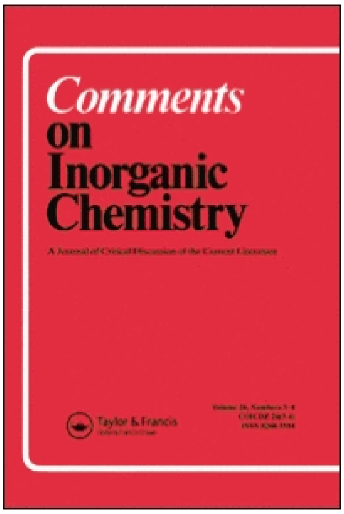

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Kinetic Studies of Colloidal Metal Complex Species Relevant to Natural Waters

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Kinetic Studies of Colloidal Metal Complex Species Relevant to Natural Waters

The dissociation reactions of colloidal complexes of Fe(III), Al(III), and Cu(II) formed by binding of the metals to naturally occurring organic ligands and by their inclusion in hydrous oxide colloids are studied by treatment with an excess of a ligand suitable for sensitive spectrophotometric detection under solution conditions favorable to formation of the complex with the color former. A range of rates varying with metal to ligand ratio are found which emphasize the importance of the extension to kinetics of the mixture polyelectrolyte approach which has gained acceptance in discussion of the equilibrium properties of similar complexes. Results do show interpretable relationships to the kinetic behavior of the better studied mononuclear chelate species and some aspects point to a role for mass transport. The ground is prepared for inorganic kineticists to enter this problem area which probably encompasses the subject of bioavailability of metal ion nutrients and toxicants.

INTRODUCTION

By the late 1960's the main mechanisms of complex formation which are at the center of current discussions, dissociative, interchange and associative, were clear. A number of studies had been done which elucidated the mechanisms of replacement of one metal by another in a chelate and some results had been reported concerning reaction kinetics of polynuclear complexes with two metal centers. This set the stage for students of natural water chemistry to ask questions about kinetics and mechanisms of metal ion speciation in fresh waters. Few of these questions have been answered in the intervening years and the literature contains very few studies of kinetic aspects of natural water metal ion

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speciation with the exception of a complex (perhaps even confused) literature on the subject of the implications of slow dissociation of complexes and nonliability for study of speciation by anodic stripping voltammetry.

A little reflection shows that this circumstance is not too surprising. Beyond the elegant early studies, such as those of Eigen and Tamm,[1] using ultrasonic absorption to characterize the kinetic properties of simple labile inorganic complexes with ligands such as sulfate and carbonate binding divalent metals like Mg, Ca, Cd, Cu and Zn, the problems of interest in natural water chemistry focus on polymeric organic ligands and metals that are extensively hydrolyzed, hence commonly present as polymeric hydroxo or oxo ions, in the pH range of natural water. The metal ions of lower intrinsic lability that are reasonably common include (Al(III), Fe(III), Cr(III) and Mn(IV). All of these are present as polymeric hydrous oxides in the pH range between 4 and 9. The important organic ligands in natural waters are dominated by the humic substances with lesser amounts of other relatively high molecular weight polyelectrolyte chelating agents.[2]

The study of the equilibrium aspects of metal ion speciation began from development of computer models which assumed that the organic ligands present in a natural system could be represented by a collection of monomeric ligands for which data on stability constants were available in standard critical compilations of laboratory data.[3] If this approach could be extended to kinetic aspects of speciation in natural waters, the information available from laboratory studies of kinetics of complex formation which were already available nearly 15 years ago would provide a substantial base for prediction of kinetic aspects since the rates of complex formation of aquo metal ions vary over only a small range as the ligand is varied. Such predictions have been attempted. An effort by one of us (C.H.L.) concerning the occurrence of mixed ligand species in natural water is probably a good example of the failure of this simple model.[4]

Recently, the application of the simple monomeric ligand model even to equilibrium properties has been extensively criticized.[5,6] It has two serious flaws: it underestimates the diversity of the ligand sites present in natural polyelectrolyte ligand mixtures and it overlooks the polyelectrolyte aspects of the problem. The equilibrium methods that are becoming accepted view the ligands in natural waters as mixtures that are sufficiently complex to be treated as continuous distributions for which thermodynamic equilibrium constants exist only as differential quantities. The methods also explicitly include polyelectrolyte electrostatic aspects. In this comment we explore the implications of this newer approach for kinetics. The effort will be to demonstrate the methods appropriate for modeling natural water inorganic kinetics and to encourage kineticists to tackle this interesting research area which probably encompasses the problem of bioavailability of trace metal nutrients and toxicants.

