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Refractive Indices, Densities, and Excess Properties for Binary Mixtures Containing Methanol, Ethanol, 1,2-Ethanediol, and 2-Methoxyethanol

Lídia Albuquerque,* Cristina Ventura, and Raquel Gonçalves

GERQ, University of Lisbon, Department of Chemistry, Cç. Bento da Rocha Cabral, 14, 1200 Lisboa, Portugal

Measurements of refractive index and density were performed for the six binary solvent mixtures containing methanol, ethanol, 1,2-ethanediol, and 2-methoxyethanol, over the entire composition range, at 298.15 K. From these results, the excess refractive indices and the excess molar volumes were calculated and fitted to the Redlich−Kister equation.

Introduction

Several solvent parameters are frequently employed to investigate and interpret medium effects in chemical reactions and other solution processes, using for instance linear solvation energy relationships analysis (Gonçalves *et al.*, 1992; Calado *et al.*, 1994; Abraham *et al.*, 1994). Moreover, selected properties of solvents are required for the control of industrial chemical processes, such as polymerization and solvolysis. The refractive index and the density are between the most relevant intensive properties of solvents.

Recently, extensive studies of thermomechanical properties and of solvatochromic parameters of binary alcohol mixtures were undertaken (Franchini *et al.*, 1991; Arce *et al.*, 1993; Corradini *et al.*, 1993; Aminabhavi and Gopalkrishna, 1994; Rosés *et al.*, 1995) in order to improve our understanding on solvation phenomena.

As a part of our experimental program on the physicochemical properties of binary mixtures of alcohols, we present here measurements on the refractive index and density for the six mixtures methanol + ethanol, methanol 1,2-ethanediol, ethanol + 1,2-ethanediol, methanol + 2-methoxyethanol, ethanol + 2-methoxyethanol, and 2-methoxyethanol + 1,2-ethanediol, at 298.15 K, over the mole fraction range. We calculated the excess refractive indices and the excess molar volumes which were fitted to the Redlich−Kister equation.

Experimental Section

Materials. The solvents were from BDH and Merck with 99% purity or better and were dried over molecular sieves for several days before use. The water content was kept lower than 0.02%. Gas chromatographic (Hewlett-Packard 5890) tests were performed, and the analysis always gives >99.0 mol % purity. Infrared spectroscopic tests were also performed.

The mixtures were prepared by mixing the appropriate volumes of liquids and weighed in a Mettler balance, to an accuracy of 0.01 mg, just before their use. The uncertainty in the mole fractions is less than 0.000 15.

Measurements. The refractive index at the sodium D line was obtained using a thermostated Abbe refractometer BS, and the values presented here are the mean values from at least five independent readings for each sample (at least three samples were taken for each solvent composition). The precision of the refractive indices is 0.000 02 units.

Table 1. Comparison of Refractive Indices (n_D) and Densities (ρ) of Pure Alcohols, at 298.15 K

alcohol	n_D expt	n_D lit.	ρ/g cm^{-3} expt	ρ/g cm^{-3} lit.
methanol	1.327 15	1.326 52[a] 1.326 4[b]	0.7893	0.786 37[a] 0.786 64[c]
ethanol	1.359 31	1.359 41[a] 1.359 2[b]	0.7852	0.784 93[a] 0.785 09[c]
1,2-ethanediol	1.430 24	1.430 6[a] 1.429 7[d]	1.1084	1.110 0[a] 1.110 0[c]
2-methoxyethanol	1.400 46	1.400 2[a] 1.400 7[d]	0.9601	0.960 24[a] 0.960 288[e]

[a] Riddick *et al.*, 1986. [b] Arce *et al.*, 1993. [c] *TRC Data Bases,* 1995. [d] Franchini *et al.*, 1991. [e] Tassi, 1993.

