Excess Molar Enthalpies and Excess Molar Volumes of the Ternary System 1,2-Dichlorobenzene + Benzene + 1-Chlorohexane at 298.15 K

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Excess molar enthalpies and excess molar volumes for the ternary system {(x_1)1,2-dichlorobenzene + (x_2)benzene + (1 − x_1 − x_2)1-chlorohexane} and the involved binary mixture {(x)benzene + (1 − x)1-chlorohexane} have been determined at the temperature 298.15 K and atmospheric pressure. Values of excess molar enthalpies were measured using a Calvet microcalorimeter, and excess molar volumes were determined from the densities of the pure liquids and mixtures, using a vibrating-tube densimeter. The experimental values were used to test the results obtained with empirical expressions for estimating ternary properties from binary data.

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1. Introduction

This work reports experimental excess molar enthalpies and excess molar volumes for the ternary system {(x_1)1,2-dichlorobenzene + (x_2)benzene + (1 − x_1 − x_2)1-chlorohexane} and the involved binary mixture {(x)benzene + (1 − x)1-chlorohexane} at the temperature 298.15 K and atmospheric pressure. The excess molar enthalpies and excess molar volumes for the binary mixtures {(x)1,2-dichlorobenzene + (1 − x)benzene} and {(x)1,2-dichlorobenzene + (1 − x)1-chlorohexane} were reported in an earlier work.[1] Values of excess molar enthalpies were measured using a Calvet microcalorimeter, and excess molar volumes were determined from the densities of the pure liquids and mixtures, using a vibrating-tube densimeter. The binary experimental data were fitted using a Redlich−Kister variable-degree polynomial.[2] The Cibulka equation[3] was used to correlate the experimental values of the ternary mixture.

The results obtained for the ternary mixtures were used to test the predicting capability of several empirical methods. These equations offer reliable estimations of excess properties for a multicomponent mixture using the involved binary experimental data. The symmetric equations used were those introduced by Kohler,[4] Jacob and Fitzner,[5] Colinet,[6] and Knobeloch and Schwartz,[7] and the asymmetric ones were due to Tsao and Smith,[8] Toop,[9] Scatchard et al.,[10] Hillert,[11] and Mathieson and Thynne.[12]

2. Experimental Section

Materials. The chemical substances employed were supplied by Aldrich and Fluka, and were subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves to eliminate residual traces of water and degassing by an ultrasound technique. The mole fraction purities of the chemicals were as follows: >0.99 mole fraction for 1,2-dichlorobenzene and 1-chlorohexane (Fluka); >0.999 mole fraction for benzene (Aldrich). The densities of the pure liquids used have been published previously by Mato et al.[1] The handling and disposal of the chemicals used has been done according to the recommendation of the *CRC Handbook of Chemistry and Physics*.[13]

Apparatus and Procedure. The mixtures were prepared by mass using a Mettler H51 balance (precision $\pm 1 \times 10^{-5}$ g), ensuring a probable error in the mole fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table.[14]

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of a vapor phase and having a calorimeter-cell volume of approximately 10 cm^3. A Philips PM2535 voltmeter and a data acquisition system were linked to the microcalorimeter. Calibration was performed electrically using a Setaram EJP30 stabilized current source. Further details about the experimental method of operation have been published.[15,16] The apparatus and procedures were tested by determining excess enthalpies for the standard system hexane + cyclohexane at 298.15 K, and the results were found to differ by less than 1% from those of Marsh[17] and Gmeling.[18] The uncertainty in excess molar enthalpy measurements is estimated to be better than 1 J·mol^{-1}.

Excess molar volumes were determined from the densities of the pure liquids and mixtures. The measurements of densities were carried out with an Anton-Paar DMA 60/602 vibrating-tube densimeter operating under static mode. The temperature inside the vibrating-tube cell was measured using an Anton Paar DT 100-30 digital thermometer and was regulated to better than ±0.01 K using a Haake F3 circulating-water bath. The experimental technique has been described previously.[19,20] The uncertainty in the densities was $\pm 2 \times 10^{-5}$ g·cm^{-3}. Before each series of

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10.1021/je025625m CCC: $25.00

Table 1. Experimental Binary Excess Molar Enthalpies, H_m^E, and Excess Molar Volumes, V_m^E, at 298.15 K for (*x*)Benzene + (1 − *x*)1-Chlorohexane

x	H_m^E / $J \cdot mol^{-1}$	x	H_m^E / $J \cdot mol^{-1}$	x	H_m^E / $J \cdot mol^{-1}$	x	H_m^E / $J \cdot mol^{-1}$
0.0723	6.1	0.2862	33.1	0.5820	95.9	0.8484	93.9
0.0744	7.1	0.3323	41.5	0.6153	102.3	0.8629	86.4
0.0805	6.1	0.3940	53.1	0.6575	107.1	0.8940	72.7
0.0888	7.0	0.4431	65.2	0.7164	110.7	0.9274	55.4
0.1407	13.0	0.5015	78.9	0.7288	111.5	0.9535	38.4
0.1427	14.7	0.5375	86.9	0.7352	109.7		
0.1437	14.7	0.5410	86.9	0.7928	104.6		
0.2125	22.5	0.5524	91.1	0.8215	101.3		