THEORY

Metal ions bound in humates and hydrous oxides may be studied kinetically at suitably low concentrations to represent natural water systems using a sensitive color forming complexing agent. The kinetic scheme is illustrated in the next few equations where for clarity the metal is assumed to be Fe(III) and the humate is a fulvic acid (FA). In the illustrations, the color forming reagent is assumed to be sulfosalicylic acid (SSA) which forms a red complex with Fe(III):

$$\mathrm{FeFA} \underset{K(2)}{\overset{K(-2)}{\rightleftharpoons}} \mathrm{Fe}^{3+} + \mathrm{FA}; \tag{1}$$

$$\mathrm{Fe}^{3+} + \mathrm{SSA} \underset{K(-1)}{\overset{K(1)}{\rightleftharpoons}} \mathrm{FeSSA}. \tag{2}$$

The reaction indicated by Eq. (2) is well understood and has a known rate law and rate. Choice of a suitable excess of SSA (or other simple color forming ligand) reduces the process characterized by $K(1)$ to a pseudo first order one characterized by the pseudo first order constant $K'(1)$ which will commonly be larger than $K(-2)$. This means that the rate of formation of Fe SSA can be expressed by the simple overall equation:

$$d[\mathrm{FeSSA}]/dt = K(-2)[\mathrm{FeFA}]. \tag{3}$$

The only problem with Eq. (1) to (3) is that they assume the existence of a single iron fulvate species. We must make allowance for the complicated polyelectrolyte mixture character of our collodial complexes.

A first step would be to write equations for an Ith component to replace Eq. (1) to (3), including summation over all components I in Eq. (3) for the rate of formation of the species which is detected:

$$\mathrm{FeFA}(I) \underset{K(2I)}{\overset{K(-2I)}{\rightleftharpoons}} \mathrm{Fe}^{3+} + \mathrm{FA}\ (I); \tag{4}$$

$$\mathrm{Fe}^{3+} + \mathrm{SSA} \underset{K(-1)}{\overset{K(1)}{\rightleftharpoons}} \mathrm{FeSSA}; \tag{5}$$

$$\frac{d[\mathrm{FeSSA}]}{dt} = \sum_I K(-2I)\ [\mathrm{FeFA}(I)]. \tag{6}$$

If an experimental signal such as an optical absorbance monitors the formation of the product complex, one can write an integrated form of Eq. (6) with P representing the product signal and $A(0,I)$ an initial concentration of the Ith component [FeFA(I) in our illustration] at t = 0:

$$P(t) = \sum_I A(0,I)\ \{1 - \exp\ [-K(I)t]\} + X. \tag{7}$$

In Eq. (7) the term X is a time independent term which will include the blank signal and any contribution to P which occurs rapidly on the time scale of the experiment.

Equation (7) is very useful for well defined mixtures. For example, Margerum *et al.*[7] have used it in an elegant kinetic method to analyze a mixture of aminopolycarboxylate ligands complexed to Ni(II) which are then reacted with cyanide. They enjoyed the advantage of being able to measure the rate constants, the $K(I)$, independently for different aminopolycarboxylates. The initial concentrations $A(0,I)$ could then be obtained by linear least squares treatment. By contrast, an attempt to study kinetic properties of metal ion containing natural water colloids is hampered by the fact that the individual component species cannot be prepared separately and the various $K(I)$ cannot be measured independently. Therefore, they must be extracted from the data. With both $K(I)$ and $A(0,I)$ to be extracted, nonlinear regression is required. Two further problems follow. First, a "correct" number of components must be chosen and second, acceptable initial guesses of the parameters must be obtained. Only then can satisfactory nonlinear fits be obtained. In our work we have treated the experimental absorbance time record initially by means of a modification of the Guggenheim method developed by Mak.[8] In this method, the number of segments of the Guggenheim plot identify the number of distinct components that can be objectively recognized and the slopes of linear regions provide good first approximation values to the $K(I)$ providing rapid convergence in nonlinear least squares. The minimum number of components required by the Guggenheim plots and required to fit the data are all that are assumed. In this sense, the number is "objective."

