ELECTROLYTIC BEHAVIOUR OF COBALT(II) COMPLEXES OF ACETONETHIO-SEMICARBAZONE HALIDES IN METHANOL AT 25°C

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The conductance of cobalt(II) complexes of acetonethiosemicarbazone (actsc) halides is measured in methanol at 25°C. The data were analyzed using the Fuoss-Onsager equation for 1:1 associated electrolytes using a fortran IV program on a PDP 11/70 computer. The characteristic parameters: the association constant K_A, the closest distance of approach a° and the equivalent conductance at infinte dilution Λ_o have been calculated. The trend of K_A has been discussed in the light of the solvent separated ion pair model.

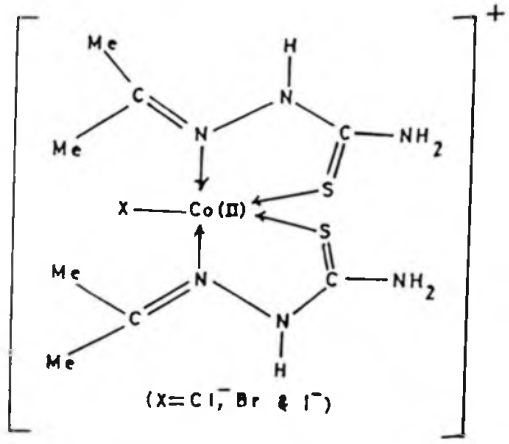
In solvents with high solvating power, small ions are well solvated and therefore the so-called solvent-separated ion pairs are predominantly formed. On the other hand, large ions are almost bare and form contact ion pairs [1]. Several 3-parameter equations [2] and 4-paramter equations [3-6], were suggested to illustrate the relation between K_a, a° and Λ_o. All these approaches are based on the model of charged hard spheres in a dielectric continuum.

This paper reports measurements of the conductances of cobalt(II) complexes of acetonethiosemicarbazone (actsc) halides in methanol at 25° C. The Fuoss-Onsager 3-parameter equation has been used to obtain the parameters K_A, a° and Λ_o. The effect of anionic size on the conductance of these salts has been discussed and a comparison is made between the summation of Stoke's electrostatic radii and a°.

EXPERIMENTAL

Materials

The Co(II) complexes were obtained by the reaction between the appropriate metal salt and actsc in ethanol solution as reported before [7]. Previous studies of X-ray [8] and electronic spectra [9] have shown that these complexes have a five-coordinate structure:



Methanol (BDH, AnalaR) was kept in contact with molecular seives (4A, BDH) for about 24 h with frequent shaking, distilled and than refluxed with silver nitrate (AnalaR) for 24 h. It was refluxed again for 24 h with magnesium turnings (AnalaR) and redistilled. The distillate was kept in contact with activated alumina fo 24 h with intermittent shaking and then distilled. A fractionating column was used in all the distillations and only the middle distillate (65.5°) was taken. Its measured properties are: density (25°) = 0.78657 g cm^{-3} ; viscosity (25°) = 0.54448 cp; specific conductance = 1.6 -3.9 x 10^{-7} ohm^{-1} cm^{-1}

Apparatus and Procedure

A Pye 11700 conductivity bridge, was used for measuring the conductance of solutions at 5K cycle/sec An Erlenmeyer conductivity cell with unplatinized electrodes was used. The cell constant is 0.05443 ± 0.43% as determined from several conductivity runs at 25 ± 0.42 using KCl (AnalaR) recrystallized from conductivity water and dried at 120°C. All solutions were prepared by weight reduced to vacuo. Dilutions were carried out successively into the cell by siphoning the solvent using a dispenser.

RESULTS AND DISCUSSION

The measured equivalent conductances (Ω^{-1} equiv.$^{-1}$ cm^2) and corresponding electrolyte concentrations (equiv. / l) are reported in Table 1. Approximate values for Λ_o were estimated from Λ vs $C^{1/2}$ plots. Figure 1 reports the reduced Λ/Λ_o vs. $C^{1/2}$ plots, which give compact representations of the data, the limiting tangents are shown by dotted lines.