Densities were measured with a digital precision system, DMA 512 (Anton Paar) with an accuracy of 0.000 05 g cm^{-3}, using a special remote cell. An average of triplicate measurements was taken in account, and they were reproducible within 0.000 02 g cm^{-3}.

In both measurements, thermostats were used with a temperature control of ±0.01 K.

Results and Discussion

Table 1 gives the observed refractive indices, n_D, and densities, ρ, for the pure components together with values obtained from the literature. The comparison shows a very reasonable agreement, except for methanol. This is difficult to explain since methanol was a high-purity-grade reagent from Merck (GR PA; 99.5% by mass; water <0.01%) and the final purity tests confirmed these values.

The refractive indices of the mixtures were determined for nine mole fractions, at 298.15 K. These values are reported in Table 2, where x_1 represents the mole fraction of the first component of the mixture. The densities, obtained for the same mixtures, are also given in Table 2.

The excess properties of the mixtures were then calculated using the following equation:

$$Y^E = Y - Y_1^* x_1 - Y_2^* x_2 \qquad (1)$$

where Y^E may represent the excess refractive index or the excess molar volume. The refractive indices or the excess molar volumes of pure liquids 1 and 2, and of the mixture, are Y_1^*, Y_2^*, and Y, respectively. The molar volume of the mixture was calculated as

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* To whom correspondence should be addressed. Fax: (351) 1 387 06 85.

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Table 2. Experimental Values of the Refractive Index (n_D), Density (ρ), Excess Refractive Index (n_D^E) and Excess Molar Volume (V^E) for Alcohol + Alcohol Mixtures, at Different Mole Fractions (x_1) and 298.15 K

x_1	n_D	n_D^E	ρ/g cm^{-3}	V^E/cm^3 mol^{-1}
		Methanol + Ethanol		
1.0000	1.327 15		0.7893	
0.9549	1.328 82	0.0002	0.7890	0.002
0.9100	1.330 46	0.0004	0.7889	−0.005
0.8099	1.334 40	0.0011	0.7883	−0.003
0.7499	1.337 08	0.0019	0.7881	−0.005
0.4999	1.345 79	0.0026	0.7871	−0.013
0.2499	1.352 81	0.0015	0.7861	−0.008
0.0860	1.357 02	0.0005	0.7855	−0.001
0.0000	1.359 31		0.7852	
		Methanol + 1,2-Ethanediol		
0.9550	1.336 07	0.0043	0.8148	−0.306
0.9103	1.343 48	0.0071	0.8397	−0.606
0.8100	1.356 49	0.0098	0.8826	−0.752
0.7499	1.365 35	0.0124	0.9050	−0.746
0.4989	1.389 67	0.0110	0.9905	−0.790
0.2500	1.413 75	0.0093	1.0570	−0.525
0.0861	1.424 88	0.0035	1.0917	−0.182
0.0000	1.430 24		1.1084	
		Ethanol + 1,2-Ethanediol		
0.9545	1.362 46	−0.0001	0.8031	−0.289
0.9104	1.366 49	0.0008	0.8204	−0.521
0.8103	1.375 12	0.0023	0.8536	−0.631
0.7500	1.379 24	0.0022	0.8747	−0.761
0.4998	1.395 72	0.0009	0.9572	−0.848
0.2499	1.412 65	0.0001	1.0372	−0.678
0.0862	1.424 94	0.0008	1.0851	−0.295
		Methanol + 2-Methoxyethanol		
0.9548	1.334 42	0.0040	0.8058	−0.111
0.9100	1.340 58	0.0068	0.8216	−0.252
0.8099	1.352 19	0.0111	0.8494	−0.361
0.7503	1.358 09	0.0126	0.8642	−0.441
0.4999	1.377 35	0.0135	0.9076	−0.350
0.2497	1.391 39	0.0093	0.9388	−0.268
0.0859	1.396 65	0.0025	0.9542	−0.159
0.0000	1.400 46		0.9601	
		Ethanol + 2-Methoxyethanol		
0.9552	1.362 08	0.0009	0.7965	−0.057
0.9104	1.364 69	0.0017	0.8083	−0.181
0.8097	1.370 12	0.0030	0.8311	−0.284
0.7502	1.373 66	0.0031	0.8443	−0.359
0.5001	1.383 71	0.0038	0.8897	−0.307
0.2496	1.392 92	0.0027	0.9281	−0.209
0.0857	1.397 99	0.0011	0.9498	−0.092
		2-Methoxyethanol + 1,2-Ethanediol		
0.9550	1.401 61	−0.0002	0.9656	−0.059
0.9098	1.402 65	−0.0005	0.9717	−0.150
0.8101	1.405 02	−0.0011	0.9842	−0.230
0.7496	1.407 34	−0.0006	0.9928	−0.331
0.5000	1.414 39	−0.0010	1.0254	−0.258
0.2503	1.421 88	−0.0009	1.0642	−0.193
0.0860	1.427 25	−0.0004	1.0924	−0.077

