Densities and Refractive Indices of Acetone + Methanol + 2-Methyl-2-butanol at 298.15 K

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Densities and refractive indices at 298.15 K for acetone + methanol + 2-methyl-2-butanol and the binary acetone + 2-methyl-2-butanol and methanol + 2-methyl-2-butanol mixtures have been measured as a function of the mole fraction at atmospheric pressure. Results have been correlated with analytical expressions.

Introduction

Due to the advantages of continuous rectification processes, azeotropic and extractive distillation continue to be among the most frequently used methods for the separation of nonideal close boiling and azeotropic mixtures in the chemical industry. The synthesis of a modified rectification system involves two main problems: choosing one or more candidate entrainers with the corresponding column sequence and determining the optimal design. In order to study the ability of aliphatic alcohols as potential entrainers for the azeotropic binary system acetone + methanol, knowledge of the different physical properties is required to calculate the bottom and head compositions of an experimental rectification system.

In previous papers (Gama and Tojo, 1992; Orge *et al.*, 1994; Iglesias *et al.*, 1994; Orge *et al.*, 1995; Iglesias *et al.*, 1995) we presented densities, refractive indices, and speeds of sound for selected binary and ternary mixtures. In this paper we present densities and refractive indices at 298.15 K of acetone + methanol + 2-methyl-2-butanol and of the binary acetone + 2-methyl-2-butanol and methanol + 2-methyl-2-butanol mixtures.

Experimental Section

Apparatus and Procedure. The densities of the pure liquids and mixtures were measured at 298.15 K with an Anton Paar DMA-46 densimeter with a precision of 10^{-4} g·cm^{-3} and the refractive indices by the automatic refractometer ABBEMAT-HP Dr Kernchen with a precision of 10^{-5}. A PolyScience controller bath, model 9510, with a temperature stability of $\pm 10^{-2}$ K was used to thermostatize the samples, which were prepared by weight using a Mettler AE-240 balance with a accuracy of 10^{-4} g, covering the whole composition range. The accuracies in the calculation of excess molar volumes and changes of refractive indices are, respectively, 10^{-3} cm^3·mol^{-1} and 10^{-4}. The experimental technique has been described previously (Iglesias *et al.*, 1995).

Purity of Materials. Acetone, methanol, and 2-methyl-2-butanol were Merck chromatographic grade. No further purification was attempted because the purities of the materials had been previously checked by gas chromatography. The analysis showed that the major peak area exceeds 99.8% for acetone and methanol and 99.5% for 2-methyl-2-butanol. The measured properties are in accordance with the literature values as can be observed in Table 1.

Table 1. Comparison of Experimental 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	0.784 40[a]	1.356 05	1.355 96[a]
		0.784 4[b]		1.356 09[c]
methanol	0.7863	0.786 64[a]	1.326 76	1.326 52[a]
		0.786 55[d]		1.326 8[e]
2-methyl-2-butanol	0.8045	0.805 0[a]	1.402 38	1.402 4[a]

[a] Riddick *et al.* (1986). [b] Wei and Rowley (1984). [c] Tasic *et al.* (1992). [d] Miyano and Hayduk (1986). [e] Aminabhavi *et al.* (1993).

Results and Discussion

The excess molar volumes and changes of refractive indices on mixing of binary mixtures are shown in the last two columns of Table 2 for each composition point. These values have been calculated by applying eq 1, where Q is

$$\delta Q = Q - \sum x_i Q_i \tag{1}$$

the molar volume of the mixture or the refractive index and Q_i the molar volume or the refractive index of the pure components. Excess properties were correlated using the Redlich–Kister expression (Redlich and Kister, 1948):

$$\delta Q = x_i x_j \sum_{p=0}^{m} B_p (x_i - x_j)^p \tag{2}$$

Figure 1 shows the experimental points of V_m^E and n_D plotted against x as well as the curves fitted. 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. These properties from Tables 2 and 3 have been fitted to a polynomial of the form

$$Q = \sum_{i=1}^{3} \sum_{j=1}^{m} A_{ij} x_i^j \tag{3}$$

where Q is v/(g^{-1}·cm^3) or n_D (v is the specific volume, n_D is the refractive index at the Na D line) and x_i is the mole

