

Studies of Acoustic and Thermodynamic Properties of Aqueous Sodium Hydroxide and Dimethyl Sulfoxide System at 303.15 K and at Frequency 4MHz

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Abstract: *The ultrasonic studies in liquids are great use in understanding the nature and strength of molecular interaction. The thermo-physical parameters viz. density (ρ), ultrasonic velocity (U) and viscosity (η) have been measured for aqueous sodium hydroxide and Dimethyl sulfoxide system at 0.0% to 100% (v/v) and at 303.15 K. Using the experimental data, some of the acoustical parameters such as, adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), and Gibb's free energy (ΔG) are evaluated at the temperature 303.15K. The present paper represents the nonlinear variation of ultrasonic velocity and the thermo-acoustical parameters lead to dipole- ion interaction between dimethyl sulfoxide and 1N aqueous sodium hydroxide is stronger than dipole- ion interaction between water and aqueous sodium hydroxide. The behavior of these parameters with composition of the mixture has been discussed in terms of molecular interaction between the components of the liquids.*

Keywords: Ultrasonic velocity, acoustical parameters, molecular interactions, ternary mixtures, normality (1N), aqueous sodium hydroxide (aq. NaOH) and dimethyl sulfoxide (DMSO).

1. Introduction

The ultrasonic study of liquid plays an important role in understanding the nature and strength of molecular interactions¹⁻³. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like, Raman Effect, Nuclear Magnetic Resonance, Ultra Violet and ultrasonic method⁴⁻⁶. In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids, owing to its ability of characterizing physio-chemical behavior of the medium. The ultrasonic velocity data for ternary liquid mixtures have been used for by many researchers⁷⁻¹⁰. In present paper we have reported the ultrasonic velocity, density, and viscosity of 1N aqueous sodium hydroxide with dimethyl sulfoxide at 303.15K over the entire range of concentrations of aqueous NaOH in DMSO. From these experimental values, number of thermodynamics parameters, namely adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i) and Gibb's free energy (ΔG) have been calculated. The variations of these parameters with concentrations were found to be useful in understanding the nature molecular interactions between the components.

2. Materials and Methods

The ultrasonic velocity in the liquid mixtures have been measured using an ultrasonic interferometer (Mittal type: Model: M-83) working at frequency 4 MHz with an overall accuracy of $\pm 0.1 \text{ ms}^{-1}$, an electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of

a steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a 10ml specific gravity bottle with an accuracy of $\pm 0.1 \text{ Kg m}^{-3}$. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with accuracy 0.001 N Sm^{-2} . The viscometer was calibrated before used. The time of flow of water (t_w) and time flow of solution (t_s) was measured with digital stop watch having an accuracy $\pm 1 \times 10^{-6} \text{ N Sm}^{-2}$. All the precautions were taken to minimize the possible experimental error.

3. Results and Discussion

The experimental values of density, velocity and viscosity of 1N aqueous NaOH with dimethyl sulfoxide & calculated acoustic parameters at 303.15 K are shown in table-1 and related graphical representation of these parameters are shown in fig.1.1 to 1.8.

Density is an important concept with respect to buoyancy, purity and packaging. It varies with temperature and pressure. **Fig. 1.1** shows the plot of density versus concentration (vol. %). It is observed that density decrease with increase in concentration (vol. %) of aqueous sodium hydroxide in Dimethyl sulfoxide. The decrease in density indicates the decrease in solute-solvent and solvent- solvent interactions which results in a structure- breaking of the solvent. **Fig. 1.2** shows the plot of ultrasonic velocity versus concentration. It is observed that ultrasonic velocity increases with increase in concentration (vol. %) of aqueous NaOH in dimethyl sulfoxide up to 50%, indicating the increase in stiffness of the mixture and hence association¹¹.

The association in the constituent molecules may involve due to hydrogen bonding or dipole-dipole interaction between Dimethyl sulfoxide and water. The association up to 50% concentration is due to stronger ion-dipole interaction between Na^+ of sodium hydroxide and dimethyl sulfoxide than the ion-dipole interaction between Na^+ of sodium hydroxide and water molecule. This is because the size of dimethyl sulfoxide is more than the size of water molecule. Hence higher the size more will be polarizability. The process may lead to strong interaction forces^{12, 13}. As the concentration goes higher (above 50%), the ultrasonic velocity gradually decreases indicating stiffness of the mixture decrease and hence dissociation. This is because of the facts that, number of dimethyl sulfoxide molecules decrease and hence more polarized molecules are not available for strong ion-dipole interaction between Na^+ of NaOH and dimethyl sulfoxide. This process leads to weak interaction. **Fig. 1.3** consists the plot of viscosity (η) versus concentration. It is observed that viscosity slightly increases with increase in concentration (vol. %) of sodium hydroxide in Dimethyl sulfoxide up to 40%, indicating strong molecular interaction. However as the concentration goes higher (above 40%), viscosity gradually decreases indicating weak molecular interaction between the constituent molecules.

