

Ion association of anhydrous ferric chloride in primary alcohols at different temperatures

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Abstract

Conductance measurements at nine different temperatures between 283.15 and 323.15 K are reported for anhydrous ferric chloride (FeCl_3) in primary alcohols: methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH) and 1-butanol (1-BuOH). Also, to analyze conductivity data, density and viscosity values of the primary alcohols have been determined experimentally at the same temperatures. The ion association constants (K_A) between ferric (Fe^{3+}) cation and chloride (Cl^-) anion were calculated by using conductivity data in terms of the Robinson–Stokes equations. The K_A values calculated for ferric chloride in primary alcohols decreased in the order of 1-BuOH > 1-PrOH > EtOH > MeOH. This was equivalent to the ion association constants increasing with a decrease in the relative permittivity of the alcohols. The K_A values increased with the increase in temperature for ferric chloride in primary alcohols.

Thermodynamic functions (Gibbs' free energy, entropy and enthalpy of ion association) were estimated from the temperature dependence of the ion association constant. Gibbs' free energy values for FeCl_3 were found to be negative in 1-PrOH and 1-BuOH whereas they were positive for MeOH and EtOH. The positive values of entropy and enthalpy found in the present study indicate that the association process is endothermic.

The limiting molar conductivities of Fe^{3+} in non-aqueous MeOH, EtOH, 1-PrOH and 1-BuOH were determined from experimental data by using the Kohlrausch equation.

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1. Introduction

Recently, ion association for unsymmetrical electrolytes and complexes in alcohol–water mixtures and alcohols at various temperatures were determined from conductance data in terms of Robinson–Stokes equations [1–3].

In a wide temperature range, conductivity measurements for electrolyte solutions can give detailed information for ion–ion and ion–solvent interactions [3,4]. From the conductivity measurements at varying temperatures between 273.15 and 323.15 K for potassium sulfate solutions, it was found that there were weak ion–ion interactions and the ion association constants were minimized at characteristic temperatures [3].

The conductance behavior of unsymmetrical electrolytes, particularly in non-aqueous solvents, has received relatively little attention. This is due in large part to the difficulty encountered in

analyzing such data since the usual methods require an arbitrary choice for some of the parameters required for the analysis [5].

Primary alcohols (MeOH, EtOH, 1-PrOH, 1-BuOH) are polar solvents having lower relative permittivity than that of water. Alcohols associate in the liquid by hydrogen bonding. In primary alcohols, ionic association is interpreted in terms of a multiple-step association process involving hydrogen-bonded solvation of anions in the homologous series methanol through 1-pentanol by Matesich et al. [6].

Anhydrous FeCl_3 is a fairly strong Lewis acid, and it is used as a catalyst in organic synthesis. In previous studies, association of Fe^{3+} ion with Cl^- ion in aqueous solutions was determined by spectrophotometric [7] and potentiometric methods [8]. In spectroscopic study, it was observed that the association constant for ferric chloride was $30 \text{ dm}^3 \text{ mol}^{-1}$ at 298.15 K and the association of Fe^{3+} ion with Cl^- ion is endothermal.

FeCl_3 is easily soluble in water and alcohols. It seems interesting to study conductometrically the association equilibrium of FeCl_3 in various primary alcohols. Thus, in this study, it

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Table 1
Molar concentrations (c) of FeCl_3 solutions used for conductivity measurements in various primary alcohols

Solution	$10^4 c$ (mol dm $^{-3}$)			
	MeOH	EtOH	1-PrOH	1-BuOH
1	2.030	2.265	2.646	3.010
2	2.665	2.880	3.326	3.785
3	3.400	3.575	4.115	4.645
4	4.185	4.567	5.078	5.450
5	4.972	5.450	5.976	6.510
6	5.880	6.480	6.990	7.590
7	6.975	7.415	8.075	8.848
8	8.065	8.568	9.084	10.050
9	9.175	9.724	10.465	11.290
10	10.295	10.865	11.735	12.678

was attempted to obtain some information on the association of Fe^{3+} ion with Cl^- ion by conductometric measurements at various temperatures. The association constants for FeCl_3 in non-aqueous MeOH, EtOH, 1-PrOH and 1-BuOH were determined by analyzing conductivity data in terms of Robinson–Stokes equations. From conductivity data, the temperature dependence of the limiting ionic conductivity of the Fe^{3+} ion in non-aqueous alcohols was also determined in the present study. Ion association constants and the thermodynamic parameters were calculated and compared with each other according to interaction of solvent at different temperatures.

