Densities and Refractive Indices for Acetone + Methanol + 1-Propanol at 298.15 K

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Densities and refractive indices at 298.15 K for acetone + methanol + 1-propanol and the binary acetone + 1-propanol and methanol + 1-propanol mixtures have been measured as a function of the mole fraction at atmospheric pressure. Parameters of analytical expressions which represent the composition dependences of physical properties and excess values are reported. The refractive index results are compared with estimation methods. The excess properties for the ternary mixture are compared with those estimated on the basis of binary property contributions.

Introduction

Our present research is focused on the use of aliphatic alcohols as solvents in atmospheric extractive rectification of binary minimum azeotropes. As part of that research, we present densities and refractive indices on mixing at 298.15 K of acetone + methanol + 1-propanol, acetone + 1-propanol, and methanol + 1-propanol.

Experimental Section

Apparatus and Procedure. A PolyScience controller bath model 9510 with a temperature stability of $\pm 10^{-2}$ K was used. The samples were prepared by mass using a Mettler AE-240 balance with a precision of $\pm 10^{-4}$ g. The densities of the mixtures and pure liquids were measured with an Anton Paar DMA-46 densimeter with a precision of $\pm 10^{-4}$ g·cm^{-3} and the refractive indices by an automatic refractometer ABBEMAT-HP Dr Kernchen with a precision of $\pm 10^{-5}$. The accuracies in the calculation of excess molar volumes and changes of refractive indices are better than 9.4×10^{-3} cm^3·mol^{-1} and 10^{-4}, respectively. The experimental technique has been described previously (Iglesias *et al.*, 1995).

Purity of Materials. Acetone, methanol, and 1-propanol were supplied as chromatographic grade by Merck Farma y Química S.A. No further purification was attempted because the chemicals were recently acquired and kept in inert argon atmosphere. The purities of the chemicals had been previously checked by gas chromatography, and they fulfilled the purchaser specifications. The analysis showed purities exceeding 99.8% for all the chemicals used. Precautions were taken such as cooling chemicals before sample preparation, in order to avoid evaporation losses during experimental work. Table 1 compares our density and refractive index values with recommended values and recent published results. The accuracy in the determination of the molar fraction of the measured samples is 10^{-4}.

Table 1. Comparison of Data with Literature Data for Pure Liquids at 298.15 K

	ρ(298.15 K)/(g·cm^{-3})		n_D(298.15 K)	
component	exptl	lit.	exptl	lit.
acetone	0.7841	0.785 47[a]	1.356 05	1.355 96[a]
		0.784 40[b]		1.355 96[b]
methanol	0.7863	0.786 64[a]	1.326 76	1.326 52[a]
		0.786 64[b]		1.326 52[b]
1-propanol	0.7993	0.799 75[a]	1.382 83	1.383 70[a]
		0.799 75[b]		1.383 70[b]

[a] *TRC Thermodynamic Tables* (1994). [b] Riddick and Bunger (1986).

Table 2. Densities ρ, Refractive Indices n_D, Excess Molar Volumes V_m^E, and Changes of Refractive Index on Mixing δn_D for Binary Mixtures at 298.15 K

