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Molar Excess Volume of *sec*- and *tert*-Butyl Chloride with Aromatic Hydrocarbons at $T = 298.15$ K

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The molar excess volumes (V^E) of *sec*-butyl chloride or *tert*-butyl chloride (A) + benzene or toluene or *o*- or *m*- or *p*-xylene (B) were measured at $T = 298.15$ K over the entire composition range using a V-shaped dilatometer. The V^E values for all these binary mixtures were found to be negative, whereas these change sign from positive to negative for *sec*-butyl chloride + benzene. Although the V^E values for an equimolar mixture of *sec*-butyl chloride + aromatics vary in the order benzene > *m*-xylene > toluene > *p*-xylene > *o*-xylene, for an equimolar mixture of *tert*-butyl chloride + aromatics, these follow the sequence benzene > *m*-xylene > *p*-xylene > toluene > *o*-xylene. Branching of the butyl group decreases the V^E in the following order: *n*-butyl chloride > *sec*-butyl chloride > *tert*-butyl chloride.

Introduction

The additions of inert solvents such as alkane generally break the orientation order of pure alkyl halide to give the positive value of excess thermodynamic functions.[1−6] However, when alkane is replaced by aromatic hydrocarbons which are potential electron donors, weak specific interactions of the electron donor−acceptor type were reported between the components in alkyl halide−aromatic hydrocarbon mixtures along with disruption in the orientational order of the pure components.[5−10] In our previous paper, excess volume and excess enthalpy of *n*-butyl chloride with aromatic hydrocarbons were reported.[10] To study the effect of branching of the carbon chain in the alkyl group, we have selected the binary systems of *sec*- and *tert*-butyl chloride (A) + benzene, toluene, *o*-, *m*-, and *p*-xylene (B) and measured their excess volumes at $T = 298.15$ K over the entire range of compositions.

Experimental Section

Butyl chloride, benzene, toluene, and xylene (Merck) were purified by a standard procedure.[11−12] The purities of the purified samples were checked by measuring their densities and refractive indices at $T = 298.15$ K as described earlier,[13] and these compared well with the literature values[11] as shown in Table 1.

Molar excess volumes were measured using a two-limb specially designed V-shaped dilatometer in the manner explained elsewhere.[14] The temperature of the water thermostat was controlled to ± 0.01 K by a mercury-in-toluene regulator. After thermal equilibrium, the change in the level of the liquid in the dilatometer was noted with a cathetometer that could read to ± 0.001 cm. The performance of the dilatometer was checked by measuring the molar excess volume of the benzene + cyclohexane mixture at $T = 298.15$ K, and these agreed to within the experimental limits with the corresponding literature values.[15] The uncertainty in the measured V^E values was ± 1 %.

Table 1. Densities (ρ) and Refractive Indices (n_D) of the Pure Components at $T = 298.15$ K

	ρ/kg·m^{-3}		n_D	
material	exptl	ref 11	exptl	ref 11
sec-butyl chloride	867.70	867.67	1.3943	1.3942
tert-butyl chloride	836.06	836.1	1.3826	1.3828
benzene	873.65	873.60	1.4980	1.49792
toluene	862.22	862.19	1.4940	1.49413
o-xylene	875.93	875.94	1.5031	1.50295
m-xylene	860.07	860.09	1.4944	1.49464
p-xylene	856.63	856.61	1.4932	1.49325

Results and Discussion

The measured molar excess volumes of *sec*- or *tert*-butyl chloride (A) + benzene or toluene or *o*- or *m*- or *p*-xylene (B) as a function of mole fraction, x_A, at 298.15 K are reported in Table 2 and also shown in Figure 1. The results were expressed by the Redlich−Kister equation

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_A x_B[V_0 + V_1(x_A - x_B) + V_2(x_A - x_B)^2 + V_3(x_A - x_B)^3] \quad (1)$$

where V_n ($n = 0$ to 3) are the adjustable parameters and x_A and x_B are the mole fraction of butyl chloride and the second component of the binary mixture, respectively. These parameters were evaluated by fitting $V^E/x_A x_B$ data to eq 1 by the method of least-squares and are given along with standard deviations, $\sigma(V^E)$, of V^E in Table 3.

