J. Chem. Eng. Data **1999,** *44,* 1195−1198

Excess Molar Enthalpies and Excess Molar Volumes of Binary Systems 1-Chlorohexane + 1-Alkanol (from 1-Butanol to 1-Octanol) at 298.15 K

P. Santana,[†] J. Balseiro,[†] J. Salgado,[†] E. Jiménez,[‡] J. L. Legido,[§] E. Carballo,[§] and M. I. Paz Andrade*,[†]

Departamento de Física Aplicada, Campus Universitario Sur, Universidad de Santiago, E-15706 Santiago de Compostela, Spain, Departamento de Física, Facultad de Ciencias, Campus A Zapateira, Universidad de A Coruña, E-15070 A Coruña, Spain, and Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Vigo, E-36200 Vigo, Spain

Excess molar enthalpies H_m^E and excess molar volumes V_m^E have been measured at 298.15 K and normal atmospheric pressure for the binary mixtures 1-chlorohexane + 1-alkanol (from 1-butanol to 1-octanol) using a Calvet microcalorimeter and a vibrating tube densimeter, respectively. The values of H_m^E and V_m^E for all of the mixtures are positive over the whole range of composition. Experimental H_m^E results are compared with the predictions of UNIFAC group-contribution models considered by Dang and Tassios (Dang, D.; Tassios, P. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25*, 22−31) and by Larsen et al. (Larsen, L.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274−2286) and discussed in terms of molecular interactions.

1. Introduction

The present work gives information about the excess molar enthalpies and excess molar volumes of {1-chlorohexane + 1-alkanol} (from 1-butanol to 1-octanol) mixtures at the temperature of 298.15 K and atmospheric pressure. The excess molar enthalpies were measured using a Calvet microcalorimeter, and the excess molar volumes were determined from the densities of the pure liquids and mixtures, using a vibrating-tube densimeter. The excess molar enthalpies were compared with the values predicted by the UNIFAC group-contribution model in the versions considered by Dang and Tassios (1986) and by Larsen et al. (1987).

Table 1. Densities ρ for the Pure Liquids at 298.15 K

	$\rho/(\mathrm{g \cdot cm^{-3}})$	
substance	present work	lit.
1-chlorohexane	0.873 38	0.873 33,[a] 0.873 11[b]
1-butanol	0.805 75	0.805 76,[c] 0.805 75[d]
1-pentanol	0.810 77	0.810 77,[e] 0.810 80[d]
1-hexanol	0.815 22	0.815 32,[f] 0.815 34[d]
1-heptanol	0.818 67	0.818 71,[g] 0.818 88[h]
1-octanol	0.821 61	0.821 63,[i] 0.821 57[d]

[a] Ortega et al., 1989. [b] Pico et al., 1995. [c] Jiménez et al., 1997a. [d] Riddick et al., 1986. [e] Iglesias et al., 1993. [f] Franjo et al., 1995. [g] Legido et al., 1997. [h] Andreolli-Ball et al., 1988. [i] Jiménez et al., 1997b.

2. Experimental Section

1-Chlorohexane (mole fraction > 0.99) was supplied from Aldrich, and 1-alkanols (mole fraction > 0.99) were supplied from Fluka; the purities were tested by GC. The products were subjected to no further purification other than being dried with Union Carbide 0.4 nm molecular sieves. Their densities, given in Table 1, are in close agreement with the literature values. The handling and disposal of the chemicals used has been done according to the recommendation of the *CRC Handbook of Chemistry and Physics* (CRC, 1996−1997).

The experimental excess molar enthalpies were determined using a Calvet microcalorimeter using the calibration and operating conditions described by Paz Andrade et al. (1970) and Paz Andrade (1967). This apparatus works with a calorimeter-cell volume of approximately 10 cm^3, and it is equipped with a device allowing operation in the absence of the vapor phase; a Philips PM2535 voltmeter and a data acquisition system are linked to the microcalorimeter. The accuracy of the excess molar enthalpies is estimated as better than 1%.

