Only when excess Cl⁻ was added did we obtain linear first-order plots, as expected from (12). The mechanism of Garner et al. therefore does not account for the observed Cl⁻ inhibition in the absence of added Cl⁻.

If one assumes the product of reaction 8, $MoO_2Cl_4{}^{2-}$, dissociates rapidly into MoO_2Cl_2 and $2Cl^-$, then Cl^- must be treated as a variable. Integration of (11) with this assumption gives:

$$2[MoOCl_4(DMF)^-] - (k_{-6}[DMF]/k_9 + k_7[NO_3^-]/k_9$$
$$+ 3[MoOCl_4(DMF)^-]_0) \ln [MoOCl_4(DMF)^-]$$
$$= k_6k_7[NO_3^-]t/k_9 + I \qquad (14)$$

This expression, while similar in form to our expression 13, is untestable since k_{-6}, k_7, and k_9 are not known nor can they be obtained from a plot of (11) in the presence of excess Cl⁻. Furthermore, a comparison of (14) with our expression (13) indicates it would not be consistent with the data unless 3·$[MoOCl_4(DMF)^-]_0 \gg k_{-6}[DMF]/k_9 + k_7[NO^{3-}]/k_9$ (a further assumption), in which case it would be identical with (13), with $k_{obsd} = k_6k_7[NO_3^-]/k_9$.

As evidence for their mechanism, Garner, et al. cite a plot of k_{obsd} vs. excess $[NO_3^-]$ in the absence of added Cl⁻ (Figure 1 of ref 2) which is linear, and from which they conclude $k_6 \gg k_{obsd}$. It is not possible to come to this conclusion from their integrated rate expression 14, regardless of the assumptions. On the other hand, this conclusion cannot be arrived at on the basis of (11), since this is only applicable in the presence of excess Cl⁻. The linear dependence of k_{obsd} on $[NO_3^-]$ follows directly from (13), of course, since $k_{obsd} = k'[NO_3^-]$.

Garner et al. also state a plot of $[NO_3^-]/k_{obsd}$ vs. excess $[Cl^-]$ supports eq 11. While such a plot is reasonably linear, it has a negative intercept (−52.8 ± 10.7); since the intercept equals $[NO_3^-]/k_6 + k_{-6}[DMF]/k_6k_7$ and must be positive, the plot in fact argues against the validity of their mechanism.

Finally, the mechanism of Garner et al. requires a fast isomerization of the $MoOCl_4(NO_3)^{2-}$ complex formed in reaction 7 in order that an oxygen will be in the required cis position to the Mo(V) oxo group for electron transfer[4] (the NO_3^- must of necessity enter the vacant trans position of $MoOCl_4^{-1}$). In our mechanism, a reasonable possibility exists for the NO_3^- being bidentate in the complex $MoOCl_3(NO_3)^-$, which gives the cis geometry; this possibility is strongly supported by the observed Cl⁻ inhibition, a fact of considerable importance in interpreting the mechanism:
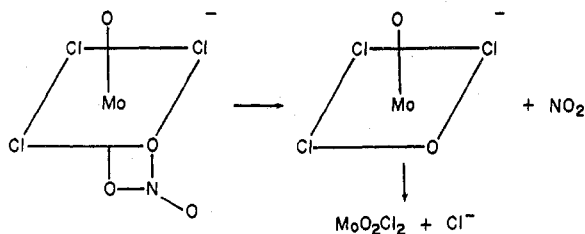
Registry No. $(NH_4)_2MoOCl_5$, 17927-44-5; NO_3^-, 14797-55-8.

References and Notes

(1) R. D. Taylor and J. T. Spence, *Inorg. Chem.*, **14**, 2815 (1975).
(2) C. D. Garner, M. R. Hyde, and F. E. Mabbs, *Inorg. Chem.*, **15**, 2328 (1976).
(3) U. Mayer and V. Gurman, *Adv. Inorg. Chem. Radiochem.*, **17**, 189 (1975).
(4) C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *Nature (London)*, **252**, 579 (1974).

