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Comparative Study of Solvolysis of Tetra Ethyl Lead in Aqueous NaOH and Aqueous KOH

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ABSTRACT

The comparative study of solvolysis of tetra ethyl lead in aqueous NaOH and aqueous KOH solution was studied with the help of ultrasonic velocity, viscosity, density and other parameters determined by using a single crystal interferometer at a frequency of 2 MHz. The ultrasonic study of tetra ethyl lead confirms that there is a significant interaction between the solute- solvent molecules and ions in aqueous alkaline solutions. The main motto of this paper is that tetra ethyl lead shows more effective interaction in which alkaline solution.

INTRODUCTION

The study of intermolecular interactions play an important role in molecular sciences, liquid-liquid mixtures and solutions have found wide applications in chemical, textile, pharmaceutical and nuclear industries[1-5]. The estimation of the speed of ultrasound is the primary requirement for investigating the transport properties of liquid and solid systems[6]. Now a days molecular and ionic interactions are mostly studied by ultrasonic interferometer[7-9]. In this paper, the speed of ultrasound waves in tetra ethyl lead in aqueous NaOH and aqueous KOH have been estimated for different concentrations at 30°C. From the experimental data various acoustical parameters such as specific acoustic impedance (Z), intermolecular free length (L_f), relative association (R_a) adiabatic compressibility (φ_K) etc. have been calculated using density, viscosity and ultrasound velocity data. These data provide useful information about interaction between solute and solvent occurring in the solution.

EXPERIMENTAL

All chemicals used in the research work are of analytical reagent (AR) grade obtained from E. Merk. The purity of the used chemicals were checked by density determination at 30°C. The values of density obtained tally with the literature values[10-12]. Weight of the samples were measured using electronic balance with an accuracy of ±0.01 mg. density, viscosity and ultrasound speed have been measured by using precalibrated bicapillary pycknometer[13-14], viscometer(Ostwald's)[15] and single frequency ultrasonic interferometer at 2MHz respectively with an accuracy of ±0.05%[16-19]. All measurements were made in a thermostatically controlled water bath with temperature accuracy of ± 1°C.

Theory and Calculations

Many acoustic parameters such as isentropic compressibility (β_s), intermolecular free length (L_f), specific acoustic impedance(Z), apperant molal compressibility (φ_k), solvation number (S_n) and relative association (Ra) have been calculated at 30°C, using ultrasonic velocity (U), density (ρ) and viscosity (Ƞ) of these solutions with the help of the following equations[20].

1. Sentropic Compressibility (β_s) $= 1/U^2\rho$ (1)

2. Specific Acoustic Impedance (Z)=U.ρ (2)

3. Intermolecular Free Length (L_f) = $K\sqrt{\beta_s}$ (3)

4. Relative Association (R_A) $= \dfrac{\rho}{\rho_o}\left[\dfrac{U_o}{U}\right]^{1/3}$ (4)

5. Solvation Number (S_n) $= \dfrac{n_1}{n_2}\left(1-\dfrac{\beta_s}{\beta_{so}}\right)$ (5)

6. Apparent Molal Compressibility (ϕ_K) =

$$(\phi_K) = \frac{1000\,(\rho_o\beta_s - \beta_{so}\rho)}{C.\,\rho_o} + \frac{\beta_{so}\,M}{\rho_o} \quad (6)$$

Where ρ, ρ_o and Uo are the densities and ultrasonic velocities of solution and solvent respectively, K is Jacobson constant, M molecular weight of solute, β_{so} the isentropic compressibility of solvent, C is concentration in mole/ litre n_1 and n_2 are the number of moles of solvent and solute respectively.

RESULT AND DISCUSSION

The measured properties in experiment like ultrasound velocity (U), density (ρ) and viscosity (Ƞ) are shown in table 1, 2. The given data shows that these three parameters increase with increase in concentration of tetra ethyl lead in alkali solution. This indicates that strong interaction observed at higher concentrations of tetra ethyl lead and suggests more association between solute and solvent molecules in the system. In these data the ultrasound velocity of tetra ethyl lead in aqueous NaOH is more than aqueous KOH solution so

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Table1. Experimental values of Tetra ethyl lead in aqueous NaOH at30^{o}C.