x_3	ρ/(g·cm^{-3})	n_D	V_m^E/(cm^3·mol^{-1})	δn_D
		Acetone (1) + 1-Propanol (3)		
0.9823	0.7990	1.382 38	0.003	0.0000
0.9289	0.7983	1.381 01	−0.006	0.0001
0.8824	0.7975	1.379 86	0.003	0.0002
0.8387	0.7970	1.378 76	−0.011	0.0002
0.7953	0.7962	1.377 63	0.002	0.0003
0.7448	0.7955	1.376 31	−0.003	0.0003
0.7005	0.7949	1.375 17	−0.010	0.0004
0.6501	0.7941	1.373 85	−0.006	0.0004
0.5954	0.7933	1.372 35	−0.009	0.0004
0.5399	0.7922	1.370 83	0.015	0.0003
0.4922	0.7916	1.369 53	0.004	0.0003
0.4472	0.7910	1.368 29	−0.004	0.0003
0.3488	0.7894	1.365 55	0.005	0.0002
0.1974	0.7870	1.361 39	0.013	0.0000
0.1554	0.7865	1.360 15	−0.001	−0.0001
0.1137	0.7856	1.358 96	0.022	−0.0001
0.0687	0.7852	1.357 62	−0.004	−0.0003
		Methanol (2) + 1-Propanol (3)		
0.9531	0.7989	1.381 32	0.006	0.0011
0.9084	0.7985	1.379 77	0.011	0.0021
0.8499	0.7979	1.377 80	0.023	0.0034
0.8296	0.7977	1.377 00	0.026	0.0037
0.8080	0.7975	1.376 26	0.027	0.0042
0.7754	0.7972	1.374 98	0.028	0.0047
0.6818	0.7962	1.371 12	0.038	0.0061
0.6729	0.7961	1.370 84	0.039	0.0063
0.6193	0.7955	1.368 39	0.043	0.0069
0.5040	0.7941	1.362 90	0.050	0.0079
0.4964	0.7940	1.362 51	0.050	0.0079
0.4516	0.7934	1.360 12	0.053	0.0080
0.4507	0.7934	1.360 03	0.052	0.0080
0.3992	0.7927	1.357 07	0.052	0.0079
0.3542	0.7921	1.354 32	0.049	0.0077
0.3106	0.7915	1.351 53	0.046	0.0073
0.2699	0.7909	1.348 82	0.042	0.0069
0.2303	0.7903	1.346 03	0.038	0.0064
0.1912	0.7898	1.343 13	0.027	0.0056
0.1585	0.7893	1.340 54	0.021	0.0049
0.1274	0.7888	1.338 05	0.015	0.0041
0.0907	0.7882	1.334 90	0.007	0.0030
0.0662	0.7878	1.332 67	0.000	0.0022
0.0396	0.7874	1.330 21	−0.010	0.0012
0.0358	0.7873	1.329 93	−0.009	0.0012

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Table 3. Densities, Refractive Indices, Excess Molar Volumes, and Changes of Refractive Index on Mixing for Acetone (1) + Methanol (2) + 1-Propanol (3) at 298.15 K

x_1	x_2	ρ/(g·cm^{-3})	n_D	V_m^E/(cm^3·mol^{-1})	δn_D
0.0541	0.1067	0.7978	1.378 03	−0.013	0.0026
0.0502	0.2273	0.7967	1.373 63	−0.002	0.0049
0.0524	0.3734	0.7953	1.367 44	−0.010	0.0069
0.0515	0.4928	0.7940	1.361 78	−0.014	0.0080
0.0362	0.5980	0.7928	1.356 29	−0.004	0.0080
0.0357	0.6858	0.7917	1.350 82	−0.015	0.0074
0.0322	0.7692	0.7904	1.345 13	−0.013	0.0063
0.0298	0.8427	0.7895	1.339 61	−0.035	0.0048
0.0290	0.9057	0.7885	1.334 43	−0.048	0.0032
0.1627	0.0714	0.7965	1.376 45	−0.022	0.0020
0.1484	0.2206	0.7956	1.371 32	−0.043	0.0048
0.1367	0.3752	0.7944	1.364 97	−0.061	0.0068
0.1248	0.4929	0.7934	1.359 52	−0.074	0.0077
0.1204	0.5947	0.7923	1.353 97	−0.087	0.0077
0.1153	0.6790	0.7915	1.348 84	−0.109	0.0072
0.1095	0.7612	0.7906	1.343 38	−0.128	0.0062
0.0984	0.8320	0.7897	1.338 28	−0.134	0.0047
0.2542	0.0436	0.7953	1.374 32	−0.020	0.0007
0.2305	0.2281	0.7945	1.368 82	−0.073	0.0049
0.2101	0.3792	0.7937	1.362 79	−0.114	0.0068
0.1979	0.4909	0.7927	1.357 47	−0.126	0.0075
0.1868	0.5955	0.7920	1.352 01	−0.162	0.0076
0.1765	0.6853	0.7913	1.346 73	−0.190	0.0070
0.3374	0.0876	0.7937	1.371 20	−0.031	0.0023
0.3144	0.2355	0.7933	1.366 18	−0.099	0.0050
0.2903	0.3829	0.7926	1.360 19	−0.147	0.0066
0.2572	0.5957	0.7913	1.349 70	−0.215	0.0072
0.2430	0.6783	0.7907	1.344 68	−0.240	0.0064
0.4476	0.0612	0.7924	1.369 12	−0.045	0.0017
0.4140	0.2238	0.7921	1.363 79	−0.129	0.0046
0.3503	0.4189	0.7917	1.356 58	−0.199	0.0066
0.3479	0.5076	0.7913	1.352 66	−0.255	0.0076
0.3298	0.5864	0.7909	1.347 94	−0.282	0.0068
0.5350	0.0759	0.7910	1.366 00	−0.057	0.0017
0.5065	0.2140	0.7909	1.361 40	−0.150	0.0041
0.4545	0.3783	0.7906	1.355 72	−0.222	0.0063
0.4226	0.4887	0.7905	1.350 53	−0.285	0.0064
0.6296	0.0794	0.7896	1.363 30	−0.070	0.0018
0.6050	0.2118	0.7895	1.358 76	−0.171	0.0040
0.5371	0.3702	0.7898	1.353 28	−0.270	0.0056
0.7180	0.0870	0.7882	1.360 52	−0.079	0.0018
0.5611	0.2074	0.7901	1.360 10	−0.154	0.0039
0.7988	0.0835	0.7870	1.358 31	−0.083	0.0015
0.1462	0.1618	0.7960	1.373 77	−0.027	0.0039
0.2501	0.1708	0.7946	1.370 35	−0.060	0.0038
0.4221	0.1591	0.7922	1.366 05	−0.086	0.0034
0.5580	0.1592	0.7902	1.362 24	−0.106	0.0033
0.7017	0.1633	0.7881	1.357 91	−0.135	0.0030
0.1740	0.3158	0.7944	1.366 48	−0.062	0.0060
0.2978	0.3172	0.7930	1.362 99	−0.127	0.0059
0.5670	0.3110	0.7895	1.355 26	−0.225	0.0050
0.6497	0.3014	0.7886	1.353 20	−0.261	0.0047
0.0482	0.3105	0.7959	1.370 14	0.000	0.0060
0.7732	0.1736	0.7871	1.355 20	−0.163	0.0028