The procedures just outlined have to recommend them that the number of components identified is objective. They have as a weakness that the rate constants are most probably not those for single well defined components of the mixture. More probably, they represent averages over a part of the distribution of components of a complicated mixture. Such a view would be consistent with the polyelectrolyte mixture models developed to deal successfully with the equilibrium properties of some of our colloidal complexes.[5,6] However, some of our species may be correctly described by a small set of kinetically distinct components and a small number of rate constants. In this case, Eq. (7) is exact.

An alternative treatment to that of Eq. (7) has recently been proposed by Schuman and his students at North Carolina.[9] This treatment is the parallel for kinetics of the continuous distribution of sites model for equilibrium. The analysis begins from theory developed for the analysis of viscoelastic relaxation in polymers.[10] Shuman *et al.* began from an expression analogous to the integrated form of Eq. (3):

$$C(t) = C(0)\exp(-kt). \tag{8}$$

In this expression, $C(t)$ represents the time course of the overall concentration of humic complexes such as the FeFAs in our initial example. This quantity is not experimentally accessible but it is assumed to relate through simple stoichiometry to the experimental quantity called P in Eq. (7). For a mixture, Eq. (8) may be rewritten as the summation of Eq. (9) or the continuous expression of Eq. (10):

$$C(t) = \sum_{I} C(0,I)\exp[-k(I)t]; \tag{9}$$

$$C(t) = S\int_{-\infty}^{+\infty} H(k)\exp(-kt)d[\ln(k)]. \tag{10}$$

In Eq. (10) the new quantity $H(K)d[\ln(K)]$ is the probability of finding a site with a dissociation rate constant in the rate constant range from

$\ln(K)$ to $\ln(K) + d[\ln(K)]$ in molar concentration units. Solutions can be obtained using the first and second derivatives of $C(t)$ and the approximate inversion of a Laplace transform expression equivalent to Eq. (10) where the integral is taken with respect to K in place of $\ln(K)$. The relevant expressions are Eq. (11) and (12).

$$H(K) = \frac{d^2C(t)}{d(\ln t)^2} - \frac{dC(t)}{d(\ln t)}; \qquad (11)$$

$$S = \frac{4C(t)}{\Sigma C(0,I)} \qquad (12)$$

$H(K)$ and S originate from the Laplace type transform and the value of S depends on whether the 1st, 2nd, or nth derivative is taken in the approximation. When $H(K)$ is plotted versus $\ln(K) = \ln(2/t)$, it gives the distribution of rate constants about a peak value $\ln(K)$ with an area under the peak proportional to the concentration of complexes, since the constraint applies that the integral over the entire range of $H(K)$ adds to the sum of $C(0,I)$s.

The approach based on Eq. (8) through (12) is fundamentally to be preferred to that based on Eq. (7) when the colloidal ligand is a complicated polyelectrolyte species. But, the complexity of the treatment and the approximations tend to lead to interpretation focused only on peaks of the distribution functions and the areas under the peaks. These are the same two parameters which can be obtained from Eq. (7) at comparable data resolution. Consequently, as long as the mixture situation and the averaging occurring is kept firmly in mind, the more kinetically conventional treatment of Eq. (7) where the approximations are physical, not mathematical, has some appeal and remains competitive. It is worth remembering that Eq. (7) is sometimes exact and not approximate at all.

RESULTS AND DISCUSSION

Hydrous Oxides of Iron

It is perhaps best to begin with the kinetically simplest system we have considered. This is the system consisting of hydrous oxide colloids of iron prepared by slow neutralization of dilute acid stock solutions with weak bases including ammonia and tris. By this route, it is possible to prepare clear solutions of Fe(III) colloids which are stable for periods of at least several months. The acid hydrolysis of the colloids followed by complexation of the Fe(III) released is an interesting reaction. It was first examined kinetically at higher concentrations by Sommer *et al.*[11] as a follow-up to a series of studies of the nature of these materials which resemble the core of ferritin. Initially they considered a kinetic treatment for the acid-catalyzed stripping of the surface from spherical particles. But they found that the results were better fit by a simple first-order rate expression. The reason for this is probably one effect of the circumstance identified by Marinsky.[12] He points out that the surface area for hydrous oxides as measured by conventional methods is so large per gram that it indicates that all of the oxide is surface. That is, these materials are water swollen gels. The material studied by Sommer *et al.* had been chromatographically purified and studied by other methods including ultracentrifugation. It was a polymer with an average of two hydroxo groups per iron atom (that is a net charge of plus one per Fe) and a relatively narrow molecular weight distribution centered on an average polymer with 90 Fe atoms.