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 thermostat. The precision of the densities was $\pm 2 \times 10^{-5}$ g·cm^{-3}. The apparatus was calibrated at atmospheric pressure before each series of measurements using bidistilled and degassed water and *n*-heptane; density data were taken from literature (Grolier and Benson (1984) for *n*-heptane and Riddick et al. (1986) for water). Binary mixtures were prepared by weight using a Mettler H51 (precision, $\pm 1 \times 10^{-5}$ g) balance, with a probable error in the mole fraction of less than 10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table (IUPAC, 1986).

3. Results and Discussion

Experimental values of H_m^E and V_m^E for the five mixtures {(x)1-chlorohexane + $(1 - x)$1-alkanol} (from 1-butanol to

---

* To whom correspondence should be addressed. E-mail: fapazand@uscmail.usc.es.
[†] Universidad de Santiago.
[‡] Universidad de A Coruña.
[§] Universidad de Vigo.

10.1021/je990104t CCC: $18.00

Table 2. 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	H_m^E/(J·mol^{-1})
		(x)1-Chlorohexane + (1 − x)1-Butanol			
0.0358	80	0.2719	599	0.6699	1001
0.0643	138	0.3137	691	0.6887	1009
0.0749	163	0.3988	833	0.7009	994
0.1386	306	0.4650	885	0.7486	972
0.1452	338	0.5026	931	0.7962	927
0.2180	495	0.567	978	0.9059	727
0.2344	537	0.6229	1001	0.9097	726
		(x)1-Chlorohexane + (1 − x)1-Pentanol			
0.0488	111	0.3279	708	0.6779	1024
0.0775	188	0.4209	853	0.7201	1006
0.1169	268	0.4344	876	0.7878	942
0.1379	316	0.4418	889	0.8195	883
0.1680	387	0.5205	968	0.8668	799
0.1923	441	0.6017	1005	0.9698	410
0.2689	590	0.6440	1023		
		(x)1-Chlorohexane + (1 − x)1-Hexanol			
0.0663	149	0.3985	810	0.6781	1016
0.1239	282	0.4204	836	0.7459	991
0.2427	534	0.4643	899	0.7829	950
0.2778	615	0.5132	958	0.8406	898
0.3071	656	0.5638	993	0.8935	778
0.3276	687	0.5699	979	0.9252	643
0.3621	750	0.6130	1016		
		(x)1-Chlorohexane + (1 − x)1-Heptanol			
0.0721	157	0.4678	925	0.8583	846
0.0841	198	0.5203	954	0.9044	770
0.1470	344	0.5618	993	0.9131	726
0.2049	485	0.6347	1026	0.9677	524
0.2991	668	0.6701	1017		
0.4380	886	0.7563	964		
		(x)1-Chlorohexane + (1 − x)1-Octanol			
0.1156	273	0.4694	896	0.7055	1023
0.2159	494	0.4858	911	0.7730	978
0.2638	577	0.5270	942	0.7957	953
0.3143	687	0.5328	958	0.8514	890
0.3859	799	0.5789	1000	0.8736	840
0.4279	867	0.6585	1011	0.9618	508

