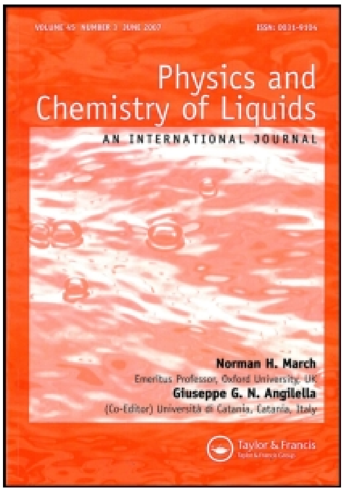

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VOLUMETRIC BEHAVIOUR OF MIXTURES OF BUTOXY ETHANOL WITH ALIPHATIC ALCOHOLS

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Excess Volumes, V^E are measured for mixtures of butoxy ethanol with aliphatic alcohols as a function of molefraction (x_1) at 308.15 K and atmospheric pressure using batch dilatometric technique. The aliphatic alcohols include methanol, *n*-propanol, *n*-butanol, isobutanol, *t*-butanol and *n*-pentanol. The measured excess volumes are negative over the entire range of composition in all the systems except for the system, 2-butoxy ethanol + *n*-pentanol, in which V^E is positive over the entire range of composition. Further increase in chain length of alcohol results in an increase in magnitude of the excess function. The data are interpreted on the basis of hydrogen bonding interaction between unlike molecules.

KEY WORDS: Excess volumes, hydrogen bonding, butoxy ethanol, aliphatic alcohols.

1 INTRODUCTION

In the chemical industry there exists a continuing need for reliable thermodynamic data of binary systems. This is particularly true for systems involved in industrial processes. A survey of the literature shows that very few attempts[1-3] have been made to study excess volumes for mixtures containing alkoxy alcohols. Alcohols and alkoxy alcohols[4-6] are selfassociated in their pure state. We are reporting here new experimental data on mixtures of butoxy ethanol with methanol, *n*-propanol, *n*-butanol, isobutanol, *t*-butanol and *n*-pentanol at 308.15 K with a view to study the intermolecular interaction between unlike molecules and also to visualise the effect of chain length and shape of aliphatic alcohols on excess volumes of these mixtures.

2 EXPERIMENTAL

Excess volumes as a function of composition are measured directly by the dilatometric method[7,8]. The experimental method is previously checked[9] for the test system, cyclohexane + benzene and the results obtained showed a standard deviation of $\pm 0.003\,\mathrm{cm^3 \cdot mol^{-1}}$. Four dilatometers with different capacities are used to cover the entire mole fraction range. Measurements are made using thermostatic bath controlled within ± 0.01 K.

Table 1 Densities of Pure Components

	Denstiy (ρ) g·cm⁻³	
Component	*Present work*	*Literature at 25°C*
2-butoxy ethanol	0.89630	0.89625
methanol	0.78650	0.78637
n-propanol	0.79972	0.79960
n-butanol	0.80580	0.80575
isobutanol	0.79790	0.79780
tertiary butanol	0.78112	0.78120
n-pentanol	0.81091	0.81080

All materials are purified by the methods described by Riddick and Bunger[10]. All alcohols are dried by refluxing with fused calcium oxide and fractionally distilled. 2-Butoxy ethanol (Fluka, Purum > 98 moles per cent) was dried over 4A molecular sieves for 1d and fractionally distilled. The purities of all substances better than 99.95 mass per cent was found by G–C analysis. The purities of the samples are checked by comparing the measured densities of the compounds with those reported in the literature[11]. Densities are determined using a bicapillary pycnometer which offered an accuracy of 5 parts in 10^5. The measured densities of the pure components are reported in Table 1 along with the literature values.

3 RESULTS AND DISCUSSION

The experimental excess volumes of the six binary systems are given in Table 2 and also graphically represented in Figure 1. The experimental values for V^E were fitted to an empirical equation of the form

$$V^E = x(1-x)\sum_{j=0}^{k} A_j(1-2x)^{j-1} \tag{1}$$

where A_j is the coefficient for order j obtained from the least square fit of the results presented in Table 2. The standard deviations, $\sigma(V^E)$ associated with this analysis, is evaluated from the equation

$$\sigma(V^E) = \left[\sum \frac{(V^E_{\text{Exp}} - V^E_{\text{Calcd}})^2}{n-p}\right]^{1/2} \tag{2}$$

where n is the number of experimental points and p is the number of coefficients in Eq. (1) and the values of the coefficients are presented in Table 3. Comparison of the experimental resutls and the values calculated according to Eq. (1) indicates that the deviations are in all cases less than 1%.

