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

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Excess molar enthalpies, $H^E_{m,123}$, and excess molar volumes, $V^E_{m,123}$, for the ternary system {x_1 1,2-dichlorobenzene + x_2 benzene + (1 − x_1 − x_2) hexane} and excess molar enthalpies H^E_m of the binary mixture {x benzene + (1 − x) hexane} 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 are compared with the results obtained with empirical expressions for estimating ternary properties from binary data.

1. Introduction

In the thermodynamic literature, experimental measurements of binary mixtures are relatively abundant, whereas experimental properties of ternary mixtures are scarce and, even, for higher-order multicomponent systems they are practically nonexistent. This work reports experimental excess molar enthalpies and excess molar volumes of the ternary system {x_1 1,2-dichlorobenzene + x_2 benzene + (1 − x_1 − x_2) hexane} and experimental excess molar enthalpies of the involved binary mixture {x benzene + (1 − x) hexane} 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) hexane} and the excess molar volumes of the binary mixture {x benzene + (1 − x) hexane} were reported in earlier works.[1,2] 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.[3] The Cibulka equation[4] 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,[5] Jacob and Fitzner,[6] Colinet,[7] and Knobeloch and Schwartz,[8] and the asymmetric ones were due to Tsao and Smith,[9] Toop,[10] Scatchard et al.,[11] Hillert,[12] and Mathieson and Thynne.[13]

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2. Experimental Section

The sources and purities of the chemicals were as follows: 1,2-dichlorobenzene and hexane were provided by Fluka (>0.99 mole fraction), and benzene was provided by Aldrich (>0.999 mole fraction). The products 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. Gas chromatographic analysis detected no significant peaks of impurities for all the components. 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*.[14]

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of 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. The accuracy in excess molar enthalpy measurements is estimated as better than 1%. Further details about the experimental method of operation have been published.[15,16]

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 controlled 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.[17,18] The uncertainty in density measurements was $\pm 2 \times 10^{-6}$ g·cm^{-3}. Before each series of 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 19 for heptane and ref 20 for water. The

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Table 1. Experimental Binary Excess Molar Enthalpies H_m^E at 298.15 K

x	H_m^E/J·mol^{-1}	x	H_m^E/J·mol^{-1}
x Benzene + (1 − x) Hexane			
0.0799	231	0.5895	916
0.1394	395	0.6314	899
0.2134	567	0.6892	849
0.2629	673	0.7456	782
0.3163	754	0.7802	724
0.3861	847	0.8154	655
0.4412	892	0.8938	432
0.4838	912	0.9310	303
0.5373	940	0.9633	168

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

A_1	A_2	A_3	A_4	A_5	A_6	s
H_m^E						
1,2-Dichlorobenzene + Benzene[a]						
620.7	−10.9					1.3
1,2-Dichlorobenzene + Hexane[a]						
2736.7	−80.0	632.3	−363.5	−373.1		4.0
Benzene + Hexane						
3689.5	584.5	353.1	446.3			5.0
V_m^E						
A_1	A_2	A_3	A_4	A_5	A_6	s
1,2-Dichlorobenzene + Benzene[a]						
0.3869	−0.0252	0.0765				0.0009
1,2-Dichlorobenzene + Hexane[a]						
−3.8357	0.1475	−0.1659				0.0078
Benzene + Hexane[b]						
1.5846	0.0576	0.1570				0.0035

[a] Reference 1. [b] Reference 2.

mixtures were prepared by weight using a Mettler H51 (precision ±1 × 10^{-5} g) balance, ensuring an accuracy in the mole fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table.[21] The accuracy 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 hexane 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 a pseudobinary mixture composed by addition of hexane and the mentioned binary mixture. Thus, the ternary excess molar enthalpy at the pseudobinary composition x_1, x_2, ($x_3 = 1 - x_1 - x_2$) can be expressed as

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

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:

