Measurement and Prediction of Excess Molar Enthalpies and Excess Molar Volumes of the Ternary System 1,3-Dichlorobenzene + Benzene + Hexane at 298.15 K

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Experimental excess molar enthalpies and excess molar volumes for the ternary system {x_1 1,3-dichlorobenzene + x_2 benzene + $(1- x_1 - x_2)$ hexane} have been determined at the temperature of 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. Several empirical expressions for estimating ternary properties from experimental binary results were applied.

Introduction

In previous papers,[1−4] we have reported experimental excess molar enthalpies and excess molar volumes at 298.15 K and atmospheric pressure of the binary and ternary nonelectrolyte mixtures containing 1,2-dichlorobenzene, 1,3-dichlorobenzene, benzene, hexane, or 1-chlorohexane. The present article continues our studies in the same line and reports experimental excess molar enthalpies and excess molar volumes at the temperature of 298.15 K and atmospheric pressure for the ternary system {x_1 1,3-dichlorobenzene + x_2 benzene + $(1- x_1 - x_2)$ hexane}. Experimental data of the three involved binary mixtures {x 1,3-dichlorobenzene + $(1 - x)$ benzene}, {x 1,3-dichlorobenzene + $(1 - x)$ hexane} and {x benzene + $(1 - x)$ hexane} were reported in earlier works.[1−3] The properties studied have proved to be meaningful from the thermodynamic point of view, as they provide direct information about the energetic effects arising between the molecules present in the mixture so they can help to explain the intermolecular interactions in solution.

Excess molar enthalpies were measured using a standard Calvet microcalorimeter, and excess molar volumes were determined from the densities of the pure liquids and mixtures, using a DMA 60/602 Anton Paar densimeter. The ternary contribution to the excess molar properties measured in this work was correlated on the basis of the Cibulka equation.[5]

The experimental data of this work were used to test several empirical equations,[6−14] who 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 that appear in the predictive multicomponent expression. These equations offer reliable estimations of excess properties for a multicomponent mixture using the involved binary experimental data.

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 degassed by ultrasound technique. The mol fraction purities of the chemicals were as follows: >0.99 mol fraction for 1,3-dichlorobenzene and hexane (Fluka) and >0.999 mol fraction for benzene (Aldrich). The densities of the pure liquids used have been published previously by Mato et al.[2] The handling and disposal of the chemicals used has been done according to the recommendation of the *CRC Handbook of Chemistry and Physics*.[15]

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 mol fraction less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table.[16]

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of the 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.[17,18] 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[19] and Gmeling.[20] The uncertainty in excess molar enthalpy measurements is estimated to be better than 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.

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Table 1. Excess Molar Enthalpies, $H^{E}_{m,123}$, at 298.15 K for the Ternary Mixture x_1 1,3-Dichlorobenzene + x_2 Benzene + (1 − x_1 − x_2) Hexane[a]

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}
$x_1' = 0.2462$, $H^{E}_{m,12} = 158$ J·mol^{-1}							
0.0158	0.0483	167	177	0.1395	0.4272	729	818
0.0282	0.0862	279	297	0.1599	0.4897	688	791
0.0479	0.1466	449	480	0.1676	0.5132	663	770
0.0652	0.1996	565	607	0.1863	0.5706	578	698
0.0779	0.2384	631	681	0.1998	0.6116	482	610
0.0920	0.2815	689	748	0.2082	0.6376	411	544
0.1048	0.3209	726	793	0.2181	0.6677	329	469
0.1163	0.3562	740	814	0.2299	0.7040	208	355
0.1254	0.3838	745	825	0.2372	0.7263	118	270
$x_1' = 0.5042$, $H^{E}_{m,12} = 171$ J·mol^{-1}							
0.0358	0.0352	181	193	0.3099	0.3048	630	735
0.0654	0.0643	310	332	0.3326	0.3271	602	714
0.1152	0.1133	459	498	0.3647	0.3586	522	645
0.1499	0.1474	546	597	0.3966	0.3900	458	592
0.1721	0.1692	612	670	0.4242	0.4171	366	509
0.2264	0.2226	653	729	0.4441	0.4367	285	435
0.2615	0.2572	656	744	0.4623	0.4546	200	357
0.2787	0.2741	649	743	0.4812	0.4732	127	290
$x_1' = 0.7602$, $H^{E}_{m,12} = 110$ J·mol^{-1}							
0.0587	0.0185	193	201	0.4603	0.1452	606	672
0.0951	0.0300	284	297	0.4943	0.1559	57l	643
0.1758	0.0555	450	476	0.5241	0.1653	539	616
0.1333	0.0421	371	390	0.5701	0.1798	480	563
0.2208	0.0696	517	549	0.6023	0.1900	429	517
0.2610	0.0823	562	600	0.6407	0.2021	343	436
0.2970	0.0937	602	645	0.6638	0.2094	279	375
0.3308	0.1044	611	659	0.7017	0.2213	177	279
0.3650	0.1151	626	679	0.7260	0.2290	105	210
0.4224	0.1333	621	682				