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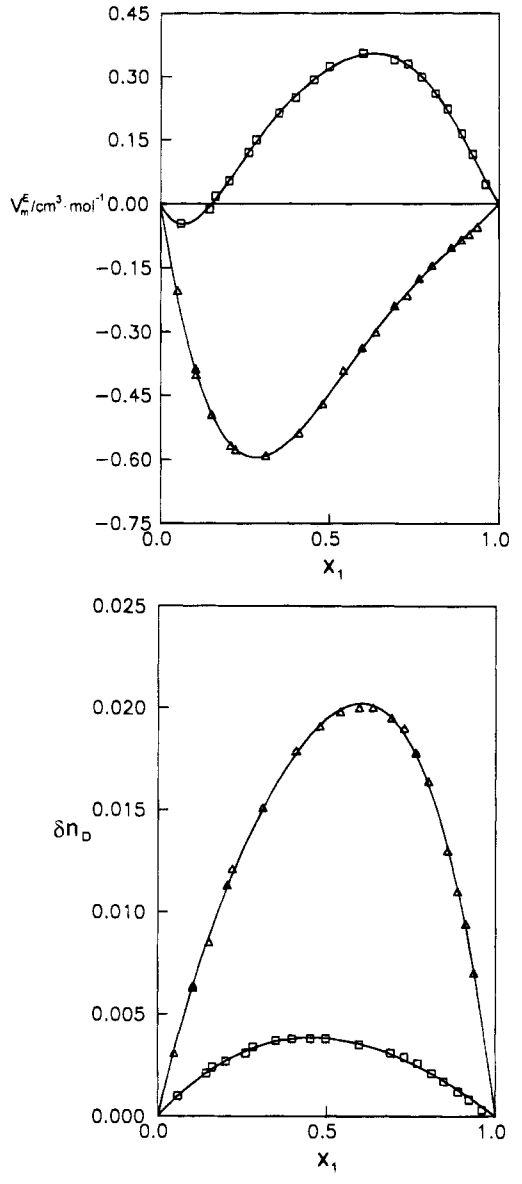

Figure 1. Variation of the (a, top) excess molar volumes and (b, bottom) changes of refractive indices on mixing with mole fraction at 298.15 for (□) acetone (1) + 2-methyl-2-butanol (2) and (△) methanol (1) + 2-methyl-2-butanol (2).

fraction of component i. Parameter m is the expansion polynomial grade. Figures 2 and 3 show, respectively, densities and refractive indices of the ternary mixture plotted against the mole fractions.

No values for the investigated ternary system have been found in the open literature. The obtained experimental results are presented in Table 3. These results were correlated with the Cibulka equation (Cibulka, 1982) for the excess properties of the ternary mixture:

$$\delta Q_{123} = \delta Q_{\text{bin}} + x_1 x_2 (1 - x_1 - x_2)(C_1 + C_2 x_1 + C_3 x_2) \quad (4)$$

where

$$\delta Q_{\text{bin}} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} \quad (5)$$

The experimental refractive indices are compared in Table 4 with the predicted results for Lorentz–Lorenz, Gladstone–Dale, and Arago–Biot mixing rules which were compiled previously (Tasic *et al.*, 1992).

The parameters A_y, B_p, and C_i of eqs 2–4 and corresponding standard deviations are given in Table 5. The unweighted least-squares method was used to fit the

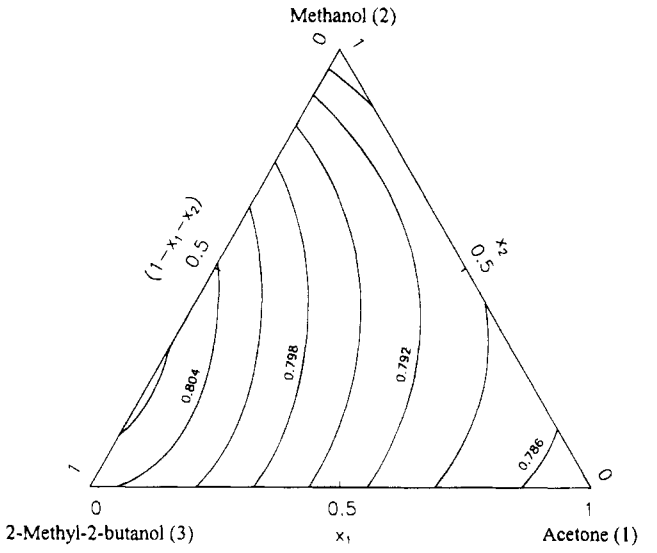

Figure 2. Density curves for acetone (1) + methanol (2) + 2-methyl-2-butanol (3) mixtures at 298.15 K.

