

**CONDUCTOMETRIC EVALUATION OF ASSOCIATION CONSTANTS
FOR AQUEOUS SOLUTIONS OF CoCl_2 IN THE ABSENCE AND
PRESENCE OF A MAGNETIC FIELD**

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ABSTRACT

The association constants K_A for CoCl_2 aqueous solutions were calculated using the experimental conductivity values at different salt concentrations. The molar conductivities were measured in the absence and presence of a magnetic field with an average power of 0.677 KGauss.

A new equation for asymmetric 1:2 salts was suggested and used. This equation was derived from Ostwald, Arrhenius and Fuoss-Shedlovsky theories. The results obtained were discussed and the effect of the magnetic field on the association constants was explained.

RESUMO

As constantes de associação, K_A , para soluções aquosas de CoCl_2 foram calculadas a partir de valores experimentais da condutividade para várias concentrações do sal. As condutividades molares foram medidas na ausência e na presença de um campo magnético médio de 0.677 KGauss.

Uma nova equação foi sugerida para sais assimétricos 1:2 e foi usada. Esta equação foi derivada a partir das teorias de Ostwald, Arrhenius e Fuoss-Shedlovsky. Os resultados obtidos foram discutidos e o efeito do campo magnético sobre as constantes de associação foi explicado.

INTRODUCTION

Association of salt solutions were studied by Barthel⁽¹⁾ and Deepa⁽²⁾. The ion-solvent interactions was explained in different electrolytes and polymers using conductivity, relaxation and FTIR measurements⁽¹⁾. Schori *et al.*,^(3,4) used conductivity as an electrical method for studying the complexation of Na⁺ with some crown ethers in DMF and in dimethoxyethane solutions.

Different Fuoss theories - Fuoss-Shedlovsky, Fuoss-Kraus, Fuoss-Edelson and Fuoss-Debye theories^(5, 6) were used for the estimation of the association constants (K_A) for symmetric electrolytes (1:1 electrolytes).

On applying these theories for the association of asymmetric electrolytes, low values of the association constants are obtained. These values lie in the same range of symmetric electrolytes which is not accepted due to the presence of increased number of ions. Therefore, a new equation was required for 1:2 asymmetric electrolytes which facilitates the calculation of K_A easily and accurately.

This paper deals with the application of a new equation for the asymmetric 1:2 salts which are ionized in solutions. This equation was derived from Fuoss-Shedlovsky and Ostwald laws⁽⁶⁾. Also, the effect of magnetic field on the association of strong electrolytes was studied. This effect has never been reported before in the literature.

EXPERIMENTAL

Cobalt chloride was provided by Merck Co. Different CoCl_2 amounts were added to 5 ml portions of doubly distilled water contained in test tubes and dissolved to give different corresponding concentrations. These solutions were thermostated at 298.15 K for two hours by using a thermostat of the type (Polyscience 8105, USA) and used for measurement of densities, conductivities and capacitance. A cell of two solid carbon electrodes with 1cm distance and cell constant = 0.96 was joined with a multimeter of the type [Macom (MX 620)] for the measurement of conductivity and

capacitance. The densities were measured by weighing 1 ml of each solution using Mettler Toledo DA analytical balance.

A two pole permanent magnet (power of 1.26 KGauss with an average value of 0.677 Kilo Gauss between the two poles, measured by a Gauss Meter Model GM-54) was used to study the effect of the magnetic field. The tube containing the solution was placed between the two poles of the magnet and the conductivity was then measured.

RESULTS AND DISCUSSION

From the densities of different CoCl_2 solutions ranging from 0.084-0.520 mole/l the molar volumes were calculated by dividing the molecular weight by the density ($V = M.W/d$) and the calculated values are shown in Table 1. From the molar volumes the solvated radii for the solutions used were also calculated by using equation 1^(7,8).

$$r = \sqrt[3]{V \cdot 0.239 N} \dots\dots\dots (1)$$

where N is Avogadro's number.

The relative capacitances of solutions ϵ were estimated by dividing the measured capacity values (in micro Farad, μF) of the electrolytes by that of pure doubly distilled water and their values are listed also in Table 1.

The mean activity coefficients (γ_{\pm}) were calculated by the use of modified Born equation^(8,9) as given in equation (2).

$$\log \gamma_{\pm} = -\frac{AZ^+ Z^- \sqrt{C}}{1 + Br\sqrt{C}} \dots\dots\dots (2)$$

where Z^+ and Z^- are the charges of the positive and negative ions of the electrolyte used, r the solvated radius and A, B are constants equal:

$$A = 1.823 \cdot 10^6 (\epsilon \cdot T)^{-3/2} \dots\dots\dots (3)$$

$$B = 50.29 (\epsilon \cdot T)^{-1/2} \dots\dots\dots (4)$$

where ϵ is the measured relative capacitances in micro Farad of the solutions. The calculated mean activity coefficients are presented in Table 1 for different CoCl_2 solutions. It was concluded that the activity coefficients increased by increasing the CoCl_2 concentrations due to more interactions in concentrated solutions.