[a] Three experimental series of measurements were carried out for the ternary compositions resulting from adding hexane to a binary mixture composed of {x_1' 1,3-dichlorobenzene + x_2' benzene}, where $x_2' = 1 - x_1'$.

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.[21,22] The uncertainty in the densities was $\pm 2 \times 10^{-5}$ 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 literature, ref 23 for heptane and ref 24 for water. The uncertainty in excess molar volumes 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' 1,3-dichlorobenzene + x_2' benzene}, where $x_2' = 1 - x_1'$. The ternary composition point is then a pseudobinary mixture composed by addition of hexane and the mentioned binary mixture. Thus, the ternary excess molar enthalpy can be expressed as

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

where $H^{E}_{m,\phi}$ is the measured excess molar enthalpy for the pseudobinary mixture and $H^{E}_{m,12}$ is the excess molar enthalpy of the initial binary {x_1' 1,3-dichlorobenzene + x_2' benzene}. Values of $H^{E}_{m,12}$ at three mol fractions were interpolated by using a spline-fit method. Equation 1 does not involve any approximation.

Table 2. Excess Molar Volumes, $V^{E}_{m,123}$, at 298.15 K for the Ternary Mixture x_1 1,3-Dichlorobenzene + x_2 Benzene + (1 − x_1 − x_2) 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}
0.0183	0.1009	0.072	0.0781	0.0517	−0.160
0.0310	0.1704	0.104	0.1009	0.0669	−0.201
0.0519	0.2855	0.155	0.1890	0.1253	−0.329
0.0718	0.3949	0.160	0.2763	0.1831	−0.393
0.0898	0.4936	0.147	0.3391	0.2247	−0.391
0.0962	0.5288	0.144	0.3704	0.2454	−0.373
0.1091	0.6001	0.125	0.4143	0.2745	−0.332
0.1243	0.6838	0.118	0.4827	0.3198	−0.226
0.1405	0.7725	0.115	0.5466	0.3622	−0.057
0.0351	0.0815	−0.008	0.0777	0.0250	−0.195
0.0612	0.1421	−0.010	0.1300	0.0419	−0.320
0.0988	0.2296	−0.023	0.2283	0.0735	−0.461
0.1476	0.3432	−0.043	0.3448	0.1111	−0.558
0.1713	0.3982	−0.051	0.4186	0.1348	−0.551
0.1847	0.4294	−0.047	0.4617	0.1487	−0.520
0.2120	0.4927	−0.038	0.5199	0.1675	−0.468
0.2409	0.5599	−0.003	0.6068	0.1955	−0.315
0.2732	0.6351	0.067	0.6814	0.2195	−0.141
0.0590	0.0717	−0.080	0.0894	0.0076	−0.260
0.0810	0.0984	−0.107	0.1319	0.0112	−0.369
0.1401	0.1701	−0.173	0.2538	0.0216	−0.589
0.2117	0.2571	−0.219	0.3885	0.0330	−0.716
0.2597	0.3154	−0.226	0.5145	0.0437	−0.707
0.2800	0.3400	−0.214	0.5621	0.0478	−0.681
0.3446	0.4186	−0.153	0.6214	0.0528	−0.619
0.3705	0.4500	−0.103	0.7441	0.0632	−0.417
0.4124	0.5009	0.016	0.8393	0.0713	−0.198

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

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

with x, M, and ρ being mol 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.

