

Figure 7—Differences between calculated and experimental fluidities and viscosities of water-propanol mixtures as a function of the mole fraction, x_2, of propanol at 25°. Key: O, Ref. 3; and ●, Ref. 24.
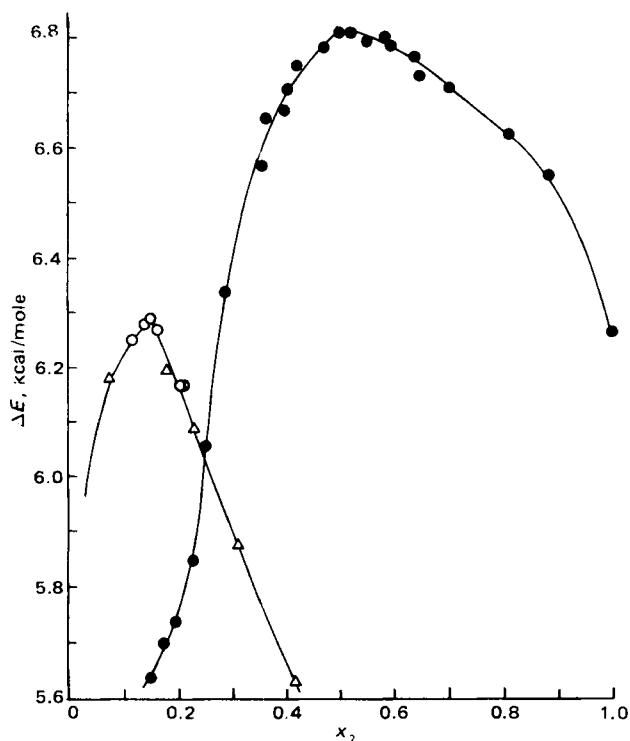
Figure 8—*Activation energies for viscous flow of water-propanol and water-pyrrolidinone mixtures as a function of the mole fraction, x_2, of the organic liquids. Key:* O, *propanol, Ref. 3;* △, *propanol, Ref. 24; and* ●, *pyrrolidinone, present work.*

$$d = \frac{\log (\phi_{12\,calc}/\phi_{12\,exp})}{x_1 x_2}$$ (Eq. 11)

They claimed that the empirical parameter d provides a useful measure of the interaction between pairs of liquids, reaching a maximum at the composition of strongest interaction (32). One shortcoming of their work is that only four mixtures were determined for each of the 14 binary systems, making the location of the composition corresponding to the maximum value of d for each system vague.

A more serious shortcoming is that the 14 pairs of liquids studied all had viscosities of the same order of magnitude. If the present data for the water-pyrrolidinone system are used to calculate d by Eq. 11, the maximum value of d is reached at a mole fraction of pyrrolidinone close to unity, corresponding to a hydration ratio close to zero. Thus, Fort and Moore's treatment has the same shortcoming as the Kendall equation, which it resembles. It fails for binary systems where one of the two components has an appreciably higher viscosity than the other. The only universal viscometric method for determining the composition of maximum association, applicable to pairs of liquids of widely differing as well as of comparable viscosities, is the one based on the activation energies of viscous flow described previously.

Other Transport Properties—Differential diffusion coefficients in the water–acetone system at 25° (33, 34), as well as at 35, 45, and 55° (33), went through minima at a mole fraction of acetone of about 0.25, confirming the maximum hydration ratio of 3:1 obtained by the viscometric methods. Relative deviation, in percent, is defined by equations analogous to Eqs. 5 and 6, with viscosity replaced by the differential diffusion coefficient. The relative deviations of the latter at the composition of maximum deviation were in the −200 to −300% range.

For the systems of deuterated water–dimethyl sulfoxide and water–deuterated dimethyl sulfoxide at 26°, self-diffusion measurements were made in x_2 increments of 0.1. Minima in the self-diffusion coefficients of water and of dimethyl sulfoxide were observed at a mole fraction of dimethyl sulfoxide of ∼0.3. This composition could correspond either to the present 3:1 or to the lower 2:1 hydration ratio. The measurements were made by NMR, using a pulsed magnetic field-gradient spin-echo technique (35).

