RESEARCH ARTICLE

Acoustic behavior of aqueous lithium Hydroxide with dimethyl foramide at different temperatures using Pulse Echo technique

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Abstract

The variation of volume ratio (v/v) and temperature of the liquid mixture dependence of thermo-acoustic properties are important parameters for the verification of intermolecular interactions. The thermo-acoustic parameters such as density (ρ), velocity (U) & viscosity (η) are determined for a ternary mixture (n=3) mixture of aqueous lithium hydroxide and Dimethylforamide system at 0.0% to 100% (v/v) and at different temperatures. Using the experimental data, adiabatic compressibility (βa), free length (Lf), free volume (Vf), internal pressure (π i), and Gibb's free energy (Δ G) are evaluated at different temperatures. The present paper shows the nonlinear characteristics of velocity and the thermodynamic properties that lead to dipole- ion interaction between dimethylforamide and 1N aqueous lithium hydroxide which is shown to be stronger than dipole- ion interaction between water and aqueous lithium hydroxide. These thermodynamic characteristics with volume ratio (v/v) of the mixture are explained in terms of weak force solutions.

Keywords: Ultrasonic velocity, acoustical parameters, molecular interactions, normality (1N), aqueous lithium hydroxide (aq. LiOH.H2O) and dimethylforamide (DMF).

Introduction

The ultrasonic studies of liquid are used to understand the behavior and strength of molecular interactions [1-5]. The studies on the physio-chemical properties of organic liquid such as: Dimethylforamide in aqueous solution of lithium hydroxide provides useful information, which is used to assess the information of molecular interaction [6].

An enormous number of studies have been made on the intermolecular forces in mixtures by different methods, such as: Raman Effect, Nuclear Magnetic Resonance, and ultra-sonic method [7-11]. The ultrasonic velocity data for ternary liquid mixtures have been used by many researchers [12-24]. In this paper the authors report on the ultrasonic velocity, density, and viscosity of 1N aqueous lithium hydroxide with dimethyl sulfoxide at different temperatures over the different volume ratio (v/v) of aqueous LiOH.H2O in DMF. From these experimental values, a number of thermodynamics parameters, namely adiabatic compressibility (βa) , intermolecular free length (Lf), free volume (Vf), internal pressure (π i) and Gibb's free energy (Δ G) were calculated. The variations of these parameters with volume ratio (v/v) were also useful toward finding the behavior of molecular forces in the ternary liquid mixtures.

Methodology

The ultrasonic velocity was measured in the ternary mixture of aqueous lithium hydroxide and dimethyl sulfoxide using an ultrasonic Pulse overlap technique working at frequency 4 MHz with an overall accuracy range of \pm 0.1 ms-1. The temperature was maintained by a constant temperature water bath using circulated water through the double walled measuring cell. The density of liquid mixtures was determined using a 10ml specific gravity bottle with an accuracy of ± 0.1 Kgm-3. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with accuracy 0.001 NSm-2. The time required for the flow of water (tw) and time required for the flow of mixture (ts) was measured with a digital stop watch having an accuracy $\pm 1 \times 10-6$ NSm-2. All precautions were taken to minimize the possible experimental error.

Results and Discussions

The experimental values of density, velocity and viscosity of 1N aq. LiOH.H2O with DMF & calculated

acoustic parameters at different temperature are shown in **Figures 1-8**.

