

## Ion association and solvation of octahedral Co(III) complexes in water + mannitol and water + sorbitol mixtures

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**Abstract.** Viscosity and conductometric studies have been made for the solutions of carbonatopentaamine Co(III) nitrate, aquopentaamine Co(III) nitrate, oxalatopentaamine Co(III) nitrate, malonatopentaamine Co(III) nitrate and succinatopentaamine Co(III) nitrate in water, water + mannitol (5 wt%) and water + sorbitol (5 wt%) at 30°C. Association constants for the complexes in these solvents have also been evaluated. The results are discussed in terms of ion–ion and ion–solvent interactions, and of structural effects on the solvent in solution.

**Keywords.** Octahedral Co(III) complexes; association constant; ion–ion and ion–solvent interactions.

### 1. Introduction

For the last two decades, physico-chemical studies involving the determination of partial molar properties, viscosity, conductance etc. have been of much interest for studying ion–ion and ion–solvent interactions in solutions of electrolytes in aqueous, non-aqueous and mixed solvent media (McDowali and Vincent 1974; Ward and Millero 1974; Blokhra and Parmer 1974; Dack *et al* 1975; Dash and Nayak 1979; Parmer and Kundra 1983; Dash and Kalia 1984; Dash *et al* 1984, 1987, 1988; Parmer and Khana 1986; Sandhu and Kashyap 1986; Naik and Dash 1990; Pattanaik and Dash 1993; Dash and Pattanaik 1994; Dash and Mohanty 1995). Since the viscosity and conductance measurements provide valuable information regarding the ion–ion and ion–solvent interactions, studies on viscosity and conductivity on ionic solutions are of great help in examining the structure and properties of solutions. Although a vast number of viscometric and conductometric studies have been made recently in various solvents involving simple and multicharged electrolytes, literature provides very little information about such studies on the solutions of octahedral Co(III) complexes. The present work reports the results of the studies of viscometric and conductometric properties of carbonatopentaamine Co(III) nitrate, aquopentaamine Co(III) nitrate, oxalatopentaamine Co(III) nitrate, malonatopentaamine Co(III) nitrate and succinatopentaamine Co(III) nitrate in water, water + 5 wt% mannitol and water + 5 wt% sorbitol at 30°C. Association constants and Walden products for octahedral Co(III) complexes have been evaluated in these solvents at 30°C.

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## 2. Experimental

Chemicals used were samples of AnalaR grade. Aquopentaamine-, carbonatopentaamine-, oxalatopentaamine-, malonatopentaamine- and succinatopentaamine Co(III) nitrates were prepared according to the methods available in the literature (Splinter *et al* 1968). The resulting crystals, which were coloured complexes, were stored in a vacuum desiccator until required.

Mannitol (BDH, AnalaR) and sorbitol (Loba chemie) were used without further purification. Water of specific conductance of the order of  $10^{-6}$  S cm $^{-1}$  was used for preparing aqueous solutions of 5 wt% each of mannitol and sorbitol. Their content in the aqueous solutions was accurate within  $\pm 0.2\%$ . All the solutions were prepared by weight and conversion of molality to molarity was done by using the standard expression (Harned and Owen 1958).

The viscosity measurements were carried out in water thermostat at  $30 \pm 0.05^\circ\text{C}$  by using an Ostwald type viscometer fitted with a silica gel guard tube. Conductivity water ( $\eta = 8.007 \times 10^{-3}$  poise,  $d = 0.9956$  g ml $^{-1}$ ) was used as reference liquid for calibration of the viscometer. The determination of viscosity involved different solutions of octahedral Co(III) nitrates ranging from 0.01 molar to 0.1 molar concentration in water, water + 5 wt% mannitol or sorbitol. Runs were repeated until three successive determinations were within  $\pm 0.1$  s. Since all the flow times were more than 100 s, the kinetic energy correction was not made.

Conductance measurements (Naik and Dash 1990) were made on a digital reading conductivity meter (Systronics Type 304) with a sensitivity of 0.1% and giving a conductance value of three digits. A dipping type conductivity cell with platinized electrode (cell constant 1 S cm $^{-1}$ ) was used. The measurements were carried out at  $30 \pm 0.05^\circ\text{C}$ . The specific and molar conductances are expressed in S cm $^{-1}$  and S cm $^2$  mol $^{-1}$ , respectively. For conductance measurements, the ionic strengths of the solutions were kept as low as practicable ( $\sim 10^{-4}$  to  $10^{-2}$  M). The experiment was repeated several times with different concentrations of the solutions (ranging from  $1 \times 10^{-2}$  to  $7.5 \times 10^{-4}$  M) in water, and 5 wt% mannitol or sorbitol. The conductances of different concentrations of octahedral Co(III) nitrates were measured several times making appropriate corrections for the conductances of the solvents concerned.

