

# CONDUCTIVITY STUDY OF ASSOCIATION OF POTASSIUM LANTHANUM HEXACYANOFERRATE(II) AND HEXACYANORUTHENATE(II) IN AQUEOUS SOLUTIONS

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Based on concentration dependences of conductivity of aqueous solutions in the region of  $10^{-4}$  to  $10^{-5}$  mol dm $^{-3}$  at 25°C, the association scheme of  $\text{KLa}[\text{Fe}(\text{CN})_6]$  and  $\text{KLa}[\text{Ru}(\text{CN})_6]$  was determined and the thermodynamic stability constants of the associates as well as their equivalent conductances were evaluated by using the two-parameter adjustment method employing the Debye-Hueckel-Onsager limiting law. The two salts associate under the conditions mentioned, yielding ion pairs, with the formation constants  $0.86 \cdot 10^6$  and  $1.02 \cdot 10^6$  dm $^3$  mol $^{-1}$  for  $\text{La}[\text{Fe}(\text{CN})_6]^-$  and  $\text{La}[\text{Ru}(\text{CN})_6]^-$ , respectively; the equivalent conductances of the pairs corresponding to the theoretical value of 12.2 of the coefficient in the Debye-Hueckel limiting relation for the association constant are 56.1 and 64.3 S cm $^2$  mol $^{-1}$ , respectively.

In our preceding work $^1$  dealing with conductometric measurements of aqueous solutions of  $\text{K}_4[\text{Ru}(\text{CN})_6]$ , a substantial similarity was proved to be between the association of potassium ions with hexacyanoruthenate(II) ions and that of potassium ions with hexacyanoferrate(II) ions: it is manifested by the close values of the stability constants of the ion pairs formed,  $\text{K}^+ \cdot [\text{Me}(\text{CN})_6]^{4-}$ , as well as of their equivalent conductances. Regarding the fact that in nuclear fission products ruthenium is accompanied by lanthanide cations, we studied in the present work the association with those ions. We employed  $\text{KLa}[\text{Fe}(\text{CN})_6]$  and  $\text{KLa}[\text{Ru}(\text{CN})_6]$  as model substances and applied again the conductometric method.

## EXPERIMENTAL

Potassium lanthanum hexacyanoferrate(II) was prepared according to Prandtl and Mohr $^2$ , potassium lanthanum hexacyanoruthenate(II) according to Králík $^3$ . The chemicals obtained were dried on air in darkness until constant weight was attained, and analyzed first by the method published by Krtíl $^4$ , determining the ratio of  $\text{La}^{3+}$  to  $[\text{Me}(\text{CN})_6]^{4-}$ ; only then the samples were mineralized by sulfuric acid and lanthanum and potassium were determined gravimetrically $^{3,5}$ . The content of water was represented by the difference from 100%.

*Analysis of the chemicals:*  $\text{KLa}[\text{Fe}(\text{CN})_6] \cdot 4 \text{H}_2\text{O}$  found (calculated) (%): La 29.90 (30.07), K 8.40 (8.47);  $\text{KLa}[\text{Ru}(\text{CN})_6] \cdot 4 \text{H}_2\text{O}$  found (calculated) (%): La 27.23 (27.38), K 7.65 (7.71).

The equipment for conductivity measurements and the corresponding procedure have been described<sup>6</sup>. Regarding the low solubility of the two compounds<sup>3,5,7</sup> ( $3$  to  $4 \cdot 10^{-4}$  mol dm<sup>-3</sup>) we performed the measurements only in a narrow concentration region,  $3 \cdot 10^{-5}$  to  $2 \cdot 10^{-4}$  mol dm<sup>-3</sup>. The conductivities of the solutions of the double salts were measured in a conductivity cell, made of hard glass, equipped with smooth platinum electrodes to prevent sorption of the electrolyte at low concentrations. The negative role of the "shaking effect", appearing during conductivity measurements in very dilute solutions<sup>8-10</sup>, could be practically removed by stirring the solution. An adapted ultrathermostat kept the temperature of the solutions measured at  $25 \pm 0.05^\circ\text{C}$ . The specific conductivity of redistilled water used for the preparation of the solutions ranged from  $5$  to  $10 \cdot 10^{-7}$  S cm<sup>-1</sup> and was subtracted from the specific conductivities of the solutions in all cases. All solutions were prepared by weighing water in a quartz flask on a balance for calibration of volumetric vessels and weighing the salts on a microbalance "Mettler". The molalities were recalculated to molarities assuming the density of the solutions to equal that of water at  $25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The molar conductance values  $\Lambda$  of the two salts, calculated from the measured specific conductivities of the aqueous solutions, are given in Table I. For a comparison, the molar conductances  $\Lambda_{\text{dis}}$  for a complete dissociation to the cations  $\text{K}^+$  and  $\text{La}^{3+}$  and anions  $[\text{Me}(\text{CN})_6]^{4-}$  were calculated for each concentration, using the limit Onsager formula for binary electrolytes<sup>11</sup>, which represents an acceptable approximation for the low concentrations applied (ionic strength of the order  $10^{-4}$  to  $10^{-3}$  mol dm<sup>-3</sup>). The transition from the formula for a binary electrolyte to that for a ternary electrolyte was realized so, that in the charge coefficients, which express the organizing

