Excess Molar Volumes of Ternary Mixtures of $\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_6OH$ or $CH_3(CH_2)_7OH\}$ at the Temperature of 298.15 K

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Excess molar volumes at the temperature 298.15 K were measured for the ternary systems ($x_1$ethyl propanoate + $x_2$hexane + $(1 - x_1 - x_2)$heptan-1-ol or $(1 - x_1 - x_2)$octan-1-ol} and for binary mixtures {$x_1$ethyl propanoate + $(1 - x_1)$*n*-hexane}, {$x_1$ethyl propanoate + $(1 - x_1)$heptan-1-ol}, {x_1*n*-hexane + $(1 - x_1)$heptan-1-ol}, {$x_1$ethyl propanoate + $(1 - x_1)$octan-1-ol}, and {x_1*n*-hexane + $(1 - x_1)$octan-1-ol}. Excess molar volumes were determined using a densimeter Anton Paar DMA 60/602. The experimental values were compared with the results obtained with some empirical methods for the estimation of ternary properties from binary results.

1. Introduction

The present article continues our studies (Souza et al., 1992; Franjo et al., 1994, 1995a,b; Lorenzana et al., 1993a,b; Ilic et al., 1990; Jiménez et al., 1996) about excess molar volumes of nonelectrolyte ternary mixtures. In this paper we present the excess volumes of {$x_1$ethyl propanoate + $x_2$hexane + $(1 - x_1 - x_2)$heptan-1-ol or $(1 - x_1 - x_2)$octan-1-ol} and of the binary mixtures {$x_1$ethyl propanoate + $(1 - x_1)$hexane}, {$x_1$ethyl propanoate + $(1 - x_1)$heptan-1-ol}, {$x_1$hexane + $(1 - x_1)$heptan-1-ol}, {$x_1$ethyl propanoate + $(1 - x_1)$octan-1-ol}, and {$x_1$hexane + $(1 - x_1)$octan-1-ol} at 298.15 K. The excess molar volumes were used to test the empirical methods of Kohler (1960), Jacob and Fitzner (1977), Colinet (1967), Tsao and Smith (1953), Toop (1965), Scatchard et al. (1952), and Hillert (1980). These methods predict excess properties of the ternary mixtures from the respective binary mixtures.

2. Experimental Section

The substances employed were supplied by Fluka and Aldrich. Their mole-fraction purities were ethyl propanoate (Fluka) >0.99, hexane (Sigma) >0.99, heptan-1-ol (Sigma) ∼0.99, and octan-1-ol (Fluka) >0.995. All chemical products were degassed by ultrasound, dried over Fluka type 0.4 nm molecular sieves, and otherwise used as supplied. The densities of the pure liquids agree well with the literature values, as Table 1 shows.

Excess molar volumes were determined from the densities of the pure liquids and mixtures measured with an Anton Paar DMA 60/602 densimeter with a resolution of $\pm 2 \times 10^{-6}$ g·cm^{-3}, thermostated at (298.15 ± 0.01) K in a Haake F3 circulating-water bath. The experimental technique has been described previously (Lorenzana et al., 1989; Legido et al., 1990). The error in the determination of V_m^E was estimated to be better than ±0.002 cm^3·mol^{-1}.

3. Results and Discussion

Experimental excess volumes of the binary mixtures determined in this work are listed in Table 2. A variable-

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Table 1. Densities of the Pure Liquids at 298.15 K

	ρ/g·cm^{-3}		
substance	exp	lit.	
ethyl propanoate	0.884 21	0.884 07[a]	0.884 0[b]
n-hexane	0.655 10	0.655 03[c]	0.655 08[d]
heptan-1-ol	0.818 75	0.818 78[e]	0.818 70[f]
octan-1-ol	0.821 63	0.821 62[g]	0.821 61[e]

[a] Jiménez et al. (1986). [b] Riddick et al. (1986). [c] Lorenzana et al. (1991). [d] Heintz et al. (1986). [e] Amigo et al. (1993). [f] Yu and Tsai (1994). [g] Franjo et al. (1995b).

