

Excess Thermo-Acoustical Parameters in Ternary Mixture Containing Aqueous Sodium Hydroxide and Dimethyl Foramide at Different Temperatures

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Abstract: Density (ρ), Ultrasonic velocity (U), viscosity (η) for the ternary mixture of aqueous sodium hydroxide and Dimethyl foramide in the whole range of composition has been carried out at different temperatures 298.15, 303.15 and 308.15K. Using experimental data ρ , U , and η , some excess thermo-acoustical parameters such as β_a^E , L_f^E , V_f^E , π_i^E , Z^E . & excess free energy ΔG^E have been calculated. The present paper shows the nonlinear characteristics of velocity and the thermodynamic properties that lead to dipole- ion interaction between dimethyl foramide and aqueous sodium hydroxide which is shown to be stronger than dipole- ion interaction between water and aqueous sodium hydroxide. These thermodynamic characteristics with composition of the mixture are explained in terms of weak force solutions.

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

I. INTRODUCTION

The ultrasonic studies of liquid are used to understand the behavior and strength of molecular interactions¹⁻⁴. The studies on the physio-chemical properties of organic liquid such as aqueous sodium hydroxide with dimethyl foramide provides useful information, which is used to assess the strength of molecular interaction⁵. The molecular behavior, interactions and their mixtures can be characterized with the help of ultrasonic studies⁶⁻⁹.

Physical and chemical properties of the molecules depend upon the structure of the molecules. Covalent bonding gives the stability of individual molecule and the non ideal behavior (thermodynamic properties) depends on the non covalent interactions among the molecular system¹⁰⁻¹¹. Vast number of Surfaces phenomena in liquid mixtures as well as solid phase structures involve due to van der Waal forces (non-covalent interactions). Most of the molecular & macro molecular phenomenon depends on the interactions¹². Ultrasonic measurements in liquid mixtures provide the information about the non-covalent molecular interaction in the molecular system¹³. Physicochemical properties of the molecular system depend on the non-covalent interactions. Theoretical and experimental studies on the molecular interactions have been studied by Flory and co-worker¹⁴⁻¹⁵, Fort and Moore¹⁶⁻¹⁷ and Ramann and Naidu¹⁸. Selected molecules have wide scope in laboratory and chemical industries as reagents as well as solvents. NaOH (sodium hydroxide) is alkali and commonly used in organic and inorganic synthesis. Acidic α - protons of carbonyl compounds such as aldehydes, ketones and esters are being abstracted by NaOH to form respective nucleophiles or enolates of these species. These species have been further used in various organic reactions such as Aldol condensation, Michael addition, Robinson Ring annulations etc. It is also important as laboratory reagents. The molecular formula of Dimethyl foramide is CHON (CH₃)₂ and the functional group is amide O=CH-N-R and the nitrogen has two methyl groups. The molecule has planar structure due to sp² hybridization in carbonyl carbon to which the nitrogen attached. Due to lone pair of electron present on nitrogen, participate in resonating structure with carbonyl carbon also becomes sp² hybridized. These are the resonating structures of dimethyl foramide. In the present work, we reported three basic experimental parameters density (ρ), ultrasonic velocity(U) and viscosity(η), using experimental data, some excess

thermo-acoustical parameters such as excess adiabatic compressibility (β_a^E), excess free length (L_f^E), excess free volume (V_f^E), excess internal pressure (π_i^E), excess acoustic impedance (Z^E) and excess Gibb's free energy (ΔG^E) of the ternary mixture of aqueous NaOH and DMF (dimethyl foramide) have been calculated at different temperatures.

II. MATERIALS AND METHODS

The chemicals used in the present investigation are AnalaR grade and are obtained from The Global Marketing, Nagpur. The chemicals are purified by standard procedure [16 is replace by 10]. The different compositions of the liquid mixtures are prepared by varying volume ratio (v/v). Ultrasonic interferometer (Mittal enterprises, India Model: F-83) is used for ultrasonic velocity measurements operating at 4MHz with an overall accuracy range of $\pm 0.1 \text{ ms}^{-1}$. The temperature of pure liquids and liquid mixtures were 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 $\pm 0.1 \text{ Kgm}^{-3}$. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with accuracy 0.001 NSm^{-2} . The time required for the flow of water (t_w) and time required for the flow of mixture (t_s) was measured with a digital stop watch having an accuracy $\pm 1 \times 10^{-6} \text{ NSm}^{-2}$. All precautions were taken to minimize the possible experimental error.

