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Excess Volumes of 1-Propanol and 2-Propanol with Aromatic Hydrocarbons at 298.15 K

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The excess volumes for binary mixtures of 1-propanol or 2-propanol + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene have been measured over the entire range of composition at 298.15 K. The excess volume curves for 1-propanol + toluene, + *o*-xylene, and + *p*-xylene systems are sigmoids. For other mixtures, the V^E values are positive over most of the concentration range, but are slightly negative at $x_1 > 0.8$. The system 2-propanol + benzene is positive over the entire range of composition.

Introduction

Alcohol molecules are known to be self-associated (*1–4*) through hydrogen-bonded linear chains into variable degrees of polymerization. The degree and strength of polymerization decrease with increasing hydrocarbon chain length and also with branching of the alkyl group. The binary solutions of alcohols with inert nonpolar solvents generally break the three-dimensional hydrogen-bonded network of pure alcohols to give positive values of excess thermodynamic properties like V^E, H^E, and G^E (*3, 5*). However, aromatic hydrocarbons are potential electron donors, and their mixtures with alkyl halides have been interpreted in terms of charge-transfer interactions between the π-electrons of the aromatic ring and the empty 3d levels of the halogens in alkyl halides (*6–9*).

A good deal of work has been reported on excess volumes of various alcohols with benzene and toluene (*3, 10, 11*). In order to obtain more information regarding the nature of interactions in 1-propanol and 2-propanol with aromatic hydrocarbons, we selected 10 systems: 1-propanol and 2-propanol with benzene, toluene, and *o*-, *m*-, and *p*-xylenes. The excess volumes, V^E, for these binary mixtures were measured over the whole range of composition at 298.15 K.

Experimental Section

1-Propanol, 2-propanol, benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene (Ranbaxy AR grade) were purified by standard procedures (*12*). The purities of the final samples were checked by density determinations at 298.15 ± 0.01 K, which agreed to within ±0.000 05 g cm^{-3} with the corresponding literature values (*10, 13–15*) as reported in Table 1.

The excess volumes as a function of composition were measured dilatometrically as described by Nigam et al. (*16*). The temperature of the water bath was controlled to 0.01 K.

Results

The results for the binary mixtures of 1-propanol and 2-propanol + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene as a function of composition at 298.15 K are recorded in Table 2 and shown graphically in Figures 1 and 2. The results were fitted to the equation

Table 1. Densities of the Pure Components at 298.15 K

	ρ/(g cm^{-3})			ρ/(g cm^{-3})	
material	present work	lit.	material	present work	lit.
1-propanol	0.799 62	0.799 59 (*10*)	*o*-xylene	0.875 81	0.875 83 (*14*)
2-propanol	0.781 02	0.781 00 (*10*)	*m*-xylene	0.860 00	0.859 99 (*15*)
benzene	0.873 73	0.873 72 (*13*)	*p*-xylene	0.856 71	0.856 73 (*15*)
toluene	0.862 23	0.862 24 (*13*)			

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3] \quad (1)$$

where x_1 and x_2 are the mole fractions of alcohols and aromatic hydrocarbons, respectively. *A–D* are adjustable parameters. These parameters were evaluated by the method of least squares and are given, together with the standard deviations of V^E, in Table 3. The plots of ΔV [$V^E_{\text{exptl}} - V^E_{\text{calcd}}$ (from eq 1)] vs x_1 show a random distribution of ΔV over the whole composition range, thus confirming a best or near best fit of data in the Redlich–Kister equation (1).

Discussion

The V^E results for 1-propanol and 2-propanol with benzene at 298.15 K have been reported by Brown and Smith (*10*) and compared with the earlier studies on these systems. Our experimental curve for the 2-propanol + benzene system is in excellent agreement with that reported by them. However, for the 1-propanol + benzene system, our V^E values are slightly greater (at the most 0.02 cm^3 mol^{-1}) at mole fractions $x_1 > 0.30$ than those of Brown and Smith. V^E values of the toluene + 1-propanol and 2-propanol systems at 303.15 K are also reported in the literature (*3*). Their values are higher than our values at each mole fraction because reported values are at a different temperature (5 K more than ours). However, the general shapes of the curves are the same.

