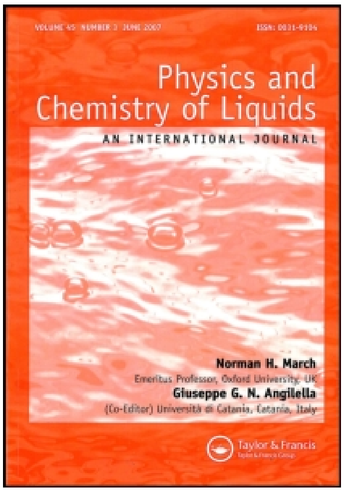

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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R. Bravo[a]; M. Pintos[a]; A. Amigo[a]
[a] Departamento de Fisica Aplicada, Facultad de Fisica, Universidad de Santiago, santiago de composa, Spain

To cite this Article Bravo, R. , Pintos, M. and Amigo, A.(1992) 'Excess Molar Volumes at the Temperature 308.15 K of the Ternary Mixtures (*o*-Xylene *n*-Heptane Toluene Or *n*-Hex-1-Ene)', Physics and Chemistry of Liquids, 24: 4, 239 — 248
To link to this Article: DOI: 10.1080/00319109208027275
URL: http://dx.doi.org/10.1080/00319109208027275

Phys. Chem. Liq., 1992, Vol. 24, pp. 239–248
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EXCESS MOLAR VOLUMES AT THE TEMPERATURE 308.15 K OF THE TERNARY MIXTURES (*o*-XYLENE + *n*-HEPTANE + TOLUENE OR *n*-HEX-1-ENE)

R. BRAVO*, M. PINTOS and A. AMIGO

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago, E-15706, Santiago de Compostela, Spain

(Received 13 November 1991)

Excess molar volumes at the temperature 308.15 K were obtained for the mixture (*o*-xylene + *n*-heptane), (*o*-xylene + toluene), (*o*-xylene + *n*-hex-1-ene), (*n*-heptane + toluene), (*n*-heptane + *n*-hex-1-ene), (*o*-xylene + *n*-heptane + toluene), and (*o*-xylene + *n*-heptane + *n*-hex-1-ene) from density measurements with a vibrating-tube densimeter. Variable-degree polynomials have been fitted to the results and several ways of predicting the excess volumes of the ternary mixture from experimental results for the binary mixtures are compared. Some of the experimental values are used to test the predictions of the Nitta–Chao model.

KEY WORDS: Excess molar volumes, ternary mixtures.

INTRODUCTION

In a previous paper[1] we have presented experimental excess molar volumes at the temperature 298.15 K and normal atmospheric pressure for the mixtures (*o*-xylene + *n*-heptane), (*o*-xylene + toluene), (*o*-xylene + *n*-hex-1-ene), (*n*-heptane + toluene), (*n*-heptane + *n*-hex-1-ene), (*o*-xylene + *n*-heptane + toluene), and (*o*-xylene + *n*-heptane + *n*-heptane-1-ene). Due to the industrial interest of mixtures containing aromatic compounds, we have extended this investigation by determining the excess molar volumes at 308.15 K for the same mixtures. The results for both binary and ternary mixtures have been fitted to adequate equations. Different methods for estimating the excess volume of multicomponent mixtures from binary data are tested.

Recent years have seen considerable promotion of theoretical group contribution methods allowing prediction of the thermodynamic excess properties of liquid mixtures. In this article, the predictions of the Nitta–Chao model[2,3] for the excess molar volumes using Koukios *et al.*'s parameters[4] are compared to our experimental results. This group contribution model is based on the Carnahan–Starling equation of state for hard spheres[5].

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* To whom correspondence should be addressed.

EXPERIMENTAL

The chemical substances employed were supplied by Fluka and Merck, and subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves. Their mole-fraction purities were: *o*-xylene (Fluka, >99.0), *n*-heptane (Fluka, >99.5), toluene (Fluka, >99.5), and *n*-hex-1-ene (Merck for synthesis, >99.0).

Binary mixtures were prepared by using a Mettler H51 balance (precision of $1 \cdot 10^{-5}$ g), and air-tight stoppered bottles. The possible error in the mole fractions is estimated to be less than 10^{-4}. Excess molar volumes were determined from the densities of the pure liquids and mixtures measured with an Anton Paar Model DMA 60/602 densimeter. The temperature of the fluid surrounding the density cell was maintained to ± 0.01 K (Heto, type 04 PT 623 circulating thermostat). The temperature of the thermostat was detected with a precision digital thermometer (Anton Paar DT 100-30). The calibration constants of the densimeter were determined using the known densities of water[6] ($0.9940296 \text{ g} \cdot \text{cm}^{-3}$ at 308.15 K) and air[7]. The reproductibility of an individual density measurement was to be better than $3 \cdot 10^{-6} \text{ g} \cdot \text{cm}^{-3}$.

