300° K were lower than final reproducible values by an amount that increased progressively from 0 at about 190° K to 0.046 cal deg^{-1} sample^{-1} (0.299 cal deg^{-1} mol^{-1}) at 300° K. A low-energy transition was suspected, but after 5 days of equilibration at 300° K, measurements from 273–300° K reproduced the higher curve. Additional measurements from 195–273° K and again from 273–300° K also reproduced the higher curve. After further equilibration for 14 days at 300° K, the higher curve was again reproduced from 273–300° K.

Auxiliary tests were made on a sample taken from the unused portion of the material that formed the calorimeter charge. After petrographic, X-ray, and infrared examination showed it to be the same as it was before charging the calorimeter, the sample was equilibrated at 77° K for 10 days. No change in its properties could be detected. The material in the calorimeter was removed and its petrographic, X-ray, and infrared properties were found to be the same as they were originally. Because there was no direct evidence of the presence of more than one form of the tetrametaphosphate in the calorimeter sample, it can only be assumed that the sample contained a small amount of a second form that underwent a monotropic transition.

The discussion by Van Wazer (*8*) of the boat and chair forms of ammonium tetrametaphosphate supports this possibility. A second form of $(NH_4PO_3)_4$ was prepared by slow neutralization of a cold aqueous solution of tetrametaphosphoric acid with a mixture of ammonium hydroxide and ethanol. Addition of acetone precipitated a mixture of triammonium hydrogen tetrametaphosphate and an unidentified gummy material. Addition of alcoholic ammonium hydroxide to the filtrate precipitated a crystalline material with a composition between that of $(NH_4PO_3)_4$ and $(NH_4)_3H(PO_3)_4 \cdot H_2O$. This form had optical and X-ray properties different from those of the usual form, but on recrystallization from water it appeared as the usual form. The new form is presumed to be the boat form described by Van Wazer (*8*). Complete neutralization of the filtrate and addition of more ethanol produced the usual form of $(NH_4PO_3)_4$.

Earlier measurements showed very similar thermal properties for an ammonium tetrametaphosphate sample found by paper chromatography to contain 1% orthophosphate, 1% pyrophosphate, and 2% tripolyphosphate. It also originally showed a low-heat capacity curve and, after the same temperature cycles, a reproducible higher curve. Cubic equations were fitted to the high and low curves of each sample. The differences between the high and low curve were integrated from 195–300° K, and the calculated enthalpy changes were nearly the same for the two samples—17 cal mol^{-1} for the pure sample and 11 cal mol^{-1} for the impure sample. The increase in enthalpy between 190° and 300° K is 10,469 cal mol^{-1}. The difference between 17 and 11 cal is 0.06% of the enthalpy increase and may be assigned to experimental error. This similar behavior of two different samples supports the assumption that a change in form occurred during the measurements. Similarity of the two samples is shown also by their thermal properties at 298.15° K; values of C_p, $S°$, and $H° - H_0°$ are 110.2, 111.1, and 17,642 for the pure sample and 110.4, 111.0, and 17,637 for the impure sample.

Measurements on the impure sample are not reported. Observed molal heat capacities for the pure sample are shown in Table I. The heat capacities below 10° K were read at 1° K intervals from a large-scale plot of C_p/T vs. T^2 over the range 10–25° K that extrapolated smoothly to 0° K. A fourth-power analytical expression derived by the method of least squares gave essentially the same results. The smoothed heat capacities and the derived properties are given in Table II.

