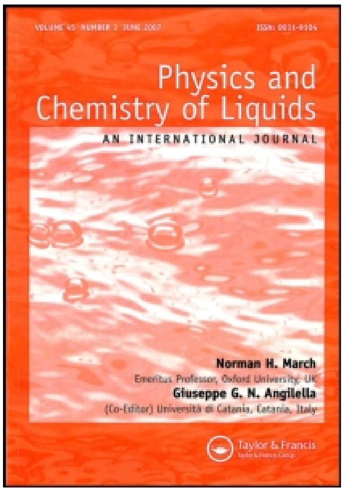

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ULTRASONIC STUDY ON CARBONATO-BIS-(ETHYLENE DIAMINE) COBALT(III) CHLORIDE IN GLYCEROL-WATER MIXED SOLVENT SYSTEMS

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Ultrasonic velocity, denisty and viscosity of the quarternary systems consisting of water, glycerol and carbonato-bis-(ethylene diamine) cobalt (III) chloride are measured at 303.15 K for different proportions of the component to evaluate various acoustic parameters. Apparent molal volume studies have also been made for the solutions of the complex at the same temperature. The results are discussed here in terms of ion-solvent, ion-ion interaction and of structural effects on the solvent in solution.

KEY WORDS: Viscosity, ion-solvent interaction, ion-ion interaction.

INTRODUCTION

Viscosity measurement studies provide information regarding ion-solvent, ion-ion and solvent-solvent interactions. Isentropic compressibility and apparent molal compressibility data computed from ultrasonic studies also provide information regarding ion-solvent interaction and the structural effects of the solute on the solvent in solution. With this aim, we report density, viscosity and ultrasonic velocity for solutions of carbonato-bis-(ethylene diamine) Co(III) chloride in water and glycerol-water mixture (10%, 20%, 30%, and 40%) at 303.15 K.

MATERIALS AND METHODS

Carbonato-bis-(ethylene diamine) Co(III) chloride was prepared according to published method[1]. A. R. Grade (B.D.H) glycerol was used to prepare 10%, 20%, 30%, and 40% (v/v) solutions in distilled water. The solutions were prepared on molar basis by dissolving known weights of the solute in appropriate volumes of the respective solvents and were kept for 2 h in a thermostat at 303.15 K, with an accuracy of 0.01 K. The densities of all the components were measured by a bicapillary pyknometer calibrated at 303.15 K, with deionised double distilled water with an acccuracy of 3 parts per 10^5. Viscosity of the solutions was measured by a calibrated Ostwald Viscometer. The viscometer was immersed in a constant temperature water bath maintained within ± 0.02 K and the time of flow was determined, the height of the liquid column being observed with the help of a cathetometer. The values of viscosities so obtained were accurate up to $\pm 0.002 \times 10^{-3}$ Ns m^{-2}. The ultrasonic velocity was measured at 303.15 K by a single crystal variable path ultrasonic interferrometer operating at 5 MHz, circulating water from thermostatically regulated bath around the sample holder with double wall to maintain the temperature of the solution constant, with a precision of ± 0.01 K. The accuracy of the velocity measurement in the interferrometer is ± 0.5 ms^{-1}.

The determination of density, viscosity and ultrasonic velocity in different solutions of $[Co(en)_2\ Co_3]$ Cl in water and also in glycerol-water mixed solvents were made. The electrolyte content in the solution varied over a range of 0.001 to 0.01 M. Five observations were taken for each measurement and difference in any two readings did not exceed 0.02%.

THEORETICAL ASPECTS

The concentration dependence of the viscosity of mixed solvent electrolytic solutions has been interpreted in terms of the semi-empirical Jones-Dole equation

$$\eta/\eta_0 = 1 + A c^{1/2} + B c \tag{1}$$

where η and η_0 are the solution and solvent viscosities, c is the molarity and A and B are adjustable parameters. The square root term represents the contribution to the viscosity from the ion-ion coloumbic interactions taken into account by Falkenhagen[2] in terms of limiting equivalent conductances and solvent properties.