Compound Formation—The most direct corroboration for the maximum hydration ratio is the existence, on the binary phase diagram, of a solid hydrate with a congruent melting point stable at lower temperatures. In agreement with the present hydration ratios of 3:1 for dimethyl sulfoxide and 1:1 for pyrrolidinone, a solid trihydrate was isolated for the former (36) and a monohydrate was isolated for the latter (16). The other solvents form no stable solid hydrates (37).

Thermodynamic Parameters—When water is mixed with aprotic solvents, hydrogen bonds between water molecules are broken while hydrogen bonds between water and solvent molecules are formed. Hydrogen bonds of protonated solvents like propanol are broken as well. The enthalpy of mixing depends in part on the difference between the numbers and energies of these two or three kinds of hydrogen bonds. The breaking up of clusters of water molecules when adding solvent or of clusters of solvent molecules when adding water increases the entropy of mixing while the association between water and solvent molecules decreases it. The net entropy change of mixing depends in part on the difference between the numbers and sizes of these two or three types of clusters. Enthalpy and entropy of mixing thus depend on the difference between two opposite processes, and their variation with composition does not provide a good indication of the composition of maximum association between water and the solvent.

Dimethyl sulfoxide and acetone can bind only two water molecules by hydrogen bonding (Ref. 27 and below). The third water molecule is held by Keesom forces, which are considerably weaker than hydrogen bonds and are probably not detected in calorimetric measurements. This difference in bond energies is another reason why thermodynamic functions are not reliable parameters for determining the maximum hydration of solvents. Excess functions are used in the discussion here since they represent the magnitude of deviation from ideality.

The maximum hydration ratio of dioxane is 4:1, with two water molecules hydrogen bonded to each ether group (1, 8, and present results, Table II). The excess enthalpy of mixing goes through a minimum at a mole fraction of dioxane of 0.14 or 0.15 (37–39), which would correspond to a hydration ratio of 6.1 or 5.7:1, while the excess entropy of mixing goes through a minimum at $x_2 = 0.27$ (37). Excess enthalpy and entropy of mixing are thus at variance with one another and with previous and present results.

Mixing of water and dimethyl sulfoxide is noticeably exothermic. The excess enthalpy of mixing at 25° goes through a minimum at mole frac-

vents at 25°. Viscosities were measured at only five compositions for each binary system, making the determination of the composition of maximum viscosity by interpolation uncertain. Their estimated x_2 values corresponding to maximum viscosity were 0.14 for acetone, 0.35 for dimethyl sulfoxide, 0.24 for dioxane, and 0.29 for propanol (29).

Viscosity maxima in binary solvent mixtures are of practical importance, e.g., when using such mixtures as reaction media, but do not necessarily coincide with the maximum association between the two solvents. As was pointed out in several publications as early as 1913 and 1917, the most extensive association between two liquids, as well as the possible formation of stoichiometric complexes of the highest solvation number between them, occurs at the composition at which the *deviation* of the experimental viscosity function goes through a maximum rather than at the composition of the viscosity maximum (1, 7, 10, 14, 22). Furthermore, the choice of the correct viscosity function for calculating additive viscosities is important. This requirement was demonstrated in the present work by the discrepancies between the compositions of maximum deviation from experimental viscosities or fluidities calculated with the Kendall (Eq. 1) and Kendall–Monroe (Eq. 4) equations.

Despite these considerations, the maximum in the viscosity of water–dimethyl sulfoxide mixtures at approximately $x_2 = 0.35$ (20, 21, 30–32) has been attributed to a 2:1 association complex (20, 21, 30, 31).

