VISCOSITY AND ACOUSTIC BEHAVIOUR OF CARBONATO PENTAMINE COBALT (III) NITRATE IN WATER AND GLYCEROL - WATER MIXED SOLVENT SYSTEM

P. K. Mishra and V. Chakravortty*

Department of Chemistry, Utkal University

Bhubaneswar-751 004, Orissa, India

ABSTRACT

The ultrasonic velocity and viscosity of carbonato pentamine Co (III) nitrate in water and different proportions of glycerol-water mixtures were determined at 303.15 K. The Jones-Dole viscosity B-coefficient of the coordination complex is found to be largest in 40% (v/v) glycerol-water mixture. Various acoustic parameters viz. isentropic compressibility, intermolecular freelength, acoustic impedance, etc. have been calculated using experimentally determined values of ultrasonic velocity and density. The variation of these acoustic parameters are discussed in the light of solute-solvent and solute-solute interactions.
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INTRODUCTION

Measurement of some bulk properties like viscosity (η), density (ρ), and ultrasonic velocity (U) provides insight into the intermolecular arrangement in solutions and helps to understand the thermodynamics and acoustic properties of the solutions. With this aim, we report the experimentally determined values of η, ρ, U and allied acoustic parameters so as to probe the nature of ion-ion and ion-solvent interactions in water and 10%, 20%, 30%, 40% glycerol-water solution of the coordination complex.

EXPERIMENTAL

Carbonato pentamine cobalt (III) nitrate was prepared following standard method [1]. A.R. Grade (BDH) 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 mass of the solute in appropriate volume of the respective solvents and were kept for 2h in a thermostat at 303.15 K with an accuracy of 0.01 K. The densities of all the solutions were measured by a bicapillary pyknometer of 10 ml capacity calibrated at 303.15 K with deionised double distilled water with an acuracy of 3 parts per 10^5. The electric balance measures mass precisely upto 0.0001 gm. 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 coloumn being

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* Author to whom correspondence should be addressed.

observed with the help of a cathetometer. The viscosity so obtained were accurate upto $\pm$ 0.002 x 10^{-3} Nsm^{-2}. The ultrasonic velocity was measured at 303.15 K by a single crystal variable path ultrasonic interferometer operating at 5 MHz, circulating water from a thermostatically regulated bath around the sample holder with double wall to maintain the temperature of the solution constant with a precision of $\pm$ 0.01 K. The accuracy of the velocity measurement in the interferometer is 0.5 ms^{-1}. The determination of density, viscosity and ultrasonic velocity in different solutions of $[Co(NH_3)_5CO_3]NO_3$ 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%.

THEORY

The variation of viscosity with solute concentration was expressed by Jones-Dole [2] equation

$$\eta/\eta_o = 1 + A\ c^{1/2} + Bc \qquad (1)$$

where η and η_o are the viscosities of the solution and solvent respectively. A and B are constants characteristic of the solute and c is the molar concentration of the solute. According to Einstein, the viscosity of a solution which contains, in suspension, rigid spherical particles is given by the equation :

$$\eta = \eta_o\ (\ 1 + 2.5\phi\ ) \qquad (2)$$

where ϕ is the volume-fraction occupied by the particles.

From Eqs (1) and (2) we get,

$$A\ c^{1/2}\ + Bc = 2.5\ \phi \qquad (3)$$

The volume fraction, ϕ, may then be expressed by

$$\phi = cV \qquad (4)$$

where V is the molar volume of the solvated ion (in l/mol). Further $Ac^{1/2}$ term is very small in comparison with Bc, and so it can safely be neglected. Accordingly, we obtain

$$B = 2.5\ V \qquad (5)$$

Equation (5) leads to

$$V_h = [4000/6.02]\ B\ \text{Å}^3 \qquad (6)$$

where V_h is the volume of the hydrated solute [3]. Thus, the average radius r_h can be calculated from the B-coefficient. The values obtained for the $[Co(NH_3)_5CO_3]^+$ are listed in table 1. The B-value of the complex ion is obtained by subtracting a relatively small correction for the NO_3^- ion. Here we have used the B-value given by Gurney [4]B_{NO3}=-0.046.

