Excess Volumes of Binary Mixtures of Benzene + 1-Alkanols at 298.15 and 308.15 K

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Excess molar volumes V^E of the binary mixtures of benzene + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, or + 1-decanol are presented at 298.15 and 308.15 K. The values of V^E are positive over the entire range of composition for these mixtures.

Introduction

Excess volumes V^E of binary mixtures containing one compound with an alkanol have been measured by many researchers (*1–3*). In a previous paper (*4*) we reported the excess molar volumes measured in binary mixtures of tetralin with 1-alkanols. Here we report the experimental V^E for seven binary mixtures of benzene + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, or + 1-decanol at 298.15 and 308.15 K. No literature V^E data are available for these mixtures except benzene + 1-butanol at 298.15 K (*5*), + 1-pentanol at 298.15 and 308.15 K (*6*), + 1-hexanol at 298.15 K (*7*), and + 1-heptanol at 298.15–313.15 K (*8*).

Experimental Section

The chemicals used in this study and their suppliers and purities are listed in Table 1. All the substances were used without further purification. Table 1 also gives density measurements for these components together with values obtained from the literature (*9–11*).

Binary mixtures were prepared by mass with an accuarcy of ± 0.0001 in mole fraction. Densities were measured to ±0.0001 g·cm^{-3} by using a Kyoto Electronics vibrating-tube densimeter (model DA-300), calibrated with redistilled, degassed water and dry air at atmospheric pressure. All the measurements were made at constant temperature, employing a thermostat that could be maintained to ±0.01 K. The error in V^E is estimated to be less than 0.02 cm^3·mol^{-1}.

Results and Discussion

Table 2 shows the excess molar volumes V^E obtained from density data for the binary mixtures studied. In each case the experimental results were fitted to an equation of the type (*12*)

$$V^E/(\mathrm{cm^3 \cdot mol^{-1}}) = \frac{x_1 x_2}{1 - h(x_1 - x_2)}[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2 + a_3(x_1 - x_2)^3] \quad (1)$$

where a_i and h are adjustable parameters and x_1 is the mole fraction of benzene. The values of a_i were obtained by the least-squares method with all points weighted equally while h was found by optimization in order to achieve the best fitting possible. The standard deviations were calculated by using the equation

$$\sigma(V^E) = [\sum (V^E_{\mathrm{exptl}} - V^E_{\mathrm{calcd}})^2/(n-p)]^{1/2} \quad (2)$$

where n is the number of measurements and p is the number of parameters.

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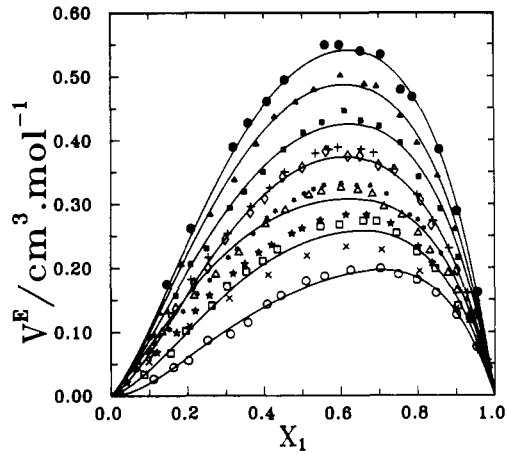

Figure 1. Excess molar volumes V^E for benzene (1) + 1-alkanol (2) at 298.15 K: ○, 1-butanol; □, 1-pentanol; △, 1-hexanol; ◇, 1-heptanol; ■, 1-octanol; ▲, 1-nonanol; ●, 1-decanol; —, eq 1; ×, 1-butanol for Rodriguez et al. (*5*); ★, 1-pentanol for Ortega and Paz Andrade (*6*); *, 1-hexanol for Ortega et al. (*7*); +, 1-heptanol for Ortega (*8*).

Table 1. Source, Purity, and Densities ρ of the Pure Components at 298.15 K

component	source	purity/ (mass %)	ρ/(g·cm^{-3}) this work	ρ/(g·cm^{-3}) lit.
benzene	Merck	99.7	0.8737	0.873 7 (*9*)
1-butanol	Fluka	min 99.5	0.8057	0.805 8 (*9*)
1-pentanol	Fluka	99.0	0.8108	0.810 92 (*10*)
1-hexanol	Fluka	99.0	0.8153	0.815 50 (*10*)
1-heptanol	Fluka	min 99.5	0.8187	0.818 91 (*10*)
1-octanol	Fluka	min 99.5	0.8215	0.821 76 (*10*)
1-nonanol	Aldrich	99.0	0.8244	0.824 32 (*10*)
1-decanol	Aldrich	99.0	0.8267	0.826 5 (*11*)

The values of the parameters a_i and h, along with the standard deviation $\sigma(V^E)$, are given in Table 3. Curves calculated from eq 1 are shown in Figures 1 and 2 at 298.15 and 308.15 K, respectively. For the binary mixture of benzene + 1-butanol the new V^E data at 298.15 K are lower than those of Rodriguez et al. (*5*). The experimental V^E values for the binary mixtures of benzene + 1-pentanol, + 1-hexanol, and + 1-heptanol compare well with those of Ortega and Paz Andrade (*6*), Ortega et al. (*7*), and Ortega (*8*), respectively.