The densities with a selection of published values[8,9] are (measured): *o*-xylene ($0.86725 \text{ g} \cdot \text{cm}^{-3}$), *n*-heptane ($0.67093 \text{ g} \cdot \text{cm}^{-3}$), toluene ($0.85286 \text{ g} \cdot \text{cm}^{-3}$), and *n*-hex-1-ene ($0.65895 \text{ g} \cdot \text{cm}^{-3}$); (literature): *o*-xylene ($0.8675 \text{ g} \cdot \text{cm}^{-3}$), *n*-heptane ($0.67105 \text{ g} \cdot \text{cm}^{-3}$), and toluene ($0.8529 \text{ g} \cdot \text{cm}^{-3}$).

RESULTS AND DISCUSSION

The experimental values of V_m^E for the five binary mixtures are listed in Table 1. Each set of results was fitted with the equation:

$$V_{m,ij}^E/(\text{cm}^3 \cdot \text{mol}^{-1}) = x_i x_j \cdot \sum_{k=0}^{m} A_k \cdot (x_i - x_j)^k, \quad (1)$$

by the ordinary (unweighted) least-squares method. The parameters A_k and the standard deviations s of the fit are listed in Table 2. The number k of coefficients was determined in each case using an F-test[9].

Figure 1 shows V_m^E plotted against x and the V_m^E curves calculated from the smoothing equations.

The experimental excess molar volumes $V_{m,123}^E$ of the ternary mixtures are shown in Tables 3 and 4. The equation:

$$V_{m,123}^E/(\text{cm}^3 \cdot \text{mol}^{-1}) = V_{m,12}^E + V_{m,13}^E + V_{m,23}^E + x_1 \cdot x_2 \cdot (1 - x_1 - x_2) \cdot \{B_0 + B_1 \cdot (2x_1 + 2x_2 - 1) + B_2 \cdot (2x_1 + 2x_2 - 1)^2\}, \quad (2)$$

was fitted to the experimental values using a non-linear regression algorithm due to Marquardt[10]. Table 5 presents the values of the parameters of Eq. 2 and the corresponding standard deviations.

Table 1 Experimental excess molar volumes V_m^E at the temperature 308.15 K.

x	$V_m^E/cm^3 \cdot mol^{-1}$	x	$V_m^E/cm^3 \cdot mol^{-1}$	x	$V_m^E/cm^3 \cdot mol^{-1}$	x	$V_m^E/cm^3 \cdot mol^{-1}$
			$xo\text{-}C_6H_4(CH_3)_2 + (1-x)CH_3(CH_2)_5CH_3$				
0.0841	−0.0512	0.3311	−0.1487	0.6405	−0.1697	0.8985	−0.0740
0.1317	−0.0782	0.4073	−0.1626	0.7235	−0.1478	0.9410	−0.0479
0.1914	−0.0962	0.4762	−0.1756	0.7634	−0.1335		
0.2539	−0.1242	0.5538	−0.1772	0.8375	−0.1018		
			$xo\text{-}C_6H_4(CH_3)_2 + (1-x)C_6H_5CH_3$				
0.0486	0.0048	0.3503	0.0326	0.6283	0.0318	0.9222	0.0074
0.1169	0.0124	0.4079	0.0356	0.6879	0.0295		
0.2014	0.0231	0.4937	0.0380	0.7709	0.0235		
0.2647	0.0286	0.5723	0.0366	0.8518	0.0145		
			$xo\text{-}C_6H_4(CH_3)_2 + (1-x)CH_3(CH_2)_3CH{:}CH_2$				
0.0527	−0.1379	0.3512	−0.5773	0.6541	−0.5493	0.9482	−0.1177
0.1271	−0.2944	0.4402	−0.6113	0.7017	−0.5043		
0.2036	−0.4173	0.5201	−0.6174	0.8209	−0.3537		
0.2761	−0.5131	0.5820	−0.5955	0.8826	−0.2472		
			$xCH_3(CH_2)_5CH_3 + (1-x)C_6H_5CH_3$				
0.0621	0.0124	0.3114	0.0798	0.6362	0.1216	0.9370	0.0299
0.1228	0.0275	0.4058	0.1031	0.7008	0.1112		
0.1990	0.0477	0.4947	0.1229	0.7582	0.0956		
0.2680	0.0713	0.5496	0.1259	0.8704	0.0586		
			$xCH_3(CH_2)_5CH_3 + (1-x)CH_3(CH_2)_3CH{:}CH_2$				
0.0546	0.0094	0.3468	0.0364	0.6285	0.0334	0.9122	0.0108
0.1190	0.0186	0.4192	0.0377	0.7164	0.0279		
0.2144	0.0277	0.4851	0.0374	0.7824	0.0212		
0.2771	0.0319	0.5442	0.0378	0.8343	0.0176		

Curves of constant $V_{m,123}^E$ have been plotted in Figure 2, and the ternary contributions, given by $(V_{m,123}^E - V_{m,12}^E - V_{m,13}^E - V_{m,23}^E)$, in Figure 3.

