

CONDUCTOMETRIC STUDY OF ASSOCIATION OF LANTHANUM
HEXACYANOFERRATE(II) AND PRASEODYMIUM
HEXACYANORUTHENATE(II) IN AQUEOUS SOLUTION

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Conclusions about association and hydrolysis of trivalent cations (M^{3+}) in the presence of cyanoferrate and cyanoruthenate were verified on solutions containing only $[Me(CN)_6]^{4-}$ anions and M^{3+} cations to eliminate influence of K^+ ions on the association. Owing to a partial hydrolysis of the anions during preparation of the starting salts, only the apparent stability constant of the ion pairs $M^{3+} \cdot [Me(CN)_6]^{4-}$ could be evaluated, which involves a small admixture of $M^{3+} \cdot H[Me(CN)_6]^{3-}$, and further the corresponding equivalent conductivity of the pairs, λ_p . An abrupt decrease of $\log K_p$ values observed with $KLa[Me(CN)_6]$ after exceeding the critical dilution and attributed to hydrolysis of the M^{3+} cation was with the simple La^{3+} and Pr^{3+} salts similar as with double salts of La^{3+} and hence is not specific for the La^{3+} ion or for the combination $M^{3+} + K^+$.

In the preceding work¹ we analysed the concentration dependence of the conductivity of diluted aqueous solutions of $KLa[Fe(CN)_6]$ and $KLa[Ru(CN)_6]$. The measured data were in the region of smaller dilutions consistently interpreted on the assumption that La^{3+} cations associate with complex anions with the formation of negatively charged ion pairs $La^{3+} \cdot [Me(CN)_6]^{4-}$. Two parameters of the Debye-Hückel-Onsager limiting equation, namely the stability constant of the ion pair at infinite dilution, K_p^0 , and its equivalent conductance, λ_p^0 , were adjusted so as to fit the experimental data. A pronounced break on the obtained curves of $\log K_p$ toward lower values observed in the region below $1 \cdot 10^{-4}$ mol/dm³ was attributed to hydrolysis of La^{3+} ions with the formation of colloidal $La(OH)_3$.

The mentioned interpretation was, however, at variance with the observation that no lanthanum was transferred into the anode space in a Hittorf apparatus, *i.e.*, no association of La^{3+} ions to negatively charged ion pairs took place. A theoretical (at least qualitative) explanation of this negative result was attempted, nevertheless there was some doubt whether it was not caused by association with K^+ ions to electroneutral species $K^+ \cdot La^{3+} \cdot [Me(CN)_6]^{4-}$ even when the conductivity curves did not suggest such a possibility. To elucidate this problem, we made analogous

measurements in solutions of lanthanum hexacyanoferrate and praseodymium hexacyanoruthenate containing no K^+ ions. Pr^{3+} cations were chosen in order to check whether the observed effects are not specific for La^{3+} ions.

EXPERIMENTAL

Lanthanum hexacyanoferrate and praseodymium hexacyanoruthenate were prepared by precipitation, the former according to Tananaev² from sodium hexacyanoferrate and lanthanum nitrate of reagent grade, the latter by neutralization of hexacyanoruthenic acid with praseodymium hydroxide³. The products were analysed similarly as the double salts in the preceding work¹. For the formula $La_4[Fe(CN)_6]_3 \cdot 25 H_2O$, it was found (calculated) in percent: La 32.60 (33.84, 32.49), $Fe(CN)_6^{4-}$ 39.55 (38.73; 39.66); for $Pr_4[Ru(CN)_6]_3 \cdot 25 H_2O$ found (calculated): Pr 29.55 (31.56; 30.25), $Ru(CN)_6^{4-}$ 44.38 (43.21; 44.17). The composition is in both cases — in spite of different methods of preparation — shifted from the expected stoichiometric ratio of 4 : 3 toward the acidic salt $HM[Me(CN)_6] \cdot 8 H_2O$ and corresponds roughly to an equimolar mixture of this salt with the normal one, namely $HM_5[Me(CN)_6] \cdot 33 H_2O$ (see the second numbers in parentheses) with an equivalent ratio of H : M equal to 1 : 15.

