Table IV. Experimental Values of Henry's Constant, $H_{1,2}$ (Solute 1 in Solvent 2) and Calculated Fugacity Coefficients

T/K	$H_{1,2}$/bar	$\hat{\phi}_1^\infty$	ϕ_2
	R 13 (1) + *n*-Butane (2)		
310.93	54.8	0.994	0.908
350.00	72.0	1.002	0.837
400.00	87.7	1.092	0.725
	R 13 (1) + Isobutane (2)		
310.93	44.7	0.987	0.881
350.00	61.9	0.996	0.802
400.00	71.1	1.164	0.677

lows then that the Henry's constant functions also have slopes equal to their respective values of b (1.30 and 1.10 K m^3/kg) in agreement with the model. It is interesting to note that the linear relationship for K_1^∞ in Figure 3 continues to hold at least down to a reduced temperature of 0.72.

The remaining task involves the evaluation of b from the initial slopes of the critical lines in eq 2. This was done by estimating the pressures and compositions at the critical points in Figures 1 and 2. These data along with the critical points of the pure components were treated with several fitting and interpolation techniques to estimate the limiting slopes. The values of b obtained were 1.24 K m^3/kg for R 13 + n-butane and 1.17 K m^3/kg for R 13 + isobutane, with estimated uncertainties of about 6–8%. We feel that the agreement is remarkably good and that these results help substantiate the work of Japas and Levelt Sengers. The values of Henry's constant are given in Table IV along with the calculated values of the fugacity coefficients.

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Registry No. R 13, 75-72-9; butane, 106-97-8; isobutane, 75-28-5.

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Densities and Viscosities of Binary Mixtures of 1-Propanol and 2-Propanol with Acetonitrile

Susana Paez and Martin Contreras*

Departamento de Quimica, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

Densities and viscosities of binary liquid mixtures of acetonitrile with 1-propanol and 2-propanol have been measured at 20, 30, 40, and 50 °C. The calculated excess volumes are positive over the whole range of composition in both systems. The behavior of V^E is discussed considering physical, chemical, and structural effects. Viscosities have also been determined for both systems and analyzed by means of the Batschinski–Hildebrand and McAllister equations. The trends of viscosities are discussed in terms of the free energy, the enthalpy, and the entropy of activation of the viscous flow.

Introduction

Mixtures containing acetonitrile and alcohols have not been sufficiently studied. We report here density and viscosity data for acetonitrile (AN) + 1-propanol (1-PrOH) and AN + 2-propanol (2-PrOH) over the entire mole fraction range at four temperatures: 20, 30, 40, and 50 °C. Recent information about viscosities of these mixtures is scarce in the literature. Viscosities of AN + 2-PrOH were studied by Katz et al. at 50 °C (*1*). Previously Mato and Coca published viscosity measurements in both systems at 25, 35, and 45 °C (*2*). On the other hand, there is enough information about the excess volumes or densities of these mixtures between 25 and 35 °C (*3–5*).

Experimental Section

All organic chemicals used in the study were reagent grade. 1-PrOH and 2-PrOH (BDH, AnalaR grade, 99.5% purity) were dried by refluxing over CaO, distilling, and finally passing through 3-Å molecular sieves. AN (Aldrich, HPLC, 99.9% purity) was only dried with 3-Å molecular sieves. Water contents were checked by Karl Fischer titration. In all cases the water contents in the liquids used were not greater than 0.05% (v/v).

