Excess Thermodynamic Properties of Aqueous Alcohol Solutions

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Heats of mixing of methanol, ethanol, and propanol-2 with water were measured for isothermal-isobaric conditions of 25° C. and 1 atm. Excess entropy of mixing values were calculated by combining the experimental results with the excess free energy of mixing values available in the literature.

HEATS of mixing were determined for methanol, ethanol, and propanol-2 with water at 25° C. and 1 atm. in the course of investigating various thermodynamic properties of solutions The term heat of mixing, ΔH^M, is defined as the change in enthalpy per mole of mixture when the pure components are mixed at constant temperature and pressure. It is identical to the excess enthalpy of mixing per mole of mixture, ΔH^E. Although experimental values for these properties are available in the literature, the discrepancy between different investigators is generally greater than the claimed experimental error. Excess entropy of mixing values were obtained by combining the heat of mixing results obtained in this investigation with the excess free energy of mixing values available in the literature.

EXPERIMENTAL

Brass calorimeters of various sizes were employed in this investigation. Each calorimeter consisted of two compartments, ranging from 8 to 15 ml. in total volume. The compartments were separated by a 0.0015 inch tin-foil diaphragm placed between Teflon gaskets. A filling opening was provided for each compartment and sealed by an 0-ring and a brass plug.

A manganin wire was used as the heating element and was wound noninductively on the lower compartment and coated with Glyptal. In the heating circuit, a standard resistor connected in series with the calorimeter heater was employed to determine the voltage drop which was measured by a K-3 potentiometer. The heating time was measured by a syncronized electric timer. A thermistor was used as the temperature sensing element and was cemented onto the lower compartment with Epoxy resin. This thermistor was used as one arm of a Wheatstone Bridge (Tinsley-type 4870); the current flowing through the thermistor was about 30 μamp. Thermistors ranging in resistance from 900 to 2100 ohms at 25° C. were employed in this investigation. They were supplied by the Veco Corp., and

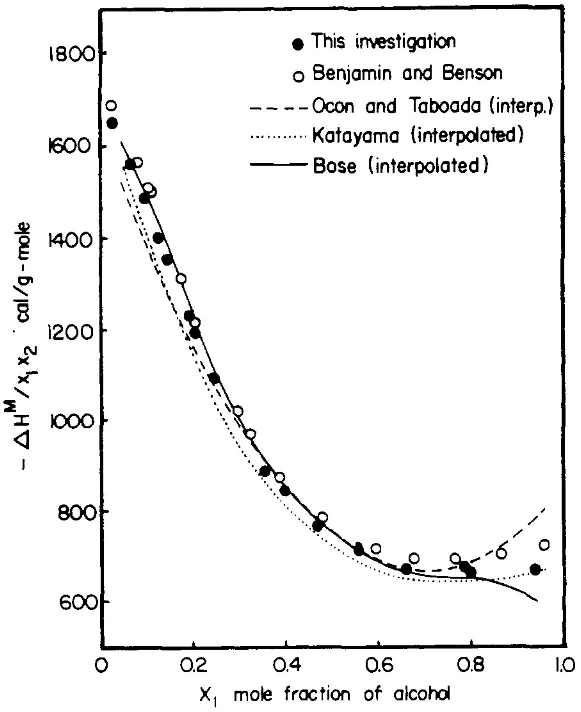

Figure 1. Heat of mixing data for system methanol-water at 25° C.