The measured values of excess molar enthalpies and excess molar volumes for the three involved binary mixtures {x 1,3-dichlorobenzene + (1 − x) benzene}, {x 1,3-dichlorobenzene + (1 − x) hexane}, and {x benzene + (1 − x) hexane} were reported in an earlier works.[1−3]

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.

Experimental values of ternary excess molar enthalpies, $H^{E}_{m,123}$ and ternary excess molar volumes, $V^{E}_{m,123}$, for the ternary system {x_1 1,3-dichlorobenzene + x_2 benzene + (1 − x_1 − x_2) hexane} are listed in Tables 1 and 2.

Data Correlation

The measured values of ternary excess properties $Q^{E}_{m,123}$, listed in Tables 1 and 2, were correlated using the Cibulka equation[5]

$$Q^{E}_{m,123} = Q^{E}_{m,bin} + x_i x_j(1 - x_i - x_j)(B_1 + B_2 x_i + B_3 x_j) \qquad (3)$$

where $Q^{E}_{m,123}$ represents $H^{E}_{m,123}$/J·mol^{-1} or $V^{E}_{m,123}$/cm^{3}·mol^{-1}, $Q^{E}_{m,bin}$ is known as the binary contribution to the excess ternary properties

$$Q^{E}_{m,bin} = Q^{E}_{m,12} + Q^{E}_{m,13} + Q^{E}_{m,23} \qquad (4)$$

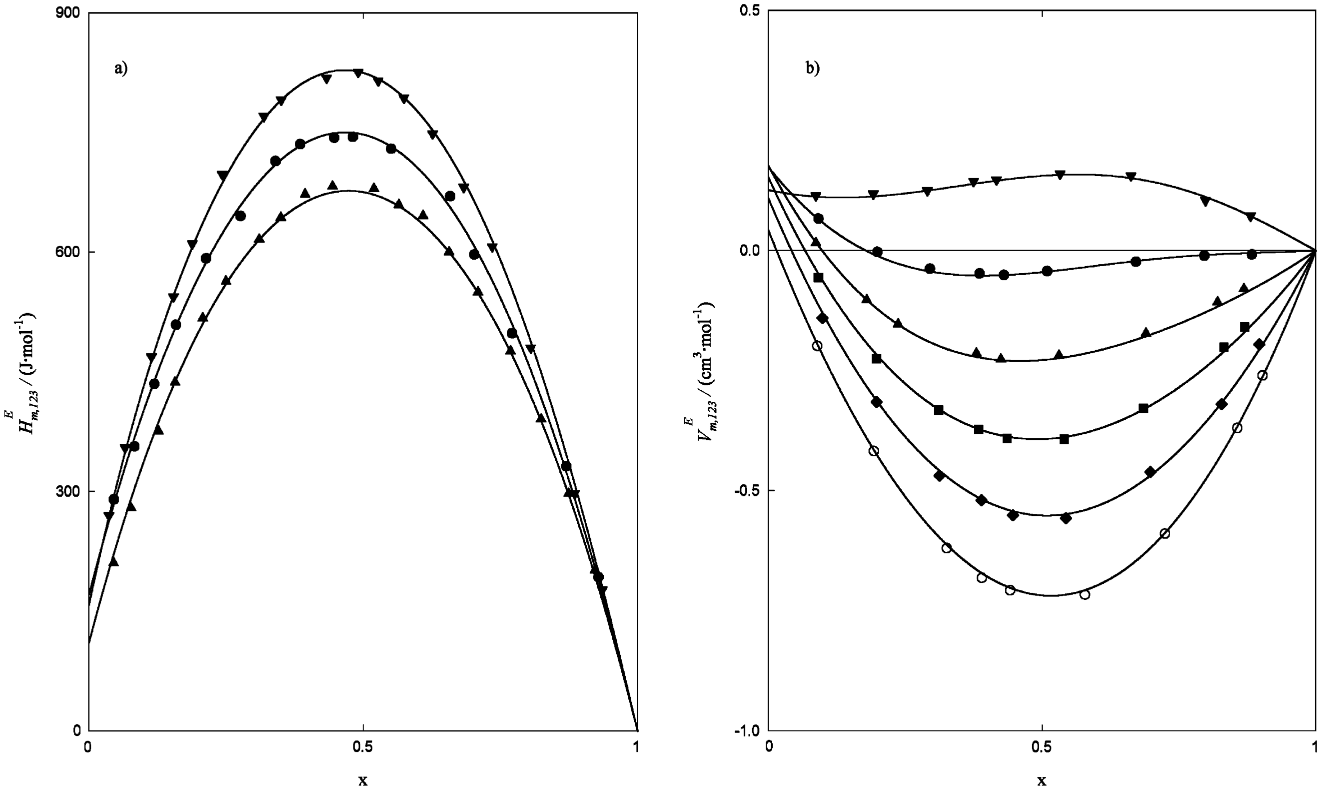

Figure 1. Pseudobinary representation of {(1 − x) (x_1' 1,3-dichlorobenzene + x_2' benzene) + x hexane} at 298.15 K. (a) Ternary excess molar enthalpies $H^E_{m,123}$/(J mol^{-1}): ▼, $x_1' = 0.2462$, $x_2' = 0.7538$; ●, $x_1' = 0.5042$, $x_2' = 0.4958$, ▲, $x_1' = 0.7602$, $x_2' = -0.2398$. (b) Ternary excess molar volumes $V^E_{m,123}$/(cm^3 mol^{-1}): ▼, $x_1' = 0.1539$, $x_2' = 0.8461$; ●, $x_1' = 0.3008$, $x_2' = 0.6992$; ▲, $x_1' = 0.4515$, $x_2' = 0.5485$; ■, $x_1' = 0.6015$, $x_2' = 0.3985$; ◆, $x_1' = 0.7564$, $x_2' = 0.2436$; ○, $x_1' = 0.9217$, $x_2' = 0.0783$; solid line, correlated using eq 3.

