

An Attempt to Interpret the Variations in Excess Viscosity in non-ideal Homogeneous Binary Liquid Systems

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In non-ideal homogeneous binary liquid systems, the occurrence of maxima or minima in the plots of excess viscosity η^E versus composition has been explained by assuming the existence of mobile liquid structures having a central molecule of one component surrounded by the molecules of the other component. Further, in order to decide which component provides the central molecule and which one provides the surrounding molecules, conditions involving a parameter obtained from η^E versus composition curves are stated for polar-polar, non-polar-polar and nonpolar-nonpolar systems.

VISCOSITY of homogeneous binary liquid systems has been investigated by various workers¹⁻⁴ in the past. However, the deviations from ideal behaviour are still to be fully understood in terms of molecular and bulk properties of the pure components⁵. It may further be added that it is not sufficient to consider the molecular parameters or the physical properties of the components only, but it is also necessary to assess the magnitude of the properties of mobile liquid structures⁶ which may originate because of the existence of polar interactions⁷, weak complex formations⁸, hydrogen bonding⁹ or cohesive attachments in such binary systems. Thus it is worth while to attempt an interpretation of the data on non-ideal homogeneous binary liquid systems by taking into consideration specific liquid structures in each case.

Results and Discussion

Let us consider a binary liquid system consisting of component A with mole fraction X_A and component B with mole fraction X_B . If the molecules of the two components are dissimilar, there is a definite interaction between them due to their polar or complexing nature, or due to the existence of a cohesive force between their molecules giving rise to the existence of definite mobile liquid structures. Let us further assume that these liquid structures consist of a central molecule of one component surrounded by a definite number of the molecules of the other component. If this is so, it follows that the surrounding molecules should bear a constant ratio C with the central molecule at any temperature ; C being necessarily equal to or greater than unity. Thus assuming arbitrarily that component A provides the central and component B provides the surrounding molecules in the structural units, we have

$$\frac{X_B \text{ combined}}{X_A \text{ combined}} = C \quad (1)$$

where $C \geq 1$

If we consider the binary system through its entire composition range, we can group the compositions in

three categories. In the first category, the compositions of the system are rich in component B and a portion of it acts as the bulk molecules whereas the rest remains in combination with the entire component A in the form of liquid structures. In the second category, the compositions of the system are rich in component A and a portion of it acts as bulk molecules whilst the rest remains in combination with the entire component B in the form of liquid structures. But in the third category, we have a situation in which both the components exist in the combined form only with no uncombined molecules of either component, giving $X_A = X_A \text{ combined}$ and $X_B = X_B \text{ combined}$. With these conditions in view and remembering that $X_A + X_B = 1$, we get from equation (1)

$$\frac{1 - X_A}{X_A} = C \quad (2)$$

Since the concentration of liquid structures is maximum in this case, X_A can be designated as $X_{A \text{ max}}$ and equation (2) can be written as

$$\frac{1 - X_{A \text{ max}}}{X_{A \text{ max}}} = C \quad (3)$$

As assumed earlier, if component A provides the central molecule and $C \geq 1$, then from equation (3) we have

$$X_{A \text{ max}} \leq 0.5 \quad (4)$$

On the other hand, if component A is to provide the surrounding molecules and component B is to provide the central one, then we have

$$\frac{X_A \text{ combined}}{X_B \text{ combined}} = C \quad (5)$$

Proceeding as before, we have from equation (5)

$$X_{A \text{ max}} \geq 0.5 \quad (6)$$

It follows as a consequence that either of the two situations is equally probable if