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

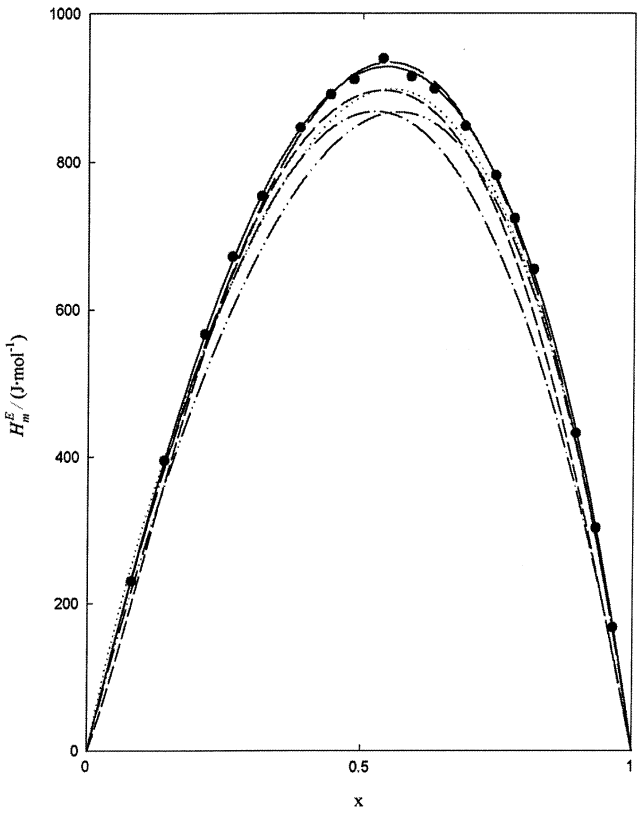

Figure 1. Excess molar enthalpies H_m^E/J·mol^{-1} at 298.15 K of {x benzene + (1 − x) hexane}: ●, experimental values of this work; —, fitted by eq 3; — —, ref 24; – –, ref 26; – · –, ref 27; ···, ref 25; – ·· –, ref 28.

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.

3. Data Correlation

Experimental values of H_m^E for the mixture {x benzene + (1 − x) hexane} 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) hexane} were reported in an earlier work,[1] and the excess molar volumes of the binary mixture {x benzene + (1 − x) hexane} were taken from ref 2. 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

$$Q_m^E = x(1-x)\sum_{i=1}^{n} A_i (2x-1)^{i-1} \quad (3)$$

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,[3] and the parameters A_i have been obtained by a fitting computer program which uses the least squares procedure and a Marquardt algorithm.[22] The number of parameters used in eq 3 was determined by applying an F test.[23] 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.

We have decided to measure experimental excess molar enthalpies for the system {x benzene + (1 − x) hexane} in order to use experimental values from the same microcalorimeter for all the binary systems involved in the ternary

