Hydration of Primary Alcohols

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The extent of hydration of three primary alcohols in aqueous solution was determined by means of the difference between the fluidities measured at various concentrations and calculated by the Kendall equation. These differences went through a single, pronounced maximum for each of the three binary systems, at compositions corresponding approximately to molar water–alcohol ratios of 3 to 2, 4 to 1, and 5 to 1 for methanol, ethanol, and 1-propanol, respectively. These are the compositions of maximal interaction between the alcohols and water.

DURING A STUDY of the hydration of solutions of cellulose derivatives, it became necessary to know the number of water molecules which are associated with primary hydroxyl groups of monomeric and polymeric molecules. Association in a binary liquid system can usually be detected by the deviation of the experimental values of an intensive property of the solutions from the additive values of the property, calculated by linear interpolation between the two values of that property of the two pure components as a function of composition. The stoichiometric composition of a complex formed between the two components is often that composition at which this deviation reaches a maximum. Among properties very sensitive to association is the fluidity, ϕ. Fluidity is the reciprocal of the viscosity.

The Kendall equation (*6*),

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

where x represents mole fraction and subscripts 1 and 2 refer to the two components, is obeyed by ideal or nearly ideal solutions (*3*), if the fluidities of the two pure liquids are of the same order of magnitude (*5*). Association between the two liquid components causes the observed fluidity of their mixtures to be smaller than that calculated by Equation 1 (*3, 5*).

The effect of association on the deviation of the experimentally observed from the calculated values is much larger for fluidity than for most other properties. In the case of binary systems comprising ethers and water, maximum deviations from a rectilinear dependence of fluidity on mole fraction was used successfully to determine the number of water molecules associated with each ether group (*10, 11*). The same technique is applied in the present work to three systems comprising primary alcohols—i.e., sterically unhindered hydroxyl groups—and water.

EXPERIMENTAL

Viscosity and density measurements were made to supplement the values reported in the literature, in order to determine accurately the composition corresponding to the maximum deviation in fluidity.

Absolute methanol, GC-spectrophotometric quality (Baker analyzed), was used as received for most measurements. It was free of acetone and formaldehyde by Hartley and Raikes' test (*4*). A few duplicate measurements, made after further purification of this material (*4*), gave identical density and viscosity values. Reagent grade 1-propanol (Baker analyzed) was purified according to Kretschmer (*7*). The water-alcohol mixtures were prepared in 100-gram batches by weighing out the two liquids to the nearest milligram.

The temperatures during the measurements were maintained constant within ±0.01° C. Densities were determined with a Sprengel-Ostwald pycnometer of 25-ml. capacity. Duplicate measurements were identical within ±0.00003 gram per ml. or better. Viscosities were measured with a Cannon-Fenske viscometer, which had the flow time of 286.4 seconds for water at 25° C. The kinetic energy correction was too small to be taken into account. Duplicate measurements, made on fresh portions of the solutions, agreed within 0.1 second.

RESULTS

The viscosities of methanol-water (*8*) and 1-propanol–water (*9*) mixtures were measured by Mikhail and Kimel over the complete range of composition at 25°, 30°, 35°, 40°, and 50° C. They expressed the viscosity of the mixtures as a function of the weight percentage alcohol by means of a power series containing six constants [Equation 8 (*8, 9*)]. The high accuracy of Mikhail and Kimel's work is shown by the fact that the viscosities calculated by their Equation 8 agree within 1.5% with those measured in the present work. The fluidities of the system ethanol-water were those of Bingham and Jackson (*1*). Values at intermediate mole fractions were obtained by graphical interpolation.

The differences between calculated (Equation 1) and experimental fluidities as a function of molar composition are plotted in Figures 1 to 3 for the three binary systems. Each curve had only one maximum, but the maxima were pronounced. The compositions at which the difference between the calculated and experimental fluidities reached a maximum are listed in Table I. The relative deviations in fluidity at those compositions, expressed as per cent of the experimental fluidities, were calculated as

$$\text{Rel. dev.} = 100\,(\phi_{12\text{ calcd.}} - \phi_{12\text{ exptl.}})/\phi_{12\text{ exptl.}} \qquad (2)$$

Table I. Compositions and Fluidities of Aqueous Alcohol Solutions at Points of Maximum Difference in Fluidities

Component 2	Temp., °C.	x_2	$\phi_{12\text{ exptl}}$, Poise,$^{-1}$	$\phi_{12\text{ calcd}}$,^{a} Poise,$^{-1}$	Rel. Dev.,^{b} %
Methanol	25	0.42	68.5	138.0	101
	30	0.41	77.3	150.7	95
	35	0.41	87.5	164.7	88
	40	0.40	97.6	177.6	82
	50	0.40	121.2	207.6	71
Ethanol	25	0.20	42.5	107.4	153
	30	0.21	49.4	119.2	141
	35	0.21	58.2	131.7	126
	40	0.21	67.5	145.1	115
	50	0.21_5	87.9	172.7	96
Propanol	25	0.15	41.2	99.6	142
	30	0.16	48.3	110.7	130
	35	0.16	56.5	123.1	118
	40	0.17	64.7	135.0	109
	50	0.18	81.3	160.0	97

^{a} Calculated by Equation 1. ^{b} Calculated by Equation 2.

