Excess Molar Enthalpies of Propyl Propanoate + 1-Hexanol + Benzene at the Temperatures 25 °C and 35 °C†

Herminio Casas, Julieta Jiménez de Llano, Sandra García-Garabal, Luisa Segade, Carlos Franjo, and Eulogio Jiménez*

Departamento de Física, Facultade de Ciencias, Universidade da Coruña, 15071 A Coruña, Spain

Jose L. Legido

Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, 36200 Vigo, Spain

As a part of our calorimetric studies, we have measured the excess molar enthalpies of the ternary system {(x_1)propyl propanoate + (x_2)1-hexanol + (1 − x_1 − x_2)benzene} and of their corresponding binary mixtures at 25 °C and 35 °C and atmospheric pressure, over the whole composition range. The excess molar enthalpies were obtained by means of a Calvet microcalorimeter. The excess molar enthalpies for the binary mixtures were fitted to a Redlich−Kister variable-degree polynomial, and the ternary excess molar enthalpies were adequately correlated by the Cibulka equation. The results obtained for the ternary mixture were used to test the empirical methods of Kohler; Jacob and Fitzner; Colinet; Tsao and Smith; Toop; Scatchard et al.; and Hillert. These methods predict excess properties of the ternary mixtures from those of the involved binary mixtures.

Introduction

This communication is a continuation of our calorimetric work with six carbon atom compounds.[1−3] We present here the ternary excess molar enthalpies at 25 °C and 35 °C and atmospheric pressure of {(x_1)propyl propanoate + (x_2)1-hexanol + (1 − x_1 − x_2)benzene} and of the binary mixtures {(x_1)1-hexanol + (x_2)benzene} at the temperatures 25 °C and 35 °C and of {(x_1)propyl propanoate + (x_2)1-hexanol} at 35 °C. The excess enthalpies for {(x_1)propyl propanoate + (x_2)benzene} at 25 °C and 35 °C and for {(x_1)propyl propanoate + (x_2)1-hexanol} at 25 °C were published elsewere.[1,2]

The results obtained for the ternary mixture were used to test the empirical methods of Kohler,[4] Jacob and Fitzner,[5] Colinet,[6,7] Tsao and Smith,[8] Toop,[9] Scatchard et al.,[10] and Hillert.[11] These methods predict excess properties of the ternary mixtures from those of the involved binary mixtures.

Experimental Section

The substances employed were supplied by Fluka and Sigma. The mass fraction purities were >0.99 for propyl propanoate (Fluka), >0.99 for 1-hexanol (Fluka), and >0.995 for benzene (Fluka). The liquids were degassed by ultrasound and dried over molecular sieves (Sigma Union Carbide, type 0.4 nm) and otherwise used as supplied. The densities of the pure liquids agree with published values, as Table 1 shows.

The excess molar enthalpies were measured by means of a Calvet microcalorimeter connected to a Philips PM 2535 voltmeter. The inaccuracy of excess molar enthalpies is better than 1%. The temperature was regulated to better than ±0.05 K. Details of calibration and procedures were described by Paz Andrade et al.[14,15] The mixtures were prepared employing a Mettler AT201 balance with a precision of 1 × 10^{-8} kg. The uncertainty of the mole fraction is estimated to be <1 × 10^{-4}. Several experimental

Table 1. Data for Pure Liquids at 25 °C

substance	ρ/g·cm^{-3} exp	ρ/g·cm^{-3} lit.
propyl propanoate	0.875 53	0.875 49[12]
1-hexanol	0.815 16	0.815 34[13]
benzene	0.873 45	0.873 60[13]

Table 2. Excess Molar Enthalpies for the Binary Mixtures at 25 °C and 35 °C

x	H_m^E/J·mol^{-1}	x	H_m^E/J·mol^{-1}	x	H_m^E/J·mol^{-1}
(x)Propyl Propanoate + (1 − x)1-Hexanol					
t = 35 °C					
0.0406	231	0.3805	1422	0.6999	1370
0.0890	487	0.4198	1486	0.7542	1250
0.1367	713	0.4667	1511	0.7995	1102
0.1766	869	0.5259	1536	0.8595	859
0.2470	1124	0.5961	1515	0.9109	597
0.3217	1320	0.6484	1459	0.9496	365
(x)1-Hexanol + (1 − x)Benzene					
t = 25 °C					
0.0619	647	0.3137	1210	0.6192	908
0.0988	823	0.3792	1216	0.7214	684
0.1383	968	0.4153	1190	0.7711	582
0.1909	1080	0.4625	1135	0.8482	380
0.2287	1142	0.5107	1093	0.8884	289
0.2675	1183	0.5648	1012	0.9790	57
t = 35 °C					
0.0370	483	0.3195	1327	0.6577	968
0.0647	723	0.3867	1347	0.7485	739
0.1001	908	0.4630	1308	0.8067	574
0.1428	1070	0.4675	1298	0.8318	498
0.1815	1169	0.5017	1268	0.8867	333
0.2272	1253	0.5463	1204	0.9323	200
0.2476	1279	0.5930	1115		