A more accurate value of Λ_o was estimated from the Fuoss-Kraus-Shedlovsky (FKS) equation [11]

$$1/\Lambda\, S_{(z)} = 1/\Lambda_o - \left[C\Lambda\, S_{(z)}\, f^2\right] / K_D\Lambda_o^2 \quad \ldots(1)$$

where K_D is the dissociation constant and $S_{(z)}$ is the Shedlovsky's function tabulated by Daggett [12] for various values of z which can be calculated as follows:

$$z = (\alpha / \Lambda_o^{3/2})\ (C\Lambda)^{1/2} \quad \ldots(2)$$

where α is the limiting tangent. The FKS plots are shown in Figure 2.

The data were analyzed using the Fuoss-Onsager equation [2]

$$\Lambda = \Lambda_o - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + (J - B\Lambda_o)\, C\gamma - K_A f^2 C\gamma\Lambda \quad \ldots(3)$$

where $E = E_1\Lambda_o - E_2$; $S = A\Lambda_o + B$ and $J = \sigma_1\Lambda_o + \sigma_2\gamma$ is the degree of dissociation and f is the activity coefficient. A and B are the Debye-Huckel constants, σ_1, σ_2, E_1 and E_2 are defined by Fuoss [2]. A, B, E_1 and E_2 are constants for a given experimental system.

TABLE 1

CONDUCTANCE OF COBALT(II) COMPLEXES OF ACETO-NETHIOSEMICARBAZONE (ACTSC) HALIDES IN METHANOL AT 25 °C.

Co(actsc) Cl		Co(actsc) Br		Co(actsc) I	
10^4 C	Λ	10^4 C	Λ	10^4 C	Λ
14.471	99.953	23.726	119.369	15.811	146.945
11.569	107.971	15.910	131.008	10.461	155.012
9.647	114.204	11.810	138.504	7.788	159.955
8.268	119.015	9.429	143.498	6.238	163.018
7.172	123.504	7.827	147.025	5.221	165.502
6.385	126.512	6.705	150.005	4.458	167.490
5.734	129.490	5.762	152.486	3.953	168.504
		5.135	154.497	3.309	170.489
		4.624	156.014		

The value of B which corrects for the effect of the added electrolyte on the viscosity of the solvent was set equal to zero. Evans and Gardam [13] showed that this approximation does not alter the value of K_A or Λ_o, but changes the value of a° by 0.2 A°.

Table 2 gives values of constants Λ_o, J, a° and K_A using a Fortran IV program written by one of us (A.A.H.) on a PDP 11/70 computer. The accuracies required for the absolute values deviation are ±0.02 for Λ_o, ±2 for J < 200, ±5 for J(200-1000) and ±10 for J >1000). The variation of J with a° are reported in Figure 3; a° corresponding to J are read out from this graph.

It can be readily seen from Table 2 that Λ_o increases for the Co(II) complexes from chloride to iodide according to the ionic equivalent conductance of the anions. The values of J and a° decrease with increasing anionic size. The trend of a° can be correlated with the increase in anion solvation in the order $Cl^- > Br^- \geq I^-$.

