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Excess Volumes for Binary Liquid Mixtures of 1,2-Dichloroethane with Benzene, Toluene, *p*-Xylene, Quinoline, and Cyclohexane

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Dilatometric measurements of excess volumes (V^E) have been made for binary liquid mixtures of 1,2-dichloroethane (CH_2ClCH_2Cl) with benzene, toluene, *p*-xylene, and quinoline at 298.15 and 308.15 K, and for mixtures of CH_2ClCH_2Cl with cyclohexane at 308.15 K. The values of V^E have been found to be positive for CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl–*p*-xylene, and CH_2ClCH_2Cl–cyclohexane and negative for CH_2ClCH_2Cl–quinoline.

Introduction

The binary systems of 1,2-dichloroethane (CH_2ClCH_2Cl) with aromatic hydrocarbons, quinoline, and cyclohexane are of considerable interest from the viewpoint of the presence of specific interaction between the components in the liquid state. The specific interaction of CH_2ClCH_2Cl with aromatic hydrocarbons and quinoline can be visualized to be due to the presence of two Cl atoms and four H atoms in CH_2ClCH_2Cl on account of which it can act as a σ-acceptor toward, and be involved in hydrogen-bond formation with, the aromatic hydrocarbons and quinoline. The aromatic hydrocarbons in their interaction with CH_2ClCH_2Cl will act as π-donors, whereas quinoline will act as an n-donor. The system CH_2ClCH_2Cl–cyclohexane, in which only dispersion, dipolar, and induction forces are believed to be present between the components, is of interest as it can be used as a reference system. Extensive studies of the interactions between the components of such systems have not been made. In the present program, we have made measurements of excess volumes for binary liquid mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, quinoline, and cyclohexane at various temperatures, and the results obtained are interpreted in this paper.

Experimental Section

Benzene (AR, BDH), toluene (AR, BDH), and *p*-xylene (Merck-Schuchardt) of synthesis quality were purified in a manner similar to that described by Nath and Tripathi (*1*). Cyclohexane (BDH) of reagent grade was subjected to treatments with nitrating mixture, with distilled water, and with dilute sodium hydroxide solution. Further, it was washed thoroughly with distilled water, and then dried over anhydrous calcium

Table I. Experimental Values of Excess Volumes for the Various Systems of CH_2ClCH_2Cl at 298.15 and 308.15 K

temp, K	x_1[a]	V^E, cm^3 mol^{-1}	temp, K	x_1[a]	V^E, cm^3 mol^{-1}
CH_2ClCH_2Cl–Benzene				0.6653	0.259
298.15	0.2699	0.193		0.7226	0.247
	0.2828	0.195		0.8547	0.161
	0.3399	0.213	308.15	0.1450	0.108
	0.4474	0.232		0.3411	0.217
	0.5467	0.228		0.4323	0.250
	0.6166	0.215		0.6021	0.273
	0.7359	0.175		0.6832	0.264
	0.7621	0.162		0.7584	0.237
308.15	0.1785	0.118		0.7768	0.225
	0.2040	0.131		0.8318	0.188
	0.2987	0.181			
	0.3643	0.205	CH_2ClCH_2Cl–Quinoline		
	0.4122	0.216	298.15	0.2266	−0.115
	0.4810	0.228		0.3594	−0.155
	0.6213	0.212		0.3624	−0.162
	0.7150	0.177		0.4125	−0.167
	0.7247	0.167		0.6100	−0.145
				0.7602	−0.096
CH_2ClCH_2Cl–Toluene			308.15	0.2630	−0.146
298.15	0.1482	0.061		0.2871	−0.154
	0.2351	0.092		0.4288	−0.182
	0.2385	0.095		0.5680	−0.169
	0.3548	0.127		0.6435	−0.154
	0.4812	0.157		0.7415	−0.120
	0.6687	0.155		0.7483	−0.114
	0.8418	0.102		0.8157	−0.089
	0.8939	0.073			
308.15	0.3370	0.141	CH_2ClCH_2Cl–Cyclohexane		
	0.3468	0.142	308.15	0.2045	0.750
	0.3990	0.156		0.2683	0.884
	0.5494	0.176		0.3361	0.978
	0.6726	0.166		0.4974	1.040
	0.7386	0.151		0.5275	1.031
	0.8751	0.092		0.7056	0.815
				0.7792	0.654
CH_2ClCH_2Cl–*p*-Xylene				0.8303	0.532
298.15	0.1577	0.100			
	0.2386	0.154			
	0.4482	0.254			
	0.5823	0.273			

[a] x_1 refers to the mole fraction of CH_2ClCH_2Cl.