Fig. 1.4 contains the plots of adiabatic compressibility versus concentration. It is observed that adiabatic compressibility (β_a) decreases with increase in concentration (vol. %) of aqueous sodium hydroxide in dimethyl sulfoxide up to 50% indicating strong intermolecular interaction between aqueous sodium hydroxide and dimethyl sulfoxide. This also shows associating tendency of the component molecules. This is because of the fact that dipole-dipole interaction of pure dimethyl sulfoxide is weaker than ion-dipole interaction of aqueous sodium hydroxide. As the concentration goes higher (above 50%), adiabatic compressibility (β_a) gradually increases indicating weak molecular interaction amongst dimethyl sulfoxide and aqueous sodium hydroxide.

Fig. 1.5 contains the plot of free length versus concentration. Graphical behavior shows that free length decreases with increase in concentration of aqueous sodium hydroxide in dimethyl sulfoxide up to 50%. The decrease in free length is

a result of dipole-dipole and ion-dipole interaction between dimethyl sulfoxide and aqueous sodium hydroxide indicating association. This leads to significant interaction between constituent molecules. As the concentration (vol.%) of aqueous sodium hydroxide in dimethyl sulfoxide goes higher (above 50%), the intermolecular free length gradually increases indicating weak interaction among constituent molecules. This is because; number of dimethyl sulfoxide molecules decrease and more polarized dimethyl sulfoxide molecules are not available for strong ion-dipole interaction. This leads to weakening of intermolecular interaction. It was observed that the variation in the free volume values show exactly the reverse trend as that of internal pressure¹⁴. In the present paper, it is observed that free volume decreases and internal pressure increases.

Fig-1.6 and Fig-1.7 respectively contains the plots of free volume and internal pressure versus concentration. It is observed that free volume decreases (V_f) and internal pressure (π_i) increases with increase in concentration (vol. %) of aqueous sodium hydroxide in dimethyl sulfoxide, indicating association in the molecules of the component liquids. The decrease in free volume with increase in concentration suggests that the molecules arrange themselves in such a way that the void space is less available showing that compressibility decreases. This ordered structural arrangement decreases the entropy. Gibb's free energy measures mobility of the medium. Higher the mobility of the medium, higher will be the entropy; lower will be the free energy. **Fig. 1.8** represents the variation of Gibb's free energy with concentration. It is observed that initially Gibb's free energy slightly increases with increase in concentration (vol. %) of aqueous sodium hydroxide in dimethyl sulfoxide up to 40%, indicating the mobility of the molecule is low i.e. highly ordered, due to outstanding salvation. As the concentration goes higher (above 50%), 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 of the fact that salvation is directly proportional to size of the molecule.

4. Tables and Figures

Table 1: Density (ρ), Velocity (U), Viscosity (η), Adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i) and Gibb's free energy of the ternary systems Aqueous NaOH + Dimethyl sulfoxide at 303.15K.

Vol. % of Aq. NaOH in DMSO	ρ (Kgm^{-3})	U (ms^{-1})	η $*10^{-3}$ (NSm^{-2})	β_a $*10^{-10}$ (m^2N^{-1})	L_f $*10^{-10}$ (m)	V_f $*10^{-7}$ (m^3mol^{-1})	π_i $*10^6$ (Nm^{-2})	ΔG $*10^{-20}$ (KJ/mol)
00	1103.62	1437.28	1.64	4.386	0.4188	0.6413	735.52	0.6273
10	1100.00	1517.60	2.96	3.947	0.3973	0.2536	1054.38	0.8091
20	1093.43	1561.60	3.18	3.750	0.3873	0.2093	1185.95	0.8162
30	1090.53	1608.00	3.41	3.546	0.3766	0.1710	1348.54	0.8211
40	1080.01	1602.00	3.30	3.606	0.3797	0.1526	1492.33	0.8155
50	1075.66	1677.60	2.79	3.303	0.3635	0.1769	1531.20	0.7197
60	1063.12	1660.00	2.21	3.413	0.3695	0.2028	1585.33	0.6448
70	1053.08	1673.60	1.75	3.390	0.3682	0.2310	1669.61	0.5562
80	1040.44	1624.00	1.38	3.644	0.3818	0.2412	1840.37	0.4943
90	1020.82	1608.00	1.21	3.788	0.3892	0.2080	2209.31	0.4601
100	997.92	1611.20	0.955	3.860	0.3929	0.1951	2680.98	0.3790