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 / $cm^3 \cdot mol^{-1}$
0.1036	0.0479	0.4951	0.1884	0.6892	0.2041	0.9086	0.1093
0.1842	0.0760	0.5461	0.1990	0.7720	0.1876	0.9485	0.0654
0.2877	0.1218	0.5969	0.2014	0.8038	0.1765	0.9642	0.0499
0.3492	0.1418	0.6390	0.2054	0.8480	0.1526		
0.3994	0.1625	0.6739	0.2047	0.8734	0.1363		

Table 2. Fitting Parameters, A_i, for Eq 3 and Standard Deviations, *s*, for H_m^E and V_m^E

H_m^E

A_1	A_2	A_3	A_4	A_5	A_6	s
(*x*)1,2-Dichlorobenzene + (1 − *x*)Benzene[a]						
620.7	−10.9					1.3
(*x*)1,2-Dichlorobenzene + (1 − *x*)1-Chlorohexane[a]						
−286.0	−22.3	24.0	237.3		−168.7	0.6
(*x*)Benzene + (1 − *x*)1-Chlorohexane						
314.3	452.8	205.7	−38.2			0.9

V_m^E

A_1	A_2	A_3	A_4	A_5	A_6	s
(*x*)1,2-Dichlorobenzene + (1 − *x*)Benzene[a]						
0.3869	−0.0252	0.0765				0.0009
(*x*)1,2-Dichlorobenzene + (1 − *x*)1-Chlorohexane[a]						
−1.3814	0.0614	0.0800				0.0030
(*x*)Benzene + (1 − *x*)1-Chlorohexane						
0.7520	0.4445	0.1982	0.0902			0.0019

[a] Reference 1.

Table 3. Excess Molar Enthalpies, $H_{m,123}^E$, at 298.15 K for the Ternary Mixture 1,2-Dichlorobenzene + Benzene + 1-Chlorohexane

x_1	x_2	$H_{m,\phi}^E$ / $J \cdot mol^{-1}$	$H_{m,123}^E$ / $J \cdot mol^{-1}$	x_1	x_2	$H_{m,\phi}^E$ / $J \cdot mol^{-1}$	$H_{m,123}^E$ / $J \cdot mol^{-1}$
$x_1' = 0.2505$, $H_{m,12}^E = 117.6$ $J \cdot mol^{-1}$							
0.0167	0.0499	−7.9	−0.0	0.1614	0.4828	−16.5	59.2
0.0346	0.1034	−16.3	−0.0	0.1711	0.5118	−11.1	69.2
0.0487	0.1457	−21.1	1.7	0.1832	0.5480	−7.9	78.0
0.0671	0.2006	−26.2	5.3	0.1940	0.5789	−6.0	84.8
0.0784	0.2344	−28.7	8.1	0.2039	0.6099	−2.7	92.9
0.0927	0.2775	−30.8	12.7	0.2129	0.6371	−0.4	99.5
0.1074	0.3212	−30.6	19.8	0.2287	0.6841	2.1	109.4
0.1176	0.3518	−29.1	26.0	0.2390	0.7151	0.8	113.0
0.1318	0.3942	−25.6	36.2	0.2415	0.7227	1.3	114.6
0.1432	0.4283	−22.8	44.3				
$x_1' = 0.5045$, $H_{m,12}^E = 155.1$ $J \cdot mol^{-1}$							
0.0317	0.0311	−16.8	−7.1	0.3187	0.3130	−68.8	29.2
0.0647	0.0635	−32.2	−12.4	0.3387	0.3326	−62.9	41.2
0.0893	0.0877	−41.7	−14.3	0.3604	0.3539	−61.8	49.0
0.1209	0.1188	−52.8	−15.6	0.3875	0.3805	−50.4	68.8
0.1532	0.1505	−61.9	−14.8	0.4066	0.3993	−42.6	82.4
0.1780	0.1748	−65.7	−10.9	0.4236	0.4160	−36.3	93.9
0.2046	0.2010	−70.0	−7.1	0.4465	0.4386	−25.8	111.5
0.2296	0.2255	−72.9	−2.2	0.4670	0.4587	−19.8	123.8
0.2612	0.2566	−74.6	5.7	0.4845	0.4759	−8.6	140.4
0.2816	0.2765	−72.3	14.3				
$x_1' = 0.7537$, $H_{m,12}^E = 114.2$ $J \cdot mol^{-1}$							
0.0468	0.0153	−19.4	−12.3	0.4362	0.1426	−82.5	−16.4
0.0831	0.0272	−33.6	−21.0	0.5013	0.1638	−74.6	1.3
0.1340	0.0438	−49.2	−28.9	0.5267	0.1721	−70.4	9.4
0.1830	0.0598	−61.3	−33.6	0.5692	0.1860	−58.2	28.0
0.2285	0.0747	−71.0	−36.4	0.5959	0.1947	−50.1	40.1
0.2677	0.0875	−76.8	−36.2	0.6250	0.2043	−43.8	50.8
0.3073	0.1004	−81.3	−34.7	0.6634	0.2168	−31.9	68.6
0.3325	0.1086	−83.2	−32.8	0.6933	0.2266	−21.2	83.9
0.3638	0.1189	−84.2	−29.1	0.7261	0.2373	−10.3	99.7
0.4087	0.1336	−83.0	−21.1				

measurements the apparatus was calibrated at atmospheric pressure using double-distilled and degassed water and heptane (Fluka, >0.995); density data were taken from the literature: ref 21 for heptane and ref 22 for water. The uncertainty in excess molar volume measurements is estimated as better than 1%.