The B coefficient has been interpreted in terms of specific ion-solvent interaction, positive values being attributed to an enhancement of the solvent association by the electrolyte and negative values being due to a weakening of the hydrogen bonding in the solvent. The Jones-Dole parameters A and B are determined from the intercept and slope of the linear plots of $(\eta/\eta_0 - 1)/c^{1/2}$ vs $c^{1/2}$. The B coefficients are related to the molar volumes of the electrolyte by

$$B = 2.5 \times \bar{V} \tag{2}$$

for concentrated solutions, $\bar{V}$ representing the volume of the hole created by the electrolyte in the solvent system.

The apparent molal volume, Φ_v, was calculated from the density data by the standard procedure[3]. The limiting apparent molar volume, Φ_v^0, was determined from the equation

$$\Phi_v = \Phi_v^0 + S_v c^{1/2} \tag{3}$$

where S_v is the slope in the Φ_v versus $c^{1/2}$ plot and c is the molarity.

Isentropic compressibility is calculated by the equation

$$\beta_s = U^{-2} \rho^{-1} \tag{4}$$

The values of β_s, calculated for solutions of different concentrations are found to obey Bachem's relationship[4]

$$\beta_s = \beta_s^0 + Cc + Dc^{3/2} \tag{5}$$

where C and D are constants and c is the concentration of the solution. The values of the constants C and D are obtained from the intercept and slope of the linear plots of $(\beta_s - \beta_s^0)/c$ vs $c^{1/2}$, respectively.

The apparent molar compressibility, Φ_k, has been computed from the relation

$$\Phi_k = \frac{1000\beta_s}{c} - \frac{\beta_s^0}{\rho_0}\left(\frac{1000\rho}{c} - M\right) \tag{6}$$

where ρ_0, β_s^0 and β_s are the densities and isentropic compressibilities of solvent and solution, respectively and M is the molar mass of the solute. The limiting apparent molar compressibility, Φ_k^0, was obtained for a set of solutions of variable concentration using the linear extrapolation of Φ_k vs $c^{1/2}$ according to the equation

$$\Phi_k = \Phi_k^0 + S_k c^{1/2} \tag{7}$$

where S_k is a constant.

The intermolecular freelength, L_f, is given by Jacobson[5] as

$$L_f = k\beta_s^{1/2} \tag{8}$$

where k is a temperature dependent constant.

The molar volume V_T of a liquid is defined as

$$V_T = M\rho^{-1} \tag{9}$$

where M is the relative molecular mass, The molar sound velocity, R and molar compressibility, W are given by

$$R = U^{1/3} \cdot V_T = U^{1/3} \cdot M\rho^{-1} \tag{10}$$

and

$$W = \beta_s^{-1/7} \cdot V_T = \beta_s^{-1/7} \cdot M\rho^{-1} \tag{11}$$

The ultrasonic velocity (U) is also influenced by acoustic impendance[6] given by

$$Z = \rho \cdot U \tag{12}$$

The isentropic compressibility data are used to determine the solvation number of the solute in the respective solution. Passynsky[7] defined the solvation number, S_n, as the number of solvent molecules present in the primary solvation sheath as

$$S_n = \frac{n_1}{n_2}\left(1 - \frac{V\beta_s}{n_1 V_1^0 \beta_s^0}\right) \tag{13}$$

where V is the volume of the solution containing n_2 moles of the solute; V_1^0 is the molar volume of the solvent and n_1 is the number of moles of the solvent. The variation of solvation number with the molar concentration of the solute leads to a limiting solvation number S_n^0 which is evaluated through the relationship,

$$\lim_{c \to 0} \Phi_k^0 = -S_n^0 V_1^0 \beta_s^0 \tag{14}$$

RESULTS AND DISCUSSION

Perusal of Table 1 reveals that Φ_v^0 values are positive indicating a strong solute-solvent interaction. It is, however, dependent on the nature of the solute and structure of the solvent. Trend of variation of Φ_v^0 reflects upon the relative strength of interaction. S_v may be considered to be a measure of the ion-ion interaction.

Table 1 Values of Φ_v^0, S_v, $\bar{V}$ and parameters A and B of the Jones-Dole equation of carbonato-bis-(ethylene diamine) Co(III) chloride in water and different proportions of glycerol-water mixture at 303.15 K.

