J. Chem. Eng. Data **2002,** *47,* 411−415

Determination of Excess Molar Enthalpies of α,ω-Dichloroalkane + 1-Butanol or 1-Heptanol Mixtures at 298.15 K. Analysis and Comparison with Predicted Values of UNIFAC

Carlos Medina,[†] Josefa Fernández,[‡] José L. Legido,[†] and María I. Paz Andrade*,[‡]

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago, E-15782 Santiago de Compostela, Galicia, Spain, and Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Vigo, E-36200 Vigo, Galicia, Spain

Excess molar enthalpies H_m^E were measured for binary mixtures containing an α,ω-dichloroalkane (from 1,3-dichloropropane to 1,6-dichlorohexane) and an alkanol (1-butanol or 1-heptanol) using a Calvet microcalorimeter at 298.15 K and normal atmospheric pressure. All mixtures exhibit endothermic behavior for the whole composition range, which means that the rupture of interactions is energetically the most important effect. Experimental values were used to test the predictions of three versions of the UNIFAC group contribution model. The experimental H_m^E values are discussed in terms of molecular interactions and the proximity effect.

Introduction

In recent years, our research has focused on the investigation of the thermodynamic properties of liquid binary mixtures of alkanols with 1-chloroalkane[1−4] and α,ω-dichloroalkane.[5] These compounds have great interest because of the complex behavior of the self-association of alcohol molecules and the possible cross-association of alcohol and solvent molecules. Therefore, a knowledge of the behavior of these mixtures constitutes a good test of the limitations of the group contribution theories.

In this work we present the excess molar enthalpies at 298.15 K for the binary mixtures of a α,ω-dichloroalkane (1,3-dichloropropane to 1,6-dichlorohexane) with a 1-alkanol (1-butanol and 1-heptanol). This systematic study is directed to analyze the behavior of these mixtures when the lengths of both molecules vary. Our analysis is done in terms of the intermolecular interactions, taking also into account the H_m^E experimental values obtained by Santana *et al.*[1−4] for binary mixtures of 1-chloroalkane with alkanols.

In addition, because the α,ω-dichloroalkanes are compounds with two main groups in the molecule, a change in distance between both groups provokes a change in their behavior and hence in the interaction parameters with other groups. This is a so-called intramolecular proximity effect.[6] Then, these H_m^E experimental values were used to test the predictions of the Dang and Tassios,[7] Larsen *et al.*,[8] and Gmehling *et al.*[9] versions of the UNIFAC group contribution model, for which there are parameters available for chloroalkane + alkanol. The main problems involved in the predictions for these mixtures are clearly the existence of hydrogen bonds and the proximity effect.

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. Their mole fraction purities were >0.99 for 1,3-dichloropropane, 1,4-dichlorobutane, and 1,5-dichloropentane (Aldrich); >0.98 for 1,6-dichlorohexane (Aldrich); and >0.99 for 1-butanol and 1-heptanol (Fluka). Their densities, measured with an Anton Paar densimeter, agreed well with the literature values.[10−12]

Apparatus and Procedure. Binary mixtures were prepared by mass using a Mettler H51 balance (precision $\pm 1 \times 10^{-5}$ g) with a probable error in the mole fraction less than $\pm 1 \times 10^{-4}$. All molar quantities are based on the IUPAC[13] relative atomic mass table.

Excess molar enthalpies were measured using a standard Calvet microcalorimeter linked to a Philips voltmeter PM2535 using the calibration and operating procedures described by Paz Andrade *et al.*[14,15] 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[16] and Gmehling.[17] The uncertainty in H_m^E is estimated to be less than 1%.

