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Thermo-Acoustical and Excess Parameters in Ternary Mixture of Containing Aqueous KOH in Dimethyl Sulfoxide at Different Temperatures

A. A. Mistry
Department of Physics, Anand Niketan College, Warora, Maharashtra, India

ABSTRACT

The thermo-physical parameters such as density (ρ), ultrasonic velocity (U) and viscosity (η) are determined for a ternary mixture (n=3) of aqueous potassium hydroxide (aq. KOH) and dimethyl sulfoxide (DMSO) system at 0.0% to 100% (v/v) and at different temperatures. Using the experimental data, adiabatic compressibility (β), free length (L_f) and free volume (V_f) are evaluated at different temperatures.. The excess values of adiabatic compressibility (β^E), excess free length (L^E_f) and free volume (V^E_f) have also been computed by using the experimental data. The behavior of these parameters with composition of the mixture has been discussed in terms of molecular interaction between the components of the liquids. The deviation in the excess values reveal that intermolecular interactions obtaining in the solution.

Keywords : *Ultrasonic velocity, acoustical parameters, molecular interactions, aqueous potassium hydroxide (aq. KOH) and* dimethyl sulfoxide (DMSO*).*

I. INTRODUCTION

The adaptable non-destructive technique like Ultrasonic interferometer is highly helpful for the characterization of various physico-chemical properties.Uitrasonic velocity jointly with density and viscosity investigations in liquid mixtures find widely applications in recognizing physico-chemical behavior**[1-2]**.The temperatures dependence of the ultrasonic parameters provide wealth of information about the interactions between the ions,dipoles,hydrogen bonding and weak Vander Waals forces between the components of the liquid mixtures**[3-5]**. The studies on the physio-chemical properties of organic liquid such as: dimethyl sulfoxide in aqueous solution of potassium hydroxide provides useful information, which is used to assess the information of molecular interaction **[6-7]**. The ultrasonic velocity data for ternary liquid mixtures have been used by many researchers **[8-10]**. The deviation from ideally is expressed by many thermo-acoustic parameters ,particular by excess properties **[11-12].**In this paper the authors report on the ultrasonic velocity, density, and viscosity of 1N aqueous potassium hydroxide with dimethyl sulfoxide at different temperatures over the different volume ratio (v/v) of aqueous KOH in DMSO. From these experimental values, a number of thermodynamics parameters, namely adiabatic compressibility (βa), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and Gibb's free energy (ΔG) were calculated and the results such as excess parameters are analyzed in the light of molecular interactions in the ternary liquid mixtures.

II. METHODS AND MATERIAL

A simple and direct device which is ultrasonic interferometer technique, operating frequencies ranging from 1 to 10 MHz has been utilized to calculate the ultrasonic velocity. 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 ± 0.1 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 $\pm 1x10^{-6}$ NSm^{-2}. All precautions were taken to minimize the possible experimental error.

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 using ultrasonic interferometer are shown in **table-1.** It is observed that density decrease with increase in concentration (vol. %) of aqueous potassium 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. If temperature of the mixture rises, 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 potassium hydroxide in dimethyl sulfoxide up to 80%, indicating the increase in stiffness of the mixture and hence association in the molecules of the component liquids. As the concentration goes higher (above 80%), the ultrasonic velocity gradually decreases indicating stiffness of the mixture decrease and hence dissociation. It is observed that viscosity slightly decreases with increase in concentration (vol. %) of potassium hydroxide in dimethyl sulfoxide. 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 potassium hydroxide in dimethyl sulfoxide up to 80%, indicating strong intermolecular interaction between aqueous potassium hydroxide and dimethyl sulfoxide. As the concentration goes higher (above 80%), adiabatic compressibility (β_a) gradually increases indicating weak molecular interaction among dimethyl sulfoxide and aqueous potassium hydroxide. It is also observed that free length decreases with increase in concentration of aqueous potassium hydroxide in dimethyl sulfoxide up to 80%. The decrease in free length is a result of dipole-dipole and ion-dipole interaction between dimethyl sulfoxide and aqueous potassium hydroxide indicating association. As the concentration (vol. %) of aqueous potassium hydroxide in dimethyl sulfoxide goes higher (above 80%), the intermolecular free length gradually increases indicating weak interaction among solvent and solute.

The excess thermo-acoustical parameters which play a major role in understanding the nature of molecular interactions in liquid mixtures have been studied by many researchers **[13-15]**.From table-3, it is clear that with the increase in concentration (vol. %) of aqueous potassium hydroxide in dimethyl sulfoxide the excess values of $\beta_a{}^E$ and $L_f{}^E$ decrease negatively in magnitude and approach to minimum at around 40% concentration of aqueous potassium hydroxide in dimethyl sulfoxide which suggest that maximum structural changes take place in this region of the mixture. Decreasing negative excess values of $\beta_a{}^E$ and $L_f{}^E$ with increase in temperature may be accounted

for the molecular dissociation which leads to less closer packing in aqueous potassium hydroxide in dimethyl sulfoxide and hence increase in compressibility and free length. The excess values of free volume (V_f^E) are negative as shown in table-3. The negative deviation of excess values of free volume is an indication of the existence of strong interaction between the component molecules. Negative free volume decreases with increasing concentration (vol. %) of aqueous potassium hydroxide in Dimethyl sulfoxide.

