Excess Volumes of 1-Butanol, 2-Butanol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol with Xylenes at 308.15 K

Umesh Bhardwaj, Sanjeev Maken, and Krishan C. Singh*

Department of Chemistry, Maharshi Dayanand University, Rohtak-124 001, India

The excess volumes V^E for 1-butanol or 2-butanol or 2-methylpropan-1-ol or 2-methylpropan-2-ol + *o*-xylene or *m*-xylene or *p*-xylene at 308.15 K have been measured over the whole range of composition. The V^E vs composition curves are skewed toward the low concentration of butanol. For systems containing 1-butanol curves are sigmoids and V^E values change sign in the 1-butanol (1) rich region ($x_1 > 0.8$). For butanol + xylene systems V^E values vary in the order 2-methylpropan-2-ol > 2-butanol > 2-methylpropan-1-ol > 1-butanol.

Introduction

The binary systems containing alkanols are of importance due to their extremely nonideal behavior and their application in chemical industry. In our earlier work we have reported the excess volumes and excess enthalpies for 1-propanol or 2-propanol + cyclohexane (Singh et al., 1996b) or an aromatic hydrocarbon (Yadav et al., 1993; Singh et al., 1994, 1996a, 1996c) and their analysis in terms of a Mecke−Kempter type of association model (Treszczanowicz and Benson, 1985). The effect of branching of the carbon chain was not clear for the systems containing 1-propanol or 2-propanol. To obtain insight into the effect of branching of an alkyl group, we have selected the binary systems of all isomers of butanol with *o*-, *m*-, and *p*-xylene and measured their excess volumes at 308.15 K over the entire range of composition.

Experimental Section

1-Butanol, 2-butanol, 2-methylpropan-1-ol, 2-methylpropan-2-ol, and *o*-, *m*-, and *p*-xylene (E. Merck) were purified by standard procedures (Vogel, 1978; Riddick and Bunger, 1970). The purities of the purified samples were checked by measuring their densities at (298.15 ± 0.01) K by a specially designed densimeter which consists of a bulb of approximate volume 35 cm^3 attached to a calibrated capillary through a B-10 standard joint in the manner described by Weissberger (1959). Buoyancy correction due to air was also applied to achieve greater accuracy. The densities agreed to within $\pm 5 \times 10^{-5}$ g cm^{-3} with their corresponding literature values (Tardajos et al., 1986; Lafuente et al., 1995), as shown in Table 1.

Molar excess volumes, V^E, at 308.15 K for the various mixtures were determined in a V-shaped dilatometer in the manner described by Singh and Bhatia (1990). The temperature of the water thermostat was controlled to ±0.01 K. The change in liquid level in the dilatometer capillary was read with a cathetometer (OSAW, India) with a precision of ±0.001 cm. The reliability of the present dilatometer was checked by measuring molar volumes for cyclohexane + benzene mixtures at 298.15 K and these agree well within the experimental error (0.5%) with the literature values (Kumaran and McGlashan, 1977).

Results

The results for the binary mixtures of an isomer of butanol + *o*-xylene or *m*-xylene or *p*-xylene as a function of composition at 308.15 K are given in Table 2 and shown graphically in Figures 1 and 2. The measured V^E results were fitted to the following equation

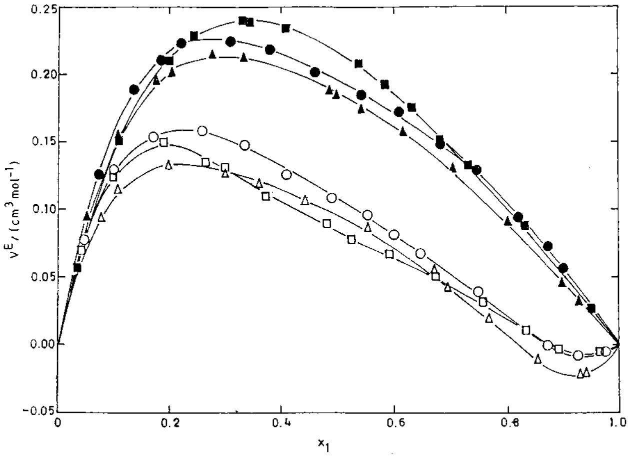

Figure 1. Variation of molar excess volume for butanol (1) + *o*-xylene (2) (△), +*m*-xylene (2) (○), and +*p*-xylene (2) (□) and 2-methylpropan-1-ol (1) + *o*-xylene (2) (▲), +*m*-xylene (2) (●), and +*p*-xylene (2) (■) at 308.15 K.