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Problems in the Study of Aluminum(III) Complexation Kinetics

Sir:

To both analytical and inorganic chemists, the dynamics of aluminum(III) complex formation has been important, useful, and—most often—puzzling. Recent studies on equilibria in aqueous acidic aluminum(III) solutions[1] and on the kinetics and mechanism of aluminum–salicylate complexation in the same medium[2] have convinced us that analytical and inorganic chemists often work—and publish—in ignorance of one another. Consequently, this letter points out several significant features of aqueous aluminum(III) solutions which constrain dynamical studies of these systems.

Speciation in Aqueous Aluminum(III) Solutions. To effect a separation of aluminum from other ions and at the same time to achieve a reliable quantitative determination of aluminum, Kolthoff and Sandell developed the method of precipitation with 8-hydroxyquinoline.[3] However, their procedure yields low and erratic results unless the analysis is carried out with the prescribed acetic acid–acetate buffer. This observation led to investigations on the species present in aqueous aluminum(III) solutions in the pH range 1–7.[4]

Attempts to characterize partially neutralized aluminum chloride solutions by means of the extent or rate of reaction of aquoaluminum(III) with an organic ligand probably begin with the work of Linnell,[5] who measured the amount of aluminum 8-hydroxyquinolinate precipitated from solution as a function of time by a gravimetric procedure. At about the same time, and independently, Okura, Goto, and Yotuyanagi studied the extraction of the aluminum 8-hydroxyquinolinate into chloroform immediately after mixing the reagents.[6] On the basis of this procedure the aluminum in solution was divided into "extractable" and "unextractable" species. This technique was modified by Turner, who subdivided the aluminum present in solutions of this type into three forms on the basis of relative reaction rates.[7] Evidence for the existence of aluminum species differing in their reactivity toward a complexing ligand could be gathered more easily and reliably following Smith's development of a single-phase spectrophotometric method.[4] This procedure uses the derivative 8-hydroxy-7-iodo-5-quinolinesulfonic acid, or "ferron", which forms a water-soluble aluminum complex whose formation may be followed spectrophotometrically.

Addition of ferron to a partially neutralized solution of $AlCl_3$ at pH 5 leads to a typical result shown in Figure 1. From the dynamics of the trace, three types of aluminum can be identified. Reacting quickest is Al^a; then, the reaction of Al^b occurs. These two reactions, usually requiring no more than 1 h for completion, are followed by the very slow reaction of Al^c, which may last for days. Current analytic investigations are concerned with the nature of Al^b and Al^c; Al^a is assumed to be monomeric.[1]

Dynamics of Aluminum(III) Complex Formation. The rate of exchange of water molecules between bulk solvent and a metal ion's inner coordination shell is a fundamental factor governing the rate of complexation. In 0.5 M $HClO_4$ solutions of $AlCl_3$, this rate constant was measured by Fiat and Connick to be 1.3×10^{-1} s^{-1} at 25 °C by using $H_2{}^{17}O$ NMR line broadening.[8] Earlier, Behr and Wendt had applied the pressure-jump method to solutions of aluminum sulfate in the pH range 1–3.[9] Hydrogen ion dependent relaxation times on the order of 10^{-1} s were measured. These results lead to a less definitive mechanism than the high-acid NMR experiments; however, it is now clear that at least one monomeric species other than Al^{3+}—probably $AlOH^{2+}$—is required to fit the data.[2,10,11]

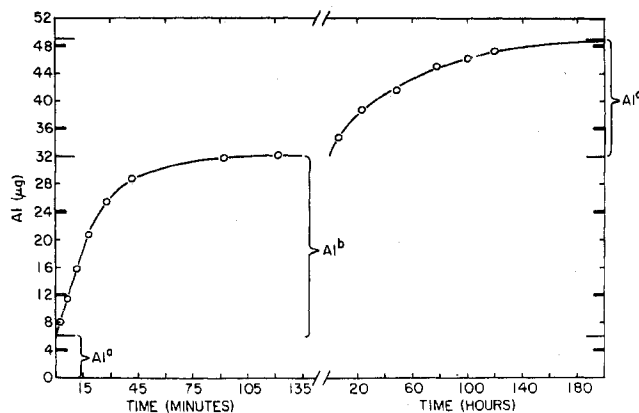**Sources of Difficulty in the Interpretation of Aluminum(III)**