The curves for the mixtures of 1-propanol + toluene, + *o*-xylene, and + *p*-xylene are sigmoids. The excess volumes for these systems are positive at lower mole fractions and negative at higher mole fractions of alcohols. For other mixtures (1-propanol + *m*-xylene, 2-propanol + aromatic hydrocarbons) the values of V^E are positive over most of the concentration range. They are slightly negative at $x_1 > 0.8$. The system 2-propanol + benzene is positive over the entire range of concentration. V^E values for 2-propanol + aromatic hydrocarbon systems are always more than those of 1-propanol

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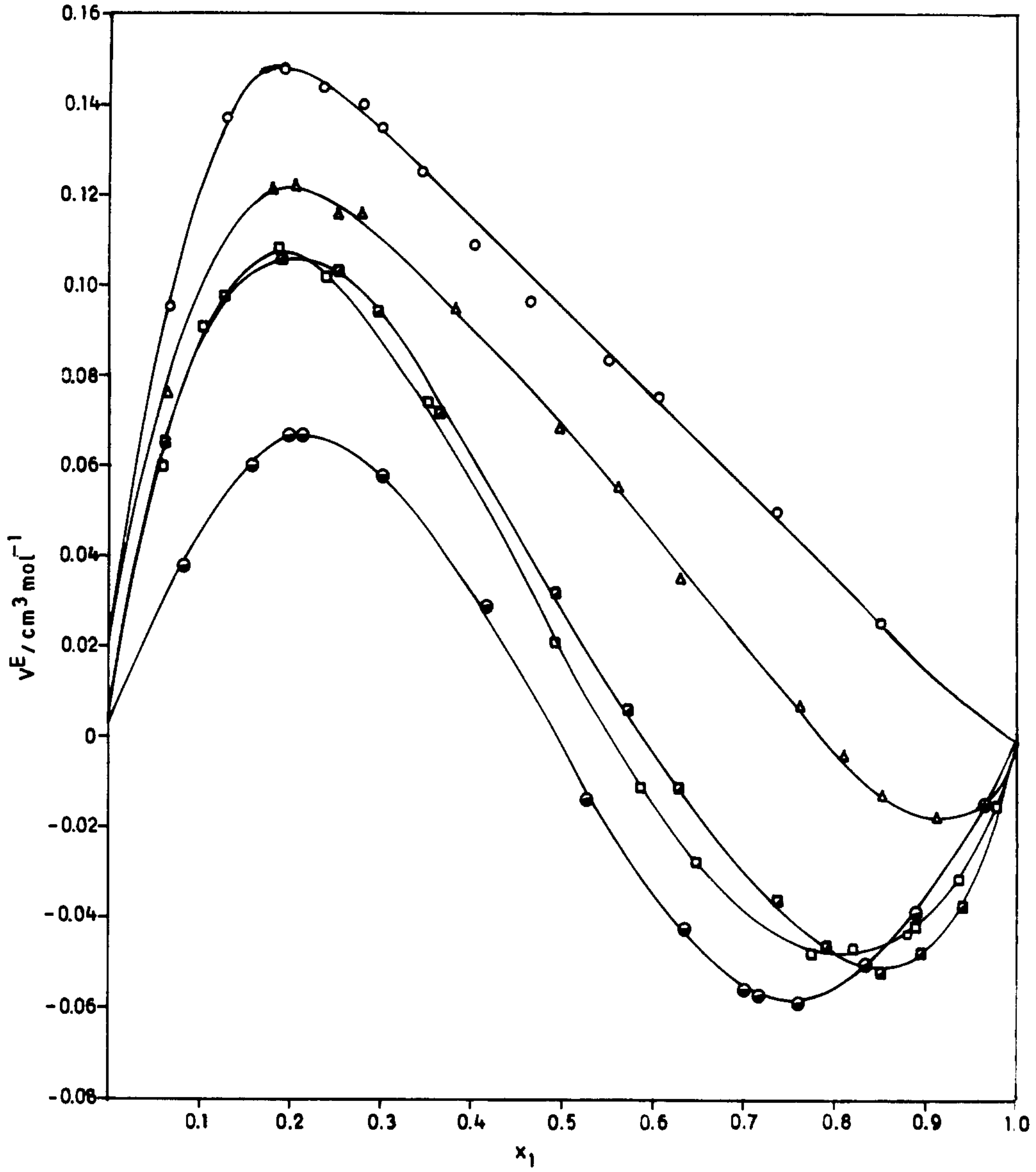