† This contribution will be part of a special print edition containing papers presented at the 9th Asian Pacific Confederation of Chemical Engineering Congress, Christchurch, New Zealand, September 29 to October 3, 2002.

* Corresponding author. E-mail: ejimenez@udc.es.

10.1021/je0201370 CCC: $25.00
Published on Web 12/19/2002

Table 3. Excess Molar Enthalpies of {(x_1)Propyl Propanoate + (x_2)1-Hexanol + ($1 - x_1 - x_2$)Benzene} at 25 °C and 35 °C

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}
			$t = 25$ °C				
$x'_1 = 0.2510$		$H^E_{m,12} = 1160$ J·mol^{-1}		$x'_1 = 0.2510$		$H^E_{m,12} = 1160$ J·mol^{-1}	
0.0065	0.0193	251	281	0.1157	0.3451	676	1211
0.0212	0.0633	541	639	0.1293	0.3859	625	1223
0.0252	0.0753	584	701	0.1388	0.4141	585	1226
0.0350	0.1044	654	816	0.1558	0.4651	501	1221
0.0472	0.1407	719	937	0.1784	0.5323	398	1223
0.0560	0.1671	738	997	0.1987	0.5929	297	1215
0.0673	0.2009	755	1066	0.2122	0.6332	214	1195
0.0783	0.2337	753	1115	0.2369	0.7069	81	1176
0.0888	0.2649	744	1154	0.2322	0.6930	106	1179
0.1015	0.3028	716	1185				
$x'_1 = 0.5008$		$H^E_{m,12} = 1601$ J·mol^{-1}		$x'_1 = 0.5008$		$H^E_{m,12} = 1601$ J·mol^{-1}	
0.0150	0.0150	182	230	0.2308	0.2300	359	1096
0.0404	0.0402	339	468	0.2569	0.2560	325	1146
0.0500	0.0498	369	529	0.2798	0.2789	291	1186
0.0872	0.0870	433	712	0.3152	0.3142	241	1249
0.0897	0.0894	438	725	0.3715	0.3703	160	1348
0.1085	0.1082	435	782	0.4062	0.4050	135	1433
0.1346	0.1341	440	870	0.4151	0.4138	122	1449
0.1566	0.1560	428	929	0.4292	0.4279	99	1471
0.1779	0.1773	408	977	0.4706	0.4690	45	1549
0.2128	0.2122	379	1059				
$x'_1 = 0.7541$		$H^E_{m,12} = 1340$ J·mol^{-1}		$x'_1 = 0.7541$		$H^E_{m,12} = 1340$ J·mol^{-1}	
0.0244	0.0079	83	126	0.4213	0.1374	84	833
0.0561	0.0183	114	214	0.4672	0.1523	56	886
0.0720	0.0235	161	289	0.5166	0.1684	65	982
0.2774	0.0905	146	639	0.5734	0.1870	55	107
0.3011	0.0982	136	671	0.6175	0.2013	30	1127
0.3418	0.1115	115	723	0.6509	0.2122	22	1179
0.3764	0.1227	100	769	0.7168	0.2337	17	1291
			$t = 35$ °C				
$x'_1 = 0.3267$		$H^E_{m,12} = 1326$ J·mol^{-1}		$x'_1 = 0.3267$		$H^E_{m,12} = 1326$ J·mol^{-1}	
0.0095	0.0195	261	299	0.1076	0.2217	714	1151
0.0246	0.0507	487	587	0.1189	0.2449	694	1177
0.0371	0.0765	589	739	0.1322	0.2723	677	1213
0.0478	0.0984	645	839	0.1522	0.3138	621	1239
0.0588	0.1211	683	921	0.1714	0.3531	561	1256
0.0749	0.1545	719	1023	0.0807	0.1663	722	1049
0.0884	0.1823	744	1103				
$x'_1 = 0.5009$		$H^E_{m,12} = 1536$ J·mol^{-1}		$x'_1 = 0.5009$		$H^E_{m,12} = 1536$ J·mol^{-1}	
0.0119	0.0119	158	194	0.1864	0.1858	453	1024
0.0391	0.0390	350	470	0.2034	0.2026	426	1049
0.0488	0.0487	389	539	0.2240	0.2232	391	1078
0.0674	0.0671	445	651	0.2589	0.2580	349	1143
0.0886	0.0883	474	745	0.3130	0.3119	252	1212
0.1106	0.1102	493	832	0.2799	0.2789	309	1167
0.1316	0.1312	484	888	0.3544	0.3532	175	1262
0.1543	0.1537	472	846				
$x'_1 = 0.7472$		$H^E_{m,12} = 1261$ J·mol^{-1}		$x'_1 = 0.7472$		$H^E_{m,12} = 1261$ J·mol^{-1}	
0.0303	0.0102	99	150	0.3366	0.1139	150	719
0.0568	0.0192	149	245	0.3773	0.1277	99	736
0.0726	0.0245	167	289	0.4350	0.1472	95	829
0.0989	0.0334	190	356	0.4655	0.1575	63	849
0.1221	0.0413	198	404	0.4955	0.1676	44	880
0.1615	0.0546	195	468	0.5824	0.1970	54	1037
0.2025	0.0685	190	532	0.6180	0.2091	40	1083
0.2292	0.0776	179	566	0.6804	0.2302	16	1164
0.2626	0.0889	164	607	0.7055	0.2387	10	1200
0.3055	0.1034	148	664				