LITERATURE CITED

(1) Coates, R. V., Woodard, G. D., *J. Chem. Soc.*, **1964**, 1780.
(2) Ebel, J. P., *Mikrochim. Acta*, **1954**, 679.
(3) Egan, E. P., Jr., Luff, B. B., Wakefield, Z. T., *J. Chem. Eng. Data*, 13, 543 (1968).
(4) Egan, E. P., Jr., Wakefield, Z. T., *J. Phys. Chem.*, **64**, 1953 (1960).
(5) Lehr, J. R., Brown, E. H., Frazier, A. W., Smith, J. P., Thrasher, R. D., *Tennessee Valley Authority, Chem. Eng. Bull.*, **6**, Muscle Shoals, Ala., May 1967.
(6) Steger, E., *Z. anorg. allgem. Chem.*, **294**, 146 (1958).
(7) Thilo, E., Rätz, R., *ibid.*, **260**, 255 (1949).
(8) Van Wazer, J. R., "Phosphorus and Its Compounds," p 699, Vol. I, Interscience, New York, N. Y., 1958.
(9) Wakefield, Z. T., Luff, B. B., Kohler, J. J., *J. Chem. Eng. Data*, **15**, 314 (1970).
(10) Warschauer, F., *Z. anorg. allgem. Chem.*, **36**, 137 (1903).

RECEIVED for review April 10, 1970. Accepted October 27, 1970.

Thermodynamic Study of Water and Propylene Oxide Solutions

KENNETH W. MORCOM[1] and ROBERT W. SMITH
Department of Chemistry, The University, Leicester LE1 7RH, England

The excess enthalpies and volumes of mixing of water and propylene oxide have been measured at 5° and 25° C over the composition regions where the components are fully miscible. The mutual solubilities of the two components have also been restudied and the upper consulate has been temperature determined.

The present work forms part of a program concerned with the thermodynamic properties of aqueous solutions of some cyclic ethers (*5*). The system water and propylene oxide shows partial miscibility and the solid-liquid, liquid-liquid, and liquid-vapor equilibria have been previously studied (*9*). Freezing point measurements (*9*) indicate weak hydrate formation, which is confirmed by low frequency dielectric studies (*4*) corresponding to the formula propylene oxide–17 H_2O. The mutual solubilities of the two components have not previously been reported above the normal boiling point, 35° C, of propylene oxide, and the present measurements complete the miscibility curve. The regions of complete miscibility are sufficiently large to allow the excess enthalpies and volumes to be determined over a

---

[1] To whom correspondence should be addressed.

substantial part of the composition range, although no such measurements have hitherto been reported.

EXPERIMENTAL

British Drug Houses laboratory grade propylene oxide was purified by refluxing over sodium for several hours in an atmosphere of dry nitrogen, followed by fractional distillation. The middle fraction, bp 35° C, was degassed and stored in ampuls with a mercury seal. Analysis of the purified material, using a Perkin-Elmer F11 Gas Chromatograph with a Carbowax 1500 DE 201 column, showed the extent of impurity to be not more than 0.1%. Deionized water was redistilled from alkaline potassium permanganate in an atmosphere of nitrogen.

The calorimeter and experimental technique used for the excess enthalpy measurements have been described elsewhere (*2*) and only brief details are included here. Two glass mixing vessels carry three thermistors each wired in parallel and form two arms of a dc Wheatstone bridge. The off-balance current is fed directly to a Kipp and Zonen Micrograph recorder. A null technique may thus be used for exothermic measurements. The accuracy of the excess enthalpy measurements is estimated to be ±1%.

The technique used for measuring the excess volumes of mixing, and the dilatometers have also been described (*1*), except that one limb of the dilatometer was enlarged to allow a larger volume of one or other component to be loaded. The precision bore capillary tubing side-arm, of nominally 0.5-mm diameter, was calibrated by weighing and measuring the length of a mercury thread. Test measurements on the system benzene–cyclohexane agreed closely with reliable literature values (*8*), and the accuracy of the measurements is estimated to be ±0.5%. Water thermostats, stable to ±0.001° C, were used to control temperature for both excess volume and enthalpy measurements, and temperatures were monitored using a platinum resistance thermometer.

