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THERMODYNAMIC PROPERTIES OF SOME BINARY LIQUID MIXTURES CONTAINING *o*-CHLOROTOLUENE. EXCESS VOLUMES AND EXCESS ENTHALPIES OF *o*-CHLOROTOLUENE + SOME AROMATIC HYDROCARBONS

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ABSTRACT

The excess volumes at 298.15 and 308.15 K and excess enthalpies at 298.15 K have been reported for *o*-chlorotoluene + cyclohexane, + benzene, + toluene and + each of the xylenes as a function of composition. It is suggested that attractive interactions exist in *o*-chlorotoluene–aromatic hydrocarbons like chlorobenzene–aromatic hydrocarbons.

INTRODUCTION

In recent years considerable attention has been given to the properties of binary liquid mixtures of halobenzene + aromatic hydrocarbons [1–8]. Benson and co-workers [5–7] have reported the excess thermodynamic properties of chlorobenzene, *o*-dichlorobenzene and *m*-dichlorobenzene with a number of aromatic hydrocarbons. They have suggested that an attractive interaction exists between unlike molecules in halobenzene–aromatic hydrocarbon mixtures and this interaction is smallest in the chlorobenzene–benzene mixture and increases significantly when benzene is replaced by one of the alkylbenzenes. The purpose of the present investigation is to report the excess volumes and excess enthalpies for the binary mixtures of *o*-chlorotoluene with cyclohexane, benzene, toluene and three isomeric xylenes as the accumulation of further information about the thermodynamic properties of such mixtures is essential to a more complete understanding of the nature of the interaction between halobenzenes and aromatic hydrocarbons.

MATERIALS AND METHODS

BDH, A.R. grade reagent cyclohexane, benzene, toluene and xylenes were further purified as described earlier [9,10]. BDH, A.R. grade *o*-chlorotoluene was distilled and used as such without further purification. The purity of the component liquids was checked by comparing their densities with the corresponding literature values [11].

Excess volumes were determined dilatometrically [12] as a function of composition at 298.15 and 308.15 K, with a temperature control to ±0.005 K using a mercury–toluene regulator. Excess enthalpies were measured in a calorimeter designed in our laboratory. Details of the apparatus and the method of operation have been described previously [13,14].

RESULTS AND DISCUSSION

The experimental results of the molar excess volumes at 298.15 and 308.15 K and molar excess enthalpies at 298.15 K are given in Tables 1 and 2, respectively. In all cases x is the mole fraction of *o*-chlorotoluene. Each set of results was fitted with a smoothing function of the form

$$\frac{X^{\mathrm{E}}}{x(1-x)} = A + B(1-2x) + C(1-2x)^2 \tag{1}$$

where X^{E} represents either H^{E} or V^{E}. Values of the coefficients A, B and C and standard deviations, determined by the method of least squares with all points weighted equally, are given in Tables 3 and 4.

The excess enthalpies are positive for the mixtures of *o*-chlorotoluene with cyclohexane and benzene, with toluene it is almost zero. For *o*-chlorotoluene + *o*- and *m*-xylenes H^{E} is positive at low mole fractions of *o*-chlorotoluene but is negative over most of the composition range, whereas it becomes negative over the whole composition range for the *o*-chlorotoluene + *p*-xylene system. The excess volumes are also positive for the two systems containing cyclohexane and benzene; however, V^{E} is negative for the remaining four systems.

An examination of Tables 1 and 2 indicates that V^{E} and H^{E} of *o*-chlorotoluene with cyclic hydrocarbons follow the sequence: cyclohexane > benzene > toluene > xylenes. The large positive excess volumes and excess enthalpies for *o*-chlorotoluene + cyclohexane may arise mainly from the breaking of strong dipole–dipole interactions between the *o*-chlorotoluene molecules. The contribution to V^{E} and H^{E} due to size factor in this system is negligible because of the nearly same molar volumes of the two components. Further, V^{E} and H^{E} decreases rapidly on going from cyclohexane to benzene and it ultimately becomes negative in toluene and xylene mixtures. This trend in V^{E} and H^{E} is in accordance with the view that attractive interactions exist between unlike molecules in *o*-chlorotoluene–aromatic hydrocarbons. Their magnitude further suggests that this interaction is smallest in the *o*-chlorotoluene + benzene system and that it increases when benzene is replaced by one of the alkyl benzenes. However, positive V^{E} and H^{E} values for benzene and negative values for the others is probably due to the