The following conclusions can be drawn from Table I and from Figures 1 to 3. Going from propanol to ethanol to methanol, the maxima in the curves become flatter, indicating that the association complexes are less well defined. For each binary system, the maxima become somewhat sharper with increasing temperature. The implication that the association complexes are better defined at the higher temperatures is plausible if one considers that there are three competing types of association in the alcohol-water systems—alcohol-alcohol, water-water, and alcohol-water—and that the first two decrease with increasing temperature. This apparently caused the alcohol-water association to increase with increasing temperature, because both alcohol and water became more "depolymerized."

Within the 25° temperature range studied, the compositions at which the differences in fluidity are at a maximum are relatively insensitive to changes in temperature. With increasing temperature, the mole fraction of alcohol corresponding to the maximum difference in fluidity decreases slightly for methanol, is almost constant for ethanol, and increases slightly for propanol. The calculated fluidities are approximately twice as large as the experimental fluidities at the compositions of maximum difference—i.e., the relative deviations are of the order of 100%.

The water-alcohol molar ratios for the compositions of maximum difference in fluidity are approximately 3 to 2 for methanol, 4 to 1 for ethanol, and 5 to 1 for propanol.

DISCUSSION

In the case of binary systems comprising water-miscible ethers and water, the maximum differences in fluidity occurred at compositions corresponding to 2 water molecules per ether group (*10, 11*), regardless of the structure of the ether. In the case of the primary alcohols, the number of water molecules per hydroxyl group at those compositions depends largely on the hydrocarbon moiety, increasing as the number of carbon atoms increases.

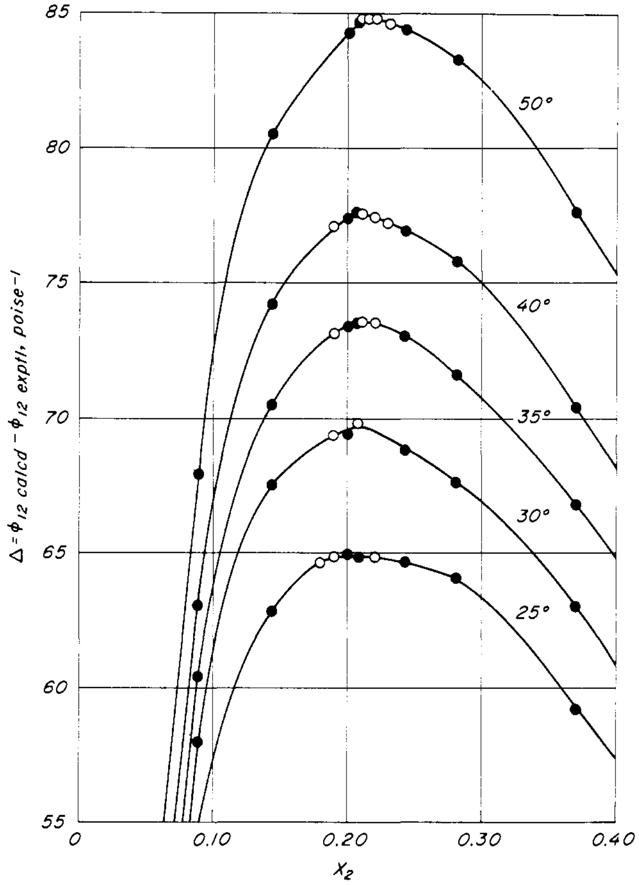

Figure 2. Differences between experimental and calculated fluidities in the system ethanol-water

● Data of Bingham and Jackson (*1*)

○ Interpolated in data of (*1*)