From the ultrasonic velocity, isentropic compressibility (β_s), intermolecular freelength (L_f), molar sound velocity (R),apparent molar compressibility (ϕ_k), and solvation number (S_n) were calculated with the help of the following equations.

$$\beta_s = U^{-2}\rho^{-1} \qquad (7)$$

$$L_f = k.\beta_s^{1/2} \qquad (8)$$

$$R = U^{1/3}.V_T \qquad (9)$$

$$\phi_k = (1000\beta_s/c) - [\beta_s{}^o/\rho_o(1000\rho/c - M)] \qquad (10)$$

$$S_n = n_1/n_2[1 - V\beta_s/n_1V_1{}^o\beta_s{}^o] \qquad (11)$$

where ρ_o and ρ are the densities of the solvent and solution; M, molecular mass of the solute; β_{s_o} and β_s, the isentropic compressibilities of the solvent and solution; c, concentration in mol. dm^{-3}; K, temperature dependent constant, n_1 and n_2 are the number of moles of the solvent and solute respectively; V_T and $V_1{}^o$ are the molar volume of the solution and solvent respectively. The value of β_s, calculated for solutions of different concentrations are found to obey Bachem's relationship [6],

$$\beta_s = \beta_s{}^o + Cc + Dc^{3/2} \qquad (12)$$

The limiting apparent molar compressibility, $\phi_K{}^o$, was obtained for a set of solutions of various concentrations using linear extrapolation of ϕ_K vs $c^{1/2}$ according to Gucker's limiting law equation

$$\phi_K = \phi_K{}^o + S_k c^{1/2} \qquad (13)$$

where S_k is a constant.

The variation of solvation number with molar concentrations of the solute leads to a limiting solvation number which is evaluated through the relationship

$$\lim \phi_K{}^o = -S_n{}^o.V_1{}^o.\beta_s{}^o \qquad (14)$$

RESULTS AND DISCUSSION

Table 1

Values of B and r_h for carbonato pentamine cobalt (III) nitrate

in different solutions at 303.15 K

Solvent	B $dm^3\,mol^{-1}$	r_h Å
Water	5.99	9.85
10% glycerol	4.61	9.04
20% glycerol	4.97	9.27
30% glycerol	7.68	10.70
40% glycerol	10.75	11.96

The B-coefficient (Table 1) is a measure of the effective hydrodynamic volume of the solvated ions and is governed by solute-solvent interaction, i.e., the structural effect of the solvent in solution [7]. The B-values (Fig. 1) show regular increase from 10% to 40%
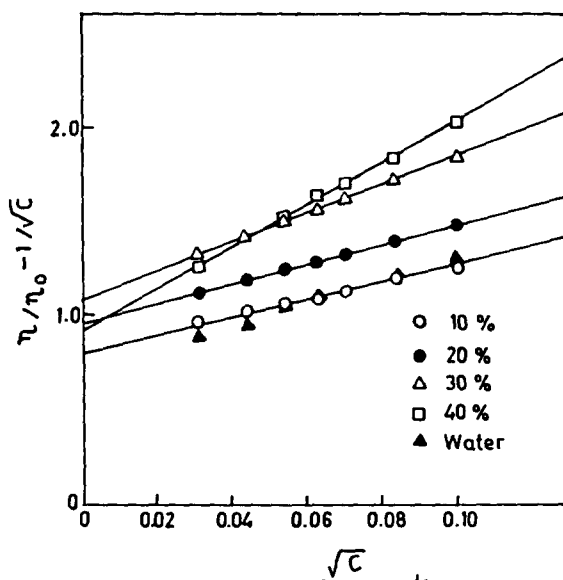
Fig.1 Plot of $\eta/\eta_0 - 1 / C^{1/2}$ Vs. $C^{1/2}$ for carbonato pentamine Co (III) nitrate.

glycerol solution indicating that the volume of the solvated complex cation $[Co(NH_3)_5CO_3]^+$ increases. The increasing values of the radius of the solvated cation Eq. (6) presented in Table 1 further confirm this. This can be explained by the fact that with increase in the glycerol content in the solution; the self association in glycerol molecules and hydrogen bonded association with water molecules increase. As a result, volume of the solvated complex cation increases. Thus it is appropriate to consider that the co-ordination complex behaves as a structure maker in the solvents investigated in the present work.

