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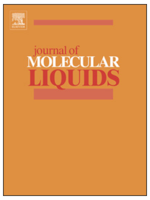

A conductivity study of dilute aqueous solutions of tetramethylammonium hexacyanoferrate(III), tetraethylammonium hexacyanoferrate(III) and benzyltrimethylammonium hexacyanoferrate(III)

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ABSTRACT

Electrical conductivities of tetramethylammonium hexacyanoferrate(III), tetraethylammonium hexacyanoferrate(III) and benzyltrimethylammonium hexacyanoferrate(III) in dilute aqueous solutions, in the 278.15 K to 313.15 K temperature range are reported. These conductivities are examined in terms of the molecular model which includes an existence of three ion species in the solution, the principal cation and anion and the additional anion formed by the association between them. Based on this molecular model, the representation of conductances was performed using the Quint-Viallard conductivity equation and the Debye-Hückel expression for activity coefficients. The thermodynamic of ion pair formation is discussed in terms of ion-solvent interactions.

1. Introduction

Tetraalkylammonium hexacyanoferrates(III) are employed as supporting electrolytes for electrochemistry measurements and oxidizing reagents with tunable redox potential in water and various non-aqueous solvents [1]. Among others, tetraalkylammonium salts are used as a model hydrophobic solute for investigation of solute-solvent, solute-solute and solvent-solvent interactions [2,3]. Recently, tetraalkylammonium ions were used in investigations of structuring and dynamical phenomena in reaction of ascorbate monoanion with hexacyanoferrate(III) [4,5]. It turned out that the association between tetraalkylammonium cation and hexacyanoferrate(III) anion plays an important role in modulating the reaction mechanism of this proton coupled electron transfer reaction.

A survey of the literature data reveals that the ion association in these systems has been studied by ^{1}H NMR in deuterated water and deuterated mixed solvents [6,7] and by potentiometry [8] and cyclic voltammetry in aqueous solutions [9]. The evidence of ion pairs or at least specific interactions between tetraalklyammonium ions and hexacyanoferrate(III) anion are reported for these systems, and the ion-pair formation constants are estimated from 8 to 21 depending on various molecular models in concentration range from 0.02 to 3.5 M. In dilute aqueous solutions no quantitative treatment was made so far.

In this work, systematic determinations of electrical conductances of tetramethylammonium hexacyanoferrate(III), $(Me_4N)_3Fe(CN)_6$, tetraethylammonium hexacyanoferrate(III), $(Et_4N)_3Fe(CN)_6$, and benzyltrimethylammonium hexacyanoferrate(III), $(BzMe_3N)_3Fe(CN)_6$, in the 278.15–313.15 K temperature range, in dilute aqueous solutions are presented. The obtained experimental data are examined by applying the Quint-Viallard conductivity equations [10] by assumption that at dissolution of tetraalkyl- or aryltrialkyl- ammonium hexacyanoferrates(III) ($(R_4N)_3Fe(CN)_6$, $R_4 = Me_4, Et_4, BzMe_3$) in water three ions exist in the solution: R_4N^+, $Fe(CN)_6^{3-}$ and $[R_4NFe(CN)_6]^{2-}$. The thermodynamic of formation process of charged ion pair $[R_4NFe(CN)_6]^{2-}$ is also discussed.

2. Experimental

2.1. Materials

Tetramethylammonium hexacyanoferrate(III), $(Me_4N)_3Fe(CN)_6$, was prepared according to the procedure described by Khoshtariya et al. [11] by mixing 3.8 g of tetramethylammonium chloride (Sigma reagent

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grade ≥ 98, previously recrystallized from acetonitrile, dried and stored under nitrogen) with 3.8 g $K_3Fe(CN)_6$ (Merck, *p.a.* grade) each dissolved in 20 ml of doubly distilled water and cooled to 0 °C for 3 h. The yellow crystals precipitate was washed with cold water, dried in a vacuum, recrystallized from water and acetonitrile (yield 3.4 g) and stored under nitrogen in dark.

Benzyltrimethylammonium hexacyanoferrate(III), $(BzMe_4N)_3Fe(CN)_6$, was prepared with similar procedure as described above by mixing 9.6 g of benzyltrimethylammonium chloride (Sigma-Aldrich, purum ≥98, previously recrystallized from acetonitrile, dried and stored under nitrogen) with 5.7 g $K_3Fe(CN)_6$ (Merck, *p.a.* grade) each dissolved in 30 ml of doubly distilled water and cooled to 0 °C for 6 h. The yellow crystals precipitate was washed with cold water, dried in a vacuum, recrystallized from water and acetonitrile (yield 4.8 g) and stored under nitrogen in dark.

Tetraethylammonium hexacyanoferrate(III), $(Et_4N)_3Fe(CN)_6$, was prepared according to the procedure described by Mascharak [1] with some modifications. The 3.2 g of $K_3Fe(CN)_6$ (Merck, *p.a.* grade) was added in solution of 4.0 g tetraethylammonium chloride (Sigma, reagent grade ≥ 98, previously recrystallized from acetonitrile, dried and stored under nitrogen) dissolved in 40 ml of acetonitrile (Merck, gradient grade for liquid chromatography) under nitrogen and in dark. After 24 h of stirring, the mixture was filtered and centrifugated, and clear yellow supernatant was concentrated under reduced pressure and shaken with 100 ml of diethyl ether. The obtained yellow powder was filtered, recrystallized from water and acetonitrile (yield 2.8 g) and stored under nitrogen in dark.

The ^1H NMR, ^{13}C NMR, UV–Vis and ESI MS spectra obtained for the prepared tetraalkyl- and aryltrialkyl- ammonium hexacyanoferrate (III) s are in accordance with the corresponding structures and no contaminants other than water and trace of organic solvents used in preparation (acetonitrile) were detected.

