

CONTRIBUTIONS TO THE CHEMISTRY OF HIGHLY  
CONCENTRATED AQUEOUS ELECTROLYTE SOLUTIONS. XXV.\*

IONOPHORETIC INVESTIGATION

OF THE ASSOCIATION OF  $\text{Al}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ga}^{3+}$  AND  $\text{In}^{3+}$  IONS  
IN CONCENTRATED SOLUTIONS OF  $\text{NaClO}_4$  AND  $\text{LiCl}$

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The paper deals with paper ionophoresis of the ions  $\text{Al}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ga}^{3+}$  and  $\text{In}^{3+}$  in the media of  $\text{ClO}_4^-$  (1.1 to 9.1 mol/l) and  $\text{Cl}^-$  (1.15 to 10.4 mol/l). From the shifts of the spots, using a modified evaluation method, the authors estimate the stability constants of the electroneutral particles  $\text{MeCl}_3$ . With scandium, gallium and indium the stability constants of anions  $\text{MeCl}_4^-$  are also assessed.

It has been shown<sup>1-3</sup> that the electrophoretic shift of a spot,  $u_i$ , is related to the concentration  $c > 1$  val/l of a background electrolyte, with whose anions the studied ion associates or forms mononuclear inner-sphere complexes, by the equation

$$u = \sum_0^n u_i^0 \beta_i m_X^i (\gamma_X^i \gamma_{\text{Me}} / \gamma_i) \exp(-k_i c) / \sum_0^n \beta_i m_X^i (\gamma_X^i \gamma_{\text{Me}} / \gamma_i), \quad (1)$$

where  $u_i^0$  is the shift of the  $i$ -th form of the studied ion (from  $i = 0$  to  $i = n$ , i.e. from the free cation Me to the highest complex in the mixture) extrapolated exponentially to  $c = 0$ ,  $\beta_i$  denotes the overall thermodynamic stability constants of these species,  $c$  the molarity of the background electrolyte,  $m_X$  the molality of its anion X;  $\gamma_X$ ,  $\gamma_{\text{Me}}$  and  $\gamma_i$  are the molal activity coefficients of the anion X, free cation Me and its  $i$ -th complex respectively (at  $c \rightarrow 10$  val/l they reach values  $10^1$  to  $10^3$ ) and  $k_i$  is a constant characterizing the physical interaction of the background electrolyte with the  $i$ -th species in its electrophoretic migration. This equation has been used as a basis for further study.

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## THEORETICAL

Experiment has confirmed<sup>1-4</sup> that the interaction constant  $k_i$  in the theoretical equation for the mobility of ions in highly concentrated solutions<sup>4</sup> is approximately the same for all normally hydrated forms of an ion added to the solution of a given background electrolyte. Consequently, we introduce the approximation of setting it equal to a common value  $k$ , and the coefficient  $\exp(-kc)$  in equation (1) can then be separated from all terms of the summation as one expressing the physical influence of the background electrolyte. This coefficient can be combined with the value  $u_0^0$  of the free ion Me and the measured shift  $u$  in Eq. (1) divided by this product. In this way we obtain a new variable  $y = (u/u_0^0) \exp(kc)$ . The remaining part of function (1) describes changes of electrophoretic migration caused by chemical processes (association, formation of complexes).

In view of the low accuracy of electrophoretic measurements it is permissible to assume<sup>5</sup> that the activity coefficients  $\gamma$  in this function will also be little different in a common background electrolyte and can be replaced by the mean activity coefficient  $\gamma_{\pm}$  of the background electrolyte, unless it is appreciably associated itself, which would distort the value of its mean activity coefficient. The chemical factor is thus transformed into a function of the product  $a = m\gamma_{\pm}$ , expressing the activity of the background electrolyte. It is advantageous to plot it in semilogarithmic coordinates as  $y = f(\log a)$ , in which every complex manifests itself by a wave, like on potentiometric titration curves. In these coordinates function (1) takes the form

$$y = \frac{\sum_0^n (u_i^0/u_0^0) \beta_i a^i}{\sum_0^n \beta_i a^i}, \quad (2)$$

which is Bjerrum's function<sup>6</sup>. From Bjerrum curves drawn through experimental points in these coordinates it is possible to assess the orders of magnitude of the constants  $\beta_i$  of the individual forms and their relative mobilities  $u_i^0/u_0^0$ ; in the case of the original, non-transformed curves this evaluation would not be directly possible in the employed concentration range of the fundamental electrolyte.