runs were carried out for the ternary mixture formed by adding benzene to a binary mixture of {(x'_1)propyl propanoate + ($1 - x'_1$)1-hexanol} where x'_1 is the mole fraction of propyl propanoate in the binary mixture. The ternary excess molar enthalpies at x_1, x_2, and x_3 can be expressed as

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

where $H^E_{m,\phi}$ is the measured excess molar enthalpy and $H^E_{m,12}$ is the excess molar enthalpy of the initial binary {propyl propanoate + 1-hexanol}. Values of $H^E_{m,12}$ at different mole fractions were interpolated by using a spline-fit method.

Results and Discussion

The excess molar enthalpies for the binary mixtures were fitted to a variable-degree polynomial of the form

$$H^E_{m,ij}/\text{J·mol}^{-1} = x_i x_j \sum_{p=0}^{n} A_p (x_i - x_j)^p \quad (2)$$

Table 4. Coefficients A_p and B_i and Standard Deviations s

t								s
°C	A_0	A_1	A_2	A_3	A_4	A_5	A_6	J·mol^{-1}
(x)Propyl Propanoate + (1 − x)1-Hexanol								
25[a]	6404	912.6	1138	510.9				6
35	6143	570.2	839.7	400.5				5
(x)Propyl Propanoate + (1 − x)Benzene								
25[b]	−408.3	63.4						4
35	−507.4	195.8	118.2	−175.6				2
(x)1-Hexanol + (1 − x)Benzene								
25	4435	−2673	1113			−3317	3585	6
35	5084	−2619			4081	−4210		7

t/°C	B_0	B_1	B_2	s/J·mol^{-1}
(x_1)Propyl Propanoate + (x_2)1-Hexanol + (1 − x_1 − x_2)Benzene				
25	8969	334.0	−14086	31
35	12308	−3657	−31106	20

[a] From ref 1. [b] From ref 2.

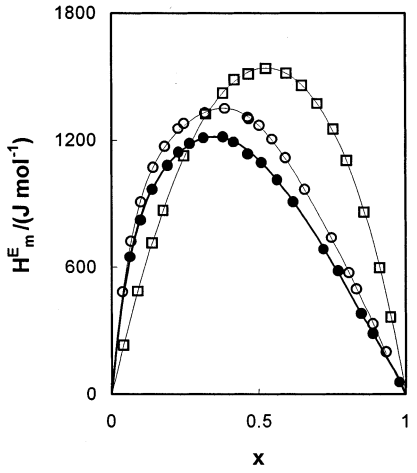

Figure 1. Excess molar enthalpies of (□) {(x)propyl propanoate + (1 − x)1-hexanol} at 35 °C; (●) {(x)1-hexanol + (1 − x)benzene} at 25 °C; and (○) {(x)1-hexanol + (1 − x)benzene} at 35 °C.

using a least-squares method. The number of parameters was determined using an F-test.[16] The experimental results for the binary mixtures are listed in Table 2.