The conductivity of solutions was measured at 25°C on an apparatus described earlier⁴ and the method of measurement was the same as in our preceding work^{1,5}, but instead of a glass cell a quartz glass cell with a quartz stirrer was used and the solutions were prepared by weighing in this cell (on a Mettler microbalance). With respect to a higher solubility, the upper concentration limit was chosen about 4 times higher for M^{3+} and 3 times higher for $[Me(CN)_6]^{4-}$ than in the preceding work¹, i.e., about 7 and $6 \cdot 10^{-4}$ mol/dm³, respectively; the lower limit was about the same (9 and $7.5 \cdot 10^{-5}$ mol/dm³).

RESULTS AND DISCUSSION

The measured values of the conductivity are given in Table I. An exact evaluation of the stability constant, K_p , of the ionic pair $M^{3+} \cdot [Me(CN)_6]^{4-}$ would involve the solution of the equilibria among the species M^{3+} , H^+ , $Me(CN)_6^{4-}$, $HMe \cdot (CN)_6^{3-}$, $M^{3+} \cdot Me(CN)_6^{4-}$, and $M^{3+} \cdot HMe(CN)_6^{3-}$ with five unknowns (three equilibrium constants and two ionic conductances), which cannot be determined separately from experimental data. Since, however, the aim of this work was not the determination of K_p but rather to see whether the experimental data are not at variance with the previous interpretation¹ and whether again a break on the concentration dependence of $\log K_p$ will appear (here K_p serves only as an auxiliary variable), approximations could be used. Since the value of λ_p^0 necessary to evaluate K_p is fitted to experimental data in the region of higher concentrations of the complex anion (of the order of 10^{-3} mol/dm³), it is possible in view of the large stoichiometric excess of anions against H^+ ions in the samples to neglect the acid dissociation of the protonated fraction of the anions. The solution conductivity can then be expressed as

$$10^3 \kappa = c_p \lambda_p z_p + (c_{Me} - c_p) \lambda_{Me} z_{Me} + (c_M - c_p) \lambda_M z_M, \quad (1)$$

where c_p denotes sum of concentrations of ion pairs $M^{3+} \cdot Me(CN)_6^{4-}$ and $M^{3+} \cdot$

. $\text{HMe}(\text{CN})_6^{3-}$, c_{Me} and c_{M} are analytical concentrations of Me and M. The products $\lambda_{\text{Me}z_{\text{Me}}}$ and $\lambda_{\text{n}z_{\text{p}}}$ represent mean molar conductances of the anions and their pairs:

$$z_{\text{Me}}\lambda_{\text{Me}} = (4[\text{Me}(\text{CN})_6^{4-}] \cdot \lambda[\text{Me}(\text{CN})_6^{4-}] + 3[\text{HMe}(\text{CN})_6^{3-}] \cdot \lambda[\text{HMe}(\text{CN})_6^{3-}]) \cdot (c_{\text{Me}} - c_{\text{p}})^{-1}, \quad (2)$$

$$z_{\text{p}}\lambda_{\text{p}} = [\text{M}^{3+} \cdot \text{Me}(\text{CN})_6^{4-}] \cdot \lambda[\text{M}^{3+} \cdot \text{Me}(\text{CN})_6^{4-}]/c_{\text{p}}, \quad (3)$$

and z_{p} , z_{Me} are their mean ionic charges. From Eq. (1) and the measured conductivities κ the pair concentration c_{p} can be determined:

$$c_{\text{p}} = (10^3\kappa - c_{\text{Me}}\lambda_{\text{Me}}z_{\text{Me}} - c_{\text{M}}\lambda_{\text{M}z_{\text{M}}})/(\lambda_{\text{p}}z_{\text{p}} - \lambda_{\text{Me}}z_{\text{Me}} - \lambda_{\text{M}z_{\text{M}}}) \quad (4)$$

as well as the apparent concentration quotient of the pair stability

$$K_{\text{p}} = c_{\text{p}}(c_{\text{Me}} - c_{\text{p}})^{-1} (c_{\text{M}} - c_{\text{p}})^{-1} \quad (5)$$

which represents, of course, an overall quantity involving besides the pairs $\text{M}^{3+} \cdot \text{Me}(\text{CN})_6^{4-}$ also a small admixture of protonated electroneutral pairs. For the system

