



ULTRASONIC STUDY OF MOLECULAR INTERACTION IN THE MIXTURE OF AQUEOUS POTASSIUM HYDROXIDE WITH N, N-DIMETHYL FORAMIDE AT DIFFERENT TEMPERATURES

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ABSTRACT

An analysis of different thermodynamic properties as a function of temperature provides valuable information about their characteristics. The concentration and temperature dependence of acoustic and volumetric properties of multi component liquid mixtures has proved to be a useful indicator of the existence of significant effect resulting from intermolecular interactions. The thermo-physical parameters such as density (ρ), ultrasonic velocity (U) and viscosity (η) have been measured at 4 MHz frequency in the ternary mixtures of aqueous potassium hydroxide with N, N-dimethyl formamide over entire range concentration (v/v) at temperature 298K-308K using ultrasonic Pulse overlap technique. The experimental data have been used to calculate acoustical parameter namely adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG). The present paper represents the nonlinear variation of ultrasonic velocity and the thermo-acoustical parameters lead to dipole- ion interaction between dimethyl formamide and 1N aqueous potassium hydroxide is stronger than dipole- ion interaction between water and aqueous potassium hydroxide.

Keywords: Ultrasonic velocity, acoustical parameters, molecular interactions, ternary mixtures, normality (1N), aqueous potassium hydroxide (aq. KOH) and dimethyl formamide (DMF).

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 researchers⁷⁻¹¹. In present paper we have reported the ultrasonic velocity, density, and viscosity of 1N aqueous potassium hydroxide with N, N-dimethyl formamide at different temperature over the entire range of concentrations of aqueous KOH in DMF. 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), relaxation time (τ) 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. Experimental

The ultrasonic velocity in the liquid mixtures have been measured using a Pulse echo overlap technique 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 10 ml specific gravity bottle with an accuracy of $\pm 0.1 \text{ Kgm}^{-3}$. An Ostwald's viscometer was used

for the viscosity measurement of pure liquids and liquid mixtures with accuracy 0.001 NSm^{-2} . The 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 $\pm 1 \times 10^{-6} \text{ NSm}^{-2}$.

3. Results & Discussion

Table 1 - Density (ρ), Velocity (U) and Viscosity (η) of the ternary systems Aqueous KOH + Dimethyl foramide at different temperature.

Vol. % of Aq.KOH in DMF	$\rho \text{ (Kgm}^{-3}\text{)}$			U (ms^{-1})			$\eta * 10^{-3} \text{ (NSm}^{-2}\text{)}$		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	958.02	957.06	955.60	1416.00	1373.28	1364.00	0.893	0.794	0.718
10	975.35	972.53	968.64	1504.00	1433.80	1411.20	1.33	1.19	1.05
20	994.57	991.55	988.84	1536.00	1496.00	1480.00	1.67	1.49	1.34
30	1009.65	1005.61	1002.08	1564.00	1512.00	1488.00	2.04	1.79	1.57
40	1025.34	1022.10	1018.54	1592.96	1575.92	1543.92	2.23	1.95	1.71
50	1027.47	1020.77	1020.77	1630.00	1622.00	1610.00	2.03	1.77	1.57
60	1031.01	1025.85	1023.09	1652.00	1625.60	1614.00	1.78	1.57	1.39
70	1038.91	1035.95	1032.28	1665.60	1637.60	1620.80	1.54	1.34	1.20
80	1047.71	1044.55	1041.07	1628.00	1624.00	1604.00	1.34	1.16	1.04
90	1050.45	1047.18	1043.80	1592.00	1572.00	1556.00	1.15	0.975	0.843
100	1058.04	1055.89	1055.42	1590.00	1598.00	1612.00	1.05	0.914	0.799

The experimental values of density, velocity and viscosity of 1N aqueous potassium hydroxide with N, N-dimethyl foramide over entire range concentration (v/v) at temperature 298K-308K using Pulse echo overlap technique are shown in table-1. It is observed that density increases with increase in concentration (vol. %) of aqueous potassium hydroxide in dimethylforamide. Increase in density decreases the volume indicating association in component molecules. The density of ternary liquid mixture may be increase due to structural reorganization indicating the closed packed structure of the molecular cluster. This makes the liquid medium less compressive. Increasing temperature of the mixtures decreases its density (ρ). The decrease in density (ρ) with increase in temperature indicates decrease in cohesive force. The increasing temperature has two opposite effects namely structure formation and destruction of structure. Thus increase of temperature favors increase of kinetic energy and volume expansion and hence decrease of density.