$$\sigma(V^E)/\text{cm}^3\cdot\text{mol}^{-1} = \{[\sum(V^E_{\text{exptl}} - V^E_{\text{calcdeq(1)}})]/(m - n)\}^{0.5} \quad (2)$$

where m is the number of experimental values and n is the number of adjustable parameters in eq 2. The number of parameters (n) was dictated by the consideration that the maximum deviation, σ_m, satisfied the relation: $\sigma_m(V^E) \leq 2\sigma(V^E)$.

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Table 2. Experimental Data of Excess Volumes for *sec*- or *tert*-Butyl Chloride (BC) (A) + Aromatic Hydrocarbon (B) Mixtures at $T = 298.15$ K

x_A	V^E / $cm^3 \cdot mol^{-1}$	x_A	V^E / $cm^3 \cdot mol^{-1}$	x_A	V^E / $cm^3 \cdot mol^{-1}$	x_A	V^E / $cm^3 \cdot mol^{-1}$	x_A	V^E / $cm^3 \cdot mol^{-1}$
sec-BC + Benzene		*sec*-BC + Toluene		*sec*-BC + *o*-Xylene		*sec*-BC + *m*-Xylene		*sec*-BC + *p*-Xylene	
0.0696	0.001	0.0856	−0.066	0.0784	−0.066	0.0694	−0.054	0.0881	−0.065
0.0840	0.002	0.1276	−0.096	0.1210	−0.112	0.1004	−0.078	0.1630	−0.126
0.1122	0.001	0.2495	−0.173	0.1509	−0.134	0.1390	−0.094	0.3481	−0.226
0.1524	0.002	0.3441	−0.212	0.1660	−0.147	0.2117	−0.122	0.4012	−0.248
0.1983	−0.002	0.4723	−0.232	0.2243	−0.201	0.2712	−0.143	0.4742	−0.254
0.2184	−0.005	0.5018	−0.234	0.3140	−0.262	0.3438	−0.150	0.5001	−0.258
0.2744	−0.005	0.5569	−0.232	0.3921	−0.292	0.4061	−0.156	0.5534	−0.252
0.3652	−0.018	0.6025	−0.221	0.4879	−0.310	0.4884	−0.162	0.6264	−0.234
0.4665	−0.026	0.6712	−0.206	0.5552	−0.295	0.5442	−0.162	0.6784	−0.206
0.5692	−0.044	0.7991	−0.146	0.6690	−0.246	0.6010	−0.156	0.7380	−0.175
0.6062	−0.048	0.9046	−0.072	0.7282	−0.212	0.7408	−0.134	0.7871	−0.146
0.7520	−0.054	0.9432	−0.044	0.8091	−0.142	0.8431	−0.106	0.8758	−0.086
0.8041	−0.046			0.8816	−0.086	0.9249	−0.062	0.9179	−0.052
0.8573	−0.040			0.9052	−0.064				
0.9032	−0.035								
0.9405	−0.025								
tert-BC + Benzene		*tert*-BC + Toluene		*tert*-BC + *o*-Xylene		*tert*-BC + *m*-Xylene		*tert*-BC + *p*-Xylene	
0.0821	−0.094	0.0932	−0.114	0.0698	−0.132	0.0875	−0.084	0.0816	−0.102
0.1115	−0.122	0.1243	−0.148	0.1023	−0.186	0.1216	−0.116	0.1212	−0.148
0.2016	−0.180	0.1832	−0.211	0.1642	−0.264	0.1973	−0.176	0.1874	−0.212
0.2989	−0.231	0.2556	−0.275	0.2090	−0.306	0.2724	−0.222	0.2585	−0.268
0.3140	−0.240	0.3342	−0.328	0.2653	−0.354	0.3516	−0.258	0.3080	−0.304
0.3587	−0.246	0.3895	−0.354	0.3321	−0.388	0.4307	−0.284	0.3746	−0.332
0.3959	−0.252	0.4280	−0.368	0.4187	−0.422	0.4832	−0.290	0.4539	−0.356
0.4460	−0.258	0.4952	−0.381	0.4979	−0.432	0.5214	−0.294	0.5117	−0.357
0.5551	−0.245	0.5467	−0.376	0.5984	−0.428	0.5768	−0.286	0.5918	−0.344
0.6721	−0.206	0.5985	−0.364	0.6627	−0.416	0.6580	−0.266	0.6635	−0.318
0.7422	−0.174	0.6356	−0.353	0.7452	−0.372	0.7305	−0.238	0.7516	−0.262
0.8280	−0.128	0.6889	−0.320	0.8056	−0.322	0.8543	−0.152	0.8683	−0.156
0.9140	−0.066	0.8102	−0.226	0.9113	−0.188	0.9112	−0.098	0.9321	−0.082
		0.8961	−0.130	0.9453	−0.124				
		0.9405	−0.074						

