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# THERMODYNAMIC STUDIES OF SOME BINARY MIXTURES CONTAINING A SELF-ASSOCIATED COMPONENT. II. EXCESS VOLUMES OF SOME MIXTURES OF TETRAHYDROFURAN WITH ALCOHOLS

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## ABSTRACT

Excess volumes of mixing, $V^E$, for binary mixtures of tetrahydrofuran (THF) with methanol, ethanol, *n*-butanol, *tert*-butanol, 2-bromoethanol and ethylene glycol have been determined from the experimental density measurements at 298.15 K over the entire composition range. The $V^E$ data follow the order: ethylene glycol < 2-bromoethanol < methanol < ethanol < *n*-butanol < *tert*-butanol. The results have been explained in terms of self-association and the hydrogen bond-donating abilities of alcohols.

## INTRODUCTION

The non-ideal behaviour of binary mixtures containing a self-associated component is primarily due to the specific interactions arising from the hydrogen bond between the polar groups of the component molecules. For example, when an alcohol is mixed with an organic liquid, a part of the alcohol aggregates will tend to break up to form hydrogen bonds with the molecules of the organic liquid being added. The degree of dissociation of the alcohol aggregates would depend upon the hydrogen bond-accepting ability of the functional group present in the other molecule. As an extension to our studies of the thermodynamic properties of binary mixtures containing a self-associated component [1], the excess volumes of mixing, $V^E$, of binary mixtures of tetrahydrofuran with methanol, ethanol, *n*-butanol, *tert*-butanol, 2-bromoethanol and ethylene glycol have been determined at 298.15 K over the entire composition range and are reported in this paper.

## EXPERIMENTAL

Fisher A.C.S. certified grade tetrahydrofuran, methanol, ethanol, *n*-butanol, *tert*-butanol and ethylene glycol were purified according to standard established procedures [2]. The sample of 2-bromoethanol (IR—GC

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TABLE 1

Excess volumes of mixing, $V^E$, for the binary mixtures of tetrahydrofuran (THF) with various alcohols at 298.15 K

| Mole fraction of THF | $V^E$ (cm$^3$ mole$^{-1}$) |
|---|---|
| *THF + methanol* | |
| 0.0780 | −0.057 |
| 0.1918 | −0.101 |
| 0.3232 | −0.127 |
| 0.4007 | −0.135 |
| 0.4883 | −0.135 |
| 0.5472 | −0.128 |
| 0.6738 | −0.106 |
| 0.7993 | −0.076 |
| 0.8764 | −0.048 |
| *THF + ethanol* | |
| 0.0826 | −0.003 |
| 0.1304 | −0.004 |
| 0.2496 | −0.009 |
| 0.3941 | −0.007 |
| 0.4922 | 0.001 |
| 0.5811 | 0.009 |
| 0.6762 | 0.015 |
| 0.7493 | 0.018 |
| 0.8598 | 0.022 |
| *THF +* n-*butanol* | |
| 0.0942 | 0.009 |
| 0.1909 | 0.012 |
| 0.2464 | 0.018 |
| 0.3368 | 0.022 |
| 0.4357 | 0.026 |
| 0.5213 | 0.030 |
| 0.6101 | 0.034 |
| 0.6830 | 0.033 |
| 0.7672 | 0.029 |
| 0.8488 | 0.022 |
| 0.9100 | 0.012 |
| *THF +* tert-*butanol* | |
| 0.0840 | 0.102 |
| 0.1691 | 0.197 |
| 0.2227 | 0.244 |
| 0.3308 | 0.335 |
| 0.4684 | 0.408 |
| 0.5618 | 0.413 |
| 0.6622 | 0.395 |
| 0.7350 | 0.351 |
| 0.8312 | 0.242 |
| 0.9229 | 0.128 |
| *THF + 2-bromoethanol* | |
| 0.2288 | −0.170 |
| 0.3541 | −0.251 |
| 0.5012 | −0.308 |
| 0.7065 | −0.286 |
| 0.7300 | −0.267 |
| 0.8649 | −0.160 |

TABLE 1 (continued)

| Mole fraction of THF | $V^E$ (cm$^3$ mole$^{-1}$) |
|---|---|
| *THF + ethylene glycol* | |
| 0.0784 | −0.155 |
| 0.1454 | −0.279 |
| 0.2630 | −0.447 |
| 0.3820 | −0.559 |
| 0.4341 | −0.575 |
| 0.5641 | −0.520 |
| 0.6768 | −0.431 |
| 0.7787 | −0.334 |
| 0.9016 | −0.169 |

analysed) supplied by Aldrich was purified by fractional crystallization followed by distillation under reduced pressure. The reagents were stored in brown bottles and fractionally distilled immediately before use. The densities and refractive indices of the solvents agreed closely with the accepted literature values [2,3].

