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Note

THERMODYNAMIC STUDIES OF BINARY MIXTURES CONTAINING AN ALIPHATIC AMINE AS ONE COMPONENT: EXCESS VOLUMES OF SOME DIETHYLAMINE SOLUTIONS

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A recent paper [1] from this laboratory reported excess volumes for binary mixtures of triethylamine with benzene, toluene, ethylbenzene, and the isomeric xylenes. As an extension of that work, we have made similar measurements for mixtures of diethylamine with the same set of aromatic compounds. The purpose of these investigations is to provide information about the thermodynamic properties of amine—aromatic hydrocarbon mixtures in an attempt to understand interactions between the molecules.

EXPERIMENTAL

The samples of aromatic hydrocarbons used were as in the previous studies [1]. These solvents were fractionally distilled immediately before use. Diethylamine (LR grade; B.D.H.) was purified by the procedure of Letcher and Bayles [2]; at 313.15 K the density (0.68355 g cm^{-3}) and at 298.15 K the refractive index (1.3822) agreed reasonably well with the values reported in the literature [2,3] (0.68472 g cm^{3} and 1.3820, respectively).

The molar excess volumes of mixing were calculated from the density measurements. The experimental details used in the preparation of solutions and measurement of densities have been described elsewhere [4]. The maximum uncertainty in excess volumes is expected to be around 0.007 cm^{3} mole^{-1}.

RESULTS AND DISCUSSION

The excess volumes of mixing for the six binary mixtures are recorded in Table 1 and plotted as a function of composition in Fig. 1. Excess volumes are expressed:

$$V^E\ (\mathrm{cm^3\ mole^{-1}}) = X_1X_2\ \{A + B(X_1 - X_2) + C(X_1 - X_2)^2 + D(X_1 - X_2)^3\} \quad (1)$$

where A, B, C and D are disposable parameters, and X_1, X_2 are the mole fractions of diethylamine and aromatic hydrocarbon, respectively. The parameters A, B, C and D evaluated by the least-squares method are recorded in Table 2 along with the standard deviation $\sigma(V^E)$.

Our data for the binary mixtures of diethylamine with benzene and with toluene at 313.15 K are compared with the results of Letcher [2,5] at 298.15 K in Fig. 1. A systematic trend in the two sets of data has been observed, with a negative temperature coefficient for V^E as expected. To the best of our knowledge, no V^E data have been reported in the literature for other binary mixtures considered here.

It can be seen from Fig. 1 that V^E decreases when a methyl group is added to the benzene ring, which is indicative of direct interaction between diethylamine and the π-electron system on the methyl-substituted benzene. The effect on the π-electron density of increasing the size of the alkyl group is significant. Increasing the length of the side chain makes the molecule more polarizable and presumably more strongly interacting via dispersion forces. If the substitution in the benzene ring is restricted to only a single alkyl group, one would expect V^E to decrease with increasing size of the alkyl group. A similar trend for V^E, decreasing in the order benzene > toluene > ethylbenzene, has also been reported for various other polar solvents as one component of the binary mixture [6—8].

TABLE 1

Excess volumes of mixing, V^E, for the binary mixtures at 313.5 K

X_1	V^E (cm^3 mole^{-1})	X_1	V^E (cm^3 mole^{-1})
Diethylamine (1) + benzene (2)		*Diethylamine (1) + o-xylene (2)*	
0.0922	−0.016	0.1166	−0.171
0.1722	−0.036	0.2207	−0.275
0.2698	−0.054	0.3374	−0.385
0.3637	−0.088	0.4347	−0.437
0.4617	−0.108	0.5397	−0.453
0.5640	−0.124	0.6318	−0.436
0.6682	−0.142	0.8216	−0.321
0.8846	−0.143	*Diethylamine (1) + m-xylene (2)*	
Diethylamine (1) + toluene (2)		0.1187	−0.131
0.1069	−0.129	0.2283	−0.222
0.2075	−0.217	0.3356	−0.280
0.3115	−0.279	0.4431	−0.305
0.4051	−0.318	0.6408	−0.296
0.6054	−0.389	0.7331	−0.282
0.8055	−0.329	0.9129	−0.152
Diethylamine (1) + ethylbenzene (2)		*Diethylamine (1) + p-xylene (2)*	
0.1186	−0.209	0.1172	−0.272
0.3392	−0.358	0.2463	−0.389
0.4435	−0.386	0.3356	−0.422
0.5402	−0.416	0.5433	−0.411
0.6377	−0.433	0.6405	−0.362
0.7341	−0.425	0.7328	−0.318
0.8239	−0.377	0.8269	−0.241

