INTRODUCTION

We have been engaged in the study of thermodynamic, acoustic and transport properties of liquid mixtures. In our previous investigations, we have reported viscosities, speed of sound, isentropic compressibilities and theoretical for various binary and ternary mixtures. 

The nature of interactions in binary systems have been explained on the basis of certain thermodynamic properties such as excess volume, deviation in viscosity, deviation incompressibility, excess enthalpies etc.

Excess volume and excess thermal expansivities for binary mixtures of 2-ethoxyethanol with n-octane, benzene and cyclohexane are reported by Ohji. Excess enthalpies, excess heat capacities, densities and cyclohexane were measured at different temperatures by Nishimoto et al.

In the present study, we have measured densities and viscosities of three binary mixtures of 2-methoxyethanol with heptane (I), benzene (II) and 1,4-dioxane (III) at 308 K.

EXPERIMENTAL

All the solvents used were fractionally distilled and their accuracy was checked by GLC. Further, viscosities and densities of these pure solvents were measured which were in good agreement with literature values of Riddick et al.

Densities and viscosities of the three systems at various compositions were measured at 308 K by the procedures reported earlier. The uncertainty in the measurement of density and viscosity are ± 0.0001 g/ml and ±0.06 % respectively.

Theory

To evaluate the viscosities of binary liquid mixtures in terms of pure component data, various semi empirical relations have been proposed.

For binary liquid mixtures, Bingham relation was modified to:

\[ \eta = \sum x_i \eta_i \] (1)

Additive relation based on Arrhenius and Eyring’s model for the viscosity of pure liquids can be modified as:

\[ \ln \eta V = \sum x_i \ln \eta_i V_i \] (2)

Where \( x_i \), \( \eta_i \) and \( V_i \) are the mole fraction, viscosity and volume of the \( i^{th} \) component respectively.

Hind et al. proposed the following equation:

\[ \eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 \eta_1 \eta_2 \] (3)
\( \eta_{12} \) is attributed to unlike pair interactions. It is approximately equal to 0.5 \((\eta_1 + \eta_2)\) but this relation is not sufficiently accurate for the predication purpose. Equation (3) has been theoretically derived by Bearman and Jones\(^{11}\) from statistical mechanical theory.

Kendall and Munroe\(^{12}\) gave the following equation for multi component system,

\[
1n \eta = (x_1 \eta_1 + x_2 \eta_2) \tag{4}
\]

The Grunberg and Nissam relation\(^{13}\) for the viscosity of non-ideal mixture is given by:

\[
1n \eta = \sum x_i 1n \eta_i + x_1 x_2 d \tag{5}
\]

Where \(d\) is an approximate measure of strength of interaction between the components of the mixture.

\[
d = -\left( \frac{\alpha F_m}{x_1 x_2 RT} \right) \tag{6}
\]

where \(\alpha F_m\) is the excess free energy of mixing and is given by

\[
\alpha F_m = - RT(1n\eta - 1n\eta_{Bing}) \tag{7}
\]

where \(\eta_{exp}\) is the experimental viscosity value and \(\eta_{Bing}\) is the viscosity calculated by eq. (1).

The Katti and Chaudhari relation\(^{14,15}\) can be written as:

\[
1n \eta V = \sum x_i 1n \eta_i V_i + (W_{vis}/RT) x_1 x_2 \tag{8}
\]

where \(W_{vis}\) is the interaction energy parameter among the components and is given by:

\[
W_{vis} = (RT/X_1 X_2) ln (V/\sum V_i x_i) + d RT \tag{9}
\]

where \(V\) is the volume of the mixture and \(V_i\) is the volume of pure components at different compositions.

**RESULTS AND DISCUSSION**

The theoretical values of viscosities and thermodynamic parameters like excess free energy of mixing, strength of interaction parameter and interaction energy etc are calculated from different equations mentioned above.

The experimental and theoretical viscosity values and thermodynamic parameters in the three systems are given in Table - 1 for all the three systems. The percentage deviations between experimental and theoretical viscosity values are given in Table - 2.

Table - 2 shows that in system 1, the deviation between experimental and theoretical values is large for almost all theories. In system II, good agreement between experimental and theoretical values is observed for Bingham relation. However, except Arrehenius relation, fair agreement is observed between experimental and theoretical values calculated. From other relations. In system III, very good agreement is observed for GN relation but except Arrehenius, all other theoretical values are in good agreement with the experimental results. The Aehrenius relation was proposed considering ideal mixing of solution, which is not true at all the composition of binary mixtures. Comparison of the three systems shows that in system III, which is methoxyethanol and 1,4-dioxane mixture, deviation is less in comparison to other two systems for all the theories.

In the mixture, quantitative estimation of interaction can be done by the strength of interaction parameter \((d)\). the \(d\) values are generally negative except in system II, where it is positive for some compositions. It is reported\(^{7}\) that if \(d\) is greater than zero, weak interaction is present. Thus, weak interactions are present in system I and III, whereas in system II, interactions are somewhat stronger in comparison to other two systems.