Table 2. Experimental Excess Molar Volumes V_m^E at 298.15 K

x	V_m^E/ cm^3·mol^{-1}	x	V_m^E/ cm^3·mol^{-1}	x	V_m^E/ cm^3·mol^{-1}
x_1Ethyl Propanoate + $(1 - x_1)$Hexane					
0.0673	0.2115	0.4520	0.6297	0.7465	0.4185
0.1654	0.4301	0.5078	0.6116	0.8078	0.3345
0.2680	0.5635	0.6122	0.5519	0.8725	0.2372
0.3234	0.6040	0.6549	0.5235	0.9360	0.1303
0.4028	0.6283	0.6855	0.4919		
x_1Ethyl Propanoate + $(1 - x_1)$Heptan-1-ol					
0.0761	0.0970	0.4731	0.3253	0.7404	0.2506
0.1506	0.1713	0.5308	0.3244	0.8004	0.2140
0.2828	0.2676	0.5561	0.3209	0.8713	0.1542
0.3686	0.3059	0.6506	0.2959	0.9411	0.0755
0.4213	0.3200	0.6717	0.2901		
x_1Hexane + $(1 - x_1)$Heptan-1-ol					
0.0476	−0.0736	0.4295	−0.3717	0.7848	−0.1775
0.0678	−0.1075	0.4876	−0.3608	0.8550	−0.1053
0.0828	−0.1355	0.4935	−0.3541	0.9142	−0.0538
0.1340	−0.1982	0.5387	−0.3479	0.9478	−0.0154
0.1959	−0.2663	0.5867	−0.3255	0.9870	0.0190
0.2737	−0.3210	0.6386	−0.2843	0.9899	0.0162
0.3350	−0.3576	0.7096	−0.2430	0.9945	0.0118
0.3951	−0.3709				
x_1Ethyl Propanoate + $(1 - x_1)$Octan-1-ol					
0.1045	0.1449	0.5013	0.3746	0.7671	0.2784
0.1238	0.1703	0.5518	0.3689	0.8225	0.2195
0.3077	0.3204	0.6003	0.3625	0.8819	0.1668
0.3918	0.3550	0.6528	0.3435	0.9425	0.0923
0.4478	0.3704	0.6861	0.3292		
x_1Hexane + $(1 - x_1)$Octan-1-ol					
0.1296	−0.2240	0.6172	−0.4200	−0.9401	−0.0556
0.2001	−0.3117	0.6887	−0.3664	0.9695	−0.0140
0.3596	−0.4342	0.7556	−0.3059	0.9877	0.0085
0.4097	−0.4574	0.8191	−0.2330	0.9905	0.0050
0.4564	−0.4711	0.8888	−0.1353		
0.5488	−0.4550	0.9160	−0.0956		

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Table 3. Coefficients A_p, K, B_p, and B_i of Equations 1−4 and Standard Deviations s

system	A_0	A_1	A_2	A_3	A_4	s
$x_1$ethyl propanoate + $(1 - x_1)$hexane	2.4699	−0.6981	0.3712			0.003
$x_1$ethyl propanoate + $(1 - x_1)$heptan-1-ol	1.3023		0.0905			0.002
$x_1$ethyl propanoate + $(1 - x_1)$octan-1-ol	1.4961		0.3571			0.003

system	K	B_0	B_1	B_2	B_3	s
$x_1$hexane + $(1 - x_1)$heptan-1-ol	−0.9916	−1.4345	1.9495	−0.3002	−0.1516	0.004
$x_1$hexane + $(1 - x_1)$octan-1-ol	−0.9765	−1.8531	2.0549	−0.0693	−0.0661	0.003

system	B_0	B_1	B_2	B_3	s
$x_1$ethyl propanoate + $x_2$hexane + $(1 - x_1 - x_2)$heptan-1-ol[a]	0.1104	−4.3258	−2.4460		0.009
$x_1$ethyl propanoate + $x_2$hexane + $(1 - x_1 - x_2)$octan-1-ol[b]	−4.8576	4.6040	5.9569	−2.2733	0.009

[a] Equation 3. [b] Equation 4.