and $Q^E_{m,ij}$ have been fitted with the variable-degree polynomial proposed by Redlich−Kister[25] of the form

$$Q^E_{m,ij} = x_i x_j \sum_{k=1}^{n} A_i (x_i - x_j)^{i-1} \qquad (5)$$

where Q^E_m is H^E_m/J·mol^{-1} or V^E_m/cm^3·mol^{-1}.

The parameters A_i and the standard deviations for H^E_m and V^E_m of the three binary mixtures involved in this ternary system are presented in previous papers.[2,3]

The B_i parameters were calculated by an unweight least-squares method using a nonlinear optimization algorithm due to Marquardt.[26] Table 3 presents the values of the B_i parameters and their corresponding standard deviations.

Figure 1 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 3 was applied.

The lines of constant ternary excess molar enthalpy, $H^E_{m,123}$ and ternary excess molar volume, $V^E_{m,123}$, respectively, calculated using eq 3 are plotted in Figure 2.

The excess molar enthalpy is positive over the whole range of concentration and shows a maximun of 928.7 J·mol^{-1} at $x_2 = 0.5450$ and $x_3 = 0.4550$. The endothermicity of this mixtures suggests then that the positive contributions to the excess enthalpy, namely, the breaking of interactions, are energetically more important than the negative contribution, which is a specific interaction between unlike molecules.

The excess molar volume shows maximum values at $x_2 = 0.5100$, $x_3 = 0.4900$, and $V^E_{m,123} = 0.3963$ cm^3·mol^{-1} and minimum values at $x_1 = 0.4850$, $x_3 = 0.5150$, $V^E_{m,123} = -0.7991$ cm^3·mol^{-1}.