Table 3 presents the excess molar enthalpies for ternary mixtures that were correlated by the equation proposed by Cibulka:[17]

$$H^{E}_{m,123}\,(\mathrm{J\cdot mol^{-1}}) = H^{E}_{m,12} + H^{E}_{m,13} + H^{E}_{m,23} + x_1x_2(1 - x_1 - x_2)(B_0 + B_1x_1 + B_2x_2) \quad (3)$$

The B_i parameters were calculated by the unweighted least-squares method using a nonlinear optimization algorithm due to Marquardt.[18] Table 4 presents the values of the parameters A_p and B_i of eqs 2 and 3, respectively, and the corresponding standard deviations.

The experimental excess molar enthalpies of binary mixtures plotted against mole fraction are shown in Figure 1. In all cases the excess molar enthalpies are positive. Figure 2 shows lines of constant ternary excess molar enthalpy, and in both cases the excess molar enthalpy decreases as the temperature increases. Figure 3 shows lines of ternary contribution, ($H^{E}_{m,123} - H^{E}_{m,12} - H^{E}_{m,13} - H^{E}_{m,23}$). Table 5 shows maxima and minima for the ternary contribution.

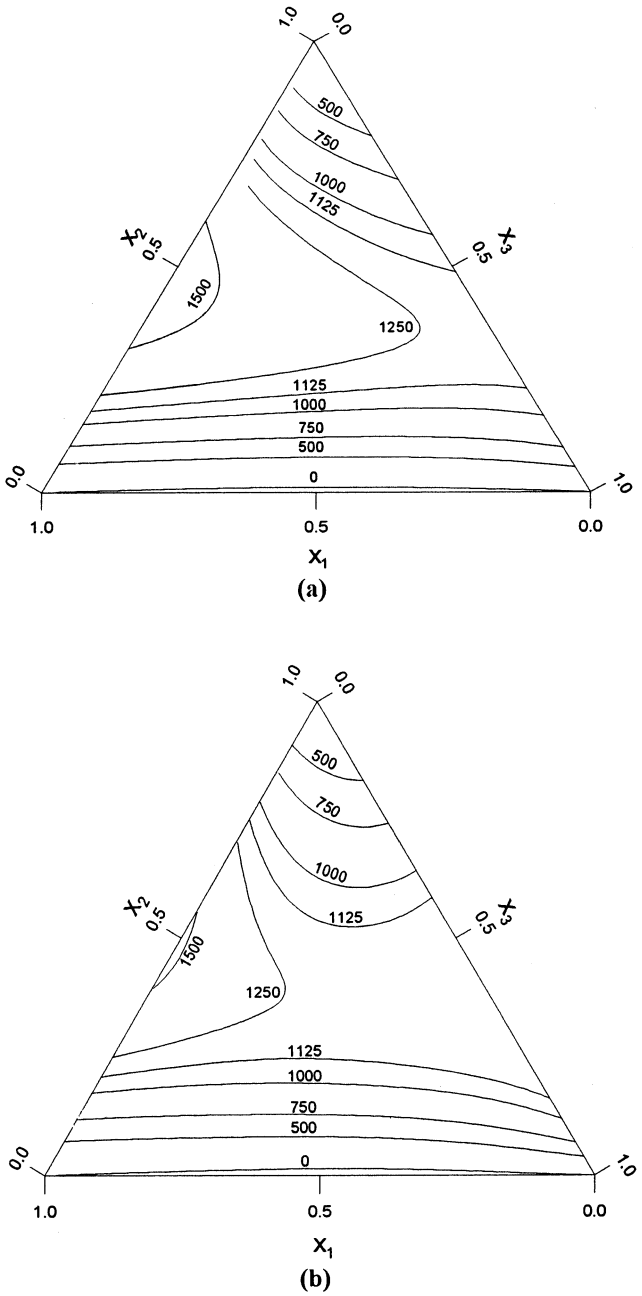

Figure 2. Curves of constant excess molar enthalpies in J·mol^{-1} at (a) 25 °C and (b) 35 °C of {(x_1)propyl propanoate + (x_2)1-hexanol + (1 − x_1 − x_2)benzene}.