Figure 1. Variation of molar excess volume for 1-propanol (1) + benzene (2) (○), + toluene (2) (⊖), + *o*-xylene (2) (□), + *m*-xylene (2) (△), and + *p*-xylene (2) (◪) at 298.15 K.

+ aromatic hydrocarbon systems. All the curves are skewed toward the low mole fractions of alcohols.

For 1-propanol + aromatic hydrocarbon mixtures the V^E falls in the order

benzene > *m*-xylene > *p*-xylene ≈ *o*-xylene > toluene

while for 2-propanol + aromatic hydrocarbon mixtures the magnitude of V^E varies:

benzene ≈ *m*-xylene > *p*-xylene > toluene ≈ *o*-xylene

The observed V^E data may be explained qualitatively by postulating that V^E is the resultant of opposing effects. The positive values arise due to the breaking or stretching of hydrogen bonds in the self-associated alcohols and physical dipole–dipole interactions between alcohol monomers and multimers and due to the disruption in the favorable orientational order of aromatic hydrocarbons. Negative contributions arise from changes of "free volumes" in the real mixtures and the presence of electron donor–acceptor-type interactions between alcohols and aromatic hydrocarbons (aromatic hydrocarbons behave as electron donors).

As the V^E values for benzene + alcohol systems are positive over the entire range of composition and also the curves are skewed toward the low mole fraction of alcohol, this clearly indicates the effects contributing to the positive V^E values outweigh the effects responsible for the negative contribution. At high mole fractions of alcohols, the V^E values tend to be negative, showing the breaking up of the three-dimensional associated network of the alcohol is not complete and the aromatic hydrocarbon molecules are more or less fitted into the alcohol network. Thus, the V^E values are negative or less positive at high concentrations of alcohols. For the 1-propanol + toluene system, the V^E values at $x_1 > 0.5$ are negative, showing more comfortable fitting of toluene molecules in the associated network of alcohol molecules. This may be due to the enhanced electron-donating power of toluene as compared to benzene. But for xylenes, it seems that the packing of these molecules is sterically hindered by two methyl groups, which are attached to the aromatic ring. With xylenes, the placement of two methyl groups in *m*-xylene seems to be such that they offer maximum steric hindrance; as a result maximum positive values of V^E are obtained.

Among the 1-propanol + aromatic hydrocarbon and 2-propanol + aromatic hydrocarbon systems, the V^E values are always higher for the latter at the respective mole fractions. This again supports our above argument that the branching of the alkyl group in 2-propanol will create more steric hindrance for the proper orientation of aromatic hydrocarbon molecules to fit in the associated network of alcohols.