Results and Discussion

The excess molar volumes and changes of refractive indices on mixing of binary and ternary mixtures have been calculated by applying, respectively, eqs 1 and 2, and they are shown in the last two columns of Tables 2 and 3 for each composition point. In eqs 1 and 2, ρ is the density of

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

$$\delta n_D = n_D - \sum_{i=1}^{N} x_i n_{D,i} \quad (2)$$

the mixture, n_D is the refractive index of the mixture, ρ_i and $n_{D,i}$ are the properties of pure components, and N is the number of components in the mixture. Excess molar volumes and changes of refractive indices on mixing for

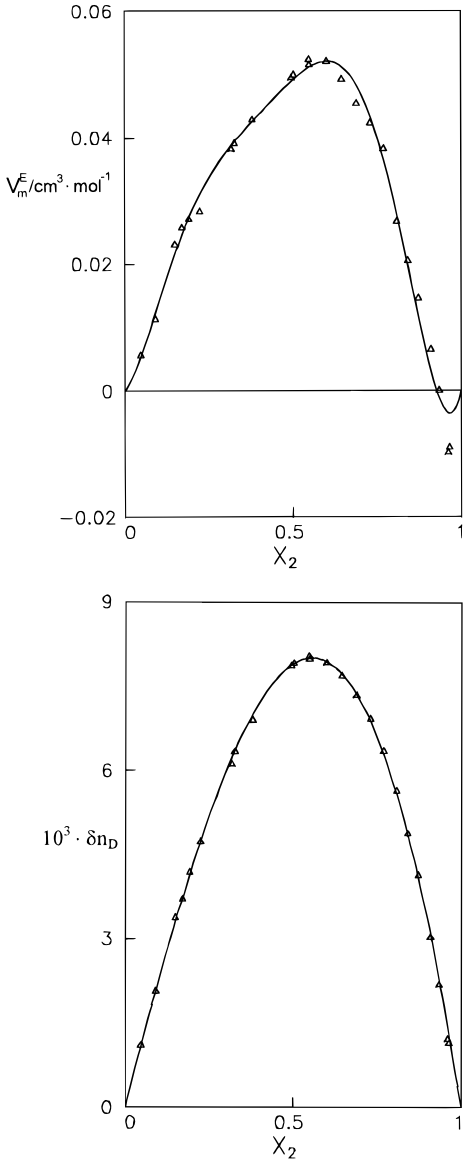

Figure 1. Variation of the (a, top) excess molar volumes and (b, bottom) changes of refractive indices on mixing with mole fraction at 298.15 K for (△) methanol (2) + 1-propanol (3).

binary mixtures were correlated using the Redlich−Kister expression (Redlich and Kister, 1948)

$$\delta Q_{ij} = x_i x_j \sum_{p=0}^{m} B_p (x_i - x_j)^p \quad (3)$$

Figure 1 shows these excess molar volumes and changes of refractive indices on mixing plotted against x. Values of the mixture acetone + methanol are available in a previous work (Orge *et al.*, 1994).