Table 2

Values of constants C and D of Eq. (12) along with ϕ_K°, S_k, and S_n°

in different solutions for carbonato pentamine cobalt (III) nitrate at 303.15 K

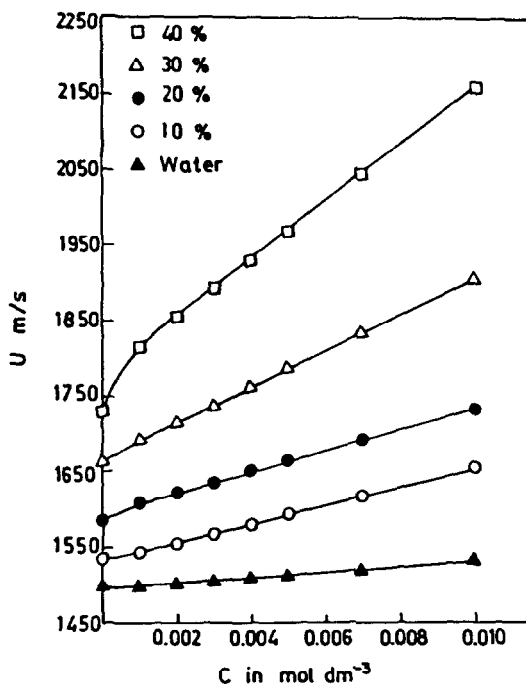| Solvent	$-C \times 10^{10}$	$D \times 10^{10}$	$\phi_K^\circ \times 10^7$	$S_k \times 10^7$	$S_n^0 \times 10^2$
Water	1.78	-3.39	1.95	1.09	2.41
10% glycerol	4.96	-12.47	6.00	0.27	7.36
20% glycerol	12.71	73.49	10.25	44.22	13.12
30% glycerol	13.42	57.53	12.15	41.06	15.44
40% glycerol	30.57	222.68	29.27	223.40	37.49

Fig. 2 Variation of 'U' Vs. 'C' for carbonato
pentamine Co (III) nitrate .

Perusal of our data shows that the ultrasonic velocity increases with increase in concentrations of the solute in all the solvents (Fig. 2). It is also found to be more in mixed solvents (glycerol-water) than in water. This corroborates our earlier conclusion on the basis of B-values that the co-ordination complex behaves as a structure maker [8].
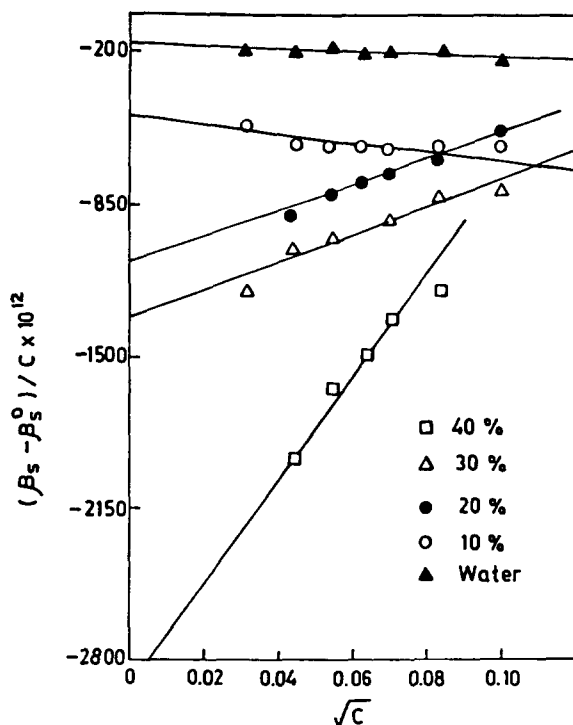

Fig.3 Variation of $(\beta_s - \beta_s^o)/C$ Vs $C^{1/2}$ for carbonato pentamine Co(III) nitrate.

The isentropic compressibility (β_s) decreases with solute concentration with all the solvents studied. That is, the compressibility of the solvation layer is smaller than that of the solvent in bulk. The value of β_s is higher in water than in the mixed solvents. This indicates that internal pressure in water is less than that in the mixed solvents. It is probably due to greater electrostatic stiffening to the adjacent water molecules in aqueous solution than in the mixed solvents. The variations of (β_s - β_s^o) with concentration are plotted for each solution (Fig. 3). The values of constants C and D of Eq. (12) are calculated by using least square method. It is observed (Table 2) that the C values are increasingly negative showing weak solute-solute interaction. The D values are positive with 20%, 30% and 40% glycerol-water mixture indicating presence of strong solute-solvent interaction.
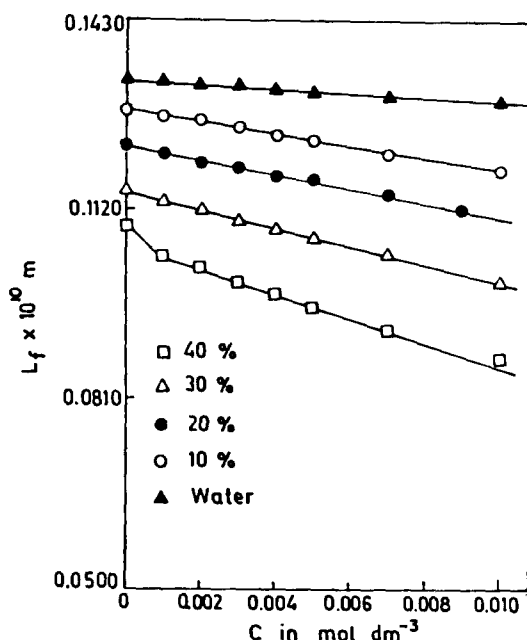
Fig.4 Variation of 'L$_f$' Vs. 'C' for carbonato
pentamine Co (III) nitrate .

