

Thermodynamical studies on ternary mixture of sodium hydroxide in aqueous medium & 1, 4 dioxane using Ultrasonic interferometer techniques at different temperature

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Abstract

As a primary goal, the abstract should render the general significance and conceptual advance of the work clearly accessible to a broad readership. References should not be cited in the abstract. Leave the Abstract empty if your article does not require one, please see the Summary Table for full details. The thermo-acoustic parameters such as density (ρ), ultrasonic velocity (U) and viscosity (η) are determined for the ternary mixture of aqueous Sodium hydroxide and 1,4 dioxane system at 0.0% to 100% (v/v) and at different temperature. These experimental data have been used to estimate 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). The behaviors of these parameters were explained on the basis of intermolecular interaction present in the mixture.

Keywords: Ultrasonic velocity, molecular interactions, normality (1N), aqueous sodium hydroxide (aq. NaOH) and 1, 4 dioxane.

Introduction

The ultrasonic studies of liquid mixture provide important information about the behavior and strength of molecular interactions [1-6]. The measurement of ultrasonic velocity in the organic liquid mixture is a useful tool to study the physicochemical properties of the liquids and also explain the mechanism of molecular interaction [7-9].

The ultrasonic velocity data for ternary liquid mixtures have been used for by many researchers [10-18]. The present work investigates thermo-acoustical properties of aqueous solution of NaOH with 1, 4 dioxane at different temperatures and at different composition. 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 in the ternary liquid mixtures.

Methodology

The ultrasonic velocity was measured in the ternary mixture of aqueous sodium hydroxide and 1,4 dioxane using an ultrasonic interferometer technique working at frequency 4 MHz with an overall accuracy range of $\pm 0.1 \text{ ms}^{-1}$. 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 $\pm 0.1 \text{ Kgm}^{-3}$. 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 $\pm 1 \times 10^{-6} \text{ NSm}^{-2}$.

Results and Discussions

The experimental values of density, velocity and viscosity of 1N aqueous sodium hydroxide with 1,4 dioxane over entire range concentration (v/v) at temperature different temperature using ultrasonic interferometer technique are shown in **Table-1**. It is observed that density decrease with increase in concentration (vol. %) of aqueous sodium hydroxide in dioxane. The decrease in density indicates the decrease in solute-solvent and solvent-solvent interactions which results in a structure-breaking of the solvent. However, when temperature of the mixture rise, its density (ρ) decreases. The decrease in density (ρ) with rise 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 dioxane indicating association in the molecules of the component liquids. The association is due to ion-induced dipole interaction between Na^+ of sodium hydroxide and dioxane is stronger than the ion-dipole interaction between Na^+ of sodium hydroxide and water molecule. Since size of dioxane molecule is more than the size of water molecule.

TABLE 1: Density (ρ), Velocity (U) and Viscosity (η) of the ternary systems Aqueous NaOH + 1,4 dioxane at different temperature.

Vol. % of Aq. NaOH in Dioxane	$\rho \text{ (Kgm}^{-3}\text{)}$			U (ms^{-1})			$\eta \times 10^{-3} \text{ (NSm}^{-2}\text{)}$		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	1050.41	1049.49	1048.39	1345.64	1337.60	1324.00	1.150	1.030	0.907
10	1050.04	1049.56	1047.39	1347.60	1298.40	1264.00	1.480	1.270	1.110
20	1046.07	1045.59	1043.43	1348.80	1330.40	1312.00	1.690	1.480	1.300
30	1040.09	1039.61	1037.14	1432.00	1416.00	1408.00	2.030	1.750	1.530
40	1033.63	1033.15	1031.80	1515.40	1450.40	1435.80	2.260	1.970	1.710
50	1030.73	1030.05	1028.90	1554.40	1509.60	1460.00	2.240	1.950	1.680
60	1026.07	1025.59	1024.24	1584.00	1536.00	1528.40	2.070	1.780	1.540
70	1019.50	1018.04	1017.69	1634.72	1592.00	1570.40	1.790	1.550	1.350
80	1011.73	1010.43	1009.13	1642.04	1624.00	1608.00	1.570	1.350	1.180
90	1005.84	1005.54	1004.28	1656.00	1625.40	1618.40	1.280	1.110	0.9522
100	998.920	997.920	995.520	1608.00	1611.20	1616.00	1.120	0.9557	0.8409

Hence higher the size more will be polarizability. The process may lead to strong interaction forces. Thus, association in the constituent molecules may involve due to dipole - induced dipole interaction between dioxane and water.

