Inorganica Chimica Acta, 21 (1977) 35–39
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Concentration Minima in Complex Chemistry

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Received May 10, 1976

On investigation of the solvation of $AlCl_3$ in a solvent system of nitromethane (NM)–dimethylformamide (D) an unusual phenomenon was observed; the concentration of the species (AlD_6^{3+}) plotted as a function of the concentration of the free ligand (D) passed through a minimum due to a change in the coordination number of the central aluminium ion. The general conditions under which a minimum in the concentration of a species in the chemistry of complexes can occur were formulated.

Introduction

A large number of different aluminium complexes were identified in the $AlCl_3$–NM–D system by using ^{27}Al-, ^{1}H NMR and conductivity measurements. All but two of the equilibrium constants of this system could be calculated directly [1]. The molality of $AlCl_3$ in the solutions used was between 1 and 3 mol per kg.

The amount of the species AlD_6^{3+} showed a maximum as a function of R when R = 1.5 (where R = weighed mole of D/weighed mol of $AlCl_3$), and a minimum when R = 1.9. The validity of this somewhat surprising effect can be confirmed by a theoretical calculation of the concentrations of the different species present in this system, using the experimentally determined equilibrium constants [1]. Only R values > 1 need be considered as it is only in this range that AlD_6^{3+} is present in measurable quantities. When R > 1.0 only D and Cl^- are found in the first coordination shell of the complex so that NM is seen as an inert solvent [1].

The following equations describe the above system when $R \geqslant 1$:

$$K_1 = \frac{[AlCl_4^-]\,[D]}{[AlCl_3D]\,[Cl^-]} \qquad (1a)$$

$$K_2 = \frac{[Cl^-]^4\,[AlD_6^{3+}]}{[D]^6\,[AlCl_4^-]} \qquad (1b)$$

$$K_3 = \frac{[AlClD_5^{2+}]\,[D]}{[AlD_6^{3+}]\,[Cl^-]} = 0.25 \pm 0.02\ (273\ K) \qquad (1c)$$

$$K_4 = \frac{[AlCl_2D_4^+]\,[AlD_6^{3+}]}{[AlClD_5^{2+}]^2} = 0.17 \pm 0.03\ (273\ K) \qquad (1d)$$

$$K_5 = \frac{[AlCl_3D]^2}{[AlCl_2D_2^+]\,[AlCl_4^-]} = 8.7\ (273\ K) \qquad (1e)$$

$$K_6 = \frac{[AlCl_3D]^2\,[AlD_6^{3+}]}{[AlClD_4^{2+}]^2\,[AlCl_4^-]} = 0.49\ (273\ K) \qquad (1f)$$

$$c_0 = [AlCl_4^-] + [AlCl_3D] + [AlCl_2D_2^+] + [AlClD_4^{2+}] + [AlCl_2D_4^+] + [AlClD_5^{2+}] + [AlD_6^{3+}] \qquad (1g)$$

$$Rc_0 = [AlCl_3D] + 2[AlCl_2D_2^+] + 4[AlClD_4^{2+}] + 4[AlCl_2D_4^+] + 5[AlClD_5^{2+}] + 6[AlD_6^{3+}] + [D] \qquad (1h)$$

$$3c_0 = 4[AlCl_4^-] + 3[AlCl_3D] + 2[AlCl_2D_2^+] + [AlClD_4^{2+}] + 2[AlCl_2D_4^+] + [AlClD_5^{2+}] + [Cl^-] \qquad (1i)$$

(c_0 = total concentration of aluminium chloride).

Although the molality of $AlCl_3$ varied between 1 and 3 mol/kg, the equilibrium constants showed no systematic dependence on the concentration due to the possible variation of the activity constants which was outside experimental error. The medium can be regarded as pure NM as long as R is below 5.5, because the concentration of free D in these solutions is small compared to NM.

Calculation of the Constants K_1 and K_2

K_1 and K_2 were determined by finding the best fit between the experimentally measured concentrations of the complexes and those calculated from eqs. (1a–i). It is not possible to determine K_1 and K_2 directly because there is no range of R in which *all* the species given in eqs. (1a) and (1b) occur in measurable quantities at the same value of R.

