Characterization of trace metal-organic interactions by anodic stripping voltammetry

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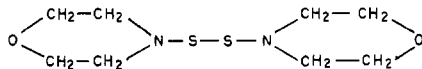**38** PUBLICATIONS **593** CITATIONS

Table I. Results of Amperometric Estimation of MDB with AgNO₃ after Reduction with NaBH₄

	Volume of AgNO₃ consumed, ml	Amount of MDB taken, µg	MDB found, µg	Deviation, %
Set A	0.990	2844	2812	−1.1
Set B	0.201	282[a]	285	+1.1

[a] Data obtained on the basis of 99% purity of MDB.

CH₂—CH₂ ... O ... CH₂—CH₂ ... N—S—S—N ... CH₂—CH₂ ... O ... CH₂—CH₂

(DTM)

The applicability of this method for the estimation of MDB in actual rubber stocks is being investigated.

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Characterization of Trace Metal–Organic Interactions by Anodic Stripping Voltammetry

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The titration of solutions of metal ions with organic ligands and solutions of ligands with metal ions in a system chosen to simulate many natural water systems is followed by anodic stripping voltammetry. The measurement of both peak current and peak potential during the course of such titrations permits the differentiation of "free" metal, labile metal complexes, and nonlabile metal complexes. Representative results of the interactions of copper, thallium, and cadmium with humic acid in a carbonate medium are presented. Copper is shown to form strong, nonlabile complexes and thallium is shown to produce predominantly labile complexes. Cadmium exhibits intermediate behavior.

The public health significance of pollution-derived and naturally-occurring trace metals in aquatic environments is not well established but has, since the metal-pollution episodes of the 1960's, received the increased attention of scientists concerned with environmental quality and the ecological effects of trace metals. This emphasis has resulted in the development of a wide range of instrumental techniques for the analysis of trace metals in an aquatic matrix (1). Of these techniques, atomic absorption spectrophotometry, neutron activation analysis, and electrochemical techniques are most frequently employed because of their capability to directly and routinely analyze trace metals at the concentration levels normally found in natural aquatic systems (2, 3). Consequently, these techniques do not normally require preconcentration, a treatment procedure which could drastically alter the physicochemical characteristics of the aqueous sample. The electrochemical techniques of particular utility in trace metal analysis are potentiometry with specific-ion electrodes (4) and anodic stripping voltammetry (5, 6).

Until recently, environmental studies and water quality standards have been concerned with the total concentration of particular trace metals in the aquatic environment; consequently, the development of analytical techniques has emphasized the determination of total metal concentration. It is now realized that knowledge of the total metal concentration alone is not always sufficient but that, to understand thoroughly the distribution and ecological implications of trace metals, the physical form and chemical speciation of the metal must be elucidated. In this regard, emphasis has focused on trace metal complexation because of the role this might play in trace metal distribution and in the availability of a metal to the biota of a natural aquatic environment. This requires an analytical technique which not only can detect trace metals at their natural concentration levels but also can differentiate the various chemical species of a given trace metal. Unfortunately, this additional restriction presently limits the available analytical techniques. Only potentiometry with specific-ion electrodes and anodic stripping voltammetry can presently differentiate, on a routine basis, the chemical forms of a trace metal in natural waters.

Potentiometric studies of trace metal complexation in natural waters have been extremely limited. This is primarily due to the lack of sensitivity of specific-ion electrodes, which respond to free metal ions only, and to the subsequent difficulty in measuring uncomplexed metal at the extremely low concentrations found in natural waters. Stiff (7) has employed the copper specific-ion electrode in the study of copper complexation in polluted fresh water, and Gardner (8) has studied the extent of formation of labile cadmium complexes with the cadmium specific-ion electrode. Gardner noted that the detection limit of the cadmium electrode was considerably higher than the concentrations usually encountered in natural waters; however, he expressed confidence in the reliability of extrapolation to lower concentrations.