The values of $V^E$ at 298.15 ± 0.001 K were calculated from the experimental density data which was obtained using a vibrating flow densimeter (Sodev Inc.). The details of the experimental technique for the preparation of solutions [4] and the measurement of density [1] have been described earlier. The maximum uncertainty in the excess volumes of mixing data reported by us is expected to be around ±0.008 cm$^3$ mole$^{-1}$.

## RESULTS AND DISCUSSION

The excess volumes of mixing, $V^E$, for the binary mixtures obtained at 298.15 are recorded in Table 1 and are plotted as a function of composition in Fig. 1. The data were fitted to the smoothing equation

$$\frac{V^E}{X_1(1-X_1)} = A + B(2X_1 - 1) + C(2X_1 - 1)^2 + D(2X_1 - 1)^3 \quad (1)$$

where $X_1$ is the mole fraction of tetrahydrofuran. The values of the constants $A$, $B$, $C$ and $D$, evaluated by the method of least squares, and the standard deviation for the excess volumes, $\sigma(V^E)$, are given in Table 2.

We find the $V^E$ values for the mixtures of tetrahydrofuran with ethylene glycol reported by Klapproth [5] at 295.15 K are consistently less negative than those reported by us. No explanation is evident to us for this difference. It is possible that the tetrahydrofuran sample used in the earlier study [5] may be contaminated. Our values were, however, carefully checked by running a duplicate measurement for each experimental point. To the best of our knowledge, no $V^E$ data has been reported in the literature for other binary mixtures considered in this paper.

