

Ion-solvent interactions studies in aqueous manganous chloride solution by ultrasonic velocity measurement at different temperatures.

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ABSTRACT

Ultrasonic velocity and density measurements of tetra hydrated manganous chloride in aqueous media have been made at 303.15, 308.15, 313.15 and 318.15K to investigate ion-solvent interactions. The gradual increase of ultrasonic velocity (U), density (ρ and acoustic impedance (Z) and gradual decrease of adiabatic compressibility (β), intermolecular free length (L_f) suggested the presence of strong ion-solvent interactions. Mn^{+2} ions possess structure making tendency for the cluster of water molecules. The solvation number (S_n) shows non linear variation with temperature and gradual decrease with concentration also confirms strong interactions between Mn^{+2} ions and dipolar water molecules.

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

INTRODUCTION

Ultrasonic study is very much useful for understanding the physiochemical properties of the liquids [1]. Ultrasonic measurements are extensively used to study the molecular interactions in pure liquids, liquid mixtures and ionic interactions in single and mixed electrolytic solutions [2,3,4] Many engineering problems require qualitative data on the ultrasonic velocity and density of liquid mixtures hence it has been a subject of active interest during the recent years[5]. Many researchers have studied acoustical properties of solutions containing transition metal ions [6, 7]. However the survey of literature shows that very less attempt has not been to study the ion-solvent interactions of some aqueous electrolytic solution at moderate concentrations and at different temperatures.

This paper is in continuation to our research work on ultrasonic investigation of ion-solvent interactions in some aqueous and non aqueous electrolytic solutions at varying temperatures [8,9]. The present work deals with the calculations and analysis of acoustical parameters which affect the ion-solvent interactions such as adiabatic compressibility's(β), acoustic impedances(Z), intermolecular free lengths(L_f) and solvation numbers(S_n) from the experimentally measured ultrasonic velocity(U) and density(ρ) values for the wide range of moderate concentrations of Manganous chloride solutions in water for temperature 303.15, 308.15, 313.15 and 318.15K.

MATERIALS AND METHODS

Ultrasonic velocity(U) 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 an accuracy of 0.4 m/Sec at 25°C. The temperature was kept constant, by constant temperature water bath with an accuracy of ± 0.1 K. 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(ρ) 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 Qualigen made hydrated salt $MnCl_2 \cdot 4H_2O$ of Anal-R grade having 99.5% assay was used without further purification for the present investigation. The aqueous solution of $MnCl_2 \cdot 4H_2O$ was prepared in double distilled water in the presence of perchloric acid to avoid hydrolysis (2).

THEORY AND CALCULATIONS

From the measured values of ultrasonic velocity (U) and density (ρ) various acoustical parameters was calculated by using the following standard expressions.

$$\text{Adiabatic compressibility } (\beta) = 1/U^2 \rho \text{ (Kg}^{-1}\text{ms}^{-2}\text{)}$$

$$\text{Intermolecular free length } (L_f) = k\sqrt{\beta} \text{ (m)}$$

Where k is temperature dependent constant called as Jacobson constant 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[10].
Specific acoustic impedance (Z) = ρU ($\text{Kg m}^{-2}\text{S}^{-1}$)

$$\text{Solvation number } (S_n) = \frac{n_s}{n_i} \left(1 - \frac{\beta}{\beta_0} \right)$$

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

Experimentally measured values of ultrasonic velocity(U) and density(ρ) and calculated values of acoustical parameters such as adiabatic compressibility(β), specific acoustic impedance(Z), intermolecular free length(L_f) and solvation number(S_n) for aqueous Manganous Chloride

solutions for a wide range of moderate concentrations at 303.15, 308.15, 313.15 and 318.15K are presented in Table1.

Table 1.: Ultrasonic velocities (U), densities (ρ), specific acoustic impedances (Z), adiabatic compressibility's (β), intermolecular free lengths (L_f), and solvation numbers (S_n) for $MnCl_2 \cdot 4H_2O$ + water system at 303.15K and 308.15K, 313.15K and 318.15K.

