Excess Enthalpies of Chloroalkylbenzene + Alkylbenzene Mixtures

Bruno Marongiu,* Alessandra Piras, Silvia Porcedda, and Enrica Tuveri

Dipartimento di Scienze Chimiche, Università di Cagliari, Cittadella Universitaria, S.P. Monserrato-Sestu Km 0,700; 09042 Monserrato (CA), Italy

The excess enthalpies, H^E, at 298.15 K for binary mixtures of chloroalkylbenzenes of general formula C_6H_5-$(CH_2)_s$-Cl (with $s = 0, 1, 2, 3$) + alkylbenzenes of general formula C_6H_5-$(CH_2)_t$-H (with $t = 0, 1, 2, 3, 4$) have been measured by flow microcalorimetry. All mixtures containing chlorobenzene ($s = 0$) and the mixtures of 1-chloro-3-phenylpropane + benzene, methylbenzene, and ethylbenzene exhibit negative H^E, and the remaining mixtures are endothermic. Data were fitted by the Redlich−Kister equation. Heats of mixing are quite low: the values at equimolar composition are in the range −143.0 J·mol^{-1} to +323.0 J·mol^{-1}. The values of partial molar excess enthalpies at infinite dilution, $\bar{H}_i^\infty$, of both components vary from −0.583 kJ·mol^{-1} to +1.295 kJ·mol^{-1}.

Introduction

In continuation of our studies[1−6] on thermodynamic properties such as excess enthalpy, H^E, and excess Gibbs energy, G^E, of chloroalkanes (tetrachloromethane,[4] 1,1,2,2-tetrachloroethane,[5] and chloroalkylbenzenes[6]) mixed with organic compounds (alkanes, cycloalkanes, alkenes, aldehydes, ketones), we have started a similar investigation on binary mixtures containing chloroalkylbenzenes and alkylbenzenes.

As the first results, in this paper we report H^E values for chloroalkylbenzenes of general formula C_6H_5-$(CH_2)_s$-Cl (with $s = 0, 1, 2, 3$) + an aromatic hydrocarbon (benzene, methyl-, ethyl-, *n*-propyl-, and *n*-butylbenzene). Among the examined systems, heats of mixing are reported in the literature only for chlorobenzene ($s = 0$) + benzene,[7−12,15] + methylbenzene,[8,10,13−15] and + ethylbenzene.[10,14,15]

From partial molar enthalpies at infinite dilution and from the known enthalpies of vaporization, the enthalpies of solution, $\Delta H^\circ_{v,2}$, have been evaluated for alkylbenzenes in chloroalkylbenzenes. No enthalpy of vaporization of chloroalkylbenzene was found in the literature. The trend of the experimental data, here reported, has been shortly discussed.

Experimental

Materials. All chemicals were commercial products from Aldrich of the best grade quality. They were used without further purification, and their purities were ≥ 99 %, with the exception of *n*-propylbenzene, which contained about 2 % impurities. The purities declared by the factories as well as the liquid densities we measured at 298.15 K along with the literature values are collected in Table 1.

Instrumentation. Heats of mixing were determined by means of a flow microcalorimeter (model 2277, LKB-producer AB, Bromma, Sweden). The apparatus and the experimental procedure are described in detail elsewhere.[16] Fully automatic burettes (ABU80, Radiometer, Copenhagen, Denmark) were used to pump the liquid into the LKB unit. The molar flow rate m_i (mol·sec^{-1}) of component i flowing into the mixing cell is given by

$$m_i = \phi_i \rho_i / M_i \quad (1)$$

* Corresponding author. Phone: +39-070-6754412. Fax: +39-070-6754388. E-mail: maronb@unica.it.

Table 1. Purities, Expressed as Percentage, and Densities at 298.15 K of Examined Compounds

compound	purity	ρ_{exptl} / g·cm^{-3}	ρ_{lit} / g·cm^{-3}
benzene	99.9	0.87358	0.87360[a]
methylbenzene	99.8	0.86219	0.86219[a]
ethylbenzene	99.0	0.86255	0.86253[a]
n-propylbenzene	98.0	0.85762	0.85780[b]
n-butylbenzene	99.0	0.85629	0.85607[a]
chlorobenzene	99.9	1.10117	1.1009[a]
benzyl chloride	99.0	1.09482	1.1004[b]
1-chloro-2-phenylethane	99.0	1.06691	−
1-chloro-3-phenylpropane	99.0	1.04184	−

[a] Riddick et al. ref 18. [b] TRC ref 19.

where ϕ_i is the volumetric flow rate; ρ_i is the density; and M_i is the molar mass. The necessary densities were determined by means of a vibrating tube densimeter (model DMA 58, Anton Paar, Graz, Austria) with a reproducibility of 1·10^{-5} g·cm^{-3}.