TABLE I
Specific Conductivities, κ (10^{-5} S cm^{-1}), of Lanthanum Hexacyanoferrate(II) and Praseodymium Hexacyanoruthenate(II) in Aqueous Solutions in Dependence on Molality, m_{La} , m_{Fe} and m_{Pr} , m_{Ru} , respectively (10^{-4} mol dm^{-3}) at 25°C

m_{La}	m_{Fe}	κ	m_{Pr}	m_{Ru}	κ
7.0383	5.5955	6.9626	7.2875	5.9955	7.3006
5.5566	4.4176	5.6180	6.0411	4.9700	6.1536
4.2426	3.3729	4.3963	5.0389	4.1455	5.2242
3.1471	2.5020	3.3656	3.8962	3.2054	4.1362
2.4708	1.9643	2.7264	3.4086	2.8042	3.6677
2.1625	1.7193	2.4249	2.4644	2.0274	2.7518
2.0049	1.5939	2.2805	1.9532	1.6069	2.2477
1.6107	1.2806	1.9266	1.3599	1.1188	1.6884
1.5614	1.2413	1.8882	1.3015	1.0707	1.6499
1.4073	1.1188	1.7537	1.0704	0.8806	1.4784
1.0790	0.8578	1.4832	1.0337	0.8504	1.4589
0.9479	0.7536	1.3633	0.9175	0.7549	1.3526

to be determined, one more independent condition must be added. Since, as already mentioned, we are interested in the break on the $\log K_p$ curves whose position cannot be much influenced by moderate changes in the distribution of protonated and non-protonated anions between the associated and nonassociated species, we can formulate this condition so that the content of both anions in pairs is the same as in the nonassociated species. The equivalent conductivities of the ions $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Ru}(\text{CN})_6]^{4-}$ at infinite dilution, λ° , were set equal to 111.0 and 108.1 S . cm²/val as in the preceding work¹. The equivalent conductivity of the anion $\text{HMe}(\text{CN})_6^{3-}$ can be, in analogy to other protonated anions (HSO_4^- , HPO_4^{2-}), assumed correspondingly smaller than for the nonprotonated anion, *i.e.*, about 80 S . cm²/val; with respect to the small admixture of this anion the choice of this value within $\pm 10\%$ is not critical for the resulting value of λ_{Me}^0 . The molar conductivity $\lambda_{\text{Me}z_{\text{Me}}}^0$ is then according to the analysis of the samples for the combination La-Fe and Pr-Ru equal to 397.7 and 364.2 S . cm²/val, respectively. The value of the parameter $\lambda_{p z_p}^0$ depends on the choice of the conductance of the nonprotonated pair, λ_p^0 , and can be therefore also chosen by iteration. For the ratio of M : H = 5 : 1 we have

$$\lambda_p^0 = 0.75\lambda_{\text{p}}^0. \quad (6)$$

The distribution of the molar conductances into the parameters λ and z is not necessary for the calculation of c_p from Eq. (4); it is needed only for the calculation of the corrections according to the Debye-Hückel-Onsager limiting relation, which are small, so that we can take for both salts the following rounded values: $z_{\text{Me}} = 3.75$, $z_p = 0.75$. These correspond to the ratio of 5 M : 1 H (analyses gave 3.77 and 3.65 for z_{Me} and 0.77 and 0.65 for z_n). The values of λ_{Me}^0 are then obtained as 106- and 97 S . cm²/val for both salts, respectively.

With the mentioned values, the parameters K_p and λ_p^0 were fitted to experimental data with the use of the same iterative scheme as earlier¹. The concentrations, c , were set equal to molalities, m . The ionic strength and mean values of λ_-^0 and z_- for the anionic species, introduced into the Onsager equation, were calculated from equations corresponding to the formula $\text{M}_5[\text{Me}(\text{CN})_6]_3 \text{H}[\text{Me}(\text{CN})_6]$:

$$I = 12.75c_{\text{Me}} - 11.25c_p, \quad (7)$$

$$\lambda_-^0 = [\lambda_{\text{Me}}^0 - (\lambda_{\text{Me}}^0 - 0.2\lambda_p^0) c_p/c_{\text{Me}}] (1 - 0.8c_p/c_{\text{Me}})^{-1}, \quad (8)$$