## 3. Results and discussion

The experimental results of viscosity were analysed by the Jones–Dole (1929) equation. As is evident from the conductivity studies, octahedral Co(III) complex behave like weak electrolytes and for the viscosity of a weak electrolyte the Jones–Dole equation becomes,

$$\eta_r = \eta_s/\eta_0 = 1 + A(\alpha c)^{1/2} + B\alpha c + B_{IP}c(1 - \alpha), \quad (1)$$

where  $\eta_r$  is the relative viscosity of the electrolyte (complex salt) solutions (i.e. the ratio of the viscosity  $\eta_s$ , of the solution to  $\eta_0$ , that of the reference liquid, e.g. water),  $c$  is the molar concentration of the solution,  $\alpha$  is the degree of ionization of the complex salt,  $A$  is the Falkenhagen (Falkenhagen and Vernan 1932) coefficient,  $B$  and  $B_{IP}$  are the Jones–Dole coefficients for the dissociated electrolyte and the ion-pairs, respectively. However, writing (1) in the form,

$$\begin{aligned} (\eta_r - 1)/c^{1/2} &= A(\alpha)^{1/2} + B\alpha(c)^{1/2} + B_{IP}(1 - \alpha)(c)^{1/2} \\ &= A(\alpha)^{1/2} + [B\alpha + B_{IP}(1 - \alpha)](c)^{1/2}, \end{aligned} \quad (2)$$

**Table 1.** Values of parameters,  $A(\text{dm}^{3/2} \text{mol}^{-1/2})$  and  $B(\text{dm}^3 \text{mol}^{-1})$ , of the Jones-Dole equation and  $\bar{v}_1^0(\text{cm}^{-3} \text{mol}^{-1})$ ,  $\bar{v}_2^0(\text{cm}^{-3} \text{mol}^{-1})$ ,  $\Delta\mu_1^{0*}(\text{kJ mol}^{-1})$  and  $\Delta\mu_2^{0*}(\text{kJ mol}^{-1})$  in water (W), water + 5 wt% mannitol (M), and water + 5 wt% sorbitol (S) for octahedral Co(III) complexes at 30°C.

| Co(III) complex* | Solvent | $A$   | $B$             | $\bar{v}_1^0$ | $\bar{v}_2^0$ | $\Delta\mu_1^{0*}$ | $\Delta\mu_2^{0*}$ |
|------------------|---------|-------|-----------------|---------------|---------------|--------------------|--------------------|
| <u>1</u>         | W       | -2.35 | $6.25 \pm 0.25$ | 18.08         | 143.16        | 9.04               | 897.70             |
|                  | M       | -1.08 | $3.09 \pm 0.27$ | 18.63         | 164.89        | 9.44               | 447.24             |
|                  | S       | -1.18 | $3.38 \pm 0.29$ | 18.63         | 161.33        | 9.41               | 485.96             |
| <u>2</u>         | W       | -2.33 | $6.22 \pm 0.54$ | 18.08         | 166.52        | 9.04               | 896.77             |
|                  | M       | -1.03 | $2.99 \pm 0.26$ | 18.63         | 134.69        | 9.44               | 429.63             |
|                  | S       | -1.16 | $3.37 \pm 0.29$ | 18.63         | 141.36        | 9.41               | 481.91             |
| <u>3</u>         | W       | -2.30 | $6.13 \pm 0.53$ | 18.08         | 182.62        | 9.04               | 886.47             |
|                  | M       | -1.01 | $2.93 \pm 0.06$ | 18.63         | 181.26        | 9.44               | 427.81             |
|                  | S       | -1.13 | $3.25 \pm 0.28$ | 18.63         | 192.19        | 9.41               | 472.55             |
| <u>4</u>         | W       | -2.29 | $6.13 \pm 0.53$ | 18.08         | 164.42        | 9.04               | 883.93             |
|                  | M       | -1.05 | $2.97 \pm 0.26$ | 18.63         | 148.05        | 9.44               | 428.73             |
|                  | S       | -1.06 | $3.09 \pm 0.27$ | 18.63         | 159.12        | 9.41               | 446.43             |
| <u>5</u>         | W       | -2.19 | $5.84 \pm 0.51$ | 18.08         | 250.90        | 9.04               | 855.56             |
|                  | M       | -0.95 | $2.80 \pm 0.24$ | 18.63         | 246.07        | 9.44               | 418.99             |
|                  | S       | -1.03 | $2.98 \pm 0.26$ | 18.63         | 246.27        | 9.41               | 443.34             |

