Viscosities and excess viscosities for binary liquid mixtures of ethylene glycol with water, dioxan and acetone at 30, 35, 40, 45 and 50°C

A B Bilkis*, S K Biswas & M Alamgir

Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Research Establishment, P.O. Box No. 3787 Savar, Dhaka, Bangladesh
and

M A Saleh

Department of Chemistry, Chittagong University, Chittagong, Bangladesh

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Viscosities of three binary systems namely, ethylene glycol (EG)-water, ethylene glycol-dioxan and ethylene glycol-acetone have been measured at five different temperatures in between 303.15 K and 323.15 K by using Ostwald Viscometer. The values of excess viscosities η\(_\text{E}\) are negative over the entire range of composition in all the phases studied except EG-water system. The positive η\(_\text{E}\) values for polar EG-water system are due to the strong intermolecular H-bond with water. But negative η\(_\text{E}\) values in the other two non-polar (acetone is less polar) systems are probably due to inclusion of smaller EG molecule and less effective H-bonding. The η\(_\text{E}\) values have been fitted to highly composition dependent Redlich-Kister equation.

Viscometric measurements often yield valuable information regarding molecular interactions in the pure liquids as well as in liquid mixtures. A familiar approach is the hypothesis that there is a direct correlation between the viscosity and the thermodynamic behaviour of the solution. Very often it is essential to know the viscosity of the liquid mixtures to solve some practical problems regarding their heat content, mass transport and fluid flow. Many scientists\(^{1,2}\) worked on the transport properties of the liquid mixtures by measuring their viscosities. The binary liquid mixtures of ethylene glycol with water, dioxan and acetone were selected for the present study and their viscosities and densities at 30, 35, 40, 45 and 50°C were measured. Though some similar works in connection with the volumetric properties of ethylene glycol-water system\(^3\)–\(^7\) are available in literature, information regarding viscometric properties are limited.

Ethylene glycol is not known to form a clathrate or well-defined hydrates\(^8\). Aqueous mixtures of clathrate forming compounds frequently exhibit a maximum in their ultrasonic absorption coefficients near the composition of the hydrate\(^9\)–\(^11\) but EG-water mixtures do not\(^11\). Acetone is known to be extensively self-associated through hydrogen bonding in the pure state\(^12\), but unlike water, its cohesive energy, density and internal pressure indicate that the molecules are weakly associated. The physical properties of mixtures of ethylene glycol with Me\(_2\)CO and iso-ProH were determined\(^13\). The data reported here for EG-water, EG-dioxan and EG-acetone systems are used to analyses the behaviour of ethylene glycol in different media. The results of the present investigation are interpreted in terms of intermolecular interactions and also inclusion of smaller molecule into bigger one in the mixtures.

**Materials and Methods**

All the chemicals (E. Merck) were further purified by distillation. Water was also doubly distilled. The densities of the pure components and the mixtures were determined by weighing a definite volume of the respective liquids in a density bottle with 98% accuracy. The viscosities of the pure compounds and the mixtures were measured in a thermostat controlled to ±0.1°C by two types of Ostwald viscometers, type-A (calibration constant = 0.034101 cm\(^2\) s\(^{-2}\)) and type-B (calibration constant = 0.138281 cm\(^2\) s\(^{-2}\)). Type-A viscometer (used for EG-water system) was calibrated by distilled water at 30°C and type-B (used for the rest) by 40% by weight sucrose solution at 30°C.

The ideal viscosities of the mixtures at all temperatures were calculated by using Eq. (1)

\[
\ln \eta_{id} = X_1 \ln \eta_1 + X_2 \ln \eta_2
\]

where \(\eta_{id}\) = ideal viscosity (expected), \(\eta_1\) = visco-
Table 1—Experimental values of density, viscosity and excess viscosities for the various systems of CH\(_2\)OHCH\(_2\)OH from 30\(^\circ\) to 50\(^\circ\)C

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<th>(\eta, mPa.s)</th>
<th>(\eta^E, mPa.s)</th>
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- Contd.
The experimental values of \( \eta^E \) have been fitted by using Eq. (4)

\[
\eta^E = X_1(1 - X_1) \sum_{i=0}^{3} A_i (2X_1 - 1)^i
\]

... (3)

The standard deviations in \( \eta^E \) have been calculated using Eq. (4)

\[
s = \left[ \frac{\sum (\eta^E_{\text{exp}} - \eta^E_{\text{calcd}})^2}{n - p - 2} \right]^{1/2}
\]

... (4)

where, \( n \) = number of measurements and \( p \) = number of coefficients. All the values are given in Tables 1 and 2.