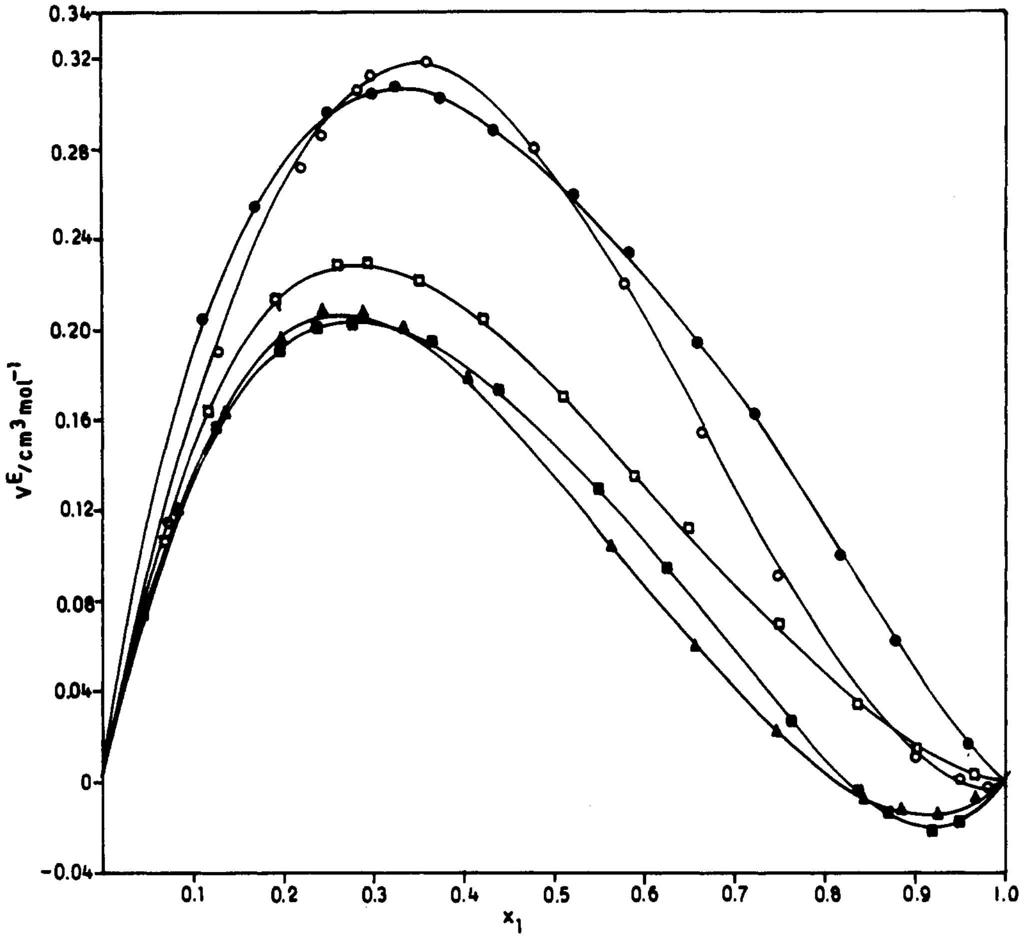

Figure 2. Variation of molar excess volume for 2-propanol (1) + benzene (2) (●), + toluene (2) (■), + *o*-xylene (2) (▲), + *m*-xylene (2) (○), and + *p*-xylene (2) (■) at 298.15 K.

