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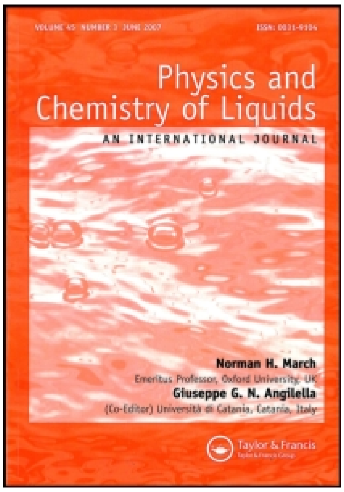

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EXCESS VOLUMES OF BINARY MIXTURES OF BENZENE + 1-ALKANOLS AT 303.15 K

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Excess molar volumes V^E of binary mixtures of benzene + 1-propanol, + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol and 1-decanol were measured at 303.15 K. The V^E values are positive over the entire range of composition for these mixtures. The results are discussed in terms of intermolecular interactions.

Keywords: Excess volume; Dilatometer; Intermolecular interactions

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INTRODUCTION

A survey of the literature has shown that V^E data for mixtures of benzene with ketones [1,2], esters [3], amines [4–7] and halogenated hydrocarbon [8] have been reported at 303.15 K. Further, V^E data for a series of 1-alkanols with benzene at 298.15 K and 308.15 K were reported earlier [9]. We present here excess volume data for benzene with 1-alkanols at 303.15 K. The work on hand was undertaken due to utilising of this data for our further study of excess thermodynamic properties at this temperature. The measured data are compared with those predicted by semi empirical equations [10,11]. The experimental results were analysed in terms of intermolecular interactions between unlike molecules and chain length of 1-alkanols.

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EXPERIMENTAL SECTION

All the chemicals were used of analytical grade and purified by described methods [12]. The purity of the samples was checked by comparing the measured densities of the components with those reported in the literature [12–14]. Densities were determined using a bicapillary-type pycnometer which offered an accuracy of 2 parts in 10 [5]. The measured densities of the pure components are reported in Table I along with literature values.

APPARATUS

The dilatometer used for measuring excess volumes in the present study is similar to that described by Rao and Naidu [15]. The mixing cell contains two bulbs of different capacities connected through a U-tube and the other end of the second bulb is closed with a ground-glass stopper. Five dilatometers with differing capacities were used to cover the entire composition range. The composition of each mixture was determined directly by weighing. The dilatometers were kept in a thermostat that controlled to ± 0.01 K. The measured V^E were accurate to $\pm 0.003\,\mathrm{cm^3\,mol^{-1}}$.

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RESULTS AND DISCUSSION

The measured excess volume (V^E) data for all the eight binary mixtures are given in Table II and the experimental data are graphically presented in Figure 1.

TABLE I Densities of pure compounds at 303.15 K

	Density ρ(g/cc)	
Compounds	*Present work*	*Literature* [12–14]
Benzene	0.86846	0.86850
1-propanol	0.79562	0.79567
1-butanol	0.80203	0.80206
1-pentanol	0.80762	0.80764
1-hexanol	0.81205	0.81201
1-heptanol	0.81572	0.81574
1-octanol	0.82188	0.82192
1-nonanol	0.82149	0.82150
1-decanol	0.82300	0.82310

TABLE II Excess molar volumes V^E for binary mixtures of benzene + 1-alkanol at 303.15 K

Mole fraction of benzene (x_1)	V^E $cm^3/mole$	*Mole fraction of benzene* (x_1)	V^E $cm^3/mole$
benzene(1) + 1-propanol(2)		benzene(1) + 1-butanol(2)	
0.1022	0.035	0.1079	0.045
0.1532	0.057	0.1642	0.072
0.2154	0.081	0.2114	0.089
0.3491	0.133	0.3270	0.136
0.4512	0.164	0.4102	0.162
0.5791	0.175	0.5327	0.180
0.6017	0.173	0.6007	0.184
0.7109	0.156	0.7461	0.153
0.8015	0.121	0.8710	0.097
0.8615	0.095	0.9219	0.064
benzene(1) + 1-pentanol(2)		benzene(1) + 1-hexanol(2)	
0.1112	0.035	0.0982	0.076
0.1734	0.059	0.1164	0.090
0.2025	0.070	0.2071	0.157
0.2936	0.115	0.3317	0.223
0.3583	0.131	0.4210	0.246
0.4496	0.172	0.5517	0.245
0.5450	0.193	0.6624	0.200
0.6037	0.200	0.7419	0.162
0.7001	0.195	0.8120	0.115
0.8525	0.140	0.8706	0.072
benzene(1) + 1-heptanol(2)		benzene(1) + 1-octanol(2)	
0.1009	0.090	0.1179	0.125
0.1537	0.140	0.1710	0.179
0.1917	0.175	0.2511	0.325
0.2610	0.225	0.3509	0.364
0.3402	0.270	0.4617	0.352
0.4389	0.291	0.5519	0.352
0.5420	0.295	0.6507	0.312
0.6680	0.242	0.7403	0.245
0.7496	0.185	0.7915	0.194
0.8417	0.115	0.8705	0.120
benzene(1) + 1-nonanol(2)		benzene(1) + 1-decanol(2)	
0.1039	0.116	0.1329	0.125
0.1742	0.198	0.2032	0.198
0.2319	0.265	0.3208	0.315
0.3539	0.383	0.4476	0.405
0.4419	0.425	0.5419	0.442
0.5271	0.444	0.6206	0.441
0.6502	0.401	0.7009	0.418
0.7129	0.350	0.7906	0.345
0.7806	0.285	0.8429	0.286
0.8817	0.155	0.9026	0.195