The molar excess enthalpies have been evaluated from the formula

$$H^E = I^2 R (E/E_c)/m \quad (2)$$

where I and R are the electrical current and resistance in the electrical calibration experiment; E and E_c are the voltage readings for measurement and electrical calibration, respectively; and m is the molar flow rate of the mixture. All enthalpy measurements were carried out at 298.15 K. The accuracy of the LKB bath temperature is 0.1 K. The reliability of the apparatus and procedure adopted were checked by performing H^E measurements on the test system benzene + cyclohexane. Our results differed by < 2 % from the literature data[17] over the entire composition range.

Results

The experimental H^E data are collected in Table 2 and plotted in Figures 1 to 4. The H^E values were fitted to the smoothing Redlich−Kister equation

$$H^E = x_1 x_2 \sum_{i=0}^{n-1} a_i (x_1 - x_2)^i \quad (3)$$

10.1021/je7002447 CCC: $37.00
Published on Web 07/11/2007

Table 2. Experimental Values of the Molar Excess Enthalpies, H^E, at Different Mole Fractions, x_1, of Chloroalkylbenzene (1) + Alkylbenzene (2) Mixtures at 298.15 K

x_1	H^E / J·mol^{-1}	x_1	H^E / J·mol^{-1}	x_1	H^E / J·mol^{-1}	x_1	H^E / J·mol^{-1}	x_1	H^E / J·mol^{-1}	x_1	H^E / J·mol^{-1}
chlorobenzene + benzene											
0.0804	−2.1	0.2258	−4.6	0.3962	−5.8	0.5675	−5.5	0.6999	−4.2	0.8235	−3.1
0.1272	−2.8	0.3043	−5.1	0.4666	−5.7	0.6363	−4.9	0.7777	−3.6	0.8974	−1.7
0.1794	−3.9	0.3684	−5.5	0.5384	−5.4						
chlorobenzene + methylbenzene											
0.1156	−52.8	0.2584	−94.4	0.4107	−114.0	0.6106	−107.0	0.8070	−67.5	0.9127	−33.4
0.2072	−82.8	0.3433	−109.4	0.5111	−114.8	0.6765	−96.3				
chlorobenzene + ethylbenzene											
0.1075	−54.9	0.1671	−78.0	0.3111	−121.3	0.4745	−144.9	0.6436	−126.1	0.8784	−62.7
0.1308	−65.5	0.2864	−115.3	0.4453	−140.2	0.5463	−142.6	0.7625	−109.3	0.9233	−40.0
chlorobenzene + *n*-propylbenzene											
0.1205	−50.5	0.2551	−88.3	0.4066	−109.4	0.5781	−109.3	0.7851	−79.0	0.9164	−32.7
0.1859	−67.8	0.3394	−102.0	0.4774	−115.8	0.6727	−100.8	0.8796	−49.5		
chlorobenzene + *n*-butylbenzene											
0.1330	−40.7	0.2036	−58.1	0.3383	−83.4	0.5350	−87.4	0.6971	−68.7	0.9020	−34.4
0.1609	−48.2	0.2772	−74.2	0.4341	−91.7	0.6054	−81.0	0.8036	−55.5		
benzyl chloride + benzene											
0.1118	60.1	0.2742	102.5	0.4304	120.1	0.6018	105.7	0.7514	78.3	0.8580	51.5
0.2012	90.1	0.3350	113.4	0.5312	113.6	0.6939	92.2	0.8193	62.6		
benzyl chloride + methylbenzene											
0.1036	24.1	0.2574	47.1	0.3813	58.5	0.5810	55.5	0.7350	45.4	0.8809	23.9
0.1877	38.7	0.3161	53.5	0.4803	60.0	0.6490	51.9	0.7871	39.5	0.9024	21.4
benzyl chloride + ethylbenzene											
0.0962	52.3	0.2102	87.4	0.4151	117.6	0.5866	116.3	0.7395	92.2	0.8646	57.1
