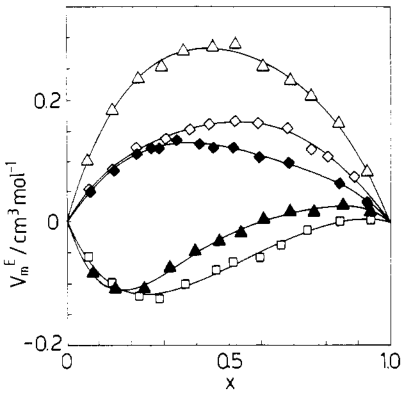

Figure 2. Excess volumes V_m^E of the mixtures of DEMSA with aliphatic alcohols at 333.15 K. The symbols are the same as in Figure 1.

Coefficients A_i of these fitting equations together with the standard deviations $\rho(V_m)$ of the fits are collected in Table III.

The excess volumes of the primary alcohols increase with the length of the alkyl chain and are smaller at the lower temperature than at the higher; the values range between −0.32 and 0.23 cm^3 mol^{-1} at 303.15 K and between −0.17 and 0.29 cm^3 mol^{-1} (methanol not measured) at 333.15 K. For 2-methyl-2-propanol, however, the values are positive at 303.15 K, but mainly negative at 333.15 K.

In the present mixtures, considerable amounts of positive contributions are expected due to the break-up of interactions between like molecules, viz., the rupture of the hydrogen-bonded chains of the alcohols and the loosening of the dipolar interactions between the amide molecules. The results indicate, however, that negative contributions predominate in the mixtures of methanol and ethanol with DEMSA. One source of negative contributions is the interactions between unlike molecules. However, since the alcohols are relatively poor proton donors (*8*, *9*) and the sulfonamides are relatively poor proton acceptors (*10*–*12*), we think that the contributions due to the DEMSA–alcohol heteroassociation equilibria are in no way sufficient to override the positive contributions. The more important source of the negative contributions may be the differences in the size and shape of the components of the mixtures. The molar volumes of DEMSA, methanol, and ethanol at 303.15 K are 138.45, 40.98, and 59.01 cm^3 mol^{-1}, respectively, which might allow the components to fit into each others' structures, so that reduction in volume occurs.

Comparison of the excess volumes with the excess enthalpies for the same mixtures supports this conclusion. The excess enthalpies, which are less sensitive to geometrical effects than are the excess volumes, are positive and great in magnitude, suggesting that as far as intermolecular interactions are concerned the break-up of interactions between like molecules predominates in all present amide–alcohol systems.

The molar volumes of the higher alcohols are greater (75.53, 92.42, 77.39, and 95.58 cm^3 mol^{-1} at 303.15 K for 1-propanol, 1-butanol, 2-propanol, and 2-methyl-2-propanol, respectively) and their proton-accepting abilities are smaller than those of methanol. As a result, the negative contributions to the excess volumes are relatively smaller for the mixtures of the higher alcohols than for the mixtures of methanol and are not sufficient to override the positive contributions. However, the magnitudes of the excess volumes are relatively small compared with the excess enthalpies and suggest that also in the mixtures of the higher alcohols there are negative contributions of geometrical origin. The fact that the excess volumes for the DEMSA–2-methyl-2-propanol system are positive at 303.15 K but mainly negative at 333.15 K seems, further, to be related to structural effects due to the globular shape of the 2-methyl-2-propanol molecule.

Registry No. DEMSA, 2374-61-0; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-methyl-2-propanol, 75-65-0.

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Excess Volumes of Ethanol + Water at 298.15 and 323.15 K at Pressures up to 220 MPa

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Excess volumes of ethanol + water mixtures at 298.15 and 323.15 K have been determined by a direct method in a mixing dilatometer at pressures up to 220 MPa. These measurements are reported and compared with relevant published data.

Introduction

The volumetric behavior of ethanol + water in the liquid phase at normal pressure has been the subject of extensive study over the years. The reader is referred to papers by Westmeier (*1*), Marsh and Richards (*2*), and Benson and Kiyohara (*3*) for relatively recent measurements and reviews.