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

Vol. % of Aq.KOH in DMSO	ρ (Kgm^{-3})			U (ms^{-1})			η*10^{-3} (NSm^{-2})		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
00	1104.91	1103.62	1102.09	1464.00	1437.28	1424.00	1.86	1.64	1.44
10	1100.32	1098.12	1095.46	1489.60	1477.60	1448.00	3.34	2.93	2.55
20	1095.52	1093.41	1090.55	1561.60	1538.40	1512.00	3.17	2.78	2.4
30	1090.74	1088.63	1085.57	1592.00	1568.00	1552.00	3.09	2.71	2.4
40	1083.45	1082.15	1080.31	1656.00	1605.60	1588.00	3.01	2.64	2.37
50	1080.21	1078.92	1077.28	1660.00	1608.00	1592.00	2.83	2.48	2.07
60	1072.51	1071.02	1069.09	1668.80	1650.40	1641.60	2.26	1.98	1.76
70	1068.25	1065.91	1065.40	1677.60	1664.00	1652.00	1.89	1.62	1.41
80	1064.19	1061.10	1058.08	1684.80	1667.20	1653.60	1.49	1.3	1.13
90	1061.52	1059.75	1057.44	1644.00	1610.40	1604.00	1.18	1.03	0.905
100	1058.04	1055.89	1055.42	1590.00	1598.00	1612.00	1.05	0.914	0.799

TABLE-2: - Adiabatic compressibility (βa), free length (Lf) and free volume (Vf) of the ternary systems Aqueous KOH + dimethyl sulfoxide (DMSO) at different temperature.

Vol. % of Aq. KOH in DMSO	βa *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	4.222	4.386	4.474	0.4068	0.4188	0.4251	0.5445	0.6413	0.7647
10	4.095	4.170	4.562	0.4007	0.4084	0.4293	0.2059	0.2481	0.2962
20	3.743	3.864	4.01	0.3830	0.3931	0.4025	0.2104	0.2508	0.3042
30	3.617	3.736	3.824	0.3765	0.3865	0.3930	0.1953	0.2327	0.2750
40	3.365	3.584	3.670	0.3632	0.3786	0.3850	0.1848	0.2150	0.2536
50	3.359	3.584	3.662	0.3629	0.3786	0.3846	0.1710	0.1983	0.2572
60	3.348	3.427	3.470	0.3622	0.3702	0.3744	0.1985	0.2376	0.2824
70	3.326	3.385	3.439	0.3611	0.3679	0.3727	0.2085	0.2587	0.3173
80	3.310	3.390	3.456	0.3602	0.3682	0.3736	0.2296	0.2787	0.3366
90	3.485	3.638	3.675	0.3696	0.3815	0.3853	0.2262	0.2698	0.3258
100	3.738	3.705	3.646	0.3828	0.3849	0.3838	0.1706	0.2111	0.2617

TABLE-3: - Excess values of adiabatic compressibility (β_a^E), intermolecular free length (L_f^E) and free volume (V_f^E), of the ternary systems Aqueous KOH + dimethyl sulfoxide (DMSO) at different temperature.

Vol. % of Aq. KOH in DMSO	β_a^E $*10^{-10}$ (m^2N^{-1})			L_f^E $*10^{-10}$ (m)			V_f^E $*10^{-7}$ (m3/mol)		
	298K	303K	308K	298K	303K	308K	298K	303K	308K
10	-0.0786	-0.1479	0.1708	-0.0037	-0.0070	0.0083	-0.3012	-0.3501	-0.4182
20	-0.3822	-0.3858	-0.2984	-0.0190	-0.0189	-0.0143	-0.2593	-0.3044	-0.3599
30	-0.4548	-0.4457	-0.4016	-0.0231	-0.0221	-0.0197	-0.2370	-0.2795	-0.3388
40	-0.6634	-0.5296	-0.4728	-0.0340	-0.0266	-0.0235	-0.2101	-0.2542	-0.3099
50	-0.6210	-0.4615	-0.3980	-0.0319	-0.0232	-0.0198	-0.1865	-0.2279	-0.2560
60	-0.5836	-0.5504	-0.5072	-0.0302	-0.0282	-0.0259	-0.1216	-0.1455	-0.1805
70	-0.5572	-0.5243	-0.4554	-0.0289	-0.0271	-0.0234	-0.0742	-0.0814	-0.0953
80	-0.5248	-0.4512	-0.3556	-0.0274	-0.0234	-0.0184	-0.0157	-0.0184	-0.0257
90	-0.3014	-0.1351	-0.0538	-0.0156	-0.0067	-0.0026	0.01821	0.0156	0.0138

IV. CONCLUSION

- The ion-dipole interactions between K^+ of potassium hydroxide and dimethyl sulfoxide 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.
- The excess values of adiabatic compressibility (β_a^E), intermolecular free length (L_f^E) and free volume (V_f^E) are sensitive to nature of interaction in liquids.

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