0.1664	75.7	0.2853	101.3	0.5156	118.8	0.6804	104.5	0.8098	75.5	0.8949	41.8
benzyl chloride + *n*-propylbenzene											
0.1315	111.2	0.3124	195.8	0.4468	220.5	0.6450	202.7	0.7842	143.8	0.8791	85.5
0.2325	158.8	0.3772	208.9	0.5478	226.5	0.7079	185.2	0.8289	102.5	0.9065	64.3
benzyl chloride + *n*-butylbenzene											
0.1194	138.0	0.2532	249.3	0.5043	318.9	0.6439	297.9	0.7834	218.6	0.8906	123.1
0.1450	168.3	0.3114	277.4	0.5756	314.7	0.7307	258.9	0.8444	173.0	0.9313	85.2
0.2028	201.2	0.4041	305.5								
1-chloro-2-phenylethane + benzene											
0.1016	30.9	0.2028	44.0	0.4042	46.9	0.5757	35.8	0.7308	24.3	0.8444	14.8
0.1450	37.5	0.3115	47.9	0.5044	41.8	0.6706	28.7	0.8028	19.7		
1-chloro-2-phenylethane + methylbenzene											
0.0750	−0.3	0.2332	2.1	0.4478	5.5	0.6186	7.9	0.8122	6.8	0.8902	4.8
0.0920	0.0	0.2885	2.7	0.5195	7.0	0.6838	7.7	0.8439	6.1	0.9068	4.1
0.1686	0.8	0.3782	4.6	0.5488	7.4	0.7643	7.3				
1-chloro-2-phenylethane + ethylbenzene											
0.1050	33.4	0.2603	62.0	0.3849	79.9	0.5847	80.9	0.7379	66.5	0.8825	34.8
0.1900	50.2	0.3194	75.7	0.4841	84.7	0.6524	77.1	0.7897	60.1	0.9037	26.8
1-chloro-2-phenylethane + *n*-propylbenzene											
0.1173	72.4	0.2099	111.2	0.4147	164.6	0.5863	169.2	0.7392	133.4	0.8500	93.0
0.1375	78.3	0.2850	138.0	0.4436	169.3	0.6145	162.4	0.8096	110.4	0.9140	57.7
0.1662	92.5	0.3470	152.2	0.5152	171.8	0.6801	154.4				
1-chloro-2-phenylethane + *n*-butylbenzene											
0.1063	99.4	0.2293	185.3	0.4424	252.8	0.6134	247.9	0.7604	199.4	0.8639	131.7
0.1295	117.0	0.3085	217.4	0.4716	254.1	0.7041	225.8	0.8264	159.9	0.9225	81.7
0.1655	143.5	0.3730	235.9	0.5434	255.1						
1-chloro-3-phenylpropane + benzene											
0.0913	−9.6	0.2316	−22.9	0.3760	−34.4	0.5466	−36.3	0.7068	−29.5	0.8282	−19.9
0.1843	−20.0	0.3113	−30.0	0.4455	−36.3	0.6164	−34.3	0.7834	−23.8	0.8577	−17.4
1-chloro-3-phenylpropane + methylbenzene											
0.1072	−52.3	0.2648	−96.9	0.4187	−113.6	0.5903	−101.6	0.6836	−85.7	0.8121	−57.1
0.1526	−69.0	0.3244	−105.8	0.4899	−108.3	0.6576	−91.1	0.7423	−75.2	0.8781	−36.9
0.1936	−81.6	0.3507	−105.8	0.5193	−106.9						
1-chloro-3-phenylpropane + ethylbenzene											
0.0766	−19.7	0.2372	−43.2	0.4534	−50.4	0.5544	−47.6	0.7133	−34.8	0.8327	−21.7
0.1214	−28.9	0.2931	−46.4	0.5251	−49.1	0.6239	−43.1	0.7684	−30.1	0.8924	−14.0
0.1717	−37.3	0.3835	−50.4								
1-chloro-3-phenylpropane + *n*-propylbenzene											
0.0863	3.7	0.2394	11.6	0.4145	17.2	0.5861	19.4	0.7391	17.9	0.9042	9.0
0.1360	6.6	0.3207	13.7	0.4856	18.6	0.6538	19.4	0.7906	15.8	0.9189	8.0
0.1910	9.2	0.3863	16.4	0.5573	19.5	0.7157	17.7	0.8343	13.0		
1-chloro-3-phenylpropane + *n*-butylbenzene											
0.1167	30.7	0.2605	69.9	0.4134	90.2	0.5849	93.2	0.6789	80.9	0.8087	57.3
0.2090	59.3	0.3458	82.4	0.5138	94.8	0.6132	89.6	0.7381	71.8	0.9136	31.4