The following are additional arguments against equating the composition of maximum viscosity with the composition of maximum association. With water–acetone mixtures, maximum viscosity at room temperature was reached at $x_2 = 0.14$ (19, 29). This composition would correspond to a hydration ratio of 6, which is improbable, because six water molecules cannot be in close contact with a single carbonyl group. In the water–pyrrolidinone system, the highest viscosity is that of pure pyrrolidinone; i.e., there is no viscosity maximum at an intermediate composition. However, there is a pronounced association maximum at the composition of the monohydrate, signaled by a maximum in the deviation of the experimental viscosity from that calculated by Eq. 4 at $x_2 = 0.50$, which amounts to one-half of the experimental viscosity.

Fort and Moore (32) introduced a correction term into the Kendall equation (Eq. 1), changing it to:

$$\log \eta_{12\,exp} = x_1 \log \eta_1 + x_2 \log \eta_2 + x_1 x_2 d$$ (Eq. 10)

Comparison of Eq. 10 with Eq. 1 results in:

Table III—Maximum Deviations of Density and Dielectric Constant for Five Water–Solvent Systems

	Maximum Deviations According to									
	Density					Dielectric Constant				
Solvent	Tempera- ture	x_2	Hydration Ratio[a]	Relative Deviation[b], %	Reference	Tempera- ture	x_2	Hydration Ratio[a]	Relative Deviation[b], %	Reference
Acetone	20°	0.45	1.2	−4.3	18, 19, p[c]	25°	0.39	1.6	−49	58
Dimethyl sulfoxide	25°	0.30	2.3	+5.6	5	25°	0.25	3.0	+4.1	5, 59
Dioxane	25°	0.24	3.2	+3.0	15	25°	0.32	2.1	−182	60, 61
Propanol	25°	0.37	1.7	−6.1	3, 24	20°	0.36	1.8	−72	58
Pyrrolidinone	35°	0.33	2.0	+4.8	17, p	35°	0.50	1.0	−17	17
	40°	0.31	2.2	+4.6	17, p	40°	0.50	1.0	−17	17

[a] Ratio water molecules to molecule solvent. [b] Calculated with equations analogous to Eqs. 5 and 6. [c] Present work.

tions of dimethyl sulfoxide of 0.34 (40, 41) or 0.36 (42), which would translate into hydration ratios of 1.9 or 1.8:1. The excess enthalpy of mixing in the water–acetone system at 20° goes through a minimum at a mole fraction of acetone of 0.18 (43). This composition would correspond to a hydration ratio of 4.6:1.

Heat capacities of liquid mixtures are perhaps more pertinent than enthalpies since they depend in part on the size of the clusters of associated molecules. The excess molal heat capacity at 25° goes through a maximum at a mole fraction of acetone of 0.24, corresponding to the present hydration ratio of 3:1. It is much smaller and nearly independent of composition in the water–dimethyl sulfoxide system (44). The cohesive energy density of binary mixtures depends in part on the extent of association since it represents the energy of vaporization per molar volume. The excess cohesive energy density at 25° goes through a maximum at a mole fraction of dimethyl sulfoxide of 0.25 (45), corresponding to the present hydration ratio of 3:1.

Spectroscopic Methods—The main difficulty in using absorption spectroscopy to determine the maximum hydration of organic solvents in binary mixtures with water is that spectroscopic methods are restricted almost exclusively to the strongest intermolecular bonds—viz., hydrogen bonds. Dipole–dipole interactions between molecules have, in most cases, only minor effects on their IR, UV, Raman, and NMR spectra and usually go undetected. Additional reasons why spectroscopic methods are not well suited for determining maximum hydration are the frequent use of a third, "inert" solvent and the difficulty of proper band assignment.

The maximum hydration ratio of pyrrolidinone was identified correctly as unity from the IR spectra (46) because the attraction between water and pyrrolidinone is based mainly on hydrogen bonds. In the water–acetone system, a maximum of two water molecules can be bound to the carbonyl group by hydrogen bonds (27), which is to be expected in view of the fact that the carbonyl oxygen has two unshared electron pairs. IR (47–49), UV (49), and NMR (50) measurements have identified mainly water–acetone "complexes" of 1:1 and 1:2 molar ratios, in part because this was the range of compositions in which most spectra were investigated. Both 2:1 and 3:1 or 4:1 complexes were reported also, although it is difficult to reconcile the binding of more than two water molecules by hydrogen bonds to one carbonyl oxygen having two lone electron pairs. Water molecules bound to acetone by dipole–dipole forces (Structure I) could not have been detected by the spectroscopic techniques used in Refs. 47–50.

