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**COMPARISON BETWEEN THE CONDUCTOMETRIC EVALUATION OF THE ASSOCIATION CONSTANTS OF  $\text{CoCl}_2$  IN EACH OF 50% ETHANOL- $\text{H}_2\text{O}$  SOLUTIONS AND MIXTURES OF 10% PVA (POLYVINYLALCOHOL) AND 50% ETHANOL- $\text{H}_2\text{O}$  SOLUTIONS IN ABSENCE AND PRESENCE OF MAGNETIC FIELD AT 298.15 K: Using A SIMPLIFIED EQUATION FOR 1:2 ASYMMETRIC ASSOCIATION.**

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### **ABSTRACT**

A study of the effect of magnetic field as a result of a permanent magnet of a power of 1.26 kG on the conductance values and association constants of  $\text{CoCl}_2$  in 50 % by weight mixed ethanol-water solvents in absence and presence of 10 % by weight PVA -water solvents was made. The results were compared with the values in the absence of magnetic field. A simplified equation for 1:2 asymmetric association constant was used for the calculation of the association constants ( $K_A$ ) for  $\text{CoCl}_2$  in both solvent mixtures, this equation was derived from the Fuoss-Shedlovsky equation and Ostwald dilution law and the evaluated values are discussed.

### **INTRODUCTION**

A variety of physicochemical methods has been applied to the study of ion-solvent and ion-ion interaction in electrolyte solution. Conductivity is used as a good method for explaining the ion- solvent interactions and the association of ions in different solutions [Dash et al. (2006)], and is used [Fuoss et al (1957) and Szwarc (1972 )] for the

determination of the association constant  $K_A$ . A number of theoretical equations for the calculation of the electrical conductance of electrolyte solution have been developed [Fuoss et al (1959), Pitts (1953) and Fuoss et al (1967)] all based on Debye-Huckel theory of interionic interaction. The values of the association constants  $K_A$  [Gilkerson et al. (1980)] was used to give information about the role played by the solvent molecules in the pair formation process. In this study, we add a conducting polymer [Naarmann (2002) and Han( 2005)] PVA (10%), as a solvent, to a solution of  $\text{CoCl}_2$  in 50% ethanol- $\text{H}_2\text{O}$  solvent mixtures. The effect of these solvent mixtures on the association constants of  $\text{CoCl}_2$  has been investigated, moreover, we study the effect of magnetic field on these association constants of  $\text{CoCl}_2$  in the same solvent mixtures, the association constants were calculated by using a simplified equation [Hamada et al (2009)] for 1:2 asymmetric salts derived from Fuoss-Shedlovsky equation and Ostwald dilution law [Shedlovsky et al.(1956), Fuoss, R. M. ( 1975), Fuoss, R. M.(1977) and Covington (1973)] using conductivity technique.

## EXPERIMENTAL

Cobalt chloride was obtained from Merck and ethanol from BDH and they were used without further purification. Polyvinylalcohol, M.W, 17,000, which is a water soluble polymer, from Arondale Laborations, England was used. Portions of 5 ml mixed 50 % ethanol- $\text{H}_2\text{O}$  were placed in test tubes then different salt concentrations of  $\text{CoCl}_2$  +10 % PVA solutions by weight were added and dissolved. The prepared solutions were left for two days in water thermostat of the type (Polyscience 8105, USA) at 298.15 K to reach equilibrium. The required volumes were withdrawn and measured using density, conductivity and capacitance techniques. The density values were measured by withdrawing 1 ml portions of the prepared solutions, transferring them to specific gravity bottles (1 ml capacity) and weighing using Mettler (Toledo USA), four digital weighing balance. The density values have been used to calculate the solvated radii [Gomaa (1988)]. Conductances and capacitances were measured experimentally by using a multimeter of the type [Macom (MX620)] with sensitivity of 1%. A dipping type cell with two carbon electrodes which are 1cm apart with a cell constant equals 0.96, was used. At least, the mean of a three readings was reported. The conductance values of all solutions were corrected by subtracting their values from that of the pure solvents. The required temperature was adjusted at 298.15 K with a precision of  $\pm 1$  K. A two poles permanent magnet was used with a power of 1.26 kG measured by Gauss meter (Model GM-54). The conductance values under the influence of the magnetic field were measured by placing the solutions between the two poles of the magnet.

## RESULTS AND DISCUSSION

From the densities measured for  $\text{CoCl}_2$  in mixed 50% ethanol- $\text{H}_2\text{O}$  solutions and in 10% PVA and mixed 50% ethanol- $\text{H}_2\text{O}$  solutions at 298.15 K, the molar volumes were evaluated in both solvent mixtures by dividing the molecular weight of  $\text{CoCl}_2$  by the densities. The evaluated volume values are represented in Tables (1) and (2) in absence and presence of 10% PVA consequently.