TABLE I  
Molar Conductances,  $\Lambda$  (S<sup>2</sup> cm<sup>2</sup> mol<sup>-1</sup>), of Potassium Lanthanum Hexacyanoferrate(II) (a) and Hexacyanoruthenate(II) (b) in Aqueous Solutions in Dependence on Concentration,  $c$  ( $10^{-4}$  mol . dm<sup>-3</sup>) at  $25^\circ\text{C}$

$c_a$	$\Lambda_a$	$c_a$	$\Lambda_a$	$c_b$	$\Lambda_b$	$c_b$	$\Lambda_b$
1.711	185.64	1.035	202.22	1.361	192.50	0.954	206.20
1.663	186.80	1.029	202.91	1.273	194.50	0.939	207.22
1.492	189.27	1.017	203.34	1.218	194.85	0.910	210.40
1.397	191.78	0.943	210.46	1.187	195.78	0.868	214.25
1.310	193.47	0.928	210.96	1.111	196.68	0.830	217.46
1.164	195.80	0.921	212.00	1.078	197.90	0.811	219.45
1.120	196.82	0.875	215.70	1.010	200.75	0.766	225.97
1.072	198.32	0.844	219.50	0.987	203.10	0.749	227.10
1.049	200.65	0.788	225.30				

Coulomb effect of the migrating ion on the surrounding ionic medium, in the ionophoretic and relaxation terms the absolute values 1 and 3 were taken for the charges of the migrating cations and the value 4 for that of the migrating anion; for the charge of the counter-ion, the value 4 was adopted for the cations and the averaged value  $(1 + 3)/2 = 2$  for the anions. On the other hand, in the parameter  $q$  of the relaxation term, which expresses the response of the ionic atmosphere as a whole to this organizing action, averaged charge values and equivalent conductances were employed in all cases for the cations as well as for the anions, hence  $|z_+| = 2$ ,  $\lambda_+^0 = (1/4) \cdot \lambda^0(\text{K}^+) + (3/4) \cdot \lambda^0(\text{La}^{3+}) = (1/4) \cdot 73.5 + (3/4) \cdot 69.7 = 70.65 \text{ S cm}^2 \text{ val}^{-1}$ , and  $|z_-| = 4$ ,  $\lambda_-^0 = 111.0 \text{ S cm}^2 \text{ val}^{-1}$  for  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $108.1 \text{ S cm}^2 \text{ val}^{-1}$  for  $[\text{Ru}(\text{CN})_6]^{4-}$  according to the previous work<sup>1</sup>.

The conductance  $\Lambda_{\text{dis}}$  so calculated attains values roughly three times higher than those measured; this indicates that the salts in solutions are associated to a high degree. The association of the anions  $[\text{Me}(\text{CN})_6]^{4-}$  with the cations  $\text{K}^+$ , investigated previously<sup>1</sup>, cannot account for such a low conductance as observed; one has to allow in addition for the association of a rather high fraction (at least 50%) of the  $\text{La}^{3+}$  ions. This means, however, that with the dilutions applied, the concentration of the free  $[\text{Me}(\text{CN})_6]^{4-}$  anions is suppressed to below  $10^{-4} \text{ mol dm}^{-3}$ ; this is a range, where — according to the stability constants of the ion pairs  $\text{K}[\text{Me}(\text{CN})_6]^{3-}$  (about  $3 \cdot 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ ) — only few per cent of the  $\text{K}^+$  ions present are subject to association, which thus can be neglected. The low conductivity found can then be explained only by the formation of ion pairs



or by association according to the equation



in the case of a high specific stability of the two electroneutral ion triplets formed.