Temp	Conc./M	(U) ms^{-1}	(ρ) Kgm^{-3}	(Z)/ 10^6 $Kgm^{-2}s^{-1}$	(β)/ 10^{-10} $Kg^{-1}ms^2$	(L)/ 10^{-11} m	S_n
303.15K	0.00	1509.00	995.10	1.509	4.391	4.348	-----
	0.11	1516.00	1013.17	1.536	4.295	4.300	10.889
	0.21	1521.88	1020.68	1.553	4.230	4.268	9.495
	0.31	1528.52	1031.29	1.576	4.150	4.227	9.530
	0.41	1536.69	1039.14	1.597	4.075	4.188	9.376
	0.51	1544.00	1046.79	1.616	4.007	4.153	9.093
	0.61	1552.21	1055.57	1.638	3.932	4.114	9.011
	0.71	1554.40	1063.83	1.654	3.890	4.092	8.385
308.15K	0.00	1519.10	994.90	1.517	4.338	4.361	-----
	0.11	1529.91	1010.96	1.547	4.226	4.304	12.900
	0.21	1531.30	1022.21	1.565	4.172	4.277	9.907
	0.31	1537.39	1029.68	1.583	4.109	4.244	9.188
	0.41	1543.82	1037.41	1.602	4.044	4.210	8.837
	0.51	1552.53	1047.05	1.626	3.962	4.167	9.005
	0.61	1559.23	1056.76	1.648	3.892	4.130	8.851
	0.71	1564.00	1062.74	1.662	3.847	4.106	8.332
313.15K	0.00	1530.00	992.27	1.526	4.284	4.370	-----
	0.11	1533.88	1009.46	1.548	4.210	4.332	8.532
	0.21	1542.24	1020.38	1.574	4.120	4.286	9.870
	0.31	1548.40	1028.67	1.593	4.055	4.251	9.300
	0.41	1552.52	1036.32	1.609	4.003	4.224	8.544
	0.51	1561.33	1043.68	1.630	3.930	4.185	8.596
	0.61	1566.13	1051.15	1.646	3.879	4.158	8.181
	0.71	1570.00	1061.43	1.666	3.822	4.127	7.934
318.15K	0.00	1536.20	990.31	1.531	4.253	4.395	-----
	0.11	1540.87	1007.88	1.553	4.179	4.357	8.749
	0.21	1546.24	1018.57	1.575	4.106	4.319	8.960
	0.31	1552.84	1026.64	1.594	4.040	4.283	8.763
	0.41	1560.17	1034.33	1.614	3.972	4.247	8.657
	0.51	1569.33	1041.84	1.635	3.897	4.207	8.740
	0.61	1572.37	1049.34	1.650	3.855	4.184	8.120
	0.71	1575.61	1060.00	1.670	3.800	4.154	7.857
	0.81	1579.34	1068.11	1.687	3.753	4.129	7.539

From Table1 and Fig.1 it is observed that for all temperatures U and ρ increases gradually with increasing concentration of $MnCl_2$ in water and as expected decrease in density with rise in temperature. The increase in ultrasonic velocity and density with increase in concentration

suggests a moderate strong electrolytic nature in which Mn^{+2} ions tend to attract water molecules. The gradual increase in U and ρ with increase in $MnCl_2$ concentration at all temperatures may be due to the increase in electrostrictive forces between Mn^{+2} ions and dipolar water molecules.

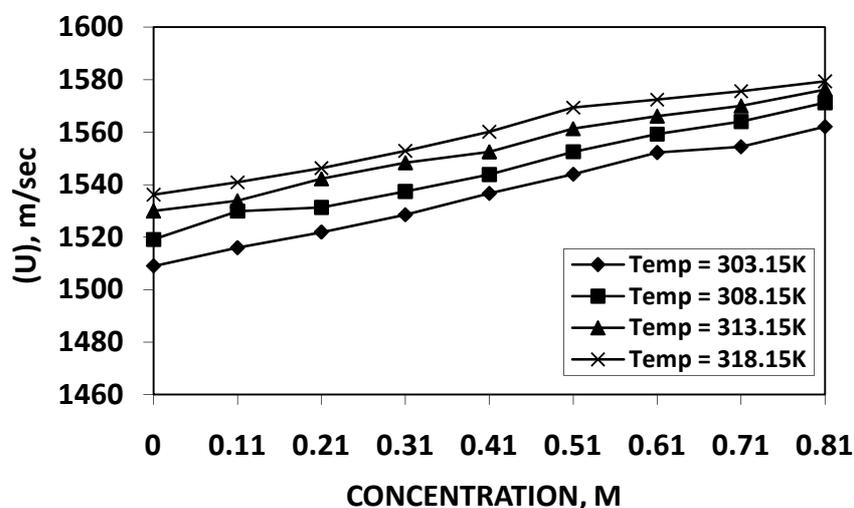


Fig. 1: Ultrasonic velocity (U) against concentration

A rise in temperature leads to less ordered structure and more spacing between Mn^{+2} ions and water molecules. The increase in ultrasonic velocity and decrease in density with rise in temperature indicates decrease in intermolecular forces due to increase in thermal energy of the system which causes increase in volume expansion and hence increase in free path length. These behaviors are similar to that of pure water, where ultrasonic velocity increases and density decrease with rise in temperature. As the temperature increases the hydrogen bonds among water molecules break and more monomeric water molecules are formed. These broken water molecules enter in the cage like water structures and thus get trapped. As a result, the number of close packed water structure increases with the increase in temperature [13]. This increase in close packed water structures forms the material medium for the propagation of ultrasonic waves. Thus ultrasonic velocity increases with the increase in temperature for pure water as well as for aqueous manganous chloride solutions in any given concentration. This show that Mn^{+2} ions behave as structure maker for the cluster of water molecules suggesting strong Mn^{+2} ion-solvent interactions [8, 9, 13].

