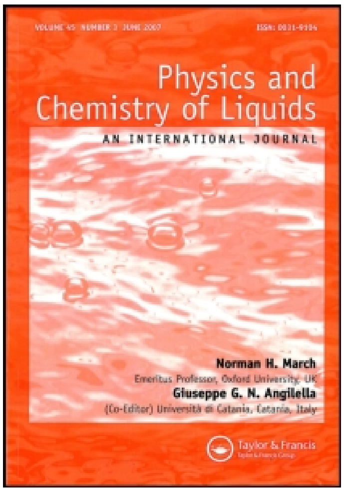

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EXCESS VOLUMES OF (2-ETHOXYETHANOL + ALCOHOLS) AT 308.15 K

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Excess volumes for mixtures containing methanol, *n*-propanol, *n*-butanol, isobutanol, *t*-butanol and *n*-pentanol as non common component and 2-Ethoxy ethanol as common component are measured at 308.15 K by batch dilatometric method. Experimental Excess Volumes are negative over the whole composition range for mixtures of methanol, *n*-propanol with 2-Ethoxy ethanol and positive in mixtures containing *n*-butanol, isobutanol, *t*-butanol and *n*-pentanol. Excess Volumes increase in magnitude with the increase in the chain length of alcohol. The results are interpreted on the basis of intermolecular interactions between unlike molecules.

KEY WORDS: Excess volume, depolymerisation, ethoxy ethanol, aliphatic alcohols.

1. INTRODUCTION

Mixing volume effects are important from both a theoretical and a practical point of view. Indeed, strong deviations from linearity are often encountered in liquid mixtures, even of similar nature.

In addition to the scientific interest, the knowledge of the mentioned phenomena is very useful for a number of practical applications in various fields; suffice it to mention were the field of paints, varnishes and printing inks, where volume effects are involved in the conversion of formulations from a gravimetric into a volumetric base (solvent mixtures and polymer solutions for mill base and let down, evaluation of pigment volume concentration, volumetric yield in application, etc.).

Mixtures containing 2- Ethoxy ethanol as one of the components have been studied in terms of thermodynamic properties[1–7]. However no systematic effort has been made to study the interaction between Ethoxy ethanol with aliphatic alcohols on the basis of excess volumes. We report new experimental results for excess volumes of six binary mixtures at 308.15 K. The mixtures included 2-Ethoxy ethanol as a common component and six alcohols as non-common components. The alcohols are methanol, *n*-propanol, *n*-butanol, isobutanol, *t*-butanol and *n*-pentanol. These systems have been selected to study the interaction between ether alcohol and alcohol and also to assess the effect of the chain length and branching of alcohols on excess volumes.

2. EXPERIMENTAL

Alcohols (Fluka Puriss) were dried by refluxing with fused calcium oxide for 5 hours and then distilled using a fractionating column containing 30 theoretical plates. 2-Ethoxy ethanol (S. Merck) was drierite over drier for 1d and fractionally distilled in vacuo from fresh calcium turnings. Purity of all substances better than 99.95 mass per cent was found by G.C. analysis. The purity of the chemicals was checked by comparing the densities and the boiling points of the components with those reported in the literature[8,9]. The densities were measured using a bicapillary pycnometer which gave an accuracy of five parts in 10^5. The boiling points were measured using a Swietoslawski type ebulliometer[10], which gave an accuracy of ± 0.2K. The measured values are included in Table 1 along with the literature values.

Excess volumes were measured using a single composition per loading type dilatometer as in earlier work[11]. The dilatometer consisted of a U-tube with mercury at the bottom to separate the two components. One arm of the U-tube was fitted with a ground glass stopper and the other arm with a capillary that can be replaced by another with thicker (or thinner) bore. Composition was determined directly by weighing. Mixing was carried out by tilting the dilatometer, thereby breaking the mercury seal. Four dilatometers with different capacities were used to cover the entire composition range. The dilatometers were kept in a thermostat maintained at ± 0.01K. The values of V^E were accurate to ± 0.003 cm^3 mol^{-1}.

3. RESULTS AND DISCUSSION

The excess volumes for the systems of 2-Ethoxy ethanol with six alcohols are included in Table 2. The date are also graphically represented in Figure 1. The values of V^E may be fitted to an empirical equation of the form,

$$V^E/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} = x(1-x) \sum_{i=0}^{K} a_i (1-2x)^i \tag{1}$$

where x is the molefraction of 2-Ethoxy ethanol. The values of a_i, determined by the method of least squares, are given in Table 3 along with the standard deviation

Table 1 Boiling points and Densities of Pure Components at 308.15K.