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

x_1	x_2	$H^E_{m,\phi}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}	x_1	x_2	$H^E_{m,\phi}$ / J·mol^{-1}	$H^E_{m,123}$ / J·mol^{-1}
			$x'_1 = 0.2393$, $H^E_{m,12} = 114$ J·mol^{-1}				
0.2298	0.7310	139	249	0.1562	0.4966	744	818
0.2283	0.7256	156	265	0.1375	0.4372	797	862
0.2230	0.7089	223	329	0.1254	0.3985	805	864
0.2210	0.7024	251	356	0.1030	0.3273	787	836
0.2117	0.6731	356	457	0.0865	0.2750	732	773
0.2026	0.6441	463	560	0.0748	0.2379	698	733
0.1950	0.6197	537	630	0.0608	0.1933	592	621
0.1860	0.5914	607	696	0.0477	0.1516	515	538
0.1750	0.5562	667	751	0.0336	0.1067	378	394
0.1736	0.5518	661	743	0.0196	0.0625	241	250
			$x'_1 = 0.4959$, $H^E_{m,12} = 155$ J·mol-1				
0.4733	0.4811	131	279	0.2563	0.2605	740	820
0.4574	0.4650	219	362	0.2719	0.2764	729	814
0.4353	0.4425	337	474	0.2384	0.2424	724	799
0.4147	0.4215	419	549	0.1973	0.2006	699	761
0.4000	0.4067	492	617	0.1727	0.1756	664	719
0.3741	0.3803	559	676	0.1530	0.1556	637	684
0.3561	0.3619	616	727	0.1164	0.1184	537	574
0.3278	0.3332	677	779	0.0578	0.0587	321	339
0.3043	0.3093	706	801	0.0345	0.0351	202	213
			$x'_1 = 0.7418$, $H^E_{m,12} = 118$ J·mol-1				
0.7035	0.2449	136	247	0.3889	0.1354	693	755
0.6813	0.2372	212	320	0.3320	0.1155	696	749
0.6451	0.2246	330	433	0.2792	0.0972	661	705
0.6190	0.2155	390	489	0.2582	0.0899	649	690
0.5837	0.2032	475	568	0.2495	0.0869	642	682
0.5578	0.1942	532	621	0.1779	0.0619	535	563
0.5155	0.1794	598	680	0.1309	0.0456	441	462
0.4842	0.1685	636	713	0.0833	0.0290	311	325
0.4464	0.1554	675	746	0.0487	0.0169	207	215
0.4136	0.1440	684	750				

system. The obtained experimental values of H^E_m are compared with literature values[24−28] in Figure 1 for the binary system {x benzene + (1 − x) hexane}. The experimental values of this work are in very close agreement with the most recent literature values, obtained by Casas et al.,[24] showing a positive deviation of 0.6%. Older literature data show higher negative deviations of 3%, 3%, 7%, and 7% for data obtained by Jones and Lu,[25] Romaní and Paz Andrade,[26] Paz Andrade et al.,[27] and Ridway and Butler,[28] respectively. The group of literature referring to this binary system is very large, and we have chosen several time sparse references for comparing our experimental values.

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

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

$$Q^E_{m,123} = Q^E_{m,bin} + x_1x_2(1 - x_1 - x_2)\Delta_{123} \quad (4)$$

where $Q^E_{m,123}$ is $H^E_{m,123}$/J·mol^{-1} or $V^E_{m,123}$/cm^3·mol^{-1} and the last term stands for the ternary contribution to the magnitude and was correlated using the equation proposed by Cibulka[4]

$$\Delta_{123} = (B_1 + B_2x_1 + B_3x_2) \quad (5)$$

and

$$Q^E_{m,bin} = Q^E_{m,12} + Q^E_{m,13} + Q^E_{m,23} \quad (6)$$

is known as the binary contribution to the excess ternary properties and $Q^E_{m,ij}$ values are given by eq 3.