Solvent	Φ_v^0 $cm^3\ mol^{-1}$	S_v $cm^{3/2}\ mol^{-3/2}$	A $dm^{3/2}\ mol^{-1/2}$	B $dm^3\ mol^{-1}$	$\bar{V}$ $dm^3\ mol^{-1}$
Water	192.70	−764.94	−0.75	4.35	1.74
10% glycerol	168.28	−482.61	−0.77	5.63	2.25
20% glycerol	148.11	−388.21	−1.52	8.50	3.40
30% glycerol	128.92	156.16	−0.82	9.13	3.65
40% glycerol	56.14	767.59	−2.42	33.65	13.46

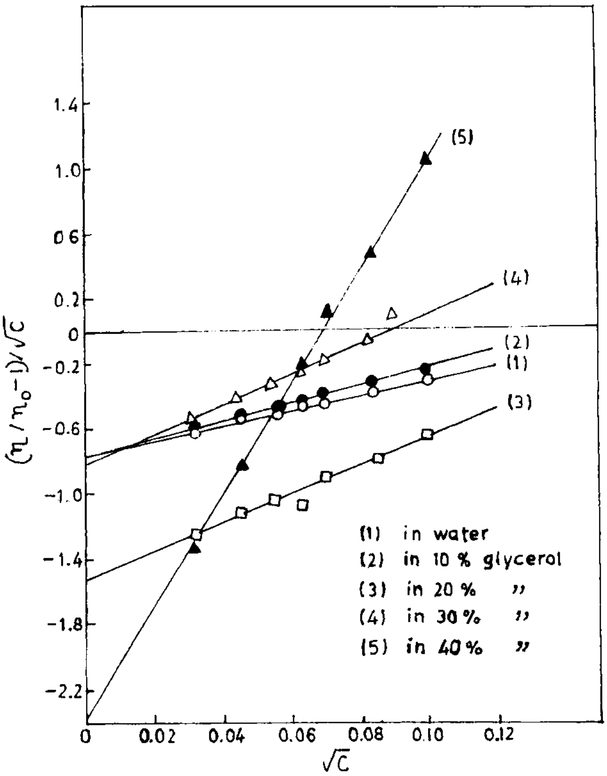

Figure 1 Plot of $(\eta/\eta_0 - 1)/c^{1/2}$ vs $c^{1/2}$ for carbonato-bis (ethylene diamine) cobalt(III) chloride in water and glycerol-water mixture.

Positive values of S_v in case of 30% and 40% glycerol show the extent of the interaction in increasing order.

The values of A (Tab. 1) are negative. The positive A value indicates ionic interaction while the negative value has no physical significance[3]. The B coefficient is a measure of the effective hydrodynamic volume of the solvated ions and is governed by solute-solvent interaction, that is, the structural effect of the solvent in solution. Stokes[8] has suggested an explanation of electrolytic viscosities based on three separate contributions to the B coefficient (Fig. 1). η^E, the viscosity increment resulting from size and shape of the ions; η^A, an increase in viscosity resulting from ordering of the solvent molecules in the immediate vicinity of the ions, as a result of ionic field; and finally η^D, a decrease in the solvent viscosity as a result of the disruptive presence of ions. The B coefficient and $\bar{V}$ values (Tab. 1) are positive showing strong solute-solvent interaction. The increase in the B coefficient with increase in concentration of glycerol in the solvent mixture may be attributed to the

