1232 *J. Chem. Eng. Data* **1997,** *42,* 1232−1234

Densities and Excess Molar Volumes of Water + Propyl Acetate + Propan-1-ol and Its Constituent Binaries at 303.15 K

Nuno A. T. Natividade, Abel G. M. Ferreira, and Isabel M. A. Fonseca*

Department of Chemical Engineering, University of Coimbra, Coimbra, Portugal

The densities of water + propyl acetate + propan-1-ol mixtures were measured in the miscible region at 303.15 K and atmospheric pressure. Derived excess molar volumes were correlated using the Redlich−Kister equation.

Introduction

Rao and Rao (1959) have determined the mutual solubility and tie-line data for some systems of the type water + ester + propan-1-ol, at 303.15 K. This investigation was undertaken to study the phase equilibrium relationships of this kind of ternary system with the purpose of finding a suitable solvent for the extraction of propan-1-ol from their aqueous solutions. One of the solvents studied was propyl acetate. In this work we report densities and excess molar volumes in the miscible region for water + propyl acetate + propan-1-ol and its constituent binaries at 303.15 K.

Experimental Section

Materials. Tridistilled water has been used. Propan-1-ol was supplied by Fluka AG with a purity >99.5 mass %, and propyl acetate was obtained from Aldrich with a purity >99 mass %. Since small concentrations of impurities have little influence on the excess volumes (Spanedda et al., 1991), both compounds were used without further purification. Table 1 lists the measured densities of the alcohol and the ester together with the values found in the literature. Water was used to calibrate the densimeter.

Apparatus. Mixtures were prepared by mass using a Mettler AT 200 balance with a precision of $\pm 10^{-5}$ g. Densities were measured in an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 602 measuring cell. Air and water have been used for the calibration of the densimeter. The control of the temperature was made using an Haake D8-G thermostated water bath, which has a temperature precision of ±0.02 K. A Pt resistance thermometer (calibrated against a precision mercury thermometer, graduated in 0.01 °C, certified by NPL, U.K.) was placed inside the vibrating tube densimeter to find the actual temperature of the measurements. The temperature was mantained at (303.15 ± 0.02) K.

Uncertainties. Densities were measured to a precision of 10^{-5} g·cm^{-3}. Keeping in mind that the error in excess molar volume, V^E, is determined by the uncertainties in mole fraction and density, the maximum error in V^E resulting from the propagation law of errors is 5×10^{-3} cm^3 mol^{-1}.

Table 1. Densities (ρ) of Pure Components at 303.15 K

component	ρ/(g·cm^{-3}) exptl	ρ/(g·cm^{-3}) lit.
water		0.995 7[a]
propyl acetate	0.876 35	0.877 0[b]
propan-1-ol	0.795 59	0.795 5[c]
		0.795 60[d]

[a] Dizechi and Marschall (1982). [b] Subrahmanyam and Murty (1964). [c] Mikhail and Kimel (1963). [d] Pikkarainen (1983).

Results and Discussion

The molar volumes V_m of the mixtures were calculated from the expression

$$V_m = \sum \frac{x_i M_i}{\rho} \tag{1}$$

where x_i is the mole fraction of component i in the mixture, M_i its molecular weight, and ρ the measured density of the mixture. The excess molar volumes V^E were calculated from

$$V^E = V_m - \sum x_i V_i^* \tag{2}$$

where V_i^* is the molar volume of pure component i. Table 2 lists the measured densities, ρ, and the corresponding values of V^E for ternary mixtures. Results for the constituent binaries water (1) + propan-1-ol (3) and propyl acetate (2) + propan-1-ol (3) are also included. For the latter system the measured values of ρ and V^E are plotted against mole fraction of propan-1-ol in Figure 1. As far as we know these values have not been previously published.

The V^E data were correlated using a Redlich−Kister type equation for the ternary system (Redlich and Kister, 1948)

$$V_{123}^E = V_{12}^E + V_{32}^E + V_{13}^E + x_1x_2x_3[A + B_1(x_1 - x_2) + B_2(x_3 - x_2) + B_3(x_1 - x_3) + ...] \tag{3}$$

where V_{123}^E represents the excess molar volume for the ternary system and V_{ij}^E is the value of the Redlich−Kister polynomial for the same property, fitted to the data for the binary system (i,j):

$$V_{ij}^E = x_i x_j \sum_k A_k (x_i - x_j)^k, \quad k = 0, 1, 2, ..., n \tag{4}$$

The optimized coefficients, A_k, and standard deviations (defined as $\sigma = [\sum(V_{exp}^E - V_{calc}^E)/M - 3]^{1/2}$, where M repre-

---

* Corresponding author. Tel: +(0.39) 28392. Fax: +(039) 27425. E-mail: eq1imf@eq.uc.pt.