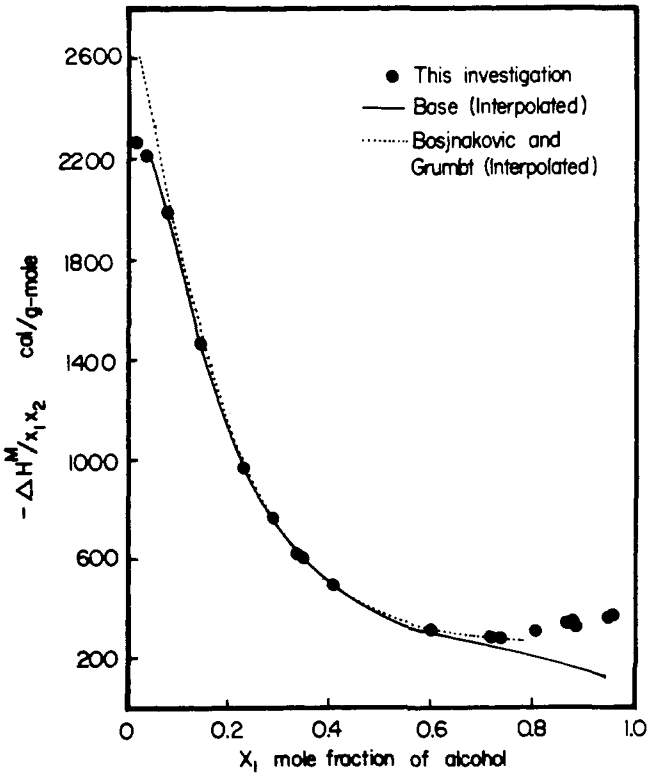

Figure 2. Heat of mixing data for system ethanol-water at 25° C.

their resistances were calibrated as a function of temperature. Output from the Wheatstone Bridge was fed to a D-C Null Detector (Leeds and Northrup, Model 9834-1) and the amplified signal drove a 50 mv. recorder (Leeds and Northrup Speedomax Model H) with a chart speed of 1 inch per minute.

A single calorimeter was used in each of the determinations. The upper and lower compartments of the calorimeter were completely filled with the desired liquid at 25° C. and 1 atm. and weighed to ±0.1 mg. The assembled vessel was then mounted in a brass jacket. Rings of styrofoam and plexiglass were used to keep the calorimeter from touching the jacket. The jacket was evacuated to a pressure less than 0.001 mm. of Hg and submerged in a 30-gallon water bath, which was controlled at 25 ± 0.01° C. by a Haake Universal Thermostat Unitherm. When thermal equilibrium was reached between the calorimeter and the bath, a gold-plated nail, initially placed in the lower compartment of the calorimeter, was energized by an external solenoid at 36 volts (D.C.) with about 40 on-off intervals per minute to rupture the tin foil and to stir the liquid mixture during the run. The change of resistance of the thermistor with time was recorded. By operating the Wheatstone Bridge near the balancing point at all times, errors resulting from unbalancing were considerably minimized (*10*). Sensitivity of the system could be varied from run to run and during the run if necessary from about 2 to 40 mv. per 0.01° C.

When the heat of mixing was exothermic, the change of resistance of the thermistor with time was recorded during the mixing period. The calorimeter was then allowed to reach thermal equilibrium with the bath overnight without stirring. The solenoid was then energized, and the change of resistance of the thermistor with time owing to the stirring effect (minus any heat loss to the bath) was followed for 10 minutes. This effect was about 0.0005° C. per minute. Electrical energy was then supplied to duplicate the change of thermistor resistance occurring during the mixing period. The heating time was recorded to ±0.05 second by a Precision electric stopwatch synchronized to the calorimeter heating circuit. The over-all heat capacity of the calorimeter and contents was evaluated, and the heat of mixing value was then calculated. When the heat of mixing was endothermic, electrical energy was supplied after a regular decrease of the thermistor resistance was indicated and until the thermistor resistance approached its original value. Heating and stirring were continued for an additional 10 minutes, and the resistance of the thermistor was recorded. The heat of mixing value was evaluated from the net heat input required for bringing the liquid mixture temperature back to the initial temperature before mixing.

Table I. Experimental Excess Enthalpy Values at 25° C.