The only significant measurements at high pressure appear to be those of Hamann and Smith (*4*), Moriyoshi et al. (*5*, *6*),

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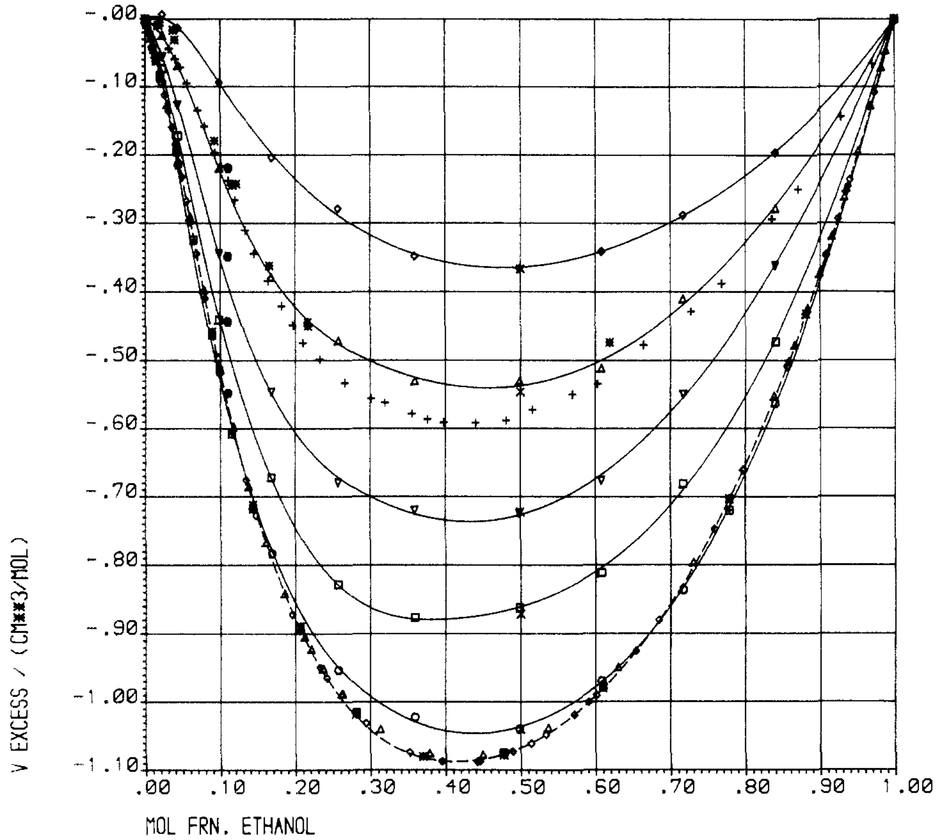

Figure 1. Excess volumes of ethanol + water at 298.15 K: (-O-) present work, 3.0 MPa; (-□-) present work, 25.3 MPa; (-▽-) present work, 54.8 MPa; (-△-) present work, 112.1 MPa; (-◇-) present work, 220.3 MPa; (×) ref *7* interpolated to above pressures ($x = 0.5$); (⊕) ref *6* interpolated to above pressures ($x = 0.11042$); (+) ref *5* 101.3 MPa; (*) ref *4* 101.3 MPa (note $T = 303.15$ K); (--◇--) ref *3*, 0.1 MPa; (△) ref *2*, 0.1 MPa; (⊞) ref *10*, 0.1 MPa; (⋇) ref *11*, 0.1 MPa.

Tanaka et al. (*13*), and Yusa et al. (*14*), who measured compressions of ethanol + water, and Götze and Schneider (*7*) who measured volumes of mixing by a direct method. This paper reports further direct measurements at high pressure.

Experimental Section

A direct method was employed to determine the isothermal, isobaric volume change on mixing known masses of the two components. These components were initially separated by a small volume of mercury and the system was brought to thermal equilibrium at the chosen conditions. The system was then caused to mix by breaking the mercury seal and agitating the mixture. The change in volume after return to the original pressure and temperature was determined by the displacement of a piston which formed the one movable boundary of the system. Details of the equipment and technique have been given previously (*8*, *9*).