$$X_{A \text{ max}} = 0.5 \quad (7)$$

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Thus for any binary liquid mixture, it is possible to decide which of the two components provides central molecule in the liquid structures if the numerical value of $X_{A \text{ max}}$ for that system is known. Recalling that $X_{A \text{ max}}$ by definition is equal to X_A for which the concentration of the liquid structures is maximum in the composition range from $X_A = 0$ to $X_A = 1$ and also that the magnitude of non-ideality represented by excess viscosity η^E in the viscosity behaviour is to be attributed to the existence of these liquid structures, it is obvious that the value of X_A for which η^E is maximum or minimum and equals η^E_{max} gives the value of $X_{A \text{ max}}$. Since a maxima is obtained in the plot of η^E versus X_A when η^E is positive, the viscosity of the liquid structures should obviously be higher than either of the pure components. If it is so, the higher viscosity of the liquid structures implies that the order among their molecules is greater than that among the molecules of either of the pure components leading to the expectation that the dipole moment of the component providing central molecule μ_C which is largely responsible for the orderliness in the liquid structures is greater than the dipole moment of the component providing surrounding molecules μ_B in case the binary components are polar or nonpolar-polar. However, in case the binary components are nonpolar-nonpolar, the central molecule is expected to possess greater orientation capacity due to its greater complexing or cohesive nature in order that liquid structures show higher viscosity. On the other hand, since a minima is obtained in the plot of η^E versus X_A when η^E is negative, the viscosity of the liquid structures should be lower than either of the pure components indicating less order among the molecules of the liquid structures and leading to the expectation that the component providing central molecule possesses lower dipole moment or acts as diluent due to its lower ability for complex formation or cohesive orientation than the component providing surrounding molecules.

To verify the above conclusions, the values of X_A and η^E for suitable binary liquid systems from the published data^{1,0} were plotted in Figures 1 to 4 and the value of $X_{A \text{ max}}$ and the corresponding value of η^E designated by η^E_{max} were determined for individual systems to decide which component provides the central molecule in the liquid structures formed in the system.

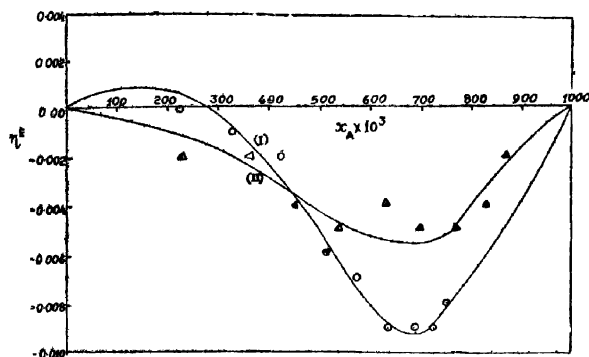


Fig. 1. Plots of excess viscosity (η^E) versus mole fraction (X_A) for binary mixtures of (I) CH_2Cl_2 (A) + Toluene (B), and (II) CH_2Cl_2 (A) + *o*-xylene (B) at 25°C.

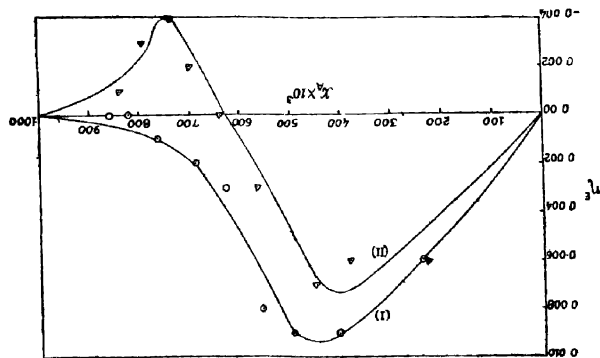


Fig. 2. Plots of excess viscosity (η^E) versus mole fraction (X_A) for binary mixtures of (I) CH_2Cl_2 (A) + *m*-xylene (B), and (II) CH_2Cl_2 (A) + *p*-xylene (B) at 25°C.