Methanol-Water (1) (2) x_1	ΔH^M, cal. per mole	Ethanol-Water (1) (2) x_1	ΔH^M, cal. per mole	Propanol-2–Water (1) (2) x_1	ΔH^M, cal. per mole
0.0287	−46.0	0.0132	−29.5	0.0275	−78.0
0.0492	−76.8	0.0172	−38.4	0.0398	−104.8
0.0495	−77.3	0.0367	−78.5	0.0767	−152.4
0.0674	−98.1	0.0772	−141.4	0.1090	−155.9
0.0973	−130.6	0.1442	−181.9	0.1446	−144.4
0.1253	−155.3	0.2288	−172.0	0.2474	−99.8
0.1468	−169.4	0.2861	−155.9	0.3079	−72.8
0.1903	−189.6	0.3366	−138.3	0.4092	−25.9
0.2041	−193.7	0.3468	−138.2	0.4689	−2.75
0.2463	−202.9	0.4018	−123.6	0.5525	22.8
0.3562	−203.7	0.6008	−77.8	0.6074	35.1
0.3955	−201.9	0.7180	−59.6	0.6529	48.8
0.4689	−191.5	0.7314	−55.6	0.7224	50.7
0.5568	−175.4	0.8070	−49.6	0.7559	51.8
0.6598	−151.6	0.8684	−38.4	0.8988	29.6
0.7823	−114.7	0.8774	−38.0		
0.7990	−106.8	0.8807	−35.4		
0.9348	−40.8	0.9487	−18.1		
		0.9596	−14.8		

Vapor space in the calorimeter resulting from the contraction of volume during the mixing process was small, and maximum errors arising from possible evaporation were estimated as follows: methanol-water 0.24%; ethanol-water 0.66%; and propanol-2–water 1.4%. Errors owing to heat exchange with the surroundings amounted to 0.5%. Other measurement errors were negligible.

Absolute ethanol (Canadian Industrial Alcohol and Chemicals Limited) and Spectro grade methanol and propanol-2 (Matheson, Coleman and Bell) were used without further purification. Their physical properties agree with those available in the literature. Redistilled water was used throughout the investigation.

RESULTS AND DISCUSSION

Excess Enthalpy of Mixing, ΔH^M or ΔH^E. The heat of mixing values obtained for the three aqueous alcohol solutions are summarized in Table I. The data are compared with values available in the literature and presented graphically in Figures 1 to 3.

METHANOL-WATER. Heats of mixing of methanol and water have been previously reported in the literature. Bose (*2*) made measurements at 0°, 19.69°, and 42.37° C.; Ocon and Taboada (*11*) at 16.0°, 35.4°, and 53.5° C.; and Katayama (*8*) at 5°, 20°, 35°, and 50° C. Graphically interpolated values from these sets at 25° C. are plotted in Figure 1. Recently, Benjamin and Benson (*1*) reported their measurements at 25° C., and these are also plotted in Figure 1. The values obtained in this investigation are in general