The excess molar volumes of mixtures of more than two components may be estimated, from binary data, using the expression[11,12]

$$V_{m,123}^E = \sum_{i<j} (x_i x_j / x_i' x_j') V_{m,ij}^E(x_i', x_j') \tag{3}$$

Table 2 Parameters A_k of Eq. 1 and standard deviations s.

	A_0	A_1	A_2	s
$xo\text{-}C_6H_4(CH_3)_2 + (1-x)CH_3(CH_2)_5CH_3$	−0.7037	−0.0902	—	0.0030
$xo\text{-}C_6H_4(CH_3)_2 + (1-x)C_6H_5CH_3$	0.1489	−0.0109	−0.0500	0.0009
$xo\text{-}C_6H_4(CH_3)_2 + (1-x)CH_3(CH_2)_3CH{:}CH_2$	−2.4702	0.1666	−0.0875	0.0023
$xCH_3(CH_2)_5CH_3 + (1-x)C_6H_5CH_3$	0.4834	0.1881	−0.1821	0.0022
$xCH_3(CH_2)_5CH_3 + (1-x)CH_3(CH_2)_3CH{:}CH_2$	0.1499	−0.0305	—	0.0007

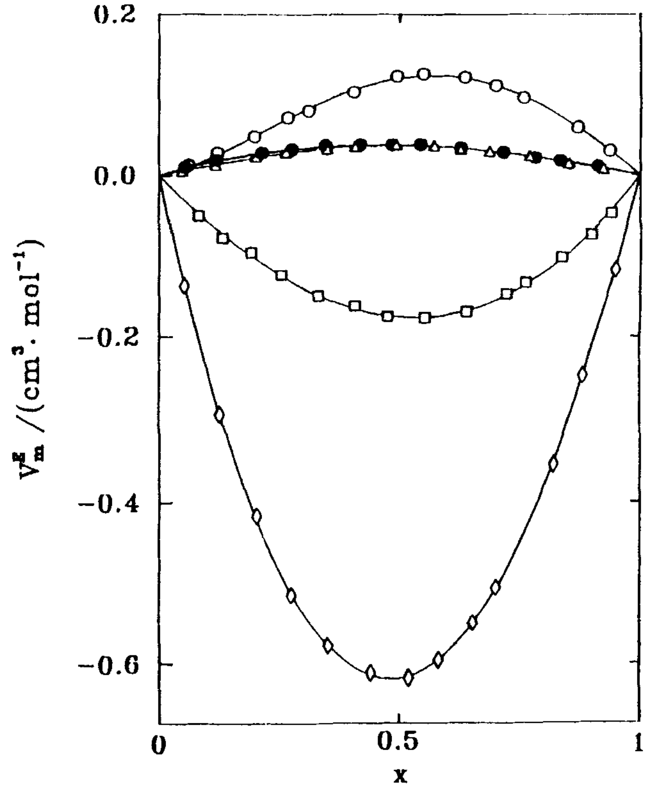

Figure 1 Excess molar volumes at 308.15 K of *o*, $\{xCH_3(CH_2)_5CH_3 + (1-x)C_6H_5CH_3\}$; ●, $(xo\text{-}C_6H_4(CH_3)_2 + (1-x)C_6H_5CH_3\}$; Δ, $(xCH_3(CH_2)_5CH_3 + (1-x)CH_3(CH_2)_3CH{:}CH_2\}$; □, $(xo\text{-}C_6H_4(CH_3)_2 + (1-x)CH_3(CH_2)_5CH_3\}$; ◇, $\{xo\text{-}C_6H_4(CH_3)_2 + (1-x)CH_3(CH_2)_3CH{:}CH_2)$; —, calculated from Eq. 1 with parameters from Table 2.

where the mole fractions x_i' and x_j' are defined so that $x_i' + x_j' = 1$. The binary contribution $V_{m,ij}^E$ is then the excess volume of the binary system (i, j) at (x_i', x_j'). The mole fractions x_i', x_j' can be obtained as projections of the ternary point composition into the axis of the respective binary system in the triangular diagram. The normal projection with $x_i' = (1 + x_i - x_j)/2$ and $x_j' = (1 + x_j - x_i)/2$ transforms Eq. 3 into

$$V_{m,123}^E = \sum_{i<j} 4x_i x_j/\{1 - (x_i - x_j)^2\} V_{m,ij}^E\{(1 + x_i - x_j)/2, (1 + x_j - x_i)/2\}. \quad (4)$$

