Influence of Permanent Magnet on the Association Constants of FeCl₃+10% PVA (Polyvinylalcohol) in 50% Ethanol-Water Solutions Conductometrically at 298.15K: Using New Equation for 1:3 Asymmetric Electrolytes

Nagah A. El-Shishtawi[1], Maany A. Hamada[2], Esam A. Gomaa[2,*]

[1]Department of Physics
[2]Department of Chemistry, Faculty of Science, Mansoura University, 35516, Mansoura, Egypt

Abstract The external poles of a permanent magnet of power 1.26 kG were used to study their effect on the conductance values of FeCl₃ plus 10% by weight , PVA (polyvinylalcohol) in 50 % by weight mixed ethanol-water solutions. A new equation for 1:3 asymmetric association constant was derived and used for calculating the association constants (K_A) for FeCl₃ solutions in 50 % ethanol (EtOH)-H₂O mixture in presence of PVA and also in absence and presence of an external magnetic field. The new equation was derived from the Fuoss-Shedlovsky equation and Ostwald dilution law and the evaluated values are discussed.

Keywords Magnetic Effect, Conductance, FeCl₃ , PVA Solutions , 50% Ethanol, Water , Association Constants

1. Introduction

Conducting polymers have received much attention due to their electroactive properties at electrode surface when they are doped by electrochemical oxidation-reduction reactions by chemical methods using electron donors or acceptors[1,2]. These properties allow the polymers to be used as modifiers of electrode surface to facilitate organic electrochemical reaction at the electrodes and to improve battery electrodes[3].

Adding cations as doped elements improve the conducting properties of polymers and also play an important role in forming thin films[3].

Conductivity is a good method for explaining the ion-interactions and the association of ions in different solutions[4]. In this work we apply new equation for the association constants for 1:3 asymmetric electrolytes by the use of conductivity data. This new equation is derived from Fuoss-Shedlovsky equation and Ostwald dilution law[5-8].

Studying the effect of external magnet on the association constants of FeCl₃+10% PVA+50% ethanol-water solutions is very important because it is not studied before.

2. Experimental

* Corresponding author:
esam1947@yahoo.com (Esam A. Gomaa)

Ferric chloride was provided from Merck and ethanol BDH was used without purification. Polyvinylalcohol, M.W, 17,000 water soluble polymer, from Arondale laborations, England was used. 5 ml of mixed 50% ethanol-H₂O were put in test tubes then different salt concentrations of FeCl₃+10% PVA by weight were added and dissolved. The prepared solutions were left for two days in water thermostate of the type (Polyscience 8105, USA) at 298.15 K to reach the necessary equilibrium. Necessary volumes were withdrawn and measured using density techniques, conductivity and capacitance.

The density measurements were done by taking 1 ml of the prepared solutions and put in specific gravity bottle (1 ml capacity) and weighing them using Mettler-Toledo USA, four digital weighing balance. The density have been used to calculate the solvated radii[9,10].

Conductances and capacitances were measured experimentally by the use of multimetter of the type [Macom (MX620)] with sensitivity of 1%. Dipping type cell with two carbon electrodes apart with 1 cm distance and with cell constant equal 0.96, was used. At least three readings were done. The conductance values of all solutions were corrected by substracting their values from that of pure solvents. The required temperature was adjusted at 298.15 K with a precision of ±1 K.

Two poles of permanent magnet was used with power 1.26 K Gauss (kG) measured by Gauss metter Model GM-54. The measured solutions were put between the two poles of the magnet and their conductivity were measured.

3. Results and Discussion

From the densities of $FeCl_3$+10% PVA in mixed 50% ethanol-water solutions at 298.15 K, the molar volumes were calculated by dividing the molecular weight of $FeCl_3$ by the densities of 50% mixed ethanol-H_2O solutions and the evaluated volume values are represented in Table 1, in presence of 10% PVA. From the molar volumes, the solvated radii r_s in Å units for $FeCl_3$+50% (EtOH-H_2O) in presence and absence of PVA were calculated by using equation 1.

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

where N_A is Avogadro's number.

The relative capacitance of $FeCl_3$ solutions in 50% (EtOH-H_2O) solvents in absence and presence of PVA were evaluating by dividing the measured capacitances in microfarad (μF) by that of water and their values are given also in Table 1.

Table 1. Molar volumes (V), relative capacitance (∈), solvated radii (r_s) in, Born equation constants A, B and mean activity coefficients ($\gamma_\pm$) of different $FeCl_3$ solutions in 50% mixed EtOH-H_2O+10% PVA solutions at 298.15 K

C_m mole/L	V cm³/mol	∈	r_sx10⁻⁸ cm	A	B	log $\gamma_\pm$
0.084	209.30	11	4.36	9.71	0.88	-4.00
0.1	207.43	12	4.35	8.52	0.84	-3.75
0.15	200.25	13.5	4.30	7.14	0.79	-3.58
0.21	202.76	15.5	4.32	5.81	0.74	-3.24
0.25	204.03	17	4.33	5.06	0.71	-2.99
0.34	197.81	19.5	4.28	4.11	0.66	-2.72
0.42	202.76	22	4.32	3.43	0.62	-2.44
0.52	202.76	25.5	4.32	2.75	0.58	-2.13