From the molar volumes, the solvated radii  $r_s$  [Gomaa (1991)] in  $\text{A}^0$  units for  $\text{CoCl}_2$  and 50% ethanol- $\text{H}_2\text{O}$  in absence and presence of PVA were calculated by using equation(1) :

$$r_s = \sqrt[3]{V \cdot \frac{3}{4} \pi N_A} \quad (1)$$

Where  $V$  is the molar volume of  $\text{CoCl}_2$  and  $N_A$  is the Avogadro's number. The relative capacitance( $\epsilon$ ) of  $\text{CoCl}_2$  solutions in 50% (EtOH- $\text{H}_2\text{O}$ ) solvents in absence and presence of 10% PVA was evaluated by dividing the measured capacitances in microfarads ( $\mu\text{F}$ ) by that of water and their values are given also in Tables (1) and (2).

Table (1): Molar volumes ( $V$ ), relative capacitances ( $\epsilon$ ), solvated radii ( $r_s$ ), Born equation constants  $A$ ,  $B$  and mean activity coefficients ( $\gamma_{\pm}$ ) of different  $\text{CoCl}_2$  concentrations in 50% mixed ethanol-water solutions at 298.15 K.

Cm $\text{CoCl}_2$ conc. mole/l	$V$ $\text{cm}^3/\text{mol}$	$\epsilon$	$r_s$ ( $\text{A}^0$ )	$A$	$B \times 10^8$	$\log \gamma_{\pm}$
0.084	129.224	8.50	3.714	14.29	0.999	3.986
0.100	128.299	10.00	3.705	11.21	0.921	3.409
0.150	128.046	12.50	3.703	8.019	0.824	2.845
0.210	127.920	16.50	3.701	5.287	0.717	2.191
0.250	127.543	18.50	3.698	4.453	0.677	1.959
0.340	126.796	23.50	3.690	3.111	0.601	1.585
0.420	126.303	28.00	3.686	2.392	0.551	1.337
0.520	125.569	34.00	3.680	1.787	0.499	1.108

Table 2: Molar volumes (V), relative capacitances ( $\epsilon$ ), solvated radii ( $r_s$ ), Born equation constants A, B and mean activity coefficients ( $\gamma_{\pm}$ ) of different  $\text{CoCl}_2$  concentrations in 50% mixed ethanol-water solvent/10% PVA solutions at 298.15 K.

$C_m$ $\text{CoCl}_2$ conc. mole/l	V $\text{cm}^3/\text{mol}$	$\epsilon$	$r_s$ ( $\text{\AA}$ )	A	$B \times 10^3$	$\text{Log } \gamma_{\pm}$
0.084	128.299	5.05	3.705	31.23	1.296	7.560
0.100	128.046	6.50	3.703	21.38	1.143	5.781
0.150	127.669	9.00	3.699	13.12	0.971	4.249
0.210	126.809	12.50	3.691	8.019	0.824	3.07
0.250	126.672	15.00	3.689	6.10	0.752	2.555
0.340	125.813	20.00	3.681	3.962	0.651	1.921
0.420	125.206	24.50	3.675	2.922	0.589	1.569
0.520	124.367	30.00	3.667	2.157	0.532	1.292

The mean activity coefficients ( $\gamma_{\pm}$ ) were calculated by the use of the modified Born equation [Born et al. (1978)] as given by equation (2):

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

And the constants are given by :

$$A = \frac{1.823 \times 10^6}{(\epsilon T)^{1.5}} \quad \text{and} \quad B = \frac{50.29}{(\epsilon T)^{0.5}}$$

where  $Z^+$  and  $Z^-$  are the charges of the positive and negative ions of the electrolyte used,  $r_s$  is the solvated radius and A and B are Born constants,  $\epsilon$  is the experimental relative capacitance for  $\text{CoCl}_2$  solutions and  $C_m$  is the cobalt chloride molar concentration. The values of  $r_s$ , A, B and  $\epsilon$  as well as the calculated mean activity coefficients ( $\gamma_{\pm}$ ) are represented in Tables (1) and (2) for  $\text{CoCl}_2$  in 50 % (EtOH- $\text{H}_2\text{O}$ ) solutions in absence and presence of 10% by weight of PVA at 298.15 K . It is noticed that their values decrease by increasing electrolyte concentrations.