It is also observed that ultrasonic velocity increases with increase in concentration (vol. %) of aqueous potassium

hydroxide in dimethylforamide up to 70%, indicating association in the constituent molecules. The association in the constituent molecules may involve due to stronger ion-dipole interaction between K^+ of potassium hydroxide & dimethylforamide than ion-dipole interaction between K^+ of potassium hydroxide & water. Since size of dimethylforamide is more as compared to size of water molecule. Hence higher the size more will be polarizability. The process may lead to strong interaction forces. However, when concentration goes higher (above 70%), the ultrasonic velocity gradually decreases indicating stiffness of the mixture decrease and hence dissociation in the constituent molecules. This is due to number of dimethylforamide molecules decreases and hence more polarize molecules are not available for strong ion-dipole interaction between K^+ of potassium hydroxide and dimethylforamide. This process may lead to weak interaction. As temperature of the mixture increases, velocity decreases because of less ordered structure and more spacing between the molecules.

It is observed that viscosity increases with increase in concentration (vol. %) of

potassium hydroxide in dimethylformamide up to 40%, indicating strong molecular interaction. The viscosity gives the strength of molecular interaction between interacting molecules. However, as the concentration goes higher (above 40%), viscosity decreases, indicating

weak molecular interaction between the constituent molecules. Increase in temperature of the mixture, increases disorder of the medium and hence entropy increases. As entropy increases, viscosity of the ternary mixture decreases.

Table 2- Adiabatic compressibility (β_a), free length (L_f) and free volume (V_f) of the ternary systems Aqueous KOH + Dimethyl formamide at different temperature

Vol. % of Aq.KOH in DMF	$\beta_a * 10^{-10}$ ($m^2 N^{-1}$)			$L_f * 10^{-10}$ (m)			$V_f * 10^{-7}$ ($m^3 mol^{-1}$)		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	5.205	5.540	5.624	0.4517	0.4707	0.4766	1.4087	1.605	1.8450
10	4.527	5.001	5.183	0.4213	0.4472	0.4576	0.7560	0.8356	0.9723
20	4.261	4.506	4.616	0.4087	0.4245	0.4318	0.4892	0.5574	0.6459
30	4.049	4.349	4.507	0.3984	0.4171	0.4267	0.3254	0.3749	0.4450
40	3.843	3.939	4.118	0.3881	0.3969	0.4079	0.2514	0.3012	0.3564
50	3.663	3.710	3.779	0.3789	0.3852	0.3907	0.2535	0.3082	0.3637
60	3.553	3.685	3.752	0.3732	0.3839	0.3893	0.2606	0.3062	0.3638
70	3.469	3.599	3.687	0.3688	0.3794	0.3859	0.2622	0.3178	0.3675
80	3.601	3.629	3.733	0.3757	0.3810	0.3883	0.2445	0.2997	0.3506
90	3.756	3.864	3.956	0.3837	0.3931	0.3998	0.2184	0.2741	0.3354
100	3.738	3.705	3.646	0.3828	0.3849	0.3838	0.1706	0.2111	0.2617

From table-2 it is observed that adiabatic compressibility (β_a) decreases with increase in concentration (vol. %) of aqueous potassium hydroxide in dimethylformamide up to 70%, indicating strong intermolecular interaction between aqueous sodium hydroxide and dimethylformamide. This shows associating tendency of the component molecules. This is because of the fact that dipole-dipole interaction of pure dimethylformamide is weaker than ion-dipole interaction of water and potassium hydroxide. As the concentration (vol. %) of aqueous potassium hydroxide increases up to 70%, the dipole-dipole and ion-dipole interaction between dimethylformamide and aqueous potassium hydroxide becomes predominant which leads to a more compact structure and decreased adiabatic compressibility. This leads to weak interaction and hence dissociating tendency of the component molecules. It is also observed free length decreases with increase in concentration of aqueous potassium hydroxide in dimethylformamide up to 70%. The decrease in free length is a result of dipole-dipole and ion-dipole interaction between dimethylformamide and aqueous potassium hydroxide indicating association. This leads to significant interaction between solvent and solute. As the concentration (vol. %) of aqueous potassium

hydroxide in dimethylformamide goes higher (above 70%), the intermolecular free length slightly increases indicating weak interaction among the constituent molecules. Above 70% concentration, the slight increase in free length is due to number of dimethylformamide molecules less and hence more polarized dimethylformamide molecules are not available for strong ion-dipole interaction. This leads to significant weak interaction.