Table 3. Excess Molar Volumes V_m^E at 298.15 K

x	V_m^E/(cm^3·mol^{-1})	x	V_m^E/(cm^3·mol^{-1})	x	V_m^E/(cm^3·mol^{-1})
		(x)1-Chlorohexane + (1 − x)1-Butanol			
0.0112	0.0001	0.2446	0.0506	0.6974	0.1775
0.0502	0.0022	0.3068	0.0745	0.7866	0.1675
0.1385	0.0200	0.3808	0.1044	0.8799	0.1368
0.1650	0.0232	0.4493	0.1294	0.9617	0.0739
0.1822	0.0325	0.5289	0.1529		
0.2363	0.0473	0.6050	0.1684		
		(x)1-Chlorohexane + (1 − x)1-Pentanol			
0.0193	0.0020	0.3626	0.0821	0.7872	0.1469
0.0760	0.0041	0.4417	0.1107	0.8627	0.1276
0.1445	0.0137	0.5135	0.1332	0.9700	0.0563
0.2080	0.0307	0.5635	0.1400	0.9757	0.0488
0.2468	0.0421	0.6167	0.1493		
0.2934	0.0574	0.6954	0.1550		
		(x)1-Chlorohexane + (1 − x)1-Hexanol			
0.0118	0.0011	0.3140	0.0644	0.6786	0.1452
0.0317	0.0029	0.3311	0.0687	0.7546	0.1421
0.0630	0.0076	0.3993	0.0881	0.8292	0.1301
0.1085	0.0103	0.4303	0.0972	0.8697	0.1155
0.1505	0.0161	0.4573	0.1079	0.9193	0.0969
0.1830	0.0249	0.5403	0.1292	0.9705	0.0559
0.2118	0.0342	0.5667	0.1316		
0.2775	0.0508	0.5988	0.1358		
		(x)1-Chlorohexane + (1 − x)1-Heptanol			
0.0493	0.0040	0.3748	0.0767	0.7532	0.1322
0.0729	0.0051	0.4505	0.0987	0.7988	0.1269
0.1238	0.0116	0.5069	0.1112	0.8510	0.1147
0.1749	0.0239	0.5565	0.1204	0.8948	0.1004
0.2335	0.0373	0.6034	0.1267	0.9451	0.0740
0.2722	0.0452	0.6561	0.1318	0.9707	0.0522
0.3239	0.0626	0.7069	0.1322		
		(x)1-Chlorohexane + (1 − x)1-Octanol			
0.0676	0.0032	0.4760	0.1008	0.8172	0.1172
0.1318	0.0158	0.5377	0.1114	0.8659	0.1052
0.1934	0.0304	0.5766	0.1178	0.9104	0.0866
0.3046	0.0601	0.6312	0.1236	0.9537	0.0621
0.3588	0.0742	0.6814	0.1271	0.9711	0.0441
0.4077	0.0854	0.7266	0.1269		

1-octanol) are listed in Tables 2 and 3, respectively. The excess molar volumes were calculated from the densities of the pure liquids and their mixtures using the following equation

$$V_m^E = x_1 M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (1)$$

with x, M, and ρ being the mole fraction, molar mass, and density, respectively; the subscripts indicate values for the pure components, whereas quantities without subscripts refer to mixtures.

The experimental results for each mixture were fitted by the following variable-degree polynomials:

$$H_m^E/(\mathrm{J{\cdot}mol^{-1}}) = \left[\frac{x(1-x)}{1+k(2x-1)}\right]\sum_i A_i(2x-1)^i \qquad (2)$$

$$V_m^E/(\mathrm{cm^3{\cdot}mol^{-1}}) = x(1-x)\sum_i A_i(1-x)^{(i-1)/2} \qquad (3)$$

Equation 2 is a modified Redlich−Kister fitting polynomial (Redlich and Kister, 1948; Redlich and Pierotti, 1959), and the parameters A_i, as well as the *skewing factor*, k, have been obtained by a fitting computer program which uses the least squares procedure and Marquardt's algorithm (Marquardt, 1963). The number of parameters used in eqs 2 and 3 for each mixture was determined by applying the F test (Bevington, 1969). The parameters A_i and the standard deviations for V_m^E are given in Table 4. The same parameters as well as the values of k for H_m^E are shown in Table 5. A plot of the experimental values together with the smoothing curves for H_m^E and V_m^E is shown in Figures 1 and 2, respectively. We are not aware of any previous measurement of H_m^E and V_m^E of the mixtures to which of this work are directed.