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

x_1	x_2	$V^E_{m,123}$ / cm^3·mol^{-1}	x_1	x_2	$V^E_{m,123}$ / cm^3·mol^{-1}
0.0161	0.0911	0.0580	0.0916	0.0597	−0.2512
0.0256	0.1444	0.0829	0.1803	0.1176	−0.4290
0.0473	0.2675	0.1259	0.2633	0.1718	−0.5321
0.0714	0.4033	0.1449	0.3375	0.2201	−0.5585
0.0919	0.5193	0.1441	0.3815	0.2489	−0.5305
0.0966	0.5459	0.1343	0.4167	0.2718	−0.4922
0.1066	0.6025	0.1277	0.4853	0.3166	−0.3659
0.1231	0.6957	0.1148	0.5482	0.3576	−0.1763
0.1382	0.7808	0.0859	0.0958	0.0317	−0.3203
0.0300	0.0691	−0.0201	0.1187	0.0393	−0.3724
0.0448	0.1032	−0.0318	0.2221	0.0736	−0.5940
0.0921	0.2124	−0.0677	0.3176	0.1052	−0.7114
0.1371	0.3161	−0.0948	0.4092	0.1355	−0.7393
0.1739	0.4011	−0.1022	0.4449	0.1473	−0.7188
0.1905	0.4394	−0.0932	0.5066	0.1678	−0.6757
0.2106	0.4858	−0.0828	0.5906	0.1956	−0.5221
0.2442	0.5631	−0.0406	0.6749	0.2235	−0.2586
0.2760	0.6365	0.0134	0.0855	0.0092	−0.3077
0.0509	0.0609	−0.1137	0.1421	0.0153	−0.4683
0.0676	0.0808	−0.1465	0.2625	0.0282	−0.7270
0.1399	0.1671	−0.2649	0.3838	0.0413	−0.8626
0.2002	0.2392	−0.3273	0.4923	0.0529	−0.8825
0.2595	0.3101	−0.3341	0.5323	0.0572	−0.8585
0.2825	0.3376	−0.3338	0.6071	0.0652	−0.7988
0.3145	0.3759	−0.2998	0.7086	0.0762	−0.6151
0.3649	0.4360	−0.2164	0.8084	0.0869	−0.3314
0.4143	0.4951	−0.0719			
0.0631	0.0412	−0.1786			

The B_i parameters were calculated by an unweighted least-squares method using a nonlinear optimization algorithm due to Marquardt.[22] Table 5 presents the values

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
	$H^E_{m,123}$		
−1095.5	1789.6	−221.8	7.7
	$V^E_{m,123}$		
−4.4905	−3.8217	3.3540	0.0052

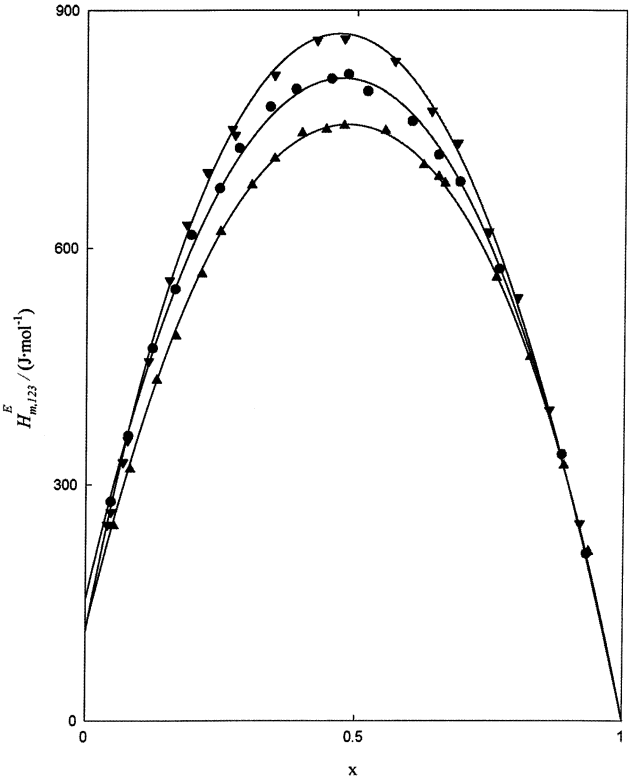

Figure 2. Pseudobinary representation of ternary excess molar enthalpies $H^E_{m,123}$/J·mol^{-1} at 298.15 K of {(1 − x)(x'_1 1,2-dichlorobenzene + x'_2 benzene) + x hexane}: (▼) x'_1 = 0.2393, x'_2 = 0.7607; (●) x'_1 = 0.4959, x'_2 = 0.5041; (▲) x'_1 = 0.7418, x'_2 = 0.2582; —, correlated using eq 4.

of the B_i parameters and their corresponding standard deviations.