Figures 1 and 2 show that excess molar volumes are positive over the whole range of composition for the seven binary mixtures at 298.15 and 308.15 K. Excess volumes increase in the sequence 1-decanol > 1-nonanol > 1-octanol > 1-heptanol > 1-hexanol > 1-pentanol > 1-butanol for each temperature. The temperature coefficients of V^E, $(\partial V^E/\partial T)_p$, are positive for all binary mixtures, and increase in the

0021-9568/94/1739-0441$04.50/0

Table 2. Excess Molar Volumes V^E for Binary Mixtures of Benzene (1) + 1-Alkanol (2) at 298.15 and 318.15 K

T = 298.15 K				T = 308.15 K				T = 298.15 K				T = 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})	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})
Benzene (1) + 1-Butanol (2)															
0.1112	0.030	0.5585	0.204	0.0561	0.016	0.6037	0.237	0.3572	0.126	0.8477	0.187	0.4283	0.179	0.8510	0.187
0.1634	0.050	0.6261	0.216	0.1152	0.045	0.6537	0.231	0.4073	0.156	0.9010	0.154	0.4956	0.205	0.9005	0.150
0.2024	0.062	0.7043	0.221	0.2258	0.094	0.6952	0.231	0.4433	0.171	0.9532	0.106	0.5524	0.234	0.9565	0.086
0.2517	0.095	0.7513	0.213	0.3003	0.134	0.7493	0.223	0.5102	0.195						
0.3115	0.107	0.7996	0.206	0.3517	0.155	0.8034	0.206								
Benzene (1) + 1-Pentanol (2)															
0.0863	0.028	0.5973	0.266	0.1298	0.064	0.5941	0.296	0.3539	0.190	0.8472	0.198	0.4479	0.261	0.8492	0.206
0.1563	0.062	0.6585	0.272	0.2075	0.118	0.6576	0.291	0.3971	0.207	0.9052	0.140	0.5073	0.278	0.9042	0.157
0.1961	0.097	0.6933	0.271	0.3029	0.179	0.7024	0.276	0.4350	0.226	0.9641	0.071	0.5485	0.281	0.9573	0.091
0.2626	0.136	0.7462	0.253	0.3566	0.215	0.7566	0.266	0.5478	0.262						
0.3039	0.167	0.7992	0.224	0.4178	0.246	0.8017	0.241								
Benzene (1) + 1-Hexanol (2)															
0.0670	0.035	0.6446	0.323	0.1185	0.061	0.5893	0.331	0.4037	0.256	0.8329	0.228	0.3977	0.267	0.8430	0.228
0.1336	0.082	0.6824	0.317	0.1862	0.117	0.6363	0.337	0.4560	0.280	0.8799	0.193	0.4517	0.292	0.8949	0.187
0.2167	0.140	0.7128	0.297	0.2466	0.156	0.6978	0.324	0.5176	0.305	0.9022	0.165	0.4827	0.304	0.9569	0.103
0.2745	0.175	0.7599	0.284	0.2925	0.197	0.7483	0.309	0.5501	0.311	0.9375	0.131	0.5477	0.334		
0.3346	0.211	0.8020	0.256	0.3442	0.229	0.7928	0.287	0.6007	0.318	0.9722	0.068				
Benzene (1) + 1-Heptanol (2)															
0.1022	0.060	0.5616	0.379	0.1114	0.092	0.5470	0.383	0.3642	0.282	0.8079	0.304	0.3958	0.317	0.8413	0.278
0.1687	0.130	0.6189	0.372	0.2100	0.184	0.6028	0.398	0.4024	0.304	0.8361	0.265	0.4494	0.356	0.9014	0.211
0.2179	0.169	0.6504	0.372	0.2589	0.226	0.6516	0.395	0.4496	0.338	0.9036	0.195	0.5085	0.375	0.9482	0.135
0.2536	0.194	0.6988	0.357	0.3047	0.258	0.7234	0.374	0.5002	0.353	0.9474	0.124				
0.2986	0.239	0.7412	0.350	0.3625	0.300	0.7994	0.312								
Benzene (1) + 1-Octanol (2)															
0.1000	0.085	0.5515	0.424	0.1202	0.122	0.6087	0.441	0.3487	0.314	0.8038	0.341	0.4081	0.367	0.8571	0.303
0.1689	0.149	0.6095	0.442	0.2127	0.209	0.6594	0.445	0.3979	0.345	0.8593	0.291	0.4530	0.397	0.9354	0.175
0.2092	0.198	0.6522	0.427	0.2706	0.267	0.6880	0.430	0.4523	0.380	0.9060	0.215	0.5551	0.440		
0.2499	0.224	0.7005	0.419	0.3070	0.294	0.7565	0.404	0.5029	0.407	0.9556	0.133				
0.3112	0.288	0.7566	0.393	0.3621	0.344	0.8040	0.361								
Benzene (1) + 1-Nonanol (2)															
0.1261	0.132	0.6012	0.502	0.0814	0.056	0.5545	0.473	0.4277	0.438	0.8525	0.345	0.3415	0.360	0.8490	0.347
0.1845	0.207	0.6635	0.489	0.1601	0.166	0.5956	0.481	0.4842	0.461	0.8981	0.262	0.4159	0.412	0.8995	0.267
0.2597	0.285	0.6949	0.485	0.1950	0.196	0.6714	0.480	0.5322	0.480	0.9532	0.151	0.4426	0.437	0.9533	0.149
0.3233	0.339	0.7552	0.439	0.2487	0.260	0.7096	0.468					0.5008	0.449		
0.3807	0.395	0.7996	0.396	0.3027	0.320	0.7505	0.438								
Benzene (1) + 1-Decanol (2)															
0.1468	0.165	0.6526	0.536	0.1579	0.186	0.5951	0.539	0.4554	0.488	0.9021	0.288	0.4070	0.447	0.8481	0.394
0.2091	0.253	0.7056	0.531	0.1732	0.200	0.6455	0.540	0.5598	0.544	0.9558	0.161	0.4684	0.480	0.8989	0.297
0.3196	0.382	0.7581	0.476	0.2501	0.285	0.7001	0.524	0.5973	0.545			0.4904	0.505	0.9419	0.204
0.3583	0.420	0.7886	0.465	0.3013	0.357	0.7498	0.492					0.5511	0.521		
0.4098	0.454	0.8545	0.368	0.3418	0.383	0.7964	0.444								