It is observed that the $V^E$ for methanol solutions are negative over the

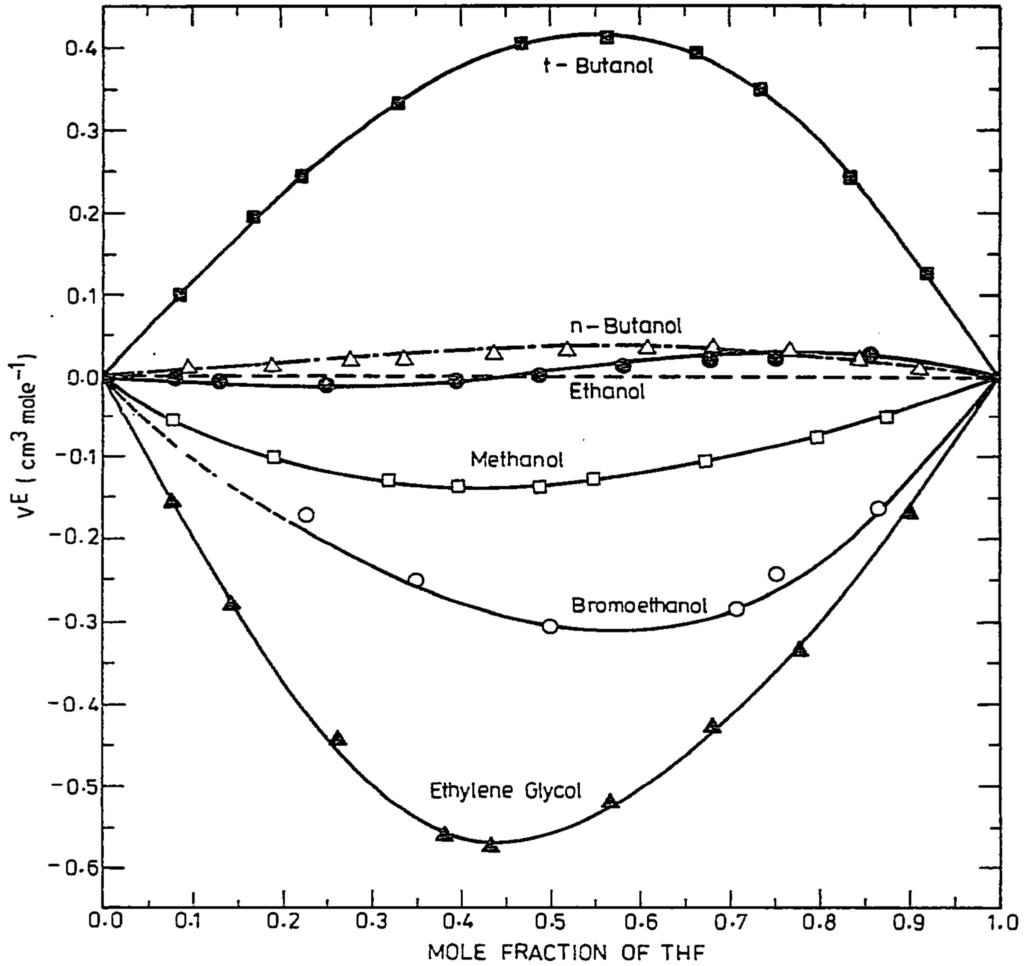

Fig. 1. Excess volume of mixing, $V^E$, as a function of the composition for binary mixtures of tetrahydrofuran with various alcohols at 298.15 K. □, Methanol; ●, ethanol; △, *n*-butanol; ▨, *tert*-butanol; ○, 2-bromoethanol; ▲, ethylene glycol.

entire composition range. It is, therefore, evident that tetrahydrofuran molecules strongly interact with the hydroxyl group of methanol. The volumetric effects arising from this interaction supercedes the positive contribution to

TABLE 2

Parameters of eqn. (1) and the standard deviation $\sigma(V^E)$ in cm$^3$ mole$^{-1}$ at 298.15 K for binary mixtures of some alcohols with tetrahydrofuran

| System | *A* | *B* | *C* | *D* | Standard deviation $\sigma(V^E)$ |
|---|---|---|---|---|---|
| THF + methanol | −0.5283 | 0.1199 | −0.0935 | 0.1057 | ±0.002 |
| THF + ethanol | 0.0020 | 0.1543 | 0.1139 | −0.0078 | ±0.001 |
| THF + *n*-butanol | 0.1203 | 0.0907 | 0.0184 | −0.0803 | ±0.002 |
| THF + *tert*-butanol | 1.6527 | 0.3876 | −0.1617 | −0.2059 | ±0.004 |
| THF + 2-bromoethanol | −1.1902 | −0.6156 | −0.0155 | 0.8468 | ±0.007 |
| THF + ethyleneglycol | −2.2208 | 0.5820 | 0.3480 | −0.7060 | ±0.007 |

the $V^E$ due to the structure breaking of the polymer aggregates of methanol. The self-associated polymer aggregates of higher alcohols are relatively easier to break. However, the hydrogen bond energy between the hydroxyl group of the alcohol and the hydrogen acceptor oxygen of tetrahydrofuran, and consequently the volumetric effects arising therefrom, decrease with the increase in alkyl chain length of the alcohol. Experimentally determined $V^E$ values for binary mixtures of alcohols follow the expected trend, viz. methanol < ethanol < *n*-butanol.

The large positive $V^E$ for mixtures containing *tert*-butanol compared with those containing *n*-butanol reflects the easiness of breaking the intermolecular structure of *tert*-butanol, and its relatively weaker hydrogen bonding interactions with tetrahydrofuran. Substitution of bromine at the $\beta$ position in ethanol increases its hydrogen bond-forming capability which results in more negative values of $V^E$ for the binary mixtures of tetrahydrofuran with 2-bromoethanol compared with those with ethanol. The rupture of intramolecular hydrogen bonding in ethylene glycol would not produce significant volumetric effects. However, because of the increase in hydrogen bonding centres in this molecule compared with that of ethanol, the decrease in volume on mixing with tetrahydrofuran is expceted to be much more and even more than that of 2-bromoethanol. The experimental results reveal this (Fig. 1).

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