III. RESULTS AND DISCUSSION

The experimental values of velocity, density and viscosity of 1N aqueous sodium hydroxide and Dimethyl foramide over entire range concentration (v/v) at different temperature range 298.15K-308.15K using ultrasonic interferometer are shown in **table-1**. It is observed that density increases with increase in concentration (vol. %) of aqueous sodium 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 mixture decreases its density (ρ). The decrease in density (ρ) with increase in temperature indicates decrease in cohesive force. It is also observed that ultrasonic velocity increases with increase in concentration (vol. %) of aqueous sodium hydroxide in dimethylforamide up to 70%, indicating association in the constituent molecules. The association in the constituent molecules may involve due to hydrogen bonding or dipole-dipole interaction between dimethylforamide and water. The association up to 70% concentration is due to stronger ion-dipole interaction between Na^+ of sodium hydroxide and dimethylforamide than the ion-dipole interaction between Na^+ of sodium hydroxide and water molecule. This is because the size of dimethylforamide is more than the size of water molecule. Hence higher the size more will be polarizability. The process may lead to strong interaction forces. As the concentration goes higher (above 70%), the ultrasonic velocity gradually decreases indicating stiffness of the mixture decrease and hence dissociation. This is due to number of dimethylforamide molecules decrease and hence more polarized molecules are not available for strong ion-dipole interaction between Na^+ of sodium hydroxide and dimethylforamide. This process leads to weak interaction. Viscosity increases with increase in concentration (vol. %) of aqueous sodium hydroxide in dimethylforamide 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.

From the **table-2**, it is clear that with the increase in concentration (vol. %) of aqueous sodium hydroxide in dimethylforamide the excess values of β_a^E and L_f^E decrease negatively in magnitude and approach to minimum at around 40% concentration of aqueous sodium hydroxide in dimethylforamide which suggest that maximum structural changes take place in this region of the mixture. It further suggests that the negative excess values have been due to closely packed molecules which account for the existence of strong molecular interaction. Decreasing negative excess values of β_a^E and L_f^E with increase of temperature in aqueous sodium hydroxide + dimethylforamide mixtures may be accounted for the molecular dissociation which leads to less closer packing in aqueous sodium hydroxide + dimethylforamide mixtures, and hence increase in compressibility and free length. The excess values of free volume (V_f^E) are negative as shown in **table-2**. The negative deviation of excess free volume is an indication of the existence of



strong interaction between the component molecules. Negative excess values of free volume leads to reduction in volume. Negative excess values of free volume decreases with increasing concentration (vol. %) of aqueous sodium hydroxide in dimethylformamide. This also indicates dissociation between the unlike molecules. The variations of excess values of internal pressure(π_i^E), may give some information regarding the nature and force existing between the molecules. The negative excess values of internal pressure (table-3) in the ternary mixture clearly confirm the existence of molecular association between the component molecules. The excess values of acoustic impedance (Z^E) is furnished in table- 3. The positive excess values of Z^E clearly suggest that there exists strong molecular interaction between the components molecules. The variations in the excess values of Gibb's free energy (ΔG^E) with increasing concentration are found to be positive. In the present investigation positive excess values of Gibb's free energy shows the strong interaction between the unlike molecules table-3.

Vol. % of aq. NaOH in DMF	ρ (Kgm ⁻³)			U (ms ⁻¹)			$\eta * 10^{-3}$ (NSm ⁻²)		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
00	958.02	957.06	955.6	1416.00	1373.28	1364.00	0.893	0.794	0.718
10	960.77	960.67	959.21	1476.00	1444.00	1436.00	1.430	1.230	1.060
20	962.29	961.48	960.02	1569.60	1512.00	1468.00	2.010	1.750	1.520
30	967.29	965.48	965.02	1595.80	1555.80	1530.80	2.470	2.110	1.760
40	971.87	970.02	968.56	1621.00	1593.60	1552.00	2.610	2.280	1.900
50	975.41	973.56	972.10	1632.00	1612.80	1584.00	2.500	2.150	1.830
60	980.59	978.74	977.28	1650.00	1630.00	1624.00	2.100	1.820	1.590
70	984.14	982.29	980.83	1666.00	1636.00	1628.00	1.860	1.620	1.400
80	990.96	989.11	987.65	1644.00	1620.00	1604.00	1.650	1.400	1.210
90	994.61	992.76	991.30	1628.00	1616.00	1588.00	1.410	1.200	1.050
100	998.92	997.92	995.52	1608.00	1611.20	1616.00	1.120	0.955	0.840

Table 1: Density (ρ), Velocity (U) and Viscosity (η) of the ternary systems Aqueous NaOH + DMF at different temperature.