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Table II. Values of the Least-Squares Constants A, B, and C of Eq 1, and the Standard Deviations $\delta(V^E)$ for the Various Systems of CH_2ClCH_2Cl at 298.15 and 308.15 K

system	T, K	A, cm^3 mol^{-1}	B, cm^3 mol^{-1}	C, cm^3 mol^{-1}	$\delta(V^E)$, cm^3 mol^{-1}
CH_2ClCH_2Cl–benzene	298.15	0.9264	−0.0783	0.0383	0.0012
	308.15	0.9080	−0.0002	−0.2705	0.0020
CH_2ClCH_2Cl–toluene	298.15	0.6296	0.2027	−0.0190	0.0020
	308.15	0.6883	0.1911	0.0160	0.0010
CH_2ClCH_2Cl–p-xylene	298.15	1.0631	0.3861	−0.0822	0.0028
	308.15	1.0681	0.3568	0.1090	0.0013
CH_2ClCH_2Cl–quinoline	298.15	−0.6665	0.1387	0.2710	0.0034
	308.15	−0.7161	0.1373	0.1143	0.0020
CH_2ClCH_2Cl–cyclohexane	308.15	4.1629	−0.6752	0.1201	0.0033

chloride, and finally distilled from phosphorus pentoxide. Quinoline (BDH) was subjected to several fractional distillations under reduced pressure. 1,2-Dichloroethane (BDH) was purified by the method described by Foster and Fyfe (*12*). The densities of the purified components measured at 303.15 K were found to be in good agreement with the available data (*2*).

Excess volumes (V^E), which are accurate to ±0.002 cm^3 mol^{-1}, were measured by using a two-limbed dilatometer which was similar to that used in earlier measurements (*3*–*7*). The working of the dilatometer was tested as described earlier (*4*).

Results and Discussion

The experimental values of the excess molar volumes V^E for binary mixtures of CH_2ClCH_2Cl with benzene, toluene, p-xylene, quinoline, and cyclohexane are given in Table I and have been fitted by least squares to the following equation:

$$V^E = X_1X_2\,[A + B(X_1 - X_2) + C(X_1 - X_2)^2] \qquad (1)$$

In eq 1, X_1 refers to the mole fraction of CH_2ClCH_2Cl, X_2 refers to the mole fraction of aromatic hydrocarbon, quinoline, and cyclohexane, and A, B, and C are constants characteristic of a system at a given temperature. The values of the constants A, B, and C along with the standard deviations $\delta(V^E)$ for the various systems of CH_2ClCH_2Cl at 298.15 and 308.15 K are given in Table II.

The values of V^E for CH_2ClCH_2Cl–benzene have been reported earlier by Coulson et al. (*8*) and by Rowlinson (*9*). Rowlinson (*9*) has discussed that V^E for this system is symmetrical with a maximum of 0.240 cm^3 mol^{-1} at 297.15 K and of 0.210 cm^3 mol^{-1} at 323.15 K. Our values of V^E at $X_1 = 0.5$ for CH_2ClCH_2Cl–benzene at 298.15 and 308.15 K are 0.232 and 0.227 cm^3 mol^{-1}, respectively, which are in good agreement with the data reported earlier (*8*–*10*).

Table I shows that throughout the whole range of composition the values of V^E are positive for CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl–p-xylene, and CH_2ClCH_2Cl–cyclohexane, and negative for CH_2ClCH_2Cl–quinoline. The values of V^E for CH_2ClCH_2Cl–cyclohexane are found to be highly positive in comparison to those for the systems CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, and CH_2ClCH_2Cl–p-xylene. V^E at $X_1 = 0.5$ for the various systems has the sequence

$$(V^E)_{\text{cyclohexane}} > (V^E)_{p\text{-xylene}} > (V^E)_{\text{benzene}} > (V^E)_{\text{toluene}} > (V^E)_{\text{quinoline}}$$

The data show that the values of the temperature coefficient $(\partial V^E/\partial T)_P$ are positive for CH_2ClCH_2Cl–toluene and CH_2ClCH_2Cl–p-xylene, and negative for CH_2ClCH_2Cl–benzene and CH_2ClCH_2Cl–quinoline. The negative values of V^E for CH_2ClCH_2Cl–quinoline indicate the existence of specific interaction between CH_2ClCH_2Cl and quinoline. Further, the positive values of $(\partial V^E/\partial T)_P$ for the systems CH_2ClCH_2Cl–toluene and CH_2ClCH_2Cl–p-xylene also indicate the existence of specific interaction between CH_2ClCH_2Cl and the aromatic hydrocarbons. The negative values of $(\partial V^E/\partial T)_P$ for CH_2ClCH_2Cl–quinoline can be explained to be due to the fact that the quinoline molecules are self-associated (*11*) through hydrogen bonding, whereas the negative values of $(\partial V^E/\partial T)_P$ for CH_2ClCH_2Cl–benzene can be visualized to be due to the predominance of the contributions to V^E from dipolar forces over those from specific interactions.

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Registry No. CH_2ClCH_2Cl, 107-06-2; benzene, 71-43-2; toluene, 108-88-3; p-xylene, 106-42-3; cyclohexane, 110-82-7; quinoline, 91-22-5.

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