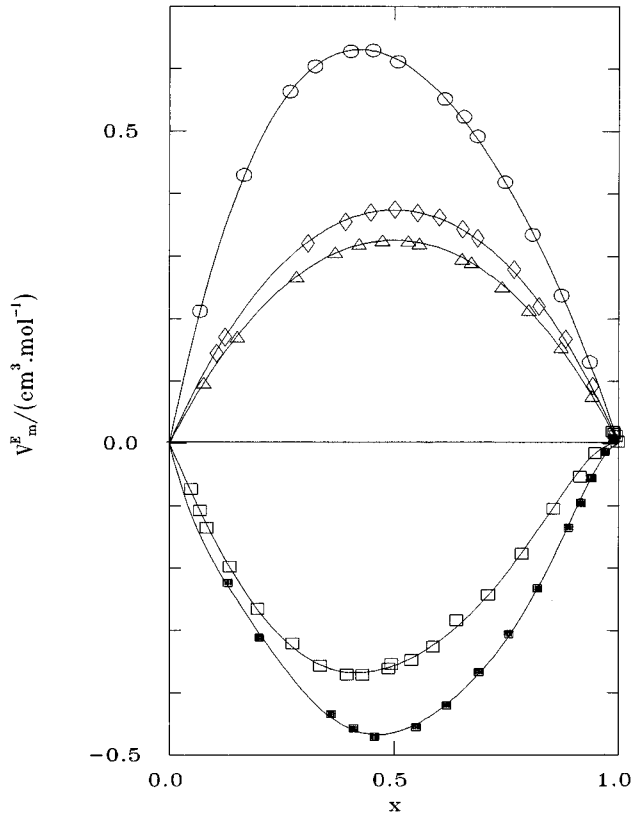

Figure 1. Excess molar volumes at $T = 298.15$ K of (○) $\{x_1CH_3CH_2COOCH_2CH_3 + (1 - x_1)CH_3(CH_2)_4CH_3\}$, (△) $\{x_1CH_3CH_2COOCH_2CH_3 + (1 - x_1)CH_3(CH_2)_6OH\}$, (□) $\{x_1CH_3(CH_2)_4CH_3 + (1 - x_1)CH_3(CH_2)_6OH\}$, (◇) $\{x_1CH_3CH_2COOCH_2CH_3 + (1 - x_1)CH_3(CH_2)_7OH\}$, and (■) $\{x_1CH_3(CH_2)_4CH_3 + (1 - x_1)CH_3(CH_2)_7OH\}$.

degree polynomial of the form

$$V^E_{m,ij}/\text{cm}^3\cdot\text{mol}^{-1} = x_i x_j \sum_{p=0}^{n} A_p (x_i - x_j)^p \qquad (1)$$

was fitted to each set of results of ethyl propanoate + hexane and ethyl propanoate + alkan-1-ol, and a polynomial function

$$V^E_{m,ij}/\text{cm}^3\cdot\text{mol}^{-1} = x_i x_j \left(\frac{\sum_{p=0}^{n} B_p (x_i - x_j)^p}{1 + K(x_i - x_j)} \right) \qquad (2)$$

was used for hexane + alkan-1-ol.

A least-squares method was employed in both cases. The number of parameters was determined in each case using an F-test (Bevington, 1994). Parameters and standard deviations are listed in Table 3. Figure 1 shows V^E_m plotted against x and the V^E_m curves calculated from the smoothing equations.

Table 4. Excess Molar Volumes for Ternary Mixtures at the Temperature 298.15 K

x_1	x_2	$V^E_{m,123}$/ cm^3·mol^{-1}	x_1	x_2	$V^E_{m,123}$/ cm^3·mol^{-1}
x_1Ethyl Propanoate + x_2Hexane + $(1 - x_1 - x_2)$Heptan-1-ol					
0.0169	0.1041	−0.1457	0.1646	0.1162	0.0457
0.0386	0.2379	−0.2449	0.2320	0.1638	0.0780
0.0722	0.4445	−0.2057	0.3094	0.2185	0.1291
0.0787	0.4845	−0.1811	0.3795	0.2680	0.2035
0.0909	0.5596	−0.1070	0.4446	0.3140	0.2856
0.0328	0.0742	−0.0800	0.5125	0.3620	0.3837
0.0449	0.1014	−0.1001	0.1118	0.0126	0.1183
0.0819	0.1851	−0.1290	0.1343	0.0152	0.1344
0.1196	0.2702	−0.1179	0.2662	0.0301	0.2240
0.1587	0.3588	−0.0745	0.3784	0.0428	0.2697
0.1740	0.3933	−0.0220	0.4907	0.0555	0.2911
0.2335	0.5277	0.1780	0.5356	0.0606	0.2928
0.2646	0.5980	0.3117	0.5954	0.0673	0.2870
0.0652	0.0461	0.0076	0.6899	0.0780	0.2683
0.0953	0.0673	0.0148	0.8068	0.0913	0.2178
x_1Ethyl Propanoate + x_2Hexane + $(1 - x_1 - x_2)$Octan-1-ol					
0.0163	0.1034	−0.1712	0.3716	0.2450	0.1713
0.0222	0.1411	−0.2142	0.0827	0.0302	0.0487
0.0398	0.2521	−0.2959	0.1246	0.0455	0.0797
0.0571	0.3620	−0.3275	0.2376	0.0867	0.1456
0.0824	0.5225	−0.2454	0.3207	0.1171	0.1823
0.0322	0.0793	−0.0985	0.4133	0.1509	0.2234
0.0854	0.2106	−0.1860	0.4568	0.1667	0.2311
0.1212	0.2989	−0.1827	0.1026	0.0117	0.1236
0.0591	0.0687	−0.0367	0.1507	0.0173	0.1647
0.0750	0.0872	−0.0511	0.2824	0.0324	0.2609
0.1364	0.1586	−0.0693	0.3982	0.0456	0.3013
0.0749	0.0494	0.0122	0.5003	0.0573	0.3209
0.1002	0.0661	0.0039	0.5555	0.0637	0.3244
0.1786	0.1177	0.0333	0.6144	0.0704	0.3087
0.3360	0.2215	0.1323			

