ABSTRACT

Excess volumes, $V^e$, of binary liquid mixtures (1) Toluene-Bromobenzene, (2) Toluene-Nitrobenzene, (3) Toluene-Cyclohexanone, (4) Cyclohexane-Nitrobenzene, (5) Cyclohexane-Cyclohexanone were measured at 30° C. The results were analysed in terms of Flory's theory. It is found that the theory, in general, is applicable to the mixtures studied.

INTRODUCTION

The excess thermodynamic functions of binary liquid mixtures can reasonably be predicted in terms of the statistical theory developed by Flory. This theory is based on the postulation that the intermolecular energy arises effectively from the interactions between the surfaces of adjoining molecules. In this paper, we have analysed the measured excess volumes and the heats of mixing reported in literature of binary liquid mixtures: (1) Toluene-Bromobenzene, (2) Toluene-Nitrobenzene, (3) Toluene-Cyclohexanone, (4) Cyclohexane-Nitrobenzene and (5) Cyclohexane-Cyclohexanone in the light of Flory Theory.

EXPERIMENTAL

Measurement of excess volume—Excess volumes at 30·0° ± 0·01° C. were computed from accurate density values of pure liquids and liquid mixtures obtained by pyknometric method described in an earlier paper. The densities are accurate to one part in $10^4$ parts and the excess volumes are accurate to $±0·02$ ml. per mole of mixture.

Purification of materials.—Toluene, Bromobenzene and Cyclohexane were purified by the methods described previously. Nitrobenzene was dried over anhydrous calcium chloride for 48 hours and then distilled. The middle fraction of the distillate was collected.
Cyclohexanone was kept over anhydrous sodium sulphate for 24 hours and then distilled in an all glass apparatus.

Purities of the samples used for the present work have been verified from densities and boiling points reported in literature.\textsuperscript{7, 8}

**THEORETICAL**

The equations for the excess volume, $V^E$, and excess heat of mixing $h^E$ due to Flory take the forms,

$$V^E = \tilde{v}^E_{\text{calc.}} \left( X_1 V_1^* + X_2 V_2^* \right)$$

$$h^E = X_1 P_1^* V_1^* \left( \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}_2} \right)$$

$$+ X_2 P_2^* V_2^* \left( \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}_{\text{calc.}}} \right) + \frac{X_1 V_1}{\tilde{v}_{\text{calc.}}} \theta X_{12}$$

$\tilde{v}^E_{\text{calc.}}$, the excess calculated reduced volume is related to the ideal reduced volume $\tilde{v}^0$, ideal reduced temperature $\tilde{T}$ and the reduced temperature $\tilde{T}$ of mixture by the relations:

$$\tilde{v}^E_{\text{calc.}} = \left( \tilde{v}^0 \right)^{3/2} \left[ \frac{4}{3} - \left( \tilde{v}^0 \right)^3 \right]^{-1} [\tilde{T} - \tilde{T}^0]$$

$$\tilde{v}^0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2$$

$$\tilde{T}^0 = \left[ \left( \tilde{v}^0 \right)^{3/2} - 1 \right] \left( \tilde{v}^0 \right)^{3/2}$$

$$\tilde{v}_i = \left[ 1 + \frac{a_i T/3}{1 + a_i T} \right], \ (i = 1, 2)$$

$$\phi_1 = 1 - \phi_2 = \frac{X_1 V_1^*}{X_1 V_1^* + X_2 V_2^*}$$

$$V_i^* = \frac{V_i}{\tilde{v}_i}$$

$$\tilde{T} = \left[ \phi_1 P_1^* + \phi_2 P_2^* \right]^{-1} \left[ 1 - \frac{\phi_1 \theta X_{12}}{\phi_1 P_1^* + \phi_2 P_2^*} \right]^{-1}$$

$$P_i^* = \frac{a_i}{(K_T)_i} \tilde{v}_i^{3/2}$$

$$\tilde{v}_{\text{calc.}} = \tilde{v}^0 + \tilde{v}^E_{\text{calc.}}$$