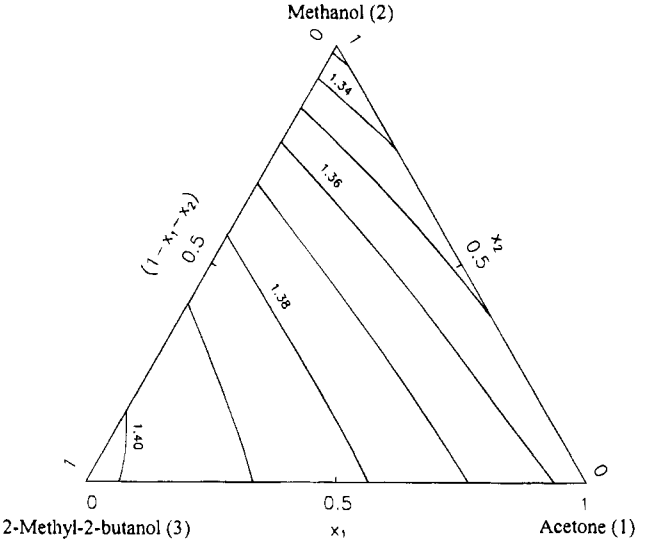

Figure 3. Refractive index curves for acetone (1) + methanol (2) + 2-methyl-2-butanol (3) mixtures at 298.15 K.

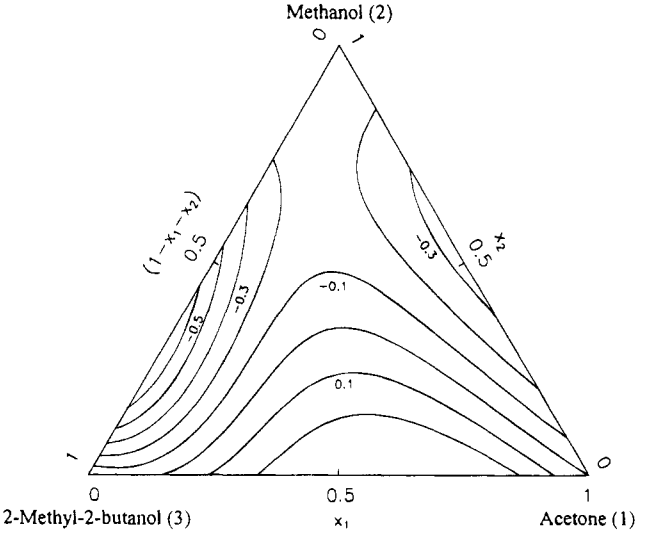

Figure 4. Excess molar volume curves for acetone (1) + methanol (2) + 2-methyl-2-butanol (3) mixtures at 298.15 K.

polynomials of eqs 2–4 to the data. The degree of eqs 2 and 3 was optimized by applying the F-test (Bevington,