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Table I. Coefficients of Eq 1

viscometer	A/cm^2 s^{-2}	B/s^3
I	1.020×10^{-4}	422.6
II	9.599×10^{-6}	4.150×10^5

Table II. Densities and Viscosities of Pure Liquids at 25 °C

	ρ/g cm^{-3}		η/cP	
liquid	obsd	lit.	obsd	lit.
acetonitrile	0.7766	0.77676 (*8*) 0.7760 (*9*) 0.7768 (*13*)	0.3415	0.342 (*8*) 0.346 (*9*) 0.3409 (*13*)
1-propanol	0.7996	0.79954 (*8*) 0.7995 (*10*) 0.7995 (*13*)	1.945	1.967 (*8*) 1.938 (*10*) 2.004 (*13*)
2-propanol	0.7809	0.7810 (*11*) 0.7804 (*12*) 0.7810 (*13*)	2.052	2.058 (*2*) 2.036 (*12*) 2.079 (*13*)

Solutions of different compositions by weight were prepared in a 50-cm^3 Erlenmeyer flask provided with a joint stopper, using a Mettler H33AR balance with an accuracy of ±0.1 mg. Densities, ρ, were measured by use of Lipkin-type pycnometer (*6*) with a volume of about 10 cm^3. The pycnometer was calibrated with deionized and degassed water at the four temperatures of this study using the accurately known densities (*7*). The uncertainty of repeated density measurements (at least three) affected the fourth decimal place. Viscosities were measured with two factory-calibrated Schott KPG Ubbelohde capillary viscometers. The equation used to calculate the viscosities was

$$\nu = \eta/\rho = A[t - Bt^{-2}] \qquad (1)$$

where ν is the kinematic viscosity, η is the dynamic viscosity, and t is the flow time in the viscometer. The viscometer constants A and B, given in Table I, were tested with deionized and degassed water. Measuring the time in seconds, the kinematic viscosities resulted in stokes. The stopwatch used, with a time resolution of 0.05 s, allowed the viscosity to be calculated to four significant figures. The reported viscosities were the averages of at least eight runs. The thermostatic bath temperature was controlled to ±0.05 °C. Densities and viscosities of the liquids at 25 °C are listed in Table II, with literature values for comparison. Densities and viscosities of the measured mixtures are informed in Tables III and IV.

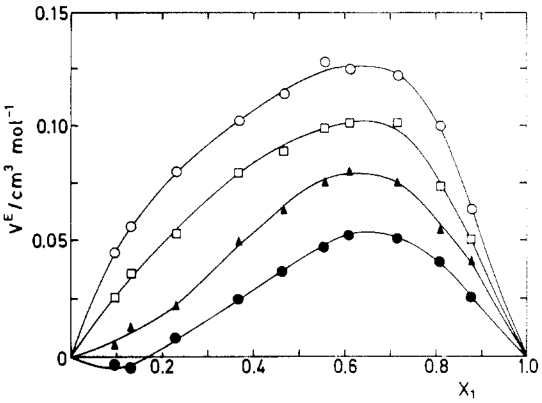

Figure 1. Excess volume of AN + 1-PrOH mixtures as a function of the mole fraction of AN at 20 (●), 30 (▲), 40 (□), and 50 °C (○).

Results and Discussion

Excess Volume. The excess volumes, V^E, have been calculated from density data according to the relationship

$$V^E = X_1M_1(1/\rho_m - 1/\rho_1) + X_2M_2(1/\rho_m - 1/\rho_2) \qquad (2)$$

For the component i, ρ_i, M_i, and X_i are the density, the molecular weight, and the mole fraction, respectively. ρ_m is the density of the mixture. The calculated V^E are shown in Figures 1 and 2. The V^E were fitted by use of the equation

$$V^E/\text{cm}^3\ \text{mol}^{-1} = X_1X_2\sum_{i=1}^{M} a_{i-1}(X_1 - X_2)^{i-1} \qquad (3)$$

Table III. Experimental Density and Viscosity Data for the Acetonitrile (1) + 1-Propanol (2) System