\*1 Carbonatopentaamine Co(III) nitrate,  $[(\text{NH}_3)_5\text{CoCO}_3](\text{NO}_3)_2$

2 Aquopentaamine Co(III) nitrate,  $[(\text{NH}_3)_5\text{Co}(\text{CH}_2)](\text{NO}_3)_3$

3 Oxalatopentaamine Co(III) nitrate,  $[(\text{NH}_3)_5\text{CoOOC}(\text{COOH})](\text{NO}_3)_2$

4 Malonatopentaamine Co(III) nitrate,  $[(\text{NH}_3)_5\text{CoOOCCH}_2\text{COOH}](\text{NO}_3)_2$

5 Succinatopentaamine Co(III) nitrate,  $[(\text{NH}_3)_5\text{CoOOC}(\text{CH}_2)_2\text{COOH}](\text{NO}_3)_2$

and plotting  $(\eta_r - 1)/(c)^{1/2}$  vs  $(c)^{1/2}$  and extrapolating to  $c = 0$ , the intercept and the slope yielded  $A'$  and  $B'$  respectively. Assuming  $\alpha = 1$  at infinite dilution,  $A'$  becomes  $A$ , the Falkenhagen coefficient since  $B_{fp}$  is dependent on  $\alpha$  and also on  $c$ , when  $c \rightarrow 0$ ,  $\alpha = 1$ ,  $B'$  becomes  $B$ , the Jones-Dole coefficient. The values of  $A$  and  $B$  thus obtained are recorded in table 1.

A perusal of table 1 shows that the values of  $A$  are negative in all cases and are more negative in water than in (water + sorbitol) and in turn in (water + mannitol) mixtures. Since  $A$  is considered to be a measure of ion-ion interaction, the negative  $A$  values may indicate the absence (as ion-ion interactions vanish at infinite dilution) or the presence of very weak ionic interactions in all the solutions in all solvents. However, in the case of ionic interactions, it is evident that the interactions are dependent on the nature of the solute and also the structure of the solvent. Thus, for a given solvent, the ion-ion interactions, for the five different types of complexes, follow the order: carbonatopentaamine- < aquopentaamine- < oxalatopentaamine- < malonatopentaamine- < succinatopentaamine-Co(III) nitrate, and for a particular complex, the interactions in the three different solvents follow the order: (water + mannitol) > water > (sorbitol + water).

The coefficient  $B$  is a measure of the effective solvodynamic volume of solvated ions, and is governed by ion-solvent interactions, that is, the structural effect of the solvent in solution. It is a fact that when a solute dissolves in a solvent, some of the solvent molecules are attached to the ions (generated from the solute) because of ion-solvent

interactions, and this causes an increase in viscosity of the solution (a positive contribution to the coefficient  $B$ ). On the other hand, these solvent molecules have to be wrenched out of the bulk solvent and this breaking of the solvent structure causes a decrease in viscosity of the solution (a negative contribution to  $B$ ). Thus, the value of  $B$  in the solution is the resultant of these two opposing factors.

The values of the coefficient  $B$  for all the five complexes are positive and large in all the solvent systems indicating thereby the existence of strong ion-solvent interactions. From the magnitude of  $B$ , it is evident that ion-solvent interactions, for a given complex, in the three different solvent systems follow the order: water > (water + sorbitol) > (water + mannitol); and for a given solvent, the ion-solvent interactions for the five complexes follow the order: carbonatopentaamine- > aquopentaamine- > oxalatopentaamine- > malonatopentaamine- > succinatopentaamine Co(III) nitrate, which is the reverse of the order with respect to  $A$ .