Several experimental series of measurements were carried out for the ternary compositions resulting from adding 1-chlorohexane to a binary mixture composed of {(x_1')1,2-dichlorobenzene + (x_2')benzene}, where $x_2' = 1 - x_1'$. The ternary composition point is then a pseudobinary mixture composed by addition of 1-chlorohexane and the mentioned binary mixture. Thus, the ternary excess molar enthalpy at the ternary composition x_1, x_2, ($x_3 = 1 - x_1 - x_2$) can be expressed as

$$H_{m,123}^E = H_{m,\phi}^E + (x_1 + x_2)H_{m,12}^E \qquad (1)$$

where $H_{m,\phi}^E$ is the measured excess molar enthalpy for the pseudobinary mixture and $H_{m,12}^E$ is the excess molar enthalpy of the initial binary {(x_1')1,2-dichlorobenzene + (x_2')benzene}. Values of $H_{m,12}^E$ at three mole fractions were interpolated by using a spline-fit method. Equation 1 does not involve any approximation.

The excess molar volumes were calculated from the densities of the pure liquids and their mixtures using the following equation

$$V_{m,123}^E = \sum_{i=1}^{n} x_i M_i(\rho^{-1} - \rho_i^{-1}) \qquad (2)$$

with *x*, *M*, and *ρ* being mole fraction, molar mass, and density, respectively; *n* is the number of the components in the mixture, and the subscript *i* indicates values for the pure components.

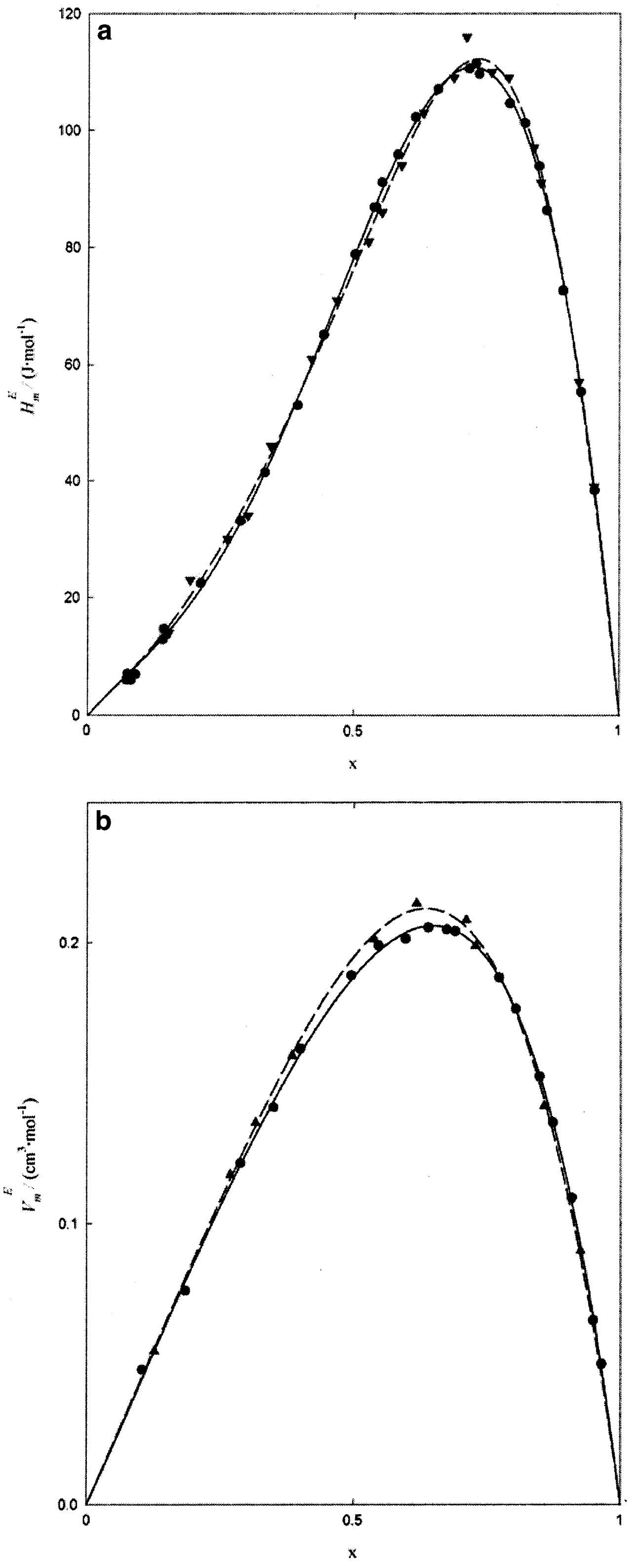

Figure 1. (a) Excess molar enthalpies, H_m^E/J·mol^{-1}, and (b) excess molar volumes, V_m^E/cm^3·mol^{-1}, at 298.15 K of {(*x*)benzene + (1 − *x*)1-chlorohexane}: ●, experimental values of this work; —, fitted by eq 3; ▼, ref 25; ▲, ref 26.