To transform the measured shifts into the values of  $y$  it is necessary to know the parameters  $k$  and  $u_0^0$ . These can be determined from experimental data obtained under such conditions that the whole chemical coefficient equals the constant  $u_0^0$ . This is the case if the free ion alone is present in the spot or is accompanied by its complex forms of the same value  $u_i^0$ . If this method cannot be used with the given ion and background electrolyte it is possible to employ the values of  $k$  and  $u_0^0$ , obtained with similar, but chemically more suited ions, in the same background electrolyte, or with the same ions but in a different, analogous electrolyte. The latter procedure was employed in this work, the background electrolyte being sodium perchlorate. To estimate the orders of magnitude of the constants the physical effects of sodium perchlorate and lithium chloride, both being uni-univalent electro-

lytes, can be assumed to be approximately the same. The chloride and the perchlorate ions have roughly the same hydration radii<sup>7</sup>,  $r'_{\text{Cl}^-} = 3.27 \text{ \AA}$  and  $r'_{\text{ClO}_4^-} = 3.14 \text{ \AA}$ , and the perchlorate ions are not likely to form highly associated particles with the metal ions, which would substantially affect the shift of the electrophoretic spot.

Hydrated bivalent ions satisfy the assumption<sup>1-3</sup> that all cationic forms migrate at about the same velocity in an electrostatic field. This is true provided the hydration of the complexes compensates for the changes in their electric charges. With trivalent ions this compensation is doubtful. The size of the univalent particle  $\text{MeX}_2^+$ , produced by association or complex formation from the ion  $\text{Me}^{3+}$ , is too big compared to a normal hydrated univalent ion.

Even two ligands  $\text{Cl}^-$  in a linear arrangement represent a prolate body with a longer semiaxis of  $4.5 \text{ \AA}$ , whereas the hydration radius of univalent ions is generally about  $3.2 \text{ \AA}$  (ref.<sup>7</sup>). Consequently, the reduction of the radius does not suffice to compensate for the decrease in electric charge and it is to be expected that the value of  $u_i^0$  for a univalent complex will be lower than for the trivalent and bivalent ions  $\text{Me}^{3+}$  and  $\text{Me}^{2+}$  or  $\text{MeX}^{2+}$ .

The anionic inner-sphere complexes, by contrast, are generally less hydrated than cations of the same size and the differences compensate for each other, but the sign of  $u_i^0$  is reversed in this case.

## EXPERIMENTAL

*Chemicals.*  $\text{LiCl}$  and  $\text{NaClO}_4$  were purified by crystallization, the other chemicals were of analytical grade purity.

*Apparatus, procedure and evaluation* of the measured data were described elsewhere<sup>2</sup>. To suppress hydrolysis all solutions of the background electrolyte were acidified by the corresponding acid ( $\text{HClO}_4$  or  $\text{HCl}$ ) to a concentration of  $0.1 \text{ mol/l}$ . The reduced shift of the spot,  $y = (u/u_i^0) \cdot \exp(kc)$ , was plotted *vs.* the logarithm of the mean activity of the ligand ion of the background electrolyte,  $a_{\pm}$ ;  $u$  [(mm/V) (20 cm/3 h)] is the measured shift of the spot corrected according to Pučar<sup>8</sup>.

*Detection of spots.* The ions of aluminium, gallium and indium were detected by an alcoholic solution of alizarine and the following exposure to vapour of ammonia. The scandic ion was detected by a solution of murexide. We also employed  $^{114\text{m}}\text{In}$ , which was detected radiometrically.

*The shift of the zero point* was determined with the aid of glucose. With  $\text{LiCl}$  it was  $0.038$  throughout its concentration range; In the case of  $\text{NaClO}_4$  the shifts varied with concentration of this salt; they were  $0.176, 0.292, 0.267, 0.304, 0.106, 0.116, 0.102, 0.091$  and  $0.011$  at concentrations  $1.1, 2.1, 3.1, 4.1, 5.1, 6.1, 7.1, 8.1,$  and  $9.1 \text{ mol/l}$ , respectively. The values of  $R_F$ , obtained by the method previously described<sup>2</sup>, are plotted in Figs 1 and 2.