Anodic stripping voltammetry (ASV) has been employed in a number of studies of trace metal complexation. Most
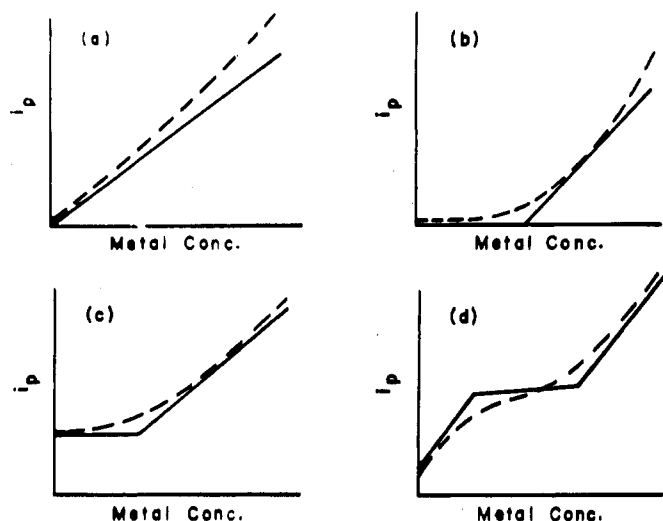
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Figure 1. Typical titration curves obtained from ASV titrations of ligands with trace metal ions

(a) Presence of only free metal or labile metal complexes, (b) formation of strong, nonlabile complexes, (c) presence of weak, nonlabile complexes, and (d) formation of strong, labile complexes followed by the formation of weak, nonlabile complexes. (———) Theoretical titration curve; (- - - -) experimentally-observed titration curve

Figure 2. Summary of diagnostic criteria for the characterization of metallic species by anodic stripping voltammetry

Figure 3. Cell and electrode arrangement for anodic stripping voltammetry

studies have used a procedure in which the concentration of metal of the sample, at its original pH, is measured and reported as either labile metal or free metal. This is then followed by acid digestion and an additional analytical measurement to obtain the total metal concentration. The concentration of complexed metal is then found by difference. Such an approach has been used by Allen et al. (9) for the determination of free and complexed Cu, Cd, and Pb in Lake Erie and the Rouge River; by Bender et al. (10) to determine the nature of the complexing agents in secondary sewage effluents; and by Chau and Lum-Shue-Chan (11) to differentiate between labile and strongly bound Cd, Cu, Pb, and Zn in a number of different lake water samples. Zirino and Healy (12) investigated the inorganic complexes of zinc in seawater by employing carbon dioxide as the acidifying agent.

Titrimetric methods of ASV analysis have also been applied to trace metal complexation studies. Shuman and Woodward (13) employed ASV to analyze the free cadmium concentration following additions of EDTA to the sample. Bradford (14) titrated solutions of zinc with sodium hydroxide to analyze the complexation of the trace metal by observing the cathodic shift in the potential of the resultant current peak. Guy et al. (15) followed the sorption of trace metals onto particulate matter by titrating solutions of the metal with MnO_2, bentonite, or solid humic acid. Chau et al. (16) titrated natural water samples containing excess ligand with copper and used ASV to determine the complexing capacity of the water.