Table 3. Fitting Parameters, B_i, for Equation 5 and Standard Deviations, s, for $H^E_{m,123}$ and $V^E_{m,123}$

B_1	B_2	B_3	s
		$H^E_{m,123}$	
−1441.0	2795.5	−1860.8	6.9
		$V^E_{m,123}$	
−2.5978	0.9795	−5.4429	0.0057

Figure 3 represents lines of constant ternary contribution to the excess molar enthalpy and excess molar volume. The so-called “ternary contribution” represents the diference between the experimental value and the predicted from binary mixtures

$$Q^E_{m,123} - Q^E_{m,bin} = x_i x_j (1 - x_i - x_j)(B_1 + B_2 x_i + B_3 x_j) \qquad (6)$$

The ternary contribution to the excess enthalpy presents maximum values of 5.3 J mol^{-1} at $x_1 = 0.7600$, $x_2 = 0.0950$, and $x_3 = 0.1450$ and minimum values of −54.6 J·mol^{-1} at $x_1 = 0.2100$, $x_2 = 0.4750$, and $x_3 = 0.3150$.

The ternary contribution to the excess molar volume is always negative, showing maximum values at 0.1629 cm^3·mol^{-1} at $x_2 = 0.2750$ and $x_3 = 0.2900$.

Empirical Equations

As the number of components in the mixture increases, the determination of thermodynamic properties becomes more laborious. Therefore, the applicability of predictive methods is of great interest for estimating ternary properties from the experimental data of the binaries involved. So, several empirical methods have been proposed to estimate ternary excess properties from experimental results on constituent binaries. These methods can be divided into symmetric and asymmetric, depending on

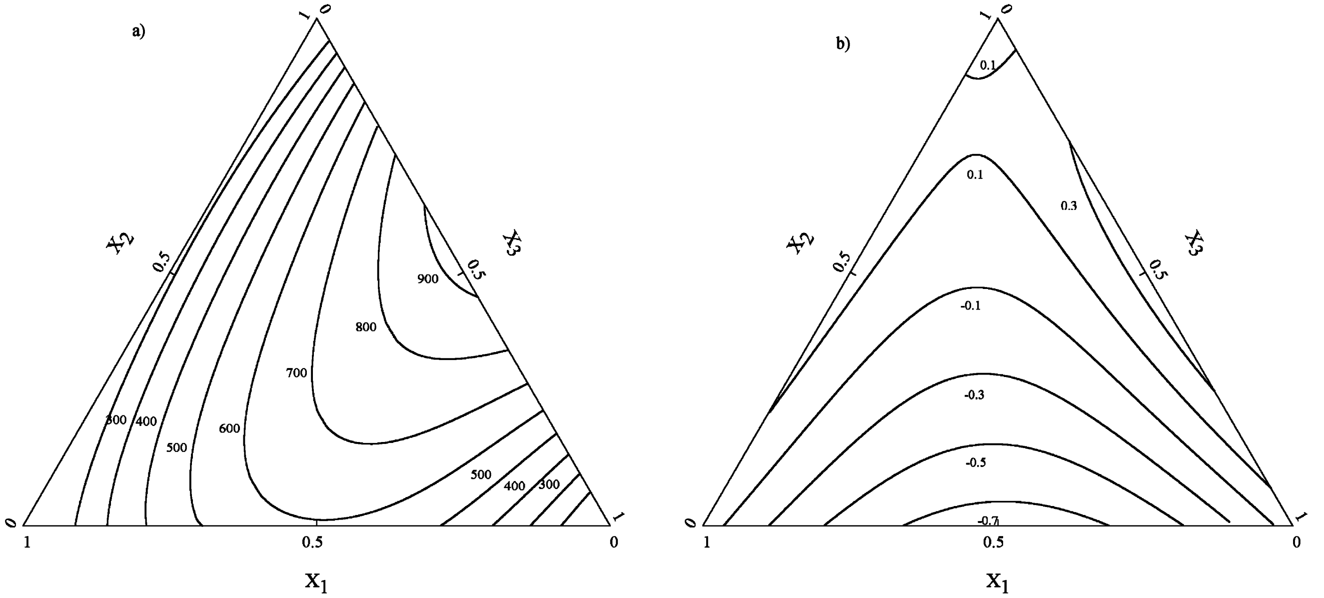

Figure 2. Curves of constant, (a) $H^{E}_{m,123}$/(J mol^{-1}) (b) $V^{E}_{m,123}$/(cm^{3} mol^{-1}), at 298.15 K for (x_1 1,3-dichlorobenzene + x_2 benzene + x_3 hexane), calculated with eq 3.