Table 5. Maxima and Minima for the Ternary Contribution

	value/J·mol^{-1}	coordinates	
		t = 25 °C	
maximum	201	x_1 = 0.40	x_2 = 0.21
minimum	−19	x_1 = 0.11	x_2 = 0.77
		t = 35 °C	
maximum	168	x_1 = 0.38	x_2 = 0.14
minimum	−172	x_1 = 0.20	x_2 = 0.62

Excess molar enthalpies of {(x)1-hexanol + (1 − x)-benzene} have been measured previously, and the difference between our results and the values presented by González et al.[19] at 25 °C for x_1 = 0.5 is less than 4%.

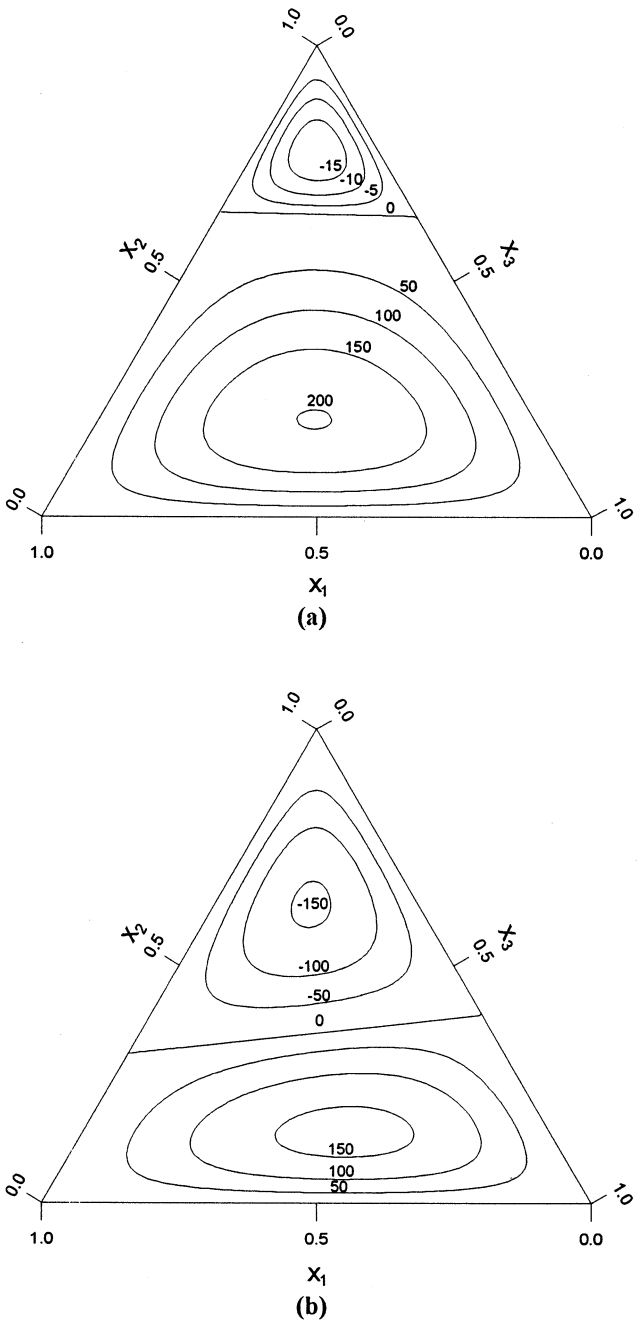

Figure 3. Curves of ternary contribution in J·mol^{-1} at (a) 25 °C and (b) 35 °C of {(x_1)propyl propanoate + (x_2)1-hexanol + (1 − x_1 − x_2)benzene}.

Several empirical methods have been proposed for estimating ternary excess enthalpy from experimental results of the constituent binary mixtures. The equations involved are asymmetric if the numerical predictions depend on the arbitrary designation of component numbering, and symmetric otherwise. The symmetric equations studied were those of Kohler; Jacob and Fitzner; and Colinet. The asymmetric expressions were those of Tsao and Smith; Toop; Scatchard et al.; and Hillert. The standard deviations between experimental and predicted values are shown in Table 6. In general, for the asymmetric equations we have found that the results agree with the rule given by Pando et al.[20] This rule consists of designating as component 1 the common component of the two mixtures with the largest absolute values of excess molar enthalpies in its maxima or minima, 1-hexanol in our case.