***Materials*.** AnalaR ethanol was used having the following specification: minimum assay 99.5 mass %, water not more than 0.3 mass %, and other alcohols not more than 0.04 mass %. Gas-liquid chromatography indicated better than 99.9% purity on a peak area basis (catharimeter detector). The water used was distilled, deionized, and degassed.

Results and Discussion

The measurements are summarized in Table I and are graphed in Figures 1 and 2 where a comparison is made with published data. The curves drawn do not represent an analytic fit to the experimental points but are cubic splines with two or three knots in the range $0 < x < 1$. The splines give a least-squares fit.

The general features of $V^E_m(x)$ at 298.15 K and various pressures found here are in good accord with what has been reported hitherto. Firstly the measurements of Götze and Schneider (*7*) for $x = 0.5$ interpolated to the five pressures reported here agree closely having a mean difference of 0.006 cm^3 mol^{-1} from the smooth curves of Figure 1. Secondly, the general shape of the $V^E_m(x)$ curve at 112.1 MPa is closely similar to the curves derived from the compression measurements of Moriyoshi et al. (*5*) at 101.3 MPa and 298.15 K and of Hamann and Smith (*4*) at 101.3 MPa and 303.15 K. Thirdly, there is fair agreement between values of V^E_m at $x = 0.110\,42$ and 298.15 K interpolated from Moriyoshi and Inubishi's compression measurements (*6*). Despite the smoothing effects of interpolation, similar treatment of the compression measurements of Tanaka et al. (*13*) and Yusa et al. (*14*) gave estimates of $V^E_m(x)$ showing considerable scatter.

Agreement between interpolated results of Götze and Schneider (*7*) at 323.15 K and the smooth curves of Figure 2 is within an average of 0.014 cm^3 mol^{-1}.

A few of the finer details of the results are worth noting. Firstly, both at 298.15 K and at 323.15 K there appears to be a region at near-ambient pressures with $x > 0.6$ where $\partial V^E_m/\partial p < 0$. Secondly, the inflection in $V^E_m(x)$ at around $0.05 < x < 0.1$, which corresponds to a minimum in V^E_1, persists over the whole experimental pressure range and ultimately gives rise to a maximum in $V^E_m(x)$ both at 298.15 K and at 323.15 K. Another point is that an inflection in $V^E_m(x)$ corresponding to a maximum in V^E_1 develops at 323.15 K at pressures in excess of about 100 MPa. Within experimental ac-

Table I. Excess Molar Volumes (V^E_m/(cm^3 mol^{-1})) of xEthanol + (1 − x)Water as a Function of Pressure at 298.15 and 323.15 K[a]

		p/MPa					
T/K	10^2x	3.0	10.4	25.3	54.8	112.1	220.3
298.15	2.26	−0.094	−0.846	−0.073	−0.055	−0.023	+0.007
	4.34	−0.214	−0.200	−0.172	−0.126	−0.069	−0.013
	9.85	−0.516	−0.491	−0.441	−0.344	−0.219	−0.094
	16.80	−0.783	−0.744	−0.672	−0.546	−0.378	−0.204
	25.68	−0.953	−0.909	−0.828	−0.679	−0.471	−0.278
	35.86	−1.022	−0.971	−0.876	−0.720	−0.530	−0.348
	49.81	−1.039	−0.969	−0.862	−0.724	−0.530	−0.366
	60.76	−0.969	−0.915	−0.811	−0.676	−0.511	−0.340
	71.63	−0.836	−0.780	−0.681	−0.549	−0.410	−0.287
	83.98	−0.563	−0.532	−0.472	−0.361	−0.277	−0.196
323.15	2.34	−0.103	−0.094	−0.078	−0.055	−0.026	+0.002
	4.91	−0.238	−0.220	−0.191	−0.145	−0.092	−0.046
	10.56	−0.507	−0.482	−0.435	−0.348	−0.227	−0.117
	17.18	−0.698	−0.660	−0.583	−0.457	−0.326	−0.176
	25.65	−0.848	−0.797	−0.705	−0.558	−0.407	−0.229
	36.13	−0.927	−0.869	−0.766	−0.617	−0.447	−0.284
	49.95	−0.955	−0.893	−0.791	−0.619	−0.459	−0.298
	60.60	−0.866	−0.810	−0.717	−0.592	−0.430	−0.288
	71.99	−0.783	−0.736	−0.642	−0.505	−0.385	−0.222
	86.20	−0.464	−0.429	−0.364	−0.289	−0.165	−0.099