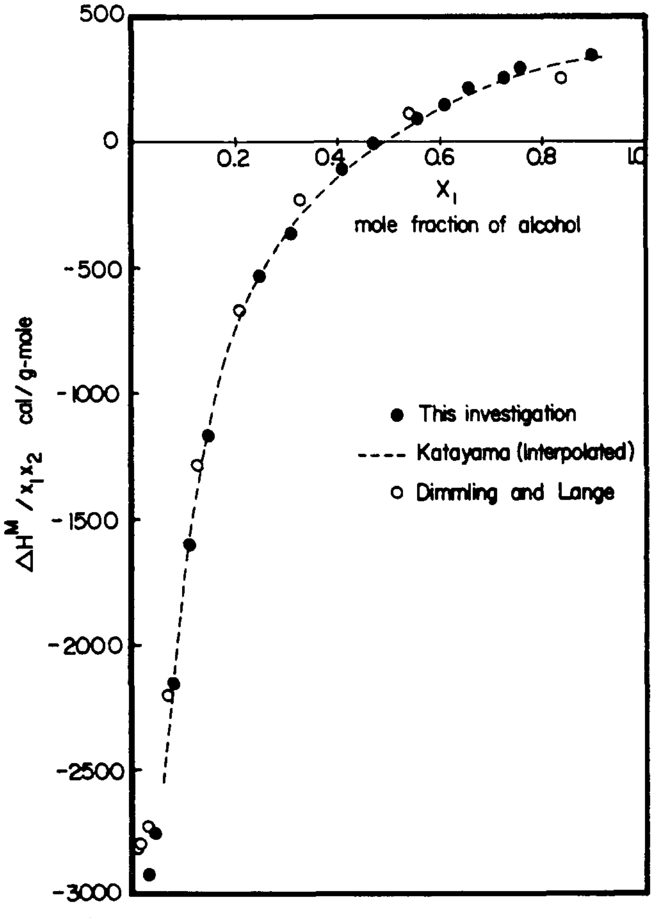

Figure 3. Heat of mixing data for system propanol-2–water at 25° C.

somewhat smaller than those of Benjamin and Benson but higher than those of Katayama. At higher mole fractions of methanol, the difference between the values reported by Benjamin and Benson and those obtained in this study is higher.

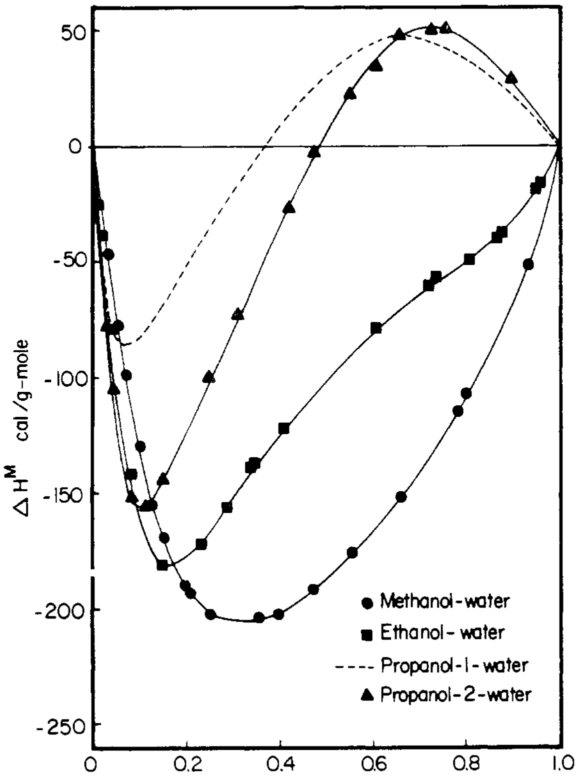

Figure 4. Heats of mixing of alcohols with water at 25° C.

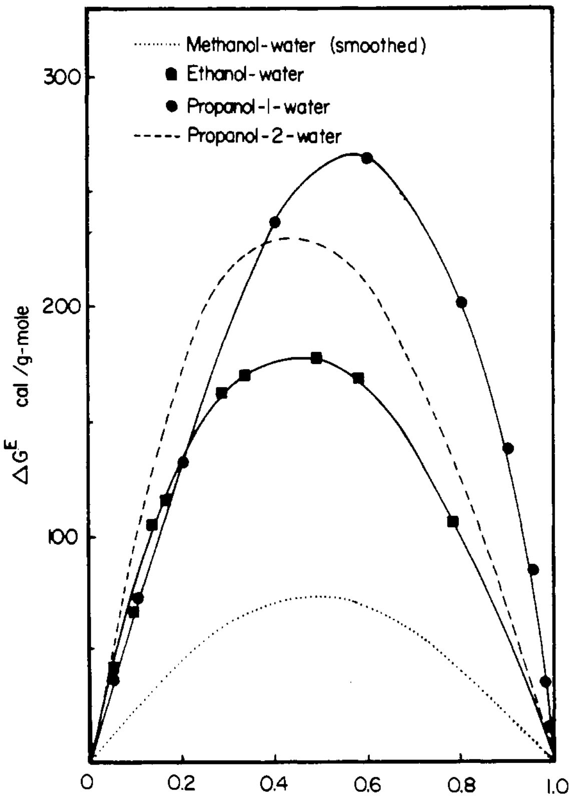

Figure 5. Excess free energies of mixing of alcohols with water at 25° C.