Table 2. Excess Volumes of Alcohols + Aromatic Hydrocarbons at 298.15 K

x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})
		1-Propanol (1) + Benzene (2)						2-Propanol (1) + Benzene (2)			
0.0632	0.095	0.2968	0.135	0.6038	0.075	0.1121	0.204	0.3747	0.303	0.7238	0.162
0.1238	0.137	0.3455	0.125	0.7368	0.050	0.1689	0.255	0.4379	0.289	0.8182	0.100
0.1912	0.148	0.3962	0.109	0.8511	0.025	0.2487	0.296	0.5249	0.260	0.8801	0.062
0.2335	0.144	0.4662	0.096	0.9333	0.006	0.2996	0.304	0.5837	0.234	0.9614	0.017
0.2786	0.140	0.5491	0.083			0.3262	0.308	0.6629	0.194		
		1-Propanol (1) + Toluene (2)						2-Propanol (1) + Toluene (2)			
0.0793	0.038	0.4158	0.029	0.7571	−0.059	0.0469	0.075	0.3662	0.195	0.8356	−0.003
0.1536	0.060	0.5266	−0.014	0.8365	−0.050	0.1278	0.158	0.4392	0.174	0.8722	−0.014
0.1965	0.067	0.6339	−0.042	0.8923	−0.039	0.1959	0.192	0.5510	0.129	0.9173	−0.021
0.2122	0.067	0.6969	−0.056	0.9651	−0.015	0.2364	0.201	0.6239	0.095	0.9492	−0.018
0.2998	0.058	0.7172	−0.057			0.2758	0.203	0.7611	0.026		
		1-Propanol (1) + *o*-Xylene (2)						2-Propanol (1) + *o*-Xylene (2)			
0.0568	0.060	0.4892	0.021	0.8788	−0.043	0.0832	0.120	0.3369	0.200	0.8392	−0.005
0.1027	0.091	0.5866	−0.011	0.8927	−0.042	0.1332	0.164	0.4063	0.179	0.8839	−0.012
0.1869	0.108	0.6432	−0.028	0.9361	−0.031	0.1861	0.193	0.5661	0.105	0.9242	−0.014
0.2356	0.102	0.7734	−0.048	0.9731	−0.015	0.2468	0.208	0.6551	0.060	0.9647	−0.007
0.3489	0.074	0.8182	−0.047			0.2922	0.207	0.7436	0.022		
		1-Propanol (1) + *m*-Xylene (2)						2-Propanol (1) + *m*-Xylene (2)			
0.0626	0.076	0.3787	0.095	0.8111	−0.004	0.0736	0.115	0.3009	0.313	0.7490	0.091
0.1732	0.121	0.4951	0.068	0.8499	−0.013	0.1293	0.190	0.3627	0.319	0.8989	0.011
0.2001	0.122	0.5589	0.055	0.1928	−0.018	0.2176	0.271	0.4827	0.280	0.9523	0.001
0.2498	0.116	0.6291	0.035	0.9680	−0.013	0.2477	0.286	0.5793	0.220	0.9793	−0.002
0.2739	0.116	0.7623	0.007			0.2833	0.306	0.6641	0.155		
		1-Propanol (1) + *p*-Xylene (2)						2-Propanol (1) *p*-Xylene (2)			
0.0598	0.065	0.3627	0.072	0.7872	−0.046	0.0634	0.108	0.3501	0.222	0.7494	0.070
0.1235	0.098	0.4877	0.032	0.8559	−0.051	0.1166	0.165	0.4211	0.205	0.8372	0.035
0.1925	0.106	0.5722	0.006	0.8967	−0.047	0.1889	0.215	0.5103	0.170	0.9020	0.017
0.2491	0.103	0.6252	−0.011	0.9375	−0.037	0.2582	0.229	0.5929	0.137	0.9667	0.004
0.2932	0.094	0.7339	−0.036			0.2951	0.230	0.6527	0.112		