Table 2. Molar conductance (Λ in ohm⁻¹ cm²), dissociation degrees (α) and association constants (K_A) for $FeCl_3$ in 50% EtOH-H_2O+10% PVA solutions in absence and presence of magnetic field of power 1.26 K Gauss at 298.15 K

C_m mole/L	A			P		
	Λx10³	α	K_A	Λx10³	α	K_A
0.084	2.8	0.8	1.06x10¹⁴	3.01	0.717	2.81x10¹⁴
0.1	2.7	0.771	1.4x10¹³	2.9	0.690	3.6x10¹³
0.15	2.5	0.714	5x10¹²	2.65	0.631	6.1x10¹²
0.21	2.35	0.671	1,2x10¹¹	2.4	0.571	3.65x10¹¹
0.25	2.2	0.629	1.9x10¹⁰	2.2	0.524	6.2x10¹⁰
0.34	2.01	0.574	1.9x10⁹	1.9	0.452	7.5x10⁹
0.42	1.9	0.543	1.97x10⁸	1.7	0.405	9.98x10⁸
0.52	1.7	0.486	2.1x10⁷	1.4	0.333	1.44x10⁸

A: $\Lambda_o = 3.5$x10³
P: $\Lambda_o = 4.2$x10³

The mean activity coefficients ($\gamma_\pm$) were calculated by the use of the modified Born equation[12] as explained by equation (2)

$$\log \gamma_\pm = \frac{-A Z^+ Z^- \sqrt{C}}{1 + B\, r_s\, \sqrt{C}} \qquad (2)$$

$$A = \frac{1.823 x 10^6}{(\varepsilon.T)^{1.5}} \text{ and } B = \frac{50.29}{(\varepsilon.T)^{0.5}} \qquad (3)$$

Where

Z^+, Z^- are the charges of the positive and negative ions of the electrolyte used, r_s the solvated radii and A, B are constants. ∈ is the experimental relative capacitance for $FeCl_3$

solutions.

The calculated mean activity coefficients are presented in Table 2 for $FeCl_3$+50% (EtOH-H_2O) solutions in presence of 10% by weight of PVA at 298.15 K are presented also in Table 1, with decreasing their values by increasing electrolyte concentrations.

For calculating the association constants for 1:3 asymmetric electrolytes new equation can be derived as follows:

$$A^{+3} + 3B^- \xrightleftharpoons{K_A} AB_3 \qquad (3)$$

$$K_A = \frac{1-\alpha}{27 C_m^3 \alpha^4} \qquad (4)$$

$$\alpha \text{ (dissociation degree)} = \frac{S(Z)\Lambda}{\Lambda_O} \qquad (5)$$

By substitute α value from equation (5) in equation (4) we get:

$$K_A = \frac{\Lambda_o^3 (\Lambda_o - \Lambda)}{27 C_m^3 \gamma_\pm^3 \Lambda^4 S(Z)^3} \qquad (6)$$

This last equation is simple and derived from Fuoss-Shedlovsky theory and the Ostwald dilution law[8]. Knowing that S(Z) factor is approximately equal one for $FeCl_3$+50% (EtOH-H_2O) solutions in presence of PVA.

The molar conductance of $FeCl_3$ were estimated from the measured specific conductance by the apply the equation[13] 8.

$$\Lambda = \frac{K_s . K_{cell} . 1000}{C_m} \qquad (7)$$

K_s is the measured specific conductance, K_{cell} is the cell constant which equal 0.96 and C_m is $FeCl_3$ concentrations in mole/L. On drawing the relation between molar conductances and square root of molar $FeCl_3$ concentrations, straight lines are obtained in 50% (EtOH-H_2O) solvents in presence of 10% by weight PVA. Extrapolating there lines to $\sqrt{C} = 0$, the limiting molar conductivity Λ_o was obtained.

The same relation was obtained from the measured specific conductivities in presence of two poles of permanent magnet of power 1.26 K. Gauss.

From Λ, Λ_o values, the association constants (K_A) for $FeCl_3$+50% (EtOH-H_2O)+10% PVA solvents in presence and absence of magnetic field were calculated by applying equation (7) and their data are presented in Table 2.

The dissociation degrees (α) were also evaluated for $FeCl_3$+50% (EtOH-H_2O)+10% PVA in absence and presence fo magnetic field (see Table 2) and for $FeCl_3$+50% EtOH-H_2O+10% PVA in absence and presence of magnet (see Table 2).

It was observed that K_A) values decrease with increase $FeCl_3$ concentrations due to the decrease in the dissociation degree. PVA favour very high $FeCl_3$ associations, i.e., increase the K_A values. This prove that the association of electrolyte ions took place easier through polymer media. Also the magnet increase also the association constants of $FeCl_3$+50% EtOH-H_2O+10% PVA which indicate that the magnet attract the cations and therefore facilitate the association through its surface.

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