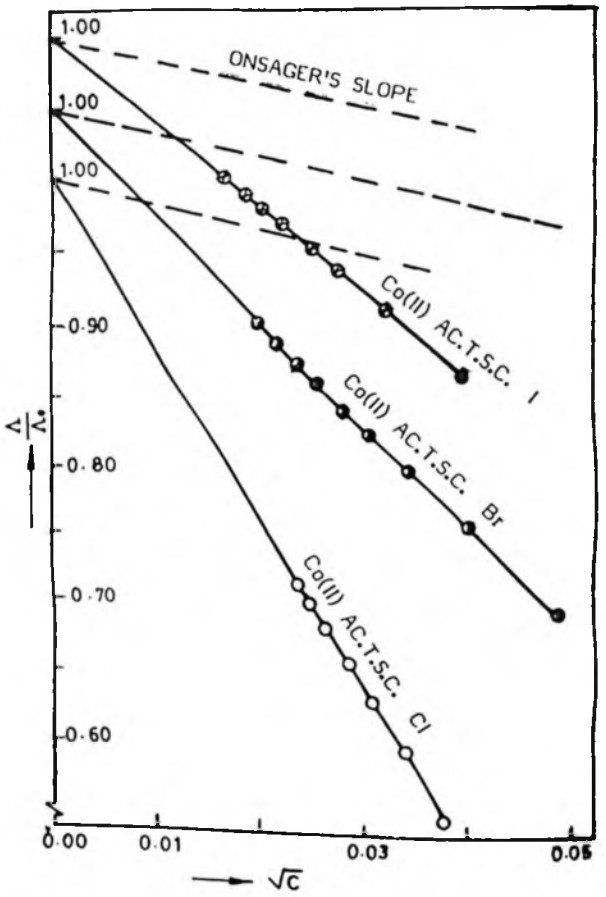


Fig. 1 Plots for cobalt(II) complexes of Acetone thiosemicarbazone halides in Methanol at 25 °C

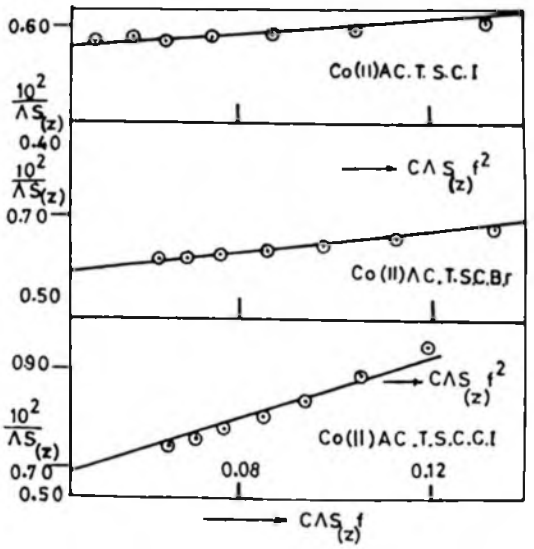
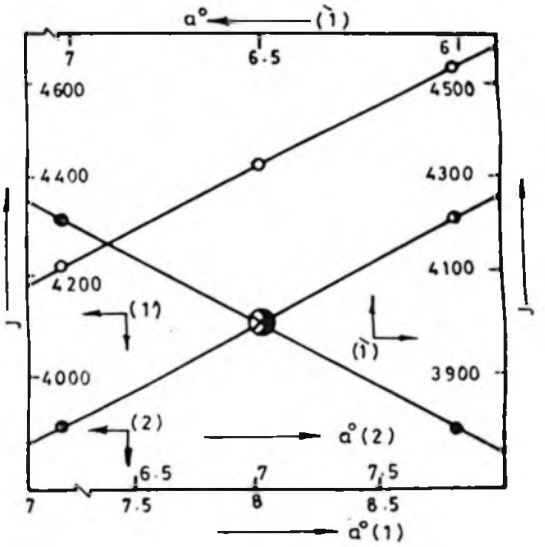


Fig. 2 (F.K.S) plots for cobalt(II) complexes of acetone thiosemicarbazone halides in methanol at 25 °C



O Co(II) AC.T.S.C. Cl ● (Co(II) AC.T.S.C. Br
⊛ Co(II) AC.T.S.C. I

Fig. 3 Variation of J with in methanol at 25 °C

TABLE 2

CHARACTERISTIC PARAMETERS CALCULATED FOR Co(II) COMPLEXES OF ACTSC HALIDES IN METHANOL AT 25 ° C.