S0021-9568(97)00135-0 CCC: $14.00

Table 2. Densities, ρ, and Excess Molar Volumes, V^E, for Water (1) + Propyl Acetate (2) + Propan-1-ol (3) at 303.15 K

x_1	x_2	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x_1	x_2	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})
0.0680	0.5956	0.857 01	0.095	0.4108	0.1149	0.848 49	−0.505
0.0756	0.7770	0.868 29	0.109	0.4372	0.0580	0.844 76	−0.559
0.0771	0.2279	0.826 14	−0.041	0.4419	0.2204	0.864 72	−0.483
0.1034	0.8738	0.873 84	0.049	0.4641	0.0000	0.840 46	−0.611
0.1056	0.7518	0.869 54	0.047	0.5035	0.1118	0.861 12	−0.557
0.1070	0.4152	0.845 44	−0.015	−0.5669	0.0000	0.856 06	−0.638
0.1109	0.5029	0.852 49	0.030	0.5885	0.0000	0.859 70	−0.634
0.1132	0.5779	0.858 32	0.036	0.5923	0.1090	0.876 07	−0.606
0.1175	0.3150	0.838 17	−0.106	0.6283	0.0548	0.874 70	−0.581
0.1181	0.4100	0.846 07	−0.039	0.6648	0.0000	0.874 34	−0.612
0.1233	0.2165	0.829 14	−0.133	0.6896	0.0000	0.880 39	−0.625
0.1265	0.1217	0.819 37	−0.169	0.7617	0.0000	0.899 27	−0.598
0.1440	0.0000	0.807 10	−0.313	0.7699	0.0000	0.901 65	−0.592
0.1468	0.6416	0.866 12	−0.021	0.8335	0.0000	0.922 07	−0.523
0.2150	0.1206	0.827 39	−0.307	0.8400	0.0000	0.925 00	−0.530
0.2154	0.5112	0.863 65	−0.155	0.8862	0.0000	0.941 98	−0.422
0.2166	0.5892	0.869 56	−0.144	0.9236	0.0000	0.958 91	−0.343
0.2209	0.4407	0.858 62	−0.178	0.9304	0.0000	0.961 95	−0.320
0.2249	0.3603	0.852 55	−0.238	0.9677	0.0000	0.980 44	−0.189
0.2296	0.0608	0.821 97	−0.374	1.0000	0.0000	0.995 70	0.000
0.2304	0.2765	0.845 53	−0.286	0.0000	1.0000	0.876 35	0.000
0.2350	0.4890	0.837 08	−0.139	0.0000	0.9196	0.870 64	0.180
0.2444	0.0000	0.815 93	−0.449	0.0000	0.8406	0.865 52	0.253
0.2718	0.0000	0.818 54	−0.478	0.0000	0.7520	0.859 91	0.274
0.2765	0.2296	0.845 30	−0.321	0.0000	0.6516	0.853 24	0.279
0.3165	0.1193	0.837 69	−0.423	0.0000	0.5657	0.847 22	0.267
0.3267	0.3809	0.865 49	−0.338	0.0000	0.4649	0.839 64	0.248
0.3345	0.3094	0.860 23	−0.393	0.0000	0.3592	0.831 11	0.210
0.3589	0.0000	0.827 52	−0.549	0.0000	0.2470	0.821 13	0.166
0.3594	0.2255	0.854 52	−0.417	0.0000	0.1288	0.809 67	0.092
				0.0000	0.0000	0.795 59	0.000

Table 3. Coefficients and Standard Deviations of the Excess Volume−Composition Curves Fitted to the Data for the Binary Systems

system	A_0/cm^3·mol^{-1})	A_1/(cm^3·mol^{-1})	A_2/(cm^3·mol^{-1})	σ/(cm^3·mol^{-1})
water + propan-1-ol	−2.428	0.846	−1.821	0.020
propyl acetate + propan-1-ol	0.998	−0.668	0.830	0.011