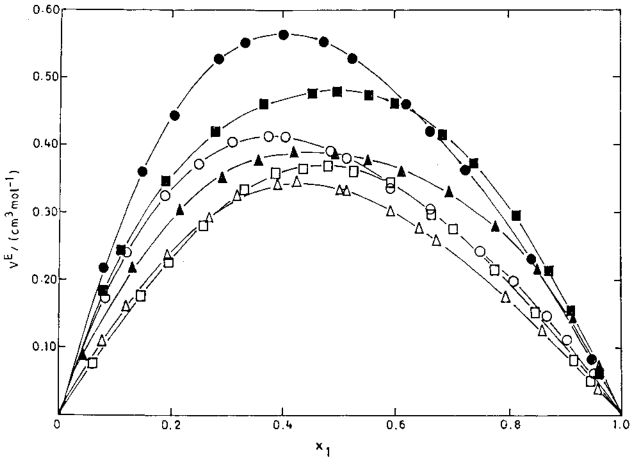

Figure 2. Variation of molar excess volume for 2-butanol (1) + *o*-xylene (2) (△), +*m*-xylene (2) (○), and +*p*-xylene (2) (□) and 2-methylpropan-1-ol (1) + *o*-xylene (2) (▲), +*m*-xylene (2) (●), and +*p*-xylene (2) (■) at 308.15 K.

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

Table 1. Densities of the Pure Components at 298.15 K

material	ρ/g cm^{-3}		material	ρ/g cm^{-3}	
	present work	lit.		present work	lit.
1-butanol	0.806 02	0.8060[a]	*o*-xylene	0.875 01	0.875 05[b] 0.875 90[c]
2-butanol	0.802 39	0.8024[a]	*m*-xylene	0.860 02	0.859 99[b]
2-methylpropan-1-ol	0.797 81	0.7978[a]	*p*-xylene	0.856 72	0.856 73[b]
2-methylpropan-2-ol	0.780 09	0.7810[a]			

[a] Lafuente et al., 1995. [b] Tardajos et al., 1986. [c] TRC thermodynamic Tables, Version 2.0S, Jan 1996.

Table 2. Excess Volumes of Alcohols + Aromatic Hydrocarbons at 308.15 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}
		1-Butanol (1) + *o*-Xylene (2)			
0.0780	0.094	0.3613	0.118	0.7713	0.018
0.1115	0.115	0.4459	0.107	0.8565	−0.011
0.2016	0.131	0.5551	0.086	0.9318	−0.024
0.2989	0.126	0.6721	0.054	0.9401	−0.021
0.3587	0.119	0.6978	0.042		
		1-Butanol (1) + *m*-Xylene (2)			
0.0472	0.077	0.4109	0.126	0.7502	0.039
0.0998	0.129	0.4918	0.109	0.8723	−0.001
0.1727	0.154	0.5537	0.096	0.9245	−0.008
0.2583	0.158	0.5989	0.081	0.9733	−0.006
0.3350	0.148	0.6466	0.067		
		1-Butanol (1) + *p*-Xylene (2)			
0.0429	0.069	0.3711	0.110	0.7555	0.031
0.1007	0.124	0.4809	0.089	0.8322	0.010
0.1893	0.149	0.5232	0.077	0.8909	−0.003
0.2636	0.135	0.5912	0.067	0.9664	−0.005
0.2981	0.130	0.6739	0.051		
		2-Butanol (1) + *o*-Xylene (2)			
0.0773	0.107	0.4261	0.343	0.7957	0.176
0.1189	0.162	0.4985	0.332	0.8608	0.125
0.1925	0.236	0.5107	0.330	0.9102	0.080
0.2681	0.292	0.5916	0.301	0.9611	0.036
0.3207	0.323	0.6464	0.276		
0.3915	0.341	0.6751	0.258		
		2-Butanol (1) + *m*-Xylene (2)			
0.0816	0.173	0.4025	0.411	0.8080	0.199
0.1212	0.241	0.4839	0.390	0.8683	0.147
0.1873	0.324	0.5117	0.380	0.9021	0.112
0.2481	0.371	0.5918	0.346	0.9513	0.061
0.3094	0.403	0.6635	0.303		
0.3746	0.412	0.7516	0.242		
		2-Butanol (1) + *p*-Xylene (2)			
0.0572	0.074	0.4350	0.364	0.7737	0.216
0.1432	0.176	0.4802	0.367	0.8462	0.152
0.1931	0.225	0.5241	0.362	0.9159	0.082
0.2562	0.280	0.5937	0.342		
0.3291	0.332	0.6658	0.305	0.9461	0.050
0.3868	0.357	0.7043	0.277		