	ρ/g cm^{-3}				η/cP			
X_1	20 °C	30 °C	40 °C	50 °C	20 °C	30 °C	40 °C	50 °C
0.000	0.8036	0.7956	0.7874	0.7792	2.187	1.705	1.380	1.109
0.0214	0.8033	0.7952	0.7869	0.7786	2.052	1.623	1.298	1.052
0.0926	0.8022	0.7939	0.7853	0.7767	1.636	1.329	1.089	0.8994
0.1310	0.8016	0.7931	0.7844	0.7757	1.467	1.195	0.9876	0.8269
0.2287	0.7998	0.7911	0.7821	0.7731	1.114	0.9375	0.7852	0.6650
0.3661	0.7971	0.7879	0.7786	0.7693	0.8314	0.7000	0.5983	0.5179
0.4647	0.7950	0.7855	0.7760	0.7664	0.6986	0.5975	0.5164	0.4510
0.5532	0.7930	0.7832	0.7735	0.7636	0.5951	0.5163	0.4519	0.3984
0.6088	0.7917	0.7817	0.7719	0.7619	0.5441	0.4725	0.4163	0.3701
0.7151	0.7892	0.7789	0.7687	0.7584	0.4665	0.4106	0.3663	0.3284
0.8071	0.7870	0.7765	0.7661	0.7554	0.4122	0.3683	0.3317	0.3003
0.8778	0.7853	0.7745	0.7640	0.7532	0.3835	0.3450	0.3126	0.2849
1.0000	0.7821	0.7710	0.7602	0.7491	0.3579	0.3254	0.2974	0.2729

Table IV. Experimental Density and Viscosity Data for the Acetonitrile (1) + 2-Propanol (2) System

	ρ/g cm^{-3}				η/cP			
X_1	20 °C	30 °C	40 °C	50 °C	20 °C	30 °C	40 °C	50 °C
0.0000	0.7851	0.7767	0.7678	0.7591	2.290	1.778	1.331	1.032
0.0526	0.7849	0.7762	0.7672	0.7583	1.921	1.464	1.125	0.9024
0.0771	0.7847	0.7759	0.7668	0.7578	1.736	1.361	1.047	0.8427
0.1018	0.7845	0.7756	0.7664	0.7574	1.572	1.239	0.9910	0.7839
0.2227	0.7838	0.7743	0.7648	0.7553	1.150	0.9168	0.7301	0.6091
0.3314	0.7831	0.7734	0.7634	0.7538	0.8622	0.7097	0.5949	0.5031
0.3989	0.7827	0.7727	0.7626	0.7528	0.7354	0.6154	0.5253	0.4466
0.5500	0.7818	0.7715	0.7611	0.7509	0.5657	0.4831	0.4201	0.3731
0.6250	0.7815	0.7709	0.7605	0.7501	0.5020	0.4366	0.3817	0.3434
0.6893	0.7813	0.7707	0.7601	0.7497	0.4639	0.4070	0.3610	0.3290
0.7624	0.7812	0.7704	0.7597	0.7462	0.4194	0.3780	0.3321	0.3054
0.8640	0.7815	0.7705	0.7597	0.7489	0.3823	0.3440	0.3081	0.2835
1.0000	0.7821	0.7710	0.7602	0.7491	0.3579	0.3254	0.2974	0.2729

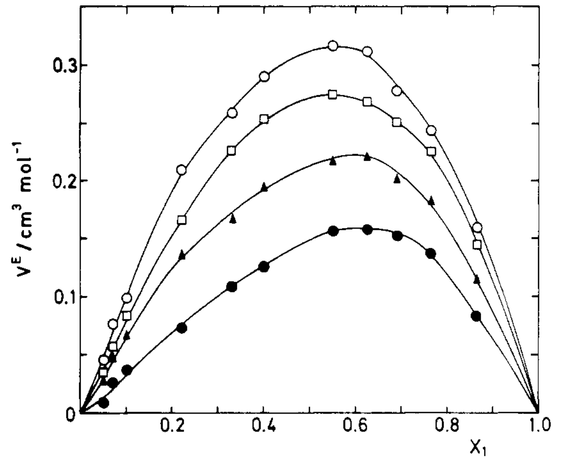

Figure 2. Excess volume of AN + 2-PrOH mixtures as a function of the mole fraction of AN at 20 (●), 30 (▲), 40 (□), and 50 °C (○).