These approaches to trace metal complexation generally suffer from two serious drawbacks; namely, (a) they alter the equilibria and general chemical nature of the natural water by the pH changes caused by either acidification or the addition of a suitable buffer, and (b) they group labile metal complexes and free metal together rather than differentiating between these two broad categories of chemical species. This report describes a titrimetric ASV procedure in which nonlabile metal complexes, labile metal complexes, and free metal may be differentiated in a natural water sample at its original pH. The original pH is maintained by the addition of appropriate amounts of carbon dioxide, a natural component of aquatic systems. Although the results which are presented are somewhat qualitative, the development of a quantitative approach to the extent and type of trace metal complexation
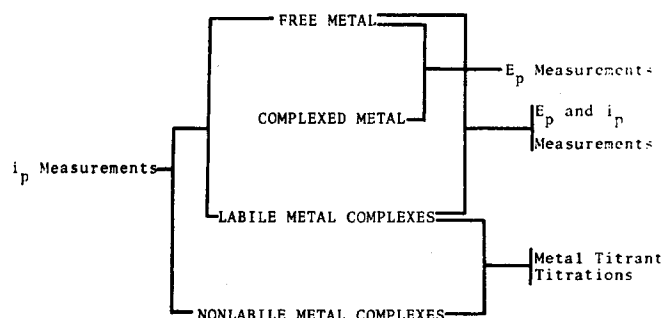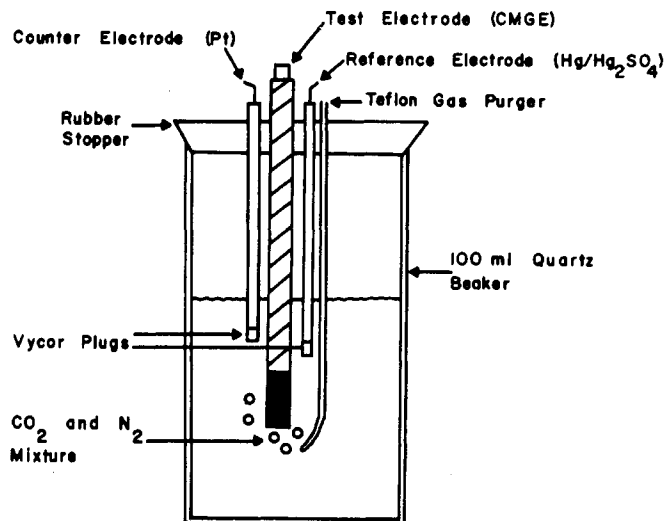
can be readily accomplished. More detailed results and applications will be presented in a subsequent publication.

THEORY

The theory of anodic stripping voltammetry has been adequately reviewed (9, 17–20). Its use in the characterization of trace metal complexes has also been extensively discussed (9, 19, 20). In this regard, the utility of ASV depends upon its ability to differentiate free metal, labile metal complexes, and nonlabile metal complexes by the measurement of both peak current (i_p) and peak potential (E_p) during the titration of the metal–ligand solution with either trace metal or ligand. The shape of the resultant titration curve depends on the particular metal–ligand interactions taking place within the solution and on the rate and degree of interaction between the trace metal and the working electrode. Four typical titration curves are graphically depicted in Figure 1 and are discussed in (19).

The pertinent diagnostic criteria for the ASV study of trace metal complexation can be summarized as follows: (a) i_p measurements can differentiate between "free" and labile metal complexes on the one hand and nonlabile metal complexes on the other hand; (b) E_p measurements can differentiate between "free" metal and complexed metal; (c) i_p and E_p measurements together can differentiate between "free" metal and labile metal complexes; (d) metal–ligand titrations in which the metal is the titrant can differentiate between labile and nonlabile metal complexes; and (e) metal–ligand titrations in which the ligand is the titrant can isolate the type of interaction between the trace metal and a particular ligand. These criteria are summarized in Figure 2.

EXPERIMENTAL

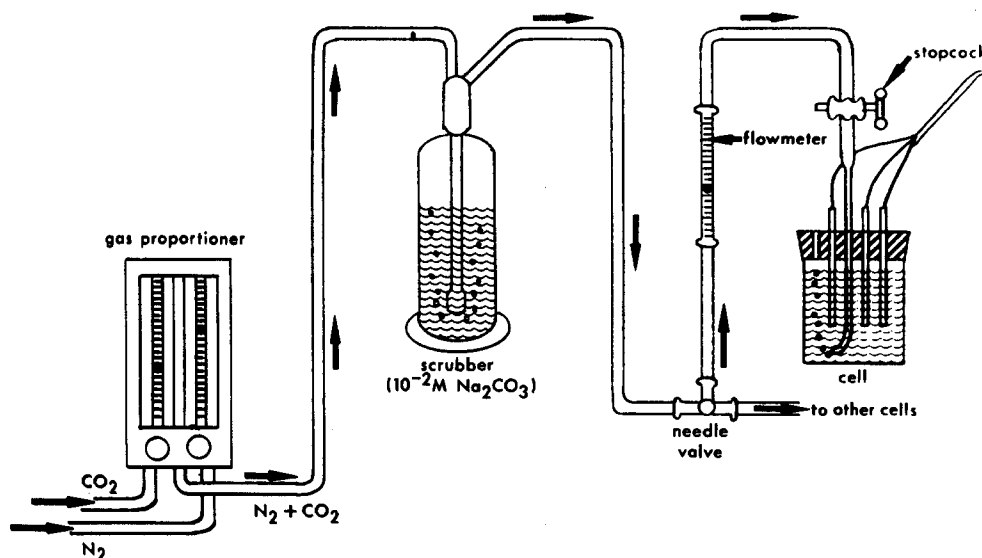**Apparatus.** A Heath Polarography System Model EUW-401, in