For the direct projection $x_i' = x_i/(x_i + x_j)$ and $x_j' = x_j/(x_i + x_j)$, Eq. 3 becomes

$$V_{m,123}^E = \sum_{i<j} (x_i + x_j)^2 V_{m,ij}^E\{x_i/(x_i + x_j), x_j/(x_i + x_j)\}, \quad (5)$$

Table 3 Excess molar volumes for $\{x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)\ C_6H_5CH_3$ at 308.15 K; $\delta V^E_{m,123} = V^E_{m,123}(\text{exp.}) - V^E_{m,123}(\text{Eq. 2})$; $\Delta V^E_{m,123} = V^E_{m,123} - V^E_{m,123}$((a) Eq. 3; (b) Eq. 4; (c) Eq. 5)

x_1	x_2	$V^E_{m,123}$ / $cm^3 \cdot mol^{-1}$	$\delta V^E_{m,123}$ / $cm^3 \cdot mol^{-1}$	$\Delta V^E_{m,123}(cm^3 \cdot mol^{-1})$ (a)	(b)	(c)
0.0218	0.0510	0.0153	0.0032	0.0052	0.0058	0.0053
0.0452	0.0442	0.0127	−0.0017	0.0017	0.0027	0.0018
0.0505	0.1185	0.0374	0.0040	0.0109	0.0128	0.0110
0.0546	0.0232	0.0187	0.0077	0.0099	0.0106	0.0100
0.0794	0.1862	0.0502	−0.0015	0.0081	0.0108	0.0084
0.0990	0.2322	0.0625	0.0034	0.0123	0.0150	0.0127
0.1247	0.2926	0.0652	0.0047	0.0094	0.0114	0.0102
0.1305	0.0555	0.0333	0.0060	0.0137	0.0166	0.0138
0.1379	0.1349	0.0410	−0.0015	0.0100	0.0145	0.0105
0.1592	0.3734	0.0488	0.0022	−0.0025	−0.0024	−0.0012
0.1612	0.0180	0.0227	0.0006	0.0038	0.0053	0.0039
0.1799	0.4220	0.0327	0.0027	−0.0081	−0.0092	−0.0065
0.2134	0.5006	0.0020	0.0095	−0.0085	−0.0104	−0.0065
0.2294	0.2244	0.0344	0.0002	0.0027	0.0068	0.0042
0.2327	0.0990	0.0340	−0.0018	0.0071	0.0128	0.0078
0.2329	0.5463	−0.0247	0.0094	−0.0098	−0.0114	−0.0078
0.2512	0.5893	−0.0544	0.0070	−0.0105	−0.0113	−0.0087
0.2622	0.0294	0.0251	−0.0058	−0.0017	0.0012	−0.0014
0.2637	0.2580	0.0124	−0.0075	−0.0119	−0.0090	−0.0099
0.2664	0.6251	−0.0778	0.0076	−0.0063	−0.0062	−0.0049
0.2967	0.2902	−0.0054	−0.0065	−0.0179	−0.0164	−0.0155
0.3274	0.1392	0.0256	0.0031	0.0041	0.0103	0.0058
0.3371	0.3298	−0.0336	−0.0064	−0.0250	−0.0250	−0.0222
0.3525	0.3448	−0.0389	0.0003	−0.0203	−0.0207	−0.0173
0.3590	0.0402	0.0266	−0.0052	−0.0026	0.0014	−0.0020
0.3792	0.3709	−0.0627	−0.0015	−0.0242	−0.0248	−0.0211
0.3934	0.3848	−0.0770	−0.0036	−0.0265	−0.0272	−0.0235
0.4284	0.1822	−0.0075	0.0050	−0.0066	−0.0022	−0.0039
0.4308	0.4214	−0.1097	−0.0031	−0.0233	−0.0233	−0.0206
0.4558	0.0510	0.0187	−0.0058	−0.0068	−0.0021	−0.0058
0.4747	0.4644	−0.1512	−0.0043	−0.0148	−0.0138	−0.0133
0.4965	0.2112	−0.0420	0.0025	−0.0153	−0.0128	−0.0122
0.5246	0.2231	−0.0566	0.0022	−0.0168	−0.0149	−0.0136
0.5461	0.0612	0.0044	−0.0067	−0.0166	−0.0069	−0.0102
0.5709	0.2428	−0.0810	0.0023	−0.0163	−0.0151	−0.0133
0.5890	0.2505	−0.0950	−0.0019	−0.0195	−0.0185	−0.0167
0.6182	0.2629	−0.1137	−0.0048	−0.0196	−0.0187	−0.0172
0.6565	0.2792	−0.1345	−0.0046	−0.0138	−0.0128	−0.0122
0.6588	0.0738	−0.0137	−0.0017	−0.0097	−0.0061	−0.0081
0.6726	0.2860	−0.1449	−0.0062	−0.0124	−0.0115	−0.0113
0.7218	0.0808	−0.0271	−0.0003	−0.0084	−0.0058	−0.0069
0.7435	0.0833	−0.0341	−0.0020	−0.0098	−0.0076	−0.0083
0.7642	0.0856	−0.0381	−0.0009	−0.0083	−0.0064	−0.0069
0.8105	0.0908	−0.0511	−0.0025	−0.0081	−0.0070	−0.0070
0.8260	0.0925	−0.0546	−0.0022	−0.0070	−0.0062	−0.0061
0.8405	0.0941	−0.0570	−0.0011	−0.0051	−0.0045	−0.0043
0.8643	0.0968	−0.0647	−0.0029	−0.0055	−0.0051	−0.0049