The values of K_1 and K_2 determined by the method of best fit are not very accurate as the concentrations of the complexes do not change very much with these equilibrium constants. The maximum change of a mol fraction with $\log K_2$ was (Δx_i/

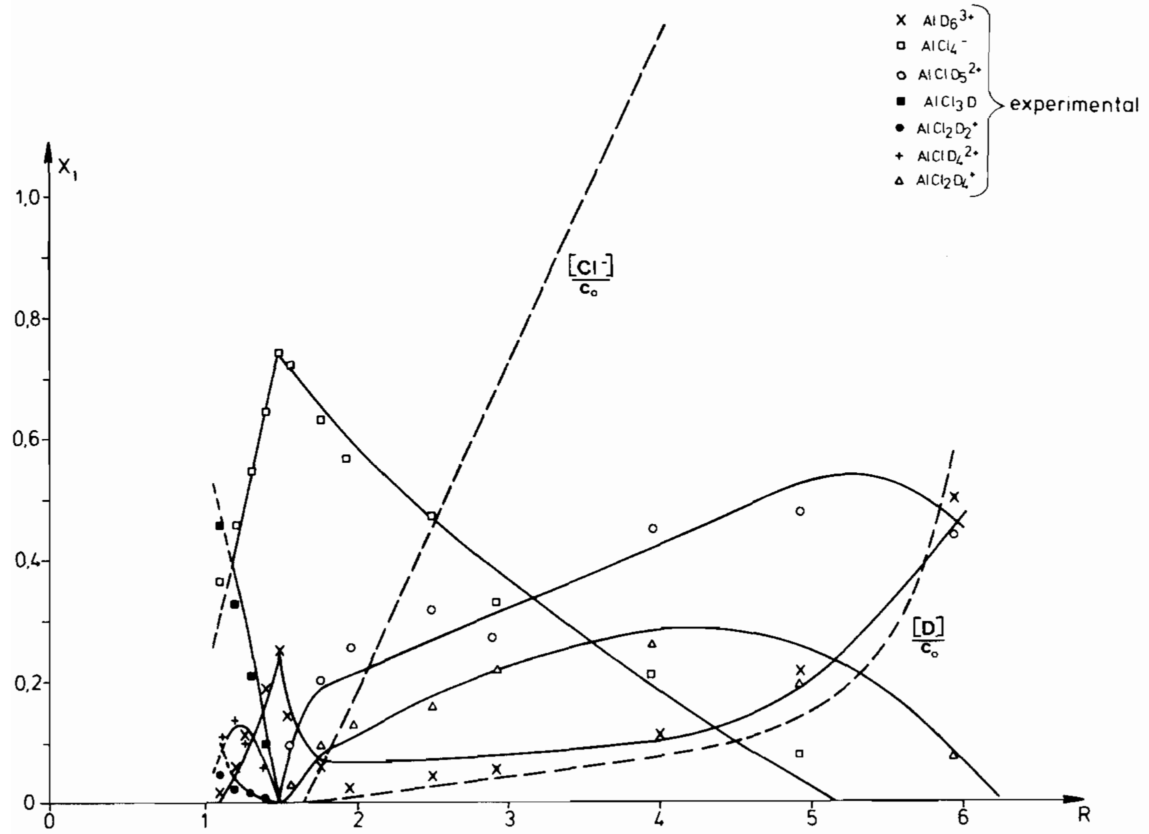

Fig. 1. Mol fractions of the species found in the system AlCl$_3$–D–NM at R ⩾ 1. The lines represent the values calculated by solving the equation systems (1a) to (1i).

Δ log$K_2)_{max}$ = 0.04. When R < 1.8 or > 5, K_2 has little influence on the values of the calculated concentrations. The fit of K_1 is even less accurate than that of K_2, since it only influences the calculated concentrations of the complexes in the region near R = 1.5. Only a lower limit for K_1 can be given. The following values are found: log$K_1 > 2$, logK_2 = 6.6 ± 1. The standard deviation of the mean between the experimentally determined and the calculated mol fractions of the complexes is

$$\frac{\sqrt{\Sigma(\kappa_i \text{ exp} - \kappa_i \text{ calc})^2}}{n-1} = 0.022$$

in the range 1.9 < R < 5.9. The maximum absolute error for the measurement of x_i is ±0.05.