x_1	V^E cm^3 mol^{-1}	x_1	V^E/cm^3 mol^{-1}	x_1	V^E/cm^3 mol^{-1}
		2-Methylpropan-1-ol (1) + *o*-Xylene (2)			
0.0531	0.093	0.3326	0.211	0.7077	0.129
0.1074	0.151	0.4888	0.187	0.8022	0.090
0.1749	0.195	0.4998	0.184	0.8976	0.045
0.2059	0.201	0.5435	0.174	0.9302	0.032
0.2781	0.214	0.6171	0.158		
		2-Methylpropan-1-ol (1) + *m*-Xylene (2)			
0.0738	0.126	0.3795	0.219	0.7483	0.129
0.1362	0.189	0.4598	0.201	0.8209	0.094
0.1867	0.211	0.5423	0.184	0.8743	0.072
0.2257	0.223	0.6091	0.172	0.9023	0.056
0.3084	0.224	0.6826	0.149		
		2-Methylpropan-1-ol (1) + *p*-Xylene (2)			
0.0325	0.056	0.3439	0.239	0.6845	0.151
0.1096	0.151	0.4079	0.234	0.7321	0.132
0.1993	0.210	0.5372	0.208	0.8314	0.088
0.2430	0.229	0.5822	0.192	0.9486	0.027
0.3281	0.240	0.6310	0.175		
		2-Methylpropan-2-ol (1) + *o*-Xylene (2)			
0.0448	0.089	0.4269	0.389	0.7755	0.280
0.1312	0.218	0.4901	0.385	0.8514	0.216
0.2147	0.302	0.5488	0.376	0.9131	0.144
0.2934	0.350	0.6123	0.360	0.9596	0.073
0.3553	0.375	0.6958	0.331		
		2-Methylpropan-2-ol (1) + *m*-Xylene (2)			
0.0794	0.218	0.4011	0.563	0.7241	0.364
0.1471	0.361	0.4690	0.554	0.8398	0.231
0.2039	0.445	0.5221	0.528	0.9481	0.084
0.2832	0.528	0.6182	0.461	0.9596	0.068
0.3328	0.552	0.6640	0.421		
		2-Methylpropan-2-ol (1) + *p*-Xylene (2)			
0.0777	0.184	0.4513	0.476	0.7412	0.371
0.1106	0.244	0.4960	0.478	0.8123	0.296
0.1910	0.344	0.557	0.474	0.8725	0.214
0.2785	0.419	0.6026	0.461	0.9083	0.156
0.3647	0.459	0.6866	0.414		

where x_1 and x_2 are the mole fraction of butanols and xylenes, respectively. A, B, C, and D are the adjustable parameters. These parameters were evaluated by fitting V^E data to eq 1 by the least squares method and are recorded in Table 3 together with the standard deviation of V^E, σ, defined by

$$\sigma/\text{cm}^3\ \text{mol}^{-1} = [\sum(V^E - V^E(\text{calcd}))^2/(m - n)]^{1/2}$$

where V^E is the experimentally measured value, V^E(calcd) is the value calculated from eq 1, m is the number of data points, and n is the number of adjustable parameters in eq 1. The random distribution of δV over the whole composition range confirms the best or near best fit of Redlich−Kister eq 1.

Discussion

We are unaware of any previous V^E data for the present systems with which to compare our results. V^E data for all isomers of butanol (1) + xylene (2) systems are positive except for 1-butanol (1) + xylene (2) mixtures where V^E values become negative at $x_1 > 0.8$. All the V^E vs x_1 curves are skewed toward the low mole fractions of butanol. For 2-methylpropan-1-ol + xylene mixtures the V^E values follow the sequence

$$p\text{-xylene} > m\text{-xylene} < o\text{-xylene} \tag{A}$$

while for all the other butanol + xylenes mixtures V^E values vary in the order

$$m\text{-xylene} > p\text{-xyelene} > o\text{-xylene} \tag{B}$$

Table 3. Values of the Constants $A-D$ and $\sigma(V^E)$ at 308.15 K[a]

system	A	B	C	D	$\sigma(V^E)$
1-butanol (1) + *o*-xylene (2)	0.3846	−0.3728	0.1447	−0.7930	0.0019
1-butanol (1) + *m*-xylene (2)	0.4280	−0.4826	0.3868	−0.6800	0.0019
1-butanol (1) + *p*-xylene (2)	0.3316	−0.3929	0.5119	−0.7465	0.0017
2-butanol (1) + *o*-xylene (2)	1.3357	−0.4494	−0.1088	0.1991	0.0019
2-butanol (1) + *m*-xylene (2)	1.5457	−0.7471	0.3827	0.1870	0.0018
2-butanol (1) + *p*-xylene (2)	1.4673	−0.2074	−0.3717	0.0164	0.0020
2-methylpropan-1-ol (1) + *o*-xylene (2)	0.7372	−0.3923	0.5062	−0.4875	0.0021
2-methylpropan-1-ol (1) + *m*-xylene (2)	0.7803	−0.4163	0.6290	−0.4428	0.0020
2-methylpropan-1-ol (1) + *p*-xylene (2)	0.8655	−0.5254	0.3269	−0.1386	0.0014
2-methylpropan-2-ol (1) + *o*-xylene (2)	1.5438	−0.1976	0.5107	0.1612	0.0018
2-methylpropan-2-ol (1) + *m*-xylene (2)	2.1602	−0.9180	0.2692	0.2222	0.0019
2-methylpropan-2-ol (1) + *p*-xylene (2)	1.9158	−0.0469	0.4451	−0.5230	0.0018

[a] $A-D$ and $\sigma(V^E)$ are in cm^3 mol^{-1}.

As far as butanols are concerned, V^E data for these systems with corresponding xylene fall the order

$$\text{2-methylpropan-2-ol} > \text{butan-2-ol} > \text{2-methylpropan-1-ol} > \text{butan-1-ol} \quad \text{(C)}$$

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