We attempted to decide between the two alternatives by transference measurements in a Hittorf apparatus, since the transport of lanthanum into the anodic section would present a direct evidence of association according to the scheme (A). The experiments did not, however, give results, from which unambiguous conclusions could be drawn; almost all the lanthanum (87–92%) was found in the cathodic section together with roughly the same fraction of potassium. In the anodic section, reactions for  $\text{La}^{3+}$  and  $\text{K}^+$  were negative in all cases, which might rather indicate the association according to the scheme (B).

The data obtained were therefore first treated based on that scheme by using the method of successive approximations. From the ratio of the measured molar conductance,  $\Lambda_{\text{exp}}$ , and the conductance calculated for a completely dissociated electro-

lyte,  $\Lambda_{\text{dis}}$ , the dissociation degree was estimated for each concentration. From this, the approximate value of the actual ionic strength of the solution,  $I = 13\alpha m$ , was calculated and inserted into the Onsager formula (in the above-mentioned modification for a ternary electrolyte) to obtain corrected conductance  $\Lambda_{\text{dis}}$  and corrected values of  $\alpha$ . Iteration of this procedure yielded values of the dissociation degree,  $\alpha$ , and ionic strength,  $I$ , corresponding to the equilibrium (B), from which the values of the stability constants of the ion triplet,  $K_t = (1 - \alpha)/\alpha^3 m^2$ , were calculated.

The points obtained by plotting  $\text{p}K_t$  versus  $I^{1/2}$  lie approximately on a straight line in the whole concentration range, thus conforming with the Debye-Hueckel theory of activity coefficients, but the slopes of the straight lines for the two substances lie between 65 and 70 instead of the value of 13.3 resulting from that theory for the equilibrium constant of the reaction (B). The rapid increase of the constant  $K_t$  with increasing dilution arises from the square of molality  $m$  in the denominator, whose decrease cannot be compensated by the mild increase of the dissociation degree  $\alpha$  amounting to less than 20% in this case (from 0.28 to 0.33). In order to attain an agreement with the Debye-Hueckel theoretical slope one would have to reduce the power of  $m$ , which corresponds to the substitution of the formation of the ion triplets by that of ion pairs, hence to the substitution of the association scheme (B) by the scheme (A). On the other hand, the agreement cannot be reached by assuming polymerization of the associate or formation of polynuclear complexes, as the power of  $m$  in the formula for the equilibrium constant would further increase.

The absence of lanthanum from the anodic section in the transference experiments does not rule out the possibility that a part of the  $\text{La}^{3+}$  ions is present as negatively charged species in the solution. As shown by Lederer<sup>12</sup>, the cations which are in the solution in an equilibrium with their kinetically unstable complexes, migrate in an electrostatic field, with the potential gradient  $\partial V/\partial x$ , with the common mean velocity  $v = (\partial V/\partial x) \sum p_i u_i$ ; here  $u_i$  are the mobilities of the individual forms, in which the ion in question occurs in the solution, and  $p_i$  are the respective fractions of the overall concentration of the cation. If in this sum the positive components, corresponding to the cationic species, prevail over the negative components, belonging to negatively charged associates (whose mobilities are usually low), the resultant direction of motion is preserved also in systems with a high amount of the anionic species. From this it follows that a negative result of the transference experiments does not rule out an evaluation of the conductivity measurements based on the scheme (A), which we therefore performed.

Under the justified assumption of a negligibly low association of the  $\text{K}^+$  ions with the complex anions themselves, the stability constant of the ion pair,  $K_p$ , is given by the relation

$$K_p = [\text{LaMe}(\text{CN})_6^-] / [\text{La}^{3+}] [\text{Me}(\text{CN})_6^{4-}] = (1 - \alpha)/\alpha^2 m \quad (1)$$

and including activity coefficients of the ions according to the Debye-Hueckel limiting law we have

$$pK_p = -\log [(1 - \alpha)/\alpha^2 m] = pK_p^0 + 12 \cdot 2 I^{1/2}, \quad (2)$$

where  $\alpha$  is the dissociation degree of the salt corresponding to the scheme (A), evaluated from experimental molar conductances  $\Lambda_{\text{exp}}$  by employing the relation

$$\Lambda_{\text{exp}} - \lambda_K = 3\alpha\lambda_{\text{La}} + 4\alpha\lambda_{\text{Me(CN)}_6} + (1 - \alpha)\lambda_p; \quad (3)$$