Further, comparison of \(d\) values with \(\alpha F_m\) shows that \(d\) values have opposite sign than that of \(\alpha F_m\). Values of \(\alpha F_m\) are generally positive except for system II where it is negative for some compositions. A positive value indicates weak interaction whereas negative value suggests strong interaction in the mixture. This is further confirmed by \(W_{vis}\) values, which are highly positive for system II in comparison to other two systems, suggesting there by strong interaction in II system than in system I and III.

Thus, it may be concluded that all these relations can be used to calculate the viscosity of binary systems. However, Arrehenius relation does not give results due to non-ideal nature of selected binary systems. In methoxyethanol + benzene system, interactions are stronger than those in other two systems.
### Table 1: Values of thermodynamic parameters and experimental and theoretical viscosities for the three systems

|  | $\chi_{\text{Meth}}$ | $\eta_{\exp}$ | $\eta_{\text{Bing}}$ | $\eta_{\text{Ken}}$ | $\eta_{\text{GN}}$ | $\eta_{\text{Hin}}$ | $\eta_{\text{KM}}$ | $\eta_{\text{Arr}}$ | $D$ | $\alpha F_m$ | $W_{\text{vis}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 0.1028 | 0.4045 | 0.4863 | 0.4475 | 0.3748 | 0.4084 | 0.4575 | 0.5971 | -1.9216 | 104.944 | -1523.5 |
|   | 0.1966 | 0.4187 | 0.5652 | 0.4982 | 0.3690 | 0.4373 | 0.5170 | 0.6296 | -1.8993 | 177.637 | -784.4 |
|   | 0.3097 | 0.4444 | 0.6615 | 0.5669 | 0.3809 | 0.4994 | 0.5953 | 0.6712 | -1.8605 | 235.520 | -369.5 |
|   | 0.3965 | 0.4829 | 0.7354 | 0.6262 | 0.4112 | 0.5724 | 0.6605 | 0.7050 | -1.7576 | 249.035 | -104.6 |
|   | 0.5023 | 0.5763 | 0.8255 | 0.7068 | 0.4935 | 0.7019 | 0.7462 | 0.7485 | -1.4373 | 212.757 | -265.2 |
|   | 0.6045 | 0.6451 | 0.9125 | 0.7945 | 0.5617 | 0.8271 | 0.8356 | 0.7931 | -1.4504 | 205.321 | -347.0 |
|   | 0.6955 | 0.7914 | 0.9899 | 0.8817 | 0.7048 | 0.9191 | 0.8349 | -1.0569 | 132.547 | 171.530 | -103.5 |
|   | 0.8013 | 0.8084 | 0.0800 | 0.9951 | 0.7449 | 1.1835 | 1.1835 | 0.8864 | -2.8002 | 143.893 | -1985 |
| II | 0.0563 | 0.5953 | 0.5726 | 0.5584 | 0.5806 | 0.5412 | 0.5623 | 0.5016 | 0.7328 | -23.055 | 1616.45 |
|   | 0.1119 | 0.6167 | 0.6124 | 0.5855 | 0.5896 | 0.5580 | 0.5932 | 0.5222 | 0.0699 | -4.112 | 1293.38 |
|   | 0.2208 | 0.6613 | 0.6905 | 0.6425 | 0.6153 | 0.6116 | 0.6568 | 0.5649 | -0.2513 | 25.596 | 1242.28 |
|   | 0.3007 | 0.7094 | 0.7478 | 0.6879 | 0.6525 | 0.6716 | 0.7063 | 0.5985 | -0.2507 | 31.216 | 1386.81 |
|   | 0.4048 | 0.7863 | 0.8224 | 0.7518 | 0.7187 | 0.7721 | 0.7744 | 0.6452 | 0.1865 | 26.609 | 1501.19 |
|   | 0.5292 | 0.9566 | 0.9116 | 0.8359 | 0.8772 | 0.9445 | 0.8614 | 0.7059 | -0.1932 | 28.508 | 1761.76 |
|   | 0.6053 | 0.9757 | 0.9662 | 0.8920 | 0.9008 | 1.0068 | 0.9176 | 0.7458 | -0.0410 | -5.793 | 1639.91 |
|   | 0.7019 | 0.9495 | 1.0355 | 0.9687 | 0.9818 | 1.1019 | 0.9926 | 0.7998 | 0.0644 | -7.974 | 1575.95 |
|   | 0.7961 | 1.1684 | 1.1030 | 1.0497 | 1.1119 | 1.1932 | 1.0694 | 0.8566 | 0.3548 | -34.105 | 1629.49 |
|   | 0.8881 | 1.2443 | 1.1690 | 1.1354 | 1.2086 | 1.2392 | 1.1482 | 0.9148 | 0.6284 | -36.979 | 1624.12 |
| III | 0.1029 | 0.9748 | 1.0278 | 1.0254 | 0.9725 | 0.9999 | 1.0261 | 0.8745 | -0.5735 | 31.3468 | 504.66 |
|   | 0.1959 | 0.9844 | 1.0507 | 1.0466 | 0.9845 | 1.0075 | 1.0479 | 0.8860 | -0.3883 | 36.2205 | +314.17 |
|   | 0.3083 | 0.9903 | 1.0785 | 1.0728 | 0.9851 | 1.0207 | 1.0746 | 0.9001 | -0.4000 | 50.5130 | +657.27 |
|   | 0.3984 | 1.0012 | 1.1007 | 1.0943 | 0.9543 | 1.0410 | 1.0964 | 0.9116 | -0.3954 | 56.1158 | +809.38 |
|   | 0.5033 | 1.0168 | 1.1266 | 1.1198 | 1.0107 | 1.0721 | 1.1221 | 0.9251 | -0.4102 | 60.7264 | +870.84 |
|   | 0.6026 | 1.0467 | 1.1511 | 1.1447 | 1.0407 | 1.1133 | 1.1468 | 0.9381 | -0.3972 | 56.3206 | +843.14 |
|   | 0.6966 | 1.0965 | 1.1743 | 1.1685 | 1.0911 | 1.1691 | 1.1705 | 0.9505 | -0.3244 | 40.6000 | +753.78 |
|   | 0.8006 | 1.1757 | 1.2000 | 1.1955 | 1.1714 | 1.2159 | 1.1971 | 0.9645 | -0.1281 | 12.1077 | +564.54 |
|   | 0.9029 | 1.2557 | 1.2253 | 1.2228 | 1.2532 | 1.2480 | 1.2237 | 0.9785 | +0.2802 | -14.530 | +5.7635 |