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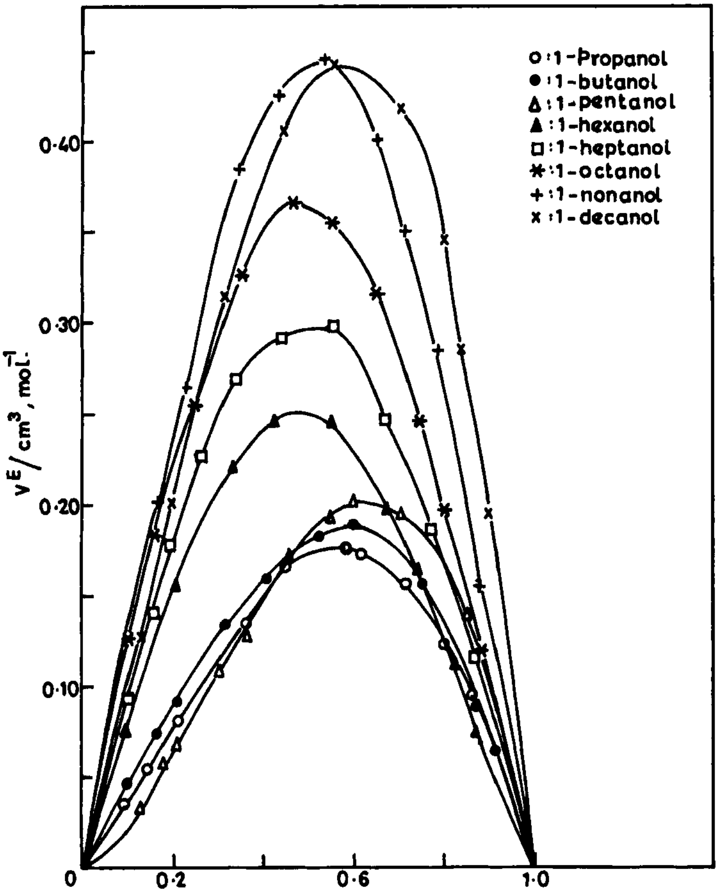

FIGURE 1 Mole fraction of benzene.

The data included in Table II show that V^E values are positive over the entire mole fraction range in all mixtures of benzene with 1-alkanols.

The dependence of V^E on composition may be expressed by an empirical equation proposed by Redlich–Kister [10] as follows

$$V^{E(12)} = x_1x_2\left[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2\right] \qquad (1)$$

where x_1 and x_2 are mole fractions of components 1 and 2 and a_0, a_1, a_2 are constants obtained by the method of least squares.

Hwang *et al.* [11], developed the relation,

$$A^{E(12)} = G^{E(12)} = x_1x_2\left[A_0 + A_1x_1^3 + A_2x_2^3\right] \tag{2}$$

for binary mixtures taking into account two body and three body interactions. Acree and Naidu [16] adopted the equation for excess volume in the following form:

$$V^{E(12)} = x_1x_2\left[V_0 + V_1x_1^3 + V_2x_2^3\right] \tag{3}$$

where x_1 and x_2 represent mole fractions of the components 1 and 2 and V_0, V_1, V_2 are constants. The computation of the V-coefficients in the above equation was described earlier [17]. The values of the two sets of constants are given in Table III along with standard deviations. The standard deviation values given in Table III point out that predictive capabilities of the expressions are similar.

The experimental data can be explained in terms of two opposing contributions:

(a) a positive term from the rupture of alkanol–alkanol hydrogen bonds and physical dipole–dipole interactions between alkanol monomers and polymers; and
(b) a negative term from the formation of OH.....π electron hydrogen-bonded complexes, changes of free volume and interstitial accommodation.