## RESULTS AND DISCUSSION

### *Solution of Sodium Perchlorate*

From the foregoing it follows that the shift of the second cationic outer- or inner-sphere complex  $\text{Me}(\text{ClO}_4)_2^+$  would probably be smaller. If its concentration is not high

enough and neither are those of  $\text{Me}(\text{ClO}_4)_3$  and anions  $\text{Me}(\text{ClO}_4)_x^{(x-3)-}$  the measured shifts plotted vs molarity of the background electrolyte  $c$  according to Eq. (1) should take an exponential course. This means that the plot of  $\log u$  vs  $c$  should be linear, at least in the range of low concentrations of the perchlorate. Fig. 3 shows that within the range of experimental error this linearity indeed exists with all the four ions, the slopes of the lines being approximately equal. These diagrams were employed to read the parameters  $u_0^0$  and  $k$ , used subsequently in evaluating the data for solutions of LiCl. The values of  $u_0^0$  and  $k$  [1/mol] respectively were: 1.39 and 0.193 for Al, 1.40 and 0.168 for Sc, 1.49 and 0.182 for Ga, 1.52 and 0.178 for In.

### Solutions of Lithium Chloride

Using the parameters  $u_0^0$  and  $k$  for solutions of  $\text{NaClO}_4$ , the values of the function  $y$  were calculated from the measured shifts  $u$ . For the coefficients in equation (2) it is necessary to substitute, empirically, chosen values of  $u_i^0$  (or  $y_i^0 = u_i^0/u_0^0$ ) and of  $\beta_i$ . From what has been said above it can be expected that the values of  $y_i^0$  for univalent ions  $\text{MeCl}_2^+$  and  $\text{MeCl}_4^-$  will be different from unity. The curves expressing the relation of  $y$  to  $\log a$  for the ions of Al, Sc and Ga (Fig. 4) are flat around the value  $y = 0.7$ . After this plateau the curves go to zero (curve 2) or to negative values (curves 3 and 4). Another plateau appears in the negative region (curve 4, the ordinate is

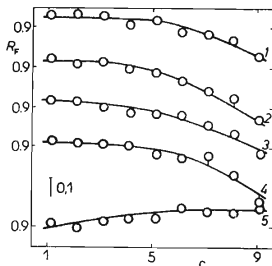


FIG. 1

$R_F$  of the Studied Ions as Function of Concentration of  $\text{ClO}_4^-$ ,  $c$  [mol/l]

1  $\text{Al}^{3+}$ , 2  $\text{Sc}^{3+}$ , 3  $\text{Ga}^{3+}$ , 4  $\text{In}^{3+}$ , 5 glucose. (The  $R_F$  scales for the individual curves are shifted, the initial value for each is given on the axis).

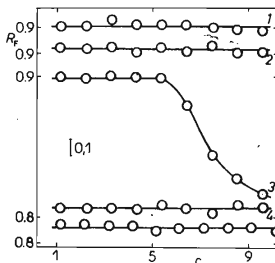


FIG. 2

$R_F$  of the Studied Ions as a Function of Concentration of  $\text{Cl}^-$ ,  $c$  (mol/l)

1  $\text{Al}^{3+}$ , 2  $\text{Sc}^{3+}$ , 3  $\text{Ga}^{3+}$ , 4  $\text{In}^{3+}$  5 glucose. (The  $R_F$  scales for the individual curves are shifted, the initial value for each is given on the axis).

ca -1). Hence it can be assumed that the shift of  $[u_4^0]$  will be the same as those of  $|u_0^0|$  and  $|u_1^0|$ , i.e.  $|y_4^0| = 1$ . In view of the rather low accuracy of electrophoretic measurements only rough estimates of the values of  $\beta_i$  and especially  $\beta_1$  are possible, since the mobilities of  $M_2^{3+}$  and  $M_2Cl^{2+}$  (the first outer- or inner-sphere complex) are supposed to be the same. The stability constant of this complex can show itself only in the slope of the wave of the second complex. The estimate of the ratio  $\beta_2/\beta_1 = K_2$  is somewhat safer, because the mobility of the second complex is smaller. The estimates of  $\beta_3/\beta_2 = K_3$  and  $\beta_4/\beta_3 = K_4$  are relatively good, since in these cases the mobility differences are the greatest. The first two constants are quite impossible to estimate if the curve of shifts approaches zero even at the lowest concentration of the background electrolyte, or if it even starts in the negative region. The consecutive constants higher than  $K_4$  cannot be assessed from the electrophoretic data since for the reasons mentioned above the method does not allow us to distinguish polyvalent anionic inner- or outer-sphere complexes from the univalent ones.

