



Effect of Temperature on the Ion- Solvent Interaction of Cerium Chloride with Aqueous Formic Acid by Ultrasonic Measurement

Neha Shakya^{1,*}, Neelam Shakya¹ and R.S.Gangwar²

¹Kr. R.C. Mahila Degree College, Mainpuri.

²Ganjdundwara P.G. College, Ganjdundwara, Etah.

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ABSTRACT

Ultrasonic velocity and density have been determined in cerium chloride and aqueous formic acid at 30°C, 35°C and 40°C. Different acoustic parameters were calculated using measured value of ultrasonic velocity and density at these three temperatures. These data provide useful information about change in interaction at different temperatures. The main target of this paper is to highlight the type and extent of molecular interaction between component molecules and to reflect effect of on them.

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Introduction

Ultrasonic technique is highly useful for the investigation of various acoustical properties. Ultrasonic study of cerium chloride with aqueous formic acid gives useful information to understand the behavior of liquid systems¹. The derived acoustic parameters like specific acoustic impedance (Z), intermolecular free length (L_f), relative association (Ra), isentropic compressibility (β_s) etc. have been calculated using density and ultrasound velocity data. The variation in the acoustical properties with the temperature provides added information regarding the binary and ternary system². It plays an important role to understand the physico - chemical behavior of liquids³⁻⁷. The study of intermolecular interaction plays an important role in molecular sciences, liquids liquid mixtures and solutions have found wide applications in chemical, textile, pharmaceutical and nuclear industries⁸⁻¹¹.

Experimental

Cerium chloride and formic acid used in the research work are of analytical reagent (AR) grade obtained from E. Merk. The purity of the chemicals were checked by density determination at 30,35 and 40°C. The densities of various concentrations have been measured by using precalibrated bicapillary pycnometer¹²⁻¹³ and digital balance with the accuracy 0.01mg. The values of densities obtained from experiment tally with the literature values¹⁴⁻¹⁶. Ultrasound speed have been measured by using single frequency ultrasonic Interferometer at 2MHz respectively with an accuracy of ± 0.052 ¹⁷⁻²⁰. All measurements were made in a thermostatically controlled water bath with temperature accuracy of $\pm 1^\circ\text{C}$.

Theory and Calculations

Different acoustical parameters such as isentropic compressibility, specific acoustic impedance, relative association, solvation number and intermolecular free length have been calculated at 30, 35 and 40°C using ultrasonic

velocity and density of these solutions with the help of the following equations²¹⁻²² –

$$1) \text{Isentropic Compressibility } (\beta_s) = \frac{1}{U^2 \rho} \quad (1)$$

$$2) \text{Specific Acoustic Impedance } (Z) = U \cdot \rho \quad (2)$$

$$3) \text{Relative Association } (R_A) = \left[\frac{\rho}{\rho_0} \right] \left[\frac{U_0}{U} \right]^{1/3} \quad (3)$$

$$4) \text{Solvation Number } (S_n) = \frac{n_1 (1 - \beta_s)}{n_2 \beta_{s0}} \quad (4)$$

$$5) \text{Intermolecular Free Length } (L_f) = K \sqrt{\beta_s} \quad (5)$$

Where ρ , ρ_0 and U, U_0 are the densities and ultrasonic velocities of solution and solvent respectively, K is Jacobson constant, M molecular weight of solute, β_{s0} and β_s the isentropic compressibility of solvent and solution, n_1 and n_2 are the number of moles of solvent and solute respectively.

Result and Discussion

The experimentally measured properties like ultrasound velocity (U), density (ρ) and calculated values of other acoustic parameters like isentropic compressibility (β_s), specific acoustic impedance (Z), intermolecular free length (L_f), relative association (R_A) and solvation number (S_n) for cerium chloride in aqueous formic acid solutions with the range of concentrations at 30, 35 and 40°C are represented in table 1, 2 and 3.

From table 1, 2 and 3 ultrasound velocity increases with increase in concentration of cerium chloride in aqueous formic acid solution but decreases with increase in temperature. This indicates that strong interaction observed at high concentration of cerium chloride and suggests more association between solute and solvent molecules in the system but with increase in temperature this interaction becoming weak so at 30°C temperature shows more interaction and high association with aqueous formic acid.

Density is measured of solvent- solvent and ion-solvent interactions.

Table 1. Experimental and calculated values of Cerium chloride in aqueous formic acid at 30° C.

C Mol/lit	U M/sec	ρ g/cm ³	$\beta_s \times 10^{12}$ cm ² /dyne	$Z \times 10^5$ g/s.cm	L_f A	Ra	Sn
0.0493	1251	1.3245	48.24	0.0166	0.0152	0.3610	31.6069
0.0986	1255	1.3268	47.85	0.0167	0.0151	0.3605	15.2364
0.1479	1258	1.3286	47.56	0.0167	0.0150	0.3601	9.7616
0.1972	1261	1.3308	47.26	0.0168	0.0149	0.3599	7.0072
0.2465	1265	1.3316	46.93	0.0168	0.0148	0.3589	5.3438
0.2958	1268	1.3332	46.65	0.0169	0.0147	0.3585	4.2256
0.3451	1271	1.3356	46.35	0.0170	0.0146	0.3583	3.4158
0.3944	1274	1.3378	46.05	0.0170	0.0145	0.3581	2.8016
0.4437	1278	1.3395	46.71	0.0171	0.0144	0.3574	2.3161
0.4930	1281	1.3408	45.45	0.0172	0.0143	0.3569	1.9253

Table 2. Experimental and calculated values of Cerium chloride in aqueous formic acid at 35° C.