Figure 4. Cell arrangement and deaeration system for anodic stripping voltammetric studies in Na_2CO_3 medium

conjunction with the Model EUA-19-4 Chopper Stabilizer, was used for control of the stripping process. An Environmental Science Associates Model 1014 Polarographic Module Interface Unit, in conjunction with a Heath Model EUW-19A Operational Amplifier, was used to provide the plating modes necessary for the simultaneous operation of four cells. Cell potentials were adjusted and measured with the aid of a Simpson Model 312 VTVM. Voltammograms were recorded on a Honeywell Electronik 194 Strip Chart Recorder.

Cell and Electrode System. The cells consisted of 100-ml fused quartz beakers. The electrodes were inserted into the cells through rubber stoppers. The cell and electrode arrangement is shown in Figure 3. Details concerning the construction of reference and counter electrodes and the composite mercury–graphite electrode (CMGE) can be found in (9, 19, 21).

The reference electrode was a saturated mercury–mercurous sulfate (Hg/Hg_2SO_4) electrode. This was chosen over the more conventional calomel or silver–silver chloride reference electrodes as a precaution against the possible leakage of chloride ion, a potential ligand, into the test solution.

Deaeration was performed by bubbling mixtures of nitrogen and carbon dioxide into the test solution. In addition to removing oxygen from the test solutions and providing the stirring necessary for increased mass transport during the plating process, this gas mixture also buffered the test solutions. This was accomplished by controlling the proportions of nitrogen and carbon dioxide in the mixture so that the partial pressure of the carbon dioxide determined the pH of the sodium carbonate supporting electrolyte (22). The proportions of the two gases were controlled with a Matheson Gas Proportioner provided with the appropriate flowmeters. The gaseous mixture was then passed through a scrubber containing supporting electrolyte to saturate the gas mixture with water vapor and thereby minimize evaporative losses in the test solutions. The flow of gas into each cell was monitored by an additional flowmeter mounted next to the cell. This flowmeter permitted adjustment of the flow rate into each individual cell so that the stirring rate could be duplicated from one analysis to the next. The gas flowed into the cell through a Teflon tube made rigid by an insert of platinum wire. The tube was adjusted so that the gas flow impinged directly on the test electrode. A schematic diagram of the cell arrangement and accompanying deaeration system is shown in Figure 4.

Reagents. All reagents except the humic acid were reagent grade chemicals. Double distilled water was used throughout the investigation. Standard stock solutions (10^{-3} M) of the trace metals to be studied were prepared either by dissolving the metal in the minimum amount of concentrated nitric acid or from the appropriate nitrate salt. Dilute stock solutions (10^{-5} M) were made daily from the standard solutions. Humic acid solutions were prepared by dissolving 50 mg of commercial grade humic acid (K & K Laboratories, Plainview, N.Y.) in a minimum amount of 0.1 M KOH and diluting to 50 ml with distilled water. The resulting solution had a humic acid concentration of 1.0 mg/ml.

The supporting electrolyte consisted of 10^{-3} M Na_2CO_3 in 9.0 × 10^{-3} M K_2SO_4. Carbonate was chosen because (a) it simulates those

aquatic conditions in which the hydroxy and carbonato ligands are the most predominant, and (b) it is an acid–base buffer system commonly found in natural waters. Additionally, the carbonate system is easily buffered between pH 6 and 8 by deaerating with the appropriate N_2–CO_2 mixture; ions not commonly found in natural waters do not have to be added to the solutions to achieve pH control. The use of sulfate, a very weak and insignificant ligand, enabled the ionic strength of the solutions to be maintained at a relatively constant value and minimized the junction potential associated with the sulfate reference electrode.