Conc.	U	ρ	η	βs	L_f	Z	Φ_K	Sn	Ra
0.0275	1472	1.1922	0.7988	38.71	0.3926	0.1755	-32.9581	11.0654	0.0231
0.0550	1476	1.1949	0.8015	38.41	0.3911	0.1764	-21.9279	15.6021	0.0461
0.0826	1481	1.1977	0.8043	38.09	0.3895	0.1773	-18.6399	20.4840	0.0691
0.1101	1485	1.2004	0.8070	37.79	0.3879	0.1782	-16.8191	25.1566	0.0920
0.1376	1490	1.2032	0.8098	37.46	0.3862	0.1792	-15.8996	30.0852	0.1149
0.1651	1493	1.2059	0.8125	37.20	0.3849	0.1800	-14.7431	34.0486	0.1378
0.1926	1497	1.2087	0.8153	36.90	0.3833	0.1810	-14.1891	38.5758	0.1606
0.2202	1501	1.2114	0.8180	36.65	0.3820	0.1818	-13.5024	42.4608	0.1834
0.2477	1505	1.2142	0.8208	36.36	0.3805	0.1827	-13.1758	46.8985	0.2061
0.2752	1510	1.2169	0.8235	36.04	0.3788	0.1838	-13.0459	51.7250	0.2288

Table 2. Experimental values of Tetra ethyl lead in aqueous KOH at 30^{o}C.

Conc.	U	ρ	η	βs	L_f	Z	Φ_K	Sn	Ra
0.0275	1455	1.1752	0.7857	40.20	0.4001	0.1710	-108.3854	7.3801	0.0234
0.0550	1459	1.1779	0.7884	39.88	0.3985	0.1719	-59.2712	13.5620	0.0468
0.0826	1463	1.1807	0.7912	39.57	0.3969	0.1727	-42.8482	19.6796	0.0702
0.1101	1467	1.1834	0.7939	39.26	0.3954	0.1736	-34.5984	25.7339	0.0935
0.1376	1471	1.1862	0.7967	38.96	0.3939	0.1745	-29.6184	31.7256	0.1168
0.1651	1475	1.1889	0.7994	38.66	0.3923	0.1754	-26.2735	37.6556	0.1400
0.1926	1479	1.1917	0.8022	38.36	0.3908	0.1762	-23.8633	43.5246	0.1632
0.2202	1483	1.1944	0.8049	38.07	0.3893	0.1771	-22.0375	49.3334	0.1864
0.2477	1487	1.1972	0.8077	37.78	0.3878	0.1780	-20.6015	55.0829	0.2095
0.2752	1491	1.1999	0.8104	37.49	0.3863	0.1789	-19.4385	60.7737	0.2326

aqueous NaOH shows more interaction and high association with tetra ethyl lead.

Density is measure of solvent-solvent and ion- solvent interactions. Increase in density (in table1,2) with concentration indicates the increase of solvent- solvent and solute- solvent interactions. In both tables density value of tetraethyl lead in aqueous NaOH is more than in aqueous KOH. This indicates that increase in density is due to structure breaking property of the aqueous NaOH solution due to addition of tetra ethyl lead.

The isentropic compressibility for the solution of tetra ethyl lead decreases with increase in solute concentration but the value of isentropic compressibility of tetra ethyl lead on aqueous KOH is more than that in aqueous NaOH. This attributed to the fact that the solute molecules in dilute solution are ionized into simple metal ion and anions. These ionic particles are surrounded by a layer of solvent ions. Firmly, bound and oriented towards the ions. The orientation of solvent ions around the ions of solute is attributed to the influence of electrostatic field of ions and thus the internal pressure increases which lowers the compressibility of solutions.

Intermolecular free length is the distance between the surfaces of the neighboring molecules and variation in free length with concentration and temperature is similar to that of isentropic compressibility[21].

The specific acoustic impedance is a product of the density of solution and velocity has shown the reverse trends to that of intermolecular free length[22]. Thus, the fact that increase of specific acoustic impedance with increase in inter molecular forces with the addition of solute forming aggregates of solvent ions around the solute ions and supports the strong solute- solvent interactions due to structural arrangement affected.

According to table1 and 2 the value of specific acoustic impedance of tetra ethyl lead in aqueous NaOH solution is more than in aqueous KOH solution. This indicates that strong inter- molecular forces produce in aqueous NaOH solution.

Values of apperant molal compressibility increases with increase in concentration at the 30^{o}C temperature, which indicates occurrence of solute- solvent interaction and solvent effect is more dominating than the electrolyte. In both table the value of apparent molal compressibility of tetraethyl lead in aqueous NaOH is more than in aqueous KOH solution. This indicates that the solute-solvent interaction is more powerful in aqueous NaOH and solvent effect is more dominating in aqueous NaOH solution.

Values of solvation numbers are listed in table 1,2 and results show that the solvation number are found to increase in aqueous NaOH solution which shows close association between solute and solvent.

Relative association[23] depends on the breaking up of solvent molecules on the addition of solute to it. In the present case relative association of tetra ethyl lead in aqueous KOH is higher than aqueous NaOH solution at 30^{o}C which is due to the breaking up of molecules in the solution which also indicates prominent solute- solvent interaction.

CONCLUSION

From the data available in table 1&2, it is concluded that the tetra ethyl lead shows more significant interaction in aqueous NaOH solution than aqueous KOH solution and this interaction increases with increase in concentration.

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