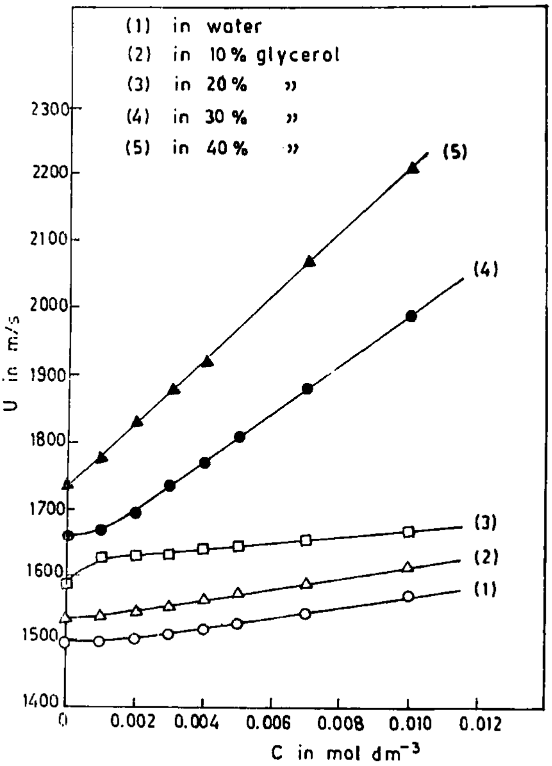

Figure 2 Variation of U with c for carbonato-bis-(ethylenediamine) cobalt(III) chloride in water and glycerol-water mixture.

large size of the solvent molecules and also to the strong association between water and glycerol through multiple hydrogen bonding and for solvated ions; it would lead to larger values of η^E and η^A. Consequently the B coefficient becomes larger with increase in glycerol content in the solvent mixture. The distortion effect (η^D term) in the systems investigated is lower and with increasing concentration of glycerol, this effect further decreases. As a result $\eta^E + u^A \gg \eta^D$. The high values of the B coefficient and $\bar{V}$ indicates that carbonato-bis-(ethylene diamine) Co(III) chloride acts as a structure promoter in glycerol-water mixed solvent systems.

The sound velocity increases with increase in concentration of the solution in all the solvents (Fig. 2) and it is also found to be greater in mixed solvents than that in water. Ultrasonic velocity increases with increasing glycerol content.

The isentropic compressibility, β_s, decreases with solute concentration; that is the compressibility of the solvation layer is smaller than that of the solvent in bulk. It is thus considered that the complex behaves as a weak electrolyte and ionizes. The ions in solution are surrounded by a layer of oriented solvent molecules tightly bound. The internal pressure increases (i.e. compressibility decreases) with increase in concentration of the solution. In other words, at higher concentration, the primary effect of dissolving a solute is to lower the compressibility of the solvent. This is in agreement with the lowering of β_s with increasing concentration. The values of β_s are higher in water than in the mixed solvents. This indicates that the internal pressure in water is higher than in the mixed solvents. It is probably due to greater electrostatic stiffering to the adjacent water molecules in aqueous solution than in the mixed solvent. The variations of $(\beta_s - \beta_{so})$ with concentration are plotted for each solution (Fig. 3). The values of constants C and D of the Eqn. (5) are calculated by using least square method. It is observed that the C values are increasingly more negative showing weak solute-solute interaction. The D values are high and positive with 10% and 40% glycerol solution of the complex, indicating presence of solute-solvent interaction.

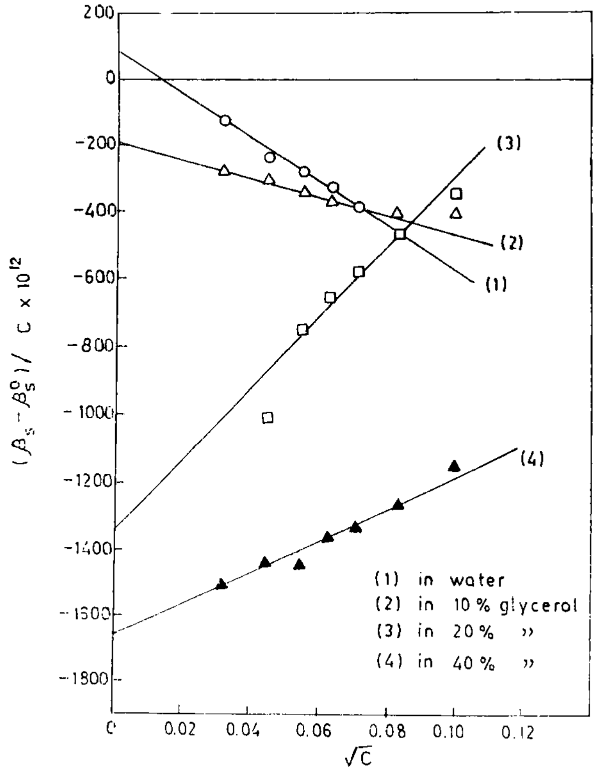

Figure 3 Variation of $(\beta_s - \beta_s^0)/c$ vs $c^{1/2}$ for carbonato-bis-(ethylene diamine) cobalt(III) chloride in water and glycerol-water mixture.