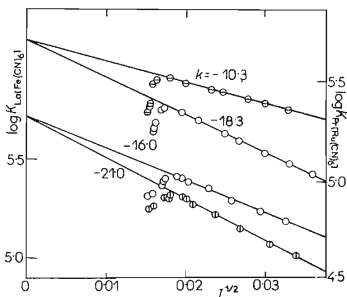
$$|z_-^0| = 3.75 - 3c_p/c_{\text{Me}}, \quad (9)$$

whereas the cationic component is formed by La^{3+} or Pr^{3+} ions with $\lambda_+^0 = 69.7$ or 70.0 S . cm²/val and $z_+ = 3$.

The dependence of the logarithm of the thus obtained constant K_p for both salts on the square root of ionic strength is shown in Fig. 1 for different values of λ_p^0 . At smaller dilutions, *i.e.*, $I > 0.0003$ for cyanoruthenate and > 0.00035 for cyanoferrate, or in both cases from about $1.5 \cdot 10^{-4}$ to $7 \cdot 10^{-4}$ mol/dm³ M³⁺, the evaluated values of $\log K_p$ lie on a straight line in accord with the limiting Debye-Hückel-Onsager equation. The linear character of the dependence was owing to a higher solubility of the simple salts shown to be valid in a much wider concentration range (more than 1 : 4) than with the double lanthanum-potassium salts in the preceding work¹ (where the concentration range was 1 : 1.35 and 1 : 1.6). Extrapolated values of $\log K_p^0$ turn out to be equal to 5.70 and 5.72 for Me = Ru and Fe, respectively, and are independent of the choice of the equivalent conductivity of the ion pair, λ_p^0 . However, the slope of the straight line, k , depends much on this choice. The theoretical value of $k = -12.2$ from the limiting Debye-Hückel-Onsager equation is in accord with $\lambda_p^0 = 86.9$ S . cm²/val for Pr³⁺ . [Ru(CN)₆]⁴⁻ and 83.5 S . cm²/val for La³⁺ . [Fe(CN)₆]⁴⁻, which are higher values than those obtained from measurements on lanthanum-potassium double salts (about 60 S . cm²/val). In contrast, the stability constants are lower than found on the double salts (where $\log K_p^0 = 6.01$ and 5.93). These differences are explained by the fact that the acid dissociation of the H[Me . (CN)₆]³⁻ anions, which contributes to the solution conductivity through the formation of very mobile hydrogen ions, was neglected for the sake of simplification. In our simplified model, this conductivity increment enters the calculated value of λ_p^0 and leads to a seemingly diminished association of the salt. If the admixture of acidic anions is neglected and it is assumed that the whole weighed amount is formed by the normal salt (taking account of the crystal water) M₄[Me(CN)₆]₃ the value of λ_p^0 turns out to be equal to 50.3 and 50.8 S . cm²/mol for Me = Ru and Fe. The values of $\log K_p^0$ remain practically unchanged (5.73 and 5.72).

FIG. 1
Dependence of the Stability Constant of the Ion Pair M³⁺ . [Me(CN)₆]⁴⁻, K_p , in Solutions of Lanthanum Hexacyanoferrate(II) (lower part) and Praseodymium Hexacyanoruthenate(II) (upper part) on Ionic Strength, I

Values of λ_p^0 of the ion pair (S . cm²/mol):
M, Me = La, Fe ⊙ 65, ○ 75; M, Me = Pr, Ru ⊙ 90, ○ 75; 25°C.



With either way of evaluation, however, even in the absence of K^+ ions the curves of $\log K_p$ show with decreasing concentration a similar sharp break toward lower apparent association (*i.e.*, higher conductivity) as was observed with double salts containing potassium. This substantiates the conclusion of the earlier work¹ that the break is due to hydrolysis of free M^{3+} cations and not to precipitation of little soluble products containing potassium. The equivalent concentration at which the break is observed in the case of the pure lanthanum or praseodymium salt is the same ($4-5 \cdot 10^{-4}$ val/dm³) as in the case of lanthanum-potassium double salts.

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