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Table - 2: Comparison between the various viscosity data in the three systems

| $X_{ME}$ | $\Delta \eta_{ex-bin}$% | $\Delta \eta_{ex-Ken}$% | $\Delta \eta_{ex-GN}$% | $\Delta \eta_{ex-hi}$% | $\Delta \eta_{ex-KM}$% | $\Delta \eta_{ex-arrh}$% |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| I        |                 |                 |                 |                 |                 |                 |
| 0.1028   | -19.38          | -10.08          | 7.79            | -0.19           | -12.54          | -46.88          |
| 0.1966   | -34.99          | -18.98          | 11.87           | -4.44           | -23.47          | -50.37          |
| 0.3097   | -48.85          | -27.56          | 14.28           | -12.37          | -33.95          | -51.03          |
| 0.3987   | -52.29          | -29.67          | 14.84           | -18.53          | -36.77          | -45.99          |
| 0.5023   | -43.24          | -22.64          | 14.36           | -21.79          | -29.48          | -29.88          |
| 0.6045   | -41.45          | -23.19          | 12.92           | -23.37          | -16.38          | -5.49           |
| 0.6955   | -25.08          | -11.41          | 10.94           | -23.37          | -16.38          | -5.49           |
| 0.8013   | -33.59          | -23.09          | 7.85            | -33.00          | -27.11          | -9.64           |
| 0.9040   | -27.51          | +2.41           | 4.12            | -29.25          | -24.34          | -2.59           |
| II       |                 |                 |                 |                 |                 |                 |
| 0.0563   | 3.81            | 6.19            | 2.46            | 9.08            | 5.54            | 15.73           |
| 0.1119   | 0.69            | 5.05            | 4.39            | 9.51            | 3.81            | 15.32           |
| 0.2208   | -4.41           | 2.84            | 6.95            | 7.51            | 0.68            | 14.57           |
| 0.3007   | -5.41           | 3.03            | 8.02            | 5.32            | 0.43            | 15.63           |
| 0.4048   | -4.59           | 4.38            | 8.59            | 1.80            | 1.51            | 17.94           |
| 0.5292   | 4.70            | 12.61           | 8.30            | 1.26            | 9.95            | 26.20           |
| 0.6053   | 0.97            | 8.57            | 6.67            | -3.18           | 5.95            | 23.56           |
| 0.7019   | 1.33            | 7.69            | 6.45            | -4.99           | 5.42            | 23.79           |
| 0.7916   | 5.59            | 10.15           | 4.83            | -2.12           | 8.47            | 26.73           |
| 0.8881   | 6.05            | 8.75            | 2.86            | 0.40            | 7.72            | 26.48           |
| III      |                 |                 |                 |                 |                 |                 |
| 0.1029   | -5.43           | -5.19           | 0.23            | -2.57           | -5.26           | 10.28           |
| 0.1959   | -6.30           | -5.88           | 0.39            | -1.93           | -6.01           | 10.36           |
| 0.3083   | -8.90           | -8.33           | 0.52            | -3.06           | -8.51           | 9.10            |
| 0.3984   | -9.93           | -9.29           | 4.68            | -3.97           | -9.50           | 8.94            |
| 0.5033   | -10.79          | -10.12          | 0.59            | -5.43           | -10.35          | 9.01            |
| 0.6026   | -9.97           | -9.36           | 0.57            | -6.36           | -9.56           | 10.37           |
| 0.6966   | -7.09           | -6.56           | 0.49            | -5.96           | -6.74           | 13.31           |
| 0.8006   | -2.06           | -1.68           | 0.36            | -3.41           | -1.82           | 17.96           |
| 0.9029   | 2.42            | 2.62            | 0.19            | 0.61            | 2.54            | 22.07           |

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