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_1	ρ/(g·cm^{-3})	n_D	V_m^E/(cm^3·mol^{-1})	δn_D	x_1	ρ/(g·cm^{-3})	n_D	V_m^E/(cm^3·mol^{-1})	δn_D
Acetone (1) + 2-Methyl-2-butanol (2)									
0.0601	0.8040	1.40061	−0.046	0.0010	0.5974	0.7911	1.37819	0.356	0.0035
0.1446	0.8025	1.39783	−0.012	0.0021	0.6899	0.7891	1.37347	0.339	0.0031
0.1621	0.8020	1.39729	0.018	0.0024	0.7298	0.7882	1.37147	0.331	0.0029
0.2021	0.8011	1.39576	0.053	0.0027	0.7694	0.7875	1.36933	0.299	0.0026
0.2615	0.7996	1.39341	0.120	0.0031	0.8110	0.7868	1.36686	0.260	0.0021
0.2828	0.7990	1.39269	0.150	0.0034	0.8467	0.7862	1.36486	0.223	0.0017
0.3503	0.7973	1.38983	0.213	0.0037	0.8897	0.7856	1.36240	0.165	0.0012
0.3987	0.7961	1.38770	0.250	0.0038	0.9216	0.7852	1.36045	0.115	0.0008
0.4524	0.7947	1.38525	0.293	0.0038	0.9603	0.7848	1.35821	0.046	0.0003
0.4984	0.7935	1.38305	0.325	0.0038					
Methanol (1) + 2-Methyl-2-butanol (2)									
0.0490	0.8057	1.40173	−0.203	0.0031	0.5962	0.8020	1.37726	−0.338	0.0200
0.1032	0.8068	1.40090	−0.387	0.0063	0.6359	0.8010	1.37429	−0.301	0.0200
0.1042	0.8069	1.40089	−0.400	0.0064	0.6919	0.7993	1.36957	−0.239	0.0195
0.1510	0.8074	1.39950	−0.495	0.0085	0.7285	0.7983	1.36628	−0.215	0.0190
0.2060	0.8077	1.39813	−0.567	0.0113	0.7638	0.7970	1.36241	−0.174	0.0178
0.2208	0.8077	1.39774	−0.576	0.0121	0.8009	0.7957	1.35826	−0.144	0.0164
0.3096	0.8073	1.39407	−0.591	0.0151	0.8582	0.7935	1.35051	−0.102	0.0130
0.4090	0.8061	1.38936	−0.538	0.0179	0.8872	0.7923	1.34632	−0.083	0.0110
0.4789	0.8048	1.38527	−0.470	0.0191	0.9109	0.7913	1.34290	−0.072	0.0094
0.5402	0.8033	1.38129	−0.391	0.0198	0.9355	0.7901	1.33868	−0.054	0.0070

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

x_1	x_2	ρ/(g·cm^{-3})	n_D	V_m^E/(cm^3·mol^{-1})	δn_D	x_1	x_2	ρ/(g·cm^{-3})	n_D	V_m^E/(cm^3·mol^{-1})	δn_D
0.0653	0.0751	0.8051	1.39898	−0.268	0.0053	0.5188	0.0923	0.7929	1.37770	0.166	0.0063
0.0493	0.4612	0.8033	1.38345	−0.405	0.0182	0.4642	0.2557	0.7934	1.37133	−0.067	0.0098
0.0442	0.5809	0.8009	1.37559	−0.316	0.0192	0.4055	0.4091	0.7931	1.36405	−0.192	0.0114
0.0403	0.6758	0.7985	1.36764	−0.241	0.0182	0.3711	0.5122	0.7924	1.35724	−0.253	0.0108
0.0365	0.7541	0.7962	1.36001	−0.184	0.0163	0.2179	0.5451	0.7961	1.36602	−0.243	0.0150
0.0674	0.7948	0.7939	1.35238	−0.170	0.0132	0.6283	0.0581	0.7904	1.37350	0.230	0.0046
0.0096	0.8995	0.7915	1.34338	−0.084	0.0095	0.5499	0.2450	0.7914	1.36687	−0.068	0.0085
0.0390	0.9143	0.7901	1.33742	−0.108	0.0060	0.4903	0.3873	0.7914	1.35970	−0.215	0.0093
0.2101	0.1307	0.8013	1.39114	−0.145	0.0084	0.4383	0.4996	0.7911	1.35304	−0.295	0.0087
0.1842	0.2916	0.8011	1.38523	−0.265	0.0134	0.6239	0.2456	0.7898	1.36201	−0.112	0.0071
0.1569	0.4562	0.7995	1.37723	−0.266	0.0166	0.7783	0.0794	0.7874	1.36384	0.092	0.0035
0.1439	0.5581	0.7981	1.37046	−0.261	0.0170	0.6949	0.2342	0.7885	1.35818	−0.156	0.0057
0.1326	0.6522	0.7962	1.36265	−0.234	0.0157	0.8427	0.0814	0.7864	1.35974	0.008	0.0026
0.1174	0.7312	0.7945	1.35528	−0.213	0.0136	0.0768	0.1466	0.8054	1.39664	−0.387	0.0089
0.0981	0.8502	0.7910	1.34110	−0.173	0.0076	0.1510	0.1067	0.8031	1.39468	−0.214	0.0074
0.3210	0.0654	0.7982	1.38866	0.071	0.0061	0.1626	0.1757	0.8026	1.39171	−0.251	0.0101
0.2721	0.2875	0.7983	1.38091	−0.160	0.0129	0.1819	0.0921	0.8021	1.39382	−0.138	0.0068
0.2397	0.4309	0.7975	1.37376	−0.228	0.0151	0.1379	0.1815	0.8034	1.39264	−0.301	0.0104
0.1986	0.6394	0.7946	1.35858	−0.245	0.0138	0.2947	0.1954	0.7984	1.38460	−0.085	0.0106
0.1828	0.7192	0.7930	1.35051	−0.244	0.0110	0.3799	0.1900	0.7961	1.38018	−0.022	0.0098
0.1687	0.7805	0.7916	1.34378	−0.241	0.0082	0.1139	0.3851	0.8022	1.38430	−0.344	0.0163
0.3734	0.0924	0.7967	1.38500	0.086	0.0069	0.6707	0.1151	0.7894	1.36805	0.097	0.0054
0.3664	0.2748	0.7958	1.37619	−0.103	0.0116	0.5684	0.1842	0.7914	1.36972	0.012	0.0076
0.3217	0.4299	0.7951	1.36818	−0.202	0.0132	0.7280	0.1668	0.7883	1.36100	−0.068	0.0050
0.2903	0.5383	0.7943	1.36142	−0.256	0.0132	0.1292	0.2947	0.8029	1.38814	−0.347	0.0140
0.2694	0.6257	0.7930	1.35387	−0.273	0.0113	0.5799	0.3267	0.7902	1.35850	−0.212	0.0077
0.2408	0.7039	0.7918	1.34712	−0.275	0.0091	0.4237	0.3525	0.7934	1.36715	−0.153	0.0111