Our experiments[13] were conducted first on solutions prepared by adjusting 1.00×10^{-4} M stock solutions of Fe(III) to pH 4 with sodium acetate. Analyses were conducted by mixing equal volumes of sample solutions which had been aged for 24 h with a reagent solution of 0.0100 M SSA in 0.100 M perchloric acid. Thus the kinetics were for the species of iron initially formed at pH 4 as it hydrolyzed at pH 1 and formed the FeSSA complexes. Two components with long reaction times compared to those for the monomeric Fe(III) reaction with SSA were identified. The first had a rate constant of 7.0×10^{-4} s^{-1}, very similar to that reported for the purified 90 Fe polymer of Sommer *et al.* The slower component correlated approximately in terms of total Fe concentration with material that could be removed from the solution by filtration through a 0.45 μ filter.

The solution is seen to contain material in two fairly distinct size ranges. The first is the polymer whose relative homogeneiety was demonstrated by various methods. The second is larger filterable particles, perhaps developing crystalline goethite which is the final hydrolysis product in hydrous oxide Fe(III) solutions. These are components in nearly the exact sense of Eq. (7).

Iron Fulvates

Samples similar to the hydrous oxides at pH 4 were prepared with 0.30 and 0.60 mg/ml of a well characterized fulvic acid as well as 100 μM Fe(III). Based on the functional group composition of the fulvic acid reported by Schnitzer and Gamble[14] this corresponds to 1:1 and 2:1 mole ratios of phenolic sites of the humic polymer to Fe. The kinetics of the reaction of these samples with acid SSA were recorded by conventional and stopped flow methods.

The slowest reacting component identified in these runs with fulvic acid exhibited a rate constant of 6.0×10^{-3} s^{-1}, very similar to a rate constant for the strongly bound Fe(III) that was seen complexed to the same FA in solutions initially prepared at pH = 2.[15] Remaining Fe(III) reacts more rapidly than any component of the Fe(III) colloids in the absence of fulvic acid, but as the stop flow kinetics indicate, at a rate below that for complex formation between SSA and free aquo-Fe^{3+}.

It is important to notice that the rate of this faster reaction is clearly sensitive to the FA:Fe ratio. At 1:1 the rate constant is 0.13 s^{-1} at 2:1 the value is 0.26 s^{-1}. This is well outside experimental error, a remark that cannot be made about the 10% difference in the same direction that is seen for the slower component. If it were not for the changes in the rate constants with FA:Fe ratio, one might overlook the polyelectrolyte character of the fulvic acid. However, this variation shows that speciation is not simply limited to two well defined types of complexing sites.

The simplest interpretation that might be given to the effect of adding FA to a solution in which Fe undergoes hydrolytic precipitation would be to suggest that the organic ligand dissolves the hydrous oxide. This is tempting given the above results. The slower reacting component could be assigned to Fe(III) bound at bidentate chelating sites analogous to salicylic acid and the faster reacting component to Fe(III) held at weaker binding sites analogous perhaps to monomeric carboxylate sites which are available in excess on the fulvic acid. However, it is well known from equilibrium studies[5,6] that the fulvic acid offers a broad distribution of binding strength sites. Moreover, this explanation is much too simple in one important dimension.