Figures 2 and 3 show the pseudobinary representations of the measured experimental values of and $V^E_{m,123}$, respectively, together with the correlated curves, where eq 5 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 Figures 4 and 5.

Figures 6 and 7 represent the ternary contribution, x_1x_2-(1 − x_1 − x_2)Δ_{123}, to the excess molar enthalpy and excess molar volume, correlated with eq 5.

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

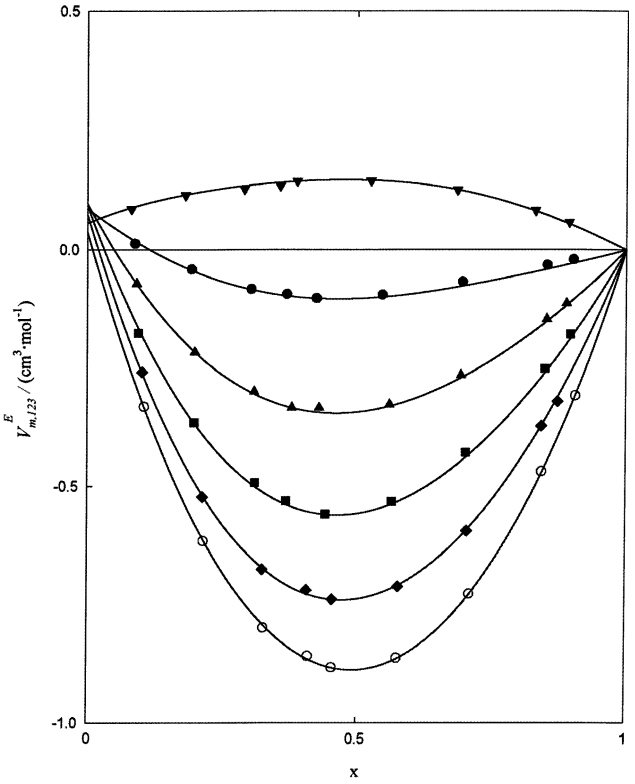

Figure 3. Pseudobinary representation of ternary excess molar volumes $V^E_{m,123}$/cm^3·mol^{-1} at 298.15 K of {(1 − x)(x'_1 1,2-dichlorobenzene + x'_2 benzene) + x hexane}: (▼) x'_1 = 0.1504, x'_2 = 0.8496; (●) x'_1 = 0.3004, x'_2 = 0.6996; (▲) x'_1 = 0.4556, x'_2 = 0.5444; (■) x'_1 = 0.6052, x'_2 = 0.3948; (◆) x'_1 = 0.7512, x'_2 = 0.2488; (○) x'_1 = 0.9030, x'_2 = 0.0970; —, correlated using eq 4.

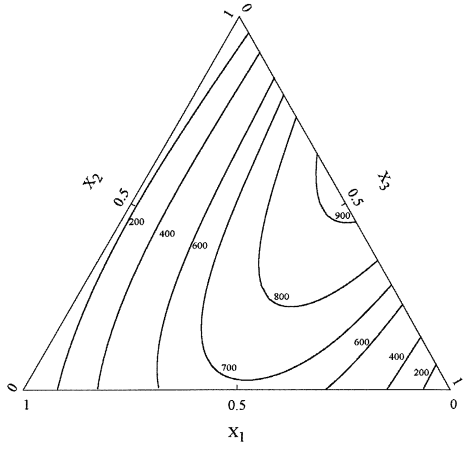

Figure 4. Curves of constant $H^E_{m,123}$/J·mol^{-1} at 298.15 K for (x_1 1,2-dichlorobenzene + x_2 benzene + (1 − x_1 − x_2) hexane), calculated with eq 4.