General Procedure. Electrodes were inserted into the test solutions and the solutions were deaerated for approximately 5 min with the appropriate N_2–CO_2 mixture. This length of time was generally sufficient for adjustment of the pH of the solutions. While continuing to deaearate, the electrodes were adjusted to the desired plating potential and maintained at this potential for a fixed period of time (plating time). Thirty seconds prior to the initiation of the stripping step, the gas flow was stopped so that the solutions could become quiescent. The electrodes were then stripped and the voltammograms recorded. The pH of the solutions was measured immediately after the electrodes were stripped. Except where noted, plating times were 10 min and the potential sweep rate was 42.9 mV/s.

Titration procedures were the same as above except that a 10-min equilibration time was included as an additional step. The equilibration time is the time between the addition of titrant and the commencement of the plating step. Its purpose was to permit any complexation reaction to approach equilibrium prior to the disruption of that equilibrium by the initiation of the electrochemical process. Peak current studies with humic acids and trace metals indicated that 10 min was a sufficient length of time.

The plating potentials were −1.000 V for copper and −1.400 V for cadmium and thallium. When not in use, the electrode system was maintained at an applied potential of −0.42 V to prevent the anodic dissolution of the mercury film.

The application of the above procedures to solutions of trace metals at concentrations of 2.0 × 10^{-8} M resulted in peak currents which were generally reproducible to within 10% and peak potentials reproducible to within 3%.

RESULTS AND DISCUSSION

The study of trace metal–organic interactions in a medium chosen to simulate both the composition and complexing capability of many natural aquatic systems requires the selection of an organic material which is both a good complexing agent and compatible with the natural environment. The choice of humic acid as the organic ligand was based on these considerations. In addition, its polymeric nature provided a potentially large number and diversity of complexing sites for trace metal interactions. Although the molecular weight of humic acid may vary between 700–2 000 000 (23), the samples used
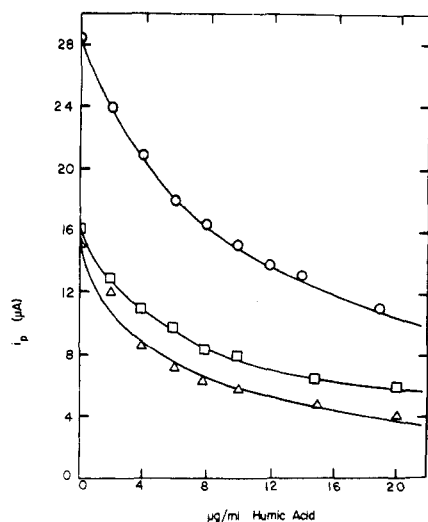
Figure 5. Variation of i_p during the titration of 5.0 $\times$ 10^{-8} M Cd with humic acid
O pH 6.2; □ pH 7.3; △ pH 9.1

Figure 6. Variation of E_p during the titration of 5.0 $\times$ 10^{-8} M Cd with humic acid

O pH 6.2; □ pH 7.3; △ pH 9.1

in this study were reported to have a molecular weight of 600–1000 (*24*). The commercial availability of these samples was fortunate in that it provided assurance that all humic acid solutions were of approximately the same composition. In addition, the low molecular weight indicated an abundance of functional groups and a relatively high solubility (*23*).

The humic acid was tested for residual trace metal content by acidifying a 5.0 μg/ml humic acid solution to pH 1.6 with 70% HClO$_4$ and analyzing by ASV. Even after periods of 3 h following acidification, analysis indicated that the trace metals which could be detected by ASV were absent from the humic acid samples.

Titration of Metal Ions with Ligands. The application of the diagnostic criteria to the complexation characteristics of a trace metal is first illustrated with cadmium. Figure 5 shows the variation in i_p when 5.0 $\times$ 10^{-8} M Cd is titrated with humic acid at pH 6.2, 7.3, and 9.1. Regardless of the pH, i_p is observed to steadily decrease as the humic acid concentration is increased to 20 μg/ml. This is indicative of an interaction between cadmium and the humic acid which decreases the availability of the metal for interaction with the test electrode; i.e., it is indicative of nonlabile complex formation. Additionally, the fact that i_p is still decreasing at 20 μg/ml humic acid shows that cadmium has not become completely complexed with the nonlabile ligands. The cadmium–organic interactions in these solutions may be described as resulting in a partitioning of the trace metal between the nonlabile form and either the labile or "free" form.