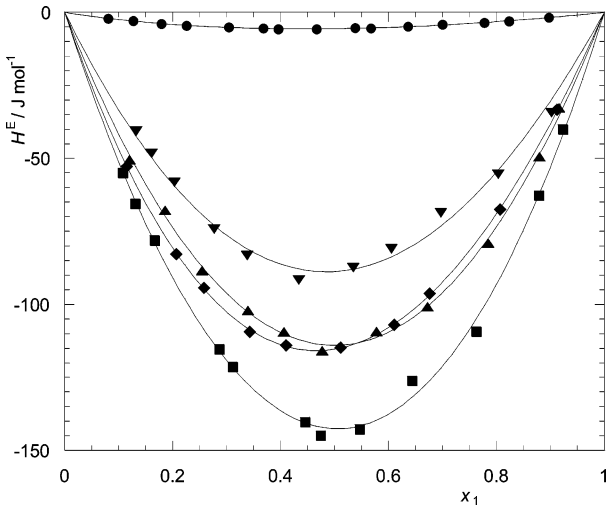

Figure 1. Molar excess enthalpies, H^E, at 298.15 K, of chlorobenzene (1) + alkylbenzene (2) mixtures vs x_1, the mole fraction of chlorobenzene. Full lines, calculated from the smoothing equation. Points, direct experimental results: ●, benzene; ◆, methylbenzene; ■, ethylbenzene; ▲, *n*-propylbenzene; ▼, *n*-butylbenzene.

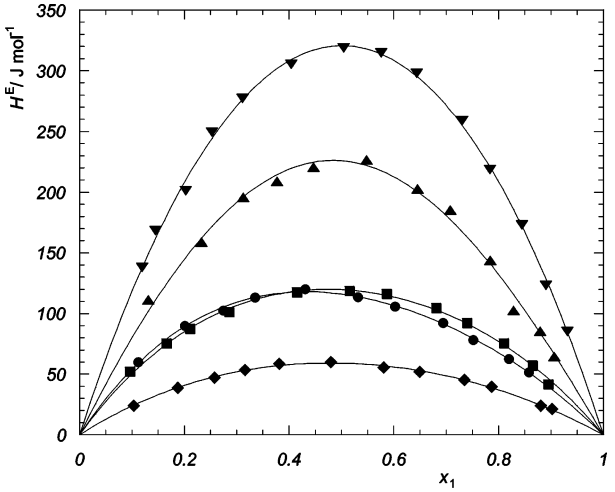

Figure 2. Molar excess enthalpies, H^E, at 298.15 K, of benzyl chloride (1) + alkylbenzene (2) mixtures vs x_1, the mole fraction of benzyl chloride. Full lines, calculated from the smoothing equation. Points, direct experimental results: ●, benzene; ◆, methylbenzene; ■, ethylbenzene; ▲, *n*-propylbenzene; ▼, *n*-butylbenzene.

where x_1 is the mole fraction of chloroalkylbenzene and n is the number of coefficients. The values of the coefficients a_i and the standard deviation of the fit, $\sigma(H^E)$

$$\sigma(H^E) = \sqrt{\frac{\Sigma(H^E_{i,\mathrm{calcd}} - H^E_{i,\mathrm{exptl}})^2}{N - n}} \qquad (4)$$

obtained by a least-squares treatment, are given in Table 3. N is the number of experimental points.

Excess enthalpies calculated at equimolar composition, H^E ($x_1 = 0.5$), are reported in Table 4 and agree with results from other authors.[7−15] In particular, it is possible to compare our results and those found in the literature for equimolar compositions, at 298.15 K (reported at the bottom of Table 4), and to notice that the discrepancy does not exceed 9 %.

In Table 4, the values of partial molar excess enthalpies at infinite dilution, $\bar{H}_i^\infty$, of both components are also collected,