Ethanol-Water. Bose (2) measured the heats of mixing of ethanol and water at 0°, 17.33°, and 42.05° C., and Bosjnakovic and Grumbt (3) reported values from 0° to 100° C. at 10-degree intervals. Figure 2 compares graphically interpolated values at 25° C. from these two sets with the values obtained in this investigation. At low mole fraction of alcohol, the values from this study agree well with those of Bose, but at high mole fractions of alcohol, the authors' values agree well with those of Bosjnakovic and Grumbt.

Propanol-2-Water. Katayama (8) measured the heats of mixing of propanol-2 and water at 20° C. and calculated heat of mixing values from 0° to 80° C. at 10-degree intervals from the experimental heat capacity values for the system. Graphically interpolated values at 25° C. are plotted in Figure 3. Dimmling and Lange (5) determined the integral heats of dilution for the system at 25° C. These values were used to evaluate the heat of mixing values which are also plotted in Figure 3. The values from this study agree well with the interpolated values of Katayama.

The heat of mixing values for methanol and water can be represented by a third-order, four-constant Margules equation

$$\frac{\Delta H^M}{x_1 x_2} = A + B(1 - 2x_1) + C(1 - 2x_1)^2 + D(1 - 2x_1)^3 \qquad (1)$$

with values of −750.9, −401.3, and −142.5 cal. per mole for the constants A, B, C, and D, respectively. The heat of mixing data for ethanol and water and for propanol-2 and water cannot be represented as well by the Margules equation with the same number of constants.

The partial molal enthalpies of alcohols in water at infinite dilution of alcohol decrease with the molecular weight of alcohols and are −1700, −2300, and −3200 cal. per mole for methanol, ethanol, and propanol-2, respec-

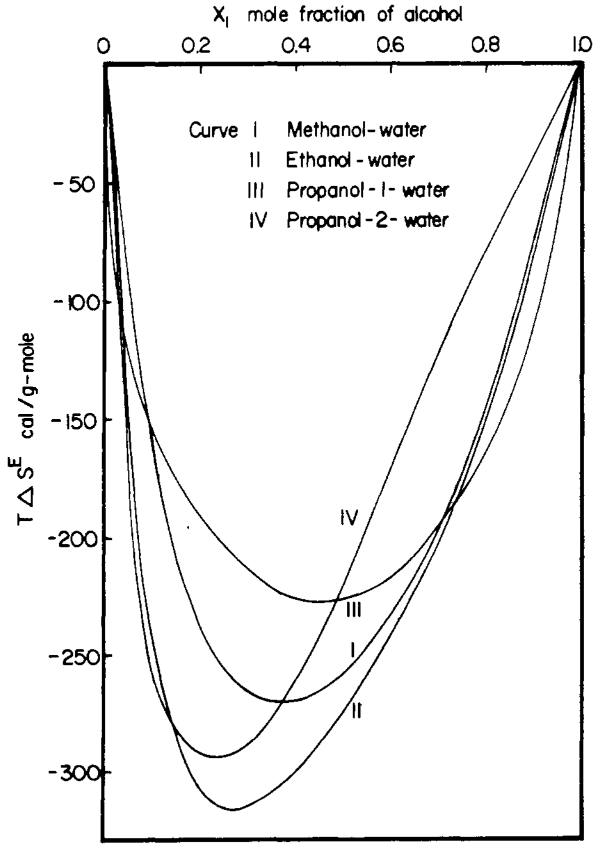

Figure 6. Excess entropies of mixing of alcohols with water at 25° C.

tively. The partial molal enthalpies of water in methanol, ethanol, and propanol-2 at infinite dilution of water increase with the molecular weight of the alcohol and are −680, −400, and +400 cal. per mole, respectively.