Results

The experimental values of H_m^E at 298.15 K are summarized in Table 1. A function of the form

$$H_m^E/(\mathrm{J\cdot mol^{-1}}) = \{x(1-x)\}/\{1-k(1-2x)\}\sum_{j=0}^{n} A_j(1-2x)^j \quad (1)$$

has been found to give the best representation of the data. This is a modified Redlich−Kister[18] equation with a skewing factor to describe the asymmetric composition dependence of the excess enthalpies. In this equation x is the mole fraction of α,ω-dichloroalkane; the coefficients A_j and k were determined by an unweighted least-squares method using the Marquardt algorithm.[19,20] The values of the coefficients A_j and k together with the standard deviations s are listed in Table 2 for each system.

---

* To whom correspondence should be addressed. E-mail: fapazand@usc.es. Fax: +34981520676.

[†] Universidad de Vigo.

[‡] Universidad de Santiago.

10.1021/je015523g CCC: $22.00

Table 1. Experimental Excess Molar Enthalpies $H_{\mathrm{m}}^{\mathrm{E}}$ for the Binary Mixtures at 298.15 K

x	$H_{\mathrm{m}}^{\mathrm{E}}$/J·mol^{-1}	x	$H_{\mathrm{m}}^{\mathrm{E}}$/J·mol^{-1}	x	$H_{\mathrm{m}}^{\mathrm{E}}$/J·mol^{-1}	x	$H_{\mathrm{m}}^{\mathrm{E}}$/J·mol^{-1}	x	$H_{\mathrm{m}}^{\mathrm{E}}$/J·mol^{-1}
(x)1,3-Dichloropropane + (1 − x)1-Butanol									
0.0952	337	0.3782	1274	0.5993	1563	0.7947	1403		
0.1939	699	0.4359	1393	0.6452	1569	0.8436	1260		
0.2788	987	0.4842	1474	0.6824	1546	0.9006	991		
0.3243	1121	0.5451	1534	0.7438	1492	0.9535	556		
(x)1,4-Dichlorobutane + (1 − x)1-Butanol									
0.0797	342	0.2585	1028	0.4367	1494	0.6642	1607	0.8791	1133
0.1216	519	0.2977	1164	0.5299	1623	0.7126	1596	0.9279	833
0.1698	729	0.3482	1308	0.5670	1629	0.7645	1513		
0.2127	881	0.3984	1419	0.6019	1638	0.8238	1354		
(x)1,5-Dichloropentane + (1 − x)1-Butanol									
0.0716	340	0.3623	1384	0.5752	1653	0.8025	1428		
0.1498	690	0.4120	1512	0.6270	1651	0.8606	1236		
0.2347	1013	0.4703	1560	0.6908	1616	0.9448	702		
0.3096	1244	0.5294	1635	0.7500	1545				
(x)1,6-Dichlorohexane + (1 − x)1-Butanol									
0.0670	309	0.2144	930	0.4192	1463	0.6594	1616	0.9155	911
0.0962	451	0.2509	1047	0.4935	1563	0.7234	1544	0.9596	549
0.1394	637	0.3246	1272	0.5385	1612	0.7766	1473		
0.1715	774	0.3844	1412	0.5997	1623	0.8530	1243		
(x)1,3-Dichloropropane + (1 − x)1-Heptanol									
0.1384	588	0.5486	1768	0.7330	1706	0.8970	1138		
0.2623	1096	0.5762	1800	0.7763	1593	0.9329	862		
0.3775	1463	0.6436	1778	0.8190	1484				
0.4812	1671	0.6900	1754	0.8568	1325				
(x)1,4-Dichlorobutane + (1 − x)1-Heptanol									
0.1291	638	0.3488	1485	0.5555	1856	0.7548	1653	0.9228	895
0.1802	873	0.4009	1626	0.6085	1844	0.7916	1588	0.9612	562
0.2282	1056	0.4454	1713	0.6523	1828	0.8307	1452		
0.2949	1330	0.5110	1803	0.6950	1784	0.8706	1278		
(x)1,5-Dichloropentane + (1 − x)1-Heptanol									
0.1125	607	0.4704	1778	0.6738	1818	0.8645	1310		
0.2156	1067	0.5065	1804	0.7291	1722	0.9065	1058		
0.3120	1425	0.5757	1838	0.7751	1636				
0.4145	1682	0.6237	1831	0.8187	1514				
(x)1,6-Dichlorohexane + (1 − x)1-Heptanol									
0.0531	280	0.2494	1144	0.4412	1617	0.6520	1737	0.8513	1298
0.1037	532	0.2942	1280	0.4953	1706	0.7015	1690	0.8981	1086
0.1482	744	0.3452	1443	0.5546	1736	0.7483	1617	0.9584	577
0.1966	945	0.3967	1557	0.5995	1753	0.7987	1492		