(the subscript p designates the ion pair). The equivalent conductances  $\lambda_i$  were calculated from the Onsager limiting law for the ionic strength of the solution  $I = m(1 + 12\alpha)$ . The Onsager formula was used for the conditions in question in the form

$$\lambda_i = \lambda_i^0 - [0.7816z_i z_{0p} q \lambda_i^0 (1 + q^{1/2})^{-1} + 30.16z_i] I^{1/2}, \quad (4)$$

where  $\lambda_i^0$  is the equivalent conductance of the migrating ion in infinite dilution,  $z_i$  is the absolute value of its charge, and  $z_{0p}$  the absolute value of the charge of the counter-ions, which involves (as did the averaged charges  $z_+$ ,  $z_-$  and conductances  $\lambda_+$ ,  $\lambda_-$  in the parameter  $q$ ), in addition to the ions  $K^+$ ,  $\text{La}^{3+}$ , and  $[\text{Me(CN)}_6]^{4-}$ , also the ion pairs  $\text{La}[\text{Me(CN)}_6]^-$ . The mutual concentration ratio of all the four ions varies with the degree of dissociation  $\alpha$ , so that the averaged values of  $z$  and  $\lambda^0$  are here functions of  $\alpha$ :

$$z_+ = (1 + 3\alpha)(1 + \alpha)^{-1}, \quad (5)$$

$$z_- = 1 + 3\alpha, \quad (6)$$

$$\lambda_+^0 = (\lambda_K^0 + 3\alpha\lambda_{\text{La}}^0)(1 + 3\alpha)^{-1}, \quad (7)$$

$$\lambda_-^0 = [\lambda_p^0 + \alpha(4\lambda_{\text{Me(CN)}_6}^0 - \lambda_p^0)](1 + 3\alpha)^{-1}, \quad (8)$$

and vary during the iteration.

The equivalent conductance of the ion pairs,  $\lambda_p^0$ , for infinite dilution cannot be determined experimentally and was therefore chosen from analogy with bulkier univalent anions. In the case of hexacyanoferrate(II) the calculation was carried out for  $\lambda_p^0 = 50.0$  and  $60.0 \text{ S cm}^2 \text{ val}^{-1}$ , in the case of hexacyanoruthenate(II) for  $\lambda_p^0 = 55$  and  $65 \text{ S cm}^2 \text{ val}^{-1}$ . For each of these chosen conductances the values of  $I$  and  $\alpha$  were again calculated for all concentrations by using the method of successive approximations, and these values served then for the evaluation of the stability constant of the ion pair,  $K_p$ , from the equation (2).

On the curves obtained by plotting the experimental values of  $\log K_p$  versus  $I^{1/2}$  (Fig. 1), a sharp break, where the slope reverses its sign, appears in all cases. On the side of dilute solutions, the slope is positive for all  $\lambda_p^0$ 's and cannot be reconciled with the Debye-Hückel limiting law. On the other hand, the slope of the section on the side of higher concentrations is negative for  $\lambda_p^0$  lower than 75 and 80 S cm<sup>2</sup> . val<sup>-1</sup> for the Fe- and Ru-salt, respectively, and attains the theoretical value of -12.2 at  $\lambda_p^0 = 56.1$  and 64.3 S cm<sup>2</sup> val<sup>-1</sup>, respectively; this is compatible with the conductances of bulkier complex univalent anions, unless they are hydrated (non-complex univalent anions display conductances  $\lambda^0$  (25°C) close to 80 S cm<sup>2</sup> val<sup>-1</sup>). From this can be inferred that in the region of higher concentrations (above 1.1 - 1.2 . 10<sup>-4</sup> mol cm<sup>-3</sup>), the two salts are subject to simple association giving ion pairs according to the scheme (A). The stability constant of the ion pair,  $K_p^0$ , is calculated to be 0.85 . 10<sup>6</sup> and 1.02 . 10<sup>6</sup> dm<sup>3</sup> mol<sup>-1</sup> for KLa[Fe(CN)<sub>6</sub>] and KLa[Ru(CN)<sub>6</sub>], respectively. These values are in an acceptable accordance with the dissociation constant (8.7 ± 1.5) . 10<sup>-6</sup> mol dm<sup>-3</sup> found spectrophotometrically by Panckhurst and Woolmington<sup>13</sup> for the ion pair La[Fe(CN)<sub>6</sub>]<sup>-</sup> in solutions of KLa[Fe(CN)<sub>6</sub>].