3. Data Correlation

Experimental values of H_m^E and V_m^E for the mixture {(*x*)-benzene + (1 − *x*)1-chlorohexane} are listed in Table 1. The excess molar enthalpies and excess molar volumes for the binary mixtures {(*x*)1,2-dichlorobenzene + (1 − *x*)-benzene} and {(*x*)1,2-dichlorobenzene + (1 − *x*)1-chlorohexane} were reported in an earlier work.[1] The experimental data of H_m^E and V_m^E corresponding to the binary mixtures were fitted by the following variable-degree polynomials of the form

Table 4. Excess Molar Volumes, $V_{m,123}^E$, at 298.15 K for the Ternary Mixture 1,2-Dichlorobenzene + Benzene + 1-Chlorohexane

x_1	x_2	$V_{m,123}^E$ / cm^3·mol^{-1}	x_1	x_2	$V_{m,123}^E$ / cm^3·mol^{-1}
0.0153	0.0881	0.0169	0.0996	0.0686	−0.0992
0.0248	0.1424	0.0283	0.1877	0.1292	−0.1522
0.0476	0.2734	0.0573	0.2178	0.1498	−0.1642
0.0681	0.3911	0.0796	0.3376	0.2323	−0.1753
0.0875	0.5022	0.0966	0.3694	0.2542	−0.1672
0.0948	0.5444	0.0987	0.4085	0.2811	−0.1510
0.1050	0.6032	0.1007	0.4750	0.3268	−0.1011
0.1200	0.6889	0.0954	0.0729	0.0245	−0.0858
0.1347	0.7733	0.0822	0.1188	0.0399	−0.1279
0.0291	0.0710	−0.0093	0.2214	0.0744	−0.2059
0.0523	0.1279	−0.0137	0.2623	0.0881	−0.2197
0.0923	0.2254	−0.0150	0.4230	0.1421	−0.2489
0.1326	0.3239	−0.0124	0.4629	0.1555	−0.2367
0.1690	0.4129	−0.0058	0.5108	0.1716	−0.2167
0.1865	0.4557	−0.0035	0.5958	0.2001	−0.1547
0.2065	0.5044	0.0090	0.6735	0.2262	−0.0610
0.2352	0.5745	0.0260	0.0980	0.0100	−0.1289
0.2635	0.6438	0.0521	0.1551	0.0159	−0.1844
0.0490	0.0605	−0.0401	0.2697	0.0276	−0.2662
0.0764	0.0944	−0.0574	0.3897	0.0399	−0.3111
0.1434	0.1771	−0.0869	0.5041	0.0516	−0.3113
0.2051	0.2533	−0.1000	0.5445	0.0558	−0.3040
0.2596	0.3205	−0.1017	0.6119	0.0627	−0.2766
0.2787	0.3442	−0.0990	0.7121	0.0729	−0.2128
0.3101	0.3829	−0.0856	0.8110	0.0831	−0.1087
0.3601	0.4447	−0.0476			
0.4037	0.4985	0.0108			
0.0589	0.0405	−0.0637			

$$Q_m^E = x_i x_j \sum_{k=1}^{n} A_k (x_i - x_j)^{k-1} \qquad (3)$$

where Q_m^E is H_m^E/J·mol^{-1} or V_m^E/cm^3·mol^{-1}.

Equation 3 is a Redlich−Kister fitting polynomial,[2] and the parameters A_k have been obtained by a fitting computer program which uses the least squares procedure and a Marquardt algorithm.[23] The number of parameters used in eq 3 was determined by applying an F test.[24]

The parameters A_i and the standard deviations for H_m^E and V_m^E of the three binary mixtures involved in this ternary system are presented in Table 2.

A plot of the obtained experimental values and literature values together with the smoothing curves for H_m^E and V_m^E of the binary mixture {(*x*)benzene + (1 − *x*)1-chlorohexane} is shown in Figure 1. García Vicente et al.[25] measured H_m^E of {(*x*)benzene + (1 − *x*)1-chlorohexane} and obtained experimental data about 2.5% higher than ours. Gallardo et al.[26] measured V_m^E of {(*x*)benzene + (1 − *x*)1-chlorohexane} and obtained experimental data about 2.8% higher than ours.

We are not aware of any previous measurement of $H_{m,123}^E$ and $V_{m,123}^E$ of the ternary mixture to which this study is directed.

The measured values of ternary excess properties, $Q_{m,123}^E$, listed in Tables 3 and 4, were correlated using the following equation:

$$Q_{m,123}^E = Q_{m,bin}^E + x_1 x_2 (1 - x_1 - x_2)\Delta_{123} \qquad (4)$$

where $Q_{m,123}^E$ is $H_{m,123}^E$/J·mol^{-1} or $V_{m,123}^E$/cm^3·mol^{-1};

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

Table 5. Fitting Parameters, B_i, for Eq 5 and Standard Deviations, s, for $H^{E}_{m,123}$ and $V^{E}_{m,123}$

B_1	B_2	B_3	s
	$H^{E}_{m,123}$		
−666.9	+921.5	−1657.1	1.2
	$V^{E}_{m,123}$		
−0.3766	−3.0402	−3.0355	0.0025

is known as the binary contribution to the excess ternary properties; the last term of eq 4 stands for the ternary contribution to the magnitude and was correlated using the equation proposed by Cibulka[3]

$$\Delta_{123} = (B_1 + B_2x_1 + B_3x_2) \tag{6}$$

and $Q^{E}_{m,ij}$ are given by eq 3.

The B_i parameters were calculated by an unweighted least squares method using a nonlinear optimization algorithm due to Marquardt.[23] Table 5 presents the values of the B_i parameters and their corresponding standard deviations.

Figure 2 shows the pseudobinary representation of the measured experimental values of the $H^{E}_{m,123}$ and $V^{E}_{m,123}$, respectively, together with the correlated curves, where eq 6 was applied to fit the ternary contribution.

