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Acoustical study of aqueous manganese chloride solutions at varying temperatures by ultrasonic technique

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ABSTRACT

Ultrasonic velocities, densities and viscosities in very dilute concentrations of aqueous $MnCl_2.4H_2O$ *system have been determined at 303.15K, 308.15K, 313.15K and 318.15K temperatures. Using this data, the acoustical parameters such as adiabatic compressibility's* (β)*, intermolecular free lengths* (L_f)*, specific acoustic impedances (Z) and solvation numbers* (S_n) *have been estimated. The results have been interpreted in light of ion-solvent interactions in terms of structure breaking and structure promoting nature of* Mn^{+2} *ions in aqueous media.*

Keywords: ultrasonic velocity, ion-solvent interactions, adiabatic compressibility, intermolecular free length, solvation number.

INTRODUCTION

The study of molecular interactions in the liquid mixtures is very much important to study the structural properties of molecules. Ultrasonic energy is used in medicine, engineering, agriculture, defence and industry. In chemical industries ultrasonic energy is found useful in studying the chemical processes and in synthesis of chemical substances. In solution of ionic solute the attraction between the solute and solvent is of ion-dipole type. When electrolyte is dissolved in solvent it causes volume contraction due to interactions between ions and solvent molecules and therefore other acoustical parameters may be affected. Many researchers have used ultrasound to investigate the ion-solvent interactions in aqueous solutions containing electrolytes [1, 6]. A survey of literature [1-18], reveals that ultrasonic waves with low amplitude have been used by many scientists to investigate the nature of molecular interactions and physiochemical behaviour of pure binary, ternary and quaternary liquid mixtures.

Recently V. Kannappan and S. Chidambara Vinayagam[6] studied ion-solvent interactions in aqueous and non-aqueous solutions of transition and inner transition metal ions by ultrasonic technique at 303.15K. However, to our knowledge it is observed from literature survey that, attempt has not been made to study ion-dipole interactions in very dilute aqueous solutions of tetra hydrated $MnCl_2$ at different temperatures. The present work deals with the measurement of ultrasonic velocity, density and viscosity. With the help of these parameters adiabatic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z) and solvation number (S_n) for very dilute aqueous solution of $MnCl_2$ at 303.15K, 308.15K, 313.15K and 318.15K have been calculated.

EXPERIMENTAL SECTION

Ultrasonic velocity for the aqueous solutions was measured using a single crystal ultrasonic interferometer at 2 MHz frequency (model F-81) supplied by Mittal enterprises, New Delhi, that has a an accuracy of 0.25 m/Sec at 25°C. The temperature was kept constant, by constant temperature water bath with an accuracy of ± 0.1K. The temperature of the circulating water near the cell was measured by using PT-100 sensor and was found to be accurate to 0.23°C. The densities of various concentrations have been measured using 25ml capacity specific gravity bottle and digital balance (Shinko, model HTR-220E, made in Japan) with an accuracy of 0.0001gm. The viscosities have been determined by using Ostwald viscometer.

The Qualigen made hydrated salt $MnCl_2.4H_2O$ of Anal-R grade having 99.5% assay was used without further purification for the present investigation. The aqueous solution of $MnCl_2.4H_2O$ was prepared in double distilled water in the presence of perchloric acid to avoid hydrolysis [6].

THEORY AND CALCULATIONS

Various physical parameters were calculated from the measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) using the following standard expressions.

Adiabatic compressibility (β) = $1/U^2\rho$ ($Kg^{-1}ms^{-2}$)
Intermolecular free length (Lf) = $k\sqrt{\beta}$ (m)

Where k is temperature dependent constant called as Jacobson constant [7] it is 2.075×10^{-6}, 2.095×10^{-6}, 2.115×10^{-6} and 2.135×10^{-6} for 303.15, 308.15, 313.15 and 318.15K respectively.

Specific acoustic impedance (Z) = ρU ($Kgm^{-2}s^{-1}$)
Solvation number (S_n) = $\frac{n_s}{n_i}\left(1-\frac{\beta}{\beta_0}\right)$, n_s = number of moles of solvent (mol/kg)
n_i = number of moles of solute (mol/kg)
β = Adiabatic compressibility of solution at a particular temperature ($N^{-1}m^2$)
β_0 = Adiabatic compressibility of solvent at a particular temperature ($N^{-1}m^2$)

RESULTS AND DISCUSSION

The experimental values of ultrasonic velocity (U), density (ρ) and viscosity (η) and the calculated values of adiabatic compressibility's (β), intermolecular free lengths (L_f), acoustic impedances (Z), and solvation numbers (S_n) for very dilute aqueous solution of $MnCl_2.4H_2O$ at 303.15K, 308.15K, 313.15K and 318.15K are summarized in Table 1.

