# CONDUCTIVITY STUDY OF ASSOCIATION OF $K_2Mg[Fe(CN)_6]$, $K_2Ca[Fe(CN)_6]$ AND $K_2Ba[Fe(CN)_6]$ IN AQUEOUS SOLUTIONS

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The stability constants, $K_p^0$, of ion pairs $M^{2+}.[Fe(CN)_6]^{4-}$ and their equivalent conductivities, $\lambda_p^0$, at infinite dilution were evaluated by means of two-parameter fitting from the conductivities measured in very diluted aqueous solutions of double hexacyanoferrates of the type $K_2M(II).[Fe(CN)_6]$ at 25°C with the use of the limiting Debye–Hückel formula for ionic activity coefficients and Onsager limiting formula for the conductivity of strong electrolytes extended to electrobyte mixtures. Thus, $K_p^0 = 0{\cdot}66, 0{\cdot}72$, and $0{\cdot}76 \,.\, 10^4$ dm$^3$/mol and $\lambda_p^0 = 46, 49$, and 53 S cm$^2$/val, respectively.

We found in our preceding work[1,2] that the curves of the concentration dependence of $\log K_p$ for ionic pairs $M^{3+}.[Fe(CN)_6]^{4-}$, determined from the molal conductivity $\Lambda$ according to the Debye–Hückel theory, reveal sharp breaks at a certain critical dilution, where the slope changes its sign. These breaks, observed with simple[2] cyanoferrates and cyanoruthenates of $La^{3+}$ and $Pr^{3+}$ as well as with double salts[1] $KLa[Fe(CN)_6]$ and $KLa[Ru(CN)_6]$, were interpreted as a result of a two-step hydrolysis of $M^{3+}$ cations accompanied with exceeding the solubility product of the hydroxide $M(OH)_3$ during diluting the solution. It was shown[1] that with three-valent cations the ionic product $[M^{3+}].[OH^-]^3$ can in the homogeneous region increase during diluting the solution only if the prevailing equilibrium in the solution is a hydrolytic equilibrium of the order $j < 3$.

A generalization of the calculation expressed by Eqs (*12*) and (*13*) in ref.[1] to $n$-valent cations leads in the homogeneous region to the expression for the ionic product of the hydroxide:

$$[M^{n+}].[OH^-]^n = \text{const.}\; j^{3/(j+1)}.[M^{n+}]^{(j-n+1)/(j+1)}\,, \qquad (1)$$

whence it follows that for $n = +3$ it is possible to obtain the desired negative value of the exponent on the right side only for $j = 1$, *i.e.*, when cation hydrolysis to the first stage prevails in the solution; and for $n = +2$ no physically real value of $j$

exists for which the ionic product of the hydroxide would increase with increasing dilution. Hence, in the case of divalent cations no breaks on the log $K_p$ dependences should be formed if they are really due to a transition from a homogeneous system to a system with a precipitated (or colloidal) hydroxide; and in the case of cations such as $Ca^{2+}$ and $Ba^{2+}$ they should not be formed simply because the solubility of their hydroxides is higher than the concentrations used in our work.

To verify this conclusion and to compare the stability and conductivity of ion pairs of the type $M^{2+}.[Fe(CN)_6]^{4-}$ with previously studied $M^{3+}.[Fe(CN)_6]^{4-}$, similar conductivity measurements as in the previous work[1,2] were carried out with solutions of double salts of the type $K_2M(II)[Fe(CN)_6]$ at concentrations smaller than $10^{-3}$ mol dm$^{-3}$, where according to James[3] practically no association of $K^+$ ions with divalent ion pairs $M^{2+}.[Fe(CN)_6]^{4-}$ takes place, hence only the latter need to be taken into account in evaluating the experimental data.

## EXPERIMENTAL

Potassium-magnesium, potassium-calcium, and potassium-barium hexacyanoferrates were prepared according to Abegg[4] from $K_4Fe(CN)_6$ and the corresponding chlorides $MeCl_2$. The obtained products were recrystallized from redistilled water and dried on the air to constant weight. The complex was in all three cases determined by potentiometric titration with 0·1M-AgNO$_3$, barium and calcium gravimetrically as carbonates, and magnesium gravimetrically as $MgNH_4PO_4$. Potassium was determined gravimetrically after precipitation with sodium tetraphenylboranate. Analysis gave the following results (calculated composition is given in parentheses):

| Formula | K, % | M(II), % | $Fe(CN)_6$, % |
|---|---|---|---|
| $K_2Mg[Fe(CN)_6].5\,H_2O$ | $19{\cdot}5_0$ (19·33) | $5{\cdot}8_5$ (6·00) | $52{\cdot}1_0$ (52·40) |
| $K_2Ca[Fe(CN)_6].3\,H_2O$ | $20{\cdot}5_0$ (20·35) | $10{\cdot}2_0$ (10·43) | $54{\cdot}7_5$ (55·15) |
| $K_2Ba[Fe(CN)_6].3\,H_2O$ | $16{\cdot}5_0$ (16·24) | $28{\cdot}3_0$ (28·52) | $43{\cdot}8_5$ (44·01) |