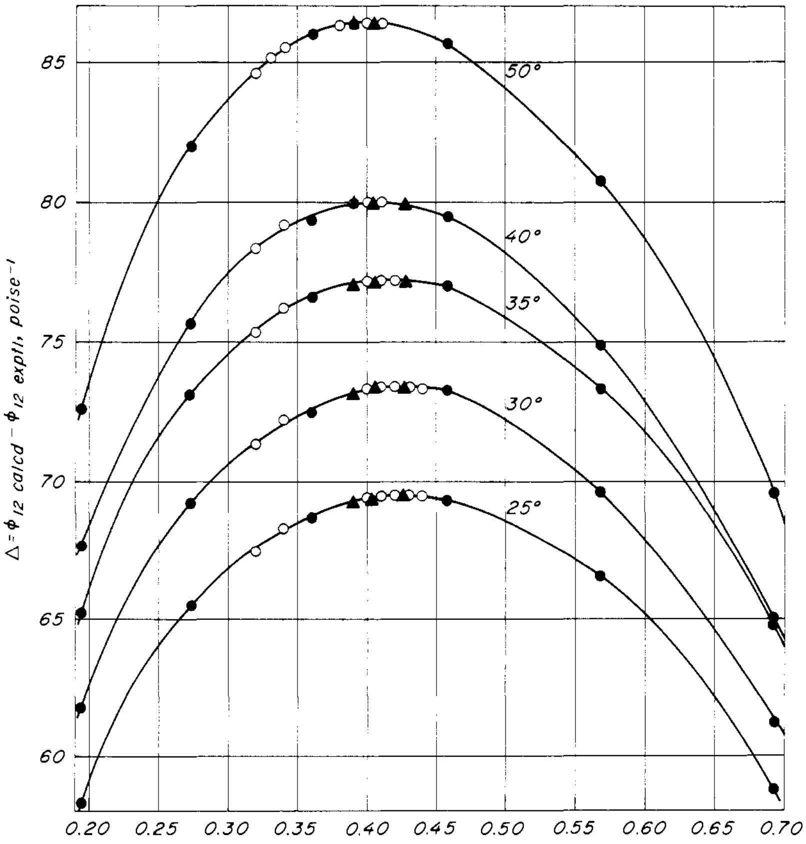

Figure 1. Differences between experimental and calculated fluidities in the system methanol-water

● Measurements of Mikhail and Kimel (*8*)

○ Calculated by Equation 8 of (*8*)

▲ Measurements, this work

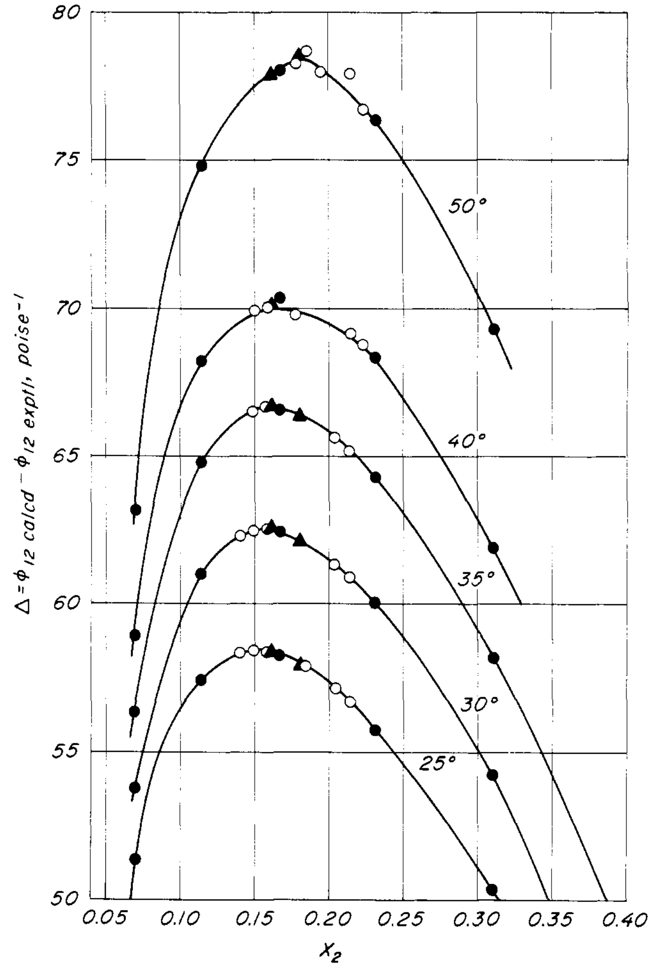

Figure 3. Differences between experimental and calculated fluidities in the system propanol-water

● Measurements of Mikhail and Kimel (9)

○ Calculated by Equation 8 of (9)

▲ Measurements, this work

Ethers are essentially nonassociated liquids and can act only as proton acceptors in hydrogen bonding. Upon mixing with water, they destroy the water structure and reduce the interaction between water molecules in favor of hydration of the ether groups. Alcohols are associated because they can act as proton donors as well as acceptors in hydrogen bonding. In pure liquid alcohols, association through hydrogen bonds produces short-chain linear polymers. In pure water, association results in three-dimensional clusters (2). When water and an alcohol are mixed, the alcohol-alcohol and water-water interactions are reduced in favor of hydration of the alcoholic hydroxyl groups, which reaches its maximum at the composition of maximum difference in fluidity. Most likely, the original structures of water and alcohol have disappeared before that point is reached.

Because both components are capable of self-association, the composition of maximum intercomponent attraction does not correspond to a simple stoichiometric relationship as it did for the ethers. In the alcohol-water systems, a balance between intracomponent hydrogen bonding and probably also hydrophobic bonding of the alcohol molecules determines the composition of maximum intercomponent attraction.

The plots of heat of mixing (ΔH^M) *vs.* composition for the three binary systems (2) resemble Figures 1 to 3. Mixing water and the alcohols in the range of temperatures studied here is an exothermic process except for the alcohol-rich part of the propanol-water system. There, a shallow endothermic maximum at $x_2 = 0.7$ exists even at 25° in addition to a steep exothermic minimum at $x_2 = 0.1$. For all three systems, the exothermic minimum in ΔH^M occurred at roughly the same x_2 values at which the maximum differences in fluidity were observed. These are then the compositions of maximal interaction between the alcohols and water. Moreover, the maxima in the ΔH^M *vs.* x_2 plots became increasingly more shallow when going from propanol to ethanol to methanol; this was also observed for the maxima in difference of fluidity.

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