TABLE 1

Experimental results for the molar excess volumes V^E for mixtures of *o*-chlorotoluene with some cyclic hydrocarbons

x	V^E(cm^3 mole^{-1})	x	V^E(cm^3 mole^{-1})
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ c-C_6H_{12}			
298.15 K			
0.1019	0.172	0.5032	0.402
0.1939	0.289	0.5838	0.362
0.2781	0.375	0.6514	0.322
0.3156	0.399	0.7025	0.294
0.3871	0.412	0.8428	0.175
308.15 K			
0.0693	0.158	0.5308	0.389
0.1333	0.241	0.6196	0.342
0.1939	0.288	0.7548	0.245
0.3079	0.370	0.8298	0.188
0.4159	0.414	0.8799	0.137
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ C_6H_6			
298.15 K			
0.0865	0.056	0.3631	0.176
0.1284	0.079	0.4321	0.178
0.1461	0.096	0.4818	0.181
0.1480	0.098	0.6151	0.150
0.1986	0.125	0.6840	0.133
0.2450	0.146	0.8093	0.091
0.2617	0.153	0.9361	0.035
0.3155	0.167		
308.15 K			
0.0621	0.038	0.4991	0.153
0.1719	0.097	0.5904	0.148
0.2963	0.133	0.7292	0.116
0.3617	0.142	0.7807	0.100
0.4419	0.152	0.8752	0.066
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ $C_6H_5CH_3$			
298.15 K			
0.0307	−0.002	0.6049	−0.030
0.1498	−0.014	0.6713	−0.025
0.2532	−0.025	0.8227	−0.014
0.3181	−0.031	0.8723	−0.010
0.4405	−0.036	0.9392	−0.003
0.5157	−0.034		
308.15 K			
0.1180	−0.018	0.5929	−0.045
0.2152	−0.030	0.6509	−0.041
0.3415	−0.043	0.7012	−0.036
0.4023	−0.046	0.7926	−0.025
0.4790	−0.047	0.9071	−0.012

TABLE 1 (continued)

x	V^E(cm^3 mole^{-1})	x	V^E(cm^3 mole^{-1})
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ 1,2-$C_6H_4(CH_3)_2$			
298.15 K			
0.1443	−0.015	0.5414	−0.042
0.2434	−0.025	0.6160	−0.041
0.3501	−0.035	0.6933	−0.035
0.4500	−0.041	0.7931	−0.024
0.4898	−0.042	0.8718	−0.015
308.15 K			
0.0950	−0.009	0.5687	−0.040
0.1885	−0.018	0.5795	−0.039
0.2393	−0.024	0.6525	−0.037
0.3520	−0.031	0.7422	−0.030
0.3979	−0.035	0.8427	−0.020
0.4620	−0.037	0.9260	−0.010
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ 1,3-$C_6H_4(CH_3)_2$			
298.15 K			
0.0933	−0.031	0.4412	−0.076
0.1301	−0.039	0.5101	−0.076
0.1734	−0.049	0.6348	−0.069
0.2060	−0.052	0.7521	−0.051
0.2383	−0.057	0.8462	−0.038
0.3489	−0.070	0.9646	−0.008
308.15 K			
0.0790	−0.026	0.4826	−0.075
0.1666	−0.045	0.5373	−0.074
0.2060	−0.052	0.5874	−0.071
0.2812	−0.062	0.6955	−0.061
0.3214	−0.065	0.7614	−0.052
0.4245	−0.073	0.9231	−0.023
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ 1,4-$C_6H_4(CH_3)_2$			
298.15 K			
0.1067	−0.031	0.5068	−0.081
0.1489	−0.046	0.5302	−0.081
0.2030	−0.056	0.6332	−0.076
0.2804	−0.067	0.7668	−0.060
0.3545	−0.075	0.8101	−0.051
0.4680	−0.080	0.8965	−0.031
308.15			
0.1111	−0.026	0.6540	−0.060
0.2068	−0.043	0.7510	−0.052
0.2823	−0.056	0.8592	−0.026
0.4205	−0.075	0.9540	−0.010
0.5171	−0.076		