Table 4. Fitting Parameters, A_i, for Equation 3 and Standard Deviations, s, for V_m^E

A_1	A_2	A_3	A_4	A_5	s
		1-Chlorohexane + 1-Butanol			
2.3749	−4.7735	4.2721	−1.1036		0.0009
		1-Chlorohexane + 1-Pentanol			
2.5161	−7.5047	11.0918	−8.5181	2.7524	0.0003
		1-Chlorohexane + 1-Hexanol			
2.1070	−5.4523	5.3704	−1.9548		0.0008
		1-Chlorohexane + 1-Heptanol			
3.4760	−13.5796	25.8690	−23.5292	7.7950	0.0010
		1-Chlorohexane + 1-Octanol			
2.4686	−6.7712	8.2421	−3.9770		0.0011

The presence of hydrogen bonds in the pure alkanols determines their properties as associated liquids. In contrast, the pure chloroalkanes that do not have hydrogen bonds are not associated liquids. Therefore, their behavior must be much different, not only when they are in the pure state but also when forming part of a binary system. The effect of the presence of a chloroalkane in the systems

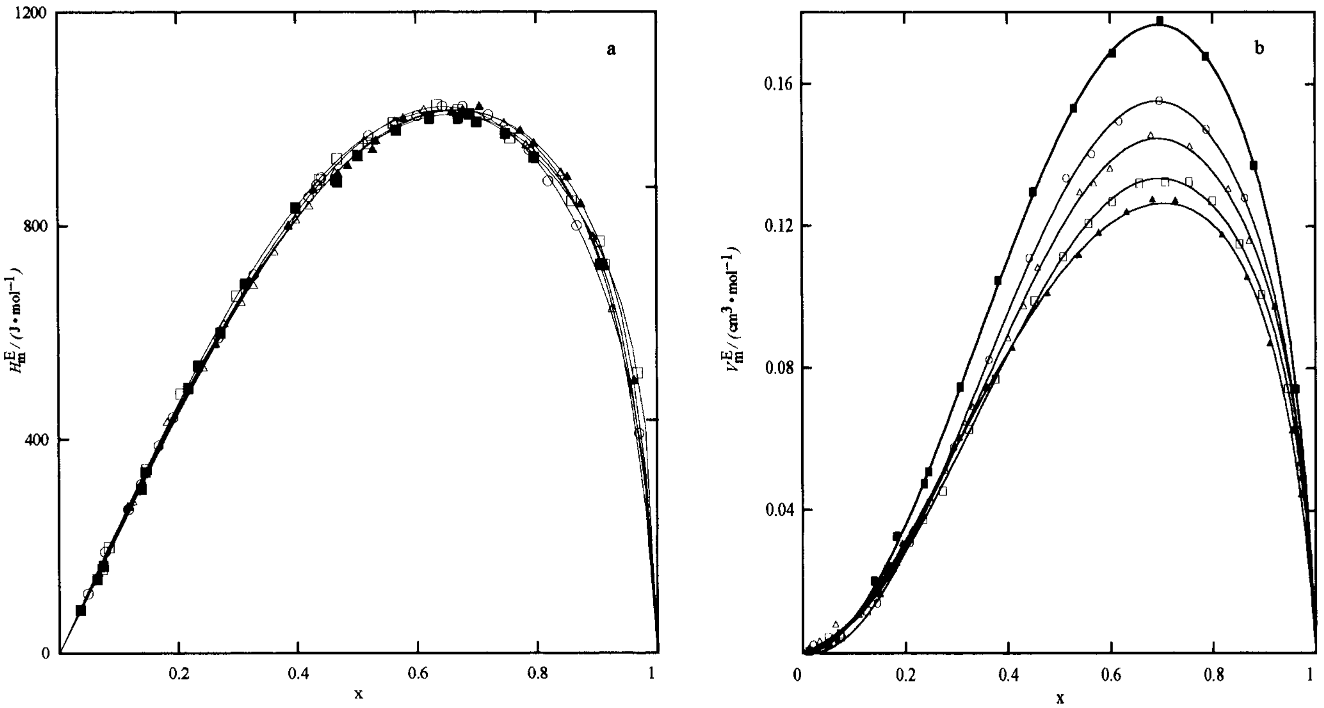

Figure 1. (a) Experimental excess molar enthalpies, H_m^E, and (b) experimental excess molar volumes, V_m^E at 298.15 K of (x)1-chlorohexane + (1 − x)alkanol: experimental values (n = number of alkanol carbon atoms), (■) n = 4, (○) = 5, (△) = 6, (□) = 7, and (▲) = 8; calculated values, (—) from eqs 2 and 3.