Two techniques were used for the determination of the miscibility curve. Above 35° C a conventional method was used in which the samples were sealed in borosilicate glass tubes, heated in a water bath, and visual observations of critical mixing were made with both rising and falling temperature. At the higher temperatures involved, propylene oxide begins to hydrolyze so that the maximum of the curve is subject to some uncertainty, as indicated by

Table I. Excess Enthalpies of Mixing of Water and Propylene Oxide

Temp, 5° C		Temp, 25° C	
x_2	H^E J mol^{-1}	x_2	H^E J mol^{-1}
0.0120	−140.8	0.0229	−192.8
0.0657	−523.4	0.0476	−335.9
0.0976	−597.3	0.0675	−411.0
0.1220	−602.2	0.0957	−447.7
0.1504	−571.6	0.1256	−429.3
0.7579	372.7	0.1492	−404.8
0.8100	412.7	0.6645	433.4
0.8780	403.7	0.7748	542.1
0.9445	265.0	0.8490	530.4
		0.8965	458.2
		0.9702	180.9

Table II. Excess Volumes of Mixing of Water and Propylene Oxide

Temp, 5° C		Temp, 25° C	
x_2	V^E cm^3 mol^{-1}	x_2	V^E cm^3 mol^{-1}
0.0096	−0.0579	0.0097	−0.0633
0.0205	−0.1332	0.0104	−0.0680
0.0297	−0.1996	0.0202	−0.1337
0.0397	−0.2700	0.0305	−0.2062
0.0496	−0.3436	0.0305	−0.2085
0.0705	−0.4824	0.0385	−0.2610
0.1486	−0.8216	0.0477	−0.3285
0.7474	−0.5813	0.0706	−0.4658
0.7721	−0.5340	0.1224	−0.7036
0.8031	−0.4708	0.1500	−0.7877
0.8540	−0.3564	0.6737	−0.7283
0.9498	−0.1142	0.6838	−0.7079
		0.7558	−0.5796
		0.8564	−0.3577
		0.9520	−0.1035