The viscosity data were also analysed on the basis of the transition state theory for relative viscosity of the octahedral Co(III) complex solutions as suggested by Feakins *et al* (1974) using the equation

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + (RT/\bar{v}_1^0)1000B - (\bar{v}_1^0 - \bar{v}_2^0), \quad (3)$$

where  $\Delta\mu_2^{0*}$  is the contribution per mole of the solute to free energy of activation for viscous flow of solution,  $\Delta\mu_1^{0*}$  is the corresponding value for pure solvent,  $\bar{v}_1^0$  is the partial molar volume of the solvent,  $\bar{v}_2^0$  is the partial molar volume of the solute and  $B$  is the Jones-Dole parameter.  $\Delta\mu_1^{0*}$  was calculated from (Glasstone *et al* 1941),

$$\Delta\mu_1^{0*} = RT \ln(\eta_0 \bar{v}_1^0 / \hbar N), \quad (4)$$

where  $\hbar$  is Planck's constant,  $N$  is Avogadro number, and  $\eta_0$  is the viscosity of the pure solvent. The values of  $\bar{V}_1^0$  and  $\bar{V}_2^0$  (Dash and Supkar 1995), and that of  $\Delta\mu_1^{0*}$  and  $\Delta\mu_2^{0*}$  are recorded in table 1. The positive and large values (as compared to that of  $\Delta\mu_1^{0*}$ ) of  $\Delta\mu_2^{0*}$  indicate that the behaviour of  $\Delta\mu_2^{0*}$  is quite similar to that of  $B$  in all solvents, i.e., stronger ion-solvent interaction. In other words, the formation of the transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure.

The experimental data of conductance measurements for Co(III) complexes in water and (water + mannitol) and (water + sorbitol) after solvent correction were analysed using the Fuoss and Shedlovsky extrapolation technique (Maniah *et al* 1986):

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + (K_A/\Lambda_0^2)(c\Lambda f_{\pm}^2 S(z)), \quad (5)$$

where

$$S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} + \dots,$$

$$z = S(\Lambda c)^{1/2} / \Lambda_0^{3/2},$$

$$S = a\Lambda_0 + b,$$

$$a = 82.04 \times 10^4 / (DT)^{3/2},$$

$$b = 82.501 / \eta(DT)^{1/2},$$

and

$$\log f_{\pm} = -A(zc)^{1/2} / (1 + Ba^0(zc)^{1/2}). \quad (6)$$

In (6)  $\alpha = \Lambda S(z)/\Lambda_0$ ,  $A$  and  $B$  are the Debye-Hückel constants,  $a^0$  is the ion-size parameter, and the Fuoss-Kraus extrapolation technique,

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + (K_A/\Lambda_0^2)(c\Lambda f_{\pm}^2/F(z)), \quad (7)$$

where  $F(z) = (4/3)\cos^2[(1/3)\cos^{-1}(-3)^{1.5}(z/2)]$  and  $z$  and  $\log f_{\pm}$  are the same as above, and  $\alpha = \Lambda/(\Lambda_0 F(z))$ . In (5) and (7),  $c$  is the molar concentration,  $\Lambda$  and  $\Lambda_0$  are the molar and limiting molar conductances, respectively, and  $K_A$  is the association constant for the reaction of the type,



given by

$$K_A = c_{[MX_n]}f_{[MX_n]}/c_{M^{n+}}f_{M^{n+}}c_{X^-}^n f_{X^-}^n. \quad (9)$$

To start the Shedlovsky method an initial value of  $\Lambda_0$  was obtained from the Onsager  $\Lambda$  vs  $c^{1/2}$  plot. Using  $\Lambda_0$ ,  $a$  and  $b$ ,  $S$  (the Onsager slope) was calculated. Using these  $S$  and  $\Lambda_0$  values,  $z$ ,  $S(z)$  and  $\alpha$  values were evaluated. The activity coefficients were, however, determined using (6) with  $a^0 = 0$ ,  $q$ , and  $2q$ , where  $q = (z_+ z_- e^2/2DkT)$ , and the other symbols have their usual meanings. From the linear plot of  $1/\Lambda S(z)$  vs  $c\Lambda f_{\pm}^2 S(z)$ ,  $\Lambda_0$  and  $K_A$  values were evaluated from the intercept and the slope ( $K_A/\Lambda_0^2$ ), respectively. The procedure was repeated using the new value of  $\Lambda_0$  until there was no further change in the values of  $\Lambda_0$  and  $K_A$ .

The procedure for applying the Fuoss-Kraus technique is similar to that described in the Shedlovsky technique.

All calculations were carried out on an HCL Horizon III Mini computer. The conductance parameters and constants obtained by the Shedlovsky and Fuoss-Kraus techniques are given in tables 2 and 3.