It is observed that free volume decreases (V_f) and internal pressure (π_i) increases with increase in concentration (vol. %) of aqueous potassium hydroxide in dimethylformamide 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. It was observed that the variation in the free volume values show exactly in the reverse trend as that of internal pressure. Further, the decrease in free volume and increase in internal pressure with increase in concentration (vol. %) clearly show the increasing magnitude of interactions. Such behavior of free volume and internal pressure generally indicate the association through dipole-dipole interaction or

hydrogen bonding between dimethylformamide and water. This suggests that both solute- solute and solute solvent interaction exist in the system. If the temperature is rise, there is reduction in molecular interaction as they move

away from each other. This reduces the cohesive force. Thus increase in free volume and decrease in internal pressure occurs with rise in temperature.

Table 3- Internal pressure (π_i), relaxation time (τ) and Gibb's free energy of the ternary systems Aqueous KOH + Dimethyl foramide at different temperature.

Vol. % of Aq.KOH in DMF	$\pi_i * 10^6$ (Nm ⁻²)			$\tau * 10^{-12}$ (S)			$\Delta G * 10^{-20}$ (KJ/mol)		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	529.43	515.07	499.28	0.6199	0.5865	0.5389	0.4514	0.4446	0.4261
10	694.67	681.35	655.72	0.8027	0.7907	0.7291	0.5462	0.5559	0.5406
20	859.79	835.34	805.92	0.9483	0.8954	0.8225	0.6073	0.6022	0.5863
30	1057.4	1022.88	979.69	1.0987	1.0380	0.9444	0.6612	0.6575	0.6386
40	1245.19	1189.46	1140.52	1.1409	1.0250	0.9389	0.6750	0.6528	0.6364
50	1339.78	1273.78	1222.38	0.9892	0.8754	0.7924	0.6228	0.5938	0.5721
60	1447.14	1390.74	1331.48	0.8417	0.7714	0.6951	0.5636	0.5467	0.5225
70	1598.17	1521.22	1469.86	0.7142	0.6408	0.5899	0.5034	0.4776	0.4603
80	1841.13	1745.62	1680.32	0.6414	0.5630	0.5152	0.4639	0.4294	0.4090
90	2192.56	2062.65	1955.88	0.5756	0.5026	0.4452	0.4243	0.3871	0.3537
100	2835.65	2683.63	2537.09	0.5227	0.4517	0.3886	0.3889	0.3473	0.3022

From table-3 it is observed that relaxation time increases slightly with increase in concentration (vol. %) of aqueous potassium hydroxide in dimethylformamide up to 40% indicating high stability. The stability of the mixture depends on the size of component molecules. Higher the size of the molecule more will be polarizability and hence greater will be the molecular interaction. Therefore relaxation time increases. As the concentration goes higher (above 40%), the relaxation time slightly decrease indicating less stability. It is observed that initially Gibb's free energy increases with increase in concentration (vol. %) of aqueous potassium hydroxide in dimethylformamide up to 40%, indicating the mobility of the molecule is low i.e. highly ordered due to outstanding salvation. Such solution generally absorbs more ultrasonic 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. As the concentration goes higher (above 40%), the Gibb's free energy slowly decreases, indicating increases mobility of the mixture hence disorder increases. This leads to the higher entropy and hence salvation decrease. Since salvation is directly proportional to size of the molecule

4. Conclusion

The decrease in adiabatic compressibility and free length up to 50% for the system- aqueous potassium 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 K⁺ of potassium hydroxide and dimethyl foramide are found to be responsible for association in the ternary liquid mixture. The ion-dipole interactions between K⁺ of potassium hydroxide and water molecules are found to be responsible for dissociation in the liquid mixtures.

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