Table V. Coefficients a_i of Eq 3 and Standard Deviations

T/°C	a_0	a_1	a_2	a_3	$\sigma(V^E)$/cm^3 mol^{-1}
			AN + 1-PrOH		
20	0.1757	0.1893	-0.1149		0.002
30	0.2718	0.1839	-0.0369		0.004
40	0.3859	0.2532	0.0062	-0.2668	0.003
50	0.4872	0.2536	0.1273	-0.3296	0.003
			AN + 2-PrOH		
20	0.6135	0.2691	-0.1394		0.005
30	0.8731	0.2116	-0.0554		0.006
40	1.111	0.1511	-0.0920	0.2179	0.006
50	1.270	0.0962	-0.0832	0.1924	0.007

The estimates of the coefficients a_i were obtained by the method of least squares and are summarized in Table V. The standard deviation $\sigma(V^E)$ was calculated as

$$\sigma(V^E) = [\sum(V^E_{\text{exp}} - V^E_{\text{calc}})^2/(N - M)]^{1/2} \qquad (4)$$

where N is the number of observations and M is the number of parameters in eq 3.

Figures 1 and 2 show a clear dependence of V^E with temperature. For both systems the maximum of V^E lies between X_1 = 0.55 and 0.65, which has also been observed in AN + $CH_3(CH_2)_{n-1}OH$ mixtures for n = 2, 3, 4, and 5 (*3-5*). At the same temperatures, the V^E values in 2-PrOH mixtures are larger than those observed in 1-PrOH mixtures. In several alcohol mixtures the V^E values for secondary and tertiary alcohols are larger than those corresponding to primary alcohols (*14*). In general, the V^E in AN + propanol mixtures are smaller than those observed in propanol + inert solvent mixtures (*14*).

The observed V^E can be discussed in terms of several effects, which may be arbitrarilly divided into physical, chemical, and structural contributions (*15*). These effects have been contemplated to different extents in the literature (*1*, *5*, *11*, *15-17*). Physical contributions comprise dispersion forces and nonspecific physical interactions that add positive terms to V^E. Chemical contributions consider the breaking up of the H-bond structure which tends to make V^E larger and specific interactions such as the formation of H bonds and charge-transfer complexes resulting in contraction of volume. Structural contributions arising from geometrical fitting of one component into the other, due to differences in molar volume and free volumes between components, lead to negative contributions to V^E (*15*). In the case of AN and the propanols the latter contribution is negligible, since free volumes are similar (*16*). AN and propanols show clear associations as pure liquids. Acetonitrile, due to its high dipole moment (3.92 D (*13*)), favors dipole-dipole interactions. On the other hand, alkanols, in general, are strongly self-associated through H bonds with degrees of association depending on chain length, branching of the alkyl group, temperature, and dilution by other substances (*4*, *16*). Due to the branched structure of 2-PrOH, self-association in pure liquid is somewhat less pronounced than in pure 1-PrOH (*18*). The excess molar enthalpies of AN + propanol systems at 25 °C are about 2000 J mol^{-1} for equimolar mixtures (*11*), being somewhat high compared to the observed expansion. It can be concluded that in the observed V^E the prevailing effect appears to be the disruption of H bonds between alcohol molecules, involving absorption of energy, compensated partially through H-bond formation between unlike molecules. The more pronounced expansion observed in AN + 2-PrOH mixtures can be attributed to a lower degree of alcohol-alcohol and alcohol-AN association than in AN + 1-PrOH mixtures.