By examining the behaviour of the  $\Lambda_0$  values (table 2) derived from the Shedlovsky and Fuoss-Kraus extrapolation techniques in the solvents concerned, we note that the  $\Lambda_0$  values are slightly different. In most cases the  $\Lambda_0$  values obtained by the Fuoss-Kraus technique are found to be slightly less than those obtained by the Shedlovsky technique. The small differences in  $\Lambda_0$  values can be interpreted as being a superposition of two effects: (1) various limiting conductivities of the complex cations, and (2) different extents of the association in solutions. Both effects seem to result from such structural factors as the symmetry perturbation and the effective sizes of  $[(NH_3)_5Co(III)]$  complexes. These effects are probably more marked with the values of  $\Lambda_0$  derived from the more general conductivity equation proposed by Fuoss and Hsia (1966, 1967) using the Fernandez-Prini (1969) coefficients where the  $\Lambda_0$  values show a large difference from those evaluated by the former two techniques. Therefore, the  $\Lambda_0$  values computed from the Fuoss-Hsia equation are excluded from the present discussion.

As observed, the  $\Lambda_0$  values in any solvent increase from carbonatopentaamine- to aquopentaamine-Co(III) nitrate. However, when the ligand is replaced by a carboxylato-group, remarkable changes in  $\Lambda_0$  values are observed. For oxalato- the  $\Lambda_0$  value becomes maximum, then decreases for the malonato- and further decreases for succinato-complex. Thus the obtained  $\Lambda_0$  values for the octahedral Co(III) complexes may be interpreted, as a first approximation, in terms of the coordination model of solutions. According to this model, two solutions, in which the total concentrations of any kind of complexes present are equal, have approximately the same specific conductivities, independent of the central metal ion. Since the central metal ion is

**Table 2.** Conductance parameters ( $\Lambda_0$ ) obtained by the Shedlovsky and Fuoss-Kraus techniques for octahedral Co(III) complexes in water (W), water + 5 wt% mannitol (M) and water + 5 wt% sorbitol (S) at 30°C.

| Complex                      | Solvent | $\Lambda_0/S(\text{cm}^2 \text{mol}^{-1}), a^0 =$ |                  |                  | Walden product* |
|------------------------------|---------|---|------------------|------------------|-----------------|
|                              |         | 0   | $q$              | $2q$             |                 |
| <i>Shedlovsky technique</i>  |         |   |                  |                  |                 |
| <u>1</u>                     | W       | 148.39<br>± 0.08                                  | 144.91<br>± 0.03 | 143.96<br>± 0.05 | 1.16            |
|                              | M       | 136.80<br>± 0.07                                  | 133.89<br>± 0.01 | 133.08<br>± 0.04 | 1.21            |
|                              | S       | 149.31<br>± 0.08                                  | 145.45<br>± 0.03 | 144.39<br>± 0.05 | 1.31            |
| <u>2</u>                     | W       | 412.61<br>± 0.60                                  | 390.03<br>± 0.01 | 385.24<br>± 0.02 | 3.12            |
|                              | M       | 369.58<br>± 0.53                                  | 349.49<br>± 0.01 | 345.27<br>± 0.02 | 3.17            |
|                              | S       | 315.98<br>± 0.09                                  | 304.94<br>± 0.08 | 302.77<br>± 0.12 | 2.74            |
| <u>3</u>                     | W       | 777.42<br>± 0.17                                  | 690.75<br>± 0.04 | 660.80<br>± 0.61 | 5.53            |
|                              | M       | 888.50<br>± 1.84                                  | 797.63<br>± 0.03 | 762.95<br>± 0.04 | 7.24            |
|                              | S       | 852.28<br>± 1.73                                  | 766.34<br>± 0.01 | 733.82<br>± 0.03 | 6.89            |
| <u>4</u>                     | W       | 520.74<br>± 0.37                                  | 475.21<br>± 0.06 | 460.13<br>± 0.13 | 3.80            |
|                              | M       | 338.24<br>± 0.55                                  | 320.32<br>± 0.01 | 315.04<br>± 0.04 | 2.90            |
|                              | S       | 287.65<br>± 0.32                                  | 275.98<br>± 0.02 | 272.48<br>± 0.02 | 2.48            |
| <u>5</u>                     | W       | 120.46<br>± 0.16                                  | 116.79<br>± 0.06 | 115.73<br>± 0.03 | 0.93            |
|                              | M       | 111.95<br>± 0.08                                  | 106.22<br>± 0.01 | 104.72<br>± 0.14 | 0.96            |
|                              | S       | 86.37<br>± 0.09                                   | 86.26<br>± 0.11  | 86.23<br>± 0.13  | 0.77            |
| <i>Fuoss-Kraus technique</i> |         |   |                  |                  |                 |
| <u>1</u>                     | W       | 146.15<br>± 0.03                                  | 143.44<br>± 0.04 | 142.74<br>± 0.04 | 1.15            |
|                              | M       | 134.88<br>± 0.01                                  | 132.65<br>± 0.02 | 132.05<br>± 0.04 | 1.20            |
|                              | S       | 147.33<br>± 0.01                                  | 144.13<br>± 0.03 | 143.27<br>± 0.06 | 1.29            |
| <u>2</u>                     | W       | 410.08<br>± 0.43                                  | 391.56<br>± 0.01 | 385.97<br>± 0.01 | 3.13            |
|                              | M       | 367.23<br>± 0.34                                  | 350.89<br>± 0.01 | 345.94<br>± 0.01 | 3.18            |
|                              | S       | 314.13<br>± 0.04                                  | 305.31<br>± 0.06 | 302.81<br>± 0.08 | 2.74            |
| <u>3</u>                     | W       | 772.57<br>± 1.20                                  | 686.18<br>± 0.76 | 656.51<br>± 0.96 | 5.49            |