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,[5] Jacob and Fitzner,[6] Colinet,[7] and Knobeloch and Schwartz,[8] while the asymmetric ones have been suggested by Tsao and Smith,[9] Toop,[10] Scatchard et al.,[11] Hillert,[12] and Mathieson and Thynne.[13] The average percent deviations from the experimental data are listed in Tables 6 and

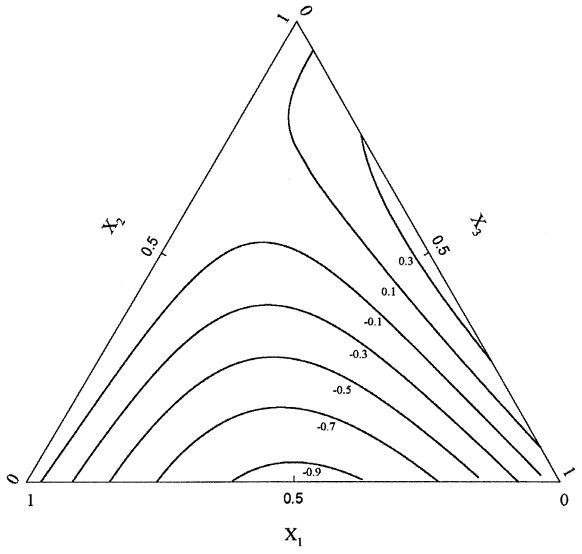

Figure 5. Curves of constant $V^E_{m,123}/cm^3 \cdot mol^{-1}$ at 298.15 K for (x_1 1,2-dichlorobenzene + x_2 benzene + (1 − x_1 − x_2) hexane), calculated with eq 4.

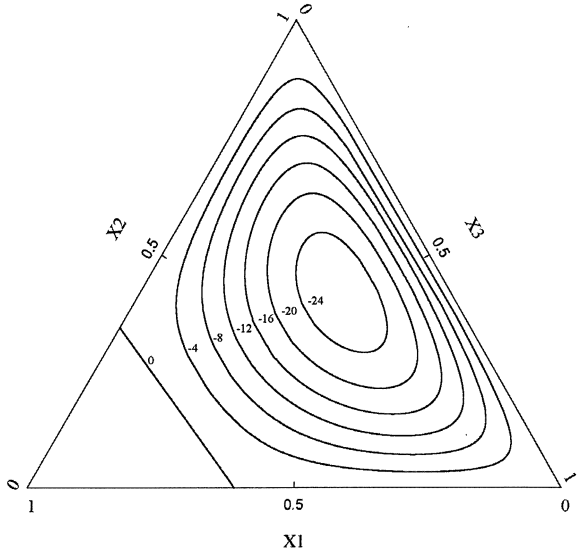

Figure 6. Curves of constant ternary contribution $x_1x_2(1 - x_1 - x_2)\Delta_{123}/J \cdot mol^{-1}$ to the excess molar enthalpy $H^E_{m,123}$ for {x_1 1,2-dichlorobenzene + x_2 benzene + (1 − x_1 − x_2) hexane}, correlated using eq 5.

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 witch ordering should be used in each case. 1,2-Dichlorobenzene, benzene, or hexane was respectively named as 1, 2, or 3. Then, the rows *A*, *B*, and *C* of Table 7 fit to 1,2-dichlorobenzene + benzene + hexane as 123, 231, and 321, respectively.

5. Results and Discussion

Experimental enthalpies for the three binary mixtures involved in the ternary system are positive over the whole range of composition, showing maximum values for the mixture with benzene + hexane. The curves for all these systems are almost symmetrical. For the ternary system there exists a maximum at $x_2 = 0.5450$, $x_3 = 0.4550$, and $H^E_{m,123} = 928.7$ J·mol^{-1}, corresponding to the binary system benzene + hexane.