The experimental excess volumes $V^E_{m,123}$ of the ternary systems are shown in Table 4. Equations:

$$V^E_{m,123}/\text{cm}^3\cdot\text{mol}^{-1} = V^E_{m,bin} + x_i x_j (1 - x_i - x_j)(B_0 + B_1 x_i + B_2 x_j) \qquad (3)$$

$$V^E_{m,123}/\text{cm}^3\cdot\text{mol}^{-1} = V^E_{m,bin} + x_i x_j (1 - x_i - x_j)(B_0 + B_1 x_i + B_2 x_j + B_3 x_i^2) \qquad (4)$$

where

$$V^E_{m,bin} = V^E_{m,12} + V^E_{m,13} + V^E_{m,23} \qquad (5)$$

have been fitted to the experimental values. The $(V^E_{m,12} + V^E_{m,13} + V^E_{m,23})$ are given by eqs 1 and 2. The B_i

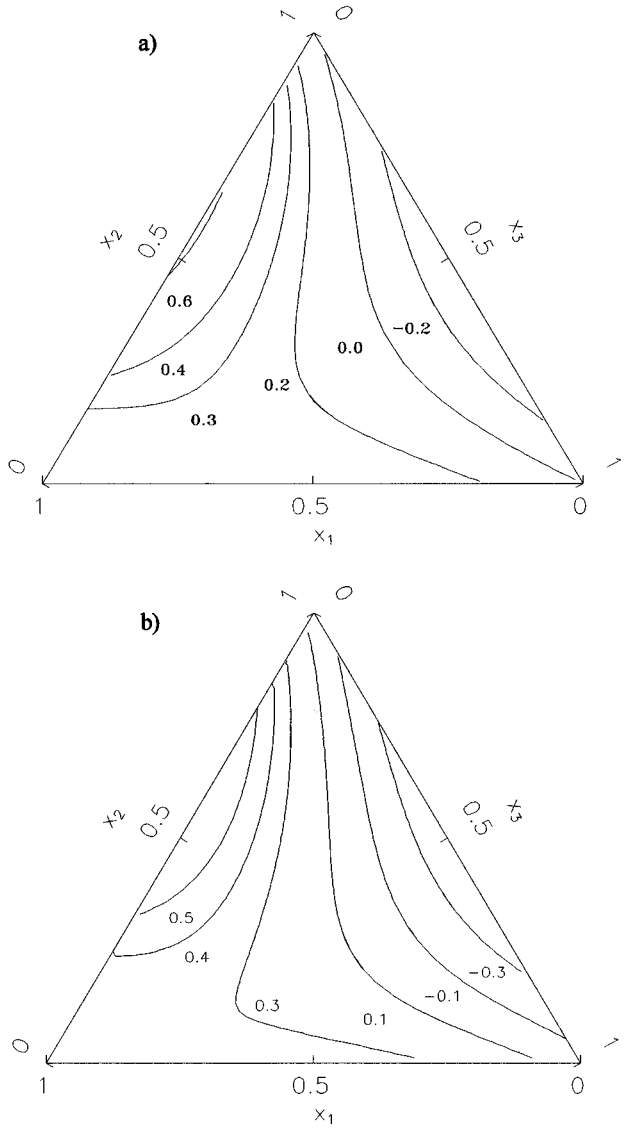

Figure 2. Curves of constant $V^E_{m,123}/cm^3 \cdot mol^{-1}$ for (a) $\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_6OH\}$ and (b) $\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_7OH\}$.