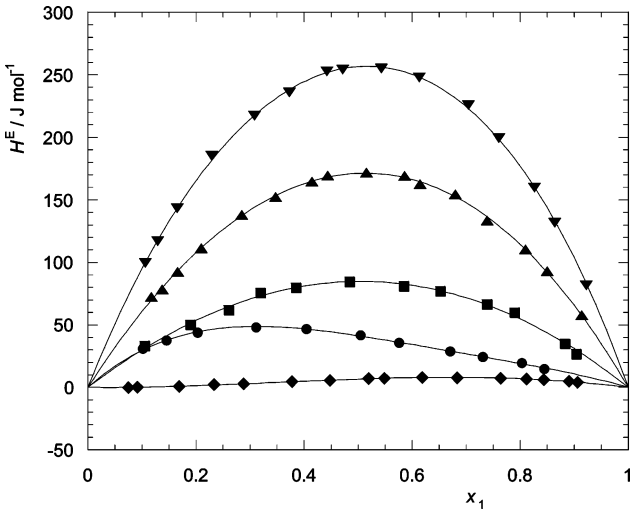

Figure 3. Molar excess enthalpies, H^E, at 298.15 K, of 1-chloro-2-phenylethane (1) + alkylbenzene (2) mixtures vs x_1, the mole fraction of 1-chloro-2-phenylethane. Full lines, calculated from the smoothing equation. Points, direct experimental results: ●, benzene; ◆, methylbenzene; ■, ethylbenzene; ▲, *n*-propylbenzene; ▼, *n*-butylbenzene.

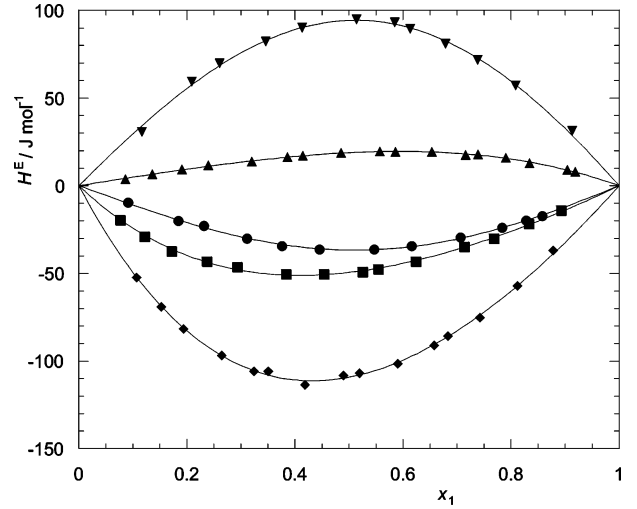

Figure 4. Molar excess enthalpies, H^E, at 298.15 K, of 1-chloro-3-phenylpropane (1) + alkylbenzene (2) mixtures vs x_1, the mole fraction of 1-chloro-3-phenylpropane. Full lines, calculated from the smoothing equation. Points, direct experimental results: ●, benzene; ◆, methylbenzene; ■, ethylbenzene; ▲, *n*-propylbenzene; ▼, *n*-butylbenzene.

obtained from the parameters a_i of eq 3 by means of the following equations

$$\bar{H}_1^\infty = a_0 - a_1 + a_2 - a_3 + \ldots$$

$$\bar{H}_2^\infty = a_0 + a_1 + a_2 + a_3 + \ldots \qquad (5)$$

In the same table, the standard enthalpies of vaporization and the derived standard heat of solution of alkyl benzenes in the mixtures under investigation are also reported, calculated by means of

$$\Delta H_i^\circ = \bar{H}_i^\infty - \Delta H_{\mathrm{v},i}^\circ \qquad (6)$$

where $\Delta H_{\mathrm{v},i}^\circ$ is the standard molar heat of vaporization of pure liquid, which was taken from the literature.[18]

All mixtures containing chlorobenzene with an aromatic hydrocarbon as the second constituent exhibit negative H^E and $\bar{H}_i^\infty$ values. Mixtures of 1-chloro-3-phenylpropane are exother-

Table 3. Redlich−Kister Parameters, a_i, and Standard Deviations, $\sigma(H^E)$, of Experimental Molar Excess Enthalpies, H^E, at 298.15 K, for Chloroalkylbenzene (1) + Alkylbenzene (2) Mixtures

