Influence of Permanent Magnet on the Association Constants of $FeCl_3$ in 50 % Ethanol−H_2O Solutions (Conductometrically) at 298.15 K Using a New Equation for 1:3 Asymmetric Electrolytes[†]

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The external two poles of a permanent magnet of a power of 1.26 kG were used to study their effect on the conductance values of $FeCl_3$ in a 50 % by weight mixed ethanol−H_2O solvent. The results were compared with values in the absence of the magnet. A new equation for the 1:3 asymmetric association was obtained and used for the calculation of the association constants (K_A) for $FeCl_3$ solutions in a 50 % ethanol (EtOH)−H_2O solvent in the 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.

Introduction

Many authors have studied the association constants of many salts in solutions conductometrically like Barthel[1] and Deepa.[2] Ion−solvent interactions have been explained in different electrolytes and polymers using conductivity, relaxation, and Fourier transform infrared (FTIR) measurements,[1] Shchori et al. and Luz[3,4] used conductivity to study the complexation of Na^+ with some crown ethers in DMF solutions.

Different Fuoss theories have been used for the estimation of the association constants (K_A) for symmetric electrolytes, like the Fuoss−Shedlovsky, Fuoss−Kraus, Fuoss−Edelson, and Fuoss−Debye theories.[5,6]

A new equation is needed for 1:3 asymmetric electrolytes which facilitate the calculation of K_A (association constant) easily.

The purpose of study is to apply a new equation for the asymmetric 1:3 salts in solutions derived from the Fuoss−Shedlovsky theory and Ostwald dilution law,[6] which are needed for evaluating chemical engineering data. This work also studied the effect of a magnet on the association of strong 1:3 electrolytes which had not been studied before in the literature.

Ferric chloride has many applications like, etching copper in ferric chloride solutions[7] and forming with phenylalanine agar used for the differentiation of enteric bacilli on the basis of their ability to produce phenylpyruvic acid by oxidative deamination. The $FeCl_3$ reagent visualizes the phenylalanine deamination reaction.[8]

Experimental Section

Ferric chloride was obtained from Merck and ethanol from BDH and were used without further purification; 5 mL aliquots of mixed 50 % bidistilled water and ethanol (by volume) were put in test tubes, and then different concentrations of $FeCl_3$ were added and dissolved. After preparing the solutions, they were left for more than one day in a water thermostat of the type Polyscience 8105 (USA) at 298.15 K.

The necessary volumes from each test tube were withdrawn and measured using conductivity, capacitance, and density techniques.

The density measurements were done by taking 1 mL of the prepared solutions, placing them in a specific gravity bottle (1 mL capacity), and weighing using a digital Mettler (Toledo, USA) analytical balance. The density values have been used to calculate the solvated radii.[9,10] Conductances and capacities were measured by using a multimeter of the type Macom (MX620) with a sensitivity of 0.1 %.

A dipping type conductivity cell, with two carbon electrodes with 1 cm apart and a cell constant equal to 0.96, was used. At least two readings were done for each measurement.

The conductance values of all $FeCl_3$ solutions were corrected by subtracting their values from that of the mixed 50 % by ethanol−H_2O solvent. The temperature was adjusted to 298.15 K with a precision of ± 0.05 K.

Two poles of a permanent magnet (model G.M-54) was used with a power of 1.26 kG by touching the magnet to the surface of the tube containing the solution.

The measured $FeCl_3$ solutions were put between the two external magnetic poles, and the conductivities were remeasured.

Results and Discussion

From the densities measured for $FeCl_3$ in a 50 % by volume ethanol−H_2O solvent, the molar volumes were evaluated by dividing the molecular weight of $FeCl_3$ by the densities, and the evaluated volumes are represented in Table 1.

From the molar volumes, the solvated radii r_s in Å units for $FeCl_3$ in 50 % EtOH−H_2O solutions were calculated by using eq 1.[11]

$$r_s = \sqrt[3]{V.0.239N_A} \qquad (1)$$

where V is the molar volume of $FeCl_3$ (molecular weight divided by the solution density) and N_A is Avogadro's number.

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Table 1. Molar Volumes (*V*), Relative Capacitance (∈), Solvated Radii (r_s), Born Equation Constants *A* and *B*, and Mean Activity Coefficients ($\gamma_\pm$) of Different $FeCl_3$ Solutions in a 50 % Mixed EtOH−H_2O Solvent at 298.15 K

C_m	V					
$mol \cdot L^{-1}$	$cm^3 \cdot mol^{-1}$	∈	$r_s \cdot 10^{-8}$	A	$B \cdot 10^8$	$\log \gamma_\pm$
0.084	212.03	24	4.38	3.01	0.60	−1.49
0.1	214.84	26	4.40	2.67	0.57	−1.41
0.15	221.90	28.5	4.45	2.33	0.55	−1.39
0.21	231.72	32.5	4.51	1.91	0.51	−1.28
0.25	238.19	35	4.55	1.71	0.49	−1.21
0.34	252.66	41	4.64	1.35	0.46	−1.06
0.42	269.89	47	4.75	1.10	0.43	−0.93
0.52	293.32	54	4.88	0.89	0.40	−0.81

The relative capacitance (∈) for $FeCl_3$ in 50 % EtOH−H_2O solutions was evaluated by dividing the measured capacitances in microfarads (μF) by that of water, and their values are also given in Table 1.