Figure 1 shows a comparison between the mol fractions calculated using eqs. (1a–i) (where K_1 = 100 and $K_2 = 4 \times 10^6$ kg^2/mol^2) and the mol fractions obtained from experimental measurements. The agreement between these values confirms the existence of a minimum for [AlD$_6^{3+}$] as a function of R when R = 1.9 and unusually sharp maxima for [AlCl$_6^{3+}$](R) and [AlCl$_4^-$](R) when R = 1.5.

General Conditions for a Minimum of a Concentration

The general conditions under which a species can show a minimum of the concentration as a function of R during the solvation of a salt (cation M^{q+} and anion A^-) by a ligand L, can be formulated as follows.

The (monomolecular) complexes which occur have the formula $MA_nL_m^{(q-n)+}$. For a given value of m_i, n can have different values ranging from a minimum (n_{min}) to a maximum (n_{max}). c_0 is the total concentration of the complexes and R is defined as above. There is a negatively charged complex

$$MA_{n_k}L_{m_k}^{(n_k-q)-}, \quad n_k - q > 0,$$

and a positively charged complex

$$MA_{n_l}L_{m_l}^{(q-n_l)+}, \quad q - n_l > 0.$$

If the solution only contains these complexes and $[A^-]$, $[L] \ll c_0$ then the system would have a hypothetical coordination number CN_0 where

$$CN_0 = \frac{(q-n_l)(m_k+n_k) + (n_k-q)(m_l+n_l)}{n_k-n_l}$$

at

$$R_0 = \frac{(q-n_l)m_k + (n_k-q)m_l}{n_k-n_l}$$

Necessary conditions for $[MA_{n_l}L_{m_l}^{(q-n_l)+}]$ having a minimum value are now the following:

$$1)\ CN_0 \geqslant CN(R_0) = \frac{1}{c_0} \sum_n \sum_m [MA_nL_m^{(q-n)+}](m+n)$$

where the summations are over all really occurring values of m and n and where all combinations of the concentration of individual complexes are allowed as long as they satisfy the conditions for electroneutrality and balance of mass:

$$c_0 = \sum_n \sum_m [MA_nL_m^{(q-n)+}]$$

$$R_0 = \frac{1}{c_0} \sum_n \sum_m [MA_nL_m^{(q-n)+}]m + \frac{[L]}{c_0}$$

$$q = \frac{1}{c_0} \sum_n \sum_m [MA_nL_m^{(q-n)+}]n + \frac{[A]}{c_0}$$

except for the combination

$$[MA_{n_k}L_{m_k}^{(n_k-q)-}] = c_0\frac{q-n_l}{n_k-n_l};$$

$$[MA_{n_l}L_{m_l}^{(q-n_l)+}] = c_0\frac{n_k-q}{n_k-n_l}$$

where $CN(R_0) = CN_0(R_0)$.

2) For a value of R, R_1, where $R_1 > R_0$, a hypothetical maximum coordination number, CN_1, exists which can only occur through one or more combinations of species where

a) $[MA_{n_l}L_{m_l}^{(q-n_l)+}] < c_0\frac{n_k-q}{n_k-n_l}$

and b) all the values of m for these combinations are less than m_l except, of course, for the complex $MA_{n_l}L_{m_l}$ itself.

The physical basis for these conditions is easily explained: if a reaction

$$MA_nL_{m-1} + L \longrightarrow Ma_nL_m$$

or

$$MA_{n-1}L_m + A \longrightarrow Ma_nL_m$$

is associated with a gain in free enthalpy for all the complexes present in the solution even if [L] and $[A^-]$ are very small, the equilibrium will be changed on addition of L such that, to a first approximation, the increase in the concentrations of the free ligands $[A^-]$ + [L] is minimal; this means that the change in the total coordination number is maximal. If the coordination numbers of the different species are not all the same the situation may occur where, at a value of R, R_0, a certain composition of the solution gives a higher total coordination number than all other feasible combinations (condition 1). When R has a value R_1, where $R_1 > R_0$, and when there are compositions of the solution which only make a maximum total coordination number, CN_1, possible if

$[MA_{n_l}L_{m_l}^{(q-n_l)+}] < c_0 \frac{n_k-q}{n_k-m_l}$ (condition 2), the equilibrium will change with R_1, so that the complexes predominate which give the largest total coordination number.