We extended our work on the Fe(III) colloids by the use of a reagent which allowed detection at much lower total Fe concentration but led to more complicated kinetics. This was a combination of hydrazine hydrochloride as a reducing agent with the very sensitive reagent for reduced Fe(II), ferrozine.[16] In experiments concerning the relationship between hydrous oxide colloids and feric fulvates at pH 6, we observed that the iron that had been dissolved by the organic ligands was retained on filters which would pass the hydrous oxide colloids prior to such dissolution! This led us to check the effect of the FA:Fe ratio on the light scattering of solutions. Figure 1 shows that complexing of Fe to FA leads to aggregation. The colloidal particles associated with the Fe–FA complexes are in fact larger than the colloidal particles of the hydrous oxides which we grew under the same general conditions, but

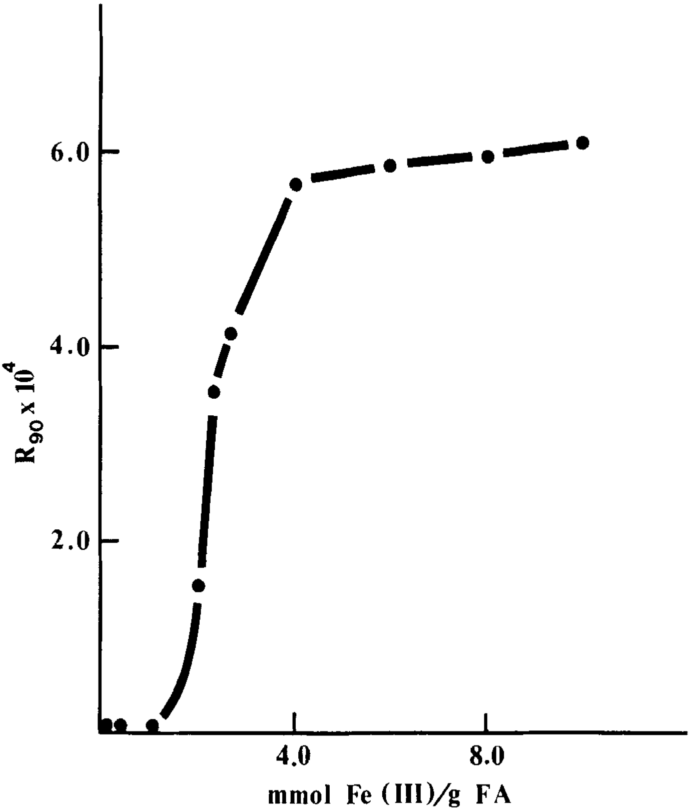

FIGURE 1 Effect of addition of Fe(III) on light scattering, hence particle size of fulvic acid. The large increase corresponds approximately to a 1:1 ratio of Fe(III) to strong binding phenol carboxylate sites.

the Fe in the fulvate complexes is more labile. It would appear that dechelation from phenol carboxylate complexes requires fewer steps to become irreversible than does the dechelation of an Fe atom in an imperfect oxide lattice.

There is a final factor which must not be overlooked in this context. The experiments at pH 4 revealed that between 25% and 35% of the Fe was not recovered as Fe(III). This was available to an Fe(II) complexing agent. Similarly, ferrozine reaction with samples prepared at pH 6 was found to recover Fe(II) from solutions containing fulvic acid *without* the addition of the reducing agent, hydrazine hydrochloride. This recovery was much slower than the recovery using the reducing agent and it did not occur at all when the sample was a straight hydrous oxide colloid. The possibility must be considered that the lability of Fe(III) complexes of fulvic acid involves electron transfer catalysis in a manner analogous to the effect of Zn on the dissolution of anhydrous $CrCl_3$.

Hydrous Oxides of Al(III)

Recently[17] we have completed a study of the reactions of hydrous oxide colloids of Al(III) that were prepared under various conditions with calcein blue, CB, a reagent which forms a fluorescent complex with Al(III) suitable for very sensitive detection. The reaction medium for conversion of the species prepared at different initial pH was an acetate buffer at pH 5 which was chosen as a compromise between the desire to have an acidic medium favoring decomposition of the Al(III) colloids to the CB complex and the negative effect of lower pH on the fluorescence intensity of CB. Kinetic components with total concentration as low as 5×10^{-7} M were readily detectable with this reagent system. Thus it seemed promising for work at low enough Al(III) concentrations to model natural water.

In each individual kinetic run the results obtained were easily fitted to either one or two kinetic components. But the variation of rate constants already found in the case of ferric fulvates becomes a much more obvious feature of the results, indicating that the components found are not well defined molecular species. That the simplicity of the treatment of the data is warranted, however, is illustrated by the two representative Guggenheim plots shown in Figures 2 and 3. To use more than two rate constants to fit the more complicated of these two would not improve the fits at all!