Table 2. Coefficients A_j (J·mol^{-1}) and k of Eq 1 and Standard Deviations s for $H_{\mathrm{m}}^{\mathrm{E}}$ at T = 298.15 K

system	A_0	A_1	A_2	A_3	A_4	k	s/J·mol^{-1}
(1 − x)1-butanol +							
(x)1,3-dichloropropane	5952	570	25	−1932		−0.5078	7
(x)1,4-dichlorobutane	6327	2166	−87	−1146		−0.6857	9
(x)1,5-dichloropentane	6437	2504	348	−1142		−0.6821	10
(x)1,6-dichlorohexane	6296	2413	362	−470	−903	−0.8424	7
(1 − x)1-heptanol +							
(x)1,3-dichloropropane	6856	2782	−1224	−947		−0.8096	11
(x)1,4-dichlorobutane	7183	2851	−414	−1079		−0.7131	13
(x)1,5-dichloropentane	7207	2478	585	−1369		−0.6078	8
(x)1,6-dichlorohexane	6824	3194	194	−552		−0.7548	8

Discussion

The results obtained for these mixtures may be understood in terms of the competition of the different energetic effects involved. The alkanol molecules present self-association due to the presence of a hydrogen bond, and the chloroalkanes are molecules with high dipole moment; during the mixing process both interactions are broken, giving an energetic positive contribution. On the other hand, in these mixtures the formation of hydrogen bonds between of the alcohol group and the Cl of dichloroalkanes might be possible, resulting in an energetic negative contribution.

Figures 1 and 2 show the experimental $H_{\mathrm{m}}^{\mathrm{E}}$ versus x curves together with the fitted curves. For all the mixtures studied, the excess enthalpies are positive all through the composition range. The endothermicity of the 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 maxima of the $H_{\mathrm{m}}^{\mathrm{E}}(x)$ curves are slightly shifted around the rich composition in α,ω-dichloroalkane, and this fact means that the presence of chlorine atoms helps the breaking of the hydrogen bonds. In this way, it is important to take into account that for mixtures containing 1-chloroalkane with alcohol[1−4] the excess molar enthalpies present the same characteristics. Nevertheless, the maximum excess enthalpy values are around 700 J·mol^{-1} lower

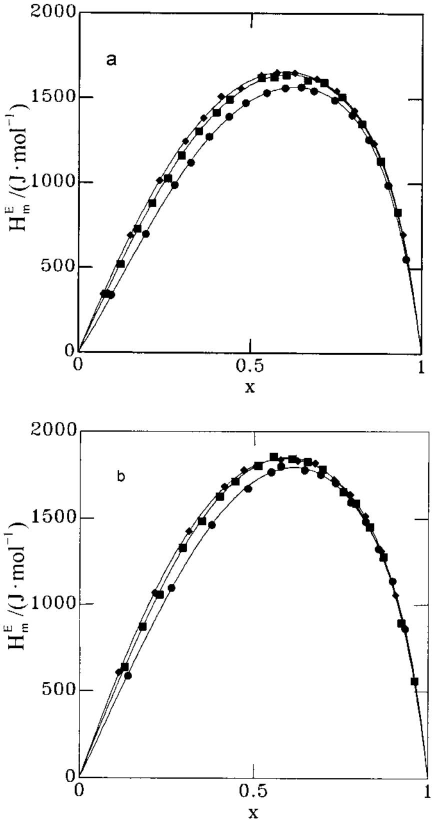

Figure 1. Excess molar enthalpies H_m^E against mole fraction x for {(x)α,ω-dichloroalkane + (1 − x)alkanol} at 298.15 K. Experimental results: (a) 1-butanol; (b) 1-heptanol; (●) 1,3-dichloropropane; (■) 1,4-dichlorobutane; (◆) 1,5-dichloropentane; (—) eq 1.