	Co(actsc) Cl	Co(actsc) Br	Co(actsc I
Λ_o	177.14	181.35	187.45
J	4152	3875	3993
a_o	7.31	6.48	6.47
K_A	1094.50	341.80	185.75
K_1	10.32	9.71	9.70
K_2	105.11	34.22	18.15
U	4.67	3.56	2.95
λ_o^-*	52.31	56.26	62.80
λ_o^+#	124.76	124.80	124.70
R^-	2.87	2.66	2.46
R^+	1.21	1.21	1.21
a_o	7.31	6.48	6.47

* from ref.18 # average value = 124.75 + 0.05

For trans-dinitrobis (ethylenediamine) Co(III) halides in water also the order of a° was found to be $Cl^- > Br^- > I^-$. Since a° is a measure of the distance between cation and anion, the force of attraction should increase in the order I > Br > Cl . In the present case an opposite trend for K_A was obtained. This can be explained in the light of the U term in the following equations [15]

$$\ln K_A = \ln(4\pi N a_o^3/3000) + e^2/a^\circ DkT + U \quad ..(4)$$

$$U = \Delta S/k - E_s/kT \quad ..(5)$$

where Δ S/k is the entropy/Boltzmann constant ratio which illustrates the probability of the orientation of solvent molecules around free ions, and E_s /kT is an energy relationship which includes the energy of the solvent molecules with respect to the two free ions and to the pair which they can form. It can be easily seen from the Table 2 that U decreases as the anionic size increases. This may indicate that the ion-dipole interaction term (E_s /kT) is higher than the entropy term.

The solvent separated ion-pair model used by Evans and Gardam [16] for tetraalkylammonium salts with common cation has been applied for the Co(II) complexes where a multiple step association is assumed to occur. The solvent separated and contact ion pairs can be illustrated as follows

$$\begin{array}{l} (\text{Co complex})^+ + X^- (\text{solvent})_n \\ \qquad\qquad \uparrow\downarrow K_1 \\ (\text{Co complex})^+ \ (\text{solvent})_n \ X^- \qquad \text{I} \\ \qquad\qquad \uparrow\downarrow K_2 \\ (\text{Co complex})^+ \quad X^- (\text{solvent}) \qquad \text{II} \end{array}$$

The association constants are given by:

$$K_A = \frac{[\text{ion pairs}]}{[(\text{Co Complex})^+]\,[X^-(\text{Solvent})_n]} = K_1(1 + K_2) \quad ...(6)$$

where $K_1 = 4\pi N a_o^3 / 3000\, e^b$ ...(7)

The calculated values of K_1 and K_2 are also given in Table 2. It can be readily seen that K_2 decreases as the anionic size increases. This indicates that as the anionic size increases, the ion-pair prefers the more solvated form and distrubance due to orientation of solvent molecules around the ion decreases by increasing the anionic size.

The electrostatic ionic radii R^+ and R^- can be determined using the Stoke's equation in the following form

$$R^{\pm} = 0.8194 \times 10^{-8} / \lambda^{\pm} \eta_o \qquad ...(8)$$

In our case λ_o^- were obtained from the intercepts of the straight lines obtained from the plots of the Walden products Λ_o , η_o vs the reciprocal of the molecular weight as previously discussed [17]. To calculate λ_o^+ for (Co complex)$^+$ the results of λ_o^+ are first calculated and the average value was used in the calculations. Applying equation (8) both R^+ and R^- are obtained and included in the Table 2. It is clear from this table that the values of a° are greater than the sum of the electrostatic radii ($R^+ + R^-$) obtained from Stoke's equation. The electrostatic radius of the anion (R^-) is found to decrease with increasing anionic size in the order $Cl^- > Br^- > I^-$, as expected. It has been found that ionic equivalent conductance of (Co complex)$^+$ cations are nearly constant for all the halide salts. This may indicate that the chloride, bromide and iodide within the chelate structure does not affect the equivalent ionic conductance of the cation. Also, it was found that the Cl, Br or I within the chelate structure has no effect on the radius of the cation, since the calculated electrostatic Stoke's radius for the cation (R^+) was found to be the same. The low values of a° calculated from Stoke's radii for these different Co(II) complexes in methanol are probably due to ion association.

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