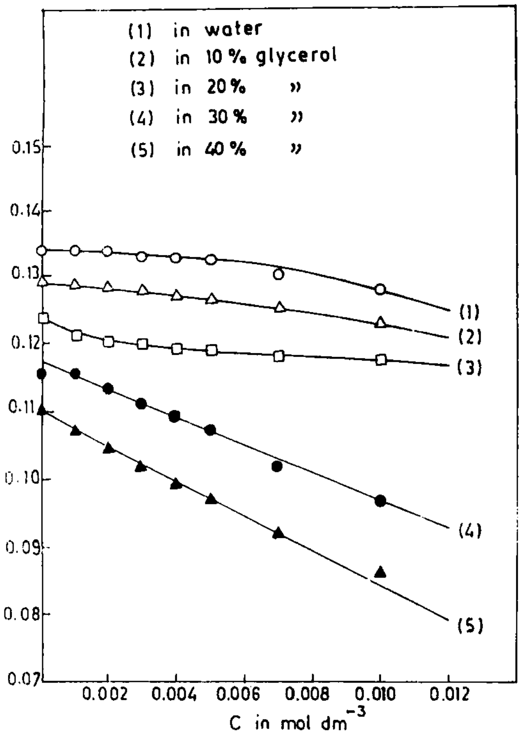

Figure 4 Variation of L_f with c for carbonato-bis-(ethylene diamine) cobalt(III) chloride in water and glycerol-water mixture.

The intermolecular freelength (L_f) values decrease with increasing concentration of the complex in all the solvents studied (Fig. 4). The values are comparatively higher in case of solutions in water than that in mixed solvents. This variation is probably due to higher internal pressure in water than that in the water-glycerol mixture.

It is observed that the limiting apparent molal compressibility (Φ_k^0) values are negative for all solutions and decrease with higher glycerol content in the solvent, indicating poor compressibility of the solutions. The slope S_k of Eqn. (7) is negative in each case (Tab. 2).

The molar sound velocity (R) increases with increase in concentration of the complex and with the increase in glycerol percentage, almost linearly (Fig. 5). This shows that the relative association in the solution increases with the increase in solute concentration. It is inferred that when the complex is added to the solvent, the association in the solvent increases due to increased solvation of the ions in the complex.

The molar compressibility (W) and acoustic impedance (Z) both increase with increase in concentration of the solutions in an almost linear manner (Fig. 6 and 7).

Table 2 Values of constants C and D of Eqn. (5) along with Φ_k^0, S_k and S_n^0 in different solutions for carbonato-bis-(ethylene diamine) Co(III) chloride at 303.15 K.

Solvent	$-C \times 10^{12}$	$D \times 10^{10}$	$-\Phi_k^0 \times 10^9$	$S_k \times 10^7$	S_n^0
Water	118.46	−32.70	38.02	42.05	46.86
10% glycerol	122.40	−37.79	205.08	23.65	251.70
20% glycerol	224.00	−20.99	190.88	73.14	244.35
30% glycerol	400.38	−64.31	166.99	95.17	212.30
40% glycerol	1696.46	52.05	153.33	70.87	196.39