$$V/\text{cm}^3\ \text{mol}^{-1} = (x_1M_1 + x_2M_2)/\rho \qquad (2)$$

where x_1, x_2, M_1, and M_2 represent the mole fraction and the molecular mass of components 1 and 2 and ρ is the experimental density.

The values of the excess refractive indices and the excess molar volumes are also presented in Table 2. They were fitted to the Redlich−Kister (Redlich and Kister, 1948) polynomial relationship:

$$Y^E/\text{cm}^3\ \text{mol}^{-1} = x_1x_2\sum_{i=0}^{n} a_i(x_2 - x_1)^i \qquad (3)$$

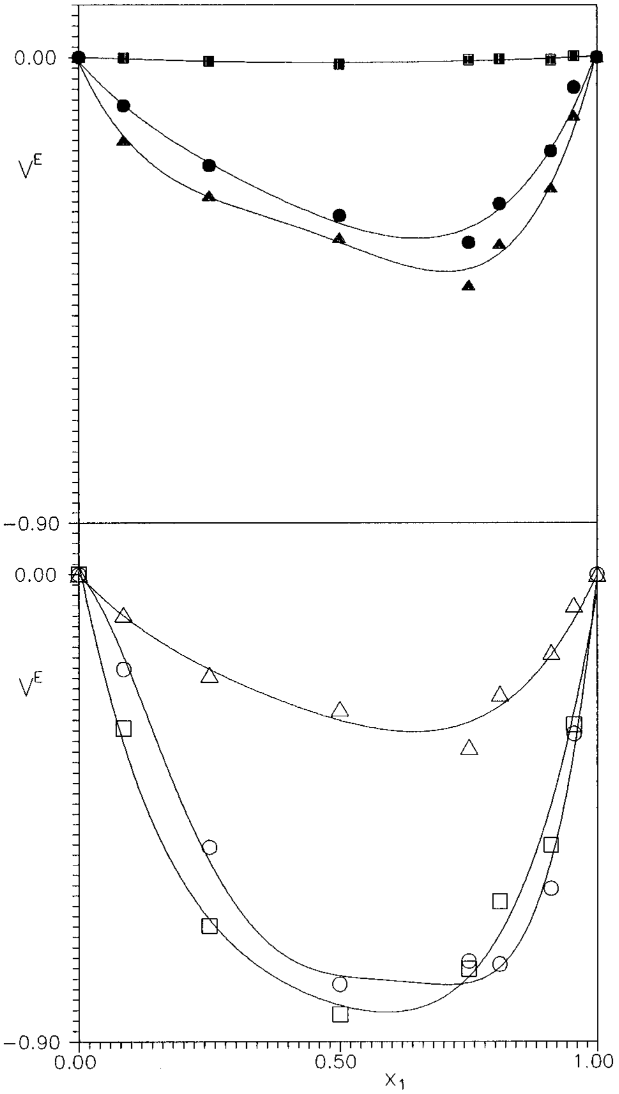

Figure 1. Dependence of excess molar volume (cm^3 mol^{-1}) on the mole fraction of the first component of the mixtures, at 298.15 K: (■) methanol + ethanol; (▲) methanol + 2-methoxyethanol; (●) ethanol + 2-methoxyethanol; (○) methanol + 1,2-ethanediol; (□) ethanol + 1,2-ethanediol; (△) 2-methoxyethanol + 1,2-ethanediol.