[a] $\delta T = \pm 0.05$ K, $\delta p = \pm 0.3$ MPa, $\delta x = \pm 0.001$, $\delta V^E_m = \pm 0.009$ cm^3 mol^{-1}.

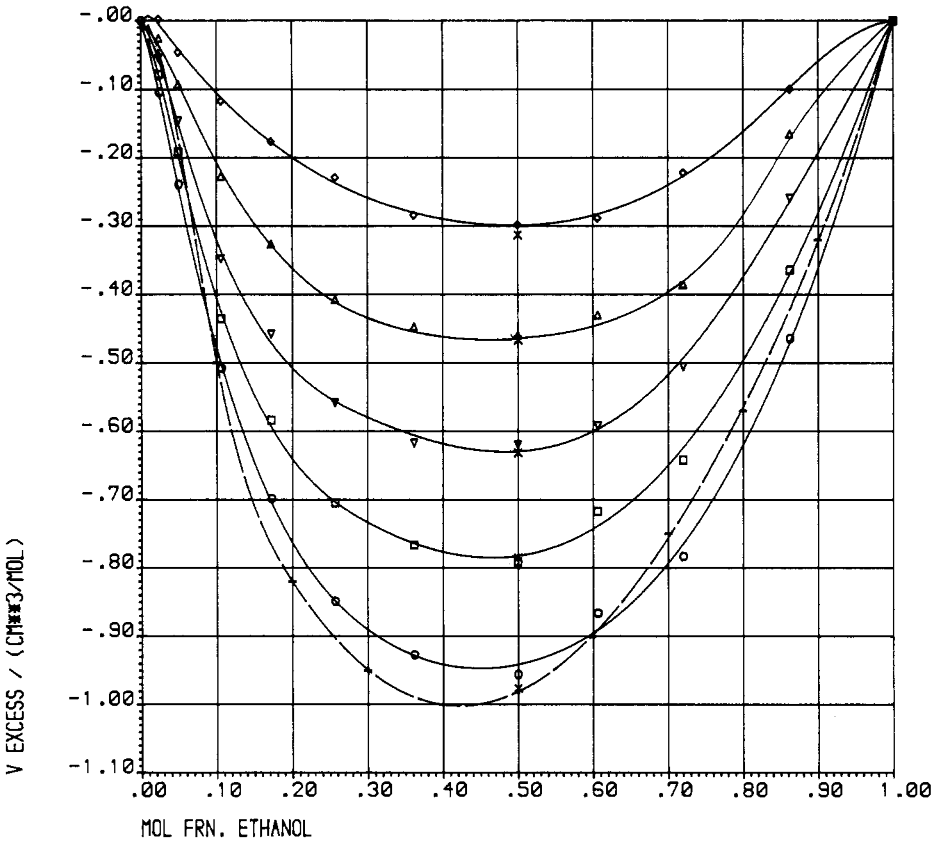

Figure 2. Excess volumes of ethanol + water at 323.15 K: (-○-) present work, 3.0 MPa; (-□-) present work, 25.3 MPa; (-▽-) present work, 54.8 MPa; (-△-) present work, 112.1 MPa; (-◇-) present work, 220.3 MPa; (×) ref *7* interpolated to above pressures (x = 0.5); (-+-) ref *12*, 0.1 MPa.

curacy V^E_m appears always to be less negative at the higher temperature.

Similar complex behavior is shown by other aqueous solutions of polar organic compounds giving little hope of finding convenient analytical expressions to describe volumetric behavior.

Glossary

p	pressure, MPa
T	temperature, K
V^E_m	molar volume of mixing, cm^3 mol^{-1}
V^E_i	partial molar excess volume of ethanol, cm^3 mol^{-1}
x	mole fraction ethanol

Registry No. Ethanol, 64-17-5; water, 7732-18-5.