Table 1.Ultrasonic velocities (U), densities (ρ), viscosities (η), specific acoustic impedances (Z), adiabatic compressibility's (β), intermolecular free lengths (L_f), and solvation numbers (S_n) for $ZnSo_4$ + water system at 303.15K and 308.15K, 313.15K and 318.15K.

Temp	Conc./M	U ms^{-1}	ρ Kgm^{-3}	$\eta/10^{-4}$ Nsm^{-2}	$\beta/10^{-10}$ $Kg^{-1}ms^2$	$Z/10^6$ $Kgm^{-2}S^{-1}$	$L/10^{-11}$ m	S_n
303.15K	0.0000	1509.00	995.11	7.980	4.391	1.507	4.348	-----
	0.0011	1510.78	1003.08	7.983	4.368	1.515	4.337	263.15
	0.0021	1512.17	1002.55	7.983	4.362	1.516	4.334	173.97
	0.0041	1508.88	1003.79	8.147	4.376	1.515	4.341	46.10
	0.0061	1512.52	1003.90	8.077	4.354	1.518	4.330	76.40
	0.0081	1511.32	1006.12	8.022	4.351	1.521	4.329	62.05
	0.081	1517.72	1011.41	8.227	4.292	1.535	4.299	15.28
308.15K	0.0000	1519.10	994.90	7.200	4.338	1.511	4.361	-----
	0.0011	1521.74	1001.46	7.042	4.312	1.524	4.348	302.63
	0.0021	1521.20	1001.54	7.084	4.315	1.524	4.349	142.10
	0.0041	1520.36	1001.80	7.227	4.318	1.523	4.351	61.50
	0.0061	1520.35	1003.60	7.217	4.311	1.526	4.347	57.32
	0.0081	1520.52	1003.19	7.187	4.312	1.525	4.348	41.92
	0.081	1524.16	1009.23	7.319	4.265	1.538	4.324	11.41
313.15K	0.0000	1530.00	992.27	6.530	4.284	1.518	4.370	-----
	0.0011	1529.91	999.06	6.680	4.276	1.528	4.366	84.55
	0.0021	1529.04	999.59	6.520	4.279	1.528	4.367	28.25
	0.0041	1526.28	1001.46	6.650	4.286	1.529	4.371	-9.13
	0.0061	1532.00	1001.50	6.630	4.254	1.534	4.355	62.01
	0.0081	1530.60	1001.50	6.610	4.262	1.533	4.359	34.25
	0.081	1533.60	1008.29	6.820	4.217	1.546	4.336	10.58
318.15K	0.0000	1536.20	990.31	5.960	4.253	1.521	4.395	-----
	0.0011	1536.88	998.76	6.210	4.239	1.535	4.388	168.81
	0.0021	1537.40	998.12	6.050	4.239	1.535	4.388	89.45
	0.0041	1535.64	998.95	6.180	4.245	1.534	4.391	26.11
	0.0061	1535.13	995.87	6.050	4.261	1.529	4.399	-16.70
	0.0081	1534.80	999.40	6.130	4.248	1.534	4.393	8.80
	0.081	1541.39	1007.77	6.300	4.177	1.553	4.356	12.26

At all temperatures the values of U, ρ, and η varies non-linearly with concentration. With increase in temperature the ρ, η shows the decreasing trend whereas U increases with increasing concentration. The increase in the values of ρ, η with small change in concentration suggests the moderate strong electrolyte nature of Mn^{+2} ions which tend to attract water molecules. The non-linear variation of U with small change in concentration for all temperatures shows the strong molecular interactions between Mn^{+2} ions and H_2O molecules.

However for 0.0041M and 0.0081M concentration at 303.15K ultrasonic velocity decreases which suggest that Mn^{+2} ions behaves as structure breaker for the cluster of water molecules suggesting weak ion-solvent interactions. For other temperatures similar structure breaking tendency of Mn^{+2} ions was observed for some other concentration as shown in Table 1 showing weak molecular interactions[8].

The non-linear variation of ultrasonic velocity with concentrations indicates occurrence of complex formation between molecules of $MnCl_2$ and H_2O [9]. The molecular association becomes maximum at those concentrations where velocity maxima occur. The chemical interaction may involve due to the association between ion and dipole molecule [10].