Densities and refractive indices are given in Tables 2 and 3. Binary and ternary values of the density and refractive index have been fitted to a polynomial of the form

$$Q = \sum_{i=1}^{3} \sum_{j=1}^{m} A_{ij} x_i^j \quad (4)$$

where Q is v/(g^{-1}·cm^3) or n_D, the former being the specific volume and the latter the refractive index. In this equation, the expansion polynomial grade is expressed by the parameter m and the mole fraction of the component i by x_i. Figures 2 and 3 show, respectively, densities and refractive indices of the ternary mixture plotted against

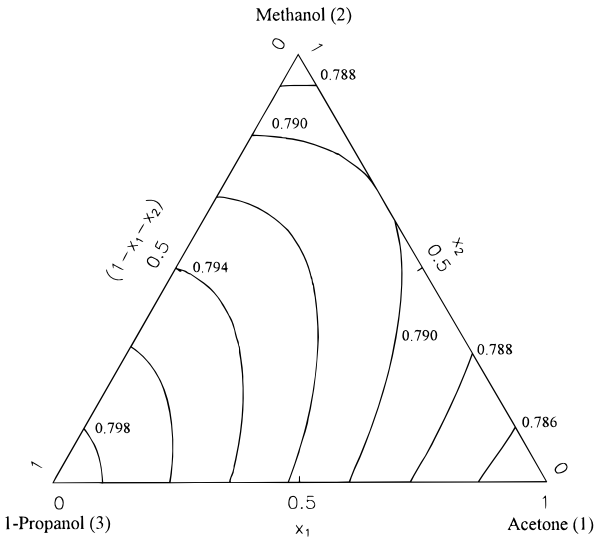

Figure 2. Density curves for the acetone (1) + methanol (2) + 1-propanol (3) mixture at 298.15 K.

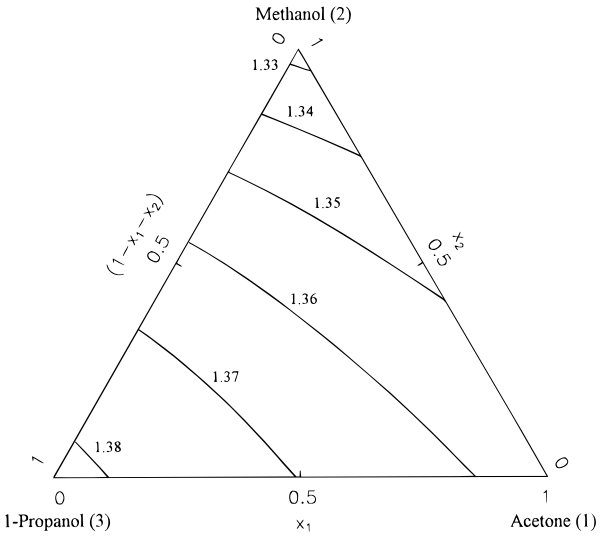

Figure 3. Refractive index curves for the acetone (1) + methanol (2) + 1-propanol (3) mixture at 298.15 K.

Table 4. Standard Deviations of the Experimental Results from the Prediction Results for the Lorentz−Lorenz (L−L), Dale−Gladstone (D−G), Arago−Biot (A−B), Eykman (Eyk), Newton (Nw), Oster (Os), and Eyring−John (E−J) Equations

