

Thermo Acoustic Study of Different Parameters for Ternary Mixture of Aqueous Potassium Hydroxide & 1, 4 Dioxane Using Ultrasonic Interferometer

S. G. Rathod*, A. A. Mistry, N. S. Ugemuge

Department of Physics, Anand Niketan College, Warora, Maharashtra, India

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-acoustic parameters such as density (ρ), ultrasonic velocity (U) and viscosity (η) are determined for the ternary mixture of aqueous potassium 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 present paper represents the nonlinear variation of ultrasonic velocity and the thermo-acoustical parameters lead to dipole- ion interaction between 1,4 dioxane 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, aqueous potassium hydroxide (aq. KOH) and 1,4 dioxane.

I. INTRODUCTION

Ultrasonic is widely useful for the investigation of various thermo-acoustic parameters such as adiabatic compressibility, free volume, intermolecular free length and relaxation time¹⁻³. The molecular behavior and interactions and their mixtures can be characterized with the help of ultrasonic studies⁴⁻⁶. The measurement of ultrasonic velocity in the organic liquid mixture is a useful tool to study the physiochemical properties of the liquids and also explain the mechanism of molecular interaction⁷⁻¹⁰. The ultrasonic velocity data for ternary liquid

mixtures have been used for by many researchers¹¹⁻¹⁴. The present work investigates thermo-acoustical properties of aqueous solution of KOH 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.

II. METHODS AND MATERIAL

The ultrasonic velocity was measured in the ternary mixture of aqueous potassium hydroxide and 1,4 dioxane using an ultrasonic interferometer 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 $\pm 1 \times 10^{-6} \text{ NSm}^{-2}$.

III. RESULTS AND DISCUSSION

The experimental values of density, velocity and viscosity of 1N aqueous potassium hydroxide with 1,4 dioxane over entire range concentration (v/v) at different temperature range 298K-308K using ultrasonic interferometer are shown in **table-1**. It is observed that density increases with increase in concentration (vol. %) of aqueous potassium hydroxide in dioxane. Due to increase in density, the volume decreases indicating association in component molecules. The decrease in density (ρ) with rise in temperature indicates decrease in cohesive force. It is also observed that ultrasonic velocity increase with increase in concentration (vol. %) of aqueous potassium hydroxide in dioxane indicating association in the molecules of the component liquids. The association is due to ion-induced dipole interaction between K^+ of potassium hydroxide and dioxane is stronger than the ion-dipole interaction between K^+ of potassium hydroxide and water molecule. Since size of dioxane molecule is more than the size of water molecule and hence more will be polarizability of

dioxane. Thus association in the constituent molecules may involve due to dipole - induced dipole interaction between water and dioxane. It is observed that viscosity increases with increase in concentration (vol. %) of potassium 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.

From table-2, it is observed that adiabatic compressibility (β_a) decreases with increase in concentration (vol. %) of aqueous potassium hydroxide in dioxane indicating strong intermolecular interaction in the molecules of component in the ternary liquid mixtures shows associating tendency of the component molecules. As the concentration (vol. %) of aqueous potassium hydroxide increases, the induced dipole- induced dipole and ion-dipole interaction between dioxane and aqueous potassium hydroxide becomes predominant which leads to a more compact structure and decreased adiabatic compressibility. It is also observed that free length decreases with increase in concentration of aqueous potassium hydroxide in dioxane. Free length decreases with concentration due to lack of perfect symmetry and decrease in available space between the component molecules. The decrease in free length with increase in concentration (vol. %) of aqueous potassium 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 dioxane and water. 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 dioxane, indicating association in the molecules of the component liquids.

From table-3, 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 - induced dipole interaction between water and dioxane. This suggests that both solute- solute and solute solvent interaction exist in the system. Thus increase in free volume and decrease in internal pressure occurs with increase in temperature. It is also observed that relaxation time increases slightly with increase in concentration (vol. %) of aqueous potassium hydroxide in dioxane up to 40%, indicating high stability. As the concentration goes higher (above 40%), the relaxation time slightly decrease indicating less stability. Gibb's free energy measure mobility of the medium. Higher the mobility of the medium, higher will be the entropy; lower will be the free energy. It is observed that initially Gibb's free energy slightly increases with increase in concentration (vol. %) of aqueous potassium hydroxide in dioxane 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 40%), 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 due to salvation is directly proportional to size of the molecule.