5. Graphs

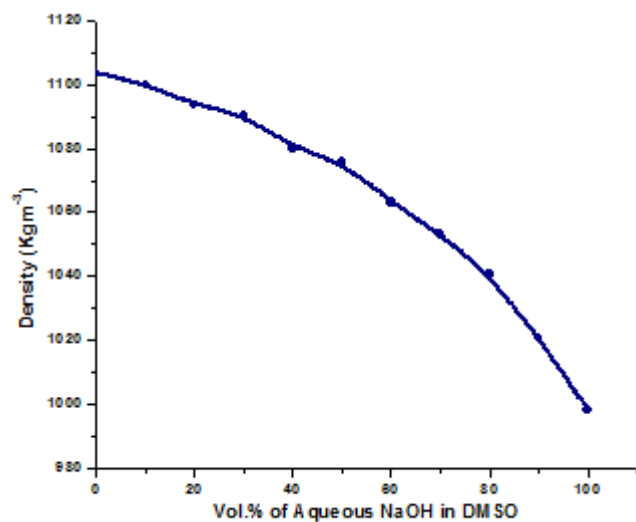


Fig.1.1: Variation of Density with concentration at 303.15K.

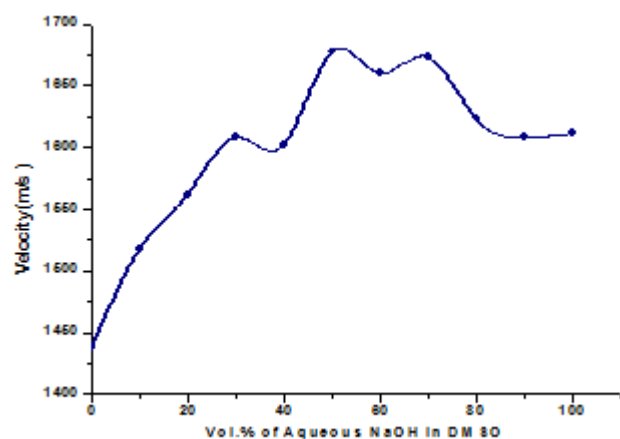


Fig.1.2: Variation of Velocity with concentration at 303.15K.

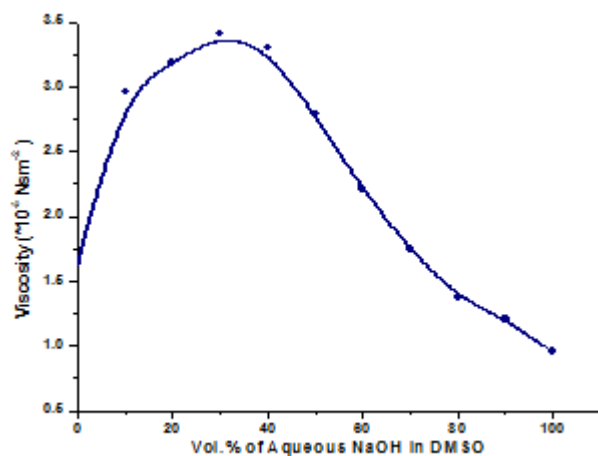


Fig.1.3: Variation of Viscosity with concentration at 303.15K.

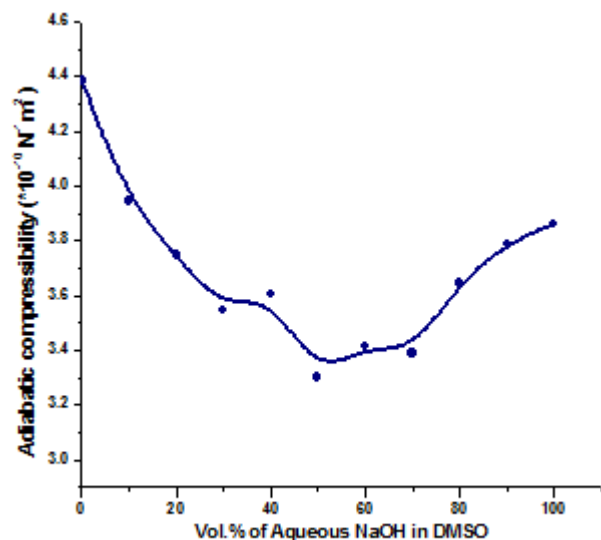


Fig.1.4: Variation of Compressibility with concentration at 303.15K.

