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Effect of Potassium Bromide on the Volumetric Behaviour of Binary Mixtures of Ethylene and Propylene Glycols with Methanol

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Abstract

The effect of potassium bromide (KBr) on the volumetric properties of binary mixtures of ethylene and propylene glycols with methanol has been studied using experimental density values of the mixtures and pure component solvents at varying compositions (0.1, 0.3, 0.5, 0.7 and 0.9) of the glycols and concentrations (0.01, 0.03, 0.07, 0.09 M) of KBr, at 298 K. The data obtained were used to compute the excess molar volumes (V^E) of the binary mixtures at the various compositions and concentrations. The results show that the V^E values of all the binary mixed systems were negative over the entire range of solvent compositions and concentrations of KBr investigated except at 0.7 and 0.9 compositions of propylene glycol mixtures with positive values of V^E. The magnitude of the negative excess molar volumes gradually increased with composition of the glycol and concentration of ethylene glycol to a maximum, beyond which the values steadily decreased. For propylene glycol mixtures, excess molar volumes became less negative as the concentration of KBr increased. These observations have been discussed on the basis of molecular interactions due to structural differences between the binary mixed solvents.

1. Introduction

Solvent mixtures are widely used in chemical and biochemical practice to modify molecular environments in order to modulate interesting phenomena such as organic synthesis, reaction kinetics etc. Solvent mixtures are also used in order to modify physical properties of liquids such as viscosity, density, vapour pressure etc. [1].

Mixing of solvents usually results in either ideal (weak or no interactions between molecules of component single solvents) or non-ideal (specific interactions such as hydrogen bonding, dipole-dipole interactions and charge transfer reactions) mixtures [2]. The deviation from ideal behaviour of mixing solvents is often a function of the composition and temperature, as well as type and extent of association between unlike molecules of the mixture. Among various parameters, density, viscosity and apparent molar volumes have been recognized as quantities sensitive to molecular interactions and thus, structural changes in mixed solvent systems [3, 4]. These properties have been used to investigate molecular packing, molecular motions, and various types of molecular interactions which are influenced by size, shape and chemical nature of component molecules [5].

Ethylene and propylene glycols are good antifreeze liquids. Though ethylene glycol has better heat transfer properties due to its low viscosity, propylene glycol is a preferred antifreeze agent as it

possesses low toxicity. Propylene glycol is also a valuable solvent in many industries such as cosmetics, food, pharmaceuticals, paints and plastics as well as in aviation industry where it serves as a de-icing agent in aeroplanes especially during snowfalls. Methanol is used as automotive antifreeze in rocket fuels. Based on the unquantifiable uses of these hydroxyl based solvents, it becomes pertinent to study their mixing behaviour with a view to improving the properties of the solvents in the various areas of application. In this paper, we present our findings on the mixing behaviour of methanol with ethylene and propylene glycols at different compositions of methanol in the presence of potassium bromide and at 298 K.

2. Methodology

Ethylene glycol, propylene glycol, methanol and potassium bromide (KBr) were of analytical grade and used as received. All density measurements were carried out using a 10ml pyknometer. Densities of the pure solvents as well as those of the binary mixtures were first measured at 0.1, 0.3, 0.5, 0.7 and 0.9 compositions of the glycols without potassium bromide. The densities of the various binary mixtures were then made at the different compositions and concentrations (0.01, 0.03, 0.07 and 0.09 M) of KBr. All measurements were done under atmospheric pressure and 298K. Each measurement was done four times and the average of the closest three values was taken. Excess molar volumes (V^E) of the solutions were computed from the density data using Equation 1 [6].

$$V^E = \frac{x_1M_1+x_2M_2}{\rho_{mix}} - \left[\frac{x_1M_1}{\rho_1} + \frac{x_2m_2}{\rho_2}\right] \quad (1)$$

In Equation 1, V^E is excess molar volume; x_1 and x_2, m_1 and m_2, ρ_1 and ρ_2 represent mole fractions, molar masses and densities of solvents 1 and 2 respectively while ρ_{mix} is the density of the mixture.

3. Results and Discussion

The plot of excess molar volume of the binary mixtures of ethylene glycol and methanol versus mole fraction of ethylene glycol without KBr is presented in Figure 1.