Components	*Boiling Point (K)* *Experiment*	*Literature*	*Density* *Experiment*	*(g cm^{-3})* *Literature*
2-Ethoxy ethanol	408.7	408.8	0.92517	0.92520
Methanol	337.5	337.7	0.78650	0.78637
Propanol	370.2	370.3	0.79972	0.79960
Butanol	390.7	390.9	0.80580	0.80575
Pentanol	411.0	411.1	0.81091	0.81080
Iso Butanol	380.9	381.0	0.79790	0.79780
Tertiary Butanol	355.3	355.5	0.78112	0.78120

Table 2 Excess Volume V^E ($cm^3 \cdot mol^{-1}$) of 2-Ethoxy Ethanol with alcohols at 308.15K.

X_1	V^E	X_1	V^E
	$cm^3 \cdot mol^{-1}$		$cm^3 \cdot mol^{-1}$
2-Ethoxy Ethanol + Methanol		2 Ethoxy Ethanol + *n*-propanol	
0.0940	−0.080	0.0990	−0.014
0.2160	−0.210	0.1640	−0.016
0.3143	−0.308	0.2411	−0.022
0.3594	−0.348	0.4162	−0.024
0.5092	−0.415	0.5464	−0.025
0.6476	−0.424	0.6400	−0.030
0.7823	−0.320	0.7904	−0.022
0.9350	−0.110	0.8670	−0.020
2-Ethoxy Ethanol + *n*-Butanol		2-Ethoxy Ethanol + Iso Butanol	
0.0922	0.025	0.1118	0.035
0.2636	0.058	0.1716	0.048
0.3724	0.066	0.2846	0.066
0.4523	0.071	0.4432	0.076
0.6107	0.069	0.6088	0.070
0.7068	0.063	0.6732	0.065
0.8098	0.040	0.8162	0.048
0.8743	0.031	0.9026	0.029
2-Ethoxy Ethanol + tertiary butanol		2-Ethoxy Ethanol + *n*-Pentanol	
0.1315	0.028	0.1046	0.112
0.2885	0.055	0.2014	0.185
0.3719	0.068	0.3211	0.243
0.4696	0.084	0.4566	0.270
0.6089	0.091	0.5514	0.262
0.7043	0.080	0.6415	0.240
0.8044	0.062	0.7298	0.202
0.8811	0.044	0.8933	0.099

(X_1 is the molefraction of 2-Ethoxy Ethanol)

Table 3 Values of the parameters a_0, a_1 and a_2 of the Eq. (1) and the standard deviation $\sigma(V^E)$ of Eq. (2) at 308.15K.

System *2-Ethoxy ethanol*	a_0	a_1	a_2	$\sigma(V^E)$
		$cm^3 \cdot mol^{-1}$		
methanol	−1.697	−0.565	0.447	0.005
n-propanol	−0.102	−0.021	−0.096	0.002
n-butanol	0.290	−0.011	−0.007	0.002
iso butanol	0.299	−0.017	0.068	0.001
tertiary butanol	0.337	0.123	−0.021	0.003
n-pentanol	1.068	−0.103	0.073	0.002