The conductivity of the solutions was measured at 25°C in a quartz glass conductivity cell with the same apparatus as earlier[1,2]. The solutions were prepared by weighing the samples on a Mettler microbalance and dissolving in a weighed quantity of water in the mentioned cell. Differences between molal and molar concentrations were neglected in view of the very low concentrations (of the order of $10^{-4}$ mol/dm$^3$ or about 0·03—0·2 g/dm$^3$, the volume effects being beyond the accuracy of the conductivity measurements). The dissolution was promoted by means of a quartz glass stirrer. The values of the molal conductivity $\Lambda$ were calculated from the measured conductivities corrected by subtracting the conductivity of water (the latter was in the range 5—10 . $10^{-7}$ S cm$^{-1}$, *i.e.*, by two orders of magnitude smaller than the solution conductivity).

## RESULTS AND DISCUSSION

The obtained values of $\Lambda_{exp}$ are given in Table I. They were used to calculate the dissociation degree $\alpha$ of the ion pair by an iterative procedure[1] from the equation

$$\Lambda_{exp} = 2\lambda_K + 2(1 - \alpha)\,\lambda_p + 4\alpha\lambda_{Fe(CN)_6} + 2\alpha\lambda_M\,. \tag{2}$$

The quantities $\lambda$ with subscripts are the equivalent conductivities of $K^+$ ions, ion pairs $M^{2+}.[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$, and $M^{2+}$ ions at a given composition of the solution. These were calculated from the Onsager's limiting equation for binary electrolytes, in which the following averaged values were substituted for the charge numbers $z$ and limiting equivalent conductivities $\lambda^0$:

$$z_+ = 2(1 + \alpha)/(2 + \alpha)\,, \quad z_- = -2(1 + \alpha)\,, \qquad (3), (4)$$

$$\lambda_+^0 = (\lambda_K^0 + \alpha\lambda_M^0)/(1 + \alpha)\,, \qquad (5)$$

$$\lambda_-^0 = [(1 - \alpha)\,\lambda_p^0 + 2\alpha\lambda_{Fe(CN)_6}^0]/(1 + \alpha)\,. \qquad (6)$$

The value of $\lambda_p^0$ was set by trial equal to 45 and 50 S cm$^2$ val$^{-1}$ for $M = Mg$, 50 and 60 S cm$^2$ val$^{-1}$ for $M = Ca, Ba$. In the first iteration, all values of $\lambda$ in (2) were set equal to their limiting values $\lambda^0$ and the dissociation degree $\alpha$ thus obtained

$$\alpha = (0{\cdot}5\Lambda_{exp} - \lambda_K - \lambda_p)/(2\lambda_{Fe(CN)_6} + \lambda_M - \lambda_p) \qquad (7)$$

TABLE I

Molar Conductivities $\Lambda$ (S cm$^2$ mol$^{-1}$) of Potassium–Magnesium (*a*), Potassium–Calcium (*b*), and Potassium–Barium (*c*) Hexacyanoferrates(II) in Aqueous Solutions in Dependence on Molality $m$ ($10^{-4}$ mol/kg) at 25°C

| $c_a$ | $\Lambda_a$ | $c_b$ | $\Lambda_b$ | $c_c$ | $\Lambda_c$ |
|---|---|---|---|---|---|
| 5·650 | 444·9 | 5·696 | 446·3 | 4·288 | 469·1 |
| 4·137 | 465·7 | 4·997 | 456·0 | 3·822 | 477·8 |
| 3·579 | 476·8 | 4·207 | 467·6 | 3·508 | 483·6 |
| 3·038 | 489·3 | 3·715 | 476·1 | 3·136 | 492·4 |
| 2·948 | 491·2 | 3·116 | 489·7 | 2·600 | 505·2 |
| 2·517 | 502·8 | 2·638 | 501·0 | 2·387 | 511·1 |
| 2·216 | 510·4 | 2·340 | 509·1 | 2·188 | 517·4 |
| 2·120 | 512·5 | 1·943 | 521·2 | 1·887 | 525·2 |
| 1·935 | 518·6 | 1·745 | 527·6 | 1·648 | 535·9 |
| 1·694 | 527·7 | 1·483 | 538·4 | 1·417 | 545·6 |
| 1·551 | 533·1 | 1·308 | 546·3 | 1·318 | 550·4 |
| 1·253 | 544·6 | 1·129 | 555·5 | 1·212 | 556·5 |
| 1·188 | 549·1 | 0·927 | 565·4 | 1·035 | 566·6 |
| 1·054 | 556·2 | 0·799 | 577·5 | 0·914 | 573·2 |
| 0·856 | 567·2 | — | — | 0·772 | 583·0 |

was used in Eqs (*3*)–(*6*) to calculate approximate values of the parameters for the Onsager's limiting formula, which after introducing the approximate ionic strength given as

$$I = (3 + 8\alpha)\, m \tag{8}$$

gave the corrected values of $\lambda$. These were in turn introduced in Eq. (*7*) to obtain the second iteration, and so on.