Table 3. Adjustable Parameters of Equation 1 and Standard Deviation (σ) for Various Butyl Chloride (BC) (A) + Aromatic Hydrocarbon (B) Mixtures at $T = 298.15$ K

system	A_0	A_1	A_2	A_3	$\sigma \cdot 10^3$
sec-BC + benzene	−0.1358	−0.2600	−0.0681	0.0249	2.3
sec-BC + toluene	−0.9401	0.0111	0.1214	−0.0164	2.3
sec-BC + *o*-xylene	−1.2287	0.1536	0.5440	−0.0355	2.5
sec-BC + *m*-xylene	−0.6417	0.0116	−0.3091	−0.0415	2.4
sec-BC + *p*-xylene	−1.0260	0.0582	0.3671	0.0165	2.1
tert-BC + benzene	−1.0270	0.2144	−0.0462	0.0320	2.9
tert-BC + toluene	−1.5170	−0.0591	0.2236	0.0552	1.6
tert-BC + *o*-xylene	−1.7332	−0.1379	−0.6444	−0.0463	1.9
tert-BC + *m*-xylene	−1.1659	−0.0820	0.0269	−0.0175	1.6
tert-BC + *p*-xylene	−1.4320	−0.0094	0.1154	0.0506	1.6

The V^E values for all the binary (A + B) systems were found to be negative, whereas these change sign for *sec*-butyl chloride + benzene from positive to negative at $x_A = 0.17$.

Although the V^E values for an equimolar mixture of *sec*-butyl chloride + aromatics vary in the order benzene > *m*-xylene > toluene > *p*-xylene > *o*-xylene, for an equimolar mixture of *tert*-butyl chloride + aromatics, they follow the sequence benzene > *m*-xylene > *p*-xylene > toluene > *o*-xylene. Diguet and Jadzyn[5] and Polo et al.[6] reported V^E data of *tert*-butyl chloride + benzene mixtures at $T = 293.15$ K. Our values are a little more negative than their values because of different temperatures in our case, although the shape of the V^E vs x_A curve is the same.

At the simplest qualitative level, the observed V^E values may be attributed to the resultant of two opposing effects. The positive contribution to V^E values arises from the disruption of orientation order of the pure component, and the negative contribution arises due to the formation of specific interactions of the electron donor−acceptor type between the chloride atom and π-electrons of aromatic hydrocarbons. When a methyl group is introduced in benzene (as in toluene), the electron density of the π-electron cloud increases, and these interactions become stronger which leads to a higher negative contribution and consequently the more negative values of V^E than the benzene + butyl chloride mixture. The introduction of two methyl groups in benzene (as in xylenes) should cause further enhancement of these attractive interactions, and it should further yield more negative values of V^E. However, it is not observed experimentally in all xylenes. It may be due to the presence of steric hindrance between the two methyl groups of xylene and the alkyl groups of butyl chloride, which might have restricted the proper orientation of these molecules and obstructed the chlorine atom toward the ring thus making interactions weaker as well as making the packing arrangement less effective in these mixtures. Among the three xylenes, *o*-xylene seems to offer minimum steric hindrance thus increasing electron donor−acceptor interaction to the maximum and hence making the V^E minimum.