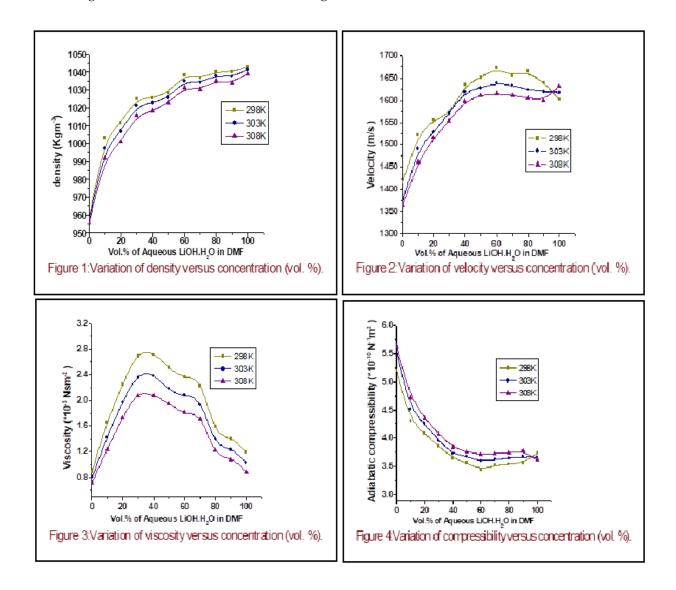
Figure 1 represents the graphical variation of density versus concentration (vol. %). From the graph notice how density rises with change in volume ratio (v/v) of aqueous lithium hydroxide in dimethylforamide. An increase in density decreases the volume indicating association in constituent molecules. In turn the density of mixture is increased due to physical changes which indicate the molecules are closed packed. This means that the liquid mixtures are less compressed. Increasing temperature of the mixtures decreases its density (ρ) . The decrease in density (ρ) with rise in temperature indicates a decrease in cohesive force. The increase of temperature indicates rise of kinetic energy and volume expansion and therefore decrease of density. Figure 2 is the graphical variation of velocity against concentration (vol. %). From the graph it is found that velocity rises with a change in concentration (vol. %) of aqueous lithium hydroxide in dimethylforamide up to 70%, indicating association in the liquid mixtures. The association in the mixtures is due to dipole-dipole interaction between dimethylforamide and water. The association up to 60% concentration is due to stronger ion-dipole interaction between Li+ of lithium hydroxide and Dimethylforamide than the ion-dipole interaction between Li+ of lithium hydroxide and water molecule. Since the size of Dimethylforamide is more than the size of water molecule. Hence the higher size more will be polarizibility. This process is due to the existence of strong interaction forces. As concentration goes higher (above 60%), the ultrasonic velocity gradually decreases indicating stiffness of the mixture decrease and hence dissociation in the constituent molecules. This is due to, a number of dimethylforamide molecules decreases and hence more polarized molecules are not available for strong ion-dipole interaction between Li+ of lithium hydroxide and dimethylforamide. This process may lead to a weak interaction in the ternary mixtures.

Figure 3 consists of the plot of viscosity (η) versus concentration. It was observed that viscosity rises with a change in concentration (vol. %) of aqueous lithium

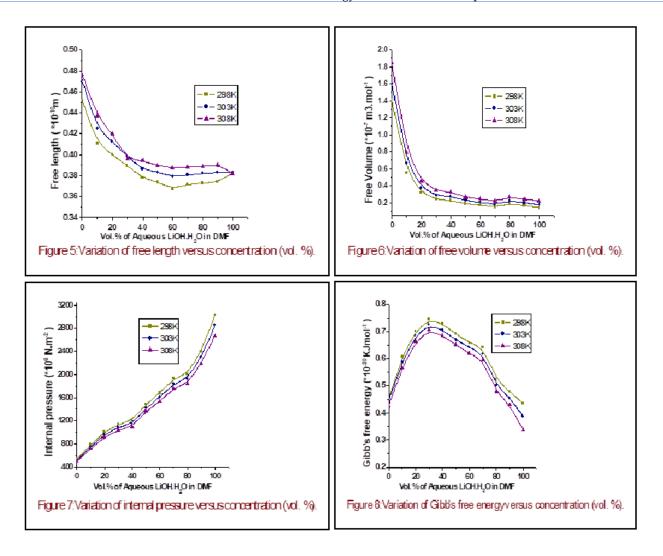
hydroxide in dimethylforamide up to 40%, indicating strong molecular interaction. The viscosity gives the strong molecular forces between interacting molecules. However, as the concentration goes higher (above 40%), viscosity decreases indicating weak molecular forces between the constituent molecules. Increasing temperature of the mixture, increases disorder of the medium and hence entropy increases. As entropy increases, viscosity of the ternary mixture decreases.

Figure 4 consists of the plots of adiabatic compressibility versus concentration (vol. %). Adiabatic compressibility (β a) decreases with change in concentration (vol. %) of aqueous lithium hydroxide in dimethylforamide up to 60%, indicating intermolecular forces are strong

between lithium aqueous hydroxide and dimethylforamide. This also shows associating tendency of the mixtures. This is due to the fact that dipole-dipole interaction of pure dimethylforamide is weaker than ion-dipole interaction of water and lithium hydroxide. As the concentration (vol. %) of aqueous lithium hydroxide dimethylforamide increases up to 60%, the dipole-dipole and ion-dipole interaction between dimethylforamide and aqueous lithium hydroxide becomes predominant. This leads to the liquid mixtures being a more compact structure & decrease of adiabatic compressibility. The observed decrease of adiabatic compressibility with change in concentration (vol. %) represents the association tendency between molecules.