It is observed that viscosity slightly increases with increase in concentration (vol. %) of sodium hydroxide in dioxane up to 40%, indicating strong molecular interaction. The viscosity of a mixture strongly depends on molecular interaction as well as on the size and shape of the molecules. As the concentration goes higher (above 40%), viscosity gradually 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 Table 2, it is observed that adiabatic compressibility (β_a) decreases with increase in concentration (vol. %) of aqueous sodium hydroxide in dioxane indicating strong intermolecular interaction in the component molecules. As the concentration (vol. %) of aqueous sodium hydroxide increase, the induced dipole-induced dipole interaction and ion-dipole interaction between dioxane and aqueous sodium hydroxide

becomes predominant which leads to a more compact structure and decreased adiabatic compressibility.

It is also that free length decreases with increase in concentration of aqueous sodium hydroxide in dioxane. The decrease in free length with increase in concentration (vol. %) of aqueous sodium hydroxide in dioxane indicates increase in closed packed structure of component molecules i.e. enhancement of the closed structure. The decrease in free length may due to dipole - induced dipole interaction between water and dioxane. 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 1, 4 dioxane indicating association in the molecules of the component liquids. It is also 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. 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 2: Adiabatic compressibility (β_a), free length (L_f) and free volume (V_f) of the ternary systems Aqueous NaOH + 1,4 dioxane at different temperature.

Vol. % of Aq. NaOH in Dioxane	$\beta_a * 10^{-10}$ (m^2N^{-1})			$L_f * 10^{-10}$ (m)			$V_f * 10^{-7}$ (m^3mol^{-1})		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	5.249	5.323	5.441	0.4536	0.4614	0.4688	1.1853	1.3885	1.6472
10	5.322	5.651	5.975	0.4568	0.4754	0.4913	0.7119	0.8519	1.0014
20	5.254	5.403	5.567	0.4538	0.4649	0.4742	0.5128	0.6177	0.7323
30	4.688	4.797	4.863	0.4287	0.4380	0.4432	0.3683	0.4521	0.5509
40	4.218	4.601	4.694	0.4066	0.4290	0.4355	0.2888	0.3343	0.4064
50	4.015	4.260	4.559	0.3967	0.4127	0.4291	0.2544	0.299	0.3543
60	3.884	4.132	4.179	0.3902	0.4065	0.4109	0.2384	0.2861	0.3531
70	3.67	3.875	3.984	0.3793	0.3937	0.4012	0.2421	0.2900	0.3474
80	3.664	3.752	3.832	0.379	0.3874	0.3934	0.2232	0.2739	0.3314
90	3.621	3.759	3.801	0.3768	0.3877	0.3919	0.2127	0.2591	0.3198
100	3.871	3.86	3.842	0.3895	0.3929	0.394	0.1536	0.1951	0.2375

TABLE 3: Internal pressure (π_i), relaxation time (τ) and Gibb's free energy of the ternary systems Aqueous NaOH + 1,4 dioxane at different temperature.

Vol. % of Aq. NaOH in Dioxane	$\pi_i * 10^6$ (Nm ⁻²)			$\tau * 10^{-12}$ (Sec.)			$\Delta G * 10^{-20}$ (KJ/mol)		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	525.43	507.62	485.95	0.8041	0.7288	0.658	0.5468	0.5256	0.5017
10	659.04	631.12	605.91	1.0476	0.9584	0.8853	0.6438	0.6276	0.6141
20	778.57	743.79	713.39	1.1862	1.0628	0.9641	0.6893	0.6661	0.6464
30	925.01	878.12	834.38	1.2696	1.1204	0.9901	0.7142	0.6858	0.6565
40	1074.57	1040.29	989.94	1.2731	1.2064	1.0705	0.7152	0.7134	0.6861
50	1244.55	1169.62	1122.77	1.197	1.1073	1.0237	0.6926	0.6814	0.6691
60	1358.58	1299.02	1230.53	1.0707	0.9784	0.8557	0.6518	0.6353	0.6012
70	1500.62	1435.31	1373.52	0.878	0.8004	0.7197	0.5790	0.5605	0.5357
80	1745.98	1657.81	1580.03	0.7647	0.6756	0.6017	0.5284	0.4973	0.4678
90	2080.66	1979.10	1873.39	0.6175	0.5519	0.4826	0.4500	0.4219	0.3843
100	2857.16	2680.98	2550.13	0.5773	0.4919	0.4308	0.4252	0.379	0.3413

From **Table 3**, it is observed that relaxation time increases slightly with increase in concentration (vol. %) of aqueous sodium hydroxide in 1,4 dioxane up to 40% indicating high stability. 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 sodium hydroxide in 1,4 dioxane up to 40%, indicating the mobility of the molecule is low. 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.

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 desparation forces in the constituent molecules.

The non regular changes of ultrasonic velocity and the thermodynamics parameters lead to dipole-ion interaction between 1,4 dioxane 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 1,4 dioxane are found to be responsible for association whereas 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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Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author Contributions

Both authors have equal contribution in this research article.

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