A discrepancy could be found in the fact that it is not very probable that the strongly hydrated La<sup>3+</sup> cation would lose completely its hydration shell during the association with the complex anions investigated. For solvent-separated ion pairs the experimental equivalent conductances are extraordinarily high. In addition, with so high a conductance of the negatively charged ion pair and the low degrees of dissociation of the associate as found, lanthanum would have to migrate to the anode, which does not occur here. All this indicates that the actual conductance of the ion pair is rather lower than as derived from the slope of the curves  $\log K_p - I^{1/2}$ . The cause of this might be sought in the inadequacy of the Onsager limiting law or in the superposition of other effects (*e.g.* the transition from one association mechanism to another), which might give rise to an additional monotone shift of the  $\log K_p$  values with concentration and so a change of the slope of the plotted straight lines. The  $K_p^0$  value is, however, virtually independent of the selection of  $\lambda_p^0$  (and so of the slope of the experimental curves) and is not appreciably influenced by those effects (Fig. 1).

As to the sharp break on the curves  $\log K - I^{1/2}$ , this can be explained only by a transition from a homogeneous system with predominant equilibrium (A) to a system, where some of the products of the parallel reactions, whose activity increased continuously up to the break point, reaches its solubility limit and its activity is maintained at a constant level, which forms a discontinuous transition of the association equilibrium followed to a different curve. Since no formation of a macrodisperse precipitate or visible turbidity was observed, the separation can be assumed to proceed in the form of a colloidal sol, where the activity of the disperse component is virtually as independent of the concentration as with the macrodisperse forms; the latter fact has been confirmed during the study of alkalimetric titration of Al<sup>3+</sup> ions in dilute

aqueous solutions<sup>14</sup>. Probably the colloidal sols are formed by the products of hydrolysis in solutions of  $\text{KLaMe}(\text{CN})_6$ ; in contrast to the case of  $\text{Al}^{3+}$ , the point of coagulation cannot be reached at all (probably owing to the high dilution).

The colloidal sol, separating at a defined dilution, can clearly be only such an ion combination, whose ionic product increases with the dilution of the solution; so it is not an associate composed only of ions of the electrolyte under study, as the equilibrium concentration of any of such associates decreases with increasing dilution. It is then only the products of hydrolysis that are to be taken into consideration. Since such effects have not been observed in solutions of  $\text{K}_4[\text{Ru}(\text{CN})_6]$  itself, only one possibility remains, *viz.* that the component, which attains saturation at the turning point, is the hydrolytic product of the  $\text{La}^{3+}$  cation or of its electroneutral combination with the products of hydrolysis of the complex anion, *i.e.* with the anions  $\text{H}_i[\text{Me}(\text{CN})_6]^{(4-i)-}$ , where  $i = 1, 2, \text{ or } 3$ , or with  $\text{OH}^-$  ions formed by proton transfer from molecules of water. Accordingly, there are three possibilities: *a*) association of  $\text{La}^{3+}$  with the  $\text{H}_i[\text{Me}(\text{CN})_6]^{(4-i)-}$  anions formed by gradual hydrolysis of the  $[\text{Me}(\text{CN})_6]^{4-}$  anions; *b*) formation of  $\text{La}(\text{OH})_3$  through the association of  $\text{La}^{3+}$  with the  $\text{OH}^-$  ions with a proton transfer to the  $[\text{Me}(\text{CN})_6]^{4-}$  anions; *c*) formation of  $\text{La}(\text{OH})_3$  through the association of  $\text{La}^{3+}$  with the  $\text{OH}^-$  ions without a proton transfer to the complex anions. The fourth alternative — the association of the  $\text{La}(\text{OH})_3^{(3-j)+}$  cations with the  $\text{H}_i[\text{Me}(\text{CN})_6]^{(4-i)-}$  anions — represents an intermediate step between the above three cases.

The case *a*) can be treated as the association of the  $\text{La}^{3+}$  and  $[\text{Me}(\text{CN})_6]^{4-}$  ions with the  $\text{H}^+$  ions, whose concentration is affected by the hydrolysis of the former two ionic species. The hydrolysis of the  $\text{La}^{3+}$  ions produces immediately  $\text{H}^+$  ions, the concentration of the latter decreases therefore with the dilution and so does the

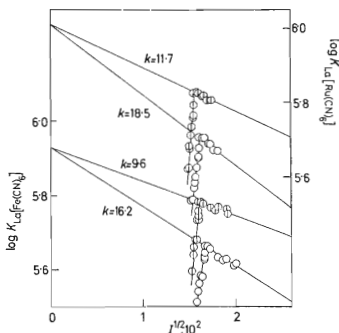


FIG. 1

Dependence of the Stability Constant of the Ion Pair  $\text{La}^{3+} \cdot [\text{Me}(\text{CN})_6]^{4-}$ ,  $K_p$ , in Solutions of  $\text{KLa}[\text{Me}(\text{CN})_6]$  on the Ionic Strength,  $I$  (25°C), for  $\lambda^0$  of the Ion Pair ( $\text{S cm}^2 \text{ mol}^{-1}$ ): Me = Fe (lower part) ○ 50, ⊙ 60; Me = Ru (upper part) ○ 55, ⊙ 65