In the water–dimethyl sulfoxide system, IR (41, 51), UV (41), Raman (52, 53), and NMR (54) spectra have identified 2:1, 1:1, and 1:2 complexes. The third water molecule, bound to dimethyl sulfoxide by dipole–dipole forces (5, 36), cannot be disclosed by these spectroscopic techniques.

NMR relaxation techniques are better suited to determine maximum hydration because they depend largely on the size and symmetry of water–solvent clusters. The reorientation of these clusters or complexes is the most important motion in the relaxation process. In particular, excess nuclear spin-lattice relaxation times, T_1, reach a minimum and excess relaxation rates, $1/T_1$, reach a maximum at the composition corresponding to the maximum intermolecular association (55, 56). Use of mixtures of deuterated acetone with water and heavy water with acetone resulted in a maximum relaxation rate at 25° at a mole fraction of acetone of ~0.20 (55). Since the authors only studied compositions of x_2 = 0.10, 0.20, and 0.40 in the pertinent range, the maximum could equally well be located at x_2 = 0.25 but not as high as 0.33. Accordingly, the maximum hydration ratio of acetone lies between 4 and 2.7:1, a result compatible with the present 3.0:1 value. The use of excess functions might have shifted the x_2 value corresponding to maximum hydration.

The water–dimethyl sulfoxide system was investigated over narrower composition intervals. The absolute value of the excess relaxation time went through a maximum at a mole fraction of dimethyl sulfoxide of 0.25,

leading the author to describe "compound formation" resulting in a 3:1 molecular complex (56). While this result does not preclude the existence of a 2:1 complex in mixtures of lower water content, the most highly hydrated complex has a 3:1 hydration ratio, in agreement with the present results. Other studies of proton spin-lattice plus spin-spin relaxation times over a range of temperatures found maxima in relaxation rates at a mole fraction of dimethyl sulfoxide of about 0.35 (57), but these authors used $1/T_1$. The use of excess relaxation rates would shift the maxima toward somewhat lower dimethyl sulfoxide mole fractions or higher hydration ratios.

Density—Compositions of maximum deviations and relative deviations of calculated from experimental densities for the five binary systems are summarized in Table III. Positive relative deviations indicate that experimental densities were higher than calculated densities, i.e., that volume contractions occurred during mixing. In aqueous mixtures of acetone and propanol, experimental densities were actually smaller than those calculated. The absolute values of the relative deviations are small, ranging from 3 to 6%.

If the compositions of maximum density deviation corresponded to maximum hydration ratios, these would be quite different from the ratios obtained by viscometry. However, excess densities do not necessarily reach maxima at the composition of most extensive association for the following reason. When two highly structured liquids like water, propanol, or pyrrolidinone are mixed, the structures of both liquids are broken up and new structures or association complexes are formed. Even acetone and dioxane, which have little structure of their own in the pure state,
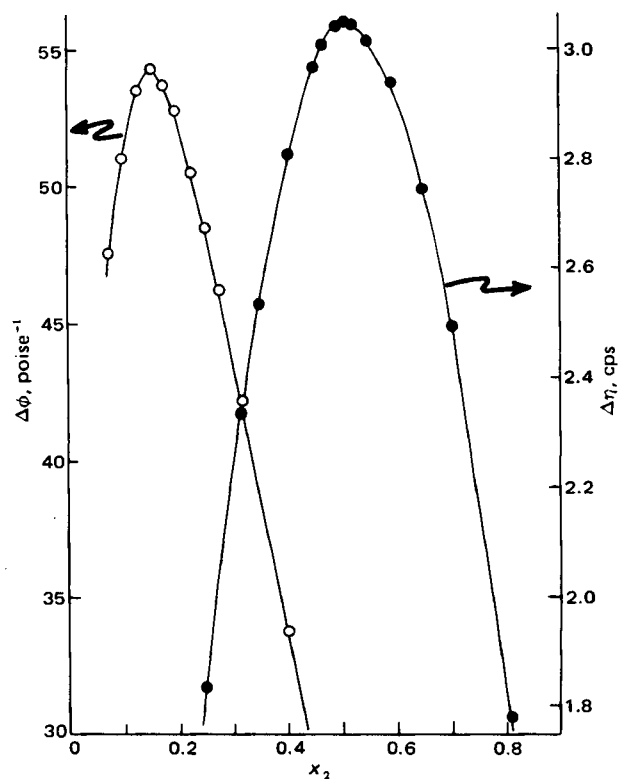