The resulting degree of dissociation $\alpha$ was used to calculate at any given molality $m$ the concentration stability constant of the ion pair ("concentration quotient" or "stability quotient" after Nancollas):

$$K_p = m\alpha^2/(1 - \alpha) \tag{9}$$

(again, we neglect the difference between molar and molal concentrations). Fig. 1 shows a plot of $\log K_p$ thus obtained as a function of the square root of the ionic strength $I$ calculated from Eq. (*8*). Except for the highest concentrations (around $5 \cdot 10^{-4}$ mol dm$^3$, where apparently association of $Fe(CN)_6^{4-}$ with $K^+$ ions takes place), the experimental points lie on a straight line at each chosen value of the equivalent conductivity $\lambda_p^0$ of the ion pair. The logarithm of the thermodynamic constant $K_p^0$ of the ion pair obtained by extrapolation of these straight lines to $I = 0$ depends only slightly on the choice of $\lambda_p^0$, similarly as in the association with three-valent cations[1,2]. However, the latter influences considerably the slope of the straight

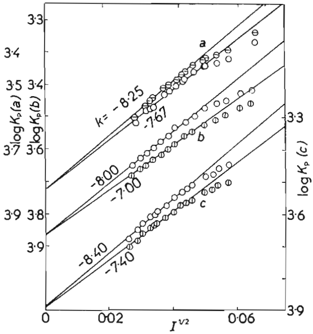

FIG. 1

Dependence of Stability Constant $K_p$ of $M^{2+}.[Fe(CN)_6]^{4-}$ Ion Pair in Solutions of $K_2M[Fe(CN)_6]$ on Ionic Strength $I$ at 25°C

Values of $\lambda_p^0$ for the ion pair (S cm$^2$ . . mol$^{-1}$): ⊖ 45, ○ 50, ⦶ 60; M = Mg (*a*), Ca (*b*), and Ba (*c*).

lines. By interpolating these slopes, we derived for each of the three systems under study such a value of $\lambda_p^0$ for which the slope of the experimental straight line coincides with the theoretical value of $-8{\cdot}14$ deduced from the Debye–Hückel limiting law for the given valence type of the associate. Thus, for M = Mg, Ca, and Ba we found $\lambda_p^0 = 46$, 49, and 53 S cm$^2$ val$^{-1}$ and the stability constants of ion pairs $K_p^0 = 6{\cdot}61$, 7·24, and 7·59 . $10^3$ dm$^3$ mol$^{-1}$, respectively. These are in fair agreement with the published data: James[3] and Davies[5] give p$K^0 = -3{\cdot}77$ for $CaFe(EN)_6$, Bjerrum[6] gives p$K^0 = -3{\cdot}87$ for $MgFe(CN)_6$. By logarithming our values of $K_p^0$ we obtain −3·82, −3·86, and −3·88, respectively.

The evaluated equivalent conductivities of ion pairs $\lambda_p^0$ are in a rough agreement with those found for associates with three-valent cations[1,2], namely they are somewhat lower, which can be attributed to a stronger hydration of the ion pair as a whole owing to its doubled total charge. The values of $\lambda_p^0$ decrease moderately in the sequence Ba–Ca–Mg similarly as the equivalent conductivities of the ions $M^{2+}$. Hence it seems that the reason is similar, *i.e.*, that $Mg^{2+}$ and $Ca^{2+}$, ions, which are in aqueous solutions more hydrated than $Ba^{2+}$, preserve this hydration order also in the ion pairs.

Breaks on the log $K_p - I^{1/2}$ curves, observed in systems with three-valent cations, were not observed with divalent ones even at the highest dilutions, as was expected on the assumption that the breaks are due to a two-stage hydrolysis with the formation of a precipitated (or colloidal) hydroxide during diluting the solution. This can be taken as a further evidence in favour of the mentioned assumption. Moreover, the earlier interpretation of both branches of the curve is substantiated, according to which the branch from the break toward higher concentrations (which in the case of divalent ions remained solely from both ones) corresponds to the dissociation of the ion pair.

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