chloroalkylbenzene	alkylbenzene	a_0 / J·mol^{-1}	a_1 / J·mol^{-1}	a_2 / J·mol^{-1}	$\sigma(H^E)$ / J·mol^{-1}
chlorobenzene	benzene	−22.426	4.771	−1.7187	0.12
	methylbenzene	−461.32	60.708	−17.089	0.46
	ethylbenzene	−571.99	−11.223	−	2.6
	n-propylbenzene	−457.46	1.0044	−	1.7
	n-butylbenzene	−354.77	21.115	−	3.0
benzyl chloride	benzene	463.86	−112.64	71.208	1.4
	methylbenzene	236.45	−19.213	18.529	0.95
	ethylbenzene	478.75	−41.792	75.235	0.71
	n-propylbenzene	903.42	−65.526	−107.38	6.8
	n-butylbenzene	1291.8	3.2854	−	4.6
1-chloro-2-phenylethane	benzene	165.22	−130.58	90.177	0.72
	methylbenzene	26.439	29.438	−2.4918	0.18
	ethylbenzene	338.54	6.3418	−	2.1
	n-propylbenzene	688.52	33.559	−	1.8
	n-butylbenzene	1026.2	60.067	118.81	1.7
1-chloro-3-phenylpropane	benzene	−146.79	−7.5526	30.871	0.58
	methylbenzene	−436.95	117.98	−25.676	1.3
	ethylbenzene	−197.84	71.486	−21.267	0.82
	n-propylbenzene	76.041	30.141	−	0.36
	n-butylbenzene	370.76	22.211	−	2.4

Table 4. Molar Excess Enthalpies at Equimolar Composition, H^E ($x_1 = 0.5$), Excess Partial Molar Enthalpies at Infinite Dilution, $\bar{H}_i^\infty$ ($i = 1, 2$), for Chloroalkylbenzene (1) + Alkylbenzene (2) Mixtures, Standard Enthalpies of Vaporization of Component 2, ΔH_2°, and Standard Enthalpies of Solution of Component 2, ΔH_2°, at 298.15 K

chloroalkylbenzene	alkylbenzene	H^E ($x_1 = 0.5$) / kJ·mol^{-1}	$\bar{H}_1^\infty$ / kJ·mol^{-1}	$\bar{H}_2^\infty$ / kJ·mol^{-1}	$\Delta H_{v,2}^\circ$ / kJ·mol^{-1}	ΔH_2° / kJ·mol^{-1}
chlorobenzene	benzene	−0.006[a]	−0.029	−0.019	33.83	−33.85
	methylbenzene	−0.115[b]	−0.539	−0.418	38.01	−38.43
	ethylbenzene	−0.143[c]	−0.561	−0.583	42.24	−42.82
	n-propylbenzene	−0.114	−0.459	−0.456	46.22	−46.68
	n-butylbenzene	−0.887	−0.376	−0.334	51.36	−51.70
benzyl chloride	benzene	0.116	0.648	0.422	33.83	−33.41
	methylbenzene	0.059	0.274	0.236	38.01	−37.77
	ethylbenzene	0.120	0.596	0.512	42.24	−41.72
	n-propylbenzene	0.226	0.862	0.731	46.22	−45.49
	n-butylbenzene	0.323	1.289	1.295	51.36	−50.07
1-chloro-2-phenylethane	benzene	0.041	0.386	0.125	33.83	−33.70
	methylbenzene	0.007	−0.006	0.053	38.01	−37.96
	ethylbenzene	0.085	0.332	0.345	42.24	−41.90
	n-propylbenzene	0.172	0.655	0.722	46.22	−45.50
	n-butylbenzene	0.257	1.085	1.205	51.36	−50.20
1-chloro-3-phenylpropane	benzene	−0.037	−0.108	−0.124	33.83	−33.95
	methylbenzene	−0.109	−0.581	−0.345	38.01	−38.36
	ethylbenzene	−0.049	−0.291	−0.148	42.24	−42.39
	n-propylbenzene	0.019	0.046	0.106	46.22	−46.11
	n-butylbenzene	0.093	0.349	0.394	51.36	−50.97

[a] Tanaka and Benson (ref 10) obtained −0.006. [b] Amaya (ref 14) obtained −0.124. Tanaka and Benson (ref 10) obtained −0.119. Muensh (ref 15) obtained −0.126. [c] Muensh (ref 15) obtained −0.156. Tanaka and Benson (ref 10) obtained −0.153.

mic with benzene, methylbenzene, and ethylbenzene and are endothermic with propylbenzene and butylbenzene, whereas mixtures of benzyl chloride and of 1-chloro-2-phenylethane with alkylbenzenes are endothermic.

Partial molar excess enthalpies at infinite dilution of both components in the mixture, $\bar{H}_i^\infty$, with respect to the number of carbon atoms in the chain of the alkylbenzene, show a characteristic trend with a minimum value, for a given chlorobenzene, corresponding to a mixture with methylbenzene, with the exception of chlorobenzene that exhibits this minimum for the mixture with ethylbenzene. The evolution of $\bar{H}_1^\infty$ is represented in Figure 5. The same trend is shown also by the excess enthalpy values at equimolar composition (Figure 6).