Table 4 Excess molar volumes for $\{x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)\ CH_3(CH_2)_3CH{:}CH_3$ at 308.15 K; $\delta V^E_{m,123} = V^E_{m,123}(\text{exp.}) - V^E_{m,123}(\text{Eq. 2})$; $\Delta V^E_{m,123} = V^E_{m,123} - V^E_{m,123}$((a) Eq. 3; (b) Eq. 4; (c) Eq. 5)

x_1	x_2	$V^E_{m,123}$ / $cm^3 \cdot mol^{-1}$	$\delta V^E_{m,123}$ / $cm^3 \cdot mol^{-1}$	$\Delta V^E_{m,123}(cm^3 \cdot mol^{-1})$ (a)	(b)	(c)
0.0130	0.0306	−0.0213	0.0057	0.0074	0.0075	0.0074
0.0368	0.0374	−0.0816	−0.0005	0.0048	0.0051	0.0048
0.0493	0.1160	−0.0815	−0.0013	0.0151	0.0162	0.0152
0.0632	0.0271	−0.1428	0.0015	0.0078	0.0082	0.0078
0.0837	0.1971	−0.1105	0.0039	0.0346	0.0367	0.0348
0.0976	0.2298	−0.1270	−0.0008	0.0336	0.0360	0.0339
0.1233	0.2901	−0.1467	−0.0005	0.0365	0.0391	0.0370
0.1382	0.0592	−0.2605	0.0068	0.0277	0.0291	0.0277
0.1392	0.1415	−0.2292	−0.0091	0.0276	0.0299	0.0277
0.1553	0.3654	−0.1672	0.0005	0.0334	0.0356	0.0342
0.1643	0.0186	−0.3429	−0.0004	0.0079	0.0084	0.0079
0.1911	0.4497	−0.1836	0.0010	0.0228	0.0237	0.0240
0.2153	0.5067	−0.1983	−0.0093	0.0040	0.0038	0.0053
0.2272	0.0973	−0.3652	−0.0015	0.0329	0.0349	0.0330
0.2374	0.2190	−0.2994	0.0015	0.0447	0.0469	0.0452
0.2379	0.0269	−0.4471	−0.0082	0.0045	0.0053	0.0045
0.2385	0.5614	−0.1941	−0.0081	−0.0018	−0.0027	−0.0005
0.2569	0.2611	−0.2993	−0.0002	0.0392	0.0410	0.0400
0.2976	0.3025	−0.3087	0.0012	0.0322	0.0331	0.0332
0.3186	0.1364	−0.4143	0.0048	0.0412	0.0429	0.0415
0.3356	0.3411	−0.3148	−0.0045	0.0170	0.0169	0.0181
0.3405	0.0385	−0.5283	−0.0050	0.0109	0.0118	0.0110
0.3437	0.3493	−0.3075	0.0016	0.0210	0.0207	0.0221
0.3740	0.3801	−0.3073	−0.0078	0.0044	0.0036	0.0055
0.3897	0.3961	−0.2991	−0.0077	0.0012	0.0002	0.0023
0.4155	0.1779	−0.4232	0.0094	0.0361	0.0368	0.0366
0.4396	0.4468	−0.2483	0.0022	0.0038	0.0031	0.0047
0.4590	0.4665	−0.2368	−0.0087	−0.0083	−0.0088	−0.0077
0.4958	0.2123	−0.3974	0.0083	0.0230	0.0230	0.0236
0.5206	0.2229	−0.3918	−0.0021	0.0091	0.0090	0.0097
0.5672	0.2429	−0.3408	0.0084	0.0140	0.0138	0.0145
0.5857	0.2508	−0.3245	0.0048	0.0086	0.0085	0.0091
0.6202	0.2655	−0.2788	0.0073	0.0087	0.0088	0.0091
0.6473	0.0731	−0.4557	0.0091	0.0150	0.0152	0.0151
0.6516	0.2790	−0.2349	0.0048	0.0050	0.0052	0.0053
0.6703	0.2870	−0.2035	0.0056	0.0055	0.0057	0.0057
0.7153	0.0808	−0.3932	−0.0034	−0.0006	−0.0004	−0.0005
0.7434	0.0840	−0.3591	−0.0072	−0.0053	−0.0050	−0.0052
0.7594	0.0858	−0.3290	−0.0003	0.0011	0.0014	0.0012
0.7849	0.0887	−0.2827	0.0061	0.0069	0.0072	0.0070
0.8058	0.0910	−0.2488	0.0050	0.0054	0.0057	0.0054
0.8280	0.0936	−0.2125	0.0014	0.0015	0.0018	0.0016
0.8474	0.0957	−0.1797	−0.0026	−0.0026	−0.0023	−0.0025
0.8696	0.0983	−0.1253	0.0068	0.0067	0.0069	0.0067