As the humic acid concentration varies from 0–20 μg/ml, i_p is reduced by 63.2%, 65.6%, and 76.5% at pH 6.2, 7.3, and 9.1, respectively. The nonlabile complexation which gives rise to these reductions is thus appreciable and the degree of nonlabile complexation of cadmium with humic acid increases significantly with increasing pH.

The variation in E_p as 5.0 $\times$ 10^{-8} M Cd is titrated with humic acid is shown in Figure 6. E_p becomes more cathodic with increasing concentration; furthermore, the magnitude of the cathodic shift increases with increasing pH. The decrease in i_p observed in Figure 5 and the nature in which E_p shifts cathodically with pH and increasing ligand concentration correlate well with one another and indicate that nonlabile complex formation is the predominant mode of interaction between cadmium and humic acid. The extent of this interaction increases both with increasing humic acid concentration and also with increasing pH.

An additional observation from Figures 5 and 6 is that the initial i_p (i_p for 0.0 μg/ml humic acid) decreases and the initial
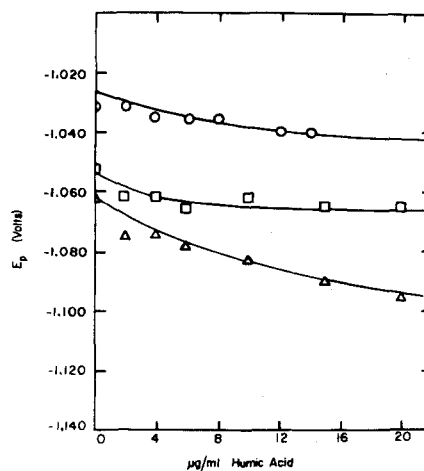
E_p becomes more cathodic as the pH increases. This trend suggests the existence of nonlabile interactions with the carbonato and hydroxo ligands present from the inorganic supporting electrolyte. It is, therefore, not unreasonable to assume the partitioning of trace metals between both nonlabile inorganic and nonlabile organic ligands in a natural water system.

The titration of 5.0 $\times$ 10^{-8} M Cu with humic acid is similar to Figures 5 and 6 and is another example of nonlabile complex formation. Initial i_p values of 21, 15, and 8 μA and initial E_p values of −0.424, −0.472, and −0.528 V were obtained at pH 6.2, 7.3, and 8.7, respectively. Copper thus forms nonlabile complexes with the inorganic supporting electrolyte; the extent of this complex formation increases with increasing pH. The addition of as little as 4.0 μg/ml humic acid to these solutions results in the complete extinction of the copper signal. This effect is independent of the pH. Consequently, the "free" or labile copper available in these solutions interacts completely and rapidly with humic acid to form relatively strong, nonlabile complexes.

Thallium exhibits another mode of behavior. The initial i_p and E_p values for 5.0 $\times$ 10^{-8} M Tl are unchanged as the pH is varied from 6.2 to 9.1. This indicates that thallium forms neither labile nor nonlabile complexes with the inorganic carbonate medium used as the supporting electrolyte. As humic acid is added, i_p values remain unchanged at pH 6.2 and 7.2 but the E_p values exhibit a slight cathodic shift of 15 mV as the humic acid concentration is increased from 0.0 to 20 μg/ml. The constancy of i_p indicates that nonlabile complexation is nonexistent under these conditions; however, this constancy in i_p, along with the cathodic shift in E_p, does suggest the formation of labile complexes. At pH 9.1, i_p is reduced 18.2% and E_p is shifted 25 mV in the cathodic direction as the humic acid concentration is varied. The decrease in i_p indicates the existence of nonlabile thallium–humic acid complexes at this high pH.