The content of water in the samples was analyzed through Karl Fischer titration and was taken into account in calculating the concentrations. Stock solutions were prepared by mass from pure compounds and demineralized distilled water. Demineralized water was distilled two times in a quartz bidestillation apparatus (Destamat Bi 18E, Heraeus). The final product with specific conductivity $<6 \cdot 10^{-7}$ S cm^{-1} was distilled into a flask permitting storage and transfer of water into the measuring cell under an atmosphere of nitrogen. The concentration of stock solutions was additionally checked by extinction measurements ($\varepsilon(\lambda = 420 \text{ nm}) = 1040 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

2.2. Conductivity measurements

The conductivities of the solutions were determined with the help of a three-electrode measuring cell, described elsewhere [12]. The cell was calibrated with dilute potassium chloride solutions [13] and immersed in the high precision thermostat described previously [14]. The temperature dependence of the cell constant was taken into account [13]. The water bath can be set to each temperature using a temperature program with a reproducibility of 0.005 K. The temperature in the precision thermostat bath was additionally checked with calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) in connection with a HP 3458A. The resistance measurements of the solutions in the cell were performed using a precision LCR Meter Agilent 4284A.

The three-electrode measuring cell was filled with a known mass of water (~660 g). Water conductivity was measured at all investigated temperatures. The change of concentration in the cell was carried out by successive additions of weighed amounts of stock solution, using a gas-tight syringe. The measuring procedure, including corrections and the extrapolation to infinite frequency in determination of specific conductivity values, has been previously described [14].

The densities, *d*, of the stock solutions and the final solutions in the conductivity cell were determined by the method of Kratky et al. [15] using a Paar densimeter (DMA 5000) combined with a precision thermostat. Their values are collected in Table S1 in Supplementary material. A linear change of *d* with increasing salt content for diluted solutions was assumed, $d(T) = d_0(T) + b\tilde{m}$, where $d_0(T)$ is the density of water, $\tilde{m}$ is the molonity of the electrolyte (moles of electrolyte per kilogram of solution) and b-coefficients are assumed as temperature independent. Thus, the molar concentrations *c* were determined from the masses and the corresponding densities of solutions *d*.

In all sets of the reported conductivity-concentration data (Table 1), the concentrations are given at 298.15 K and can be converted to other temperatures by using the relationship $c(T) = \tilde{m} \cdot d(T)$ by help of b-coefficients. These coefficients are given in the footnote of Table 1 and in Table S1 in Supplementary material. Considering the sources of error (calibration, measurements, impurities), the specific conductivities are estimated to be accurate within 0.5%.

3. Data analysis

According to the evidence from the ^1H NMR study of ion association between quaternary ammonium cations and hexacyanoferrate(III) anions [6, 7] it can be assumed that under dissolution in water of tetraalkyl- or aryltrialkyl- ammonium hexacyanoferrates(III) ($(R_4N)_3Fe(CN)_6$, $R_4 = Me_4, Et_4, BzMe_3$) three ions exist in the solution. The dissolution process can be represented by the following ionic reactions

$$\begin{aligned} &(R_4N)_3Fe(CN)_6 \rightarrow 3R_4N^+ + Fe(CN)_6^{3-} \\ &R_4N^+ + Fe(CN)_6^{3-} \rightleftharpoons [R_4NFe(CN)_6]^{2-} \end{aligned} \tag{1}$$

and the formation constant of the divalent anion formation is

$$K = \frac{\left[[R_4NFe(CN)_6]^{2-}\right]}{[R_4N^+]\left[Fe(CN)_6^{3-}\right]} Q \tag{2}$$

where Q is quotient of activity coefficients.

$$Q = \frac{f_{\{R_4NFe(CN)_6\}^{2-}}}{f_{R_4N^+} f_{Fe(CN)_6^{3-}}} \tag{3}$$

The activity coefficients of the individual ions in dilute solutions, f_j, can be approximated by the Debye-Hückel equations

$$\begin{aligned} &\log f_i = -\frac{z_i^2 A(T)\sqrt{I}}{1 + a_i B(T)\sqrt{I}} \\ &A(T) = \frac{1.8246 \times 10^6}{[D(T)T]^{3/2}} \quad ; \quad B(T) = \frac{50.29 \times 10^8}{[D(T)T]^{1/2}} \end{aligned} \tag{4}$$

where $D(T)$ is the dielectric constant of water, a_i is the ion size parameter and *I* denotes the ionic strength of the solution, which is $I = c(6\text{-}3\alpha)$. Values of the size parameters were prescribed and are assumed to be temperature independent [16,17]. They are: $a(Fe(CN)_6)^{3-} = 4.0$ Å, $a(Me_4N^+) = a(Et_4N^+) = 7.0$ Å, $a(Me_3BzN^+) = 8.0$ Å, $a([Me_4NFe(CN)_6]^{2-}) = a([Et_4NFe(CN)_6]^{2-}) = 5.5$ Å, and $a([Me_3BzNFe(CN)_6]^{2-}) = 6.5$ Å.

Concentrations of existing species in the solution are denoted by.

$$\begin{aligned} &[(R_4N)_3Fe(CN)_6] = c \\ &[R_4NFe(CN)_6]^{2-} = c\alpha \\ &[Fe(CN)_6]^{3-} = c\beta = c(1-\alpha) \\ &[R_4N^+] = c(3-\alpha) \end{aligned} \tag{5}$$

and the formation constant from Eq. (2) can be written as

$$K = \frac{\left[[R_4NFe(CN)_6]^{2-}\right]}{[R_4N^+]\left[Fe(CN)_6^{3-}\right]} Q = \frac{\alpha}{c(1-\alpha)(3-\alpha)} Q \tag{6}$$

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