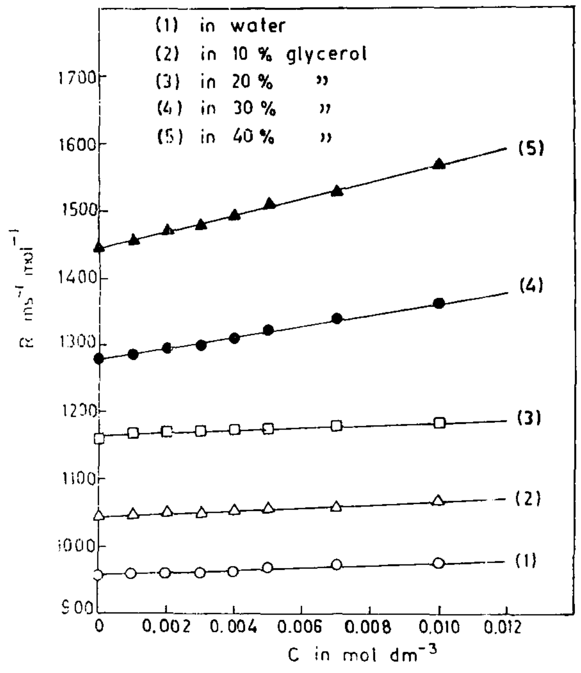

Figure 5 Variation of R with c for carbonato-bis-(ethylene diamine) cobalt (III) chloride in water and glycerol-water mixture.

The increasing order of 'Z' with concentration can be explained on the basis of the decreasing number of aggregates of solvent molecules with increase in concentration of the complex. Addition of more complex to the solvent leads to the acceleration of the process of breaking of aggregates of the solvent molecules.

The higher values of S_n^0 (Tab. 2) in case of mixed solvents suggest that the solvation layer formed around the ions is thick and/or hard. The degree of hard electrostrictive solvation decreases with increasing glycerol content in the solution.

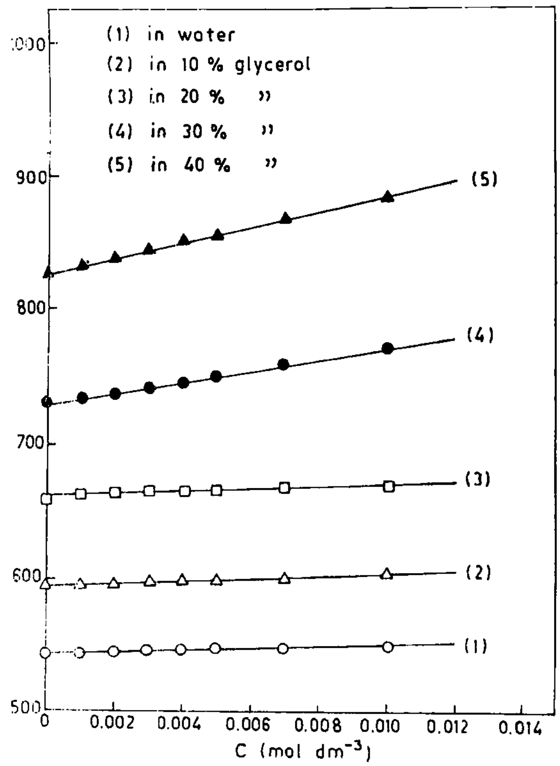

Figure 6 Variation of W with c for carbonato-bis-(ethylene diamine) cobalt(III) chloride in water and glycerol-water mixture.

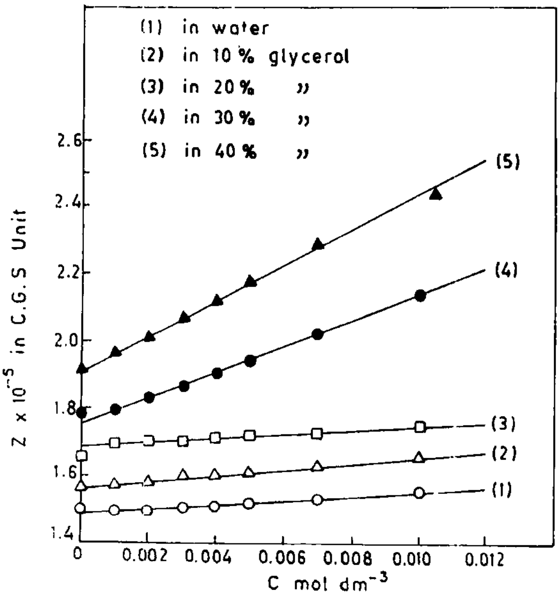

Figure 7 Variation of Z with c for carbonato-bis(ethylene diamine) cobalt(III) chloride in water and glycerol-water mixture.

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