Finally, if condition 2b is also satisfied, when $R > R_1$ (*i.e.* more L is added) the equilibrium will change such that the concentrations of the complexes in which $m > m_l - 1$ (*e.g.* the complex $[MA_{n_l}L_{m_l}^{(q-n_l)+}]$) will increase (this only holds, of course, if R is so large that [L] and/or $[A^-]$ must be larger than 0).

The following examples illustrate the above. The simplest system in which a minimum in the concentration of a species occurs under conditions 1–2b is:

a) $MA_2^- - MAL_2 - ML_3^+ - A^- - L$

All conditions are satisfied:

$$[MA_2^-] = \frac{1}{2}c_0$$

$$1)\ CN_0 = \frac{1}{2} \times 2 + \frac{1}{2} \times 3 = \frac{5}{2}$$

$$[ML_3^+] = \frac{1}{2}c_0$$

at

$$R_0 = 0 \times \frac{1}{2} + \frac{1}{2} \times 3 = 1.5$$

In this system when R_0 = 1.5, the composition $[MA_2^-]$ = 1/2 c_0, $[ML_3^+]$ = 1/2 c_0 is the only one possible.

2) $CN_1 = 3$

at

$$R_1 = \frac{[MAL_2]}{c_0} \times 2 = 2$$

When R = 2, there is apparently no composition of the solution in which the complex ML_3^+ occurs in a finite concentration which would give a total coordination number of 3, as is the case when only the complex MAL_2 is present.

3) $m_1 = 3 > 2$, *i.e.* at $R \rightarrow \infty$, $[ML_3^+] \rightarrow c_0$

In the appendix it is shown that in this system

[ML_3^+](R) always passes through a minimum, independent of the equilibrium constants. In contrast, a minimum in the concentration of the complex with the highest content of L (solely for which in the systems condition 2a is satisfied) exist in the following similar systems.

b) $MA_3^- - MAL_2^+ - ML_3^{2+} - A^- - L$

It can immediately be seen that CN_0 (condition 1) cannot exist if the coordination numbers of the individual species are constant.

c) $MA_2 - MAL_2^+ - ML_3^{2+} - A^- - L$

Here also CN_0 (condition 1) does not exist because there is no negatively charged complex.

d) $MA_3^- - MAL^+ - ML_2^+ - A^- - L$

Condition 1 is satisfied:

$$[MA_3^-] = \frac{2}{3} c_0$$

$$1)\ CN_0 = 3 \times \frac{2}{3} + 2 \times \frac{1}{3} = \frac{8}{3}$$

$$[ML_2^{2+}] = \frac{1}{3} c_0$$

at

$$R_0 = 0 \times \frac{2}{3} + 2 \times \frac{1}{3} = \frac{2}{3}$$

2) It is easy to see that when $R > R_0 = 2/3$, the higher [ML_2^{2+}], the larger the total coordination number which can be obtained; this means that condition 2 is not satisfied.

e) $MA_3^- - MAL^+ - ML_3^{2+} - A^- - L$

Condition 1 is satisfied

$$[MA_3^-] = \frac{2}{3} c_0$$

$$1)\ CN_0 = \frac{2}{3} \times 3 + \frac{1}{3} \times 3 = R$$

$$[ML_2^{2+}] = \frac{1}{3} c_0$$

at

$$R_0 = 0 \times \frac{2}{3} + 3 \times \frac{1}{3} = 1$$

2) Here too condition 2 is not satisfied because when $R > R_0 = 1$ and [MAL^+] > 0, the total coordination number falls below 3.

Thus, in general, it can be stated that in the following systems a species concentration *cannot* pass through a minimum:

1) The coordination numbers of all the species present are the same.
2) There are no negatively charged complexes.
3) The coordination number of a negatively charged complex is the same or larger than those of all the species present.

In the system of $AlCl_3$ in D and NM investigated above, minima of not only 1 but 2 species are possible under conditions 1–2b; firstly the experimentally determined minimum of [AlD_6^{3+}](R) and secondly a minimum of [$AlClD_5^{2+}$](R).