To estimate the values of the stability constants from the measured shifts  $u$  we have introduced a simplifying assumption that the activity of the chloride ions in systems LiCl-HCl, of a constant concentration of HCl (0.1M), approximately equals the product  $m_{LiCl}\gamma_{LiCl}$  in solutions of lithium chloride alone, if the concentration of  $Cl^-$  ions is the same as in the systems LiCl-HCl.

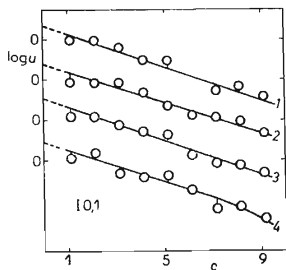


FIG. 3

Corrected Shifts of the Spots,  $u$ , in Relation to Concentration of  $ClO_4^-$ ,  $c$  (mol/l)

1  $Al^{3+}$ , 2  $Sc^{3+}$ , 3  $Ga^{3+}$ , 4  $In^{3+}$  (The scales of  $\log u$  for the individual curves are shifted, each initial value is marked on the axis).

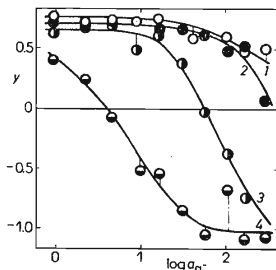


FIG. 4

Experimental Values of  $y = (u/u_0^0) \log(kc)$  of the Studied Ions in Relation to  $\log a_{Cl^-}$   
1  $Al^{3+}$ , 2  $Sc^{3+}$ , 3  $Ga^{3+}$ , 4  $In^{3+}$ .

### The Aluminic Ion

From the plot of  $y$  vs  $\log a$  (Fig. 5) it can be judged that at the lowest concentration of the background electrolyte the spot also contains bivalent cations  $\text{AlCl}_2^{2+}$ , which are transformed into univalent ions of a lower mobility ( $y = 0.7$ ); these ions strongly predominate at medium concentrations of the background electrolyte and are gradually further converted into the neutral particles  $\text{AlCl}_3$ . Under the assumption that the three forms in the spot are in an equilibrium the Bjerrum function becomes

$$y = (1 + 0.7K_2a)/(1 + K_2a + K_2K_3a^2). \quad (3)$$

On the basis of what has been said above the order of magnitude of the third consecutive constant of stability of the inner- or outer-sphere complex,  $K_3$  can be estimated reliably. The relative shifts  $y$  best fit a calculated curve for  $K_3 = 2 \cdot 10^{-3}$  and  $K_2 = 3 \cdot 10^0$ . If other values are chosen for  $K_2$  and  $K_3$  the conversions of the first inner-sphere complex into the second one (from  $y = 1$  to  $y = 0.7$ ) and of the second into the third ( $y$  reduces to zero) manifest themselves on the calculated curves by shifts on the axis of  $\log a$  to the left or the right side from the measured data; for each order of magnitude of these constants the shift is a unity of  $\log a$ , which is well detectable despite the low accuracy of the electrophoresis.

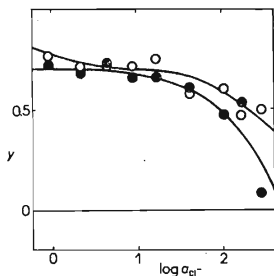


FIG. 5

The Quantity  $y = (u/u_0^0) \log(kc)$  of  $\text{Al}^{3+}$  and  $\text{Sc}^{3+}$  Ions in Relation to  $\log a_{\text{Cl}^-}$

The points are experimental data, the curves were calculated from equations (3) and (4)  $\circ \text{Al}^{3+}$ , for  $K_2 3 \cdot 10^0$ ,  $K_3 2 \cdot 10^{-3}$ ,  $\bullet \text{Sc}^{3+}$ , for  $K_3 3 \cdot 10^{-3}$ ,  $K_4 10^{-3}$ .