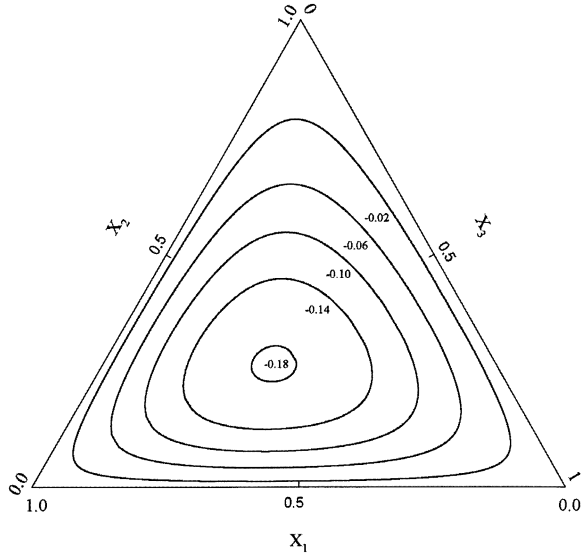

Figure 7. Curves of constant ternary contribution $x_1x_2(1 - x_1 - x_2)\Delta_{123}/cm^3 \cdot mol^{-1}$ to the excess molar volume $V^E_{m,123}$ for {x_1 1,2-dichlorobenzene + x_2 benzene + (1 − x_1 − x_2) hexane}, correlated using eq 5.

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

Kohler	Jacob−Fitzner	Colinet	Knobeloch−Schwartz
	$H^E_{m,123}/J \cdot mol^{-1}$		
21.9	15.8	20.8	160.4
	$V^E_{m,123}/cm^3 \cdot mol^{-1}$		
0.093	0.094	0.093	0.076

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

	Tsao−Smith	Toop	Scatchard et al.	Hillert	Mathieson−Tynne
			$H^E_{m,123}/J \cdot mol^{-1}$		
A	149.8	27.5	25.2	26.6	19.4
B	102.0	11.8	9.2	10.6	11.0
C	159.8	165.7	165.7	165.7	21.2
			$V^E_{m,123}/cm^3 \cdot mol^{-1}$		
A	0.142	0.091	0.091	0.091	0.093
B	0.058	0.091	0.092	0.091	0.093
C	0.117	0.109	0.109	0.109	0.096

[a] Three numberings of the components have been compared, in this order, 123, 231, 312.

The experimental volumes for the binary mixtures 1,2-dichlorobenzene + benzene and benzene + hexane are positive over the whole range of composition, and for the binary mixture 1,2-dichlorobenzene + hexane, they are negative over the whole range of composition. Then the ternary mixture 1,2-dichlorobenzene + benzene + hexane shows maximum values for benzene + hexane at $x_2 = 0.5100$, $x_3 = 0.4900$, and $V^E_{m,123} = 0.3963$ cm^3·mol^{-1} and minimum values for the mixture 1,2-dichlorobenzene + hexane at $x_1 = 0.4900$, $x_3 = 0.5100$, and $V^E_{m,123} = -0.9593$ cm^3·mol^{-1}.

The ternary contribution to the excess molar enthalpy is always negative, with the exception of a small range located at high compositions of 1,2-dichlorobenzene, showing maximum values at $x_1 = 0.7690$, $x_2 = 0.1100$, $x_3 = 0.1200$, and $H^E_{m,123} = 2.6$ J·mol^{-1} and minimum values at $x_1 = 0.2060$, $x_2 = 0.4180$, $x_3 = 0.376$, and $H^E_{m,123} = -26.5$

$J \cdot mol^{-1}$. The ternary contribution to the excess molar volume is negative over the whole range of composition, showing minimum values at $x_1 = 0.4150$, $x_2 = 0.2650$, $x_3 = 0.3200$, and $V^E_{m,123} = -0.1827$ $cm^3 \cdot mol^{-1}$. In both cases, the representation is asymmetric, as can be seen in Figures 6 and 7. This means that the position of the minimum does not coincide with the center of the Gibbs triangle.

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 Scatchard et al.,[11] choosing 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). Meanwhile, the best results obtained using symmetric equations are those predicted by the Jacob−Fitzner equation.[6]

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