The interaction coefficients, a_i, and standard deviations, s, of the best fits were obtained through the application of multiple linear regression analysis and a least-squares method. All points were equally weighted. The criterion of Ehrenson (Ehrenson, 1979) for relative fitting to a more restricted equation form was used to give the statistically preferred equations. The values of the estimated parameters as well as s values are collected in Table 3. The best-fit equations reproduce the values within the limits of experimental uncertainty. Graphical presentations of the experimental results are provided in Figures 1 and 2. The continuous curves also shown in Figures 1 and 2 were calculated from eq 3 using the values of the coefficients given in Table 3.

It seems useful to examine how excess volumes depend on the composition of the mixtures. Deviations from ideality for the systems under study can be related to intermolecular hydrogen bonding and other interactions between the components of the mixtures. Since both solvents of each mixture are alcohols, the progressive addition of a cosolvent inhibits hydrogen bonding in a solvent, these network interactions being progressively replaced by a solvent−cosolvent mixed connectivity.

Excess volumes are, in general, negative and strongly dependent on the mixture. In the mixture methanol + ethanol, an almost ideal behavior is observed. In the case

Table 3. Parameters (a_i) and Standard Deviations (s) ofthe Redlich–Kister Equation

system	a_0	a_1	a_2	a_3	s
Excess Molar Volumes (V^E)—Composition					
methanol + ethanol	−0.049 36	−0.007 68	0.047 96		0.002
methanol + 1,2-ethanediol	−3.047 44	0.201 39	−2.020 6	3.991 75	0.049
ethanol + 1,2-ethanediol	−3.332 24	−0.466 59	−2.011 64	2.782 60	0.047
methanol + 2-methoxyethanol	−1.432 64	1.088 26	−1.542 09	−0.915 19	0.024
ethanol + 2-methoxyethanol	−1.282 93	0.989 26	−0.578 66	−0.839 00	0.027
2-methoxyethanol + 1,2-ethanediol	−1.121 87	0.540 18	−0.482 29		0.032
Excess Refractive Indices (n_D^E)—Composition					
methanol + ethanol	0.009 90	0.000 40	−0.007 72		0.0005
methanol + 1,2-ethanediol	0.044 89	−0.015 96	0.036 14		0.0005
ethanol + 1,2-ethanediol	0.003 62	−0.018 92	0.010 10	0.029 95	0.0003
methanol + 2-methoxyethanol	0.056 93	−0.012 00	0.000 69	−0.034 25	0.0003
ethanol + 2-methoxyethanol	0.015 77	0.002 99	0.003 25	−0.014 40	0.0002
2-methoxyethanol + 1,2-ethanediol	−0.004 55				0.0003