Figure 9—Differences between calculated and experimental fluidities and viscosities of water–pyrrolidinone mixtures as a function of the mole fraction, x_2, of pyrrolidinone at 37°. Key: O, $\Delta\phi$; and ●, $\Delta\eta$.

are effective in breaking up the structure of water in aqueous mixtures. Calculated densities depend on the density and, hence, on the short-range order and structure in pure water and in the second pure liquid. These properties of one pure liquid are unrelated to corresponding properties of the second pure liquid and of the clusters formed by association between the two. A highly structured liquid like propanol and a liquid with little association like acetone both caused monotonic decreases in density when mixed with water while aqueous mixtures of the nonpolar dioxane had a density maximum at an intermediate composition. Therefore, excess density does not constitute a suitable property for determining the composition of maximum association, contrary to what had been assumed by the author (15).

Dielectric Constants—Deviations of experimental dielectric constants from those interpolated according to equations analogous to Eqs. 5 and 6 were calculated from literature data for the five aqueous systems. Compositions corresponding to the maximum deviations, hydration ratios corresponding to these compositions, and relative deviations are listed in Table III. Hydration ratios agree with those obtained from the viscometric methods in the cases of dimethyl sulfoxide and pyrrolidinone. However, in the former system, the experimental dielectric constants were higher than those calculated for the corresponding compositions, resulting in positive relative deviations; in the latter system and in the other three, the calculated dielectric constants were higher than the corresponding experimental values.

Pure propanol and, presumably, liquid pyrrolidinone as well have high values for the Kirkwood correlation factor (62). Those of the aprotic solvents acetone and dimethyl sulfoxide are low, namely, close to unity, while dioxane has a zero dipole moment (62). When added to water in low concentrations, propanol, acetone, and dioxane decrease the dielectric constant of water. In the water–acetone and water–dioxane systems, the correlation factors (62) and the experimental dielectric constants (58, 60, 61) decrease monotonically with increasing mole fraction of the organic component over the entire range of compositions. The addition of water to propanol and of propanol to water break their respective structures, and the correlation factor of the mixtures reaches a minimum around $x_2 = 0.5$ (62). Surprisingly, the experimental dielectric constants of water–propanol (58) and water–pyrrolidinone (17) mixtures decrease monotonically with increasing x_2 over the entire range of compositions.

The case of dimethyl sulfoxide is even more puzzling since its aqueous mixtures constitute the only one of the five systems studied in which experimental dielectric constants are larger than the corresponding calculated values. The cause for the high dielectric constant of pure dimethyl sulfoxide (46.4 at 25° from Ref. 59) is poorly understood (63). Therefore, it seems useless to speculate on why the deviations of the dielectric constants are positive in the water–dimethyl sulfoxide system and negative in the other four systems. The agreement between the compositions corresponding to a maximum positive deviation in the dimethyl sulfoxide mixtures and a maximum negative deviation in the pyrrolidinone mixtures and the compositions of maximum hydration obtained by the viscometric methods may be fortuitous. Until the theory for dielectric constants of aqueous solutions of nonelectrolytes is better understood (62), it seems preferable not to use the excess dielectric constants of such mixtures for determining the composition of maximum hydration.