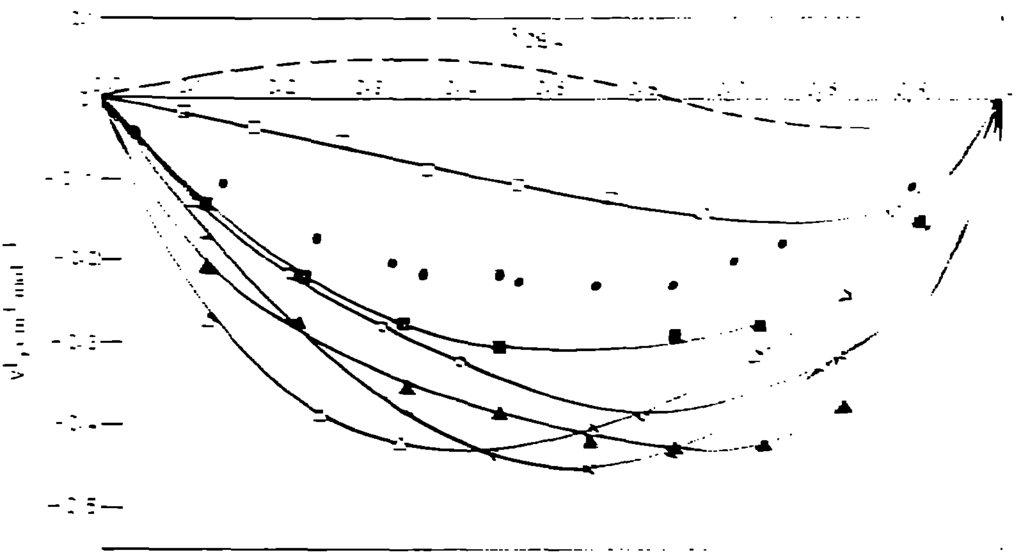

Fig. 1. Molar excess volumes of mixing at 313.15 K for the binary mixtures of diethylamine (DEA) + benzene (○), + toluene (□), + ethylbenzene (▲), + o-xylene (✕), + m-xylene (■), + p-xylene (△). (— — —) Calculated from smoothing equation in ref. 2 for DEA + benzene at 298.15 K. (●) Values of Letcher [5] for DEA + toluene at 298.15 K.

Introduction of a methyl group into toluene at the *meta* position increases V^E, where as introduction at *ortho*- and *para* positions causes a further decrease in V^E. This corresponds to the order *m*-xylene > toluene > *p*-xylene > *o*-xylene at $X_1 = 0.5$. This trend is in accordance with the expected magnitude of interactions of isomeric xylenes in view of the inductomeric effect caused by methyl groups and a nucleophilic molecule like diethylamine.

For a complete understanding of the nature of the interactions, further investigations on the thermodynamic properties of such mixtures are under way.

TABLE 2

Parameters of eqn. (1) and standard deviation $\sigma(V^E)$ of experimental values at 313.15 K

System (1) + (2)	Parameters of eqn. (1) *A*	 *B*	 *C*	 *D*	Standard deviation $\sigma(V^E)$ ($cm^3\ mole^{-1}$)
Diethylamine + benzene	−0.4357	−0.419	0.615	0.598	0.007
Diethylamine + toluene	−1.4462	−0.663	0.688	0.030	0.006
Diethylamine + ethylbenzene	−1.6147	−0.518	1.443	0.140	0.002
Diethylamine + *o*-xylene	−1.7880	−0.360	0.307	0.130	0.005
Diethylamine + *m*-xylene	−1.2355	−0.064	0.500	0.518	0.003
Diethylamine + *p*-xylene	−1.6482	−0.387	0.884	0.356	0.007

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