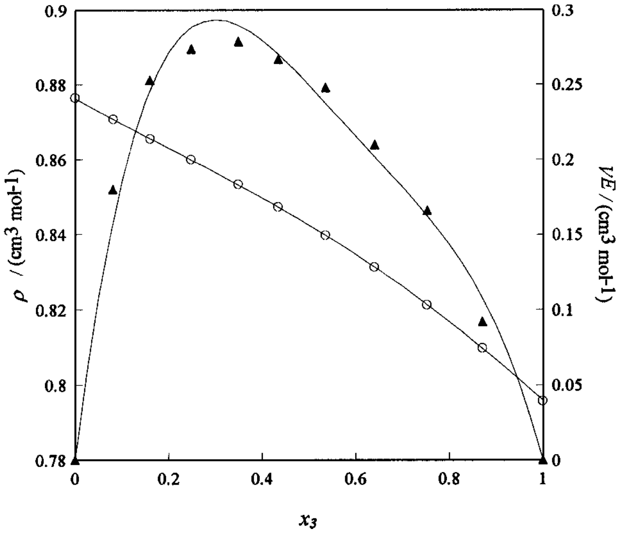

Figure 1. Density ρ (○) and excess molar volume, V^E, (△) of propyl acetate (2) + propan-1-ol (3) as functions of mole fraction of propyl acetate at 303.15 K and atmospheric pressure.

Table 4. Coefficients and Standard Deviation of the Excess Volume−Composition Surface Fitted to the Data for the Ternary System Water + Propyl Acetate + Propan-1-ol

A/(cm^3·mol^{-1})	B_1/(cm^3·mol^{-1})	B_2/(cm^3·mol^{-1})	σ/(cm^3·mol^{-1})
−5.513	−2.876	6.433	0.016

sents the number of the experimental points) are listed in Table 3. V^E_{12} is taken to be identically zero, since water and propyl acetate are practically immiscible. The fitted coefficients A, B_i for the ternary polynomial and the corresponding standard deviation of fit are in given Table 4. Since the sum of the mole fractions is unity, one of the coefficients B_i in eq 3 is reductant, so we have settled on $B_3 = 0$.

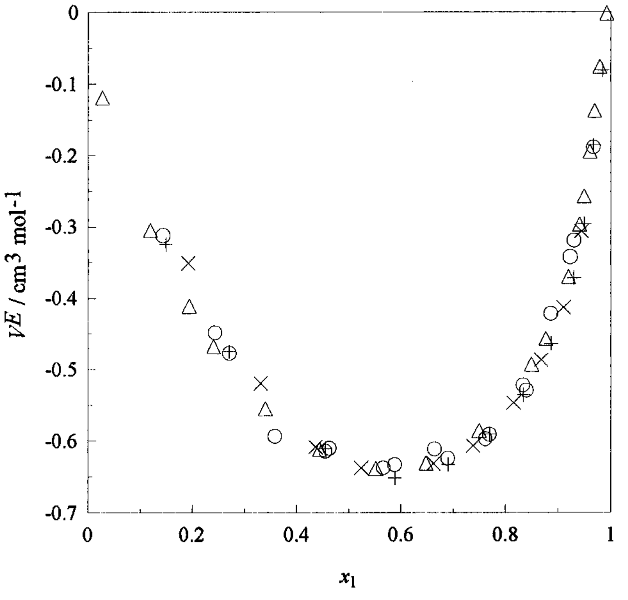

Figure 2. V^E of water (1) + propan-1-ol (3) as a function of mole fraction of water: (○) this work, (△) Benson and Kiyohara, (×) Dizechi and Marschall, (+) Mikhail and Kimel.

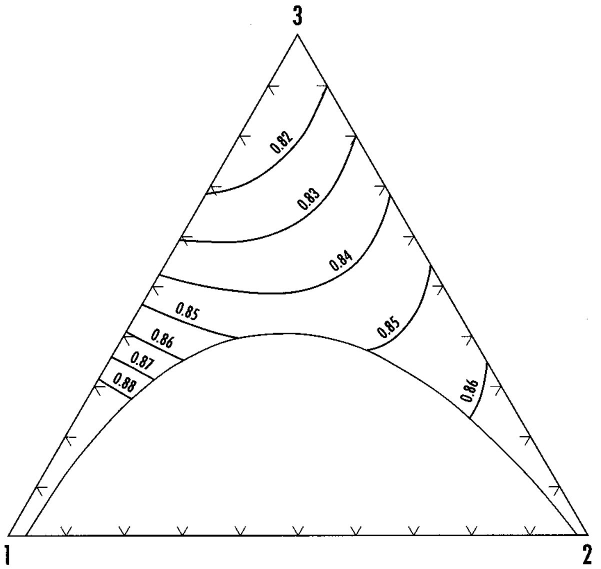

Figure 3. Density isolines for water (1) + propyl acetate (2) + propan-1-ol (3) at 303.15 K and atmospheric pressure.