C Mol/lit	U M/sec	ρ g/cm ³	$\beta_s \times 10^{12}$ cm ² /dyne	$Z \times 10^5$ g/s.cm	L_f A	Ra	Sn
0.0493	1225	1.2886	51.71	0.0158	0.0165	0.3637	31.5726
0.0986	1229	1.3006	50.90	0.0160	0.0162	0.3659	15.1660
0.1479	1232	1.3024	50.59	0.0160	0.0161	0.3655	9.6967
0.1972	1235	1.3048	50.25	0.0161	0.0160	0.3653	6.9474
0.2465	1239	1.3065	49.86	0.0162	0.0159	0.3646	5.2864
0.2958	1242	1.3088	49.53	0.0163	0.0158	0.3644	4.1711
0.3451	1245	1.3106	49.23	0.0163	0.0157	0.3640	3.3684
0.3944	1249	1.3125	48.84	0.0164	0.0155	0.3633	2.7576
0.4437	1252	1.3142	48.54	0.0165	0.0154	0.3629	2.2793
0.4930	1256	1.3168	48.14	0.0165	0.0153	0.3625	1.8880

Table 3. Experimental and calculated values of Cerium chloride in aqueous formic acid at 40° C.

C Mol/lit	U M/sec	ρ g/cm ³	$\beta_s \times 10^{12}$ cm ² /dyne	$Z \times 10^5$ g/s.cm	L_f A	Ra	Sn
0.0493	1205	1.2526	54.98	0.0151	0.0176	0.3622	31.5793
0.0986	1208	1.2548	54.61	0.0152	0.0175	0.3619	15.2187
0.1479	1212	1.2569	54.16	0.0152	0.0174	0.3613	9.7420
0.1972	1216	1.2585	53.74	0.0153	0.0172	0.3606	6.9901
0.2465	1219	1.2602	53.40	0.0154	0.0171	0.3602	5.3306
0.2958	1223	1.2623	52.96	0.0154	0.0170	0.3596	4.2104
0.3451	1226	1.2647	52.61	0.0155	0.0169	0.3594	3.4040
0.3944	1230	1.2664	52.19	0.0156	0.0168	0.3587	2.7914
0.4437	1234	1.2685	51.77	0.0157	0.0166	0.3581	2.3076
0.4930	1237	1.2704	51.44	0.0157	0.0165	0.3578	1.9178

In table 1, 2 and 3 increase in density with increasing concentration indicates the increase of solvent –solvent and solute- solvent interactions.

In these tables density value of cerium chloride in aqueous formic acid decreases with increase in temperature, this indicates that increase in density is due to structure breaking property of the aqueous formic acid solution due to added cerium chloride, but with the increase in temperature this property decreases and the density value at 30°C shows more structure breaking property in the system 23-25.

The isentropic compressibility for the solution of cerium chloride decreases with increase in solute concentrations but increase with the increase temperature, this attributed to the fact that the solute molecules in dilute solution ionize in 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 solution.

The product of ultrasound velocity (U) and density (ρ) is known as specific acoustic impedance 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, 2 and 3. It is observed that like ultrasound velocity, specific acoustic impedance exhibits a gradual increase with concentration and decrease with the increase of temperature. The increase in cerium ions interaction with dipole water molecules. When the addition of cerium chloride forming aggregates of solvent ions around cerium chloride and supports the strong ion-solvent interactions due to structural arrangement affected.

Intermolecular free length is the distance between the surfaces of the neighboring molecules. The variation in free length with concentration and temperature is similar to that of isentropic compressibility 26.

Relative association depends upon the breaking up solvent molecules on the addition of electrolyte or solvation of ions. In this case relative association decreases with increase of concentration and increases with increase in temperature. This is due to the breaking up of molecules in the solution and also indicates prominent ion – solvent interactions.

From table 1, 2 and 3 it is observed that solvation number values decreases with increase in concentration and variation in solvation number with increase in temperature. This is due to three different solvent layer regions in the near solute, outermost layer is of immobilized and compressed and electrostrictive layer and other attractive forces exerted by the cerium chloride.

This is primary layer of solvation; this layer is surrounded by slightly less compressed region of solvent molecule. The solvation number in the primary layer corresponds to coordination number and also concentration dependent, while the solvation number in the secondary layer is concentration dependent.

Conclusion

The available experimental and calculated data from table 1, 2 and 3 show that the significant ion-solvent interaction between the solute and solvent molecules with the increase of concentration of cerium chloride in aqueous formic acid at 30°C, 35°C and 40°C.

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