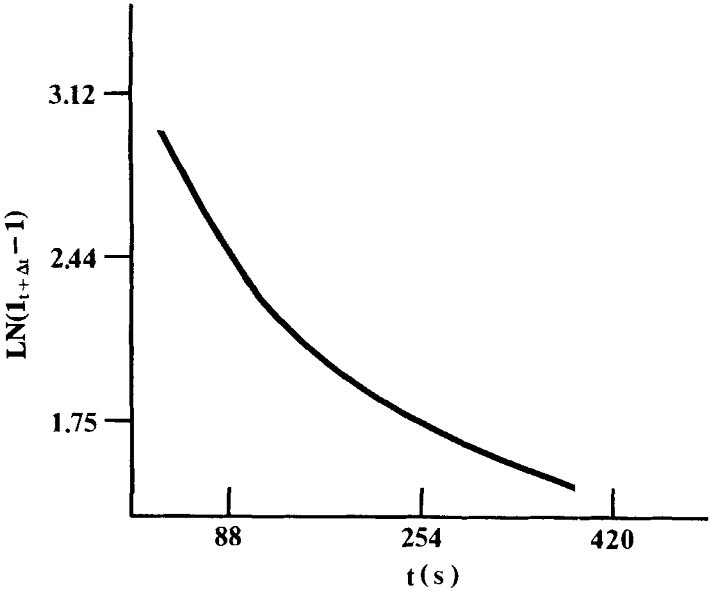

FIGURE 2 Guggenheim plot of fluorescence intensity for reaction of CB (see text) with a sample prepared from 2 × 10^{-5} M Al^{3+} at pH = 5, T = 19.5C. The presence of only one objectively definable component is evident.

A problem that is immediately obvious in the Al(III) experiments is the failure of total recovery. In every case some Al(III) forms irreversibly insoluble oxide material. This is quite recalcitrant and boiling of some samples in perchloric acid failed to render the lost aluminum accessible to the fluorimetric reagent. Clearly, we don't report kinetics for this unreactive species domain but we do keep a difference accounting. Table I is an overall summary of data. Entries A and F in the Table refer to experiments on hydrous Al(III) oxides at pH 5 in the absence of fulvic acid.

At pH 5 and total Al(III) at 20 × 10^{-6}M, 78% of the Al(III) is recoverable in a reaction with a rate constant within 12% of that reported for the reaction of this reagent with monomeric Al(III) at pH 3, 2.8 × 10^{2} s^{-1}. The value is quite reasonable for a simple Al(III) species. The surprise comes when the total Al(III) concentration is *reduced* to 2 × 10^{-6}M at this lower concentration: more aluminum has disappeared into unreactive oxide and that remaining in the solution reacts with CB *less* rapidly.

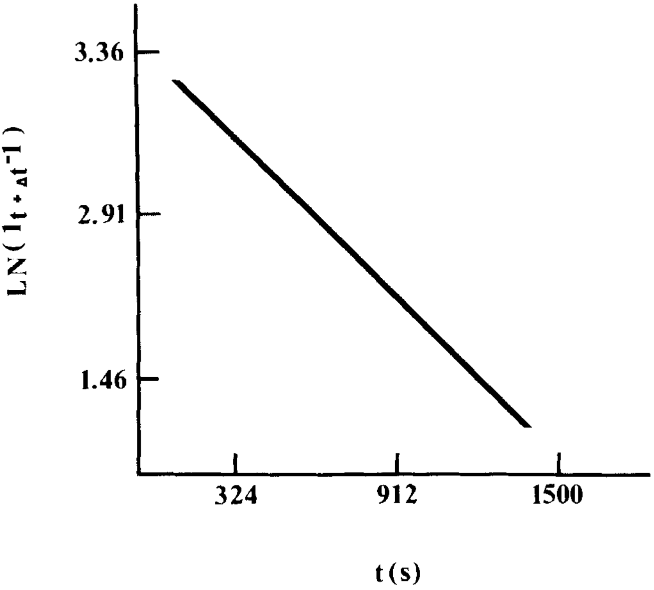

FIGURE 3 Guggenheim plot of fluorescence intensity of CB (see text) with a sample prepared from 2 × 20^{-5} M Al^{3+} plus 2 × 10^{-5} M fulvic acid at pH = 5, T = 19.5C. The presence of two but probably not more definable components is seen.