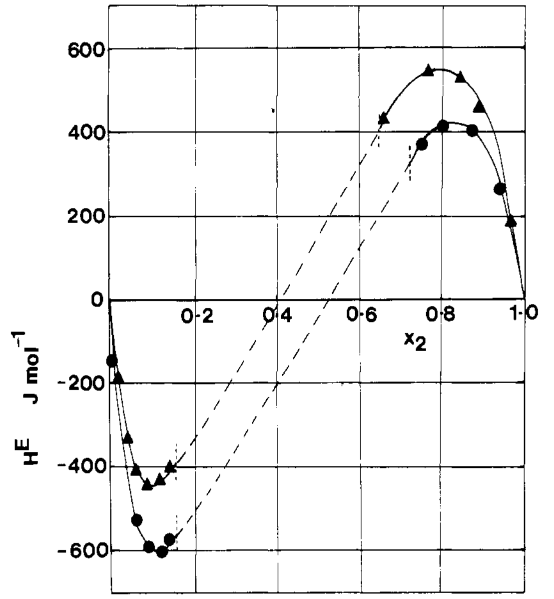

Figure 1. Excess enthalpies of mixing of water and propylene oxide

● 5° C; ▲ 25° C

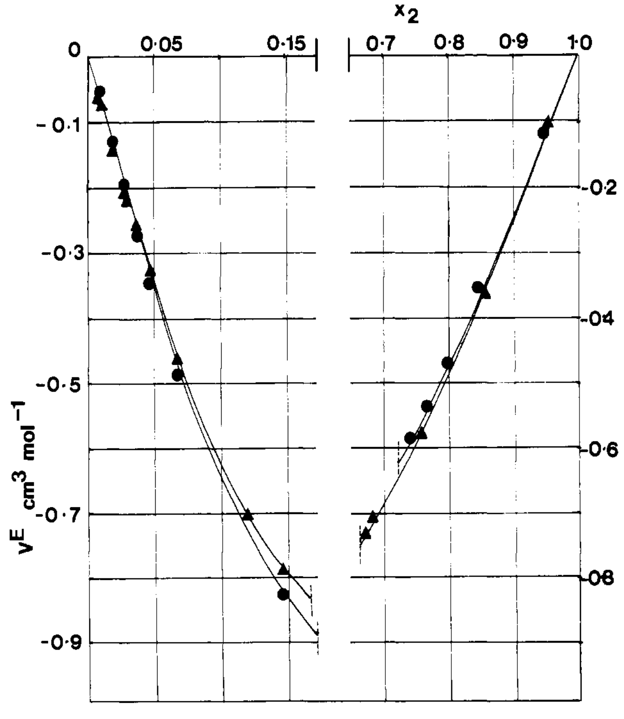

Figure 2. Excess volumes of mixing of water and propylene oxide

● 5° C; ▲ 25° C

Table III. Mutual Solubilities of Water and Propylene Oxide Mixtures

x_2	Temp, °C
0.200	92.0 ± 2.0
0.242	95.5 ± 1.5
0.297	95.0 ± 2.0
0.351	95.0 ± 1.0
0.402	89.0 ± 1.0
0.501	71.0 ± 1.0
0.599	46.5 ± 0.5
0.643	26.7 ± 0.5
0.657	24.2 ± 0.5
0.676	20.7 ± 0.5
0.699	12.9 ± 0.5
0.723	6.2 ± 0.5
0.742	−1.2 ± 0.5

the enhanced scatter in this region. Below 35° C, some measurements were made using a previously described spectrophotometric technique (*1*).

RESULTS AND DISCUSSION

The excess enthalpies, H^E, and excess volumes of mixing, V^E, at 5° and 25° C are recorded in Tables I and II together with the mole fraction, x_2, of propylene oxide, and are plotted in Figures 1 and 2. As found with other cyclic ethers, the enthalpies of mixing are negative at high concentrations of water and positive at high concentrations of propylene oxide, while the volumes of mixing are negative everywhere.

Our mutual solubility data are given in Table III, and are plotted in Figure 3, together with existing data taken below 35° C (*8*). The agreement is seen to be satisfactory. The upper consulate temperature (UCT) is 86° C at $x_2 = 0.28$. The increase in pressure inside the sample tubes at elevated temperatures is likely to cause the UCT to decrease since V^E is negative, but the effect is likely to be small. The almost constant value of the solubility of propylene oxide in water over an appreciable temperature range makes the determination of this part of the curve difficult by the present techniques. The results of Wickert et al. (*9*) suggest that the solubility curve for propylene oxide has a negative slope. The slope $(\partial x_2/\partial T)'_p$ of the solubility curve for propylene oxide in water at constant pressure is given by the expression (*6*)

$$\left(\frac{\partial x_2}{\partial T}\right)'_p = \frac{(H'_1 - H''_1)x''_1 + (H'_2 - H''_2)x''_2}{T(\partial^2 G/\partial x^2)'(x''_2 - x_2')} \qquad (1)$$

where the superscripts ′ and ″ denote the water-rich and propylene oxide–rich phases, respectively, and H_1 and H_2 denote the partial molar enthalpies of components 1 and 2. Since $\partial^2 G/\partial x^2$ must be >0 for any composition where the components are fully miscible, the denominator in Equation 1 is positive. Approximate values of the differences in the partial molar enthalpies, $H' - H''$, may be obtained from the gradients of the excess enthalpy curves. The numerator in Equation 1 is clearly small since $H'_1 \approx H''_1$ and $H'_2 \approx H''_2$, and appears to be negative at both temperatures. The enthalpy data thus satisfactorily confirm the slope of the mutual solubility curve of Wickert *et al.* (*9*) in the water-rich phase.

The present excess enthalpies and volumes may be compared with similar data for aqueous solutions of other cyclic ethers (*5*) in particular the isomeric but 4-membered trimethylene oxide. The excess enthalpy curve is much less negative, whereas the excess volume curve is more negative, than those obtained with trimethylene oxide. Searles and Tamres (*7*) have measured the enthalpy of mixing of a series of ethers with chloroform. They concluded that ability of the ether to form a hydrogen bond, as a function of ring size, was in the order 4- > 5- > 6- > 3-membered for single oxygen cyclic ethers. Similar conclusions were reached by Clemett (*3*) by studying the nmr chemical shifts of water containing cyclic ethers. The same order occurs with the series trimethylene oxide, tetrahydrofuran, and propylene oxide for the excess enthalpy of mixing with water, thus suggesting that ether-water hydrogen bonding is the dominant process determining the enthalpy of mixing over most of the composition range. The excess heat capacity C_p^E for the water and propylene oxide system is positive and approximately independent of composition, being about 8 JK^{-1} mol^{-1}.

