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Excess Volumes for Binary Liquid Mixtures of Acetone with Benzene, Toluene, *p*-Xylene, Mesitylene, and Cyclohexane

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Excess volumes (V^E) for binary liquid mixtures of acetone with benzene, toluene, *p*-xylene, and mesitylene at 298.15 and 308.15 K, and for mixtures of acetone with cyclohexane at 298.15 K, have been measured by using a dilatometer. Values of V^E for the various systems have been fitted by least squares to the equation $V^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$ where x_1 refers to the mole fraction of acetone, x_2 refers to the mole fraction of aromatic hydrocarbon or cyclohexane, and A, B, and C are constants characteristic of a system. At both temperatures, 298.15 and 308.15 K, values of V^E have been found to be negative for acetone–benzene, acetone–toluene, and acetone–*p*-xylene and positive for acetone–mesitylene. For acetone–cyclohexane at 298.15 K, the values of V^E have been found to be positive. The negative values of V^E for the systems of acetone with benzene, toluene, and *p*-xylene suggest the existence of specific interaction between acetone and aromatic hydrocarbons.

Introduction

Murrell and Gil (*1*) have observed from NMR spectral studies that benzene forms a weak hydrogen bond with pyridine in the liquid state. Further, Rastogi, Nath, and Yadava (*2*) have made measurements of excess volumes and excess enthalpies for binary liquid mixtures of benzene with diethyl ether, and on the basis of these measurements these workers have suggested the formation of a weak hydrogen bond between benzene and diethyl ether on account of the partial positive charge on the hydrogen atom of benzene and the negative charge on the oxygen atom of diethyl ether. Pyridine and diethyl ether are n-type electron donors. We are interested in knowing if excess volumes for binary liquid mixtures of benzene and other aromatics with acetone give indications of the existence of similar types of interactions of aromatics with acetone, which is also an n-type electron donor. Hence, in the present program, we have made measurements of excess volumes for binary liquid mixtures of acetone with benzene, toluene, *p*-xylene, and mesitylene at 298.15 and 308.15 K. Excess volumes for the system acetone–cyclohexane have also been measured at 298.15 K, and the results of measurements of excess volumes for the various systems have been discussed in this paper.

Experimental Section

Benzene (AR, BDH) and toluene (AR, BDH) were purified as described earlier (*3*, *4*). *p*-Xylene (Pfizer) of reagent grade was subjected to treatments with concentrated sulfuric acid, with distilled water, with dilute sodium carbonate solution, and again with distilled water. The sample so obtained was dried over anhydrous calcium chloride and then subjected to fractional crystallizations, followed by fractional distillation. Mesitylene (E. Merck) was purified by the method described by McGlashan, Stubley, and Watts (*5*). Cyclohexane (BDH) of reagent grade was subjected to treatments with nitrating mixture, with distilled water, with dilute sodium hydroxide solution, and again with distilled water. Further, it was thoroughly dried over anhydrous calcium chloride and then fractionally distilled from phosphorus pentoxide. Acetone (Rechem) of electronic grade was placed over anhydrous calcium chloride overnight and then fractionally distilled from P_2O_5 several times. The densities of the purified components measured at 303.15 K were found to be in good agreement with the available data (*6*).

Excess volumes (V^E) correct to ±0.002 cm^3 mol^{-1} were measured by using a dilatometric technique similar to that used by Nath and Dubey (*3*). The working of the dilatometer was tested as described earlier (*3*).

Results and Discussion

The experimental values of V^E for the various systems of acetone are given in Table I and have been fitted by the method of least squares to the following equation:

$$V^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (1)$$

In eq 1, x_1 refers to the mole fraction of acetone, x_2 refers to the mole fraction of aromatic hydrocarbon or 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 $\sigma(V^E)$ for the various systems at 298.15 and 308.15 K are given in Table II. The values of V^E for the various systems at 298.15 K have been plotted against x_1 in Figure 1.

The measurements of V^E for acetone–benzene at 298.15 K have also been made by Brown and Smith (*7*) and by Campbell, Kartzmark, and Chatterjee (*8*). The results of V^E for this system as obtained by Brown and Smith (*7*) are in good agreement with our results. The results of Campbell, Kartzmark, and Chatterjee (8), which we obtained from the Depository of Unpublished Data, National Science Library, National Research Council, Ottawa, Canada, are in good agreement with our results at low mole fractions of acetone. At mole fractions x_1 equal to 0.8708 and above, Campbell, Kartzmark, and Chatterjee (*8*) have obtained positive values of V^E, their highest positive value of V^E being 0.033 cm^3 mol^{-1} at x_1 equal to 0.9563. We have made measurements of V^E for acetone–benzene at 298.15 K up to mole fraction x_1 equal to 0.9593 and have not obtained positive values of V^E. Brown and Smith (*7*) have also not obtained positive values of V^E for this system, and the reason for the discrepancy concerning the positive values of V^E at higher mole fractions of acetone as obtained by Campbell et al. (*8*) is not obvious.