Miscellaneous Methods—Ultrasonic velocity in water–dimethyl sulfoxide mixtures reaches a maximum at a mole fraction of dimethyl sulfoxide of 0.27 at 20° (64). The excess velocity, i.e., the deviation of the experimental velocity from the velocity calculated by equations analogous to Eqs. 5 and 6, reaches a maximum at $x_2 = 0.25$. The maximum relative deviation, which occurs at that composition, amounts to 16%.

The adiabatic compressibility at 20°, calculated as the reciprocal of the product of density and the square of the sound velocity, goes through a minimum at $x_2 = 0.27$ (64). The excess adiabatic compressibility goes through a minimum at a slightly lower x_2 value. The relative deviation reaches a maximum value of −42% at that composition. The excess compressibility of a mixture is expected to reach a minimum and the excess sound velocity is expected to reach a maximum at the composition at which the intermolecular association is most extensive. Therefore, these data confirm the present hydration ratio of 3:1.

The solubility of hydrogen at 25° and a constant partial pressure of 1 atm in water–dimethyl sulfoxide mixtures goes through a minimum at a mole fraction of dimethyl sulfoxide of about 0.28 (65). Since solubilities were measured in mole fraction increments of 0.2, the minimum could be located equally well at $x_2 = 0.25$ or 0.33, corresponding to hydration ratios of 3:1 or 2:1. The hydrogen molecule, as a small and nonpolar probe, should cause only minimal disturbance of the association clusters between

water and dimethyl sulfoxide molecules, so the minimum solubility should occur at the composition of maximum association. Symons (65) interprets his measurements in terms of an equilibrium between a 3:1 and a 2:1 water–dimethyl sulfoxide complex. His maximum hydration of 3:1 is in agreement with the present findings.

The reason why excess molar refraction is not suitable for determining the composition of maximum hydration is given in Ref. 5.

CONCLUSION

The composition at which water and the second liquid component are most extensively associated is marked by a minimum or maximum in an excess property of the binary mixture that expresses the difference between the experimental and the calculated values of this property rather than by a minimum or maximum in the experimental value of the property. Excess enthalpy and entropy of mixing as well as absorption spectroscopy methods only detect intermolecular association by hydrogen bonding but not by dipole–dipole attraction. When the two components interact mainly by hydrogen bonding, as in the water–pyrrolidinone system, maximum hydration ratios obtained from excess thermodynamic functions or by absorption spectroscopy agree with those obtained by viscometric methods. When additional water molecules are bound by dipole forces, spectroscopic methods result in erroneously low maximum hydration ratios comprising only hydrogen-bonded water molecules. This is the case with the water–dimethyl sulfoxide and water–acetone systems, where absorption spectra and thermodynamic excess functions identified the 2:1 hydrogen-bonded complex as possessing the highest hydration ratio, whereas transport and relaxation methods revealed the existence of the 3:1 complex.

Relaxation methods that depend on the size of the clusters or complexes give maximum hydration ratios in good agreement with viscometric methods. Since all transport properties depend on cluster size, they result in identical maximum hydration ratios when properly interpreted. These hydration ratios are relevant to chemical and biological processes affected by the solvation of functional groups.

The most direct validation of the hydration ratios determined by viscometric methods is that they agreed with the composition of solid hydrates stable at lower temperatures in the two instances where such solid hydrates exist. For instance, the fact that a solid dimethyl sulfoxide trihydrate was found demonstrates that dimethyl sulfoxide possesses the bonding capacity and geometric requirements to bind three water molecules. Any method producing a hydration ratio of <3:1 as the *maximum* ratio is in error.

The use of the activation energy for viscous flow of binary mixtures to determine the composition of maximum association requires a greater number and more accurate viscosity measurements than the use of isothermal viscosities or fluidities. By comparison with the other suitable methods already discussed, viscometric techniques require less elaborate equipment that is easier to operate, have comparable or better reproducibility, and result in relative deviations that are as large or larger.