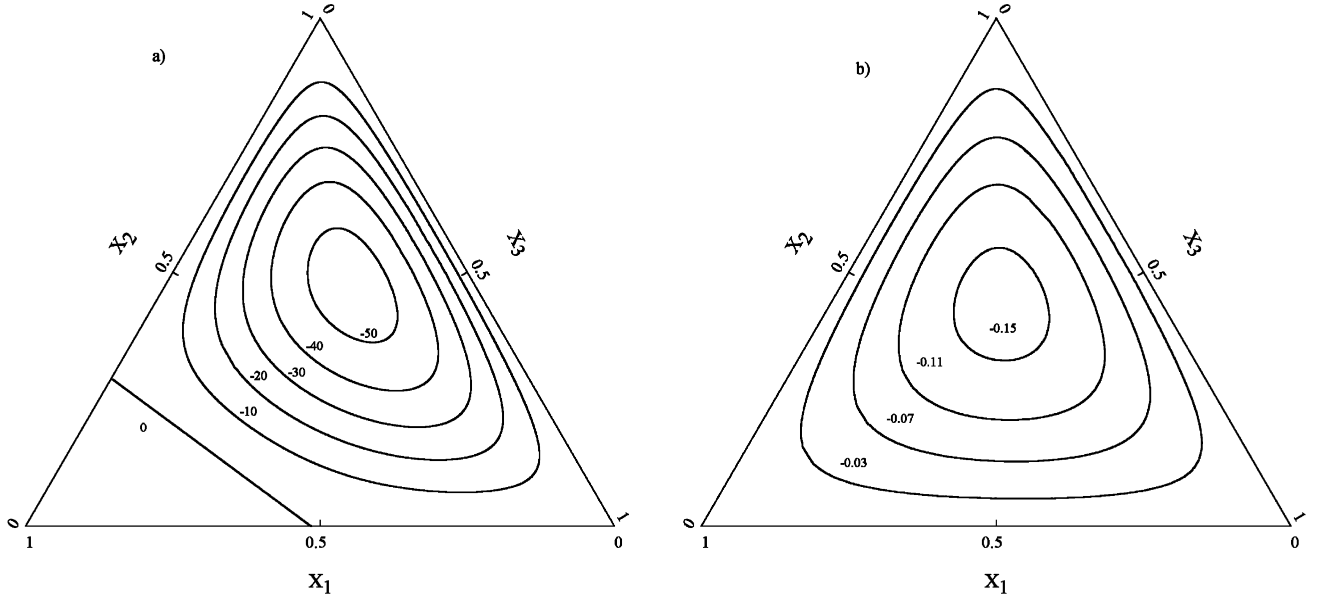

Figure 3. Curves of constant ternary contribution, (a) to the excess molar enthalpy $H^{E}_{m,123}$/(J mol^{-1}) and (b) to the excess molar volume $V^{E}_{m,123}$/(cm^{3} mol^{-1}), for {x_1 1,3-dichlorobenzene + x_2 benzene + x_3 hexane} at 298.15 K, correlated using eq 6.

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 ternary composition with the contributing binary compositions.

The symmetric equations tested have been suggested by Kohler,[6] Jacob and Fitzner,[7] Colinet,[8] and Knobeloch and Schwartz,[9] while the asymmetric ones have been suggested by Tsao and Smith,[10] Toop,[11] Scatchard et al.,[12] Hillert,[13] and Mathieson and Thynne.[14] Table 4 lists the mean-square deviations of the excess molar enthalpies and excess molar volumes for ternary system predicted by empirical equations and the experimental values. For the asymmetric equations, three different numberings of the components have been tested to check the differences in the predicted values and to find a rule to decide which ordering should be used in each case. 1,3-Dichlorobenzene, benzene, or hexane were respectively named as 1,2,3. Then, the rows A, B, and C of Table 4 fit to the 1,3-dichlorobenzene + benzene + hexane system as 123, 231, 312, respectively, ordered, the first element considered in each case being 1,3-dichlorobenzene, benzene, or hexane in this order.