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. When a plane ultrasonic wave is setup in a liquid the pressure and hence density of the liquid shows a periodic variation with distance from the source along the direction of propagation. From Table1 and Fig.2 it is observed that like ultrasonic velocity, ‘ Z ’ exhibits a gradual increase with concentration and temperature. This proves the increase in Mn^{+2} ions interactions with dipolar water molecules. When the concentration of $MnCl_2$ increased, the thickness of oppositely charged ionic atmosphere may decrease due to increase in ionic strength. This is suggested by the increase in acoustic impedance with concentration and temperature [2].

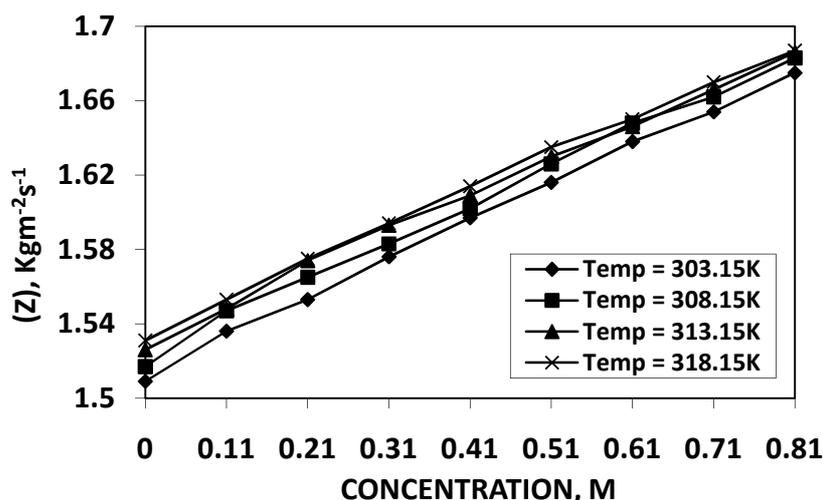


Fig. 2: Acoustic impedance (Z) against concentration

When an ion is added to a solvent it attracts certain solvent molecules towards itself by wrenching the molecule in bulk of the solvent due to the forces of electrostriction. Because of this the available solvent molecules for the next incoming ions gets decreased. The ease with which a medium can be compressed is given by the compressibility. The compressibility of a solvent is higher than that of solution and it decreases with the increase in concentration of the solution. With increase in ionic concentration the electrostrictive forces causes the structure to break and the solute surrounded water molecules are more compactly packed and therefore compressibility is decreases with increase in MnCl_2 concentration. From Table 1 Fig. 3 it is observed that compressibility decreases with increase in temperature and MnCl_2 concentration. This proves the strong interactions between Mn^{+2} ions with water molecules [12, 13].

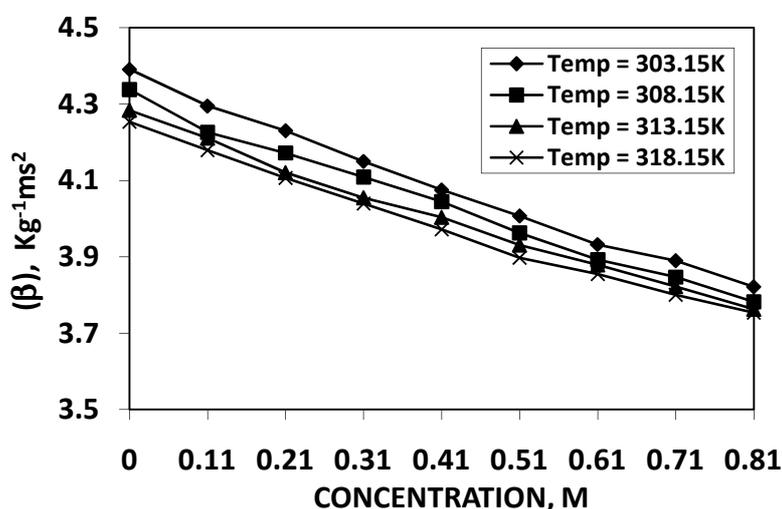


Fig. 3: Adiabatic compressibility against concentration

From Table 1 and Fig. 4 it is observed that intermolecular free length decreases with increase in Mn^{2+} ions concentrations confirms that there is a significant interactions between Mn^{+2} ions and water molecules suggesting a structure promoting behavior of Manganous chloride. However with increase in temperature the intermolecular free length also shows the increase as expected due to the thermal expansion of the solution.