Table 1. Molar volumes (V), relative capacitances (ϵ), solvated radii (r), Born constants A, B and mean activity coefficients (γ_{\pm}) of different CoCl₂ concentrations at 298.15 K.

Cm CoCl ₂ conc. Mol/gl	$\sqrt{C_m}$	V Cm ³ /mol	ϵ^*	r in (Å ^o)	A	B × 10 ⁸	- Log γ_{\pm}
0.084	0.29	130.623	32.5	3.727	1.913	0.511	0.712
0.100	0.32	130.491	34.5	3.726	1.749	0.496	0.699
0.150	0.39	130.229	44.0	3.722	1.214	0.439	0.577
0.210	0.46	129.839	56.0	3.719	0.834	0.388	0.460
0.250	0.50	129.580	64.0	3.717	0.692	0.364	0.413
0.340	0.58	129.809	80.5	3.709	0.491	0.325	0.336
0.420	0.65	128.299	96.5	3.705	0.374	0.297	0.283
0.520	0.72	127.543	115.5	3.698	0.286	0.271	0.240

* The capacity measured for solutions are in micro Farrad (μ F) where that of water is equal to 0.18 μ F.

The association constant K_A of different 1:1 (symmetric) electrolytes can be estimated by applying Fuoss-Shedlovsky equations^(9, 10) (equation 5):

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o^2}\right) (C \cdot \Lambda \cdot \gamma_{\pm}^2 \cdot S(Z)) \dots \dots \dots (5)$$

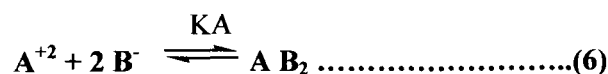
where

$$S(Z) = \left[\frac{Z}{2} + \left(1 + \left(\frac{Z}{2}\right)^2\right)^{1/2} \right]^2, \quad Z = S \cdot (\Lambda_o)^{-3/2} (C \cdot \Lambda)^{1/2},$$

$$S = a \Lambda_o + b, \quad a = 8.2 \times 10^5 (\epsilon \cdot T)^{1/2} \quad \text{and} \quad b = \frac{0.825}{\eta_o (\epsilon T)^{1/2}}$$

Λ , Λ_o are the molar and limiting conductance, ϵ is the dielectric constant, η_o is the viscosity of the solvent, T absolute temperature and S (Z) is the Fuoss Shedlovsky factor.

With the use of equation (5) for 1:2 electrolytes very low values are obtained for K_A (the association constant). Therefore we are in need of a new equation, which can be derived as follows:



$$K_A = \frac{(1-\alpha)}{(2\alpha)^2 \cdot C_m \cdot \alpha} = \frac{1-\alpha}{4 C_m^2 \cdot \alpha^3} \dots\dots\dots(7)$$

$$\alpha \text{ (dissociation degree)} = \frac{\Lambda \cdot S(Z)}{\Lambda_o} \dots\dots\dots(8)$$

$$K_A = \frac{1 - \frac{\Lambda \cdot S(Z)}{\Lambda_o}}{4 C_m^2 \left(\frac{\Lambda \cdot S(Z)}{\Lambda} \right)^3} \dots\dots\dots(9)$$

$$K_A = \frac{\Lambda_o^2 (\Lambda_o - \Lambda)}{4 C_m^2 \gamma_{\pm}^2 \Lambda^3 S(Z)^2} \dots\dots\dots(10)$$

Thus equation (10) can be easily applied for 1:2 electrolytes for diluted solution because this equation is derived from Fuoss-Shedlovsky theory and the Ostwald dilution law, knowing that S (Z) factor for $CoCl_2$ solutions was found to be approximately one. The specific conductance of different $CoCl_2$ solutions were measured and the molar conductance was evaluated by applying equation (11):

$$\Lambda = \frac{K_s \cdot K_{cell} \cdot 1000}{C_m} \dots\dots\dots(11)$$

K_s is the measured specific conductance, K cell is the cell constant and is equal 0.96 Cm is the molar concentration.