Deviations obtained with these expressions are rather high, and this fact can be attributed to the importance of the ternary contribution term to the studied magnitude. By use of this kind of expression, lower deviations are usually obtained for those properties where the ternary contribution is not impostant. The best agreement with the experimental data to excess molar enthalpies was achieved by the asymmetric equation from Scatchard et al.,[12] choosing benzene as the first component in the numbering, whereas the Tsao and Smith equation,[10] with benzene being the asymmetric component, performs the best predictions for ternary excess volumes. It can observed that the

Table 4. Mean-Square Deviations from the Experimental Values Obtained with the Empirical Predictive Methods Listed Above[a]

empirical equations	$H^{\mathrm{E}}_{\mathrm{m},123}$/J·mol^{-1}		
Kohler	33.5		
Jacob Fitzner	27.5		
Colinet	32.5		
Knobeloch-Schwartz	162.6		
Tsao-Smith	160.9[b]	91.6[c]	159.1[d]
Toop	40.2[b]	15.8[c]	66.7[d]
Scatchard et al.	38.0[b]	14.4[c]	167.7[d]
Hillert	39.8[b]	15.7[c]	166.8[d]
Mathieson-Tynne	31.9[b]	19.7[c]	34.1[d]

empirical equations	$V^{\mathrm{E}}_{\mathrm{m},123}$/cm^3·mol^{-1}		
Kohler	0.085		
Jacob Fitzner	0.084		
Colinet	0.085		
Knobeloch-Schwartz	0.069		
Tsao-Smith	0.136[b]	0.031[c]	0.111[d]
Toop	0.087[b]	0.076[c]	0.099[d]
Scatchard et al.	0.087[b]	0.077[c]	0.098[d]
Hillert	0.087[b]	0.077[c]	0.099[d]
Mathieson-Tynne	0.085[b]	0.080[c]	0.086[d]

[a] For the asymmetric equations, three numberings of the components have been compared, in this order, 123, 231, 312. [b] Order 123. [c] Order 231. [d] Order 312.

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 to the ternary excess enthalpies obtained using symmetric equations are those predicted by Jacob and Fitzner equation,[7] whereas to the ternary excess volumes the best predictions using symmetric equations were obtained with Knobeloch and Schwartz.[9]

Supporting Information Available:

Experimental densities and excess molar volumes at 298.15 K for the ternary system 1,2-dichlorobenzene (x_1) + benzene (x_2) + hexane (x_3). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Casas, H.; Segade, L.; Franjo, C.; Jiménez, E.; Paz Andrade, M. I. Excess Properties for Propyl Propanoate + Hexane +Benzene at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 756−762.

(2) 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 1,3-Dichlorobenzene + (Benzene, Hexane, Hexane) and 1,3-Dichlorobenzene + (Benzene, Hexane, Hexane) at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 4−7.

(3) Mato, M. M.; Balseiro, J.; Jiménez, E.; Legido, J. L.; Galiñanes A. V.; Paz Andrade, M. I. Excess Molar Enthalpies and Excess Molar Volumes of the Ternary System 1,2-Dichlorobenzene + Benzene + Hexane at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 1436−1441.

(4) Mato, M. M.; López, M.; Legido, J. L.; Salgado, J.; Verdes, P. V.; Paz Andrade, M. I. Excess Molar Enthalpies and Excess Molar Volumes of the Ternary System 1,2-Dichlorobenzene + Benzene + 1-Chlorohexane at 298.15 K. *J. Chem. Eng. Data* **2003**, *48*, 646−651.

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

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

(7) 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.

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

(9) 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.

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

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

(12) Scatchard, G.; Ticknor, L. B.; Goates J. R.; McCartney, E. R. Heats of Mixing in Some Nonelectrolyte Solutions. *J. Am. Chem. Soc.* **1952**, *74*, 4, 3721−3724.

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

(14) 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.

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

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

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

(18) 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.

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

(20) Gmehling, J. Excess Enthalpy. Cychlohexane + Hexane System. *Int DATA Ser. Sel. Data Mixtures, Ser. A* **1992**, *3*, 144.

(21) 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$_n$H$_{2n+2}$)}, (n=6 to 10). *J. Chem. Thermodyn.* **1989**, *21* (10), 1017−1022.

(22) 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.

(23) 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.

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

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

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

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