total ionic product of the resulting electroneutral combination. For this reason, that alternative can be ruled out. The hydrolysis of the anions, on the contrary, produces  $\text{OH}^-$  ions, so that the dilution leads to a decrease of the concentration of the  $\text{OH}^-$  ions and to an increase of that of the  $\text{H}^+$  ions, which conforms with the precipitation hypothesis. With the concentration of  $\text{KLa}[\text{Me}(\text{CN})_6]$  of the order of  $10^{-4} \text{ mol dm}^{-3}$  and the dissociation degree  $\alpha$  about 0.1, the concentration of the free  $\text{La}^{3+}$  and  $[\text{Me}(\text{CN})_6]^{4-}$  ions makes about  $10^{-5} \text{ mol dm}^{-3}$ , which is two orders higher than that of the  $\text{H}^+$  and  $\text{OH}^-$  ions in water. At the very beginning of the hydrolysis we can therefore neglect the two latter items in respect to the two former ones, and put  $[\text{La}^{3+}] = [\text{Me}(\text{CN})_6^{4-}]$  and  $[\text{OH}^-] = [\text{HMe}(\text{CN})_6^{3-}]$ . Then, denoting the dissociation constant of the complex acid  $K_4$  and the ionic product of water  $K_w$ , we have

$$[\text{H}^+] = (K_4 K_w / [\text{La}^{3+}])^{1/2}, \quad (9)$$

which in fact is a value increasing with the dilution of the solution. For the ionic product of the neutral associate we obtain in this case

$$[\text{La}^{3+}]^{4-i} [\text{H}^+]^{3i} [\text{Me}(\text{CN})_6^{4-}]^3 = (K_4 K_w)^{3i/2} [\text{La}^{3+}]^{7-5i/2}, \quad (10)$$

which for  $i = 1$  or  $2$  decreases with increasing dilution; for  $i = 3$ , however, the ionic product of the associate —  $\text{La}[\text{H}_3\text{Me}(\text{CN})_6]$  in this case — would increase slightly with decreasing concentration of the  $\text{La}^{3+}$  ions. There are no unique data available from the literature concerning the consecutive hydrolytic constants of the  $[\text{Me}(\text{CN})_6]^{4-}$  anions or the existence and solubility of the associate of the composition mentioned, which would make it possible to assess in detail the conditions of its formation. It can be stated only that owing to the binding of the protons in the products of hydrolysis the solution should exhibit an alkaline reaction. Tentative pH measurements revealed, however, a weakly acidic reaction — pH 6.5 to 6.7. The turning point is therefore not likely to be accounted for by the formation of polymeric lanthanum hydrogen cyanoferrates or cyanoruthenates.

In the case *b*) an analogous approximate solution with respect to the concentration of the  $\text{OH}^-$  ions leads to the expression

$$[\text{OH}^-] = [K_w / (j\beta_j K_4)]^{1/(j+1)}, \quad (11)$$

whose value is independent of the dilution ( $\beta_j$  is the overall stability constant of the predominant  $j$ -th  $\text{La}^{3+}$  hydroxocomplex; the hydrolysis of the anion only to the first degree is assumed). The ionic product  $[\text{La}^{3+}][\text{OH}^-]^3$  is in this case directly proportional to the concentration of free  $\text{La}^{3+}$  ions and decreases with increasing dilution. This alternative can be therefore neglected too.



In the case *c*), for predominant hydrolysis of the  $\text{La}^{3+}$  cations to the  $j$ -th degree we can put in an approximation  $[\text{H}^+] = j[\text{La}(\text{OH})_j^{3-j}]$  under the conditions given. Then we obtain

$$[\text{OH}^-]^{j+1} = [K_w/(j\beta_j[\text{La}^{3+}])], \quad (12)$$

hence a quantity increasing with increasing dilution, and for the ionic product of  $\text{La}(\text{OH})_3$  we have

$$[\text{La}^{3+}][\text{OH}^-]^3 = [K_w/(j\beta_j)]^{3/(j+1)} [\text{La}^{3+}]^{(j-2)/(j+1)} \quad (13)$$

which increases with decreasing concentration of the solution only if  $j = 1$ . Accordingly, the occurrence of a break on the curves  $\log K_p - I^{1/2}$  owing to the formation of colloidal lanthanum hydroxide is feasible, if the hydrolysis of the  $\text{La}^{3+}$  cation only to the first degree predominates in the solution.