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The measured V^E data in Table II show that the values are positive over entire composition range in all systems of benzene + 1-alkanols. This suggest that the first factor '*a*' is dominant in all the systems. This observation is similar to that of Rodriguez-nunez *et al.* [18].

The algebraic values of V^E for all mixtures of benzene with 1-alkanols fall in the order:

1-decanol ≈ 1-nonanol > 1-octanol > 1-heptanol > 1-hexanol > 1-pentanol > 1-butanol > 1-propanol. This order is similar to that of Chun-Hung Yu and Fuan-Nan Tsai [9]. Further, the above order suggest that excess volume data in the present investigation increases with increase in chain length of 1-alkanols and also suggests that an increase in carbon chain length of 1-alkanols increases Van der Waals interactions, also enhance the association of molecules in the order specified which would in turn increase the volume of mixtures.

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TABLE III Standard deviations $\sigma(V^E)$ and values of the constants from the Redlich–Kister, Eq. (1) and the Hwang *et al.*, Eq. (2)

	a_0	a_1	a_2	$\sigma(V^E)$	b_0	b_1	b_2	$\sigma(V^E)$
Systems		$cm^3/mole$				$cm^3/mole$		
benzene + 1-propanol	0.6789	0.2527	−0.1489	0.002	0.7283	0.1036	−0.4989	0.002
benzene + 1-butanol	0.7109	0.2540	−0.0616	0.002	0.7317	0.2188	−0.3850	0.002
benzene + 1-pentanol	0.7324	0.5084	0.0311	0.003	0.7225	0.6460	−0.5667	0.003
benzene + 1-hexanol	1.0040	−0.1575	−0.4231	0.002	1.1449	−0.7512	−0.3762	0.002
benzene + 1-heptanol	1.1963	−0.1602	−0.4906	0.003	1.3597	−0.8437	−0.4636	0.003
benzene + 1-octanol	1.4477	−0.1022	−0.5711	0.002	1.6386	−0.8857	−0.6414	0.002
benzene + 1-nonanol	1.7683	0.1538	−0.6614	0.003	1.9888	−0.6986	−1.0647	0.003
benzene + 1-decanol	1.7168	0.7403	−0.1525	0.002	1.7673	0.6803	−1.0845	0.002

References

[1] Jayalakshmi, T. and Reddy, K. S. (1985). *Can. J. Chem.*, **63**, 2824.

[2] Jayalakshmi, T. and Subramanyam Reddy, K. (1985). *J. Chem. Eng. Data*, **30**, 51.

[3] Iloukhani, H., Reddy, K. D. and Rao, M. V. P. (1984). *J. Chem. Eng. Data*, **29**, 474.

[4] Venkatesu, P. and Rao, M. V. P. (1994). *Fluid Phase Equilibria*, **93**, 369.

[5] Krishnaiah, A. and Naidu, P. R. (1979). *Can. J. Chem.*, **57**, 915.

[6] Dharmaraju, D., Narayanaswamy, G. and Raman, G. K. (1981). *J. Soln. Chem.*, **79**, 10.

[7] Prabhavathi, C. L., Siva Kumar, K., Venkateswarlu, P. and Raman, G. K. (1999). *Indian J. Chem.*, **38A**, 934.

[8] Chandrasekhar, A. C. H., Surendranath, K. N. and Krishnaiah, A. (1988). *Chem. Scr.*, **28**, 421.

[9] Hungyu, C. and Fuan-Nan Tsai (1994). *J. Chem. Eng. Data*, **39**, 441.

[10] Redlich, O. and Kister, A. T. (1948). *Ind. Eng. Chem.*, **40**, 345.

[11] Hwang, C. A., Hoste, J. C., Hall, K. R. and Mansoori, G. A. (1991). *Fluid Phase Equilibria*, **62**, 1739.

[12] Riddick, J. A. and Bunger, W. S., *Organic Solvents Techniques of Chemistry*, Vol. II (Wiley-Inter Science, New York, 1970).

[13] Timmermans, *Physico-Chemical constants of pure organic compounds* (Elsevier, Amsterdam, 1950).

[14] *Thermodynamics Tables*, Thermodynamic Research Center, Texas TX 77843-3111, 1996.

[15] Rao, M. V. P. and Naidu, P. R. (1974). *Can. J. Chem.*, **52**, 788.

[16] Acree, W. E. Jr. and Naidu, P. R. (1994). *Phys. Chem. Liqs.*, **27**, 69.

[17] Siva Kumar, K. and Naidu, P. R. (1994). *J. Chem. Engg. Data*, **39**, 2.

[18] Rodriguez-nunez, E., Paz-Andrade, M. I. and Ortega, J. (1986). *J. Chem. Thermodynamics*, **18**, 303.

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