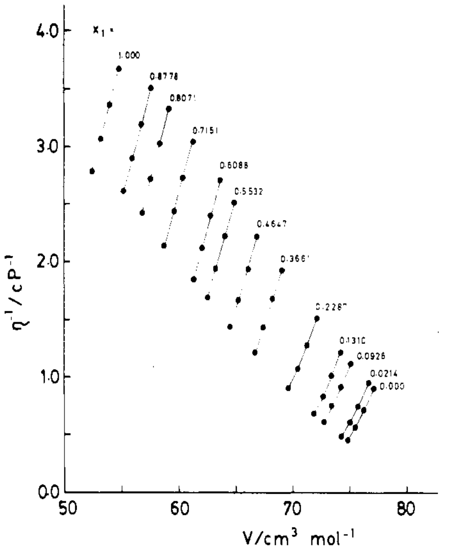

Figure 3. Fluidity versus molar volume for AN + 1-PrOH mixtures.

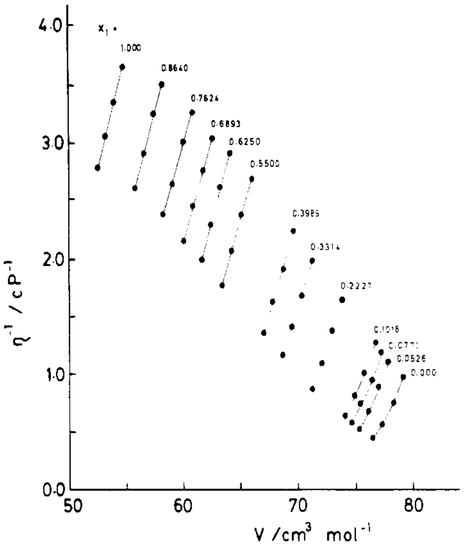

Figure 4. Fluidity versus molar volume for AN + 2-PrOH mixtures.

Viscosity. The Batschinski-Hildebrand equation (*19*, *20*)

$$\eta^{-1} = B(V - V_0)/V_0 \qquad (5)$$

shows that the fluidity, η^{-1}, for a liquid of constant composition depends linearly on the molar volume, V. V_0 and B are constants for a liquid. V_0 is the smallest volume into which 1 mol of liquid can be compressed when $\eta^{-1} \rightarrow 0$, and B depends on the forces acting between the molecules. $V - V_0$ represents the free volume necessary for flow. Figures 3 and 4 show the fluidity behavior of these systems. Below $X_1 \approx 0.2$ it can be seen that eq 5 is not obeyed, which is typical for strongly

Table VI. Interaction Parameters in Eq 6 and Percent Standard Deviations

T/°C	ν_{12}	ν_{21}	$(\Delta\%)_{av}$	$(\Delta\%)_{max}$
		AN + 1-PrOH		
20	0.5666	0.9457	1.464	2.430
30	0.4925	0.8469	1.066	1.709
40	0.4473	0.7276	0.9648	1.689
50	0.4024	0.6527	0.8295	1.289
		AN + 2-PrOH		
20	0.5308	0.9026	1.238	2.543
30	0.4965	0.7117	1.195	2.566
40	0.4363	0.6345	1.156	2.074
50	0.4132	0.5503	0.9434	1.991

associated liquids (*21*). For $X_1 > 0.2$ in the temperature interval studied, according to eq 5 our systems do not exhibit marked associations. The kinematic viscosities were correlated by means of the McAllister equation based upon a three-body interaction model, which for two-component mixtures reads (*22*)

$$\ln \nu_m = X_1^3 \ln \nu_1 + X_2^3 \ln \nu_2 + 3X_1^2X_2 \ln \nu_{12} + 3X_1X_2^2 \ln \nu_{21} - \ln [X_1 + X_2M_2/M_1] + 3X_1^2X_2 \ln [(2 + M_2/M_1)/3] + 3X_1X_2^2 \ln [(1 + 2M_2/M_1)/3] + X_2^3 \ln [M_2/M_1] \quad (6)$$

where ν_m, ν_1, and ν_2 are the kinematic viscosities of the mixture and of components 1 and 2. M_i and X_i have the same meaning as before. The interaction parameters ν_{12} and ν_{21} were obtained by solving eq 6 using nonlinear regression analysis. The percent average deviation, $(\Delta\%)_{av}$, was defined as