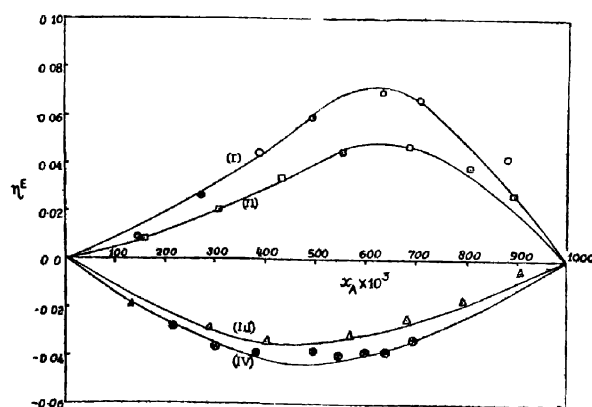


Fig. 3. Plots of excess viscosity (η^E) versus mole fraction (X_A) for the binary mixtures of (I) CHCl_3 (A) + Acetone (B), (II) CHCl_3 (A) + Ether (B), (III) Acetone (A) + Benzene (B), & (IV) CH_2Cl_2 (A) + Benzene (B) at 25°C.

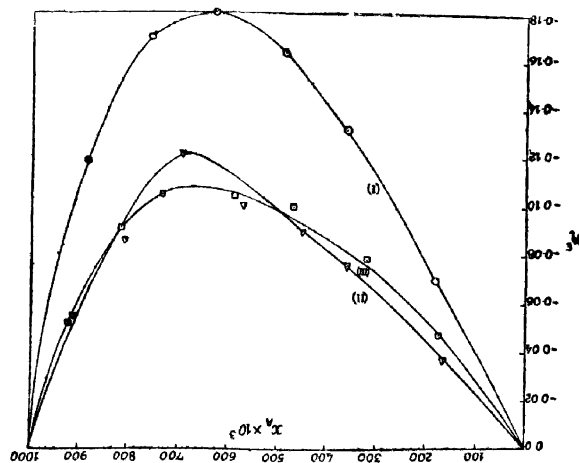


Fig. 4. Plots of excess viscosity (η^E) versus mole fraction (X_A) for the binary mixtures of (I) Cyclohexane (A) + η -Pentane (B), (II) Benzene (A) + η -Pentane (B) at 25°C, & (III) Benzene (A) + η -Hexane (B) at 25°C.

From the curves in Figure 1 to 4, it is clear that we get a single value of $X_{A \text{ max}}$ and consequently a single value of η^E_{max} for all the systems considered except for $\text{CH}_2\text{Cl}_2 + \text{C}_6\text{H}_5\text{CH}_3$ and $\text{CH}_2\text{Cl}_2 + \text{p-C}_6\text{H}_4(\text{CH}_3)_2$

TABLE 1—VALUES OF X_A^{max} , η^E_{max} AND COMPARATIVE SIGNS OF $\Delta\mu_{cs}$ OR ORIENTING TENDENCIES OF THE COMPONENT MOLECULES IN NON-IDEAL BINARY LIQUID SYSTEMS