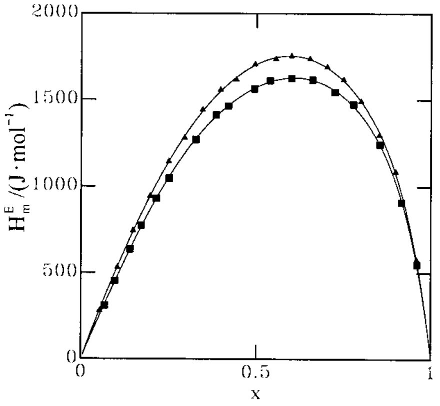

Figure 2. Excess molar enthalpies H_m^E against mole fraction x for {(x)1,6-dichlorohexane + (1 − x)alkanol} at 298.15 K. Experimental results: (■) 1-butanol; (▲) 1-heptanol; (—) eq 1.

than those of mixtures containing molecules with two chlorine groups.

Comparing the present experimental data with the excess molar enthalpy values obtained in a previous work[5] for binary mixtures of α,ω-dichloroalkane (1,3-chloropropane to 1,6-dichlorohexane) with pentanol or hexanol, we conclude that the excess enthalpies increase when the alkanol length increases, as Figure 3 shows. This effect is sustained for the four dichloroalkanes used. For 1-chlorobutane[3] with these alkanols, the sequence is the same, but for mixtures with 1-chlorooctane,[4] the sequence is the contrary.

The sequence obtained for 1-heptanol or 1-butanol with the dichloroalkane chain is more complicated: the values of the excess enthalpies increase from 1,3-dichloropropane to 1,5-dichloropentane and decrease for the 1,6-dichlorohexane, like the trend obtained with the alcohols 1-pentanol and 1-hexanol,[5] as can be seen in Figure 3. The diminution of H_m^E from 1,5-dichloropentane to 1,6-dichlorohexane is in agreement with the proximity effect: as the distance separating the two chlorine groups of the α,ω-dichloroalkane increases, they become more independent, and therefore, the behavior of their mixtures is more similar to the one of 1-chloroalkane mixtures.

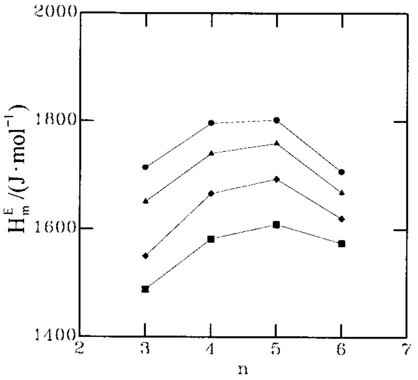

Figure 3. Excess molar enthalpies H_m^E(x = 0.5) at equimolecular mole fraction against the number of carbons of the α,ω-dichloroalkane (n): (■) butanol; (◆) pentanol; (▲) hexanol; (●) heptanol (present work and ref 5).