Figure 1. Aluminum determination by ferron complex formation at pH 5. The total amount of aluminum in the sample is known independently; it is indicated by the uppermost light line on the ordinate. The experimental points are calculated from the measured absorbance, the absorptivity coefficient of the tris complex at 368 nm (6.1×10^3 M^{-1} cm^{-1}), and a 34-mL sample volume. Smooth curves have been drawn between the data points. Extrapolation to zero time of the curved portion of the analysis curve in the minutes region of the plot yields the Al^a value (lowest light line on ordinate). The horizontal portion of this curve is asymptotic to the amount of $Al^a + Al^b$ (middle light line on ordinate); subtraction of Al^a gives the Al^b value. A considerable amount of slowly reacting material remains, as shown by the continuation of the time scale in hours. Subtraction of the $Al^a + Al^b$ amounts from the total aluminum present yields Al^c.

Complexation Kinetics. (1) Rate Constants for Reactions of Monomeric Aluminum(III). The ferron assay shows that freshly prepared solutions of partially neutralized Al(III) may be as much as 90% polymeric at pH 5. As the pH is reduced, the relative reactivity patterns change, leading to decreases in the concentrations of higher molecular weight polymeric forms. How meaningful, then, are the concentrations of free aluminum(III) that have been used to determine rate constants? How valid are mechanistic assignments that overlook polynuclear hydrolytic species? These questions should be considered in future studies of aluminum complex formation.

(2) Ferron Assay. Problems with the ferron assay arise from its qualitative nature. Systematic rate law determinations have not been carried out; a first-order rate law for Al^b reaction has been assumed.[1,4] However, under the conditions of the

ferron assay, second-order kinetics fit equally well. Ligand-dependent rate constants could lead to different reactivity patterns, but no ligands other than ferron have been studied for this purpose. Due to the relatively high charge on aluminum(III) and the probable polyelectrolytic nature of Al^b and Al^c, specific anion effects are expected to influence the kinetics; these effects have not been investigated. In short, although the dynamical approach to aluminum analysis is valid, the lack of systematic rate studies makes some of the conclusions less certain than they could be.

Summary. Homogeneous solutions of aluminum(III) in aqueous acid media contain species which differ in their reactivity toward complexing ligands. Kineticists should consider this information in studying the rates and mechanisms of aluminum(III) complexation. Analysts should avail themselves of the results and methodologies of chemical kinetics to develop a more quantitative dynamical assay of the aluminum species present in solution.

References and Notes

(1) (a) R. C. Turner, *Can. J. Chem.*, **53**, 2811 (1975); (b) *ibid.*, **54**, 1528 (1976); (c) *ibid.*, **54**, 1910 (1976).
(2) F. Secco and M. Venturini, *Inorg. Chem.*, **14**, 1978 (1975).
(3) I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928).
(4) R. W. Smith, *Adv. Chem. Ser.*, No. **106**, 250 (1971).
(5) R. H. Linnell, *J. Inorg. Nucl. Chem.*, **22**, 55 (1961).
(6) T. Okura, K. Goto, and T. Yotuyanagi, *Anal. Chem.*, **34**, 581 (1962).
(7) R. C. Turner, *Can. J. Chem.*, **47**, 2521 (1969).
(8) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **90**, 608 (1968).
(9) B. Behr and H. Wendt, *Ber. Bunsenges. Phys. Chem.*, **66**, 223 (1962).
(10) J. Miceli and J. Stuehr, *J. Am. Chem. Soc.*, **90**, 6967 (1968).
(11) C. Kalidas, W. Knoche, and D. Papadopoulos, *Ber. Bunsenges. Phys. Chem.*, **75**, 106 (1971).

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