Published data<sup>15</sup> on the stability constant of the first  $\text{La}^{3+}$  hydroxo complex in aqueous solutions spread over a wide range of  $\log \beta_1$ , from 5.6 to 10.1. For  $[\text{La}^{3+}] = 10^{-5} \text{ mol dm}^{-3}$ , to pH 6.7–6.5 the value of  $\log \beta_1$  5.5–6.0 would correspond, which is close to the lower limit of the range mentioned. For the logarithm of the solubility product  $K_s = [\text{La}^{3+}][\text{OH}^-]^3$  the value of –25 to –27.5 then results. The book<sup>15</sup> reports also a series of mutually different values of  $\log K_s$ , which are the higher the more recently they were determined, probably as the separation of the lower degrees of hydrolysis improved due to the application of computers. The difference between the latest value, –23, which seems to be the most reliable, and the values following from the above considerations may be explained so, that lanthanum hydroxide forms in a solution first a colloidal sol at concentrations of  $\text{OH}^-$  lower than as corresponds to the tabulated solubility product, and only with a further increase of the concentration of the  $\text{OH}^-$  ions coagulation occurs, due to salting-out effects or ion sorption and the consequent change of potential of the micelles. Based on this the high differences in the  $\beta_1$  and  $K_s$  values as published by various authors could be also understood.

In order to verify the hypothesis concerning the slope of the  $\log K_p$  curves and the estimate of the constants, we compared the results following from them with the experimental findings. We treated first the question of how deeply the hydrolytic equilibrium according to the alternative *c*) can be perturbed by the partial (orders of magnitude lower) hydrolysis of the complex anion, considered in the alternative *a*). Denoting the concentration of the  $\text{OH}^-$  ions produced by that hydrolysis  $c_{\text{OH}}$  we can write for the overall balance of the  $\text{H}^+$  ions

$$[\text{H}^+] = 3(c_{\text{La}} - [\text{La}^{3+}] - [\text{LaOH}^{2+}]) + [\text{LaOH}^{2+}] + ([\text{OH}^-] - c_{\text{OH}}), \quad (14)$$

where the first term of the right side expresses the production of the  $H^+$  ions associated with the formation of the colloidal  $La(OH)_3$  and the second term the production of the  $H^+$  ions by the hydrolysis of the  $La^{3+}$  ions to the first degree;  $c_{La}$  is the total concentration of lanthanum not associated with the complex anions, in our case a value of the order of  $10^{-5}$  mol  $dm^{-3}$ . If we express  $[La^{3+}]$  as a function of  $[H^+]$  from the condition of a constant solubility product,  $K_s$ , and neglect the  $[OH^-]$  term in respect to  $[H^+]$ , then Eq. (14) takes on the form

$$3(K_s/K_w^3)[H^+]^3 + 2\beta_1(K_s/K_w^2)[H^+]^2 + [H^+] = 3c_{La} - c_{OH}. \quad (15)$$

From this the buffering sensitivity of the system is

$$\partial pH/\partial(c_{OH}/c_{La}) = 0.434c_{La}([H^+] + 4[LaOH^{2+}] + 9[La^{3+}])^{-1}. \quad (16)$$

If at the point of the beginning separation of  $La(OH)_3$  all the lanthanum not associated with the  $[Me(CN)_6]^{4-}$  anion were hydrolyzed to the first degree, the equality  $[LaOH^{2+}] = c_{La}$  would approximately hold and the two other terms in the parentheses could be neglected. The regulation coefficient of the system would be then 0.11. For  $\beta_1 = 10^6$   $dm^3$   $mol^{-1}$  and  $c_{La} = 10^{-5}$  mol  $dm^{-3}$  the terms  $[LaOH^{2+}]$  and  $[H^+]$  make only about 3% of  $[La^{3+}]$ , so that at the beginning of the formation of the polymeric  $La(OH)_3$ ,  $[La^{3+}]$  equals approximately  $c_{La}$  and  $\partial pH/\partial(c_{OH}/c_{La})$  is 0.05. This is a buffering capacity one or two orders of magnitude higher than that of common homogeneous regulation systems composed of monohydric acid (or base) and its salt, where the analogous calculation performed for the point of half neutralization (which is the optimum from the regulation point of view) leads to the value of  $\partial pH/\partial(c_{OH}/c) = 4/2.303 = 1.7$ . Such very efficient two-step regulation systems, where the concentration of the  $H^+$  ions is stabilized by the formation of a soluble product whose concentration is additionally stabilized by the equilibrium with its polymeric form, has been previously denoted<sup>14</sup> a "second order buffer". According to the above considerations, a solution of  $KLa[Me(CN)_6]$  of the concentration corresponding to the break point on the  $\log K_p$  curve is such a second order buffer, and the production of  $OH^-$  ions during the slight hydrolysis of the anion can affect neither the pH value nor the course of the curve near the turning point; for  $c_{OH} = 20\%$   $c_{La}$  the shift of pH should be 0.01, whereas in a homogeneous regulator such an addition of the  $OH^-$  ions would bring about a change of pH higher than 0.3.