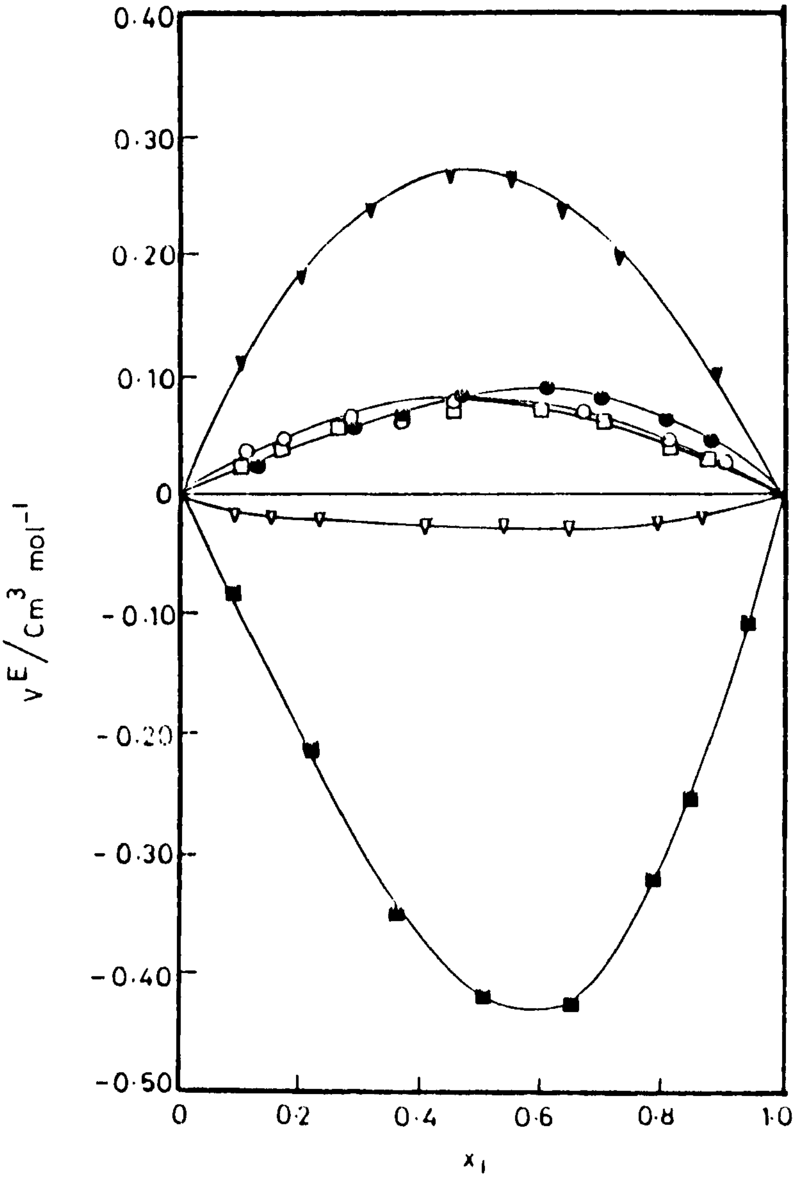

Figure 1 Excess volumes vs molefraction at 308.15K for 2-Ethoxyethanol with methanol (■), *n*-propanol (∇), *n*-butanol (□), isobutanol (○), *t*-butanol (●) and *n*-pentanol (▼).

$\sigma(V^E)$. The values of $\sigma(V^E)$ are obtained by using the equation,

$$\sigma(V^E) = \left[\sum (V^E_{\text{calcd}} - V^E_{\text{exptl}})^2/(N-P)\right]^{1/2} \tag{2}$$

where N is the number of experimental data and P is the number of coefficients.

The molecules of the alkoxy alkanols are self-associated like the alcohols[12]. The effect of the simultaneous presence of etheric and alcoholic oxygen atoms in the same molecule of alkoxy alkanol and 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.

The values of V^E are negative over the entire range of composition for methanol, propanol systems and positive in case of butanol, isobutanol, *t*-butanol and pentanol systems at 308.15K.

The excess volumes, which are strikingly large, may be explained on the basis of two opposing effects.

1. Depolymerisation of selfassociated alkoxy alkanols by the alcohols and selfassociated alcohols by the alkoxy alkanols.
2. Hydrogen bond formation between alkoxy alkanols and alcohols. The former effect results in expansion of volume and the later contributes contraction in volume. The experimental results suggest that the later effect is dominant in methanol and proponal systems while the former effect is dominant in the remaining systems. The positive deviations are mainly due to H—bond breaking. Negative deviations might be due to weak specific interactions between unlike molecules. The positive V^E values increase with an increase in the chainlength of the alcohol. The differences in the size and shape of unlike molecules is the predominating factor. When the alkyl group of the alkanol molecule becomes more and more branched steric hinderance is expected to increase from primary to tertiary and hence the interaction between 2-Ethoxy ethanol and alkanol should fall in the sequence primary > secondary > tertiary.

The results in Table 2 obeyed the same sequence. The positive values of V^E for the binary mixtures of 2-Ethoxy ethanol fall in order:

methanol < *n*-propanol < *n*-butanol < isobutanol < *t*-butanol < and *n*-pentanol.

Finally, the V^E of 2-Ethoxy ethanol and alkanol mixtures result from a shifting imbalance between negative and positive contributions and the magnitudes of these being sensitive to the length of the component molecules.

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