Table 5 Parameters B_1 of Eq. 2 and standard deviation s.

B_0	B_1	B_2	s
$x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)C_6H_5CH_3$			
−0.0681	−1.6082	0.9064	0.0048
$x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_3CH{:}CH_3$			
1.3073	−2.4423	1.0934	0.0058

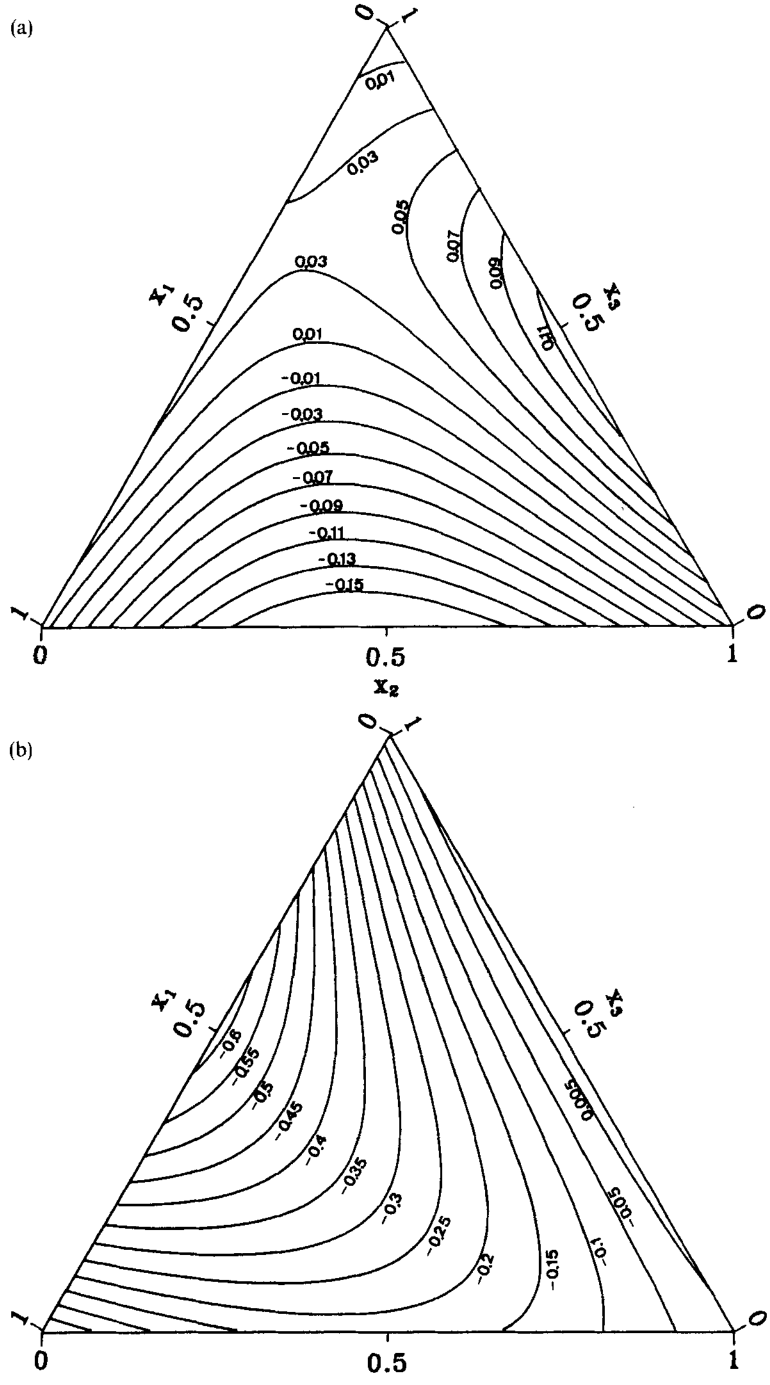

Figure 2 Curves of constant $V^E_{m,123}/(\mathrm{cm^3 \cdot mol^{-1}})$ for: (a), $\{x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)C_6H_5CH_3\}$, and (b), $\{x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_3CH{:}CH_2\}$.