The limiting equivalent conductance Λ_o was obtained by extrapolating the relation between Λ and $\sqrt{C_m}$ for different solutions to zero concentration

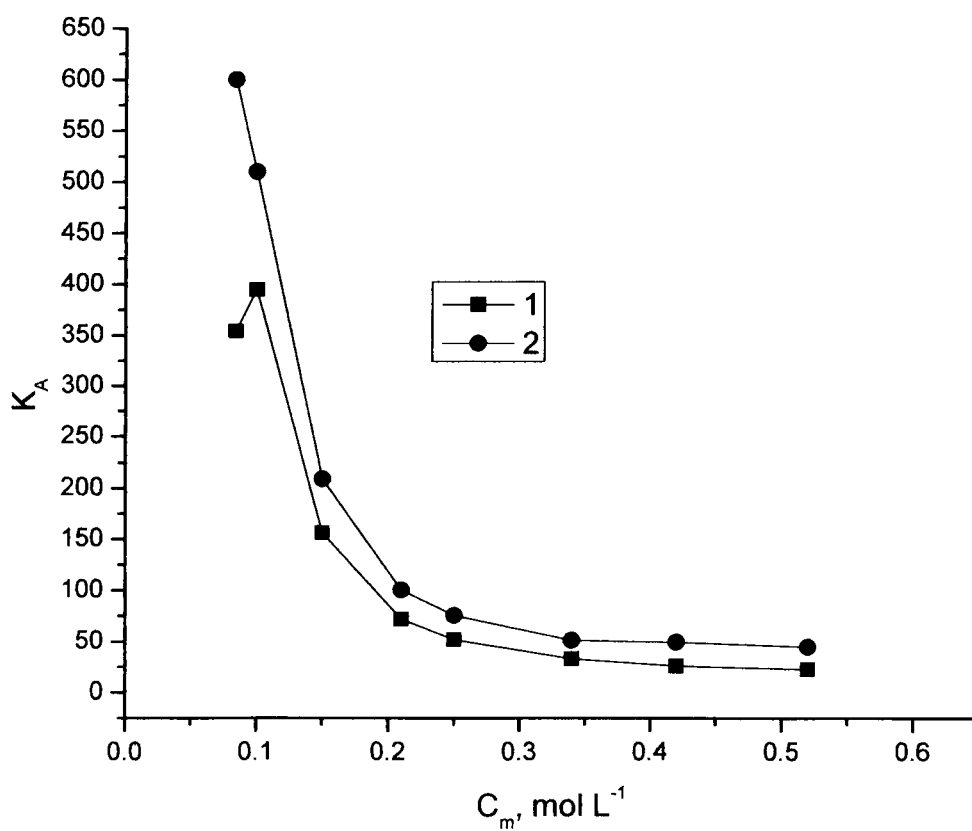


Figure 1. Plot of association constants (K_A) versus concentration (C_m) of CoCl_2 solutions in the absence (1) and presence (2) of a magnet at 298.15 K.

The same relation was drawn for CoCl_2 solution using a permanent magnet of average power of 0.677 Kilo Gauss and the net results are also illustrated in Fig. 1.

From Λ , Λ_o , the association constants (K_A) for CoCl_2 in the absence and presence of magnet were calculated using equation (10) and the results are shown in Table 2.

Table 2. Molar conductance (Λ), limiting molar conductance (Λ_o), dissociation degrees (α) and association constants (K_A) of CoCl_2 solutions in the absence and presence of a magnet at 298.15 K.

C_m Molar Conc.	In absence of magnet			In presence of magnet		
	Λ (in mS. $\text{cm}^2 \text{mol}^{-1}$)	α	K_A ($\text{dm}^3 \text{mol}^{-1}$)	Λ in (m S $\text{cm}^2 \text{mol}^{-1}$)	α	K_A ($\text{dm}^3 \text{mol}^{-1}$)
0.084	7.25	0.764	353.80	8.15	0.741	599.70
0.100	7.05	0.74	394.39	7.80	0.709	509.96
0.15	6.50	0.684	155.99	7.10	0.645	208.61
0.21	5.95	0.626	71.61	6.40	0.582	99.96
0.25	5.65	0.595	51.72	6.00	0.545	75.19
0.34	5.00	0.526	33.06	5.20	0.473	50.98
0.42	4.50	0.474	25.86	4.40	0.400	48.95
0.52	3.95	0.416	22.65	3.80	0.345	44.24

$\Lambda_o = 9.5$ m. Siemens ($\text{m S cm}^2 \text{mol}^{-1}$) in the absence of the magnet and 11.0 ($\text{m S. cm}^2 \text{mol}^{-1}$) in the presence of the magnet.

The dissociation degree, α , was also estimated for the electrolyte studied in the absence and presence of the magnet and the results are also shown in Table 2.

It was concluded that the K_A increases with decreasing CoCl_2 concentrations, mainly due to the increase of the degree of dissociation and the activity coefficient, both in the absence and presence of the magnet.

Using the magnet, K_A values increase due to the more association near that magnet which attracts the ions near it.

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