$$(\Delta\%)_{av} = \left[\frac{1}{N}\sum_j^N \epsilon_j^2\right]^{1/2} \quad (7)$$

where $\epsilon_j = 100(\nu_j - \nu_{j\,calcd})/\nu_j$. ν_j and ν_{calcd} are the experimental and the calculated viscosities for a particular mole fraction of AN. For each temperature, the percent maximal deviation $(\Delta\%)_{max}$ was determined as

$$(\Delta\%)_{max} = |\epsilon_j|_{max}$$

The values of the interaction parameters along with those of percent average deviation and percent maximal deviation for both systems are given in Table VI. In both mixtures the percent average deviation at four temperatures was 1.11%. This value is smaller than 1.65% informed by Skubla for similar systems (*23*).

The free energy of activation of the viscous flow $\Delta G_m^{\ddagger}$ have been calculated from Eyring's equation (*24*)

$$\eta_m = (hN/V) \exp[\Delta G_m^{\ddagger}/RT] \quad (8)$$

By plotting ln $(\eta_m V/hN)$ against $1/T$ we found a linear behavior which enables us to obtain directly the entropy $(\Delta S_m^{\ddagger})$ and the enthalpy $(\Delta H_m^{\ddagger})$ of activation of viscous flow considering

$$\Delta G_m^{\ddagger} = \Delta H_m^{\ddagger} - T\Delta S_m^{\ddagger} \quad (9)$$

The results are given in Tables VII and VIII.

At lower temperature $\Delta G_m^{\ddagger}$ or η_m for 2-PrOH is slightly greater than that observed for 1-PrOH. With increasing temperature this situation is changed. From Tables III and IV it can be estimated that around 35 °C the viscosities for both alcohols are the same. The trends of $\Delta G_m^{\ddagger}$ for the mixtures can be better understood by analyzing the enthalpies and entropies of activation. The enthalpy of activation depends on geometrical effects as well as intermolecular interactions, which explains the high $\Delta H_m^{\ddagger}$ in the alcohol-rich region. For the pure components, $\Delta H_m^{\ddagger}$ follow the order 2-PrOH > 1-PrOH > AN. Although 1-PrOH is more associated than 2-PrOH, the branched structure of 2-PrOH prevails as a determinant of viscosity. With decreasing alcohol concentration $\Delta H_m^{\ddagger}$ gradually diminishes as is expected due to the breaking of H bonds, and the values of $\Delta S_m^{\ddagger}$ change from positive to negative. The positive values of $\Delta S_m^{\ddagger}$ show that the formation of activated complexes involves less order due to destruction of H bonds, and the negative values indicate that the formation of activated complexes introduces molecular order, probably due to attractions between

Table VII. Activation Parameters for the Acetonitrile (1) + 1-Propanol (2) System

