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Evaluation of Interaction Parameters from Viscosity Data of Liquid Mixtures

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Following the relations for the viscosity of binary mixtures due to Grunberg and Nissam[1] and that due to Katti *et al.*[2], the excess free energy of mixing, strength of interaction parameter, interaction energy term and viscosity of binary system of chloroform-triethylamine have been evaluated. The strength of interaction has been discussed.

Key Words: Interaction parameters, Viscosity data, Liquid mixtures.

INTRODUCTION

Various attempts[1–6] have been made to study the interactions in binary liquid mixtures in the light of excess thermodynamic functions. However, very few attempts[7–12] have been made to study the interactions from viscosity data. The present investigation deals with the evaluation of strength of interaction parameter (d), excess free energy of mixing $\alpha\Delta F_m$, interaction energy term (W_{vis}) and viscosity (η) for chloroform + triethylamine at 25°C using viscosity data of Das[17].

The free energy of activation (ΔF^*) is related to energy of vaporization (ΔE) by

$$\Delta F^* = \frac{\Delta E}{2.45} \tag{1}$$

Eyring *et al.*[13] observed the following relation of the actual value of the fluidity of the mixture:

$$\phi_m(a) = \frac{V_m}{hN} \exp\left\{-\left[\frac{(x_1\Delta E_1 + x_2\Delta E_2)}{2.45} - \frac{\Delta F_m}{2.45}\right]\Big/ RT\right\} \tag{2}$$

where the various symbols have the usual meaning. The fraction $\left(\frac{1}{2.45}\right)$ of the excess free energy of mixing in the above equation is representd by the letter α and different workers[14, 15] gave different values for it.

Rewriting the equation (2) in terms of viscosity of the mixture [$\eta_{m(a)}$] and taking logarthims on both sides, we get

$$\ln \eta_{m(a)} + \ln \frac{V_m}{hN} = \left(\frac{x_1\Delta E_1 + x_2\Delta E_2}{2.45RT}\right) - \frac{\alpha\Delta F_m}{RT} \tag{3}$$

In the light of Eyring's[13] equation for the fluidity of ideal mixtures, the viscosity of an ideal mixture [$\eta_{m(a)}$] is given by the following relation:

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$$\ln \eta_{m(i)} + \ln \frac{V_m}{hN} = \left(\frac{X_1\Delta E_1 + X_2\Delta E_2}{2.45RT}\right) \tag{4}$$

and from eqns. (3) and (4) we obtain

$$\alpha\Delta F_m = -RT(\ln \eta_{m(a)} - \ln \eta_{m(i)}) \tag{5}$$

From eqn. (5), $\alpha\Delta F_m$ can be calculated if viscosity data are available. The value of R used in these calculations is 1.987 cal mol^{-1} deg^{-1}.

According to Grunberg and Nissam[16] the viscosity of non-ideal mixtures is represented by the relation:

$$\ln \eta_{m(a)} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1X_2d \tag{6}$$

where η_1 and η_2 stand for the viscosities of components 1 and 2 respectively. Assuming that eqn. (6) is valid for estimating the strength of interaction parameter (d), from a knowledge of experimental viscosity data, one can get

$$d = -\left[\frac{1}{X_1X_2} \cdot \frac{\alpha\Delta G_m}{RT}\right] \tag{7}$$

Theoretical evaluation of viscosity has been made using Katti and Chaudhure's expression[7]

$$\ln \eta_{m(a)}V_m = X_1 \ln \eta_1V_1 + X_2 \ln \eta_2V_2 + X_1X_2\frac{W_{vis}}{RT} \tag{8}$$

Assuming that eqn. (8) enables the estimation of W_{vis} from a knowledge of experimental viscosity data, one can get from eqns. (6) and (8)

$$W_{vis}\frac{X_1X_2}{RT} = \left[\ln \frac{V_m}{V_1^{x_1}V_2^{x_2}}\right] + dRT \tag{9}$$

The viscosity of the mixture from ideal mixing rule may be given as:

$$\eta_{m(i)} = X_1\eta_1 + X_2\eta_2 \tag{10}$$

where X_1, X_2 are the mole fractions of first and second components and η_1 and η_2 are viscosities of the pure components.

RESULTS AND DISCUSSION

The value of excess free energy of mixing ($\alpha\Delta G_m$), the interaction parameter (d), and interaction energy term (W_{vis}) for the binary mixture of chloroform-trimethylamine at 25°C were calculated by eqns. (5), (7) and (9) respectively.

The necessary data required for the calculation where taken from the literature[24]. The results obtained have been shown in Table-1, in its columns 5th, 6th and 7th respectively.