APPENDIX: VARIATION IN SELF-ASSOCIATION OF LIQUID WATER WITH TEMPERATURE DETERMINED FROM TEMPERATURE DEPENDENCE OF ACTIVATION ENERGY FOR VISCOUS FLOW

In this section, the variation of the activation energy for viscous flow of water with temperature is used to provide a relative estimate of the degree of self-association in the pure liquid as a function of temperature. The activation energy of water, unlike that of most liquids, depends markedly on temperature because of an exceptionally extensive self-association (66–68).

The activation energies for viscous flow at constant volume of nonassociated liquids are small and independent of temperature. The experimental activation energies, ΔE, measured at constant pressure and defined by Eqs. 7–9 vary with temperature to the same limited extent as do the specific volumes and, hence, the free space or volume of the holes in these liquids (11, 13, 69). For associated liquids, the size of the holes and, therefore, the viscosities and activation energies for viscous flow are larger than for nonassociated liquids of comparable molecular size because the flow units are larger.

The degree of association decreases with increasing temperature. Since the activation energy for viscous flow is primarily expended in creating the holes or vacant sites required for flow, it too should decrease with increasing temperature. The activation energy is proportional to the size of a hole which, in turn, is proportional to the size of a flow unit and the degree of association. Therefore, any decrease of the latter with increasing

Table IV—Activation Energy for Viscous Flow, Slope of the ΔE versus Temperature Curve, and Median Cluster Size for Liquid Water

Temperature	ΔE, kcal/mole	$\dfrac{d(\Delta E)}{dT}$, kcal/mole/°K	j^a
0°	5.5		11.2[b]
10°	4.58	0.043	8.8[b]
20°	4.20	0.034	7.8[b]
30°	3.89	0.026	7.0[b]
40°	3.66	0.020	6.5[b]
50°	3.47	0.015	6.1[b]
60°	3.34	0.014	5.6[b]
70°	3.22	0.010	5.3[c]
80°	3.12	0.008	5.1[c]
90°	3.06	0.004	4.9[c]
100°	2.9		4.5[c]

[a] Median cluster size [b] From Ref. 68. [c] Calculated by Eq. 12.

temperature should be reflected in a comparable decrease in the activation energy. The variation of the activation energy with temperature can, therefore, be used as a measure of the variation in the degree of association of the liquid with temperature.

Three sets of data for the viscosity of water at 1 atm from 0 to 100° in increments of 5° are reported in the literature (66, 70). The activation energies for viscous flow derived from the three sets are in good agreement up to 70°. Table IV lists the best values of ΔE as a function of temperature and the values of the slope of the ΔE versus temperature curve, $\Delta(\Delta E)/\Delta T$, in kcal/mole/°K. As shown, ΔE decreases fast with increasing temperature near the melting point where the association of water molecules is extensive and, consequently, the reduction in association per degree temperature increase is appreciable. This reduction and the slope of the ΔE versus temperature curve level off as the temperature approaches the normal boiling point. Considering the association in liquid water in the range between its freezing point and normal boiling point, over half of the association disappears between 0 and 20° because over half of the drop in ΔE occurs over that temperature range.

The extensive dissociation of clusters of associated water molecules over a relatively narrow temperature interval above the melting point of ice is confirmed qualitatively by several techniques. Most of the investigations dealing with self-association in water are based on spectroscopic methods and provide estimates mainly for the fraction of unbonded and hydrogen-bonded protons. The various results differ considerably (51).

In a statistical thermodynamic treatment, water was assumed to consist of clusters in equilibrium having a continuous size distribution. The median cluster size, j, was calculated from partition functions and found to decrease with increasing temperature (68). These values of j, estimated between 0 and 60°, are included in Table IV. The following linear relation between ΔE and j is obtained from the tabulated data, with a correlation coefficient of 0.9995:

$$j = -2.884 + 2.555 \, \Delta E \qquad \text{(Eq. A1)}$$

The close correlation between cluster size and activation energy for viscous flow corroborates the use of the latter in estimating the relative size of the flow unit and its variation with temperature for pure, extensively associated liquids like water.