For calculating the association constants for 1:2 asymmetric electrolytes, a simplified equation has been used [Hamada et al (2009)] as follows:



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

Where  $\alpha$  is the dissociation degree and is given by:

$$\alpha = \frac{S(Z)\Lambda}{\Lambda_o} \quad (5)$$

Where  $S(Z)$  is the Fuoss-Shedlovsky parameter,  $\Lambda$  is the molar conductance and  $\Lambda_o$  is the molar conductance at infinite dilution

By substituting the  $\alpha$  value from eq. (5) in eq. (4) we get:

$$K_A = \frac{\Lambda_o^3(\Lambda_o - \Lambda)}{4C_m^2\gamma_{\pm}^2\Lambda^3S(Z)^2} \quad (6)$$

The simplified equation (6) is derived from Fuoss-Shedlovsky theory and the Ostwald dilution law. It is known that  $S(Z)$  factor for all strong electrolytes [Hamada et al. (2009)] is approximately equal to one in different solvents. The molar conductance of  $\text{CoCl}_2$  was estimated from the measured specific conductance by applying equation (7) [Hamada et al. (2009) and El-Shishtawi et al. (2011)].

$$\Lambda = \frac{K_s \cdot K_{\text{cell}} \cdot 1000}{C_m} \quad (7)$$

Where  $K_s$  is the measured specific conductance,  $K_{\text{cell}}$  is the cell constant which equals 0.96 and  $C_m$  is the  $\text{CoCl}_2$  concentrations in  $\text{mole L}^{-1}$ . On drawing the relation between molar conductance and square root of the  $\text{CoCl}_2$  concentrations, straight lines are obtained in 50 % (EtOH- $\text{H}_2\text{O}$ ) mixed solvents in absence and presence of 10 % by weight PVA. Extrapolating these lines to zero concentration, the limiting molar conductance,  $\Lambda_o$ , were evaluated. The same relation was obtained from the measured specific conductivities in presence of the magnetic field established from a permanent magnet of a power equals 1.26 kG. From  $\Lambda$ ,  $\Lambda_o$  values, the association constants ( $K_A$ ) for  $\text{CoCl}_2$  in 50 % (EtOH- $\text{H}_2\text{O}$ ) and 50 % (EtOH- $\text{H}_2\text{O}$ )+10 % PVA solvents in presence and absence of magnetic field were evaluated by applying equation (7) and the results are given in Tables (3) and (4). The dissociation degrees ( $\alpha$ ) for  $\text{CoCl}_2$  in both solvent mixtures were also evaluated in absence and presence of magnetic field, Tables (3) and (4).

Table (3): Molar conductance ( $\Lambda$ ), dissociation degrees ( $\alpha$ ) and association Constant ( $K_A$ ) for  $\text{CoCl}_2$  in 50% ethanol- $\text{H}_2\text{O}$  solvents in absence (A) and presence (P) of magnetic field of average power 1.26 K. Gauss at 298.15 K.

Cm of $\text{CoCl}_2$ (Mole/l)	A			P		
	$\Lambda$ (m S. $\text{cm}^2 \text{mol}^{-1}$ )	$\alpha$	$K_A$ ( $\text{d m}^3 \text{mol}^{-1}$ )	$\Lambda$ (m S. $\text{cm}^2 \text{mol}^{-1}$ )	$\alpha$	$K_A$ ( $\text{d m}^3 \text{mol}^{-1}$ )
0.084	3.85	0.847	$9.354 \times 10^8$	5.9	0.791	$1.4 \times 10^9$
0.10	2.85	0.792	$7.567 \times 10^7$	5.70	0.722	$1.219 \times 10^8$
0.15	2.70	0.75	$3.493 \times 10^6$	5.20	0.658	$6.512 \times 10^6$
0.21	2.50	0.694	$1.340 \times 10^5$	4.70	0.595	$2.629 \times 10^5$
0.25	2.40	0.667	$4.819 \times 10^4$	4.40	0.557	$1.026 \times 10^5$
0.34	2.05	0.611	$5.803 \times 10^3$	3.85	0.487	$1.417 \times 10^4$
0.42	2.00	0.556	$1.840 \times 10^3$	3.40	0.430	$4.786 \times 10^3$
0.52	1.85	0.514	$5.756 \times 10^2$	2.85	0.360	$2.069 \times 10^3$

A:  $\Lambda_0 = 3.6 \text{ m S. C}_m^{-2} \text{ mol}^{-1}$ .

P:  $\Lambda_0 = 7.90 \text{ m S. C}_m^{-2} \text{ mol}^{-1}$ .

Table 4: Molar conductance ( $\Lambda$ ), dissociation degrees ( $\alpha$ ) and association constants ( $K_A$ ) for  $\text{CoCl}_2$  in 50% ethanol- $\text{H}_2\text{O}$  solvents and 10% PVA in absence (A) and presence (P) of magnetic field of average power 1.26 K. Gauss at 298.15 K.