The lines of constant ternary excess molar enthalpy, $H^{E}_{m,123}$, and excess molar volume, $V^{E}_{m,123}$, respectively, calculated using eq 4 are plotted in Figure 3.

Figure 4 represents the ternary contribution, $x_1x_2(1 - x_1 - x_2)\Delta_{123}$, to the excess molar enthalpy and excess molar volume, correlated with eq 6.

4. Empirical Equations

Experimental values were used to test several empirical equations that have been suggested for parametrizing and predicting excess properties of ternary mixtures from the experimental data of the involved binary systems and require the binary coefficients which appear in the predictive multicomponent expression. A wide variety of empirical methods have been proposed to estimate multicomponent properties on mixing from experimental results on constituent binaries. These methods can be divided into symmetric and asymmetric, depending on whether the assumption of the three binaries contributing equally to the ternary mixture magnitude is accepted or not.

Asymmetry is usually understood to be caused by the strongly polar or associative behavior of any of the compounds in the mixture. In these cases, different geometric criteria are applied to match each point of the ternary composition with the contributing binary compositions.

The symmetric equations tested have been suggested by Kohler,[4] Jacob and Fitzner,[5] Colinet,[6] and Knobeloch and Schwartz,[7] while the asymmetric ones have been suggested by Tsao and Smith,[8] Toop,[9] Scatchard et al.,[10] Hillert,[11] and Mathieson and Thynne.[12] The average percent deviations from the experimental data are listed in Tables 6 and 7. Asymmetric equations were applied for three different numberings of the components, to check the differences in the predicted values and also to seek a rule to decide which ordering should be used in each case. 1,2-Dichlorobenzene, benzene, or 1-chlorohexane were respectively named as 1, 2, and 3. Then, the rows A, B, and C of Table 7 fit to the 1,2-dichlorobenzene + benzene + 1-chlorohexane system as 123, 231, and 321, respectively.

5. Results and Discussion

The excess enthalpies for the binary mixtures benzene + 1-chlorohexane and 1,2-dichlorobenzene + benzene are positive over the whole range of composition. The obtained curve for the system benzene + 1-chlorohexane is asym-