In the case of [AlD_6^{3+}](R) the conditions 1–2b are:

$$[AlD_6^{3+}] = \frac{1}{4} c_0$$

$$1)\ CN_0(R_0) = CN_0(1.5) = 6 \times \frac{1}{4} + 4 \times \frac{3}{4} = 4.5$$

$$[AlCl_4^-] = \frac{3}{4} c_0$$

at

$$R_0 = 0 \times \frac{3}{4} + 6 \times \frac{1}{4} = 1.5.$$

No other combination of the concentrations of the species present, which satisfy also conditions 2 or 3, gives a total coordination number of 4.5 when R = 1.5.

$$[AlClD_5^{2+}] = \frac{1}{3} c_0$$

$$2)\ CN_1(R_1) = CN_1\ \frac{5}{3} = 6 \times \frac{1}{3} + 4 \times \frac{2}{3} = 4\frac{2}{3}$$

$$[AlCl_4^-] = \frac{2}{3} c_0$$

at

$$R_1 = 0 \times \frac{2}{3} + 5 \times \frac{1}{3} = 1\frac{2}{3}.$$

When R = 5/3, there is apparently no composition with [AlD_6] ≥ 1/4 c_0, which would give a total coordination number of 4 2/3.

3) $m_1 = 6 > 5.0$

In the case of [$AlClD_5^{2+}$] the conditions 1–2b are:

$$[AlClD_5^{2+}] = \frac{1}{3} c_0$$

$$1)\ CN_0(R_1) = CN_1(R_1) = CN_0\ \frac{5}{3}$$

$$= 6 \times \frac{1}{3} + 4 \times \frac{2}{3} = 4\ \frac{2}{3}$$

$$[AlCl_4^-] = \frac{2}{3} c_0$$

at

$$R_1 = 0 \times \frac{2}{3} + 5 \times \frac{1}{3} = 1\frac{2}{3} \text{ (see above).}$$

No other combination of the concentrations of the species present, which satisfy also conditions 2 or 3, gives a total coordination number of 4 2/3 when R = 2.

$$[\mathrm{AlCl_2D_4^+}] = \frac{1}{2}c_0$$

$$2)\ \mathrm{CN_1}(\mathrm{R_2}) = \mathrm{CN_1}(2) = 6 \times \frac{1}{2} + 4 \times \frac{1}{2} = 5$$

$$[\mathrm{AlCl_4^-}] = \frac{1}{2}c_0$$

at

$$\mathrm{R_2} = 0 \times \frac{1}{2} + 4 \times \frac{1}{2} = 2.$$

When $R_2 = 2$, there is apparently no composition in which the complex $\mathrm{AlClD_5^{2+}}$ occurs in a finite concentration which would give a total coordination number of 5.

3) $m_1 = 5 > 4.0$

The minimum of $[\mathrm{AlClD_5^{2+}}](R)$ was not observed experimentally, however it can be calculated with the suitable equilibrium constants if, for example,

$$K_1 \approx K_2 \gg K_3 \approx K_4 \approx K_5 \approx K_6 \approx 1.$$

Since $[\mathrm{AlClD_5^{2+}}] \rightarrow 0$ as $R \rightarrow 1.0$ and $R \rightarrow \infty$, a concentration profile with 2 maxima and 1 minimum is obtained.

Appendix: Proof that a Minimum of $[\mathrm{ML_3^+}]$ always exists in the System $\mathrm{MA_2^-}$–$\mathrm{MAL_2}$–$\mathrm{ML_3^+}$–$\mathrm{A^-}$–L