TABLES

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

Vol. % of Aq. KOH in Dioxane	ρ (Kg ^m ⁻³)			U (ms ⁻¹)			η *10 ⁻³ (NSm ⁻²)		
	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	1051.52	1050.86	1049.21	1336.00	1322.40	1306.00	1.420	1.210	1.050
20	1052.90	1051.50	1050.11	1388.80	1344.00	1329.60	1.710	1.480	1.320
30	1053.21	1052.32	1051.00	1398.40	1365.60	1345.60	1.850	1.610	1.400
40	1054.12	1053.21	1052.11	1481.60	1467.20	1444.80	2.080	1.790	1.480
50	1055.32	1054.08	1052.96	1529.60	1509.60	1481.60	1.870	1.640	1.430
60	1056.08	1055.02	1053.82	1573.60	1533.60	1516.00	1.750	1.530	1.340
70	1057.10	1055.90	1054.71	1593.60	1580.00	1568.00	1.590	1.360	1.180
80	1057.95	1055.50	1055.30	1600.00	1556.00	1549.60	1.320	1.130	0.983
90	1058.50	1057.01	1055.83	1592.00	1540.00	1547.20	1.180	1.020	0.890
100	1058.04	1055.89	1055.42	1590.00	1598.00	1612.00	1.050	0.914	0.799

TABLE-2: - Adiabatic compressibility (β_a), free length (L_f) and free volume (V_f) of the ternary systems Aqueous KOH + 1,4 dioxane at different temperature.

Vol. % of Aq. KOH in Dioxane	β_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	5.249	5.323	5.441	0.4536	0.4614	0.4688	1.1853	1.3885	1.6472
10	5.328	5.441	5.587	0.4570	0.4665	0.4751	0.7543	0.9494	1.1498
20	4.924	5.264	5.386	0.4393	0.4589	0.4665	0.5288	0.6238	0.7323
30	4.855	5.095	5.254	0.4362	0.4514	0.4607	0.4111	0.4857	0.5884
40	4.321	4.410	4.553	0.4116	0.4200	0.4289	0.3189	0.3923	0.511
50	4.050	4.162	4.326	0.3984	0.4080	0.4180	0.3248	0.3895	0.4631
60	3.823	4.030	4.128	0.3871	0.4015	0.4084	0.305	0.36	0.4287
70	3.724	3.799	3.856	0.3821	0.3895	0.3947	0.2819	0.3511	0.4281
80	3.692	3.909	3.946	0.3804	0.3954	0.3992	0.2802	0.3399	0.4158
90	3.727	3.989	3.956	0.3822	0.3994	0.3998	0.2299	0.2726	0.336
100	3.738	3.705	3.646	0.3828	0.3849	0.3838	0.1706	0.2111	0.2617

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

Vol. % of Aq. KOH in Dioxane	π_i *10 ⁶ (Nm ⁻²)			τ *10 ⁻¹² (Sec.)			ΔG *10 ⁻²⁰ (KJ/mol)		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	525.43	507.62	486.00	0.8041	0.7288	0.6580	0.5468	0.5256	0.5017
10	645.89	608.95	580.11	1.0080	0.8743	0.7804	0.6297	0.5934	0.5663
20	773.58	743.74	716.04	1.1224	1.0402	0.9461	0.6690	0.6581	0.6393
30	898.4	863.59	822.74	1.1914	1.0957	0.9797	0.6920	0.6775	0.6525
40	1051.92	997.64	927.90	1.1969	1.0537	0.8980	0.6926	0.6629	0.6195
50	1135.07	1085.44	1040.78	1.0124	0.9098	0.8269	0.6312	0.6082	0.5883
60	1272.20	1223.45	1172.37	0.8922	0.8206	0.7396	0.5849	0.5697	0.5460
70	1456.06	1374.86	1307.20	0.7892	0.6883	0.6084	0.5399	0.5042	0.4720
80	1660.10	1581.35	1501.87	0.6500	0.5885	0.5172	0.4688	0.4459	0.4105
90	2081.10	1997.22	1892.20	0.5864	0.5418	0.4697	0.4311	0.4151	0.3740
100	2835.65	2683.63	2537.09	0.5227	0.4517	0.3886	0.3889	0.3473	0.3022

IV. CONCLUSION

- The non regular changes of ultrasonic velocity and the thermodynamics parameters lead to dipole-ion interaction between 1,4 dioxane and 1N aqueous potassium hydroxide is stronger than dipole-ion interaction between water and aq. potassium hydroxide.
- The ion-dipole interactions between K⁺ of potassium hydroxide and 1,4 dioxane are found to be responsible for association whereas the ion-dipole interactions between K⁺ of potassium hydroxide and water molecules are found to be responsible for dissociation in the liquid mixtures.

V. REFERENCES

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