Fortunately, this apparent contradiction has a precedent and an explanation and serves in fact as a good test of the sensitivity of the kinetic methods to subtle phenomena. Matijevic *et al.*[18] reported a turbidity maximum at an Al(III) concentration of 1 × 10^{-5} M. At lower concentration, sol stability was attributed to adsorption of polyhydroxo cations of Al(III). At higher concentration, anion adsorption is thought to stabilize the colloid. It does finally seem reasonable to describe the Al(III) at the lower concentration as more extensively hydrolyzed. Perhaps this is a point of biochemical significance. If so, bioavailability of aluminum will be complex nonmonotonic function of pH and concentration. This will be seen to hold for complexes with soil organic ligands as well.

Aluminum Fulvates

The objectively definable fractions of AlFA mixtures recognized by their rate constants collected in Table I fall into two well defined ranges

TABLE I
Kinetic analysis of aluminum fulvates[a]

Sample	[A1] Total × 10^6M	[FA] Total × 10^5M	pH of mixture	[CB] Total × 10^4M	*K* (A1) $M^{-1}s^{-1}$	*K* [A1-FA(I)] × $10^2 s^{-1}$ (obs)	*K* [A1-FA(II)] × $10^3 s^{-1}$ (obs)	*K* [A1-FA(III)] × $10^4 s^{-1}$ (obs)	Equilibrium (24 h) recovery (%)	Total kinetic recovery (%)
A	20.0	0	5.0	20.0	2.81×10^2	—	—	—	86.28	78.51
B	20.0	2.0	5.0	20.0	—	2.71	3.36	—	65.22	61.44
C	20.0	5.0	5.0	20.0	—	2.62	3.30	—	33.33	35.13
D	20.0	2.0	6.0	20.0	—	2.35	1.98	—	56.52	48.02
E	20.0	5.0	6.0	20.0	—	2.64	3.54	—	33.33	31.31
F	2.00	0	5.0	2.00	6.24×10^1	—	—	—	51.11	40.96
G	2.00	0.10	6.0	2.00	—	2.34	3.57	—	17.41	15.91
H	2.00	0.20	6.0	2.00	—	1.85	1.92	—	40.00	26.16
I	2.00	0.50	6.0	2.00	—	1.66	1.76	—	51.85	39.39
J	2.00	2.0	6.0	2.00	—	1.35	1.53	—	75.93	56.95
K	2.00	5.0	6.0	2.00	—	—	5.51	37.06	35.07	
L	2.00	5.0	5.0	2.00	—	—	—	7.77	38.46	42.04
M	2.00	0.20	8.0	2.00	—	16.6	30.9	—	35.09	31.69
N	2.00	2.0	8.0	2.00	—	—	—	18.7	29.83	20.29

[a] T = 19.5C. The reagent is calcium blue (see text).

in solutions of pH 5 or 6. These ranges are denoted Al-FA(I) and Al–FA(II). The average rate constant for the first is 2.2×10^{-2} s^{-1}. The average rate constant for the second is 2.6×10^{-3} s^{-1}. These components are probably representative of a *distribution* of sites on the fulvic acid which behave most nearly like simple Al(III) complexes. Aluminum citrate reacts with these reagents system with a rate constant of 4.8×10^{-3} s^{-1}.[8] Secco and Venturini[19] report a dissociation rate constant of 7.9×10^{-3} s^{-1} for aluminum salicylate at 25C (*T* slightly higher than our value of 19.5C).

The observation of important *less* labile Al(III) in cases K and L where Al/FA ratios are smaller illustrates an important feature of the site distribution of fulvic acid which is well recognized in equilibrium studies. At low metal coverage the strongest binding sites dominate the averages. These appear to correspond to the kinetically less labile sites in these dilute solutions where coverage is expected to be low. We identify an average rate constant an order of magnitude smaller.

We will not discuss here the pattern of the amounts of Al(III) associated with each of the rate constant values reported in any detail. That is considered in Ref. 17. But, it is interesting to note that a common feature is an increase in FA leading to an increase in nonrecoverable Al(III). We believe this supports Bourg's[20] report of ternary surface complexes between aluminum oxides, humic substances and metal ions from solution. In this case aluminum is both the ion of the oxide and the ion from solution which is bound in the surface complex to complete the ternary complex.