Table 5. Fitting Parameters A_i and k for Equation 2 and Standard Deviations, s, for H_m^E

A_0	A_1	A_2	A_3	s	k
		1-Chlorohexane + 1-Butanol			
3742	1520	−504	−763	8	−0.8610
		1-Chlorohexane + 1-Pentanol			
3794	1691	−917	4	6	−0.9586
		1-Chlorohexane + 1-Hexanol			
3737	1302	−549	−410	9	−0.8653
		1-Chlorohexane + 1-Heptanol			
3808	1932	−830	−367	9	−0.9686
		1-Chlorohexane + 1-Octanol			
3729	1572	−479	−129	8	−0.9283

discussed in this work can be interpreted if we consider the chloroalkane as the solvent and the alkanol as the solute. In this way, the behavior of the systems can be explained by taking into account the higher or lower dilution of the alkanol with the chloroalkane.

Hydrogen bonds are established between molecules that have hydrogen atoms with partial positive charge, as it happens with the O−H bonds, and other atoms with a strongly partial negative charge present in other molecules, such as the chloroalkanes, producing an electrostatic attraction of higher magnitude than the dipolar attraction (Vinogradov and Linnell, 1971). In our case we could think that in a mixture containing alkanols, R−OH, and chloroalkanes, R−Cl, the formation of hydrogen bonds between the alkanol and the chloroalkane might be possible.

The experimental excess molar enthalpies H_m^E are positive for all the studied systems over the whole range of composition. This suggests the predominance of the rupture of the existing hydrogen bonds of the pure alkanol instead of the establishment of new interactions during the mixing process, given that the hydrogen bond established between an alkanol and a chloroalkane is very weak. The maximun values corresponding to those interactions oscillate between 1009 J·mol^{-1} and 1026 J·mol^{-1}.

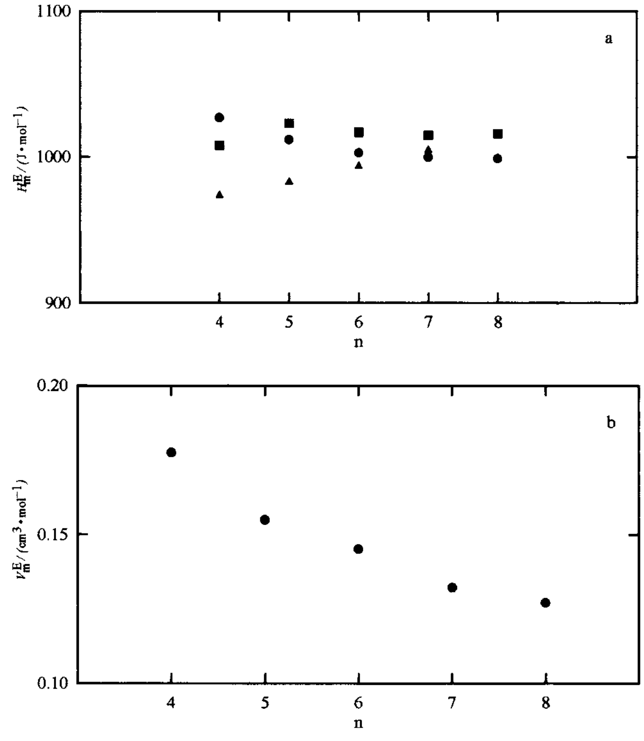

Figure 2. Maximum excess molar enthalpies, H_m^E, and maximum excess molar volumes, V_m^E, at 298.15 K of (x)1-chlorohexane + (1 − x)alkanol (n = number of alkanol carbon atoms): (a) H_m^E; (■) experimental values, (●) calculated from UNIFAC I (Tassios), and (▲) calculated from UNIFAC II (Larsen); (b) V_m^E, (●) experimental values.

The obtained curves are asymmetric, with their maxima displaced toward a high mole fraction of chlorohexane. This displacement can be interpreted on the basis of the rupture of hydrogen bonds present on the pure alkanol. At those compositions, the rupture of hydrogen bonds reaches its maximun and it is not compensated by the new possible interactions established during the mixing process. It can be seen in Figure 2a that the maximum values of H_m^E show almost no variation as the length of the alkanol carbon chain increases.