The mean activity coefficients of $FeCl_3$ in 50 % EtOH−H_2O solutions were calculated by the use of the modified Born equation[12] as given in eq 2.

$$\log \gamma_\pm = -\frac{AZ^+Z^-\sqrt{C_m}}{1 + Br_s\sqrt{C_m}} \tag{2}$$

The constants:

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

where Z^+ and Z^- are the charges of the positive and negative ions of the electrolyte used, r_s the solvated radii, and *A* and *B* are Born constants. ∈ is the relative capacitance for 50 % EtOH−H_2O, $FeCl_3$ solutions. C_m is the ferric chloride concentration. The calculated activity coefficients are presented in Table 1 also.

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

$$A^{+3} + 3B^- \overset{K_A}{\rightleftharpoons} AB_3 \tag{3}$$

$$K_A = \frac{1 - \alpha}{27{C_m}^3\alpha^4} \tag{4}$$

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

where $S(Z)$ is the Fuoss−Shedlovsky parameter, Λ is the molar conductivity, and Λ_o is the molar conductance at infinite dilution.

By substituting the α value from eq 5 in eq 4, we get:

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

Equation 6 is simple in application and derived from the Fuoss−Shedlovsky theory and Ostwald dilution law.[5] It is known that the $S(Z)$ factor for all stong electrolytes[13] is approximately equal to one in different solvents.

Table 2. Molar Conductance (Λ) in $cm^2 \cdot \Omega^{-1}$, Dissociation Degrees (α), and Association Constants (K_A) for $FeCl_3$ in a 50 % EtOH−H_2O Solvent in the Absence (*A*) and Presence (*P*) of a Magnetic Field of Power 1.26 kG at 298.15 K[a]

C_m	*A*			*P*		
$mol \cdot L^{-1}$	$\Lambda \cdot 10^3$	α	K_A	$\Lambda \cdot 10^3$	α	K_A
0.084	2.1	0.84	$6.13 \cdot 10^5$	2.8	0.683	$2.78 \cdot 10^6$
0.1	2.0	0.80	$3.05 \cdot 10^5$	2.65	0.646	$1.27 \cdot 10^6$
0.15	1.9	0.76	$1.23 \cdot 10^5$	2.4	0.585	$6.06 \cdot 10^5$
0.21	1.8	0.72	$2.8 \cdot 10^4$	2.1	0.512	$1.90 \cdot 10^5$
0.25	1.7	0.68	$1.49 \cdot 10^4$	1.9	0.463	$1.16 \cdot 10^5$
0.34	1.6	0.64	$2.97 \cdot 10^3$	1.55	0.378	$4.21 \cdot 10^4$
0.42	1.5	0.60	$9.15 \cdot 10^2$	1.3	0.317	$2.00 \cdot 10^4$
0.52	1.4	0.56	$3.1 \cdot 10^2$	0.95	0.232	$1.85 \cdot 10^4$

[a] *A*: $\Lambda_o = 2.5 \cdot 10^3$. *P*: $\Lambda_o = 4.1 \cdot 10^3$.

The molar conductance of $FeCl_3$ solutions was estimated from the measured specific conductances by applying eq 7.[13]

$$\Lambda = \frac{K_s \cdot K_{cell} \cdot 1000}{C_m} \tag{7}$$

where K_s is the measured specific conductance, K_{cell} is the cell constant which equals 0.96, and C_m is the $FeCl_3$ concentration in $mol \cdot L^{-1}$. On drawing the relation between molar conductances and the square root of the $FeCl_3$ concentration, straight lines are obtained in the absence and presence of the magnet in a 50 % EtOH−H_2O mixed solvent. Extrapolating these lines to zero concentration, the limiting molar conductances, Λ_o, were obtained.

The measured molar conductance values for ferric chloride agree well with that of literature values.[14]

From Λ and Λ_o values, the association constants (K_A) for $FeCl_3$ in 50 % EtOH−H_2O solutions in the presence and absence of a magnetic field were calculated, and their results are given in Table 2. The dissociation degrees α were also calculated for $FeCl_3$ solutions in the absence and presence of the permanent magnet, and these data are also given in Table 2. It was observed from Tables 1 and 2 that the activity coefficients increase with an increase in the $FeCl_3$ concentrations due to the increase of ion−ion interactions.

It is concluded from Tables 1 and 2 that the association constants decreased for all solutions in the presence of the magnet due to more cation attraction near the magnet. This indicated that the ferric ion prefers to attract to the magnet than migrate to the bulk solution, causing a decrease in both association constants and dissociation degrees.

It is also concluded that a simple equation could be used for evaluating the association constant, giving logical data, rather than that of the complicated Fuoss−Shedlovsky theory.[6]

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