The viscosity obtained from ideal mixing rule (eqn. 10) has been shown in the column 3rd of Table-1. The result obtained from [$\ln \eta_{m(a)} - \ln \eta_{m(i)}$] relation have been shown in the 4th column of Table-1.

Persual of the table shows that the viscosity obtained from ideal mixing rule shows a regular trend of increase with increase in mole fraction of chloroform following the trend of viscosity obtained experimentally.

A thorough examination of Table-1 reveals that experimental viscosity value differs from ideal viscosity value of the mixture which shows the presence of some complexing in the system under investigation. If the mixture would have been an ideal one, the value of viscosity $\eta_{m(i)}$ should not differ.

TABLE-1

VALUES OF THE INTERACTION PARAMETER (d), EXCESS FREE ENERGY OF MIXING ($\alpha\Delta G_m$) AND INTERACTION ENERGY TERM (W_{vis}) FOR BINARY SYSTEM OF CHLOROFORM-TRIETHYLAMINE AT 25°C

X_1	$\eta_{m(a)}$[15] MPa	$\eta_{m(id)}$ (eq. 10)	$[\ln \eta_{m(a)} - \ln \eta_{m(i)}]$	$\alpha\Delta F_m$ cal/mole (eq. 5)	d (eq. 7)	W_{vis} cal/mole (eq. 9)
0.0000	0.358	0.3580	—	—	—	—
0.1020	0.406	0.3756	0.0779	–46.1957	0.8513	580.7646
0.2103	0.463	0.3942	0.1609	–95.3475	0.9691	653.7063
0.3058	0.527	0.4106	0.2496	–147.8722	1.1758	1497.4812
0.4087	0.592	0.4283	0.3237	–191.7713	1.3395	877.9460
0.5115	0.638	0.4459	0.3581	–212.1391	1.4331	936.5130
0.6009	0.651	0.4614	0.3443	–204.0028	1.4358	941.0747
0.6932	0.639	0.4773	0.2919	–172.9321	1.3725	906.8115
0.8215	0.596	0.4993	0.1770	–104.8908	1.2074	813.9745
0.9103	0.564	0.5146	0.0917	–54.3387	1.1233	767.9706
1.0000	0.530	0.5300	—	—	—	—

Persual of Table-1 also reveals that values of $\alpha\Delta G_m$ are all negative at all mole fractions of chloroform. A negative excess function is a strong indication of the presence of interaction in the system.

The negative magnitude of $\alpha\Delta G_m$ varies with the composition of the mixture and is maximum at $x_1 = 0.5115$, showing greater internal flexibility of triethylamine, which allows more favourable accommodation within the available volume, in the liquid structure.

Nigam *et al.*[9] and Rammoorthy[10] observed that if $d > 0$ and large in magnitude, strong specific interaction is indicated. If $d > 0$ but not very large in magnitude, weak specific interactions are present. If $d < 0$ and large in magnitude there are no specific interactions.

Persual of Table-1 shows that the value of d is positive and is in increasing order with rise in mole fraction of chloroform; intermolecular interaction is obvious. It is maximum at $x_1 = 0.6009$ and then shows is reducing trend. Presence of chlorine in chloroform makes it a polar and electron repelling group. Ethyl group also makes in triethylamine a polar molecule; thus a dipole-dipole interaction is possible which is maximum at approximatly equal mole fraction of the component of the mixture, and reduces after $x_1 = 0.6009$.

W_{vis} are all positive at all mole fractions and maximum at $x_1 = 3058$ but generally in increasing order, up to equal mole fraction and then show a reducing trend, similar to d.

The value of $[\ln \eta_{m(a)} - \ln \eta_{m(i)}]$ also shows increasing trend up to mole fraction of $x_1 = 0.5115$ and then shows reducing trend.

The present observation well supports the dipole-dipole interaction in the binary system of chloroform and triethylamine. This view has also been supported by other workers[17]. According to them there exists an equilibrium between chloroform-triethylamine with the formation of 1 : 1 chloroform-triethyl complex of the type given below:

$$A + B = AB.$$

This complex is of charge transfer type. Here Triethylamine (because of increased electron density on the nitrogen atom arising due to electron replacing inductive effect of ethyl groups) acts as donor, while chloroform (because of the electron-deficiency on the carbon atom due to electron withdrawing inductive effect of the chlorine atoms) behaves as accepter.

Thus it is obvious that chloroform-triethylamine forms complex of the type AB, suporting the idea of ideal associated solution model theory[17].

Thus it may be concluded that viscosity may be used to evaluate the extent and magnitude of interaction within the molecules of liquid mixtures. The ideality of the component of the mixture can be evaluated, if the data other than viscosity are not available.

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