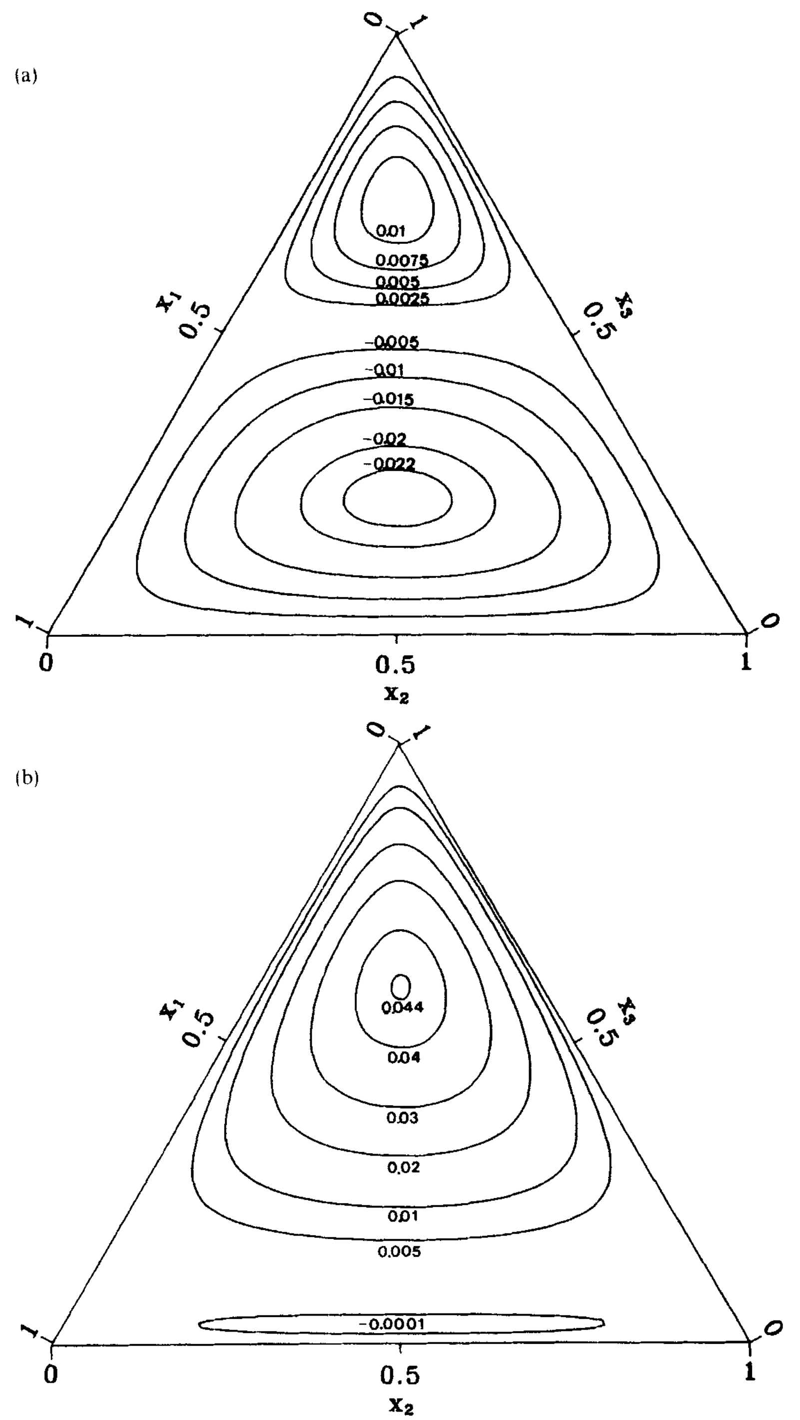

Figure 3 Curves of constant ternary contribution ($V^E_{m,123} - V^E_{m,12} - V^E_{m,13} - V^E_{m,23}/\mathrm{cm^3 \cdot mol^{-1}}$) to the excess molar volumes of: (a), $\{x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)C_6H_5CH_3\}$, and (b), $\{x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_3CH{:}CH_2\}$.