The asymmetry of the curves on a ΔH^M *vs.* x_1 plot (Figure 4) increases with the increase of molecular weight of the alcohols. Interpolated ΔH^M values for propanol-1-water (*2*) are also included in Figure 4 for comparison. For aqueous solutions of nonelectrolytes, Rowlinson (*7, 12*) suggested that the increase of the proportion of CH_2 groups in the molecules makes hydrogen bonding more difficult for steric reasons. If the solute (alcohol) is capable of forming a small number of reasonably strong hydrogen bonds to water, ΔH^M is generally positive in mixtures rich in solute and negative in mixtures rich in water. Propanol-1 and water and propanol-2 and water systems follow this behavior. An increase in the strength or number of the solute-water bonds leads to negative ΔH^M values over the complete concentration range. Methanol-water and ethanol-water systems follow this behavior.

Excess Free Energy of Mixing, ΔG^E. Vapor-liquid equilibrium data reported at 25° C. by Butler, Thomson, and MacLennan (*4*) for the system methanol-water and by Dobson (*6*) for the system ethanol-water were smoothed and used for obtaining the ΔG^E values. For the system propanol-2-water, vapor-liquid equilibrium data reported by Wilson and Simmons (*13*) at 95 and 190 mm. of Hg were used together with the heat of mixing data of this investigation for obtaining the ΔG^E values at 25° C. This method of calculation has been reported previously (*9*). The values obtained for these systems are graphically presented in Figure 5. ΔG^E values for propanol-1-water are also included in Figure 5. They were evaluated from the vapor-liquid equilibrium data reported by Butler and coworkers (*4*). The ΔG^E values increase with the increase of the molecular weight of the alcohols, and all ΔG^E values are positive. The ΔG^E values for propanol-2-water are between that for ethanol-water and propanol-1-water.

Excess Entropies of Mixing, ΔS^E. Excess entropies of mixing are evaluated from the relationship

$$T\Delta S^E = \Delta H^E - \Delta G^E$$

and are graphically presented in Figure 6. All the values are negative. A decrease in the strength of alcohol-water bonds leads to an increasing of the excess entropy, with the exception of methanol.

ACKNOWLEDGMENT

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The Condensed System LiF–NaF–ZrF_4—Phase Equilibria and Crystallographic Data

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THE potentialities of the system LiF-NaF-ZrF_4 in molten-salt technology have been recognized and developed during the last several years. As molten solvents for ZrF_4, LiF and NaF are cheap, stable, and in combination provide a high capacity for ZrF_4. Initially of interest as a nuclear reactor fuel solvent (*9*), the system LiF-NaF-ZrF_4 has recently been adapted with marked success in chemical reprocessing of spent reactor fuel elements (*6, 14*). Although no previous comprehensive report has been made of the phase equilibria in the system LiF-NaF-ZrF_4 and the limiting binary system LiF-ZrF_4, several interim reports have indicated the progress of this investigation (*8, 19*). Precise definition of the equilibrium relationships in the ternary system has required a long and tedious investigation, because of the formation of complex solid solutions on the one hand and the difficulty of obtaining very pure reagents on the other.

This report presents composition-temperature diagrams of the system LiF-NaF-ZrF_4 and the limiting binary system LiF-ZrF_4. Phase behavior in these systems was investigated in the temperature range from the liquidus down to about 400° C. This lower temperature limit was chosen because, at temperatures below this, solid-state equilibria in these systems are established only during impractically long annealing periods.

Nine complex fluoride compounds have been observed to crystallize from molten mixtures of LiF, NaF, and ZrF_4. Unquestionably, reasons for the complex phase behavior among crystalline solids in the LiF-NaF-ZrF_4 system will be obtainable only through studies of the crystal chemistry of these nine fluorides. The structures of only two of these crystalline phases, $3NaF \cdot ZrF_4$ (*10*) and $2LiF \cdot ZrF_4$ (*12*), have been elucidated. Single-crystal studies of the compound $7NaF \cdot 6ZrF_4$ have been in progress for some