Table 2 Values of V^E for the binary mixtures of 2-Butoxy ethanol with alcohols at 308.15 K (x_1 is the molefraction of 2-butoxy ethanol)

X_1	V^E	X_1	V^E
2-Butoxy ethanol + methanol		2-Butoxy ethanol + *n*-propanol	
0.1176	−0.164	0.1286	−0.084
0.2309	−0.280	0.2072	−0.099
0.3243	−0.339	0.3051	−0.115
0.4118	−0.370	0.4440	−0.128
0.4991	−0.365	0.5500	−0.123
0.6761	−0.290	0.6465	−0.117
0.8156	−0.196	0.7629	−0.096
0.8871	−0.125	0.8763	−0.065
2-Butoxy ethanol + *n*-butanol		2-Butoxy ethanol + isobutanol	
0.1812	−0.018	0.1398	−0.018
0.2737	−0.025	0.2403	−0.028
0.4223	−0.030	0.3354	−0.032
0.4882	−0.032	0.4911	−0.034
0.6102	−0.027	0.5544	−0.032
0.7558	−0.019	0.6732	−0.027
0.8229	−0.015	0.8032	−0.018
0.8845	−0.010	0.8617	−0.013
2-Butoxy ethanol + tertiary butanol		2-Butoxy ethanol + *n*-pentanol	
0.1085	−0.084	0.1642	0.011
0.2457	−0.111	0.2952	0.016
0.4079	−0.103	0.4443	0.019
0.4977	−0.095	0.5286	0.023
0.5816	−0.082	0.6505	0.020
0.6761	−0.065	0.7220	0.018
0.7620	−0.048	0.8273	0.010
0.8812	−0.024	0.8816	0.012

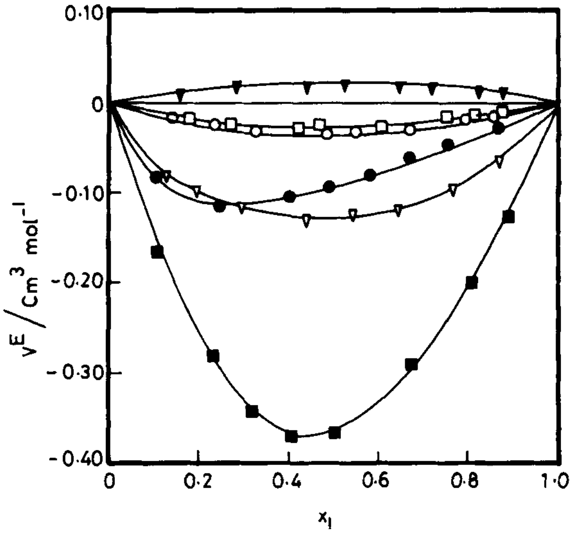

Figure 1 Excess volumes vs. mole fraction at 308.15 K for 2-butoxyethanol with methanol (■), *n*-propanol (▽), *n*-butanol (□), isobutanol (○), *t*-butanol (●) and *n*-pentanol (▼).

Table 3 Values of parameters in Eq. (1) and the standard deviation $\sigma(V^E)$ at 308.15 K

System *2-Butoxy ethanol +*	a_0	a_1	a_1	$\sigma(V^E)$
methanol	−1.464	0.233	0.074	0.006
n-propanol	−0.493	0.075	−0.299	0.005
n-butanol	−0.122	0.017	0.023	0.001
isobutanol	−0.135	0.031	0.008	0.001
tertiary butanol	−0.372	0.375	−0.284	0.005
n-pentanol	0.084	0.012	0.004	0.001

The presence of the etheric oxygen enhances the ability of the —OH group to form hydrogen bonds and we can expect intramolecular hydrogen bonds to be formed in the alkoxy ethanol molecules[12–17].

The V^E values are negative over the whole mole-fraction range for mixtures containing 2-butoxy ethanol and alcohols except with *n*-pentanol where in the V^E values are positive over the entire range of composition. The negative V^E values may be attributed to the enhanced hydrogen bonding interactions between unlike molecules. However, this interaction becomes weaker as the chain length of alcohols increases.

In the case of butanols the algebraic values of V^E follow the order:

$$n\text{-butanol} > \text{isobutanol} > t\text{-butanol}$$

This order suggests that interaction between unlike molecules increases as the aliphatic alcohol becomes more and more branched, which may be attributed to the increased number of methyl gourps.

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