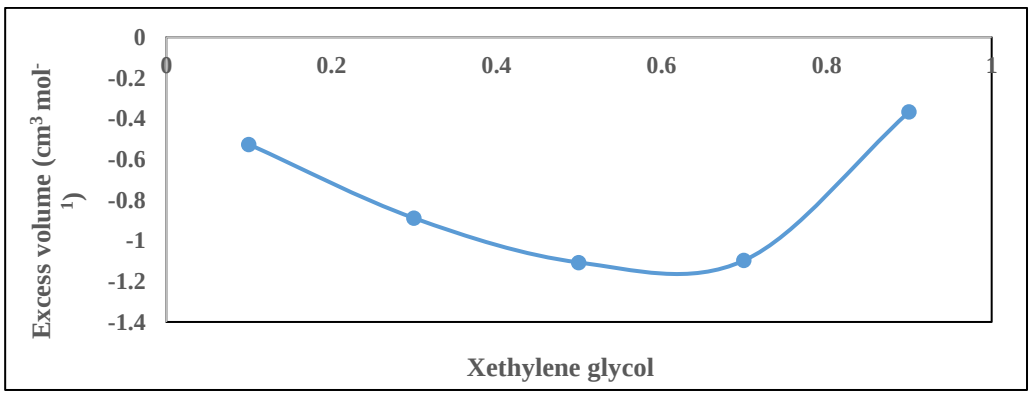

Figure 1: Plot of the excess molar volume versus mole fraction of ethylene glycol/methanol mixture at 298 K without KBr

Similarly, Figure 2 shows plot of excess molar volumes of propylene glycol/methanol mixtures against mole fractions of propylene glycol without KBr. The results show negative V^E values for the entire compositions of ethylene glycol mixtures which progressively decrease at higher compositions. For propylene mixtures, V^E values are negative at lower compositions and positive at higher values.

Methanol and the glycols are alkanols commonly known to be self-associating through hydrogen bonding. Therefore, it is expected that when these two OH-containing groups are mixed, there will be a disruption in hydrogen-bonding equilibrium [7]. Subsequently, several effects may occur including breaking of H-bonds of component solvents which leads to volume expansion and thus, positive contribution to excess molar volume. When strong specific interactions like dipole-dipole and H-bonding exist between unlike molecules of such mixed solvent system, the resulting effect on the mixture is volume contraction leading to negative excess molar volumes. In some cases, where the molar volumes of mixed solvents are largely different, geometric effects of the accommodation of one solvent into the interstitial space of the other leads to negative contribution to excess molar volume.

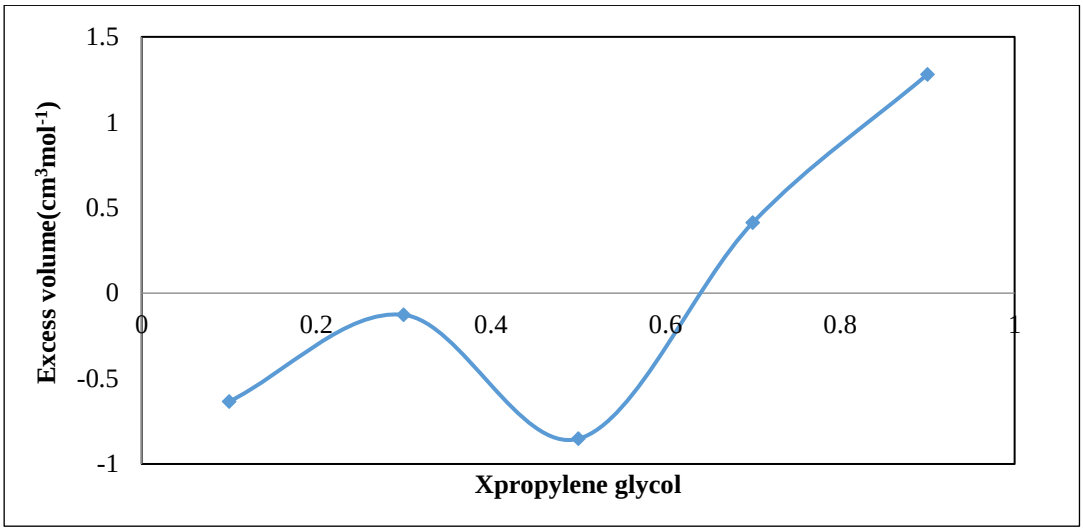

Figure 2: Plot of excess molar volume versus mole fraction of propylene glycol for propylene glycol/methanol mixture at 298.15 K without KBr