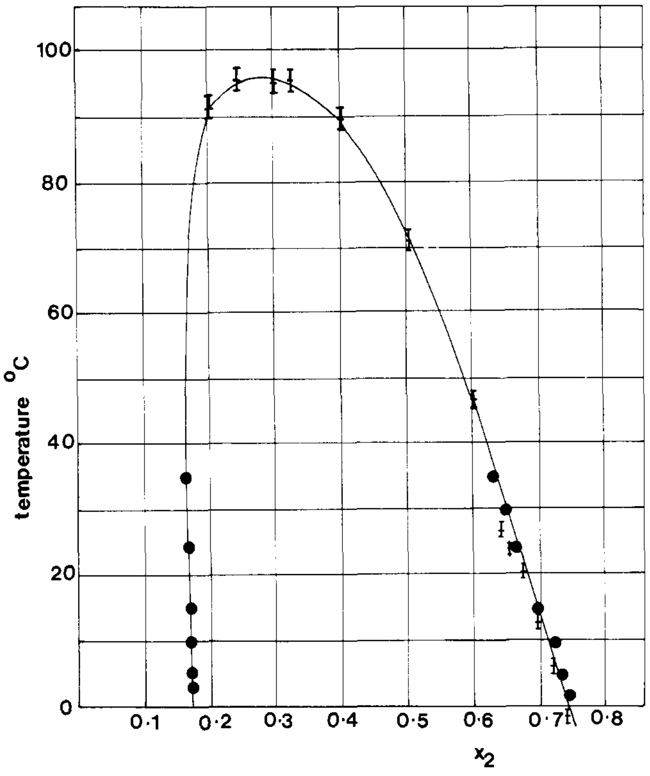

Figure 3. Mutual solubilities of water and propylene oxide
Ī present work; ● data of Wickert *et al.* (*9*)

A large-scale plot of the V^E curves at both 5° and 25° C show points of inflection at high water concentrations, which lead to minima in the plots of the relative partial molar volumes $V_2 - V_2^0$. Such minima are frequently regarded as indicating some "structuring" of the solution. The temperature dependence $(\partial V^E/\partial T)_p$ over the range $0 < x_2 < 0.03$, is very small, and negative, becoming positive above about $x_2 = 0.03$. Such behavior is not unusual and occurs with some other cyclic ethers, in particular tetrahydrofuran and tetrahydropyran. However, at high mole fractions of propylene oxide, $(\partial V^E/\partial T)_p$ has become negative again, and this behavior does appear to us to be unusual. The effect is not shown by the other ethers studied and does not permit any simple explanation at the present time.

NOMENCLATURE

C_p^E = excess heat capacity $(\partial H^E/\partial T)_p$
G = Gibbs free energy
H_1, H_2 = partial molar enthalpies of water and propylene oxide, respectively
H^E = excess enthalpy of mixing
J = Joule
K = degrees Kelvin
T = temperature
$V_2 - V_2^0$ = relative partial molar volume of propylene oxide

V^E = excess volume of mixing
x_2 = mole fraction of propylene oxide

LITERATURE CITED

(1) Armitage, D. A., Blandamer, M. J., Foster, M. J., Hidden, N. J., Morcom, K. W., Symons, M.C.R., Wootten, M. J., *Trans. Faraday Soc.*, **64**, 1193 (1968).
(2) Armitage, D. A., Morcom, K. W., *Trans Faraday Soc.*, **65**, 688 (1969).
(3) Clemett, C. J., *J. Chem. Soc (A)*, 455 (1969).
(4) Hawkins, R. E., Davidson, D. W., *J. Phys Chem.*, **70**, 1889 (1966).
(5) Morcom, K. W., Smith, R. W., *Trans. Faraday Soc.*, **66**, 1073 (1970).
(6) Rowlinson, J. S., "Liquids and Liquid Mixtures," 2nd ed, p 146, Butterworths, London, 1969.
(7) Searles, S., Tamres, M., *J. Amer. Chem. Soc.*, **73**, 3704 (1951).
(8) Watson, A. E. P., McLure, I. A., Bennett, J. E., Benson, G. C., *J. Phys. Chem.*, **69**, 2753 (1965).
(9) Wickert, J. N., Tamplin, W. S., Shank, R L., *Chem. Eng. Prog. Symp. Series* [2], **48**, 92 (1952).