Copper Humates

Shuman *et al.*[9] have studied the complexes of Cu(II) with an organic fraction extracted from estuarine waters by diafiltration–ultrafiltration and falling in a nominal size range of 1.3 to 3.1 nm. The kinetics were for reaction with an excess of 4-(2-pyridylazo)resorcinol (PAR) which forms a Cu complex at pH 7.5 that is strongly absorbent at 508 nm. The kinetics were analyzed by the affinity spectrum approach of Eqs. (10) through (12). Results are given for two Cu to organic ratios in Table II for solutions with a fixed 21 mg/l DOC. Peaks in the kinetic spectrum (average rate constants of the preceding cases) and areas under the peaks (component concentrations of the previous cases)are shown for each ratio.

Two points are reminiscent of the extensive Al(III) results: (1) the

TABLE II
Results of affinity spectrum analysis of photometric data for copper humates[a]

Total Cu concentration (μM)	Rate constants at peaks (s^{-1})	Complex concentration (μM Cu)	% of total Cu
7.1	0.016	0.080	1.1
	0.45	0.87	12.2
	15.1	0.67	9.4
	Totals		
	1.62	22.7	
34.5	0.49	0.83	2.4
	34.	2.8	8.2
	Totals		
	3.63	10.6	

[a] T = 25C. Reagent is PAR (see text).

rate constant averages vary with Cu to organic ratio; (2) a large part of the Cu is not represented kinetically. However, the reason for this second point is completely different. In the Cu case the Cu not accounted for kinetically is too labile. It reacts too fast for the stopped flow experiments. This is not surprising. The lability of typical simple Cu complexes is in the neighborhood of 1.0×10^8 M^{-1} s^{-1}. In fact, what is surprising is the fact that 20% of the copper exhibits lability many orders of magnitude below that of simple Cu(II) complexes. Indeed, 1% appears to display lability reduced by seven or more orders of magnitude.

Certainly, the complicated mixture polyelectrolyte character of the organic ligand system is again illustrated in these kinetics. The extreme range of labilities supported by the data might be interpreted by a correspondingly extreme range of stability constants. But, the results in the same study of potentiometric titration of the organic ligand material suggests stability constants grouped in three regions with log K values near 4.4, 5.3 and 6.2. These do not seem to span the required range, so that we need to consider *additional* factors in the kinetics. The obvious additional factor is a mass transport limitation into or out of the water swollen gel.

Mg Fulvates

A study parallel to the AlFA study was conducted by Lee[21] to analyze kinetics of release of Mg(II) with a fluorimetric reagent. In contrast to

Cu(II) *no* Mg(II) was found which dissociated from FA at a ratio *below* the rate of formation of the Mg complex with the fluorescent reagent. Since the lability of simple Mg(II) complexes is much below Cu(II), approximately 1 × $10^{-5}M^{-1}s^{-1}$ at 25C, there must be an important difference in binding. We suggest that in contrast to Cu(II), Al(II), and Fe(III), Mg(II) only forms outer-sphere electrostatic complexes with the fulvic acid.

CONCLUSIONS

The complex polyelectrolyte character of the organic ligands in the complexes discussed here is amply demonstrated in all cases, from the ferric fulvates, where it is delicately suggested, to the copper humates, where it is abundantly clear. Much of this kinetic behavior can be adequately understood if a distribution of sites is postulated and then the individual components of this distribution are thought of as analogous to fairly well studied mononuclear chelate species. This is illustrated by the parallels drawn throughout this paper between average values obtained here and results for mononuclear species.

There is, however, another factor. A few rates seem to be too low to be accounted for by analogy with mononuclear metal chelates. A moment's reflection suggests an additional possible factor which the hydrous oxides especially tend to call to mind. The entities involved in metal ion speciation in natural waters are large enough that the least labile sites may be those to which access is limited by mass transport.

We list, then, three factors for the foundations of the study of kinetics of metal speciation in natural waters: (1) the polyelectrolyte mixture model; (2) behaviour of mononuclear chelates; (3) mass transport into colloids.

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