Discussion

Mixtures of chlorobenzenes + alkylbenzenes are characterized by H^E and $\bar{H}_i^\infty$ values that do not have an evolution similar to those of the remaining chloroalkylbenzenes. Indeed, chlorobenzene does not belong to the class of chloroalkylbenzenes, as no alkyl group is present between the phenyl and the chlorine groups. The very low value of the exothermic effect associated with the mixing of chlorobenzene and benzene (athermal solution) suggests that the chlorine atom, characterized by an electron drawing effect, does not have a significant effect in modifying the van der Waals interaction with respect to benzene.

For chlorobenzene, benzyl chloride, and 1-chloro-3-phenylpropane, the mixture having the lowest heat of mixing, in absolute value, has as a second constituent the homologous alkylbenzene (same number of C atoms). 1-Chloro-2-phenylethane does not follow this rule.

The values of excess enthalpies at equimolar composition of alkyl chlorobenzenes, C_6H_5-$(CH_2)_s$-Cl, having $s = 1$, 2, and 3 with respect to t ($t = 0$, 1, 2, 3, 4), the number of C atoms in the chain of the alkylbenzene, exhibit a minimum in the heat

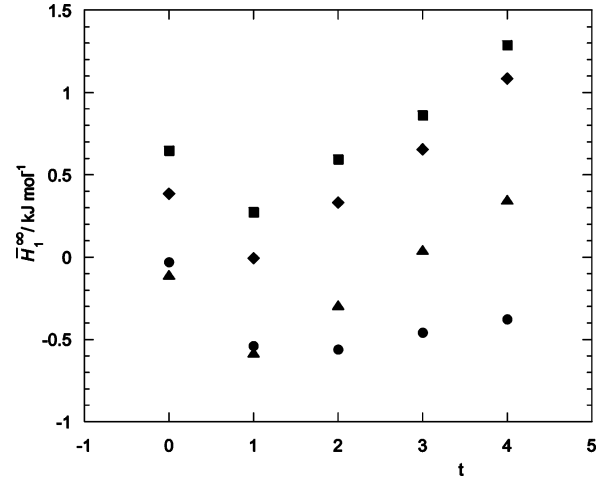

Figure 5. Molar excess enthalpies at infinite dilution of the first component, $\bar{H}_1^{\infty}$, at 298.15 K, in chloroalkylbenzene (1) + alkylbenzene (2) mixtures vs *t*, the number of C atoms in the chain of the alkylbenzene: ●, chlorobenzene; ■, benzyl chloride; ◆, 1-chloro-2-phenylethane; ▲, 1-chloro-3-phenylpropane.

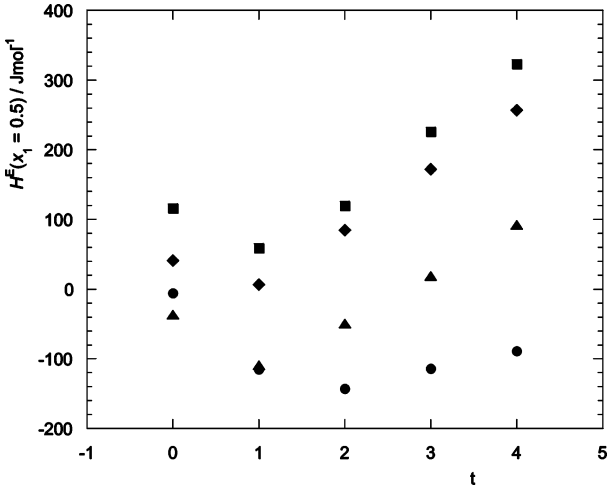

Figure 6. Molar excess enthalpies at equimolar composition, H^E (x_1 = 0.5), at 298.15 K, of chloroalkylbenzene (1) + alkylbenzene (2) mixtures vs *t*, the number of C atoms in the chain of the alkylbenzene: ●, chlorobenzene; ■, benzyl chloride; ◆, 1-chloro-2-phenylethane; ▲, 1-chloro-3-phenylpropane.

of mixing, i.e., a maximum in the exothermic contribution due to the attractive force between unlike molecules when the second constituent is methylbenzene, probably because of the relevant positive inductive effect (+*I*) exerted by the methyl group. An increase of the +*I* effect for addition of a CH_2 group is negligible.

Literature Cited

(1) Kehiaian, H. V.; Marongiu, B. A comparative study of thermodynamic properties and molecular interactions in mono - and poly-chloroalkane + n-alkane or cyclohexane mixtures. *Fluid Phase Equilib.* **1988**, *40*, 23−78.