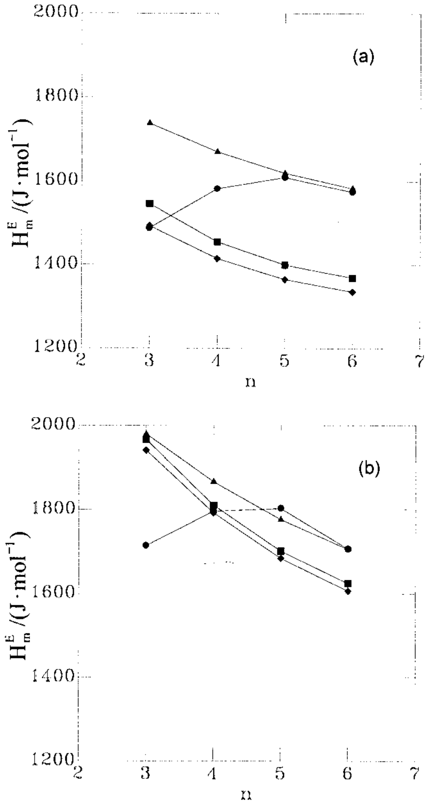

Figure 4. Excess molar enthalpies H_m^E(x = 0.5) at equimolecular mole fraction against number of carbons of the α,ω-dichloroalkane (n) with (a) 1-butanol and (b) 1-heptanol: (●) experimental values; (▲) Tassios version; (■) Larsen version; (◆) Gmehling version.

The excess molar enthalpy values at equimolecular composition (x = 0.5) are represented graphically in Figure 4, against n, the number of carbons of the α,ω-dichloroalkane, in comparison with the values predicted by the Tassios, Larsen, and Gmehling versions of the UNIFAC model. In Table 3 we have listed these predictions together

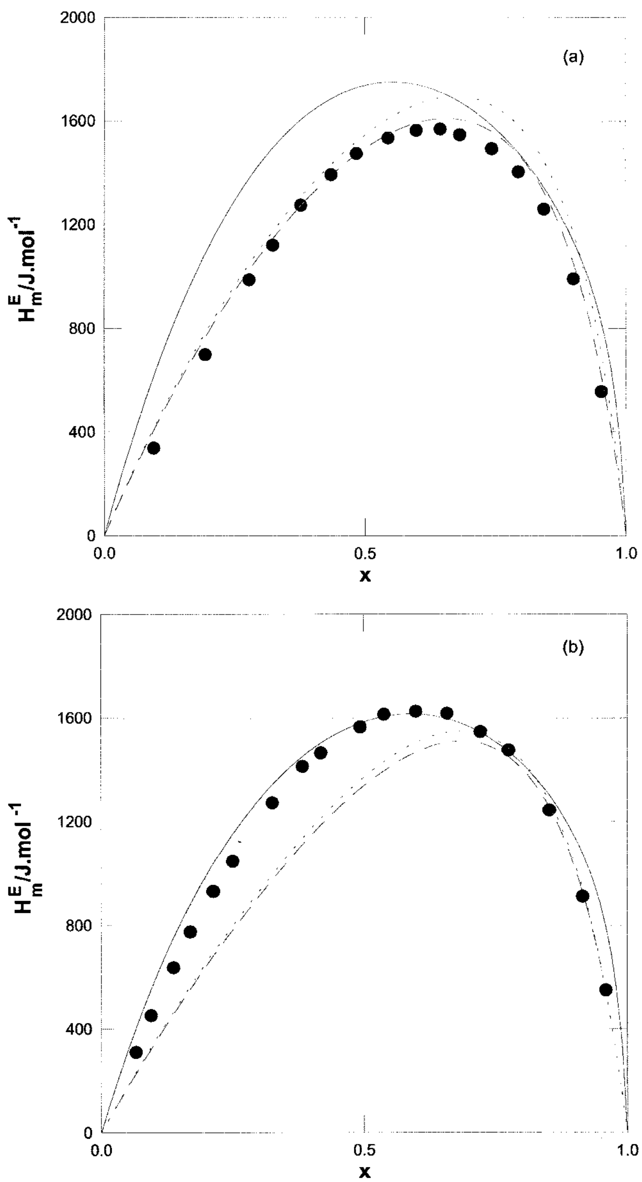

Figure 5. Excess molar enthalpies H^E_m at 298.15 K against x for (a) {(x)1,3-dichloropropane + (1 − x)1-butanol} and (b) {(x)1,6-dichlorohexane + (1 − x)1-butanol}: (●) experimental values; (—) Tassios version; (- - -) Larsen version; (— — —) Gmehling version.