Equations A1 to A5 (R and c_0 are defined as above):

$$K_1 = \frac{[\mathrm{MA_2^-}]\,[\mathrm{L}]^2}{[\mathrm{ML_2A}]\,[\mathrm{A^-}]} \qquad (A1)$$

$$K_2 = \frac{[\mathrm{ML_2A}]\,[\mathrm{L}]}{[\mathrm{ML_3^+}[\,[\mathrm{A^-}]} \qquad (A2)$$

$$c_0 = [\mathrm{MA_2^-}] + [\mathrm{ML_3^+}] + [\mathrm{ML_2A}] \qquad (A3)$$

$$1 \times c_0 = 2[\mathrm{MA_2^-}] + [\mathrm{ML_2A}] + [\mathrm{A^-}] \qquad (A4)$$

$$Rc_0 = 3[\mathrm{ML_3^+}] + 2[\mathrm{ML_2A}] + [\mathrm{L}] \qquad (A5)$$

After eliminating $[\mathrm{MA_2^-}]$, $[\mathrm{ML_2A}]$ and $[\mathrm{A^-}]$ the two following equations result:

$$\begin{aligned} 0 = f_1(\mathrm{L}, R, [\mathrm{ML_3^+}]) &= [\mathrm{L}]^2 + \\ &+ [\mathrm{L}](3[\mathrm{ML_3^+}] - Rc_0 - K_2[\mathrm{ML_3^+}]) + \\ &+ K_2[\mathrm{ML_3^+}](Rc_0 + [\mathrm{ML_3^+}] - 2c_0) \end{aligned} \qquad (A6)$$

$$\begin{aligned} 0 = f_2(\mathrm{L}, R, [\mathrm{ML_3^+}]) &= 2[\mathrm{L}]^3 + \\ &+ [\mathrm{L}]^2(4c_0 + 2[\mathrm{ML_3^+}] - 2Rc_0 - K_1) + \\ &+ [\mathrm{L}](2K_1Rc_0 - 2K_1[\mathrm{ML_3^+}] - 2K_1c_0) \end{aligned} \qquad (A7)$$

From equations (A6) and (A7) it follows that:

$$\frac{d[\mathrm{ML_3^+}]}{dR} = \frac{\left(\frac{\partial f_1}{\partial L}\right)\left(\frac{\partial f_2}{\partial R}\right) - \left(\frac{\partial f_1}{\partial R}\right)\left(\frac{\partial f_2}{\partial L}\right)}{\left(\frac{\partial f_1}{\partial [\mathrm{ML_3^+}]}\right)\left(\frac{\partial f_2}{\partial L}\right) - \left(\frac{\partial f_1}{\partial L}\right)\left(\frac{\partial f_2}{\partial [\mathrm{ML_3^+}]}\right)} \qquad (A8)$$

When $R \rightarrow 1.5$:

$$-\left(\frac{\partial f_1}{\partial L}\right), \left(\frac{\partial f_1}{\partial R}\right), \left(\frac{\partial f_1}{\partial [\mathrm{ML_3^+}]}\right) \rightarrow 0.5 \times K_2 c_0$$

as $R \rightarrow 1.5$, it follows that

$$[\mathrm{L}], [\mathrm{A^-}], [\mathrm{MAL_2}] \rightarrow 0; [\mathrm{MA_2^-}], [\mathrm{ML_3^+}] \rightarrow 0.5 \times c_0$$

As neither the nominator nor the denominator of (A8) vanish when $R > 1.5$, it follows that:

$$\left(\frac{d[\mathrm{ML_3^+}]}{dR}\right)_{R\rightarrow 1.5} = -\frac{\left(\frac{\partial f_2}{\partial R}\right) + \left(\frac{\partial f_2}{\partial L}\right)c_0}{\left(\frac{\partial f_2}{\partial L}\right) + \left(\frac{\partial f_2}{\partial [\mathrm{ML_3^+}]}\right)}$$

$$= -\frac{4c_0^2[\mathrm{L}]}{4c_0[\mathrm{L}] + 4K_1(Rc_0 + [\mathrm{ML_3^+}] - [\mathrm{L}] - 2c_0)}$$

$$= -\frac{c_0^2[\mathrm{L}]}{c_0[\mathrm{L}] + 2K_1[\mathrm{A^-}]} \qquad (A9)$$

From this it follows that:

$$-1 < \left(\frac{d[\mathrm{ML_3^+}]}{c_0\,dR}\right)_{R\rightarrow 1.5} < 0$$

As $[\mathrm{ML_3^+}]$ has a value of $0.5 \times c_0$ when $R = 1.5$ and as $[\mathrm{ML_3^+}] \rightarrow c_0$ as $R \rightarrow \infty$, it is proved that $[\mathrm{ML_3^+}](R)$ always passes through a minimum in this system.

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