2. Experimental

2.1. Materials

Anhydrous FeCl_3 was a Merck (Darmstadt, Germany) product. It was purified by sublimation under an atmosphere of hydrogen chloride gas. Alcohols used (MeOH, EtOH, 1-PrOH, 1-BuOH) in pro analysis grade were supplied by Merck. They were dehydrated by chemical methods and purified as reported previously [9,10].

2.2. Solutions

All solutions were prepared by mass. Conversion of molality to molarity was performed by using a standard equation [11]. Molar concentrations (c) of FeCl_3 solutions in primary alcohols are given in Table 1.

The specific conductances of alcohols used in the present study at 298 K were determined to be 2.84×10^{-6} , 1.57×10^{-6} , 3.92×10^{-7} and 2.94×10^{-7} S cm $^{-1}$ for MeOH, EtOH, 1-PrOH and 1-BuOH, respectively.

2.3. Density and viscosity measurements

Density (ρ) measurements of MeOH, EtOH, 1-PrOH and 1-BuOH at varying temperatures between 283.15 and 323.15 K were performed by using a Wertheim pycnometer of 50 cm 3 capacity with a coupled thermometer. The change in temperature during the density measurements was ± 0.01 K. The

Table 2
Densities (ρ) of primary alcohols at different temperatures

T (K)	ρ (g cm $^{-3}$)			
	MeOH	EtOH	1-PrOH	1-BuOH
283.15	0.8054	0.7987	0.8111	0.8177
288.15	0.8002	0.7937	0.8070	0.8135
293.15	0.7958	0.7894	0.8031	0.8095
298.15	0.7910	0.7851	0.7990	0.8058
303.15	0.7862	0.7808	0.7951	0.8023
308.15	0.7815	0.7763	0.7911	0.7990
313.15	0.7765	0.7722	0.7869	0.7958
318.15	0.7724	0.7665	0.7811	0.7929
323.15	0.7669	0.7616	0.7788	0.7902

average uncertainty of density was estimated to be lower than ± 0.002 g cm $^{-3}$. The density values measured for MeOH, EtOH, 1-PrOH and 1-BuOH are presented in Table 2.

An Ostwald-type viscometer was used for viscosity (η) measurements. The flow time for the viscometer with a precision stop watch ranged between 400 and 800 s. The experimental viscosity values were calculated on an average of five measurements. The accuracy of the experimental viscosity data was within ± 0.003 mPa s. To calibrate the viscometer redistilled water was employed. The temperature was controlled with a thermostated water bath (Veb MLW type 3230) with a precision of ± 0.01 K. The viscosity values determined for primary alcohols are shown in Table 3.

2.4. Conductivity measurements

Conductance measurements were carried out on a digital conductivity meter (CMD 750 WPA model) with a sensitivity of 0.1%. The conductivity cell used was a three-necked flask with a water jacket which was equipped with platinized electrodes. The cell constant was 0.98 cm $^{-1}$ at 298.15 K.

For every solution, the measurements were carried out by starting at 283.15 K and elevating the temperature to 323.15 K in steps of 5 K.

The conductance measurements for FeCl_3 in MeOH, EtOH, 1-PrOH and 1-BuOH were performed at ten different

Table 3
Viscosities (η) of primary alcohols at different temperatures

T (K)	η (mPa s)			
	MeOH	EtOH	1-PrOH	1-BuOH
283.15	0.661	1.460	2.387	3.631
288.15	0.623	1.328	2.495	3.291
293.15	0.590	1.308	2.201	2.925
298.15	0.552	1.083	1.970	2.620
303.15	0.503	0.990	1.721	2.300
308.15	0.462	0.915	1.591	2.020
313.15	0.422	0.822	1.376	1.761
318.15	0.383	0.764	1.251	1.542
323.15	0.353	0.702	1.131	1.341

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