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Activity Coefficients in Cyclohexane–Alcohol Systems Near the Freezing Point of Cyclohexane

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Activity coefficients of light alcohols and cyclohexane are determined by measuring freezing point lowering of solutions of alcohols in the cyclic hydrocarbon. Methanol, ethanol, 1-propanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol were used as solutes. Fits to van Laar, Wilson, and some continuous association models showed that the latter models work much better, except when the solute is 2-methyl-2-propanol, which would be in the form of tetramers as the unique species in the low concentration range. The minor species in the remaining alcohols examined would be dimers. The magnitudes of the association equilibrium constants in the low concentration range indicate that athermal models of continuous association should be reformulated in order to interpret adequately the behavior of solutions in the whole range of composition.

Introduction

Measurements of freezing point depressions of a solvent have been widely used in the determination of molecular weights and activity coefficients in the region of high dilution of the solute.

Several properties of solutions of alcohols in hydrocarbons have been measured and examined by many authors from the standpoint of models for the excess Gibbs energy, especially those based on continuous association of alcohol molecules. One conclusion is that the region of low alcohol concentration does not fit as well as in other compositions (*1*). When the solvent is cyclohexane, there are peculiar circumstances, which make it particularly interesting for a comparative study of several models in order to have some basis for a better understanding of what really happens in the low concentration region of alcohol. It has been shown (*2*) from the determination of molecular weights that dimers are the preferred form of light alcohols in cyclohexane, but 2-methyl-2-propanol would be in the form of tetramers under the same conditions.

In this paper, the experimental data by Aguirre-Ode and Rojas (*2*) are used for the calculation of activity coefficients of both components near the freezing point of cyclohexane, in order to verify the interpretative capacity of different models. Besides 2-methyl-2-propanol (*tert*-butyl alcohol), the solutes considered are methyl, ethyl, 1-propyl, 2-propyl, 2-butyl, and isobutyl alcohol.

Experimental Section

Cyclohexane and the alcohols were analytical grade reagents from Merck, most of them used without further purification after gas chromatography failed to show any significant impurity. The certified minimum purities were over 99.7%, except in the case of the butanols which reached only 99.0%. For this reason, the butanols were redistilled in a high-efficiency packed column. A heart cut was collected by discarding the first 20% of the distillate and the last 25% of the residue. The physical properties (density and refractive index) showed reasonable agreement with the values from literature. Mole fractions of the solutions were determined by weighing solvent and solute.

The experimental procedure was basically the described by Gillespie et al. (*3*). The solution was stirred by means of a mechanical device consisting of a helical stirrer connected through a fine flexible cord to a loose ring attached to an eccentric position on a rotating wheel. The cord was looped over a pulley in order to convert the circular motion of the wheel to the vertically oscillating motion required for the helical stirrer. The apparatus, shown in Figure 1, was placed in an ice-water bath.

A Beckmann thermometer was used to determine the temperature vs. time cooling curves for the solvent alone and for different concentrations of each one of the previously mentioned solutes in the solvent.

The freezing point depression, θ_m, directly obtained from the experimental measurements, was corrected for the supercooling effect in the manner suggested by Gillespie et al. (*3*)

$$\hat{\theta} = \theta_m\left(1 - \frac{c_p}{\lambda_1}S\right) \qquad (1)$$

in which c_p is the heat capacity of the liquid solvent, λ_1 is the heat of fusion of the solvent, $S = T - T_s$ is the extent of the supercooling, T is the freezing point, and T_s is the lowest temperature of the supercooled system. Figure 2 schematically shows the meaning of the different quantities.

Calculation of Activity Coefficients from Experimental Data

From the thermodynamic analysis of solid–liquid equilibrium, the following equation is derived

$$d \ln a_1 = -(\lambda_1/R)\, d(1/T) \qquad (2)$$

in which a_1 is the activity of the solvent, λ_1 is the heat of fusion of the solvent [J/mol], R is the gas constant [J/(mol K)], and

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