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Spectra of Radical Cations of Phenothiazine Derivatives in Solution and Solid State

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Abstract □ The UV and visible spectra of radical cations of several phenothiazine derivatives were studied using different solvents. The establishment of a relationship between these bands and the R_2 and R_{10} substituents was attempted. The influence of the disolvents on the bands also was studied. The characteristic charge transfer band was observed in the solid state using diffuse reflectance spectroscopy. The R_2 substituent did not appear to influence the band, while the R_{10} substituent influenced the band considerably, probably due to steric effects.

Keyphrases □ Phenothiazine—derivatives, spectra in solution and solid state, effect of R_2 and R_{10} substituents □ Psychotropic drugs—phenothiazine derivatives, spectra in solution and solid state, effect of R_2 and R_{10} substituents □ Spectroscopy—UV and visible spectra of phenothiazine derivatives, solution and solid state

Psychotropic drugs are fundamental in the treatment of mental disorders. Increased knowledge of the physicochemical properties of these products would help in understanding their interaction with live organisms.

One important property of these drugs is that they are oxidized easily (1). The idea that phenothiazines could act in humans in an oxidized form (2) was supported by the fact that several oxidized compounds are observed in the degradation products (3). This paper describes a study of the oxidized form of these phenothiazine derivatives in solution and in the solid state.

An attempt was made to relate the derivatives according to their R_2 and R_{10} substituents, semiconductor properties, dissociation constants (4), and ability to form complexes (5). The phenothiazine derivative cation radicals were prepared in a solid state, and their diffuse reflectance spectra were studied. The UV and visible spectra of these radicals in solution also were studied.

EXPERIMENTAL

Materials— Phenothiazine derivatives with R_2 and R_{10} substituents were used (Table I). The products were pharmacologically pure and were used as supplied commercially. Perchloric acid (70%) and potassium dichromate were the oxidizing agents. The solvents were distilled water, acetonitrile, and sulfuric acid (2 and 9 N).

A UV-visible spectrophotometer was used to obtain the solution spectra; for the diffuse reflectance spectra, the corresponding attachment was used.

Method—A literature method (6) was used to obtain the cation radicals in the solid state. The proposed formula for these products is (6):
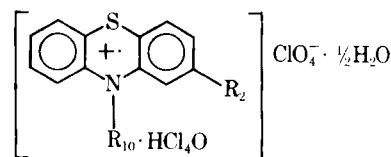
The melting points of the products ranged from 175 to 223°. The radicals rapidly dissolved in all of the solvents used. An intense color appeared, corresponding to the oxidized form. The radicals remained indefinitely stable only with 9 N H_2SO_4 due to its high acidity.

The formation of charge transfer complexes in the solid state was studied by diffuse reflectance spectroscopy. Tablet preparation was the same as that used for the IR method except that naphthalene (7) was the solvent.

RESULTS

Solutions were prepared from polycrystalline powder of the cation radicals in 9 N H_2SO_4. Table II gives the wavelengths corresponding to the absorption peaks of the radicals in 9 N H_2SO_4, both in the visible and the UV range (Fig. 1). The reference used to study the effect of the substituents was promazine.

UV Spectra—The UV spectra of derivatives with a constant R_2 substituent and various R_{10} substituents were studied. Derivatives with R_2 = H and various R_{10} substituents (I–V) showed no change from the reference spectrum. This observation showed that the R_{10} substituent does not influence the UV electron transitions. In derivatives with R_2 = Cl and various R_{10} substituents, the R_2 substituent caused a bathochromic shift of 4 nm throughout the spectrum (Table II). The second peak in the spectra of derivatives with R_2 = CF_3 and various R_{10} substituents disappeared.

Derivatives with a constant R_{10} substituent and various R_2 substituents were considered. The effect of the R_2 substituent was observed in the promazine (I and VI–VIII) and perazine (V and X–XIII) families (Table II). The chlorine derivatives featured a 4-nm bathochromic shift in all bands. The other substituents caused more pronounced shifts throughout the spectrum, together with the disappearance of the second peak [derivatives with R_2 = OCH_3 or $SO_2N(CH_3)_2$].