### Results and Discussion

Figure 1 shows the variations of viscosity of EG-water system from 30°C to 50°C with 5°C interval. The curves at lower temperatures are slightly concave while higher temperature curves are almost linear. The nature of the system appears to be quite different from those observed for monohydric alcohol-water systems, such as methanol-water, ethanol-water, 1-propanol-water,
Table 2—Parameters $A_i$ of Eq. (3) and standard deviations ($s$)

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Fig. 1—Coefficient of viscosity versus mole fraction of EG of EG-water system

Fig. 2—Excess viscosity versus mole fraction of EG of EG-water system

Fig. 3—Coefficient of viscosity versus mole fraction of EG of EG-dioxan system
2-propanol-water and tert-butanol-water. At lower concentration of EG, hydrogen bonds form between EG and water molecules. As the concentration of EG increases, EG-water H-bondings are replaced by EG-EG H-bonding. Increase in the EG-EG H-bonding leads to increase in the viscosity of the mixture. Figure 2 shows the excess viscosity curves for EG-water system. It is found that all concentrations and temperatures, excess viscosities are positive and their values are relatively high. The positive $\eta^E$ values indicate strong specific interaction between EG and water molecules.

In the case of EG-dioxan system the viscosities become increasingly greater with the increase in concentration of EG (Fig. 3). Dioxan is a spatial molecule having large volume. So, at lower concentration of EG (i.e., high concentration of dioxan), the molecules of EG have been assumed to be accommodated into the available spaces of dioxan structure resulting in lowering of viscosity than the expected theoretical value. As the concentrations of EG increases, the viscosity increases because the included EG molecules are more and more excluded and form EG-EG complexes. This leads to the viscosity of the mixture increasingly becoming closer to the viscosity of pure EG as its concentration increases. The excess viscosities ($\eta^E$) are negative throughout the whole range of concentrations (Fig. 4) and their negative values decrease on increasing temperature.

The variation of viscosity of EG-acetone system as a function of concentration of EG is shown in Fig. 5. The change in viscosity does not seem to be appreciable up to a moderate concentration of EG. After this level, the viscosity increases very rapidly with increasing concentration of EG. Acetone is 24% less compact than dioxan (density of acetone = 0.7787 gm/cc and that of dioxan = 1.0225 gm/cc at 30°C). So, at lower concentration of EG, its inclusion occurs into the acetone molecules and probably to a small extent hydrogen bonding may be formed between EG and acetone due to keto-enol tautomerism of the latter. As a result, the viscosity increases slowly at the beginning. But at higher concentration of EG, the molecules (EG) which are already included in the void spaces are dislodged by further addition of EG and form stronger EG-EG hydrogen
bonds. So, at higher concentrations, viscosity increases more rapidly with increasing concentration of EG. From Fig. 6 it is found that the values of excess viscosity are negative at all concentrations and temperatures. These curves are also similar to the corresponding curves of EG-dioxan system except more asymmetric nature of the former. The significantly large negative values of $\eta^E$ indicate much weaker interaction between EG and acetone than the EG-dioxan system.

Examination of $\eta^E$ values of all these systems at different temperatures clearly reveals that the excess properties whether positive or negative are diminished by increase of temperature. In EG-water system, the values of $\eta^E$ are positive hence $d\eta^E/dT$ values are negative. This indicates that there is strong specific interaction between EG and water molecules. So, increase in temperature will decrease this interaction resulting in the lowering viscosity of the mixture. But in other two systems, these $d\eta^E/dT$ changes are positive, which indicate that inclusion of smaller EG molecules occurs into bigger size molecules (dioxan and acetone) and there is no strong specific interaction between EG-dioxan and EG-acetone molecules.

References