Table 6. Standard Deviations *s* of Empirical Expressions for (a) (x_1)Propyl Propanoate + (x_2)1-Hexanol + (1 − x_1 − x_2)Benzene; (b) (x_1)1-Hexanol + (x_2)Propyl Propanoate + (1 − x_1 − x_2)Benzene; and (c) (x_1)Benzene + x_2 1-Hexanol + (1 − x_1 − x_2)Propyl Propanoate

	s/J·mol^{-1}
	a
t = 25 °C	
Jacob and Fitzner	6.7
Kohler	11.5
Colinet	8.8
t = 35 °C	
Jacob and Fitzner	4.0
Kohler	11.3
Colinet	7.5

	s/J·mol^{-1}		
	a	b	c
t = 25 °C			
Tsao and Smith	6.5	2.8	8.7
Toop	8.3	3.3[b]	17.1
Scatchard	12.6	3.4	17.6
Hillert	10.8	3.4	16.8
t = 35 °C			
Tsao and Smith	13.9	5.4	11.0
Toop	4.9	6.4	18.9
Scatchard	11.9	6.3	19.4
Hillert	9.0	6.4	18.6

Literature Cited

(1) García-Garabal, S.; Segade, L.; Franjo, C.; Jiménez, E.; Piñeiro, M. M.; Legido, J. L.; Paz Andrade, M. I. Excess Molar Enthalpies of the Ternary System (Propyl Propanoate + 1-Hexanol + *n*-Hexane) at 298.15 K. *Fluid Phase Equilib.* **1998**, *148*, 201−208.

(2) Casas, H.; Segade, L.; Franjo, C.; Jiménez, E.; Paz Andrade, M. I. Excess Molar Enthalpies of Propyl Propanoate + Hexane + Benzene at 298.15 and 308.15 K. *J. Chem. Eng. Data* **2000**, *45*, 445−449.

(3) Casas, H.; Segade, L.; García-Garabal, S.; Piñeiro, M. M.; Franjo, C.; Jiménez, E.; Paz Andrade, M. I. Excess Molar Enthalpies for Propyl Propanoate + Cyclohexane + Benzene at 298.15 and 308.15 K. *Fluid Phase Equilib.* **2001**, *182*, 279−288.

(4) Kohler, F. Estimation of the Termodynamic 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 Ternary Alloys 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) Souza, M. J.; Jiménez, E.; Legido, J. L.; Fernández, J.; Pérez-Martell, E.; Paz Andrade, M. I. Excess Molar Volumes at the Temperature 298.15 K of {$x_1C_2H_5CO_2(CH_2)_2CH_3$ + $x_2Cl(CH_2)_5CH_3$ + (1-x_1-x_2)c-C_6H_{12}}, {$x_1C_2H_5CO_2(CH_2)_2CH_3$ + $x_2Cl(CH_2)_5CH_3$ + (1-x_1-x_2)$CH_3(CH_2)_4CH_3$}, and {$x_1C_2H_5CO_2(CH_2)_2CH_3$ + x_2c-C_6H_{12} + (1-x_1-x_2)$CH_3(CH_2)_4CH_3$}. *J. Chem. Thermodyn.* **1992**, *24*, 119−128.

(8) Tsao, C. C.; Smith, J. M. Heat 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 of 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) Tanaka, R.; Toyama, S.; Murakami, S. *J. Chem. Thermodyn.* **1986**, *18*, 63.

(13) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Techniques of Chemistry*; Wiley: New York, 1986.

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

(15) Paz Andrade, M. I.; Castromil, S.; Baluja, M. C. Enthalpies of Mixing: *n*-Hexane + *o*-Xylene at 25, 35 and 50 °C. *J. Chem. Thermodyn.* **1970**, *2*, 775−777.
(16) Bevington, P. R.; Robinson, D. K. *Data Reduction and Error Analysis for the Physical Sciences*, 2nd ed.; McGraw-Hill: Singapore, 1994.
(17) Cibulka, I. Estimation of Excess Volume and Density of Ternary Liquid Mixtures of Nonelectrolytes from Binary Data. *Collect. Czech. Commun.* **1982**, *47*, 1414−1419.
(18) Marquardt, D. W. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *2*, 431−441.
(19) González, J. A.; García de la Fuente, I.; Cobos, J. C.; Casanova, C. Estimation of DISQUAC Interchange Energy Parameters for 1-Alkanols + Benzene, or + Toluene Mixtures. *Fluid Phase Equilib.* **1994**, *93*, 1−22.
(20) Pando, C.; Renuncio, J. A. R.; Calzon, J. A. G.; Christensen, J. J.; Izatt, R. M. Correlation and Prediction of Ternary Excess Enthalpy Data. *J. Solution Chem.* **1987**, *16*, 503−527.

Received for review July 22, 2002. Accepted October 30, 2002.

JE0201370