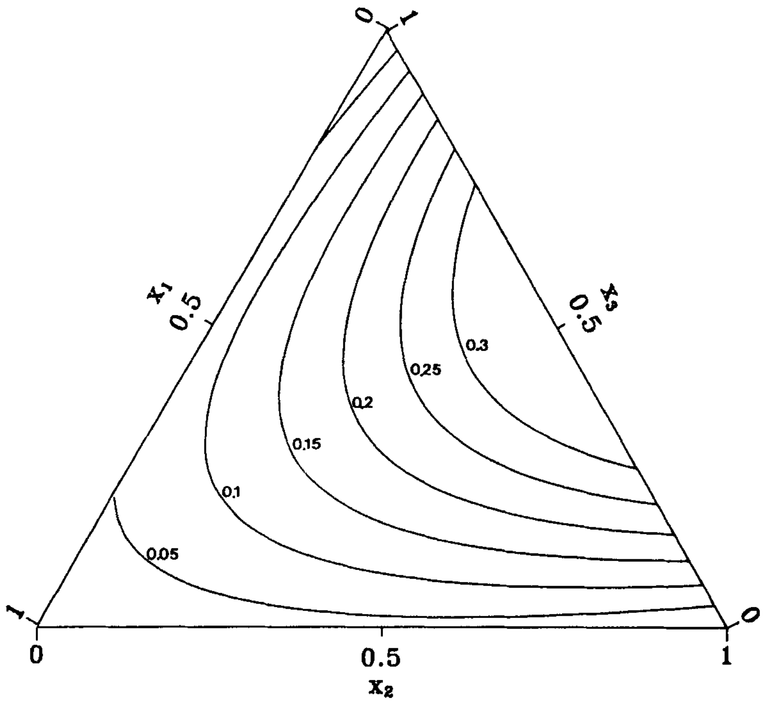

Figure 4 Curves of constant $V^E_{m,123}$/(cm^3 · (cm^3 · mol^{-1}) for $\{x_1 o\text{-}C_6H_4(CH_3)_2 + x_2CH_3(CH_2)_5CH_3 + (1 - x_1 - x_2)C_6H_5CH_3\}$ predicted by the Nitta–Chao model.

and finally, under parallel projection, the binary contribution can be written as the arithmetic mean of the contributions corresponding to $x'_i = x_i$, $x'_j = 1 - x_i$ and $x'_i = 1 - x_j$, $x'_j = x_j$, Eq. 3 becomes

$$V^E_{m,123} = \frac{1}{2}\sum_{i<j}[x_j/(1 - x_i)\cdot\{V^E_{m,ij}(x_i, 1 - x_i)\} + x_i/(1 - x_j)\cdot\{V^E_{m,ij}(1 - x_j, x_j)\}]. \quad (6)$$

Tables 3 and 4 also list the deviations between the experimental and the fitted excess molar volumes, $\delta V^E_{m,123} = \{V^E_{m,123} - V^E_{m,123}$ (Eq. 2)$\}$ together with the discrepancies between the experimental and predicted values given by: (a), Eq. 4; (b), Eq. 5; (c), Eq. 6. The results show that the best prediction is given by the parallel projection for two ternary mixtures. In all cases the error in estimating the excess volume is less than 0.05 cm^3 · mol^{-1}.

The results obtained in this work at the temperature of 308.15 K decrease slightly to those published for 298.15 K[1], both for the binary and the ternary systems.

The binary mixtures (o-xylene + n-heptane), (o-xylene + toluene), (n-heptane + toluene) and the ternary mixture (o-xylene + n-heptane + toluene) were used to test the Nitta–Chao model[2,3] using the parameters calculated by Koukios *et al.*[4].

The Nitta–Chao model predicts positive excess volumes for the aforementioned binary systems and, consequently, with this theoretical model positive V_m^E values are obtained for the ternary system analyzed (Figure 4). Figures 2(a) and 4 show that the difference between the experimental and theoretical values are very large, both qualitatively and quantitatively. This fact can be explained taking into account that the excess volumes are magnitudes which present very small values and, consequently, are very sensitive to the set of parameters needed for the use of the model. In our case, the set of parameters used for these systems was obtained by Koukios *et al.*[4] using a data base which did not contain excess volumes.

In order to improve the predictions of this model, our primary aim in a future work will be to obtain a new set of parameters using an extending data base which includes our results for V^E together with other results from the literature.

Acknowledgements

This work was supported by "Xunta de Galicia, promoción xeral do coñecemento (XUGA 8040289)" and "Universidade de Santiago de Compostela (programa de subvencions para a adquisición de material cientifico), Spain".

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