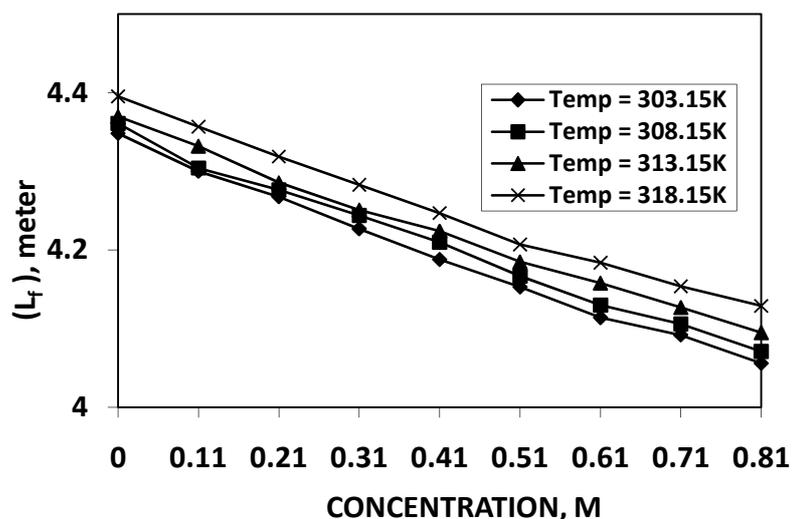


Fig. 4: Intermolecular free length (L_f) against concentration

The solvation number (S_n) of solute molecules is explained on the basis of Frank & Wen model of solute-solvent interactions[2,14], which picture three different solvent structure regions in the neighborhood of solute. Just outside the molecule, there is a layer of immobilized and compressed solvent molecules as a result of electrostrictive and other attractive forces exerted by the $MnCl_2$. This is known as primary sheath of solvation. This layer is surrounded by slightly less compressed or “structure - broken” region of solvent molecules distantly affected by these forces. This layer is called as secondary sheath of solvation. The outermost layer is bulk solvent which is not affected by any of the above forces. The solvation number in the primary sheath corresponds to coordination number and it is concentration independent, while the solvation number in the secondary sheath is concentration dependent [2, 13, 14].

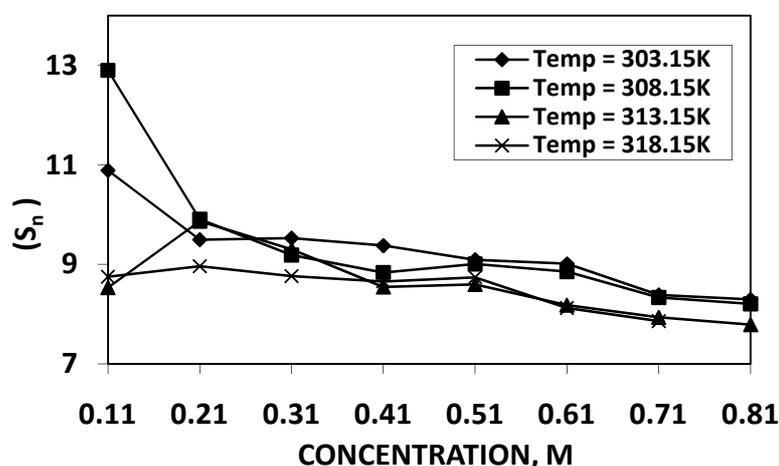


Fig. 5: Solvation number (S_n) against concentration

From Table 1 and Fig. 5 it is observed that S_n values decreases with increase in concentration and it may attain the primary solvation in pure crystalline state. The variation in S_n with temperature is non linear for moderate concentration of $MnCl_2$ in aqueous medium suggest that there is strong interactions between Mn^{+2} ions and water molecules [13, 15].

CONCLUSION

Experimentally measured and derived acoustical parameters hint to the presence of strong ion-dipole interactions between the solute and solvent molecules for the moderate range of concentration of manganous chloride in aqueous medium at different temperatures. These investigations suggest the structure promoting nature of Mn^{+2} ions in the bulk of solvent molecules.

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