(Continued)

Table 2. (Continued)

| Complex  | Solvent | $\Lambda_0/S(\text{cm}^2 \text{mol}^{-1}), a^0 =$ |                      |                      | Walden product* |
|----------|---------|---|----------------------|----------------------|-----------------|
|          |         | 0   | $q$                  | $2q$                 |                 |
| <u>4</u> | M       | 883.84<br>$\pm 1.87$                              | 793.94<br>$\pm 1.12$ | 759.06<br>$\pm 2.27$ | 7.21            |
|          | S       | 847.73<br>$\pm 1.47$                              | 762.85<br>$\pm 1.41$ | 730.02<br>$\pm 0.07$ | 6.85            |
|          | W       | 517.10<br>$\pm 0.22$                              | 471.88<br>$\pm 0.25$ | 457.05<br>$\pm 0.29$ | 3.78            |
|          | M       | 335.89<br>$\pm 0.31$                              | 318.49<br>$\pm 0.01$ | 313.39<br>$\pm 0.01$ | 2.89            |
|          | S       | 285.53<br>$\pm 0.19$                              | 274.37<br>$\pm 0.01$ | 271.05<br>$\pm 0.01$ | 2.46            |
|          | W       | 117.64<br>$\pm 0.02$                              | 114.75<br>$\pm 0.01$ | 113.96<br>$\pm 0.40$ | 0.92            |
| <u>5</u> | M       | 109.04<br>$\pm 0.01$                              | 104.02<br>$\pm 0.02$ | 102.81<br>$\pm 0.03$ | 0.94            |
|          | S       | 84.51<br>$\pm 0.01$                               | 85.50<br>$\pm 0.06$  | 85.72<br>$\pm 0.09$  | 0.77            |

\* $a^0 = q$ ; complexes 1, 2, 3, 4 and 5 are as in table 1

common in all the complexes studied in the present case, the observed differences between the  $\Lambda_0$  values of the complexes may be attributed to the difference in the nature of the substituted ligands in the complexes. Thus it follows that the differences between the values arise from the differences in the transport properties of solvated complexes which reflect factors affecting their effective sizes. The factors which influence the sizes of the complexes can be: radii of the non-solvated cations, different configuration of the complexes, distortion of the octahedral symmetry and metal–ligand bond lengths. The first two factors should be of little importance in view of the fact that the central metal ion is common in all the complexes. Therefore, the factors which influence the solvodynamic radii may be the distortion of the octahedral symmetry or the metal–ligand bond length or both.

From the  $\Lambda_0$  values presented in table 2 it is apparent that the solvodynamic radii of the complexes play an important role in influencing the ionic mobilities and hence the differentiation of the conductivities of the complexes. Unfortunately, it is not possible at present to evaluate the solvodynamic radii and to examine it quantitatively in solutions. Despite this fact, we must emphasize that the differentiation of conductivities of the investigated complexes can be most probably accounted for by the extent of ion solvation and the ion-pair association. The weaker solvation and the greater ion-pair association increase ionic mobility and hence the conductivity.

