

MOLECULAR INTERACTIONS IN BINARY LIQUID MIXTURES CONTAINING BROMOBENZENE

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Excess volumes for the binary mixtures of bromobenzene with *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *n*-pentanol, *i*-pentanol, *n*-hexanol *n*-heptanol, and *n*-octanol have been measured at 303.15 K by dilatometric method, over the entire range of composition. Values of V^E are positive at high mole fractions of bromobenzene and are negative over the rest of composition. Results are ascribed to interactions between unlike molecules.

Keywords : Mole Fraction; Excess Volume; Bromobenzene; Alcohols

INTRODUCTION

As a part of research programme the excess volumes of alcohols with toluene (Narayanaswamy *et al.*, 1980), nitrobenzene and chlorobenzene (Dharmaraju *et al.*, 1980) have been reported from our laboratory. Now we report the excess volumes of bromobenzene with a homologous series of alcohols. Alcohols chosen are *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *n*-pentanol, *i*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol. These have been selected to study the effect of chain length and branched chains in the alcohols on the measured excess volumes.

MATERIALS AND METHODS

All alcohols except *n*-heptanol were dried by refluxing with fused calcium oxide and distilling from it. Heptanol (Koch-Light Laboratories Ltd., England) was used without further purification. Bromobenzene was purified as described in earlier work (Dharmaraju *et al.*, 1981). The purities of all the liquids were checked by comparing measured densities with those reported in the literature (Timmermans, 1950).

Excess volumes as a function of composition were measured at 303.15 K directly by the dilatometric method (Narayanaswamy *et al.*, 1980). The experimental method was previously checked (Stokes *et al.*, 1970) for the test system cyclohexane + benzene and the results obtained showed a standard deviation of $\pm 0.003 \text{ cm}^3 \text{ mol}^{-1}$. Four dilatometers with different capacities were used to cover the entire mole-fraction range.

RESULTS AND DISCUSSION

The results at 303.15 ± 0.01 K are given in Table I. Values of V^E measured in all the systems are positive at high mole fractions of bromobenzene but are negative over the rest of composition range.

TABLE I
Values of V^E for the binary mixtures of bromobenzene with alcohols at 303.15 K (x is mole fraction of bromobenzene)

x	V^E cm ³ mol ⁻¹	x	V^E cm ³ mol ⁻¹	x	V^E cm ³ mol ⁻¹	x	V^E cm ³ mol ⁻¹
	<i>n</i> -propanol		<i>i</i> -propanol		<i>n</i> -butanol		<i>i</i> -butanol
0.1124	-0.092	0.0902	-0.125	0.1147	-0.123	0.1148	-0.060
0.2131	-0.128	0.1567	-0.164	0.2579	-0.178	0.2390	-0.066
0.3191	-0.121	0.2932	-0.182	0.3698	-0.153	0.3131	-0.053
0.5119	-0.052	0.3844	-0.143	0.5172	-0.080	0.4153	-0.023
0.6607	0.011	0.4635	-0.095	0.5791	-0.052	0.5178	0.010
0.7840	0.050	0.5553	-0.046	0.6739	-0.010	0.6152	0.045
0.8130	0.053	0.7150	0.044	0.7701	0.022	0.7716	0.085
0.8389	0.055	0.8450	0.083	0.8594	0.028	0.8303	0.092
	<i>i</i> -pentanol		<i>n</i> -hexanol		<i>n</i> -heptanol		<i>n</i> -octanol
0.1171	-0.061	0.1304	-0.079	0.1511	-0.061	0.1659	-0.027
0.2188	-0.070	0.2625	-0.096	0.2909	-0.072	0.3348	-0.018
0.3406	-0.055	0.3816	-0.087	0.4481	-0.033	0.3901	-0.009
0.4811	-0.010	0.4879	-0.062	0.5176	-0.022	0.5689	0.033
0.5374	0.007	0.5807	-0.025	0.6228	0.015	0.6218	0.044
0.6415	0.038	0.6883	0.001	0.7153	0.036	0.7105	0.058
0.7979	0.064	0.7911	0.026	0.8047	0.050	0.8256	0.069
0.8786	0.068	0.8815	0.038	0.9053	0.053	0.9035	0.062
	<i>n</i> -pentanol						<i>n</i> -pentanol
0.1459	-0.100	0.2544	-0.127	0.3538	-0.111	0.4848	-0.075
0.5514	-0.050	0.6561	-0.015	0.7625	0.011	0.8550	0.026

Alcohols are self-associated liquids (Franks & Ives, 1967; Rowlinson, 1969; Prigogine & Defay, 1953) in pure state. The observed values of V^E may be explained qualitatively by postulating the following factors : (i) de-polymerization of alcohols by the addition of bromobenzene and (ii) sepecific and non-specific interactions between monomers of alcohol and bromobenzene. Van Ness *et al.*, (1967) have reported spectroscopic evidence for specific interactions between the hydroxyl group and the π -electron system of an aromatic solvent. The first factor produces an increase in volume whereas the second factor contributes to decrease in volume. The observed V^E data suggest that the contributions due to factor (i) is dominant at high mole fractions of bromobenzene and the contributions due to factor (ii) become dominant at low mole fractions. The decrease in negative values of V^E (at $x = 0.25$) with increase in chain length of alcohol (except propanol) suggest that the effect of interaction decreases with increasing chain length. The lower negative values of V^E for *i*-butanol, *i*-pentanol than *n*-butanol and *n*-pentanol may be due to steric hindrance of branching alkyl groups. The compact structure of *i*-propanol might be responsible for higher negative values than *n*-propanol.

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