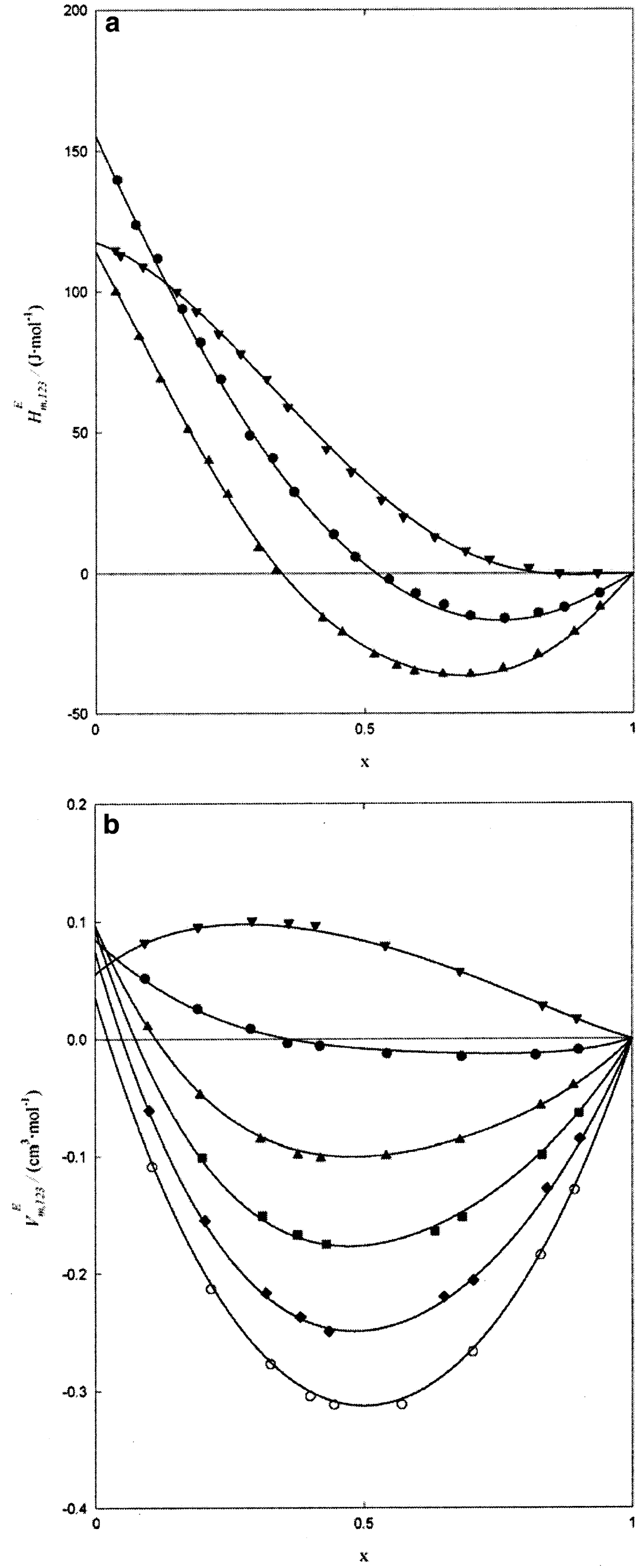

Figure 2. Pseudobinary representation of {(1 − x)[(x_1')1,2-dichlorobenzene + (x_2')benzene] + (x)1-chlorohexane} at 298.15 K. (a) Ternary excess molar enthalpies, $H^{E}_{m,123}$/J·mol^{-1}: ▼, $x'_1 = 0.2505$, $x'_2 = 0.7495$; ●, $x'_1 = 0.5045$, $x'_2 = 0.4955$; ▲, $x'_1 = 0.7537$, $x'_2 = 0.2463$. (b) Ternary excess molar volumes, $V^{E}_{m,123}$/cm^3·mol^{-1}: ▼, $x'_1 = 0.1483$, $x'_2 = 0.8517$; ●, $x'_1 = 0.3008$, $x'_2 = 0.6992$; ▲, $x'_1 = 0.4515$, $x'_2 = 0.5485$; ■, $x'_1 = 0.6015$, $x'_2 = 0.3985$; ◆, $x'_1 = 0.7564$, $x'_2 = 0.2436$; ○, $x'_1 = 0.9217$, $x'_2 = 0.0783$; —, correlated using eq 4.

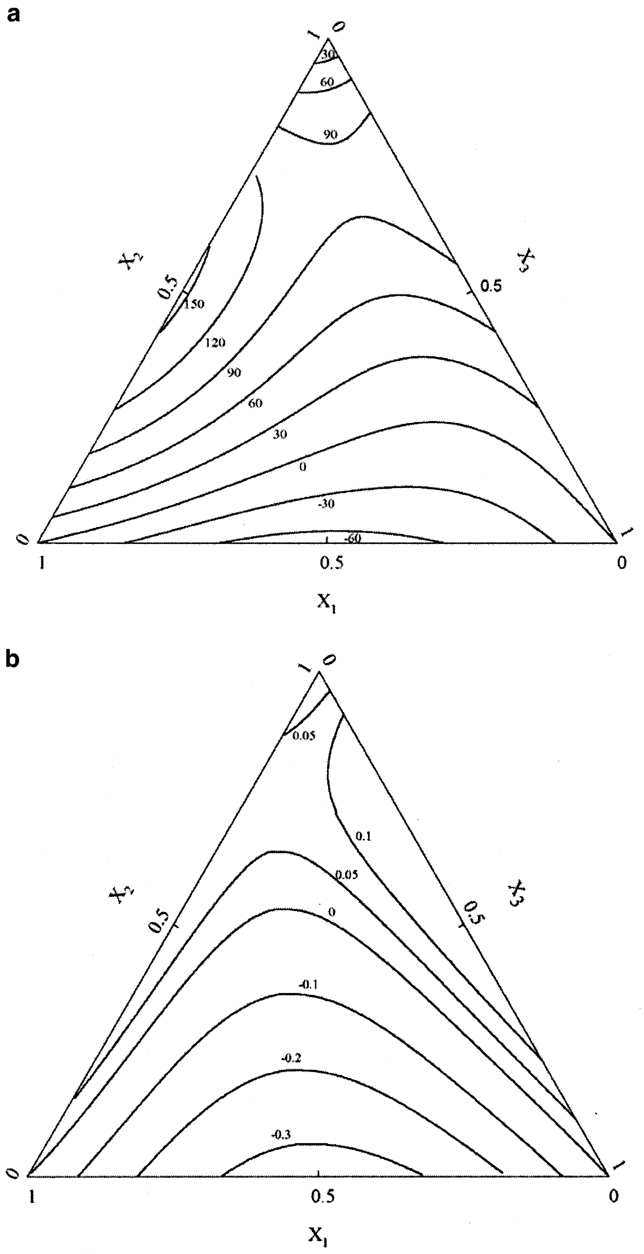

Figure 3. Curves of constant (a) $H^{E}_{m,123}$/J·mol^{-1} or (b) $V^{E}_{m,123}$/cm^{3}·mol^{-1} at 298.15 K for {(x_1)1,2-dichlorobenzene + (x_2)benzene + (1 − x_1 − x_2)1-chlorohexane}, calculated with eq 4.