L−L	D−G	A−B	Eyk	Nw	Os	E−J
Acetone + 1-Propanol						
0.00023	0.00020	0.00020	0.00021	0.00017	0.00018	0.00021
Methanol + 1-Propanol						
0.00032	0.00050	0.00050	0.00043	0.00070	0.00059	0.00040
Acetone + Methanol + 1-Propanol						
0.00096	0.00087	0.00087	0.00090	0.00077	0.00082	0.00092

the mole fraction. No values for the ternary system have been published. The excess values which are presented in Table 3 were correlated with the Cibulka equation (Cibulka, 1982)

$$\delta Q_{123} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + x_1 x_2 (1 - x_1 - x_2)(C_1 + C_2 x_1 + C_3 x_2) \quad (5)$$

where δQ_{ij} is the binary contribution expressed by the Redlich−Kister expression for every binary mixture. The correlation of the excess properties in the ternary mixture was carried out with the contribution of ternary and binary mixtures, although the measurement accuracy of the densities and refractive indices in acetone + 1-propanol are close to the value of their excess properties. Fitting parameters for excess molar volumes and the change of refractive indices of the latter binary are included in Table 5, as well as the corresponding deviations to contribute at least an approximate behavior for these excess properties.

The experimental refractive indices are compared in Table 4 with the predicted results for Lorentz−Lorenz, Dale−Gladstone, Arago−Biot (Tasic *et al.*, 1992), Eykman (Bottcher, 1952), Newton (Kurtz and Ward, 1936), Oster (Oster, 1948), and Eyring−John (Eyring and John, 1969) equations, where the lower deviation is shown by the Lorentz−Lorenz equation for methanol + 1-propanol and by the Newton equation for acetone + 1-propanol and acetone + methanol + 1-propanol.

The parameters A_{ij}, B_p, and C_i of eqs 3−5, and corresponding standard deviations are given in Table 5. The unweighted least-squares method was used to fit the polynomials to the data. The degree of eq 3 was optimized by applying the *F*-test (Bevington, 1969). Curves of constant V_m^E and n_D (eq 5) have been plotted in Figures 4 and 5, respectively. Two zones of different behavior are observed in the excess volume diagram, showing a contractive character on mixing in the greater part of the composition diagram; only the zone of low acetone composition and equal proportions of different chain alcohols shows expansive volumes on mixing. In spite of hydrogen bond attraction among alcohol molecules, a clear negative tendency can be observed in this excess property through decreasing 1-propanol mole fractions due to an easier spatial molecule packing. Positive changes of refractive indices can be observed in almost the whole composition diagram, with a small negative zone existing near the acetone pure component region.

In Table 6, the experimental and estimated excess values from different empirical binary contribution equations (Kohler, 1960; Jacob and Fitzner, 1977; Colinet, 1967; Tsao and Smith, 1953; Toop, 1965) are compared, showing

Table 5. Parameters A_{ij}, B_p, and C_i of Eqs 3−5 and Standard Deviations σ

Acetone (1) + 1-Propanol (3)						
V_m^E/(cm^3·mol^{-1})	$B_0 = 0.0087$	$B_1 = 0.0726$				$\sigma = 0.008$
δn_D	$B_0 = 0.0012$	$B_1 = -0.0017$	$B_2 = -0.0017$			$\sigma = 0.00005$
Methanol (2) + 1-Propanol (3)						
V_m^E/(cm^3·mol^{-1})	$B_0 = 0.1964$	$B_1 = 0.0971$	$B_2 = 0.0958$	$B_3 = -0.2445$	$B_4 = -0.3736$	$\sigma = 0.0024$
δn_D	$B_0 = 0.0316$	$B_1 = 0.0076$	$B_2 = -0.0006$			$\sigma = 0.00008$
Acetone (1) + Methanol (2) + 1-Propanol (3)						
v/(g^{-1}·cm^3)	$A_{11} = 1.2568$	$A_{12} = 0.0419$	$A_{13} = -0.0358$	$A_{14} = 0.0125$		
	$A_{21} = 1.2549$	$A_{22} = 0.0219$	$A_{23} = -0.0196$	$A_{24} = 0.0144$		
	$A_{31} = 1.2611$	$A_{32} = -0.0107$	$A_{33} = 0.0023$	$A_{34} = -0.0015$		$\sigma = 0.0002$
n_D	$A_{11} = 1.3561$	$A_{12} = -0.0071$	$A_{13} = 0.0125$	$A_{14} = -0.0055$		
	$A_{21} = 1.3494$	$A_{22} = -0.0158$	$A_{23} = 0.0021$	$A_{24} = -0.0090$		
	$A_{31} = 1.3838$	$A_{32} = 0.0085$	$A_{33} = -0.0193$	$A_{34} = 0.0098$		$\sigma = 0.00013$
V_m^E/(cm^3·mol^{-1})	$C_1 = -0.5779$	$C_2 = 0.7065$	$C_3 = -0.1861$			$\sigma = 0.0066$
δn_D	$C_1 = -0.0026$	$C_2 = -0.0178$	$C_3 = -0.0226$			$\sigma = 0.00017$