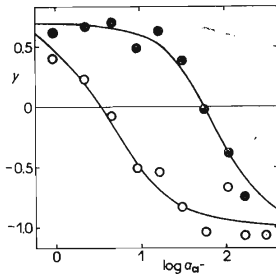


FIG. 6

The Quantity  $y = (u/u_0^0) \log(kc)$  of  $\text{Ga}^{3+}$  and  $\text{In}^{3+}$  Ions in Relation to  $\log a_{\text{Cl}^-}$

The points are experimental data, the curves were calculated from equation (4).  $\bullet \text{Ga}^{3+}$ , for  $K_3 10^{-2}$ ,  $K_4 2 \cdot 10^{-2}$ ;  $\circ \text{In}^{3+}$ , for  $K_3 3 \cdot 10^{-1}$ ,  $K_4 2 \cdot 10^{-1}$ .

In view of the small crystallographic radius of the aluminic ion ( $r_i = 0.5 \text{ \AA}$ ) and its configuration of an inert gas, the electrostatic interaction probably predominates. With small, non-deformable ions the electrostatic interaction is known to be stronger for water than for the chloride ions. Hence it seems that association of hydrated ions is more likely than the formation of true inner-sphere complexes, so that the determined values of  $K_2$  and  $K_3$  are probably the stability constants of outer-sphere complexes.

### The Scandic Ion

Even at the very beginning of the investigated concentration range of the background electrolyte the formation of the dichloroscandic cation,  $\text{ScCl}_2^+$ , is practically complete; its mobility is low ( $a = 0.7$ ). At medium concentrations these ions strongly predominate and at the highest concentrations of  $\text{LiCl}$  they are converted into the electroneutral  $\text{ScCl}_3$  (Fig. 5). The curve decreases closely to zero and is steeper than with  $\text{Al}^{3+}$ . This steepness suggests that anions  $\text{ScCl}_4^-$  are also formed, but not in a concentration high enough to reverse the migration toward the anode. In the Bjerrum function the terms in the fourth power must also be considered, which in the absence of the free ions and the first inner-sphere complexes (in the region  $K_1 K_2 a^2 \gg 1$ ) leads to the relation

$$y = (0.7 - K_3 K_4 a^2) / (1 + K_3 a + K_3 K_4 a^2). \quad (4)$$

The relative shifts of the spots,  $a$ , fit a curve calculated for the consecutive stability constants  $K_3 = 3 \cdot 10^{-3}$  and  $K_4 = 10^{-3}$ . If the fourth inner-sphere complex is not taken into the calculation it is impossible to attain agreement, within the range of experimental error, between the measured and the calculated curves of the shifts. Consequently, at the highest employed concentration of the fundamental electrolyte there are formed anions  $\text{ScCl}_4^-$ , whose constant of stability,  $K_4$ , has the same order of magnitude as  $K_3$ . The formation of the anion in the aqueous phase accords with the finding that at these high concentrations scandium is adsorbed to anion exchangers<sup>9</sup> or extracted by tri-*n*-octyl amine<sup>10</sup>.

The observed higher tendency of the scandic ion to association with  $\text{Cl}^-$  ions cannot be ascribed to Coulomb forces alone, since these are weaker with  $\text{Sc}^{3+}$ , with its greater ionic radius, than with  $\text{Al}^{3+}$ . The true explanation should probably be sought in the existence of vacant  $3d$ -orbitals, which in the ion  $\text{Sc}^{3+}$  are energetically close to its valency orbitals  $4s$  and  $4p$ .

### The Gallic Ion

The curve of the relative shifts  $y$  (Fig. 6) passes zero and enters the anionic region, where it tends to  $y = -1$ . Accordingly, at high activities of the chloride ions gallium forms not only  $\text{GaCl}_3$ , but also anions  $\text{GaCl}_4^-$ , with a mobility  $u_4^0 = -u_0^0$ , like

in the case of  $\text{Sc}^{3+}$ . The initial value of the shift at  $a_{\text{Cl}^-} = 1 \text{ mol/l}$  already corresponds to full conversion of the gallic ion into the univalent dichlorogallic cation, in analogy to scandium. The experimental points fit a curve calculated from equation (4) for  $K_3 = 10^{-2}$  and  $K_4 = 2 \cdot 10^{-2}$ . Consequently, the order of magnitude of  $K_3$  is not higher than that of  $K_4$ . The values of the two constants are close to those reported by Marcus<sup>11</sup> ( $K_3 = 6 \cdot 10^{-3}$ ,  $K_4 = 5 \cdot 10^{-2}$ ).

It is evident that the gallic ion forms even firmer complexes with  $\text{Cl}^-$  ions than the scandic ion does.