Table 4. Standard Deviations of the Experimental Results from the Prediction Results for the Lorentz–Lorenz (L–L), Gladstone–Dale (G–D), and Arago–Biot (A–B) Equations

	L–L	G–D	A–B
acetone (1) + 2-methyl-2-butanol (2)	0.0006	0.0004	0.0028
methanol (1) + 2-methyl-2-butanol (2)	0.0003	0.0002	0.0042
acetone (1) + methanol (2) + 2-methyl-2-butanol (3)	0.0004	0.0002	0.0031

1969). Curves of constant V_m^E and n_D (eq 4) have been plotted in Figures 4 and 5, respectively. Positive changes of refractive indices on the whole composition diagram can be observed while an isoline of ideal behavior in excess volumes cut the acetone + 2-methyl-2-butanol system curve, resulting from an expansion in the volumes with a growing composition of acetone.

Many papers in the past years have given extensive attention to the development of empirical expressions for predicting different thermodynamic properties of multicomponent mixtures. Some of these predictive methods that we shall use were originally proposed to reproduce excess molar Gibbs energies or excess molar enthalpies but should be applied to any other excess properties. In order to compare experimental and predicted excess values, we apply different empirical equations (Kohler, 1960; Jacob and Fitzner, 1977; Colinet, 1967; Tsao and Smith, 1953; Toop, 1965; Scatchard *et al.*, 1952; Hillert, 1980) which determine ternary excess values from different composition paths relating such composition to the bounding binary systems. Table 6 lists the standard deviations of the experimental data from the prediction results using eq 6,