Table 3. Standard Deviation $\sigma(V^E)$ and Values of Parameters a_i and h in Eq 1 for Benzene (1) + 1-Alkanol (2)

component 2	a_0	a_1	a_2	a_3	h	$\sigma(V^E)$/(cm^3·mol^{-1})
			T = 298.15 K			
1-butanol	0.7507	−0.0723	−0.4535	−0.0088	0.9607	0.004
1-pentanol	1.0131	−0.0547	−0.4536	0.3922	0.6002	0.005
1-hexanol	1.1929	−0.5028	−0.6559	0.1123	0.9673	0.004
1-heptanol	1.4330	−0.2065	−0.5338	0.4616	0.6001	0.006
1-octanol	1.6356	−0.7990	−0.8172	0.0694	1.0001	0.006
1-nonanol	1.8924	−0.8670	−0.7639	0.1106	0.9213	0.006
1-decanol	2.0851	−0.7639	−0.7879	0.3367	0.8129	0.007
			T = 308.15 K			
1-butanol	0.8395	−0.1222	−0.3404	0.1691	0.7952	0.004
1-pentanol	1.1071	−0.3466	−0.5741	0.3145	0.8213	0.003
1-hexanol	1.2641	−0.5050	−0.8441	0.2559	0.9679	0.005
1-heptanol	1.4994	−0.7748	−0.6647	0.0829	0.9838	0.005
1-octanol	1.6798	−0.7329	−0.5563	−0.0714	0.9209	0.003
1-nonanol	1.8717	−0.3973	−0.6762	0.8231	0.6001	0.010
1-decanol	2.0240	−0.8124	−0.7207	0.0052	0.9043	0.006

sequence 1-butanol > 1-pentanol > 1-hexanol > 1-heptanol > 1-octanol > 1-nonanol ≈ 1-decanol. The value of $(\partial V^E/\partial T)_p$ for the benzene + 1-decanol mixture is nearly zero. These results show that the main contribution to V^E may be the expansion in volume due to deassociation of self-associated alcohol aggregates (*1*).

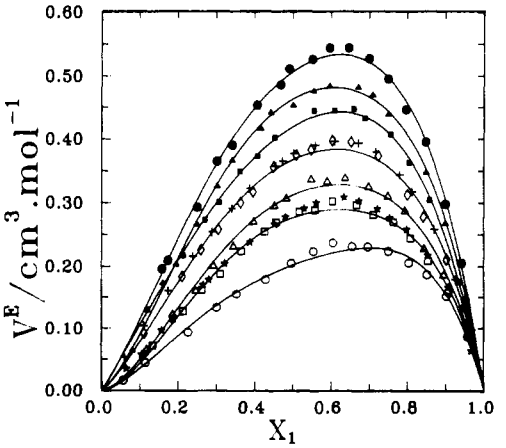

Figure 2. Excess molar volumes V^E for benzene (1) + 1-alkanol (2) at 308.15 K: ○, 1-butanol; □, 1-pentanol; △, 1-hexanol; ◇, 1-heptanol; ■, 1-octanol; ▲, 1-nonanol; ●, 1-decanol, —, eq 1; ★, 1-pentanol for Ortega and Paz Andrade (*6*); +, 1-heptanol for Ortega (*8*).

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Received for review September 13, 1993. Revised March 20, 1994. Accepted April 20, 1994.• Acknowledgment is made to the National Science Council of the Republic of China (Grant No. NSC 83-0402-E006-007) for financial support of this work.

• Abstract published in *Advance ACS Abstracts*, June 1, 1994.