Vol. % of aq. NaOH in DMF	$\beta_a^E * 10^{-10}$ (m ² N ⁻¹)			$L_f^E * 10^{-10}$ (m)			$V_f^E * 10^{-7}$ (m ³ mol ⁻¹)		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
10	-0.2946	-0.3800	-0.3908	-0.01278	-0.01612	-0.01644	-0.6212	-0.6642	-0.6974
20	-0.7202	-0.6550	-0.4346	-0.03266	-0.02864	-0.01818	-0.7753	-0.8788	-1.0000
30	-0.7503	-0.7670	-0.6654	-0.03444	-0.03416	-0.02912	-0.7811	-0.8777	-0.9715
40	-0.7594	-0.8090	-0.6252	-0.03522	-0.03668	-0.02746	-0.7034	-0.7987	-0.8976
50	-0.6890	-0.7520	-0.6340	-0.0322	-0.0344	-0.02840	-0.5969	-0.6728	-0.7600
60	-0.6596	-0.6870	-0.6758	-0.03118	-0.03182	-0.03114	-0.4549	-0.5141	-0.5830
70	-0.6112	-0.5610	-0.5306	-0.02936	-0.02624	-0.02458	-0.3334	-0.3829	-0.4279
80	-0.4048	-0.3440	-0.2634	-0.01944	-0.01596	-0.01182	-0.2252	-0.2537	-0.2838
90	-0.2114	-0.1710	-0.0202	-0.01012	-0.00798	-0.00026	-0.1153	-0.1293	-0.1524

Table 2: Excess adiabatic compressibility (β_a), Excess free length (L_f) and Excess free volume (V_f) of the ternary systems NaOH + DMF at different temperature.

Vol. % of aq. NaOH in DMF	$\pi_i^E * 10^6$ (Nm ⁻²)			$Z^E * 10^6$ (Kgm ² s ⁻¹)			$\Delta G^E * 10^{-20}$ (KJ/mol)		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
10	-43.593	-45.701	-54.915	0.036630	0.043550	0.043310	0.1424	0.13056	0.116144
20	-81.206	-65.022	-60.15	0.103960	0.080700	0.044520	0.2252	0.23432	0.244228
30	-106.029	-95.823	-115.105	0.113090	0.102250	0.081330	0.2886	0.28768	0.273512
40	-168.582	-144.274	-155.350	0.119520	0.114100	0.077040	0.2983	0.30294	0.300196
50	-250.685	-231.955	-232.645	0.110450	0.109050	0.074950	0.2797	0.2776	0.27678

60	-394.508	-359.036	-424.53	0.111580	0.104900	0.099560	0.2088	0.21216	0.211364
70	-455.191	-401.167	-394.565	0.108210	0.087250	0.078470	0.158	0.17172	0.167148
80	-412.984	-380.728	-371.580	0.072840	0.053200	0.035180	0.1231	0.12848	0.128632
90	-279.807	-260.919	-232.875	0.037970	0.025850	0.005510	0.0741	0.07684	0.089916

Table 3: Excess internal pressure (π_i^E), Excess specific acoustic impedance (Z^E) and Excess Gibb's free energy (ΔG^E) of the ternary systems NaOH + DMF at different temperature.

IV. CONCLUSION

- The non regular changes of ultrasonic velocity and the thermodynamics parameters lead to dipole-ion interaction between DMF and 1N aqueous sodium hydroxide is stronger than dipole-ion interaction between water and aq. sodium hydroxide.
- The ion-dipole interactions between Na^+ of sodium hydroxide and dimethylformamide are found to be responsible for association in the ternary liquid mixtures whereas the ion-dipole interactions between Na^+ of sodium hydroxide and water molecules are found to be responsible for dissociation in the liquid mixtures.
- The excess values of adiabatic compressibility (β_a^E), intermolecular free length (L_f^E), free volume (V_f^E), internal pressure (π_i^E), specific acoustic impedance (Z^E) and Gibb's free energy (ΔG^E) are sensitive to nature of interaction in liquids.

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