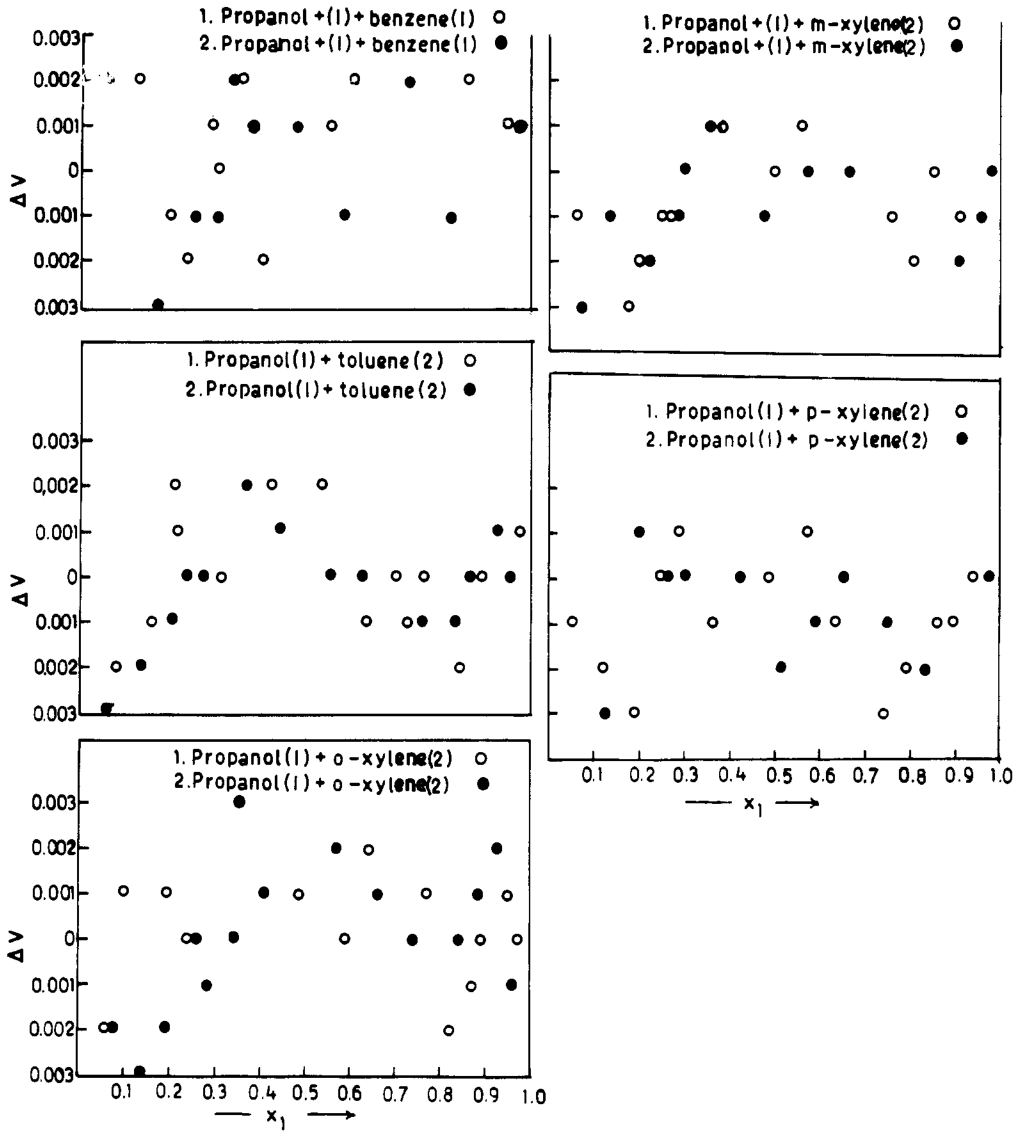

Figure 3. Variation of ΔV for 1-propanol (1) + benzene (2), + toluene (2), + *o*-xylene (2), + *m*-xylene (2), and + *p*-xylene (2) (○) and 2-propanol (1) + benzene (2), + toluene (2), + *o*-xylene (2), + *m*-xylene (2), and + *p*-xylene (2) (●) at 298.15 K.

Table 3. Values of the Constants *A*–*D* and $-(V^E)$ at 298.15 K

system	*A*	*B*	*C*	*D*	$\sigma(V^E)$/ (cm^3 mol^{-1})
1-propanol (1) + benzene (2)	0.3588	−0.3484	0.6061	−0.6644	0.0019
1-propanol (1) + toluene (2)	−0.0120	−0.7107	0.1055	0.1937	0.0016
1-propanol (1) + *o*-xylene (2)	0.0662	−0.6877	0.3207	−0.3305	0.0016
1-propanol (1) + *m*-xylene (2)	0.2635	−0.4300	0.3205	−0.6229	0.0019
1-propanol (1) + *p*-xylene (2)	0.1080	−0.6440	0.2088	−0.4675	0.0014
2-propanol (1) + benzene (2)	1.0767	−0.7219	0.3898	−0.3871	0.0015
2-propanol (1) + toluene (2)	0.6020	−0.7933	0.0960	−0.4595	0.0014
2-propanol (1) + *o*-xylene (2)	0.5456	−0.9813	0.2501	−0.1074	0.0017
2-propanol (1) + *m*-xylene (2)	1.0837	-1.1396	−0.2625	0.2427	0.0015
2-propanol (1) + *p*-xylene (2)	0.7019	−0.7793	0.3596	−0.2537	0.0014

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