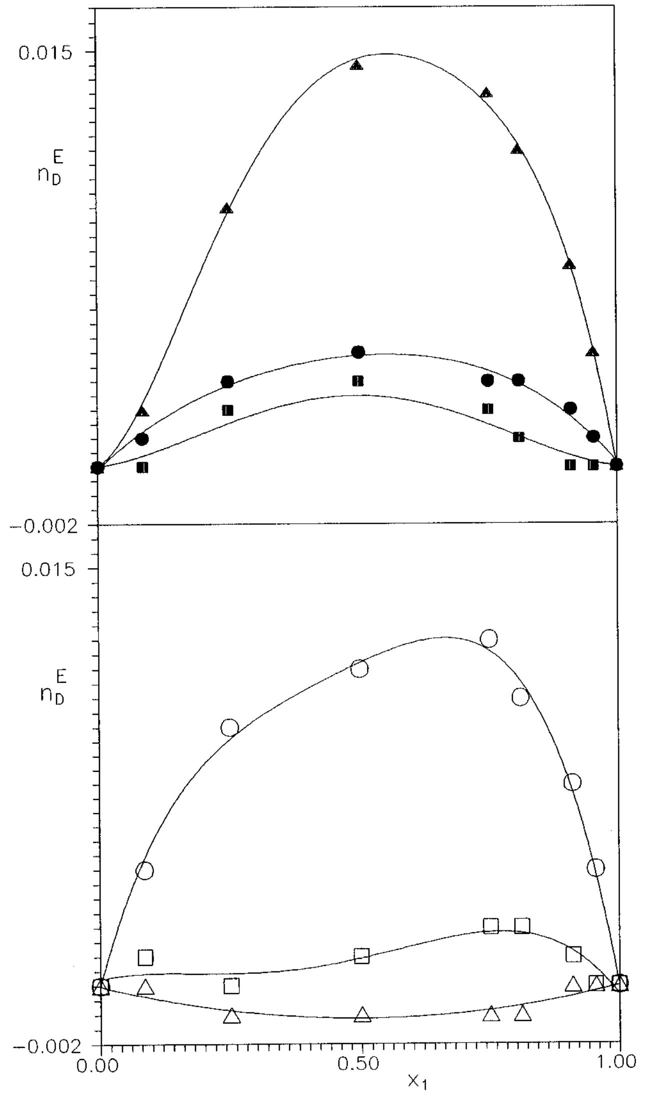

Figure 2. Dependence of excess refractive index on the mole fraction of the first component of the mixtures, at 298.15 K: (■) methanol + ethanol; (▲) methanol + 2-methoxyethanol; (●) ethanol + 2-methoxyethanol; (○) methanol + 1,2-ethanediol; (□) ethanol + 1,2-ethanediol; (△) 2-methoxyethanol + 1,2-ethanediol.

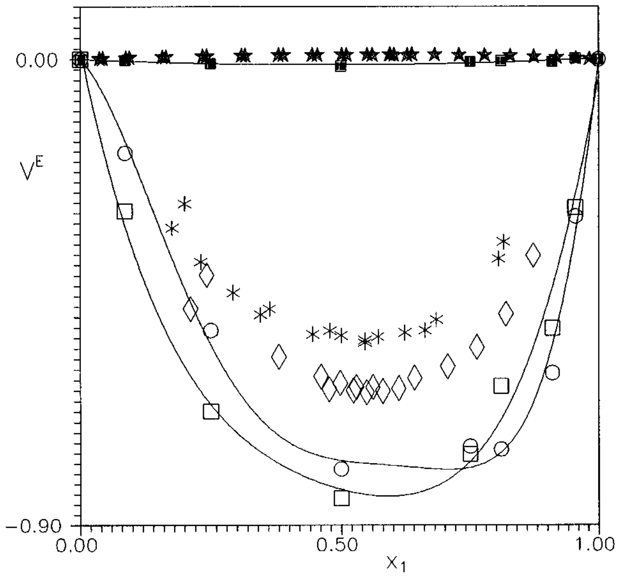

Figure 3. Dependence of excess molar volume (cm^3 mol^{-1}) on the mole fraction of the first component of the mixtures, at 298.15 K: (★) methanol + ethanol (Benson and Pflug, 1970); (◊) methanol + 1,2-ethanediol (Jimenez, 1971; Jimenez and Paz Andrade, 1974); (∗) ethanol + 1,2-ethanediol (Jimenez, 1971; Jimenez and Paz Andrade, 1974). The other symbols have the same meaning as in Figure 1.