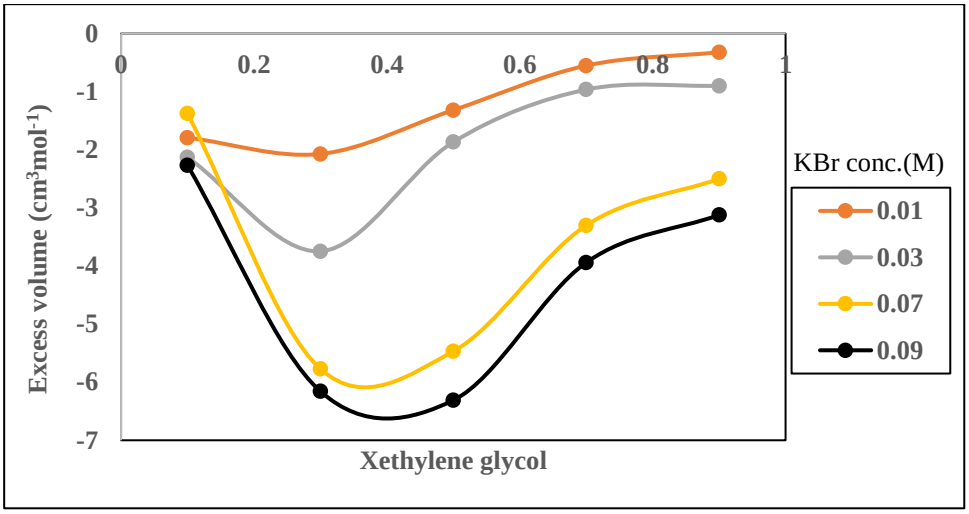

Figure 3: Effect of KBr on Volumetric Property of Ethylene Glycol/Methanol Mixtures at 298.15 K

Figures 1 and 3 show the dependence of excess molar volumes on the compositions of ethylene glycol in ethylene glycol/methanol mixtures with and without potassium bromide salt, respectively. In both figures, the V^E values are negative over the entire composition range and at all concentrations of KBr. However, the magnitude of the values of the excess molar volumes is much larger for mixtures with KBr at all compositions. The negative V^E values may be attributed to strong intermolecular interactions between the mixed solvents. As the concentration of methanol increases, the magnitude of the values of V^E decreases. This observation may be due to the fitting of smaller volume of ethylene glycol molecules into the larger volume of methanol (molar volume of ethylene glycol; 28.87cm^3mol^{-1} and methanol; 40.66cm^3mol^{-1}). The observed large negative values of V^E for mixtures with KBr may be due to a number of possible strong attractive interactions such as salt-solvent, ion-dipole and ion-ion which increased as the concentration of KBr increased.

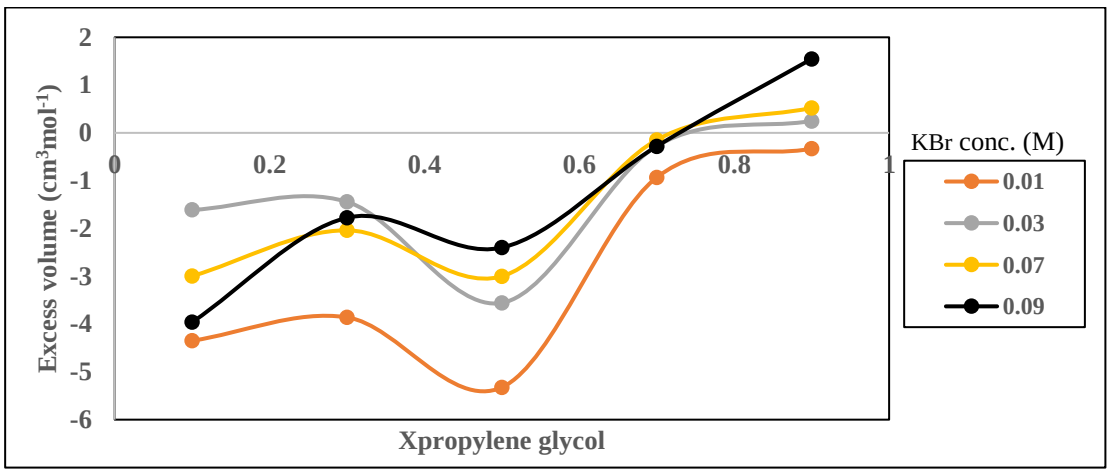

Figure 4: Effect of KBr on Volumetric Property of Propylene Glycol/Methanol Mixtures at 298.15 K

Figures 2 and 4 depict the excess molar volumes of mixtures of propylene glycol and methanol at various compositions of propylene glycol with and without KBr. The excess molar volumes are

negative at lower compositions of propylene glycol with minimum values at 0.5 mole fraction and gradually become less negative with increasing composition of methanol. Contrary to the observation for ethylene glycol and methanol mixtures with KBr, the magnitude of the excess molar volumes of KBr solutions in propylene glycol + methanol mixture decreased with increasing concentration of KBr at all compositions. It can be suggested that the decreased interactions could result from stearic hindrance posed by the bulkier nature of bromo propane formed in the mixture of propyl acetate and methanol.

4. Conclusion

The effect of potassium bromide (KBr) on the volumetric properties of mixtures of ethylene/methanol and propylene/methanol has been evaluated, using density measurement. The results indicate that KBr influenced the volumetric properties of both mixtures in various degrees. The excess molar volumes were more negative in the presence of KBr, suggesting that potassium bromide enhances attractive interaction in the binary mixtures. However, the interaction was stronger with ethylene glycol/methanol mixtures than propylene glycol/methanol binary solvent systems. The attractive interactions between the solvents could be attributed to the strong intra-molecular and inter-molecular hydrogen bonding within and between the component solvent molecules.

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