Table 3. Experimental Excess Enthalpies H^E_m at Equimolecular Composition and T = 298.15 K, and Comparison Predicted Values[7−9]

	$H^E_m(x = 0.5)/(J \cdot mol^{-1})$			
mixture	expt	Tassios	Larsen	Gmehling
1,3-dichloropropane +1-butanol	1488	1738	1546	1493
1,4-dichlorobutane + 1-butanol	1582	1670	1455	1415
1,5-dichloropentane + 1-butanol	1609	1619	1400	1365
1,6-dichlorohexane + 1-butanol	1574	1583	1369	1336
1,3-dichloropropane + 1-heptanol	1714	1980	1967	1941
1,4-dichlorobutane + 1-heptanol	1796	1866	1810	1792
1,5-dichloropentane + 1-heptanol	1802	1776	1700	1684
1,6-dichlorohexane + 1-heptanol	1706	1705	1623	1606

with the experimental values. The overall percentage mean deviations (PMDs) for all the compositions in the three versions are 12, 10, and 9%, respectively. This means that the best predictions are obtained with the Gmehling version. We observe that all versions give H^E_m values which increase with the length of the alkanol chain, a fact that agrees with the experimental sequence. The predicted $H^E_m(x = 0.5)$ values decrease when the distance between the Cl atoms of the dichloroalkane increases, in accordance with the proximity effect and the experimental results for 1,5-dichloropentane and 1,6-dichlorohexane.

The three versions give good results, the best ones being obtained for the excess molar enthalpies of mixtures with the longer dichloroalkanes with the Tassios version, as can be seen in Figures 4 and 5. For the binary mixtures of 1-chloroalkane[1−4] with 1-alkanol (from 1-butanol to 1-octanol), the Tassios version also presents better results than the Larsen one. This confirms that the choice of the database greatly affects the estimation of the predictions. Actually, for the determination of the interaction parameters between the OH group of the alcohols and the chlorine group, Larsen *et al.* used a database[21] containing experimental values of G^E_m for the binary systems containing 1,2-dichloroethane or 1-chlorobutane with ethanol or 1-propanol and of H^E_m for 1,2-dichloroethane + 1-butanol. On the other hand, the Tassios group used a database[22] comprising excess enthalpies of systems containing 1-chlorobutane, 2-chlorobutane, 1-chlorooctane, and 1-alkanol. In accordance with these databases and the proximity effect, it is expected to find that the best results for the excess enthalpies of mixtures containing short dichloroalkanes are those obtained with the Larsen model, whereas the Tassios version works better for the systems with 1,5-dichloropentane and 1,6-dichlorohexane, which have longer chains. We are not aware of the database used by Gmehling and collaborators to determine the interaction parameters needed to predict the excess enthalpies of these mixtures. It must be pointed that the maximum PMD obtained with this last version is 16% for 1,6-dichlorohexane + hexanol whereas for the Larsen version a PMD of 20% was found for 1,3-dichloropropane + 1-pentanol and for the Tassios version a PMD of 32% was found for this last system.

It would be interesting to investigate how the formation of a hydrogen bond between the Cl group and the hydroxyl group and also the interstitial accommodation of the molecules in the case of α,ω-dichloroalkane affect the excess volumes. In future work a similar study will be carried out with excess volumes.