At all temperatures, it is observed from Table1 and Fig.1 that at certain concentration ultrasonic velocity is minimum. This is probable due to maximum associated water molecules are broken into their monomers and close association is formed between Mn^{+2} ions and water molecules. It is likely that the water molecules at certain concentration of Mn^{+2} ions may stay in associated form. The associated water molecules are larger in size as compared to Mn^{+2} ions and have to be accommodated in the system and this may cause some structural changes resulting in the weakening of intermolecular forces. This may be probably would be the reason for the decrease in U suggesting weak Mn^{+2} ions - solvent interactions [11].

From Table 1 and Fig. 3, it is observed that adiabatic compressibility (β) shows an inverse trend as compared to U. Values of β decreases with increasing concentration of $MnCl_2$ in water solvent. For all temperatures and at certain concentrations e.g. 0.0041M for 303.15K, 0.0021M and 0.0041M for 308.15K etc., compressibility is maximum which suggest that Mn^{+2} ions behaves as structure breaker for the cluster of water molecules showing weak ion-solvent interactions. The occurrence of maximum U and minimum β at the same concentration indicates that there is a significant interaction between Mn^{+2} ions and water molecules [11, 12, 13].

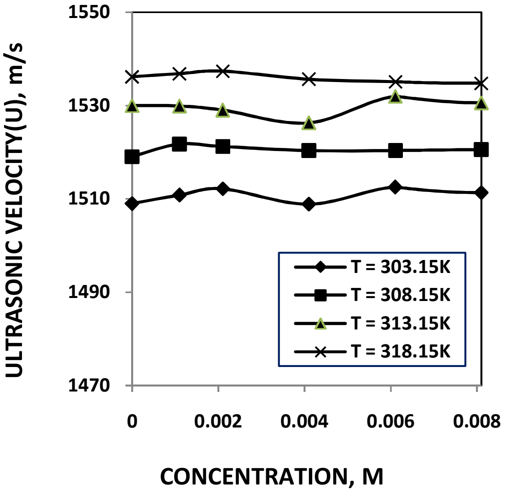

Fig. 1: U against concentration

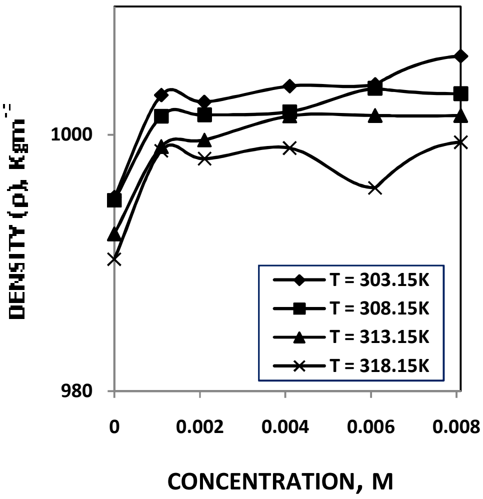

Fig. 2: ρ against concentration

Fig. 4 shows the variation of acoustic impedance with concentration and temperature for the given system. When an acoustic wave travel in a medium, there is a variation of pressure from particle to particle. The product of ultrasonic velocity (U) and density (ρ) is known as "specific acoustic impedance (Z)" of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is setup in a liquid, the pressure and hence density and refractive index of the liquid shows a periodic variation with distance from the source along the direction of propagation. If there is stationary ultrasonic wave pattern in the liquid, the density will be greater in the nodal planes than in any other plane. From Table1 and Fig. 4, it is observed that like other parameters viz. U and β, Z exhibits a non-linear variation with concentration for all temperatures. This supports the Mn^{2+} ions interactions with water molecules [15, 16, 17].