Sl No.	System Component A	Component B	X_A^{max} at 25°	η^E_{max} at 25°	Component Providing Central Molecule	Component Providing Surrounding Molecules	Predicted Sign of $\Delta\mu_{cs}$ for polar-polar and nonpolar-polar systems and orienting tendency of component providing central molecule for nonpolar-nonpolar systems
1.	CH_2Cl_2	C_6H_6	0.510	-0.0420	C_6H_6	CH_2Cl_2	-ve
2.	CH_2Cl_2	$C_6H_5CH_3$	0.150	+0.0009	CH_2Cl_2	$C_6H_5CH_3$	+ve
3.	CH_2Cl_2	$C_6H_5CH_3$	0.690	-0.0092	$C_6H_5CH_3$	CH_2Cl_2	-ve
4.	CH_2Cl_2	<i>o</i> - $C_6H_4(CH_3)_2$	0.675	-0.0053	<i>o</i> - $C_6H_4(CH_3)_2$	CH_2Cl_2	-ve
5.	CH_2Cl_2	<i>m</i> - $C_6H_4(CH_3)_2$	0.450	+0.0093	CH_2Cl_2	<i>m</i> - $C_6H_4(CH_3)_2$	+ve
6.	CH_2Cl_2	<i>p</i> - $C_6H_4(CH_3)_2$	0.410	+0.0073	CH_2Cl_2	<i>p</i> - $C_6H_4(CH_3)_2$	+ve
7.	CH_2Cl_2	<i>p</i> - $C_6H_4(CH_3)_2$	0.735	-0.0040	<i>p</i> - $C_6H_4(CH_3)_2$	CH_2Cl_2	-ve
8.	$CHCl_3$	CH_3COCH_3	0.625	+0.0730	CH_3COCH_3	$CHCl_3$	+ve
9.	$CHCl_3$	$C_2H_5OC_2H_5$	0.640	+0.0495	$C_2H_5OC_2H_5$	$CHCl_3$	+ve
10.	CH_3COCH_3	C_6H_6	0.538	-0.0350	C_6H_6	CH_3COCH_3	-ve
11.	C_6H_{12}	<i>n</i> - C_6H_{12}	0.635	-0.1800	<i>n</i> - C_6H_{12}	C_6H_{12}	Less orienting
12.	C_6H_6	<i>n</i> - C_6H_{12}	0.685	-0.1230	<i>n</i> - C_6H_{12}	C_6H_6	Less orienting
13.*	C_6H_6	<i>n</i> - C_6H_{14}	0.675	-0.1090	<i>n</i> - C_6H_{14}	C_6H_6	Less orienting

* The values for $C_6H_6 + n-C_6H_{14}$ system are at 20°C

systems for each of which two values of X_A^{max} are obtained, one corresponding to the maxima and the other to the minima in the composition range $X_A = 0$ to $X_A = 1$. For these systems the occurrence of the maxima is in the B rich composition and the minima is in the A rich composition. This signifies that in these systems the position of central and surrounding molecules in the liquid structures depends on the composition.

It is also expected that the plot of mixture viscosity η versus X_A should show an abrupt change in the slope at X_A for which the concentration of the liquid structures is maximum in any binary system and accordingly X_A^{max} can be determined from the value of X_A corresponding to this abrupt change, if it is sharp enough. Obviously, the value of X_A^{max} thus determined from η versus X_A plot should agree, within the limits of experimental error, with X_A^{max} determined from η^E versus X_A plot. The comparison showed that it is actually so except in the case of acetone-benzene system, for which the value of X_A^{max} from η^E versus X_A plot is less than 0.5 and from η versus X_A plot it is greater than 0.5. In this situation, the value of X_A^{max} determined from η versus X_A plot has been preferred for this system by us as the change in slope of the curve is quite sharp at $X_A = X_A^{max}$ and appears to give a more accurate value for X_A^{max} .

On the basis of the values of X_A^{max} and η^E_{max} as determined above, it was easy to decide which component provides the central molecule and which one provides the surrounding molecules in the liquid structures for each system. Knowing this the sign of $\Delta\mu_{cs} = \mu_c - \mu_s$ was predicted in the case of polar-polar and nonpolar-polar systems whereas the orienting tendency was predicted in the case of nonpolar-nonpolar systems. The values of X_A^{max} , η^E_{max} , comparative sign of $\Delta\mu_{cs}$ for polar-polar and nonpolar-polar systems and orienting tendencies for nonpolar-nonpolar systems have been tabulated in Table 1.

The predicted sign of $\Delta\mu_{cs}$ can easily be verified from the standard values of dipole moments¹¹ in all the cases of polar-polar and nonpolar-polar systems. For nonpolar-nonpolar systems, the predicted orientation tendency of the central molecule is in agreement with the known comparative tendencies of the central and surrounding molecules towards complex formation or cohesive attachments. This indicates that the mobile liquid structures, mainly responsible for non-ideality in the viscosity behaviour of homogeneous binary liquid systems, may safely be considered to possess a central molecule of one component surrounded by a definite number of the molecules of the other component.

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