RECEIVED for review April 23, 1970. Accepted October 2, 1970. The authors thank the Unilever Research Laboratory, Colworth House, Bedfordshire, England, for maintenance grant to R.W.S.

Salt Effects in Liquid-Liquid Equilibria

MAULIN L. DESAI[1] and EDWIN O. EISEN[2]
Lamar State College of Technology, Beaumont, Tex. 77705

The effect of magnesium chloride on the distribution of acetic acid, propionic acid, and butyric acid between benzene and water at 25° C has been studied. The Eisen-Joffe equation has been employed to relate distribution data to salt concentration. Compared with previous work, the order of decreasing salting out, on a weight basis, is

$$MgCl_2 > LiCl > NaCl > KCl$$

for all systems studied. The ternary system acetic acid–benzene–water exhibits solutropy upon the addition of magnesium chloride.

The effect of salts on the solubilities of nonelectrolytes in water has been extensively studied (*5*). Several theories have been advanced to explain this complex effect (*1*, *6*, *7*). However, the mathematical characterization of the salt effect has been semiquantitative at best, because of limitations of the theories or simplifying assumptions made in the derivation of the equations.

The effect of salts on the distribution of a solute between two relatively immiscible solvents has received little attention. Setschenow (*8*) correlated distribution data with the equation

$$\ln C^\circ/C = k_s X_s \tag{1}$$

which was valid for salt concentrations up to 3*M*. For a given solvent phase solute concentration, C and C^0 are aqueous phase solute concentrations with and without salt present, respectively. This equation was used by Swabb and Mongan (*9*) to correlate the effect of sodium sulfate on the distribution of acetic acid between benzene and isopropyl ether. The Hand (*4*) Equation,

$$\log \frac{X_{CB}}{X_{BB}} = \log A_0 + B_0 \log \frac{X_{CA}}{X_{AA}} \tag{2}$$

which gives excellent results in correlating ternary distribution data, was adapted by Eisen and Joffe (*3*) to quaternary systems containing salt. In the Eisen-Joffe Equation,

$$\log \frac{X_{CB}}{X_{BB}} = a + bX_s' + (c + dX_s) \log \frac{X_{CA}}{X_{AA}} \tag{3}$$

a, b, c, and d are constants which depend on the nature of the system, the nature of the salt, and temperature, but which are independent of salt concentration. The effects of lithium chloride, sodium chloride, and potassium chloride on the distribution of acetic acid, propionic acid, and butyric acid between benzene and water at 25° C were previously correlated using the Eisen-Joffe Equation (*2*).

EXPERIMENTAL

One to 60 ml of acid, 20 ml of aqueous magnesium chloride solution, and 20 ml of benzene were added to a tared polyethylene-stoppered Erlenmeyer flask. The weights of the respective solutions were read to ±0.1 mg on a Sartorius analytical balance. The composition of this initial mixture was then calculated, the composition of the magnesium chloride solution having been previously determined. The flasks were attached to a shaker and allowed to equilibrate for 24 hr in a constant-temperature bath maintained at 25.00 ± 0.02° C.

Two-milliliter aliquots of the aqueous phase and the organic phase were transferred to separate, tared 125-ml stoppered flasks and immediately weighed. Each aliquot was titrated with standard sodium hydroxide solution to the phenolphthalein end point, using 5-ml, 10-ml, and 50-ml class A burets. The percent of acid in the aqueous and organic phases was then calculated. A second aliquot of the organic phase was weighed and titrated with standardized Karl Fischer reagent using an electrometric "dead stop" end point indicator. The salt content of the organic phase was too low to produce a visible color change using dichlorofluorescein indicator. In previous work (*2*), a quantity of standard sodium chloride solution was added to the organic phase aliquot to improve the detection of the end point. Even then, the organic phase salt concentration could be determined only to within ±10%. In the present work, several organic phase samples were analyzed for salt

---

[1] Present address: Fluor Corporation, Houston, Tex.
[2] To whom correspondence should be addressed.