of 1,2-ethanediol + 2-methoxyethanol mixture, V^E exhibits the smaller dependence on composition (except that for methanol + ethanol). An explanation for this is that both solvents, at low temperatures, predominantly exist in the cyclic *gauche* conformation and the strong intramolecular hydrogen bonding tendency would reduce its ability to sustain interaction connectivity. In 2-methoxyethanol, the probability of achieving favorable orientations for hydrogen bonding formation is much lower than in 1,2-ethanediol. This may explain the comparable behavior of excess volumes for the mixtures containing the first solvent (methanol + 2-methoxyethanol and ethanol + 2-methoxyethanol) and those containing the second solvent; the V^E minimum observed for 1,2-ethanediol is approximately 2 times larger than for 2-methoxyethanol curves. It is interesting to compare the excess functions behavior with that of the same systems available in the literature. Several authors provided V^E values for the system methanol + ethanol (Wisniak and Tamir, 1978). We selected the more recent experimental values, those from Benson and Pflug (Benson and Pflug, 1970). Excess volumes can also be found for two other systems, methanol + 1,2-ethanediol and ethanol + 1,2-ethanediol (Jimenez, 1971; Jimenez and Paz Andrade, 1974). The comparison of our excess molar volume results with those obtained by the cited previous researchers is shown in Figure 3.

Our values are in good agreement with the values obtained by Benson and Pflug and differ from those of Jimenez and Paz Andrade. However, even in this case, the interpretation and the position of the minima are consistent.

Concerning the n_D^E properties, we present in Figure 4 a comparison of our values with those calculated from

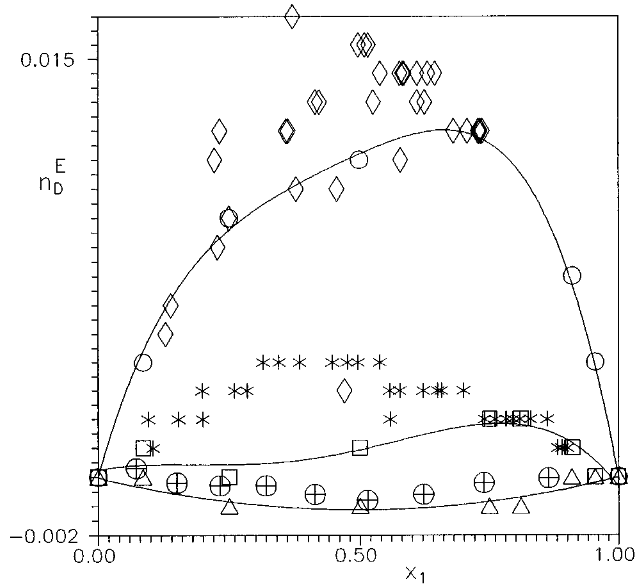

Figure 4. Dependence of excess refractive index on the mole fraction of the first component of the mixtures, at 298.15 K: (◊) methanol + 1,2-ethanediol (Jimenez and Paz Andrade, 1974); (∗) ethanol + 1,2-ethanediol (Jimenez and Paz Andrade, 1974); (⊕) 2-methoxyethanol + 1,2-ethanediol (Franchini *et al.*, 1991). The other symbols have the same meaning as in Figure 2.

Jimenez and Paz Andrade n_D data (Jimenez and Paz Andrade, 1974) for the systems methanol + 1,2-ethanediol and ethanol + 1,2-ethanediol. Also in the same figure our results for the 2-methoxyethanol + 1,2-ethanediol mixture are compared with those obtained by Franchini *et al.* (Franchini *et al.*, 1991). A poor agreement is found for the binary mixtures methanol + 1,2-ethanediol and ethanol + 1,2-ethanediol; the values presented in the literature are too scattered, and hence, its reliability and precision are scarce. Conversely, an excellent agreement is found between our results and those presented by Franchini *et al.*

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