At both temperatures, 298.15 and 308.15 K, and throughout the whole range of composition, the values of V^E have been found to be negative for acetone–benzene, acetone–toluene, and acetone–*p*-xylene and positive for acetone–mesitylene. The values of V^E at 298.15 K are highly positive for acetone–cyclohexane. For acetone–aromatics at any fixed composition, the values of V^E have the sequence

mesitylene > benzene > *p*-xylene > toluene

The above complex sequence along with the negative values of V^E for the systems acetone–benzene, acetone–toluene, and

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Table I. Experimental Values of the Excess Volumes V^E for the Various Systems of Acetone at 298.15 and 308.15 K

temp = 298.15 K		temp = 308.15 K	
x_1[a]	V^E, cm^3 mol^{-1}	x_1[a]	V^E, cm^3 mol^{-1}
	Acetone–Benzene		
0.0899	−0.019	0.0993	−0.023
0.1137	−0.027	0.1774	−0.045
0.2780	−0.058	0.2118	−0.055
0.3782	−0.066	0.3184	−0.076
0.5366	−0.069	0.4417	−0.092
0.7031	−0.052	0.5503	−0.089
0.7280	−0.049	0.6019	−0.085
0.8841	−0.023	0.6286	−0.082
0.9458	−0.011	0.7260	−0.065
0.9494	−0.010	0.7779	−0.052
0.9593	−0.007	0.8274	−0.041
		0.8689	−0.032
		0.9055	−0.025
		0.9579	−0.010
	Acetone–Toluene		
0.1219	−0.073	0.1101	−0.067
0.2066	−0.111	0.2452	−0.132
0.3454	−0.148	0.2553	−0.137
0.5265	−0.163	0.2616	−0.138
0.7054	−0.130	0.4270	−0.177
0.7852	−0.105	0.4767	−0.182
0.8823	−0.063	0.5540	−0.176
0.9188	−0.047	0.5786	−0.170
		0.6097	−0.165
		0.6340	−0.159
		0.6840	−0.145
		0.8419	−0.078
	Acetone–*p*-Xylene		
0.0984	−0.033	0.1349	−0.039
0.3074	−0.092	0.2214	−0.066
0.3933	−0.101	0.2437	−0.074
0.4696	−0.108	0.2914	−0.086
0.5518	−0.106	0.5081	−0.104
0.7217	−0.095	0.5637	−0.100
0.8420	−0.060	0.5915	−0.098
		0.6348	−0.096
		0.6878	−0.086
		0.7898	−0.066
		0.8025	−0.064
	Acetone–Mesitylene		
0.1885	0.061	0.1319	0.055
0.2301	0.086	0.1525	0.064
0.3129	0.111	0.2138	0.091
0.5005	0.156	0.3657	0.141
0.7990	0.126	0.4632	0.172
0.9267	0.060	0.7960	0.135
		0.8672	0.101
		0.9045	0.074
		0.9134	0.066
	Acetone–Cyclohexane		
0.1437	0.578		
0.3424	1.001		
0.4709	1.072		
0.5697	1.073		
0.7710	0.801		
0.8359	0.648		

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

Table II. Values of the Constants A, B, and C of Eq 1, and the Standard Deviations $\sigma(V^E)$, for the Various Systems of Acetone 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}	$\sigma(V^E)$, cm^3 mol^{-1}
acetone–benzene	298.15	−0.2797	0.0238	0.0719	0.0016
	308.15	−0.3623	0.0021	0.1397	0.0018
acetone–toluene	298.15	−0.6459	0.0426	−0.00964	0.0017
	308.15	−0.7190	0.0793	0.1650	0.0011
acetone–*p*-xylene	298.15	−0.4401	−0.0502	0.0367	0.0043
	308.15	−0.4170	−0.0146	0.0921	0.0026
acetone–mesitylene	298.15	0.6249	0.3039	−0.0163	0.0051
	308.15	0.7030	0.2512	−0.0727	0.0027
acetone–cyclohexane	298.15	4.3391	0.0217	0.7585	0.0092

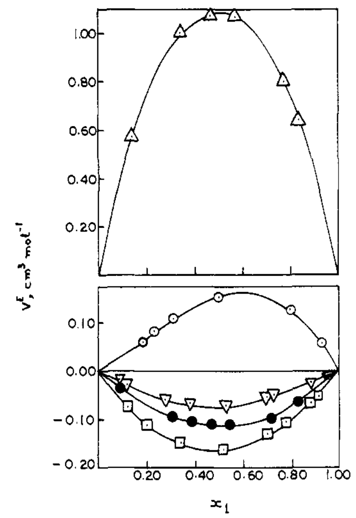

Figure 1. Excess volumes at 298.15 K: (▽) acetone–benzene; (□) acetone–toluene; (●) acetone–*p*-xylene; (○) acetone–mesitylene; (△) acetone–cyclohexane. The smoothed curves are based on the constants A, B, and C of Table II.

acetone–*p*-xylene indicates that the dipole interaction is not the only cause of the deviations and the electron donor and acceptor properties of the components also play an important part. There is the likelihood of the interaction of the hydrogen atom of the aromatic ring with the lone-pair electrons of acetone, leading to the formation of a weak hydrogen bond. The positive values of V^E for the systems acetone–mesitylene and acetone–cyclohexane can be attributed to the fact that the dispersion forces are predominant between the components in these cases.

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Registry No. Acetone, 67-64-1; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; mesitylene, 108-67-8; cyclohexane, 110-82-7.

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