Table 6. Standard Deviations of the Experimental Results from the Prediction Results for Different Empirical Equations

	$\sigma(V_m^E/(cm^3 \cdot mol^{-1}))$	$\sigma(\delta n_D)$		$\sigma(V_m^E/(cm^3 \cdot mol^{-1}))$	$\sigma(\delta n_D)$
Kohler	0.024	0.0004	Tsao−Smith[c]	0.033	0.0014
Jacob−Fitzner	0.023	0.0003	Toop[a]	0.017	0.0005
Colinet	0.021	0.0003	Toop[b]	0.027	0.0002
Tsao−Smith[a]	0.019	0.0016	Toop[c]	0.030	0.0005
Tsao−Smith[b]	0.031	0.0002			

[a] 1-Propanol is the asymmetric component in the equation. [b] Methanol is the asymmetric component in the equation. [c] Acetone is the asymmetric component in the equation.

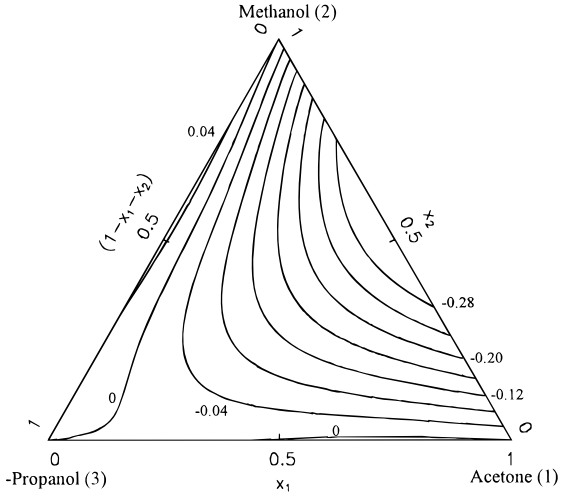

Figure 4. Excess molar volume curves for the acetone (1) + methanol (2) + 1-propanol (3) mixture at 298.15 K.

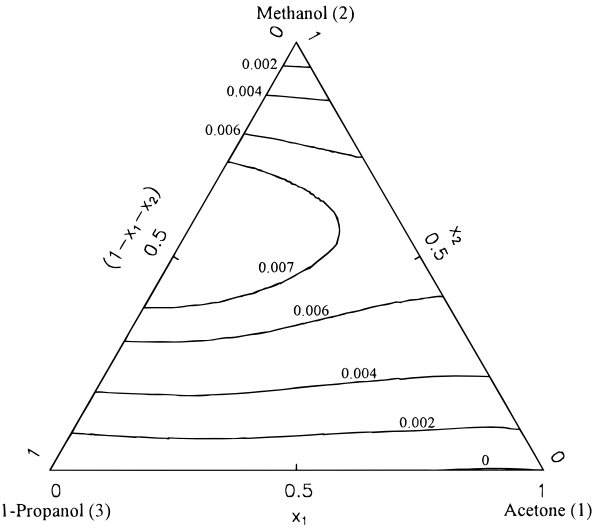

Figure 5. Changes of refractive index on mixing curves for the acetone (1) + methanol (2) + 1-propanol (3) mixture at 298.15 K.

standard deviations determined using eq 6. In this equation z is the value of the property and N is the number of experimental data. In the asymmetric rules, the asymmetry in the third component allows lower deviations in excess molar volumes and in the second allows for changes of the refractive index.

$$\sigma = \left[\frac{\sum_i^N (z_{exp} - z_{pred})^2}{N} \right]^{1/2} \quad (6)$$

Acknowledgment

The authors wish to thank Cándida Barreiro Castro and Mónica Castro Barreiro for their assistance in the experimental development of this paper.

Registry Numbers Supplied by the Author. Acetone, 67-64-1; methanol, 67-56-1; 1-propanol, 71-23-8.

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Received for review July 28, 1995. Accepted November 11, 1995.[⊗] The authors are grateful to the Xunta of Galicia (C5X560902 Project) for supporting this research.

JE950186V

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.