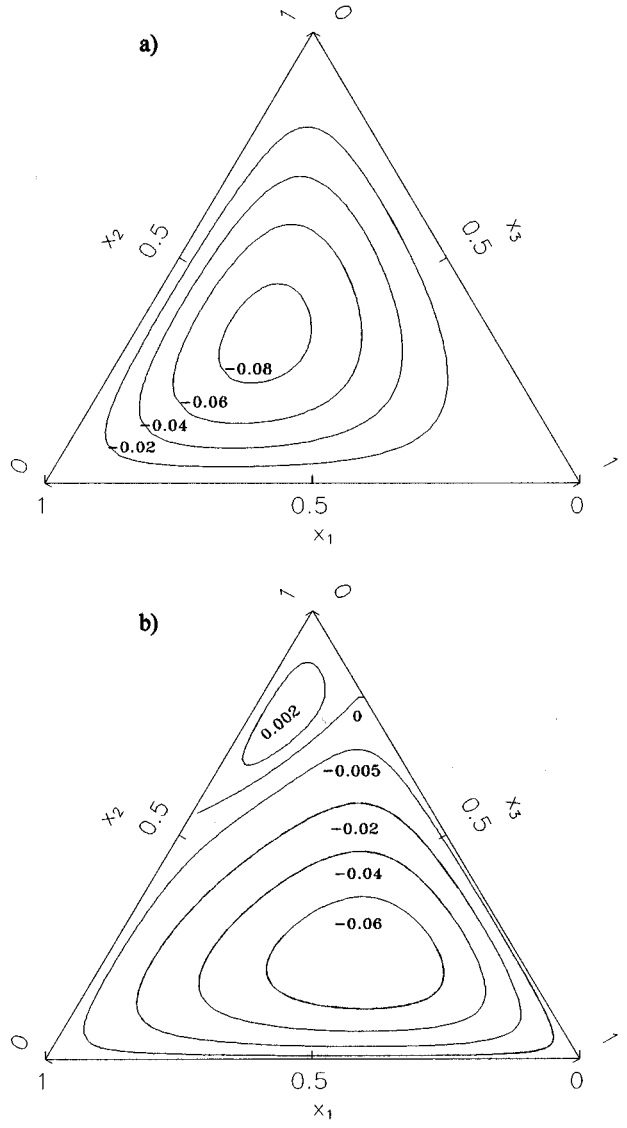

Figure 3. Curves of constant $(V^E_{m,123} - V^E_{bin})/cm^3 \cdot mol^{-1}$ for (a) $\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_6OH\}$ and (b) $\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_7OH\}$.

parameters were calculated by the unweighted least-squares method using a nonlinear optimization algorithm due to Marquardt (1963).

Table 3 presents the values of those parameters and the corresponding standard deviations between experimental and fitted values. The lines of constant ternary excess molar volume $V^E_{m,123}$ calculated by using eqs 3−5 are shown in Figure 2. Figure 3 shows lines of constant "ternary contribution". The so-called "ternary contribution" represents the difference between the experimental value and that predicted from binary mixtures ($V^E_{m,123} - V^E_{m,bin}$).

For $\{x_1$ethyl propanoate + $x_2$hexane + $(1 - x_1 - x_2)$-heptan-1-ol$\}$ there exists a maximum inside the triangular diagram, whose coordinates are $x_1 = 0.42$, $x_2 = 0.57$, $V^E_{m,123} = 0.609$ $cm^3 \cdot mol^{-1}$. The "ternary contribution" shows a minimum of -0.087 $cm^3 \cdot mol^{-1}$ at $x_1 = 0.43$, $x_2 = 0.32$. For $\{x_1$ethyl propanoate + $x_2$hexane + $(1 - x_1 - x_2)$-octan-1-ol$\}$ there exists a maximum, $V^E_{m,123} = 0.615$ $cm^3 \cdot mol^{-1}$, for $x_1 = 0.42$ and $x_2 = 0.57$. The ternary contribution shows a maximum at $x_1 = 0.16$ and $x_2 = 0.77$ with a value of 0.0035 $cm^3 \cdot mol^{-1}$ and a minimum of -0.075 $cm^3 \cdot mol^{-1}$ at $x_1 = 0.29$ and $x_2 = 0.22$.

Table 5. Standard Deviations of the Models for the Mixtures Studied

$\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_6OH\}$			
Jacob and Fitzner	0.0423	Toop	0.0593
Kohler	0.0468	Scatchard	0.0584
Colinet	0.0468	Hillert	0.0493
Tsao and Smith	0.0289		
$\{x_1CH_3CH_2COOCH_2CH_3 + x_2CH_3(CH_2)_4CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_7OH\}$			
Jacob and Fitzner	0.0409	Toop	0.0530
Kohler	0.0403	Scatchard	0.0538
Colinet	0.0447	Hillert	0.0325
Tsao and Smith	0.0194		

Several empirical methods have been proposed to estimate ternary excess properties from available experimental results on constituent binaries. The equations of Kohler, Jacob-Fitzner, Colinet, Tsao and Smith, Toop, Scatchard, and Hillert were used. Table 5 shows the mean deviations between experimental and predicted values. The most accurate predictions are given by the Tsao and Smith equation in both systems.

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