Cm of $\text{CoCl}_2$ (Mole/l)	A			P		
	$\Lambda$ (m S. $\text{cm}^2 \text{mol}^{-1}$ )	$\alpha$	$K_A$ ( $\text{d m}^3 \text{mol}^{-1}$ )	$\Lambda$ (m S. $\text{cm}^2 \text{mol}^{-1}$ )	$\alpha$	$K_A$ ( $\text{d m}^3 \text{mol}^{-1}$ )
0.084	2.80	0.848	$1.159 \times 10^{16}$	3.50	0.745	$2.888 \times 10^{16}$
0.10	2.65	0.803	$3.463 \times 10^{12}$	3.15	0.670	$9.974 \times 10^{12}$
0.15	2.45	0.742	$2.20 \times 10^9$	2.80	0.596	$6.683 \times 10^9$
0.21	2.30	0.697	$6.99 \times 10^6$	2.45	0.521	$2.639 \times 10^7$
0.25	2.20	0.667	$5.798 \times 10^5$	2.25	0.479	$2.449 \times 10^6$
0.34	2.05	0.621	$2.373 \times 10^4$	1.85	0.394	$1.493 \times 10^5$
0.42	1.90	0.576	$4.321 \times 10^3$	1.50	0.319	$4.072 \times 10^4$
0.52	1.75	0.530	$1.120 \times 10^3$	1.15	0.245	$1.833 \times 10^3$

A:  $\Lambda_0 = 3.3 \text{ m S. C}_m^{-2} \text{ mol}^{-1}$ .

P:  $\Lambda_0 = 4.7 \text{ m S. C}_m^{-2} \text{ mol}^{-1}$ .

It was observed that the increase in  $\text{CoCl}_2$  concentrations is accompanied by a decrease in the dissociation degree and consequently a decrease in  $K_A$  values. It was also, observed that addition of 10% PVA to 50% (EtOH- $\text{H}_2\text{O}$ ) increases  $\text{CoCl}_2$  associations, i.e., increases the  $K_A$  values to a several order of magnitude, Tables (3) and (4), which is always accompanied by a decrease in conductivity values, this means that the association of electrolyte ions takes place in a better manner through the polymer media. This was attributed [Sinha et al. (2001)] to the fact that PVA which has hydroxyl groups on alternate carbon atoms arranged in long backbone, chelates the cations, the complexing behavior of PVA with transition metal ions is well established [Yokoi et al. (1986) and Young et al. (1992)]. Studies [Watabe (1974)] of 10% PVA membrane complexed with cobalt ions showed the growth of  $\text{CoCl}_2$  particles arranged in circular manner at a curved polymer-polymer interface. It was reported that PVA has a combined effect of surface entrapment and weak Van Der Waals bonds [Young et al. (1992)]. It was concluded that a decrease of self-polymer (PVA) aggregation occurs due to the presence of ethanol which causes breaking of hydrogen bonds between PVA molecules which enhances the attraction of metal ions and results in the large increase in solvation. It was suggested [Toledo et al.(2008)] that the magnetic field causes hydrogen bonding to be broken. It was also suggested that magnetic field causes changes in conductivity; they [Holysz et al. (2007)] concluded that magnetic field caused hydrating water structure around the ions which explains the decrease in conductivity value in presence of the magnetic field Tables (3) and (4) which may be due to the increased solvation as a result of the rupture of different hydrogen bonding (arising from  $\text{H}_2\text{O}$ , Et-OH, PVA) resulting in less mobility of the ions. Also, the chelating tendency of PVA may be increased due to breaking hydrogen bonding between PVA molecules which helps more in reducing the value of conductivity. These factors resulting in decreased values of conductivity, also, consequently led to an increase of the association constants in presence of magnetic field.

### CONCLUSION

It was observed that addition of 10% PVA to  $\text{CoCl}_2$  +50 % ethanol-water mixture increases the association constant of  $\text{CoCl}_2$  to a several orders of magnitude. Using a magnetic field results in an increase of the association constants in both solvent mixtures.

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الملخص العربي

مقارنة بين التقدير التوصيلي لثوابت تجميع كلوريد الكربلت في كل من ٥٠٪ إيثانول - ماء ومخلوط من ١٠٪ PVA + ٥٠٪ إيثانول - ماء وقد تم ذلك في عدم وجود المجال المغناطيسي وكذلك تحت تأثيره باستخدام معادلة التجميع الغير متمثل ١:٢. وقد وجد أن ثوابت التجمع تزداد زيادة كبيرة بإضافة ١٠٪ PVA إلى كلوريد الكربلت + مخلوط من ٥٠٪ إيثانول وماء حيث يقوم الإيثانول بتكبير الروابط الهيدروجينية بين جزيئات ال PVA مما يؤدي إلى زيادة الذوبان. كما وجد أن المجال المغناطيسي يقوم أيضا بتكبير الروابط الهيدروجينية الموجودة في وسط التفاعل مؤديًا في النهاية إلى زيادة ثوابت التجمع.