In contrast with systems containing smaller chloroalkanes (Santana et al., 1999), the excess molar volumes, V_m^E, are positive for the whole composition range. This fact can be explained with a packing term which makes a negative contribution to the V_m^E. This term results from the insertion of the chloroalkane into vacancies in the hydrogen-bonded structure of the alkanol, and it is most important at low x. In the systems we discuss here, the chloroalkane is not suitable to be inserted into the hydrogen-bonded structure because of a strong steric interaction with the alkanol, and therefore the excess molar volumes is always positive. The variation of the excess molar volume with the length of the carbon chain of the alkanol presents a more regular situation than in the case of excess molar enthalpies. The maximum values of the excess molar volumes decrease as the chain length of the alkanol increases. This indicates a lower steric interaction among the long alkanol carbon chains in order to admit the molecules of chlorohexane in their environment (see Figure 2b).

The maximum values of the experimental H_m^E are compared in Figure 2a, with those predicted by both versions of the UNIFAC model mentioned above, giving a standard deviation of 6% for Dang and Tassios (1968) and 12% for Larsen et al. (1987).

The experimental results for V_m^E show high concordance with those predicted by Larsen's version; the model predicts the endothermicity of the mixtures as well as the asymmetry of the curves. If we compare the predictions of both versions of the UNIFAC model with the different studied alkanols, it can be seen that the mixtures containing 1-octanol present the lowest deviations and the deviation decreases as the length of the alkanol increases.

Literature Cited

Andreolli-Ball, L.; Patterson, D.; Costas, M.; Cáceres-Alonso, M. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3991.

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

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

Dang, D.; Tassios, P. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25*, 22−31.

Franjo, C.; Menaut, C. P.; Jimenez, E.; Legido, J. L.; Paz Andrade, M. I. *J. Chem. Eng. Data* **1995**, *40*, 992−994.

Grolier, J. P. E.; Benson, G. C. *Can. J. Chem.* **1984**, *62*, 949−953.

Iglesias, T. P.; Legido, J. L.; Romaní, L.; Peleteiro, J.; Paz Andrade, M. I. *J. Chem. Thermodyn.* **1993**, *25*, 1325−1332.

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

Jiménez, E.; Franjo, C.; Menaut, C. P.; Segade, L.; Legido, J. L.; Paz Andrade, M. I. *J. Chem. Thermodyn.* **1997a**, *29*, 117−124.

Jiménez, E.; Franjo, C.; Segade, L.; Legido, J. L.; Paz Andrade, M. I. *J. Chem. Eng. Data* **1997b**, *42*, 262−265.

Larsen, B. L.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274−2286.

Legido, J. L.; Jiménez, E.; Franjo, C.; Segade, L.; Paz Andrade, M. I. *Fluid Phase Equilib.* **1997**, *136*, 315−321.

Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431−441.

Ortega, J.; Peña, J. A.; Matos, J. S. *Int. DATA Ser., Sel. Data Mixtures, Ser. A.* **1989**, *2*, 86.

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

Paz Andrade, M. I.; Castromil, S.; Baluja, M. C. *J. Chem. Thermodyn.* **1970**, *2*, 775.

Pico, J. M.; Menaut, C. P.; Jiménez, E.; Legido, J. L.; Paz Andrade, M. I. *Can. J. Chem.* **1995**, *73*, 139.

Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 341.

Redlich, O.; Pierotti, G. *J. Am. Chem. Soc.* **1959**, *81*, 2283.

Riddick, J. A.; Bunger, W. B.; Sakano, T. *Organic Solvents*, 4th ed.; Wiley: New York, 1986; Vol. II.

Santana, P.; Balseiro, J.; Jiménez, E.; Franjo, C.; Legido, J. L.; Romaní, L.; Paz Andrade, M. I. *J. Chem. Thermodyn.* **1999**, *31*, 547−554.

Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; VNR Co.: New York, 1971.

Received for review April 12, 1999. Accepted July 7, 1999.

JE990104T