Intermolecular freelength (L$_f$) is a predominant factor in determining the variation of ultrasonic velocity in a solution [9]. As shown in (Fig. 4), L$_p$ decreases on increasing concentration in all the solvents; which results in the increase of velocity in the same order. The change in L$_f$ according to Eyring and Kincaid [9] indicates that there is significant interaction between the solute and solvent molecules due to which structural arrangement is considerably affected.

The molar sound velocity (R) increases with increase in concentration of the co-ordination complex and with the increase in glycerol percentage almost linearly (Fig. 5). This probably indicates that the relative association in the solution reinforces rather uniformly with increase in solute concentration.

The values of the $\phi_K°$ are negative for all the solutions and increases with higher glycerol concentration indicating poor compressibility of the solutions. The slope, S$_k$ of the Eq. (13) is positive with all the solvents studied.
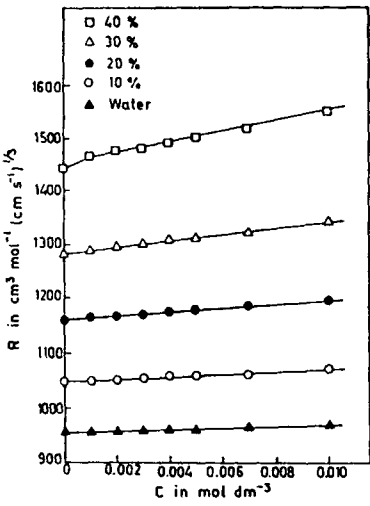
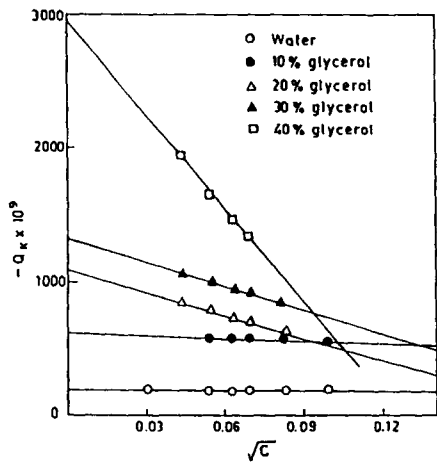Fig. 5 Variation of 'R' Vs. 'C' for carbonato
pentamine Co (III) nitrate.

Fig. 6. Variation of Q_K Vs $\sqrt{C}$ for carbonato pentamine
Co (III) Nitrate.

The isentropic compressibility data have aslo been used to measure the solvation of the co-ordination complex Eq. (11). The assumption has been made here that the ions as well as the solvent molecules in immediate vicinity of the ions are incompressible. This is because the ions add some electrostatic stiffening on the adjacent solvent molecules, which is considered to be equivalent to a large internal pressure on these solvent molecules. S_n° shows a significant increase with increase in glycerol content, being minimum in water. This is probably due to the fact that with water as the solvent, water molecules are not localised to the ion sites for long as solvent bonds alter rapidly due to switching mechanism. With increase in glycerol content the bigger glycerol molecules are rather localised on the ion sites and the degree of electrostrictive solvation increases significantly which is manifested in its increase by two orders of magnitude (Table 2).

ACKNOWLEDGEMENT

REFERENCES

1. Inorg. Synthesis, 4 (1953) 171.

2. G. Jones and M. Dole, J. Am. Chem, Soc., 51 (1929) 2950.

3. M. Yasuda, Bull. Chem. Soc. Japan, 42 (1969) 2547.

4. R.W.Gurney, Ionic Processes in Solution, McGraw Hill Book Co. New York (1953).

5. H.S.Harned and B.B.Owen, "The physical Chemistry of Electrolytic Solutions", Reinhold, New York (1958).

6. C. Bachem, Z Physik, 101 (1936) 541.

7. P.K.Mishra, B.B.Swain and V. Chakravortty, Phy. Chem. Liq., 31 (1996) 97.

8. Vishnu and R. Wadhwani, Ind. J. Chem., 34A, (1995) 954.

9. H. Eyring and J.F. Kincaid, J. Chem. Phys., 6 (1938) 620.