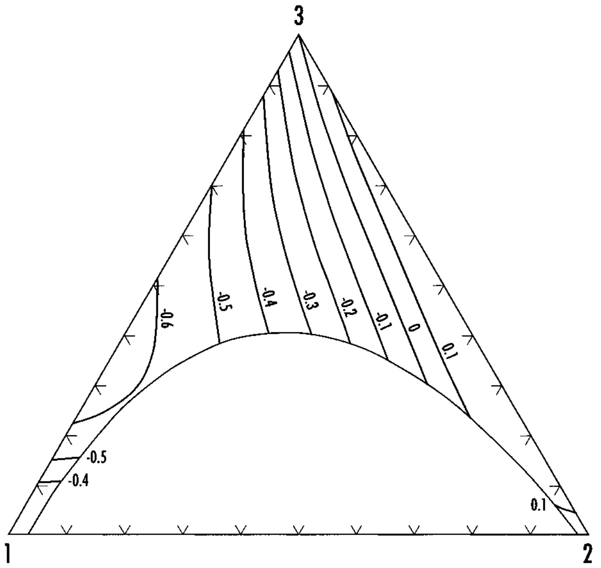

Figure 4. Excess molar volume isolines for water (1) + propyl acetate (2) + propan-1-ol (3) at 303.15 K and atmospheric pressure.

Figure 2 compares our V^E data for water + propan-1-ol with previously published results. In Figures 3 and 4 are shown isolines for the density and excess molar volume, respectively. Figure 5 represents a perspective view of the excess molar volumes for the ternary system.

Conclusions

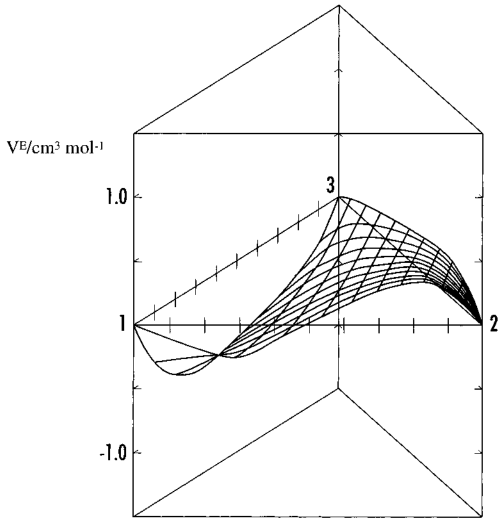

Figure 5. Perspective view of the excess molar volume of water (1) + propyl acetate (2) + propan-1-ol (3) at 303.15 K and atmospheric pressure.

The excess molar volumes of the ternary system water + propyl acetate + propan-1-ol at 303.15 K and atmospheric pressure are negative in the majority of the miscible region and become positive near the propyl acetate + propan-1-ol binary. The maximum value of V^E is 0.294 cm^3 mol^{-1} (for $x_2 = 0.300$, $x_3 = 0.700$), and the minimum value is -0.648 cm^3 mol^{-1} (for $x_1 = 0.656$, $x_3 = 0.344$).

In spite of the relatively complexity of the V^E surface, we achieve to represent it with only three adjustable parameters, which allows us to obtain a standard deviation of the same order of those for the binaries.

Literature Cited

Benson, G. C.; Kiyohara, O. Thermodynamics of Aqueous Mixtures of Nonelectrolytes. I. Excess Volumes of Water−*n*-Alcohol Mixtures at Several Temperatures. *J. Solution Chem.* **1980**, *9* (10), 791−804.

Dizechi, M.; Marschall, E. Viscosity of Some Binary and Ternary Liquid Mixtures. *J. Chem. Eng. Data* **1982**, *27*, 358−363.

Mikhail, S. Z.; Kimel, W. R. Densities and Viscosities of 1-Propanol−Water Mixtures. *J. Chem. Eng. Data* **1963**, *8* (3), 323−328.

Pikkarainen, L. Densities and Viscosities of Binary Mixtures of *N,N*-Dimethylacetamide with Aliphatic Alcohols. *J. Chem. Eng. Data* **1983**, *28*, 344−347.

Rao, R. J.; Rao, C. V. Ternary Liquid Equilibria Systems: Propan-1-ol−Water−Esters. *J. Appl. Chem.* **1959**, *9*, 69−73.

Redlich, O.; Kister, A. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Spanedda, A.; Lepori, L.; Matteoli, E. Volumes of Mixing of Ethers with Tetrachloromethane at 298.15 K. *Fluid Phase Equilibr.* **1991**, *69*, 209−222.

Subrahmanyam, V.; Murty, P. D. Vapour−Liquid Equilibria: System: (1) Acetone−Ethyl Acetate; (2) Acetone−*n*-Propyl Acetate. *J. Appl. Chem.* **1964**, *14*, 500−502.

Received for review May 27, 1997. Accepted August 4, 1997.⊗

JE970135T

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1997.