Since the radius of the gallic ion is relatively large we can probably attribute this observation to the formation of inner-sphere complexes, not to electrostatic forces alone. The great stability of these complexes is probably due to the  $d^{10}$  configuration of the gallic ion, so that it forms bonds with  $\text{Cl}^-$  ligands not only by accepting the electron pair, but also by back transfer of charge from its occupied  $d$ -orbitals to the ligands.

### The Indic Ion

With this ion in chloride solutions the conversion into the electroneutral and the negatively charged forms begins at the very lowest concentrations of the chloride ions (Fig. 6). In the investigated region the values of the shift are much smaller than would correspond to the cation  $\text{InCl}_2^+$  and rapidly decrease to zero, then enter the anionic region, already at much lower activities of the chloride ions than in the case of  $\text{Ga}^{3+}$ . At the highest activities of  $\text{Cl}^-$  there appears a marked plateau in the anionic region. This plateau indicates a practically quantitative conversion of indium into complex anions (in the case of gallium this conversion was not complete). The curve approaches the limit  $y = -1$ , from which it can be inferred that the mobility of the complex anions is roughly the same as that of the free cations  $\text{In}^{3+}$ . The conversion of the cationic forms of indium into the anionic ones proceeds in a single wave. This proves that the stability constant  $K_3$  of the electroneutral form has the same or lower order of magnitude than  $K_4$ . The reduced shifts of the spots best agree with the curve calculated from equation (4) for  $K_3 = 3 \cdot 10^{-1}$  and  $K_4 = 2 \cdot 10^{-1}$ . These results suggest that of all the ions studied the indic ion forms the stablest complexes with the ligands  $\text{Cl}^-$ . This conclusion is in accordance with the fact that the configuration of  $\text{In}^{3+}$  is again  $d^{10}$ , but the ion is even more deformable than  $\text{Ga}^{3+}$ . The values of the constants well agree with the reported ones<sup>11</sup>. In addition to the anions  $\text{InCl}_4^-$  the spot possibly contains the anions  $\text{InCl}_5^{2-}$  and  $\text{InCl}_6^{3-}$ , especially at higher concentrations of lithium chloride<sup>12-15</sup>. As has been stated above, the paper electrophoresis is not able to separate these forms visibly, because the differences in their mobilities are small. In the region of high concentrations the absolute values of mobility are very low and the errors are multiplied by the factor  $\exp(kc)$ , whose value is very high in this region. This may be the cause of the spread of experimental points in this part of the curves.



## CONCLUSION

The results show that paper electrophoresis reveals the formation of outer- and inner-sphere complexes in strongly concentrated solutions of electrolytes. Their constants of stability can be calculated from the plots of  $\log a$  vs  $(u/u_0^0) \exp(kc)$ . The procedure is based on theoretical ideas published previously.

With solutions of lithium chloride (1.15 – 10.4 mol/l) it has been found that at a concentration of 1 mol  $\text{Cl}^-$ /l all the four ions are present as univalent cations  $\text{MCl}_2^+$ . At higher concentrations of  $\text{Cl}^-$  aluminium forms the electroneutral  $\text{AlCl}_3$  of a low stability constant,  $K_3 = 2 \cdot 10^{-3}$ , but negatively charged outer-sphere complexes are not formed to a significant extent. In the case of scandium there are formed both  $\text{ScCl}_3$  and  $\text{ScCl}_4^-$ , their stability constants being  $K_3 = 3 \cdot 10^{-3}$  and  $K_4 = 10^{-3}$ . However, in the given concentration range of chlorides the curve of the shifts does not reach zero and does not enter the anionic region. The curves for the ions  $\text{Ga}^{3+}$  and  $\text{In}^{3+}$  pass the zero value at  $\log a = 1.8$  ( $K_3 = 10^{-2}$ ,  $K_4 = 2 \cdot 10^{-2}$ ) and  $\log a = 0.60$  ( $K_3 = 3 \cdot 10^{-1}$  and  $K_4 = 2 \cdot 10^{-1}$ ), respectively. In the latter case at the highest concentration of  $\text{LiCl}$  the conversion into negatively charged inner-sphere complexes is practically quantitative. The found order of stabilities of outer- and inner-sphere complexes,  $\text{Al}^{3+} < \text{Sc}^{3+} < \text{Ga}^{3+} < \text{In}^{3+}$ , agrees with the general theory of ion association and bonding in complexes.

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