Association constants estimated from Shedlovsky and Fuoss–Kraus methods taking  $a^0 = 0, q$ , and  $2q$  are given in table 3. The observed differences in the association constants indicate the octahedral distortion of the complex which facilitates the approach of solvated cations by  $\text{NO}_3^-$  ions, in different solutions. Our investigations of the complexes show a considerable ion-pair association. The distortion of octahedral symmetry may account for the strong cation–anion electrostatic interaction observed in these complexes. A larger ion-pair association of oxalatopentaamine Co(III) nitrate

**Table 3.** Values of  $K_A$  ( $\text{dm}^3 \text{mol}^{-1}$ ) obtained by Shedlovsky and Fuoss-Kraus techniques for octahedral Co(III) complexes in water (W), water + 5 wt% mannitol (M) and water + 5 wt% sorbitol (S) at 30°C.

| Complex  | Solvent | Shedlovsky technique* |            |            | Fuoss-Kraus technique |            |            |
|----------|---------|-----------------------|------------|------------|-----------------------|------------|------------|
|          |         | 0                     | $q$        | $2q$       | 0                     | $q$        | $2q$       |
| <u>1</u> | W       | 6.88                  | 4.63       | 3.97       | 4.87                  | 3.15       | 2.67       |
|          |         | $\pm 0.03$            | $\pm 0.01$ | $\pm 0.02$ | $\pm 0.01$            | $\pm 0.07$ | $\pm 0.07$ |
|          | M       | 6.75                  | 4.55       | 3.89       | 4.82                  | 3.19       | 2.72       |
|          |         | $\pm 0.03$            | $\pm 0.01$ | $\pm 0.03$ | $\pm 0.01$            | $\pm 0.03$ | $\pm 0.05$ |
|          | S       | 8.10                  | 5.41       | 4.61       | 6.24                  | 4.09       | 3.47       |
|          |         | $\pm 0.02$            | $\pm 0.01$ | $\pm 0.03$ | $\pm 0.02$            | $\pm 0.05$ | $\pm 0.07$ |
| <u>2</u> | W       | 19.16                 | 11.93      | 10.27      | 18.16                 | 12.34      | 10.52      |
|          |         | $\pm 0.01$            | $\pm 0.01$ | $\pm 0.01$ | $\pm 0.03$            | $\pm 0.02$ | $\pm 0.02$ |
|          | M       | 19.17                 | 11.93      | 10.28      | 18.17                 | 12.36      | 10.54      |
|          |         | $\pm 0.10$            | $\pm 0.01$ | $\pm 0.01$ | $\pm 0.03$            | $\pm 0.02$ | $\pm 0.01$ |
|          | S       | 9.88                  | 6.10       | 5.27       | 9.04                  | 6.08       | 5.20       |
|          |         | $\pm 0.01$            | $\pm 0.02$ | $\pm 0.03$ | $\pm 0.01$            | $\pm 0.02$ | $\pm 0.04$ |
| <u>3</u> | W       | 85.67                 | 55.24      | 45.32      | 83.69                 | 53.68      | 43.97      |
|          |         | $\pm 0.46$            | $\pm 0.08$ | $\pm 0.27$ | $\pm 0.41$            | $\pm 0.41$ | $\pm 0.42$ |
|          | M       | 114.20                | 77.96      | 64.89      | 112.13                | 76.42      | 63.53      |
|          |         | $\pm 0.12$            | $\pm 0.05$ | $\pm 0.02$ | $\pm 0.95$            | $\pm 0.50$ | $\pm 0.99$ |
|          | S       | 108.21                | 73.83      | 61.50      | 106.18                | 72.31      | 60.17      |
|          |         | $\pm 0.78$            | $\pm 0.12$ | $\pm 0.01$ | $\pm 0.72$            | $\pm 0.57$ | $\pm 1.02$ |
| <u>4</u> | W       | 53.33                 | 35.25      | 29.41      | 51.64                 | 33.90      | 28.24      |
|          |         | $\pm 1.48$            | $\pm 0.12$ | $\pm 0.17$ | $\pm 0.96$            | $\pm 0.22$ | $\pm 0.14$ |
|          | M       | 20.54                 | 13.64      | 11.55      | 19.40                 | 12.80      | 10.82      |
|          |         | $\pm 0.12$            | $\pm 0.01$ | $\pm 0.03$ | $\pm 0.03$            | $\pm 0.01$ | $\pm 0.05$ |
|          | S       | 16.22                 | 11.07      | 9.46       | 15.06                 | 10.22      | 8.72       |
|          |         | $\pm 0.04$            | $\pm 0.01$ | $\pm 0.01$ | $\pm 0.01$            | $\pm 0.01$ | $\pm 0.02$ |
| <u>5</u> | W       | 11.31                 | 7.67       | 6.58       | 7.88                  | 5.17       | 4.39       |
|          |         | $\pm 0.11$            | $\pm 0.04$ | $\pm 0.02$ | $\pm 0.16$            | $\pm 0.01$ | $\pm 0.04$ |
|          | M       | 14.86                 | 9.13       | 7.60       | 11.02                 | 6.38       | 5.23       |
|          |         | $\pm 0.02$            | $\pm 0.09$ | $\pm 0.12$ | $\pm 0.05$            | $\pm 0.36$ | $\pm 0.33$ |
|          | S       | 0.658                 | 0.482      | 0.422      | -2.11                 | -1.28      | -1.08      |
|          |         | $\pm 0.07$            | $\pm 0.04$ | $\pm 0.04$ | $\pm 0.04$            | $\pm 0.06$ | $\pm 0.06$ |