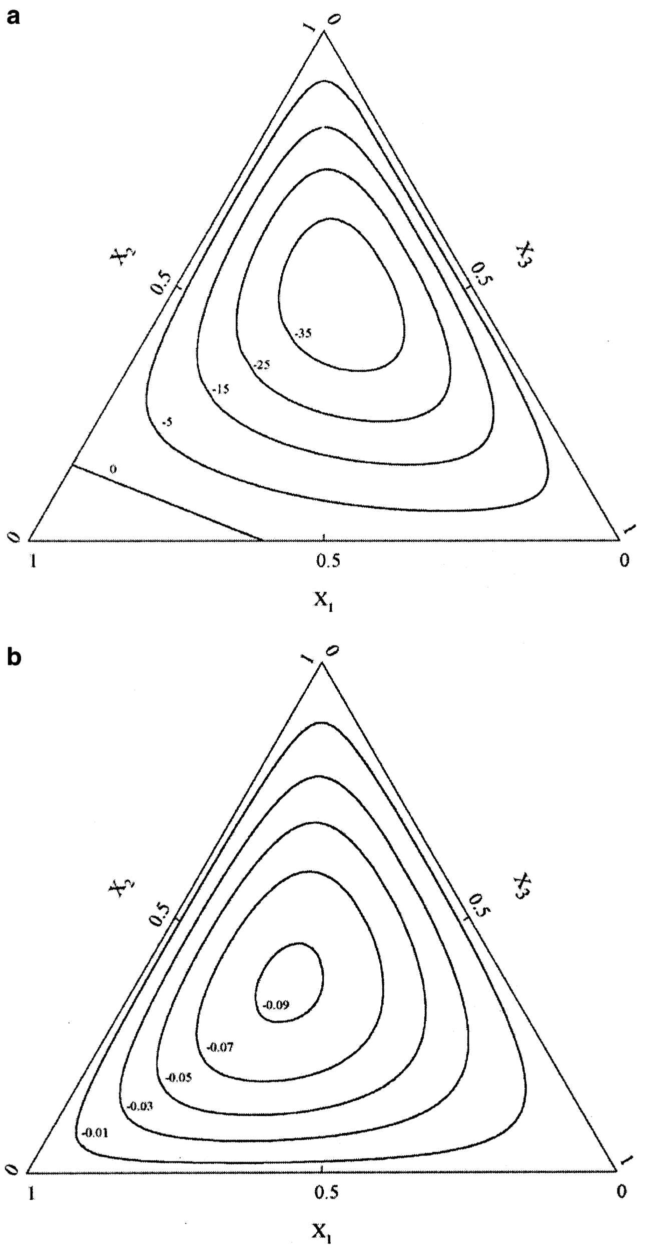

Figure 4. Curves of constant ternary contribution, $x_1x_2(1 - x_1 - x_2)\Delta_{123}$, (a) to the excess molar enthalpy, $H^{E}_{m,123}$/J·mol^{-1}, or (b) to the excess molar volume, $V^{E}_{m,123}$/cm^{3}·mol^{-1}, for {(x_1)1,2-dichlorobenzene + (x_2)benzene + (1 − x_1 − x_2)1-chlorohexane} at 298.15 K, correlated using eq 5.

Table 6. Average Percent Deviations of the Ternary Excess Properties Values Predicted by Symmetrical Empirical Equations from the Corresponding Experimental Data

Kohler	Jacob−Fitzner	Colinet	Knobeloch−Schwartz
		$H^{E}_{m,123}$/J·mol^{-1}	
22.0	20.5	21.7	35.7
		$V^{E}_{m,123}$/cm^{3}·mol^{-1}	
0.050	0.049	0.051	0.048

metric, with the maximum shifted around the rich compositions in benzene; nevertheless, the curve for the system 1,2-dichlorobenzene + benzene is symmetrical. H^{E}_{m} values for the binary mixture 1,2-dichlorobenzene + 1-chlorohexane are negative over the whole range of composition, and the curve for this system is almost symmetrical.

The ternary system shows maximum values at x_1 = 0.4950, x_2 = 0.5040, and $H^{E}_{m,123}$ = 155 J·mol^{-1}, corresponding to the binary system 1,2-dichlorobenzene + benzene, and minimum values at x_1 = 0.5170, x_3 = 0.4830, and $H^{E}_{m,123}$ = −72 J·mol^{-1}, corresponding to the binary mixture 1,2-dichlorobenzene + 1-chlorohexane. The ternary contribution presents maximum values of 0.8 J·mol^{-1} at x_1 = 0.8280, x_2= 0.0500, and x_3 = 0.1220 and minimum values of −41 J·mol^{-1} at x_1 = 0.2300, x_2= 0.4830, and x_3 = 0.2870.

The experimental volumes for the binary mixtures 1,2-dichlorobenzene + benzene and benzene + 1-chlorohexane are positive over the whole range of composition, and for the binary mixture 1,2-dichlorobenzene + 1-chlorohexane they are negative over the whole range of composition.

Then the ternary system shows maximum values for the benzene + 1-chlorohexane at x_2 = 0.6500, x_3 = 0.3500, and $V^{E}_{m,123}$ = 0.2060 cm^{3}·mol^{-1} and minimum values for the mixture 1,2-dichlorobenzene + 1-chlorohexane at x_1 =

Table 7. Average Percent Deviations of the Ternary Excess Properties Values Predicted by Asymmetrical Empirical Equations from the Corresponding Experimental Data[a]

	Tsao−Smith	Toop	Scatchard et al.	Hillert	Mathieson−Tynne
			$H^{E}_{m,123}$/J·mol^{-1}		
A	33.0	21.3	19.7	20.8	20.2
B	4.2	12.9	13.0	13.0	16.4
C	53.8	34.3	34.3	34.3	25.5
			$V^{E}_{m,123}$/cm^{3}·mol^{-1}		
A	0.074	0.050	0.049	0.050	0.049
B	0.014	0.041	0.041	0.041	0.044
C	0.075	0.066	0.066	0.066	0.054

[a] Three numberings of the components have been compared, in this order: A ≡ 123, B ≡ 231, C ≡ 312.

0.4900, $x_3 = 0.5100$, and $V^{E}_{m,123} = -0.3455$ cm^3·mol^{-1}. The ternary contribution to the excess ternary volume is negative over the whole range of composition showing minimum values at -0.0934 cm^3·mol^{-1} $x_1 = 0.3700$, $x_2 = 0.3700$, $x_3 = 0.2600$.