TABLE 2

Experimental values of the molar excess enthalpies H^E for mixtures of *o*-chlorotoluene with some cyclic hydrocarbons at 298.15 K

x	H^E(J mole^{-1})	x	H^E(J mole^{-1})
x 1,2-$C_6H_4(CH_3)_3(Cl)+(1-x)$ c-C_6H_{12}			
0.0783	152.4	0.5583	502.6
0.2397	355.2	0.6173	487.1
0.3707	449.5	0.7439	410.8
0.4433	485.1	0.8112	336.5
0.5385	505.8	0.9442	130.5
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ C_6H_6			
0.0925	62.1	0.4831	163.4
0.1743	103.4	0.5000	162.2
0.2372	121.5	0.5715	158.2
0.2716	132.5	0.6575	141.1
0.2950	139.9	0.7711	102.4
0.4022	160.6	0.8140	86.7
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ $C_6H_5CH_3$			
0.2371	−0.4	0.5238	−0.9
0.3729	−1.2	0.6323	−0.7
0.4261	−0.8	0.7838	0
x-1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ 1,2-$C_6H_4(CH_3)_2$			
0.0960	4.4	0.5093	−45.0
0.2295	−9.1	0.6206	−44.5
0.2976	−24.8	0.7053	−40.9
0.4019	−38.6	0.7494	−36.8
0.4220	−41.0	0.9020	−13.9
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$1,3-$C_6H_4(CH_3)_2$			
0.0863	4.6	0.4958	−49.1
0.1301	0	0.6357	−51.7
0.2206	−15.5	0.8090	−35.9
0.2987	−25.6	0.8601	−27.5
0.4316	−41.7	0.9433	−14.8
x 1,2-$C_6H_4(CH_3)(Cl)+(1-x)$ 1,4-$C_6H_4(CH_3)_2$			
0.0854	−22.0	0.6012	−68.5
0.1978	−45.2	0.7120	−55.2
0.2297	−52.9	0.7319	−52.0
0.3712	−69.3	0.8373	−33.5
0.4513	−75.7	0.9130	−20.2
0.4986	−75.9		

difference in relative size of the molecules. Thus the present results indicate that attractive interactions are present in mixtures of halobenzene with aromatic hydrocarbons which are in agreement with the results obtained previously by Tanaka and Benson [5] for chlorobenzene + aromatic hydro-

TABLE 3

Values of the parameters of eqn. (1) for $X^E = V^E$(cm^3 mole^{-1}) and standard deviations $\sigma(V^E)$

System	T(K)	A	B	C	$\sigma(V^E)$ (cm^3 mole^{-1})
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) c-C_6H_{12}	298.15	1.594	−0.538	0.052	0.003
	308.15	1.551	−0.518	0.121	0.009
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) C_6H_6	298.15	0.664	−0.126	0.072	0.004
	308.15	0.621	−0.056	−0.024	0.003
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) $C_6H_5CH_3$	298.15	−0.139	0.021	0.063	0.003
	308.15	−0.189	0.020	0.059	0.002
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) 1,2-$C_6H_4(CH_3)_2$	298.15	−0.156	−0.008	0.036	0.003
	308.15	−0.156	−0.009	0.056	0.002
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) 1,3-$C_6H_4(CH_3)_2$	298.15	−0.307	0.053	0.013	0.003
	308.15	−0.299	0.056	0.006	0.002
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) 1,4-$C_6H_4(CH_3)_2$	298.15	−0.330	0.008	0.000	0.003
	308.15	−0.309	0.008	0.119	0.002

TABLE 4

Coefficients of eqn. (1) for $X^E = H^E$(J mole^{-1}) at 298.15 K and standard deviations $\sigma(H^E)$

System	A	B	B	$\sigma(H^E)$(J mole^{-1})
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) c-C_6H_{12}	1978.87	−192.76	390.05	6.74
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) C_6H_6	644.69	99.16	−5.07	2.90
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) 1,2-$C_6H_4(CH_3)_2$	−185.13	122.28	205.25	2.23
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) 1,3-$C_6H_4(CH_3)_2$	−161.89	163.34	31.66	6.23
x 1,2-$C_6H_4(CH_3)(Cl)$+(1 − x) 1,4-$C_6H_4(CH_3)_2$	−296.51	25.61	54.36	4.88

carbons. From the magnitude of H^E and V^E of *o*-chlorotoluene and chlorobenzene [5] with aromatic hydrocarbons it can be inferred that the interactions in *o*-chlorotoluene mixtures are probably weaker than those present in the corresponding chlorobenzene mixtures.

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