\* $a^0$  values = 0,  $q$  and  $2q$  (given at the top of each column); complexes 1, 2, 3, 4 and 5 are as in table 1

obtained in all the solvents can be attributed to lower cation complex stability and to the lack of solvation of the complex ion, while the reverse is the case for carbonatopentaamine- and succinatopentaamine Co(III) complexes which give smaller ion-pair association. The obtained association constants of succinatopentaamine Co(III) nitrate would suggest that this complex is slightly less associated than the corresponding carboxylato complexes. This is consistent with the results reported by Jenkins and Monk (1951) that the larger the size of the ligand (in a complex) or the alkyl tail (in tetraalkyl ammonium salt), the smaller the ion-association constant. Any change in the association for a particular complex on passing from one solvent to another is due to the different extents of association in solutions.

Walden products ( $\Lambda_0\eta$ ) estimated for octahedral Co(III) complexes in various solutions are given in table 2 using both the Shedlovsky and Fuoss-Kraus techniques for the  $\Lambda_0$  values. As pointed out earlier, the mean activity coefficients of the complexes



needed for the evaluation of  $\Lambda_0$  and  $K_A$  values (5), (7) were computed using the Debye–Huckel extended law (6) with  $a^0 = 0$ ,  $q$ , and  $2q$ . For solvent-separated ion-pairs, the activity coefficient of the medium was used for evaluation of  $\Lambda_0$  values with  $a^0 = q$  and this  $\Lambda_0$  value was taken into consideration for estimation of the Walden product of the complex. Unfortunately, it is not possible at present to estimate the Walden products of single ions because of lack of data in case of single ion conductivity values. However, the Walden products as computed from the molar conductivity values,  $\Lambda_0$ , would be informative from the point of view of ion–solvent interactions.

It is evident from the comparative results in table 2 that the values of Walden product remain essentially the same, regardless of the  $\Lambda_0$  values from which they are derived. Therefore, it is convenient to consider first any information obtainable from the  $\Lambda_0\eta$  value, as it should be virtually free of ambiguity. Appreciable variation in the Walden product as a function of the solvent is generally regarded as an index of specific ion–solvent interactions including structural effects. A reasonable constancy of the Walden product in different solvents for carbonatopentaamine Co(III) nitrate, and for aquopentaamine Co(III) nitrate and succinatopentaamine Co(III) nitrate in water and 5% wt mannitol indicates that there is not much change in the solvation of the corresponding ion-pairs with change of solvent. However, as observed, oxalatopentaamine- and malonatopentaamine Co(III) complex cations exhibit considerable variation in their Walden products with the solvent. In these cases solvation effects are reflected in the variation of the Walden products of the Co(III) complexes with change of ligand in the complex cation. This variation in the values of  $\Lambda_0\eta$  can be interpreted in terms of the effect of the complex cation (since the anion is the same in all complexes) on the structure of the solutions. A structure-breaking ion, in general, possesses high mobility and decreases the local viscosity leading to a high value of  $\Lambda_0\eta$ . Indeed, the higher values of  $\Lambda_0\eta$  for oxalatopentaamine and malonatopentaamine Co(III) complexes support this view.

#### 4. Conclusion

The results of the present investigation on the octahedral Co(III) complexes reveal that the complexes which show high ion–ion interaction show minimum ion–solvent interaction and vice versa. Formation of the transition state is accompanied by ‘rupture’ of the intermolecular interaction. The observed trend of  $\Lambda_0$  values can be explained in terms of the changes in metal–ligand bond length as well as of the distortion from the octahedral symmetry of the complexes. Magnitudes of the Walden products depend on the identity of the complex. No simple straightforward correlation can be made between conductivity or viscosity data and nature of the solvent (i.e., water, water + mannitol and water + sorbitol).

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