	$\Delta G_m^{\ddagger}$/kJ mol^{-1}					
X_1	20 °C	30 °C	40 °C	50 °C	$\Delta H_m^{\ddagger}$/kJ mol^{-1}	$\Delta S_m^{\ddagger}$/J K^{-1} mol^{-1}
0.0000	14.65 ± 0.47	14.58 ± 0.48	14.50 ± 0.49	14.42 ± 0.50	16.92 ± 0.24	7.72 ± 0.79
0.0214	14.49 ± 0.08	14.42 ± 0.08	14.34 ± 0.08	14.26 ± 0.08	16.73 ± 0.04	7.63 ± 0.13
0.0926	13.89 ± 0.17	13.86 ± 0.18	13.82 ± 0.18	13.79 ± 0.18	14.86 ± 0.09	3.31 ± 0.29
0.1310	13.59 ± 0.11	13.57 ± 0.11	13.55 ± 0.11	13.53 ± 0.11	14.19 ± 0.05	2.05 ± 0.18
0.2287	12.86 ± 0.38	12.86 ± 0.38	12.87 ± 0.39	12.87 ± 0.39	12.69 ± 0.19	−0.57 ± 0.63
0.3661	12.02 ± 0.22	12.04 ± 0.22	12.05 ± 0.23	12.07 ± 0.23	11.50 ± 0.11	−1.78 ± 0.37
0.4647	11.52 ± 0.10	11.55 ± 0.10	11.58 ± 0.10	11.62 ± 0.11	10.53 ± 0.05	−3.36 ± 0.17
0.5532	11.05 ± 0.02	11.10 ± 0.02	11.15 ± 0.02	11.21 ± 0.02	9.54 ± 0.01	−5.15 ± 0.03
0.6088	10.78 ± 0.22	10.84 ± 0.23	10.89 ± 0.23	10.95 ± 0.24	9.10 ± 0.11	−5.72 ± 0.38
0.7151	10.31 ± 0.15	10.38 ± 0.15	10.46 ± 0.16	10.53 ± 0.16	8.15 ± 0.08	−7.35 ± 0.25
0.8071	9.92 ± 0.04	10.02 ± 0.04	10.11 ± 0.05	10.20 ± 0.05	7.23 ± 0.02	−9.18 ± 0.07
0.8778	9.68 ± 0.05	9.78 ± 0.05	9.88 ± 0.05	9.98 ± 0.05	6.71 ± 0.03	−10.14 ± 0.09
1.0000	9.39 ± 0.01	9.50 ± 0.01	9.62 ± 0.01	9.74 ± 0.01	5.99 ± 0.00	−11.60 ± 0.02

Table VIII. Activation Parameters for the Acetonitrile (1) + 2-Propanol (2) System

	$\Delta G_m^{\ddagger}$/kJ mol^{-1}					
X_1	20 °C	30 °C	40 °C	50 °C	$\Delta H_m^{\ddagger}$/kJ mol^{-1}	$\Delta S_m^{\ddagger}$/J K^{-1} mol^{-1}
0.0000	14.9 ± 1.1	14.7 ± 1.2	14.5 ± 1.2	14.3 ± 1.2	20.22 ± 0.58	18.3 ± 1.9
0.0526	14.36 ± 0.64	14.20 ± 0.66	14.04 ± 0.66	13.88 ± 0.67	19.04 ± 0.33	16.00 ± 1.1
0.0771	14.11 ± 0.72	13.97 ± 0.73	13.82 ± 0.74	13.68 ± 0.76	18.23 ± 0.37	14.0 ± 1.2
0.1018	13.85 ± 0.65	13.73 ± 0.66	13.61 ± 0.68	13.50 ± 0.69	17.27 ± 0.33	11.7 ± 1.1
0.2227	12.97 ± 0.71	12.87 ± 0.72	12.78 ± 0.74	12.68 ± 0.75	15.85 ± 0.36	9.8 ± 1.2
0.3314	12.18 ± 0.17	12.15 ± 0.17	12.12 ± 0.18	12.09 ± 0.18	13.12 ± 0.09	3.20 ± 0.28
0.3989	11.74 ± 0.27	11.73 ± 0.28	11.72 ± 0.28	11.71 ± 0.29	12.01 ± 0.14	0.92 ± 0.45
0.5500	10.95 ± 0.57	10.99 ± 0.58	11.03 ± 0.59	11.06 ± 0.60	9.89 ± 0.29	−3.63 ± 0.95
0.6250	10.60 ± 0.54	10.65 ± 0.54	10.71 ± 0.55	10.76 ± 0.56	8.90 ± 0.27	−5.57 ± 0.89
0.6893	10.34 ± 0.64	10.42 ± 0.65	10.50 ± 0.66	10.58 ± 0.67	8.00 ± 0.32	−8.0 ± 1.1
0.7624	10.04 ± 0.81	10.12 ± 0.82	10.21 ± 0.84	10.30 ± 0.85	7.42 ± 0.42	−8.9 ± 1.3
0.8640	9.70 ± 0.44	9.79 ± 0.45	9.89 ± 0.46	9.99 ± 0.46	6.82 ± 0.22	−9.80 ± 0.73
1.0000	9.39 ± 0.01	9.50 ± 0.01	9.62 ± 0.01	9.74 ± 0.01	5.99 ± 0.00	−11.60 ± 0.02

the two components of the mixture (*25*, *26*).