Several empirical equation methods have been proposed to estimate ternary excess properties from experimental results on constituent binaries. The deviations obtained are rather high, and this fact can be attributed to the comparatively important significance of the ternary contribution to the studied magnitude. The best agreement with the experimental data was achieved by the asymmetric equation from Tsao and Smith,[8] choosing the benzene as the first component in the numbering. It can observed that the dependence on the arrangement of the components varies in each asymmetric equation. For all cases, the best results are obtained using arrangement B (231). The best results for the ternary excess enthalpies obtained using symmetric equations are those predicted by the Jacob−Fitzner equation;[5] meanwhile, the best predictions of the ternary excess volumes are obtained with the Knobeloch and Schwartz method.[7]

Literature Cited

(1) Mato, M. M.; Balseiro, J.; Salgado, J.; Jiménez, E.; Legido, J. L.; Piñeiro, M. M.; Paz Andrade, M. I. Study on Excess Molar Enthalpies and Excess Molar Volumes of the Binary Systems 1,2-dichlorobenzene + (benzene, hexane, 1-chlorohexane) and 1,3-dichlorobenzene + (benzene, hexane, 1-chlorohexane) at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 4−7.

(2) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(3) Cibulka, I. Estimation of Excess Volume and Density of Ternary Mixtures of Nonelectrolytes from Binary Data. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1414−1419.

(4) Kohler, F. Estimatión of Thermodynamic Data for a Ternary System from the Corresponding Binary Systems. *Monatsh. Chem.* **1960**, *91*, 738−740.

(5) Jacob, K. T.; Fitzner, K. The Estimation of the Thermodynamic Properties of the Ternary Allows from Binary Data Using the Shortest Distance Composition Path. *Thermochim. Acta* **1977**, *18*, 197−206.

(6) Colinet, C. Thesis, University of Grenoble, France, 1967.

(7) Knobeloch, J. B.; Schwartz, C. E. Heats of Mixing of Ternary Systems: Sulphuric Acid−Phosphoric Acid−Water *J. Chem. Eng. Data* **1962**, *7*, 386-387.

(8) Tsao, C. C.; Smith, J. M. Heats of Mixing of Liquids. "Applied Thermodynamics". *Chem. Eng. Prog., Symp. Ser.* **1953**, *49*, 107−117.

(9) Toop, G. W. Predicting Ternary Activities Using Binary Data. *Trans. TMS-AIME* **1965**, *223*, 850−855.

(10) Scatchard, G.; Ticknor, L. B.; Goates J. R.; McCartney, E. R. Heats of Mixing in Some Nonelectrolyte Solutions. *J. Am. Chem. Soc.* **1952**, *74*, 3721−3724.

(11) Hillert, M. Empirical Methods of Predicting and Representing Thermodynamic Properties of Ternary Solution Phases. *Calphad* **1980**, *4*, 1−12.

(12) Mathieson, A. R.; Thynne, J. C. Heats of Mixing of Ternary, Quaternary, and Quinary Mixtures formed by Benzene, Cyclohexane, Heptane, Toluene and Hexane. *J. Chem. Soc.* **1957**, 3713−3716.

(13) *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL, 1996−1997; Vol. 16, pp 1−11.

(14) IUPAC. *Pure Appl. Chem.* **1986**, *58*, 1677−1692.

(15) Paz Andrade, M. I. *Les Dévelopements Récents de la Microcalorimetrie et de la Thermogenése*, 1st ed.; CRNS: Paris, 1967.

(16) Paz Andrade, M. I.; Castromil, S.; Baluja, M. C. Enthalpies of Mixing: *n*-hexane + o-xilene at 25, 35, and 50 °C. *J. Chem. Thermodyn.* **1970**, *2*, 775−777.

(17) Marsh, K. N. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1973**, *1*, 22.

(18) Gmehling, J. Excess Enthalpy. Cychlohexane + hexane system. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1992**, *3*, 144.

(19) Lorenzana, M. T.; Legido, J. L.; Jiménez, E.; Fernández, J.; Pías, L.; Ortega, J.; Paz Andrade, M. I. Thermodynamic properties of (a propyl ester + an *n*-alkane) at 298.15 K. I.{Propyl propanoate+ alkane (C_nH_{2n+2})}, (n=6 to 10). *J. Chem. Thermodyn.* **1989**, *21* (10), 1017−1022.

(20) Legido, J. L.; Lorenzana, M. T.; Jiménez, E.; Fernández, J.; Amigo, A.; Paz Andrade, M. I. Thermodynamic Propierties of Binary Mixtures of 2-Hexanone with *n*-Alkanes at 35 °C. *J. Solution Chem.* **1990**, *19* (11), 1095−1102.

(21) Grolier, J. P. E.; Benson, G. C. Thermodynamics properties of the binary mixtures containing Ketones. VIII. Heat capacities and volumes of some *n*-alkanone + *n*-alkane mixtures at 298.15 K. *Can. J. Chem.* **1984**, *62*, 949−953.

(22) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley & Sons: New York, 1986; Vol. II.

(23) Marquardt, D. W. An Algorithm for least Squares Estimation of Non- Linear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *2*, 431−441.

(24) Bevington, P. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

(25) García Vicente, I.; García-Lisbona, N.; Velasco, I.; Otin, S.; Muñoz Embid, J.; Kehiaian, H. V. Excess enthalpies of 1-chloroalkanes + benzene. Measurement and analysis in terms of group contributions (DISQUAC), *Fluid Phase Equilib.* **1989**, *49*, 251−262.

(26) Gallardo, M. A.; Garciá Vicente, I.; Velasco, I.; Otín, S. Excess volumes of some (1-chloroalkane or 1-bromoalkane + benzene)s at 298.15 K, *J. Chem. Thermodyn*, **1989**, *21*, 1101−1104.

Received for review October 7, 2002. Accepted January 20, 2003.

JE025625M