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

Table 5. Parameters A_{ij}, B_p, and C_i of Eqs 1–3 and Standard Deviations σ

			Acetone (1) + 2-Methyl-2-butanol (2)			
V_m^E/(cm^3·mol^{-1})	$B_0 = 1.2839$	$B_1 = 0.9896$	$B_2 = -0.3094$	$B_3 = 0.4492$	$B_4 = -1.1884$	$\sigma = 0.0046$
δn_D	$B_0 = 0.0153$	$B_1 = -0.0027$				$\sigma = 0.0001$
			Methanol (1) + 2-Methyl-2-butanol (2)			
V_m^E/(cm^3·mol^{-1})	$B_0 = -1.7777$	$B_1 = 2.1394$	$B_2 = -1.1985$			$\sigma = 0.0055$
δn_D	$B_0 = 0.0779$	$B_1 = 0.0276$	$B_2 = 0.0203$			$\sigma = 0.0002$
			Acetone (1) + Methanol (2) + 2-Methyl-2-butanol (3)			
ϱ^{-1}/(g^{-1}·cm^3)	$A_{11} = 1.2914$	$A_{12} = -0.0161$	$A_{13} = 0.0015$	$A_{14} = -0.0016$		
	$A_{21} = 1.2320$	$A_{22} = 0.0443$	$A_{23} = -0.0324$	$A_{24} = 0.0276$		
	$A_{31} = 1.2367$	$A_{32} = 0.0191$	$A_{33} = -0.0584$	$A_{34} = 0.0457$		$\sigma = 0.0002$
n_D	$A_{11} = 1.3310$	$A_{12} = 0.0466$	$A_{13} = -0.0432$	$A_{14} = 0.0214$		
	$A_{21} = 1.3627$	$A_{22} = -0.0324$	$A_{23} = 0.0255$	$A_{24} = -0.0290$		
	$A_{31} = 1.4481$	$A_{32} = -0.0836$	$A_{33} = 0.0693$	$A_{34} = -0.0316$		$\sigma = 0.0004$
V_m^E/(cm^3·mol^{-1})	$C_1 = 15.3220$	$C_2 = -14.7600$	$C_3 = -13.8713$			$\sigma = 0.0076$
δn_D	$C_1 = -0.0457$	$C_2 = 0.0420$	$C_3 = 0.0651$			$\sigma = 0.0002$

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

	$\sigma(V_m^E)$	$\sigma(n_D)$		$\sigma(V_m^E)$	$\sigma(n_D)$
Kohler	0.0663	0.00078	Toop[c]	0.0237	0.00124
Jacob–Fitzner	0.0396	0.00053	Scatchard[a]	0.0763	0.00076
Colinet	0.0517	0.00068	Scatchard[b]	0.0848	0.00032
Tsao–Smith[a]	0.1505	0.00374	Scatchard[c]	0.0243	0.00120
Tsao–Smith[b]	0.0798	0.00053	Hillert[a]	0.0821	0.00088
Tsao–Smith[c]	0.0307	0.00210	Hillert[b]	0.0906	0.00032
Toop[a]	0.0886	0.00095	Hillert[c]	0.0234	0.00123
Toop[b]	0.0935	0.00032			

[a] 2-Methyl-2-butanol is the polar component. [b] Methanol is the polar component. [c] Acetone is the polar component.

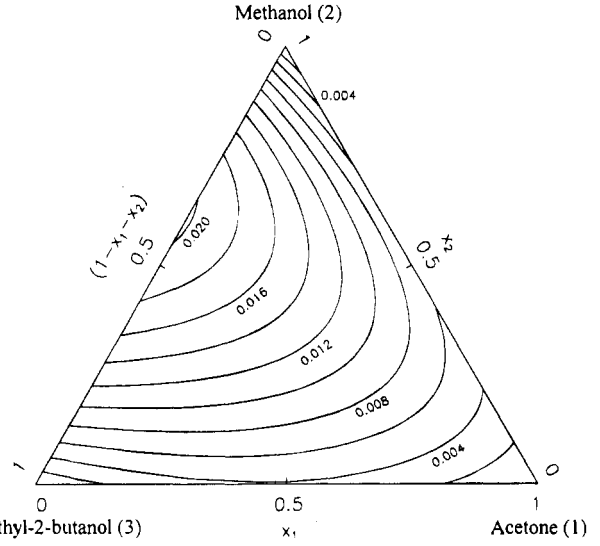

Figure 5. Changes of refractive index on mixing curves for acetone (1) + methanol (2) + 2-methyl-2-butanol (3) mixtures at 298.15 K.

where n is the number of experimental data and z is the value of the property. It can be observed that the best estimations to determine excess volumes are the Toop and Hillert asymmetric equations and those of Toop, Scatchard, and Hillert for changes of refractive indices. It can also be noted that the accuracy of estimation rises if the asymmetry is located in the alcohol components of the mixture. Comparison between fitting deviations by the Cibulka equation and the best estimation equation show that they are only comparable for changes of refractive indices.

Registry Numbers Supplied by the Author. Acetone, 67-64-1; methanol, 67-56-1; 2-methyl-2-butanol, 75-85-4.

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