Registry No. AN, 75-05-8; 1-PrOH, 71-23-8; 2-PrOH, 67-63-0.

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Mixture Properties of the Water + γ-Butyrolactone + Tetrahydrofuran System. 1. Densities of γ-Butyrolactone + Water at 303.15–343.15 K and of Tetrahydrofuran + γ-Butyrolactone at 278.15–298.15 K; Ultrasonic Velocities at 298.15 K for the Three Binary Systems Inclusive of Tetrahydrofuran + Water and the Ternary System Tetrahydrofuran + Water + γ-Butyrolactone

Devarapalli H. S. Ramkumar and Arvind P. Kudchadker*

Department of Chemical Engineering, Indian Institute of Technology, Bombay, Powai, Bombay 400 076, India

Densities of γ-butyrolactone + water and tetrahydrofuran + γ-butyrolactone systems were measured over temperature ranges of 303.15–343.15 and 278.15–298.15 K respectively, and ultrasonic velocities were measured at 298.15 K for the ternary system tetrahydrofuran + water + γ-butyrolactone and all three binary systems inclusive of the tetrahydrofuran + water system. Excess volumes and excess isentropic compressibilities were calculated from measured data and reported for all the systems studied. The data have been fitted to empirical models, and the model constants are also reported.

Introduction

The tetrahydrofuran (THF) + water system has been well studied with regards to its properties (*1*). We have earlier reported the enthalpies of mixing of THF + γ-butyrolactone (GBL) and GBL + water systems (*2*). In the present investigation we report the excess volumes and excess isentropic compressibilities from the measured density and ultrasonic velocity data of the binaries and the ternary system.

Experimental Section

Tetrahydrofuran supplied by Sarabhai Chemicals, India, was passed over activated alumina, refluxed over KOH pellets for 6 h, and finally distilled and collected over sodium wire. The purity of THF was found to be 99.6 mol % by GLC on Carbowax 29M by use of a thermal conductivity detector (TCD). γ-Butyrolactone of Fluka AG, Switzerland, was passed over a 13X molecular sieve column and distilled under reduced pressure in a 0.6-*m* packed column. A suitable fraction was collected and used for the experiment. The purity of GBL was found to be 99 mol % as determined by GLC on a column packed with 12% EGS (ethylene glycol succinate) using TCD. Double-distilled deionized water with 2×10^{-4} S·m conductivity was used for the measurements.

Densities were measured with a Lipkin pycnometer. The volume between marked lines of the pycnometer was determined by measuring the density of distilled mercury at various temperatures (*3*). The diameter of the capillary was determined by using a mercury thread with a traveling microscope. Mixtures of various compositions were prepared by weighing with an accuracy of $\pm 1 \times 10^{-5}$ in mole fraction on a Sartorius, FRG, balance. Care was taken not to allow any air bubble in the pycnometer. The pycnometer was thermostated with an accuracy of ±0.01 K. Low temperatures were achieved by using a Neslab, USA, cryounit. Temperatures were measured with an accuracy of ±0.025 K by use of a platinum resistance thermometer supplied by Minco Products, USA. The liquid levels in the pycnometer were read up to $\pm 1 \times 10^{-4}$ m with a cathetometer. Other precautions were taken, such as flushing the pycnometer with dry air and closing with caps as reported by Bauer (*4*). The overall accuracy of density measurements is estimated to be ± 0.1 kg·m^{-3}. Our pure component density data are compared with the literature values in Table I. Pure component density data of GBL measured by us from 298.15 to 453.15 K (data from 298.15 to 343.15 K

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