Literature Cited

(1) Santana, P.; Balseiro, J.; Jimenez, E.; Franjo, C.; Legido, J. L.; Carballo, E.; Paz Andrade, M. I. A study of excess molar enthalpies and excess molar volumes of binary mixtures of 1-chloropentane + 1-alkanol (from 1-butanol to 1-octanol) at 25 °C. *J. Solution Chem.* **2000**, *29*, 1115−1122.
(2) Santana, P.; Balseiro, J.; Salgado, J.; Jimenez, E.; Legido, J. L.; Carballo, E.; Paz Andrade, M. I. Excess Molar Enthalpies and Excess Molar Volumes of Binary Systems 1-Chlorohexane + 1-Alkanol (from 1-Butanol to 1-Octanol) at 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 1195−1198.
(3) Santana, P.; Balseiro, J.; Franjo, C.; Jimenez, E.; Legido, J. L.; Romani, L.; Paz Andrade, M. I. Measurements and analysis of excess molar enthalpies and excess molar volumes of the binary systems {$xCH_3(CH_2)_3Cl + (1 - x)CH_3(CH_2)_{n-1}OH$}($n$ = 4 to 8) at 298.15 K. *J. Chem Thermodyn.* **1999**, *31*, 547−554.
(4) Santana, P.; Balseiro, J.; Salgado, J.; Jimenez, E.; Legido, J. L.; Romani, L.; Paz Andrade, M. I. Excess molar enthalpies and excess molar volumes of binary systems containing {$xCH_3(CH_2)_7Cl + (1 - x)CH_3(CH_2)_n - 1OH$} ($n$ = 4 to 8) at T = 298.15 K. *J. Chem. Thermodyn.* **1999**, *31*, 1329−1336.
(5) Medina, C.; Fernández, J.; Legido, J. L.; Paz Andrade, M. I. Excess molar enthalpies of (α,ω-dichloroalkane + pentanol, or hexanol) at T = 298.15 K. *J. Chem. Thermodyn.* **1998**, *30*, 1061−1068.
(6) Kehiaian, H. V. Group contribution methods for liquid mixtures: a critical review. *Fluid Phase Equilib.* **1983**, *13*, 243−252.
(7) Dang, D.; Tassios, D. P. Prediction of enthalpies of mixing with a UNIFAC model. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25*, 22−31.
(8) Larsen, B. L.; Rasmussen, P.; Fredenslund, A. A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274−2286.

(9) Gmehling, J.; Li, J.; Schiller, M. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.
(10) Blanco, A. M.; Ortega, J. Excess volumes of α,ω-dichloroalkane (C_2−C_6) + some normal alkane (C_5−C_{17}) mixtures. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1993**, *21*, 195−231.
(11) Iglesias, T. P.; Legido, J. L.; Romani, L.; Paz Andrade, M. I. Excess dielectric permittivity and excess molar volumes of binary mixtures of *n*-hexane with 1-alkanol at the temperature 298.15 K. *Phys. Chem. Liq.* **1993**, *25*, 135−43.
(12) Legido, J. L.; Jiménez, E.; Franjo, C.; Segade, L.; Paz Andrade, M. I. Excess molar volumes of ternary mixtures of di-*n*-butyl ether + 1-heptanol + *n*-octane at the temperature of 298.15 K. *Fluid Phase Equilib.* **1997**, *136*, 315−321.
(13) IUPAC Commission on Atomic Weights and Isotopic Abundances, 1985. *Pure Appl. Chem.* **1986**, *58*, 1677−1692.
(14) 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.
(15) Paz Andrade, M. I. *Les developpements recents de la microcalorimetrie et de la Thermogenese*; CRNS: Paris, 1967.
(16) Marsh, K. N. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1973**, *1*, 22.
(17) Gmehling, J. Excess Enthalpy. Cyclohexane-hexane system. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1992**, *3*, 144.
(18) Redlich, O.; Kister, A. T. The thermodynamics of nonelectrolyte solutions and its technical applications. III. Systems with associated components. *J. Chem. Phys.* **1947**, *15*, 849−855.
(19) Marquardt, D. W. An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Ind. Appl. Math.* **1963**, *2*, 431−441.
(20) Bevington, P. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; p 200.
(21) Larsen, B. L. Prediction of phase equilibria and heats effects of mixing with a modified UNIFAC model. Ph.D. Thesis, Instituttet for Kemiteknik, The Technical University of Denmark, Denmark, 1986.
(22) Stathis, J. Prediction of heats of mixing in hydrogen-bonded solution using a UNIFAC model. Ph.D. Thesis, Faculty of the Graduate School of the New Jersey Institute of Technology, 1983.

Received for review October 1, 2001. Accepted January 15, 2002.

JE015523G