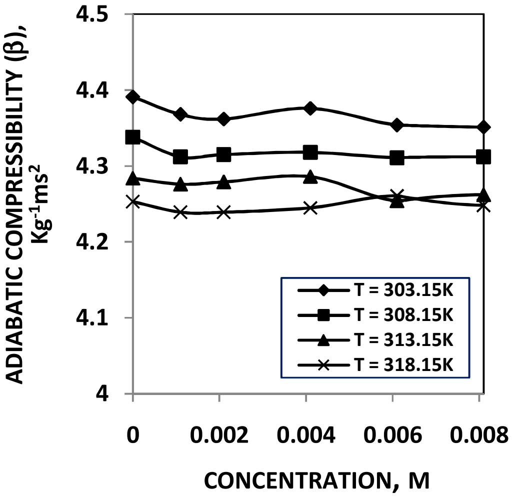

Fig. 3: β against concentration

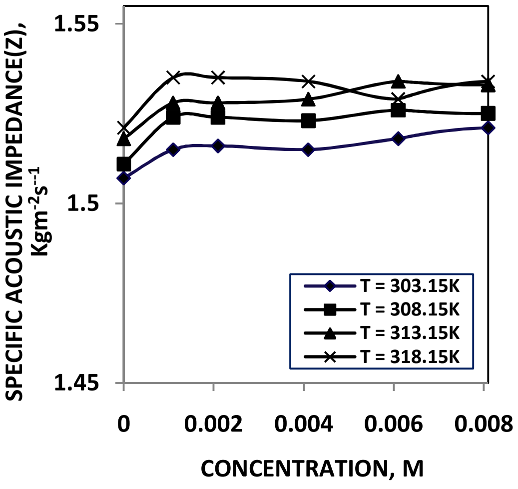

Fig. 4: Z against concentration

From Table 1 and Fig. 5, it is observed that intermolecular free length (L_f) shows similar behavior as reflected by β. The decreased compressibility brings the molecules to a closer packing resulting into a decrease of intermolecular free length [L_f]. L_f is a predominant factor in determining the variation of U in solutions. As L_f decreases U increases and vice versa, showing an inverse behavior. The interdependence of L_f and U has been evolved from a model for sound propagation proposed by Eyring and Kincaid[14].The increase in the values of β and L_f with decrease in ultrasonic velocity shows the structure breaking behavior of Mn^{+2} ions in water solvent showing weak ion-solvent interactions[13].

The solvation of the molecules in water is explained on the basis of Frank and Wen model of solute solvent interactions [18], which pictures three different solvent structures in the neighborhood of the solute. In first region, the solvent molecules are attached to the ion by strong coordination bond and it is known as primary sheath of solvation. In second region, there are weak forces of attraction between solute and solvent molecules and it is known as secondary sheath of solvation. Third region is a region of bulk solvent [6, 12].

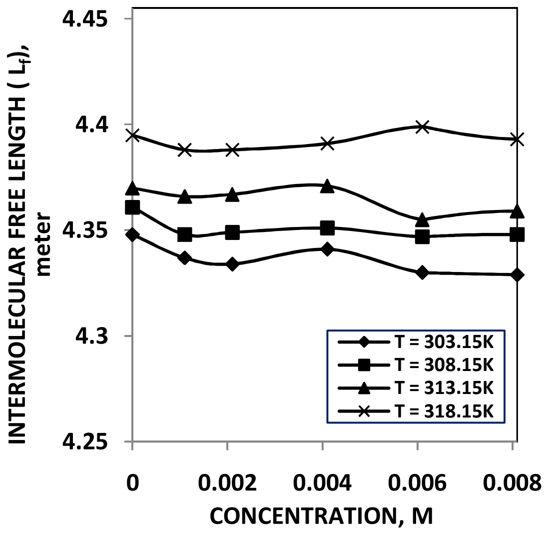

Fig. 5: L_f against concentration

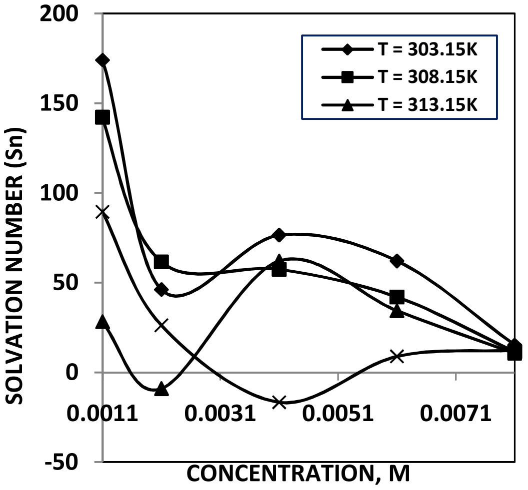

Fig. 6: S_n against concentration

From Table 1 and Fig.6 it is observed that the solvation number (S_n) in a given system decreases with increase in concentration and it may attain the primary solvation in pure crystalline state. The variation in the S_n with concentration and temperature is also non-linear for Mn^{+2} ions + water system, which suggest the presence of strong ion-dipole interactions. For 0.0041M, concentration at 303.15K and 0.0061M concentration at 318.15K S_n values are negative which shows the structure breaking nature of Mn^{2+} ions in aqueous media [12, 14].

CONCLUSION

Experimentally measured ultrasonic velocity and other calculated acoustical parameters contain valuable information about ion-solvent interactions. The non-uniform variation in the acoustical parameters proves that there is considerable amount of interactions between Mn^{+2} ions and water molecules and it shows moderate change with very small change in concentration and temperature.

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