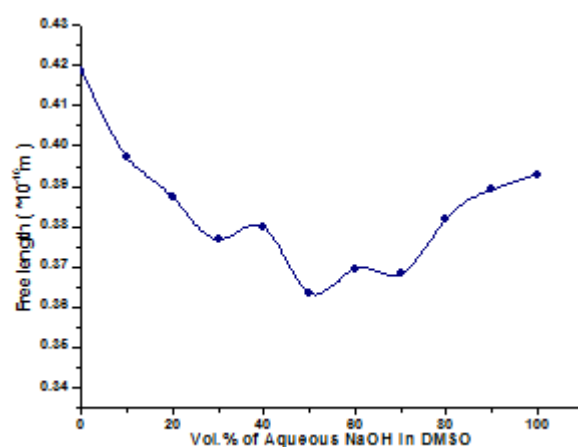


Fig.1.5: Variation of Free length with concentration at 303.15K.

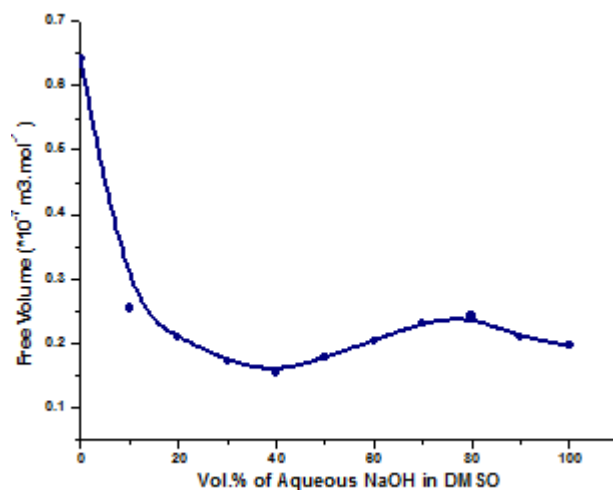


Fig.1.6: Variation of Free volume with concentration at 303.15K.

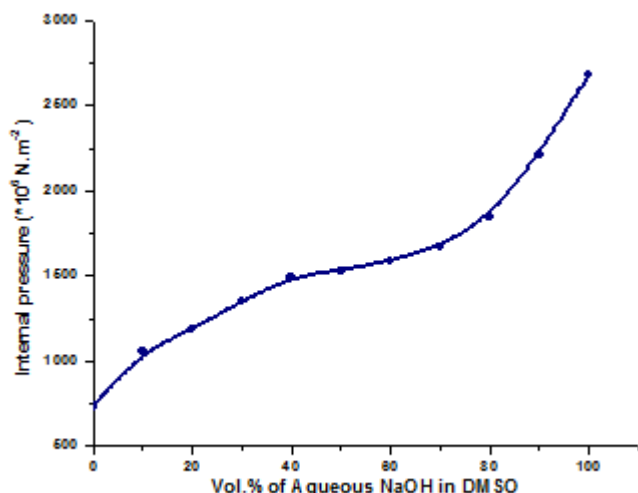


Fig.1.7: Variation of internal pressure with concentration at 303.15K.

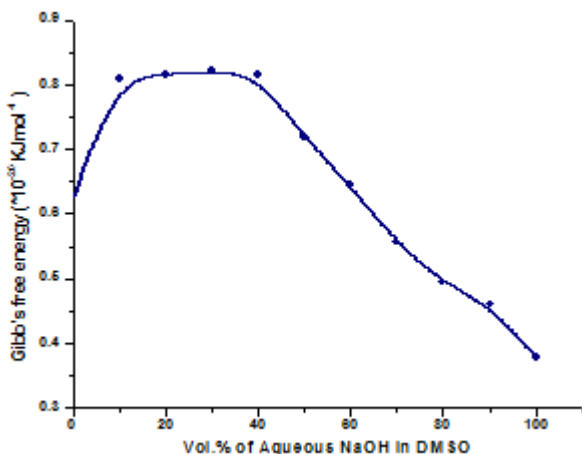


Fig.1.8: Variation of Gibbs free energy with concentration at 303.15K.

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6. Conclusion

The decrease in adiabatic compressibility and free length up to 50% for the system- aqueous sodium hydroxide + dimethyl sulfoxide is due to strong association, whereas the increase in adiabatic compressibility and free length above 50% for the systems is due to dissociation in the constituent molecules. The ion-dipole interactions between Na^+ of sodium hydroxide and dimethyl sulfoxide are found to be responsible for association in the ternary liquid mixture. The ion-dipole interactions between Na^+ of sodium hydroxide and water molecules are found to be responsible for dissociation in the liquid mixtures.

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