(2) Kehiaian, H. V.; Marongiu, B. Thermodynamic of 1-chloroalkanes of α,ω-dichloroalkanes + tetrachloromethane mixtures. *Fluid Phase Equilib.* **1988**, *42*, 141−163.

(3) Marongiu, B.; Pittau, B.; Porcedda, S.; Kehiaian, H. V. Thermodynamics of binary mixtures containing linear or cyclic alkenes. II. Mixtures with benzene or tetrachloromethane. *Fluid Phase Equilib.* **1994**, *99*, 185−198.

(4) Giannotti, A.; Lepori, L.; Matteoli, E.; Marongiu, B. Excess Gibbs energies of liquid binary mixtures. 6. A hydrocarbon or tetrachloromethane + an aldehyde or a ketone. *Fluid Phase Equilib.* **1991**, *65*, 275−290.

(5) Marongiu, B.; Piras, A.; Porcedda, S.; Tuveri, E. Excess enthalpies of chloroalkylbenzene + n-heptane or cyclohexane mixtures. DISQUAC analysis. *J. Therm. Analysis* **2007**, in press.

(6) Marongiu, B.; Pusceddu, E.; Porcedda, S.; Lepori, L.; Matteoli, E. Thermodynamic study of 1,1,2,2-tetrachloroethane + hydrocarbon mixtures. I. Excess and solvation enthalpies. *Fluid Phase Equilib.* **2006**, *250*, 105−115.

(7) Merkel, K. Uebermolekuelbildung in Fluessigkeiten. *Nova Acta Leopold.* **1940**, *9*, 243−297 (see also ref 15).

(8) Harsted, B. S.; Thomsen, E. S. Excess enthalpies from flow microcalorimetry. 3. Excess enthalpies for binary mixtures of aliphatic and aromatic hydrocarbons, carbon tetrachloride, chlorobenzene and carbon disulphide. *J. Chem. Thermodyn.* **1975**, *7*, 369−376 (see also ref 15).

(9) Canning, J.; Cheesman, G. H. Heats of mixing of liquids. *J. Chem. Soc. (London)* **1955**, 1230−1233 (see also ref 15).

(10) Tanaka, R.; Benson, G. C. Excess enthalpies and volumes for mixtures of chlorobenzene with some aromatic hydrocarbons at 298.15 K. *J. Chem. Eng. Data* **1976**, *21*, 320−324 (see also ref 15).

(11) Nigam, R. K.; Singh, P. P.; Maini, N. N. Dipolar interactions in binary mixtures of benzene & toluene with chloro- & bromo-benzenes. *Indian J. Chem.* **1970**, *8*, 908−915 (see also ref 15).

(12) Baghdoyan, A.; Fried, V. Thermodynamic investigation of carbon tetrachloride + thiophene and toluene + chlorobenzene. *J. Chem. Thermodyn.* **1975**, *7*, 409−415.

(13) Amaya, K. Thermodynamical studies on binary systems consisting of polar and non-polar liquids. II. The measurement of the heats of mixing for binary systems of polar and nonpolar liquids. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1278−1285 (see also ref 15).

(14) Muensch. E. Mischungskalorimetrie mit einem Verdraengungskalorimeter, dargestellt an den Systemen Benzol + n-Heptan, 2-Methylnaphthalen + 1-Methylnaphthalen, Toluol + Chlorbenzol und Chlorbenzol + Aethylbenzol. *Thermochim. Acta* **1978**, *23*, 237−255 (see also ref 15).

(15) Christensen, C.; Gmehling, J.; Rasmussen, P.; Weidlich, U. *Heats of mixing data collection*, part 2; DECHEMA: Frankfurt/Main, Germany, 1984; Vol. III.

(16) Monk, P.; Wadsö, I. A flow micro reaction calorimeter. *Acta Chem. Scand.* **1968**, *22*, 1842−1852.

(17) Marsh, K. N. Excess enthalpy. Cyclohexane + hexane, benzene + cyclohexane, tetrachloromethane + benzene. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1973**, *1*, 1−5.

(18) Riddick, J. A; Bunger, W. B.; Sakano, T. K. *Organic Solvents − Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1968.

(19) *Thermodynamics Research Center (TRC), Thermodynamic Tables of Hydrocarbons*, Supplement no. 95l; Texas A&M University System: College Station, 1988.

Received for review May 7, 2007. Accepted May 30, 2007.

JE7002447