The second question, which had to be considered, to verify the model, is the theoretical course of the curve after the break point. Based on the hydrolytic model and the condition of a constant solubility product, it can be shown that for low degrees of dissociation  $\alpha$  the formation of polymeric  $La(OH)_3$  is from roughly a half (more accurately  $(2 + \alpha)^{-1}$ ) made up for by the lanthanum bound in the ion pairs, the rest

by free  $\text{La}^{3+}$ . Under these conditions, 1 mol of  $\text{H}^+$  ions released by the hydrolysis is associated with the theoretical overall increment of conductance  $\Lambda^0$  of  $380 \text{ S cm}^2 \text{ mol}^{-1}$ , which in turn is a value corresponding to the dissociation of 0.7 mol of the ion pairs. The stability constant of the ion pairs,  $K_p$ , as calculated from the conductivity, is then underestimated:

$$\Delta \log K_p = -2 \cdot 0.434 \cdot 0.7[\text{H}^+]/[\text{La}^{3+}] = -0.6[\text{H}^+]/[\text{La}^{3+}]. \quad (17)$$

The dependence of that departure on the square root of the ionic strength  $I = c(1 + 12\alpha)$ , with the approximation  $\alpha = (K_p c)^{-1/2}$ , is then

$$\begin{aligned} \partial \Delta \log K_p / \partial I^{1/2} = & -1.2c^{1/2}(1 + 12\alpha)^{1/2} (1 + 6\alpha)^{-1} \partial([\text{H}^+]/[\text{La}^{3+}]) / \partial c - \\ & - 1.2c^{1/2} \partial([\text{H}^+]/[\text{La}^{3+}]) / \partial c. \end{aligned} \quad (18)$$

The deflection of the slope of the experimental curves  $\log K_p - I^{1/2}$  after the turning point (*i.e.* on the side of dilute solutions) from that before the turning point, as read from Fig. 1, makes roughly  $-2 \cdot 10^2 \text{ mol}^{-1/2} \text{ dm}^{3/2}$ . For  $c = 10^4 \text{ mol dm}^{-3}$  we have then, according to Eq. (18), the change of the ratio  $[\text{H}^+]/[\text{La}^{3+}]$  with the concentration  $c$  equal to  $-1.7 \cdot 10^4 \text{ mol}^{-1} \text{ dm}^3$ . For the concentration at the turning point  $c = 10^{-4} \text{ mol dm}^{-3}$  this implies that a 10% dilution of the solution at the very beginning of the hydrolysis brings about the production of  $\text{H}^+$  ions at the level of approximately 17% of the concentration of free  $\text{La}^{3+}$  ions, hence 1.7% of the total concentration of the salt,  $c$ , and to the hydroxide,  $\text{La}(\text{OH})_3$ , is converted the corresponding amount of lanthanum, *i.e.* 0.6% of all the lanthanum present. For an explanation of the observed decrease of the  $\log K_p$  values after exceeding the turning point, a very low extent of hydrolysis is sufficient -0.6% for a 10% dilution of the solution, which is in a good accordance with the dilution shifts of hydrolytic equilibria commonly observed. A quantitative verification of the agreement of the experimental slope with the theoretical value cannot be performed owing to the high differences in the published constants of the products of hydrolysis of the  $\text{La}^{3+}$  ion.

It can be thus concluded that potassium lanthanum hexacyanoferrate and hexacyanoruthenate associate in aqueous solutions at concentrations of the order of  $10^{-4} \text{ mol dm}^{-3}$  and lower to give only ion pairs  $\text{La}^{3+} \cdot [\text{Me}(\text{CN})_6]^{4-}$ . Association with the  $\text{K}^+$  cations does not appear appreciably at such dilutions. During a dilution, the  $\text{La}^{3+}$  cations are subject to hydrolysis, whose intermediate product is predominantly the  $\text{LaOH}^{2+}$  cation, and the final product,  $\text{La}(\text{OH})_3$ , forms a colloidal sol after exceeding the solubility product.

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