As far as the effect of branching of the butyl group is concerned, it has been found that branching decreases the V^E, and the V^E of the system containing *tert*-butyl chloride is always less than that of the respective system having *sec*-butyl chloride which is further less than *n*-butyl chloride[10] at the same mole fraction. As V^E is a packing effect, this indicates that placement of three methyl groups in tertiary butyl chloride reduces the size of the molecule as compared to that of *sec*-butyl chloride where a chlorine atom is attached at the secondary carbon atom. This is also supported by the values of molar volume of *tert*-butyl chloride (110.71 $cm^3 \cdot mol^{-1}$), *sec*-butyl chloride (106.69 $cm^3 \cdot mol^{-1}$), and *n*-butyl chloride (105.08 $cm^3 \cdot mol^{-1}$). Thus,

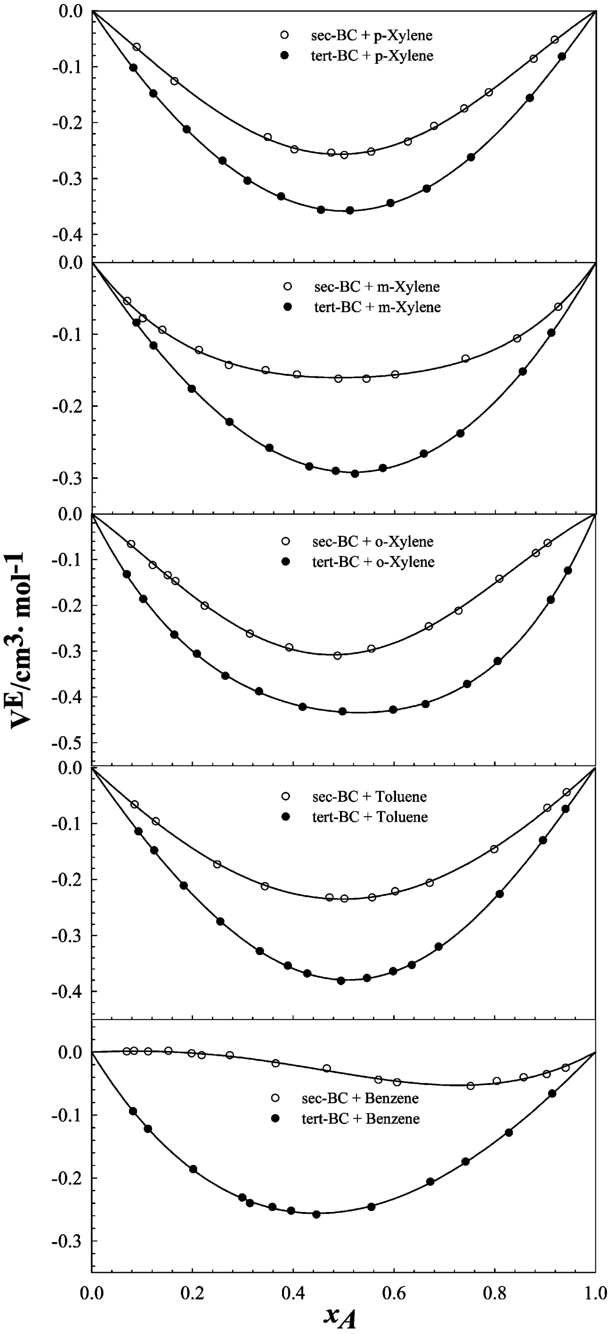

Figure 1. Molar excess volume for *sec*- and *tert*-butyl chloride (A) with aromatic hydrocarbons (B) at $T = 298.15$ K.

the small size of the *tert*-butyl chloride offers better packing with aromatics than the *sec*-butyl chloride and *n*-butyl chloride, and hence V^E decreases on branching in the following order: *n*-butyl chloride[10] > *sec*-butyl chloride > *tert*-butyl chloride. Similar behavior was also observed by Diguet and Jadzyn[5] for *n*-, *sec*-, and *tert*-butyl chloride + benzene mixtures.

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