Titration of Ligands with Metal Ions. A natural water sample is a potentially complex mixture of varying proportions of "free" trace metals, inorganic and organic ligands, and nonlabile and labile complexes. Depending on the relative concentrations of these various components, an aquatic sample can contain either (a) an excess of "free" metal if there is metal in excess of that needed to satisfy the demands of the available ligands, or (b) a deficiency of available metal. ASV titrations in which the metal ions serve as the titrant can be applied to an aquatic sample to determine the nature and relative proportions of metal ions, ligands, and complexes

present in the sample. Some expected results of such titrations are shown in Figure 1. We have applied this technique to the trace metal–humic acid–carbonate system by titrating solutions of 5 μg/ml humic acid in 10^{-3} M Na_2CO_3 with metal ions at pH 6.2, 7.1, and 8.5. Trace metal concentrations were varied from 0.0–1.0 $\times$ 10^{-7} M.

The titration of solutions of cadmium with humic acid (Figures 5 and 6) indicates the formation of nonlabile humic acid complexes in which the extent of complexation increases with increasing pH. These titration results also confirm the existence of nonlabile inorganic complexes with the supporting carbonate electrolyte. The titration of humic acid solutions with cadmium is not in complete agreement with these interpretations; i_p varies linearly with increasing cadmium concentrations. This is an indication of a system in which the metal–ligand interactions are labile and, consequently, the interaction of the metal ion with the electrode is unaffected by the dissociation kinetics of the metal–organic complexes.

Although the titration curves are linear at pH 6.2, 7.1, and 8.5, their slopes decrease as the pH increases. This effect is similar to and of the same order of magnitude as that obtained in titrations performed in the absence of humic acid. It is further evidence of nonlabile inorganic complex formation with the carbonate supporting electrolyte. Therefore, the results of these titrations with a metal ion titrant show that cadmium forms labile humic acid complexes and nonlabile inorganic complexes in a carbonate medium.

The inconsistencies indicated by Figures 5 and 6 on one hand and the titration of humic acid with cadmium on the other hand is an example of the qualitative, operational manner in which the terms labile and nonlabile are defined. Nonlabile applies to those complexes whose dissociation rates are much slower than the rate of plating and labile refers to complexes whose dissociation rates are much faster than the rate of plating. Clearly, there are also complexes whose dissociation rates are similar to the rate of plating and which might be expected to exhibit labile characteristics in some situations and nonlabile characteristics in others. In addition, many organic systems, such as humic acid, represent a mixture of different ligands, and it is highly probable that such mixtures would produce complexes of varying degrees of lability and nonlability. The interactions of cadmium and humic acid, therefore, are not labile or nonlabile in the strictest sense; they represent a series of interactions which produce complexes of intermediate dissociation rates. More definitive information on the dissociation of these complexes would be possible in situations in which the cell constant can be accurately measured and controlled.

The results of the titration of humic acid with copper are consistent with those obtained by the titration in which humic acid served as the titrant; strong, nonlabile interactions are clearly indicated. The titration curves are similar to (b) of Figure 1. At pH 6.2, no i_p is obtained until after 4.0 $\times$ 10^{-8} M Cu has been added to the solution because the added copper becomes strongly bound in nonlabile complexes with the available humic acid ligand sites; no copper is available for electron transfer at the test electrode surface. After 4.0 $\times$ 10^{-8} M Cu has been added, all the nonlabile ligand sites have been saturated and the further addition of copper causes a nonlinear increase in i_p because of either the formation of labile complexes with other ligand sites or the availability of "free" copper.

The extent of this nonlabile complexation increases with increasing pH. This is indicated by the fact that as the pH increases greater amounts of copper must be added to saturate the nonlabile ligand sites and obtain a peak current. At pH 7.1, 8.0 $\times$ 10^{-8} M Cu is needed before i_p can be detected and at pH 8.5, the copper concentration must exceed 1.0 $\times$ 10^{-7} M.

The results obtained by titrations with thallium are also consistent with those obtained when humic acid was the titrant. Labile interactions are predominant with both the organic ligand sites of the humic acid and with the inorganic ligands found in the supporting electrolyte. The titration curves were found to be similar to (a) of Figure 1; i.e., they were linear and had identical slopes at all three pH's.

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