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Hence intermolecular distance decreases with change in concentration up to 60%. This means that there exists compactness nature hence decrease of free length. As the concentration goes higher (above 60%), adiabatic compressibility (β a) slightly increases indicating weak molecular interaction among dimethylforamide and lithium hydroxide. Above 60% concentration, the dipole-dipole and ion-dipole interaction between dimethylforamide and aqueous lithium hydroxide decreases because the number of dimethylforamide molecules decrease and hence more polarized molecules are not available for strong ion-dipole interaction. This leads to weak interaction and hence dissociating tendency between the molecules.

Figure 5 contains the plot of free length versus concentration. It shows that free length decreases with change in concentration (vol.%) of aqueous lithium hydroxide in dimethylforamide up to 60%. The decrease in free length is due to dipole-dipole and ion-dipole interaction between dimethylforamide and aqueous lithium hydroxide indicating an association in the mixtures. This association leads to significant interaction between solvent and solute. As the concentration (vol. %) of aqueous lithium hydroxide indicating weak interaction among solvent and solute. Above 60% concentration, the slight increase in free length is due to the fact that, number of dimethylforamide molecules are less and hence more

polarized dimethylforamide molecules are not available for strong ion-dipole interaction. This leads us to assume a significant weak interaction.

Figure 6 and Figure 7 respectively consist of the plots of free volume and internal pressure versus concentration (vol. %). It is shown that free volume decreases (V_f) and internal pressure (π i) rises with change in concentration (vol. %) aqueous lithium hydroxide of in dimethylforamide indicating an association in the liquid mixtures. The decrease in free volume with change in concentration suggests that the molecules arrange themselves and the void space is less available showing that compressibility decreases. This ordered structural arrangement decreases the entropy. It was observed that the change in free volume values show exactly the reverse trend as that of internal pressure. In the present system, the authors noticed that free volume decreases and internal pressure increases. Further, the decrease in free volume and rise in internal pressure with change in concentration (vol. %) clearly shows the increasing magnitude of interactions. Such behavior of free volume and internal pressure indicates the association through dipole-dipole interaction or hydrogen bonding between dimethylforamide and water. If the temperature rises, there is a reduction in molecular interaction as they move away from each other. This reduces the cohesive bond. Thus an increase in free volume and decrease in internal pressure occurs with rise a rise in temperature.

Figure 8 represents the variation of Gibb's free energy with concentration (vol.%). Initially Gibb's free energy rises with a change in concentration (vol. %) of aqueous lithium hydroxide in dimethylforamide up to 30%, indicating the mobility of the molecule is low i.e. highly ordered, due to outstanding salvation. Such liquid mixtures absorb large ultrasound energy. The increase in Gibb's free energy also suggests the need of shorter time for the co-operative process to take place or for the rearrangement of molecules in the mixture. This indicates the easier flow of liquid mixture compared with the behavior of pure components. As the concentration goes higher (above 30%), the Gibb's free energy slowly decreases, indicating increase in mobility of the mixture hence disorder increases. This leads to the higher entropy and hence salvation decrease. This is

because salvation directly varies with the size of the molecule.

Conclusion

- The non-linear variation of ultrasonic velocity and adiabatic compressibility with concentration (vol. %) in the liquid mixture is due to formation of hydrogen bond or due to London desperation forces in the constituent molecules.
- The non -linear increase in internal pressure with concentration (vol. %) in the liquid mixture indicates association in the molecules of the component liquid.
- The non-regular changes of ultrasonic velocity and the thermodynamics parameters lead to dipole-ion interaction between dimethylforamide and 1N aqueous lithium hydroxide is stronger than dipoleion interaction between water and aq. lithium hydroxide.
- The ion-dipole interactions between Li+ of lithium hydroxide and dimethylforamide are found to be responsible for association whereas the ion-dipole interactions between Li+ of lithium hydroxide and water molecules are found to be responsible for dissociation in the liquid mixtures.

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