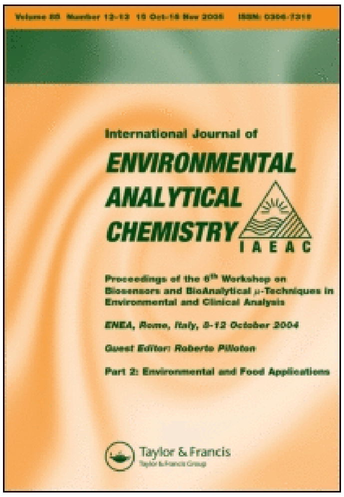

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Electrochemical Analysis of the Heavy Metal/Humic Acid Interaction

Rob F. M. J. Cleven[a]; Herman P. Van Leeuwen[b]
[a] National Institute of Public Health and Environmental Hygiene, Bilthoven, The Netherlands [b] Laboratory for Physical and Colloid Chemistry, Agricultural University, Wageningen, The Netherlands

To cite this Article Cleven, Rob F. M. J. and Van Leeuwen, Herman P.(1986) 'Electrochemical Analysis of the Heavy Metal/Humic Acid Interaction', International Journal of Environmental Analytical Chemistry, 27: 1, 11 — 28

To link to this Article: DOI: 10.1080/03067318608078388

URL: http://dx.doi.org/10.1080/03067318608078388

Intern. J. Environ. Anal. Chem., 1986, Vol. 27, pp. 11–28
0306-7319/86/2702-0011 $18.50/0

Printed in Great Britain

Electrochemical Analysis of the Heavy Metal/Humic Acid Interaction†

ROB F. M. J. CLEVEN‡

National Institute of Public Health and Environmental Hygiene,
P.O. Box 1, 3720 BA Bilthoven, The Netherlands

and

HERMAN P. VAN LEEUWEN

Laboratory for Physical and Colloid Chemistry, Agricultural University,
De Dreijen 6, 6703 BC Wageningen, The Netherlands

(*Received March 20, 1986*)

Heavy metal ion titrations of solutions of humic acid (HA) and polyacrylic acid (PAA) at different degrees of neutralization have been studied by normal pulse polarography and conductometry.

The systems Cd,Pb,Zn/HA and Cd,Zn/PAA appeared to be polarographically labile. As the diffusion coefficients of the polymeric metal complexes are very small, a mean diffusion coefficient of the reducible heavy metal ions controls the polarographic current, and is to be used to calculate binding constants of the complex formation.

The apparent binding constants for the Cd,Pb,Zn/HA systems are strongly dependent on the degree of neutralization. From comparison with corresponding results for the heavy metal binding to the synthetic polycarboxylic acid, it is concluded that polyelectrolyte effects play an important role in the interaction of heavy metals with humic acid. This finding is supported by the conductometric results.

---

†Presented at the 16th Symposium on the Analytical Chemistry of Pollutants, Lausanne, Switzerland, March 17–19, 1986.

‡Author to whom correspondence should be addressed.

Values of the intrinsic binding constants for Cd,Pb,Zn/HA are close to those for the binding with monocarboxylic acids.

KEY WORDS: Heavy metals, humic acids, polarography, conductometry, polyelectrolyte effect, speciation.

INTRODUCTION

Metal speciation is a prerequisite in environmental chemistry. It enables the assessment of bio-available fractions of heavy metals in natural waters and soil solutions.[1] Voltammetric methods are suited to distinguish different chemical forms of a number of important trace metals.[2,3] For example, stripping voltammetry is frequently practised in metal speciation schemes to determine the distiribution of heavy metal ions over the "free" and "complexed" forms.[4-6]

In the case of humic acid (HA) as complexing ligand, the interpretation of the voltammetric current-potential response curves, and thus the physico-chemical description of the complex formation, may be seriously hampered by the macromolecular and polyfunctional character of this main constituent of organic matter in ecosystems.

As a result of the macromolecular character of humic acid, the value of the diffusion coefficient of the Me/HA complex will be much smaller than that of the corresponding metal ion. For labile metal complexes, any metal ion frequently flip-flops between the bound and the free state within the time scale of the experiment. In the case of a macromolecular labile complex, the voltammetric current will be controlled by some mean diffusion coefficient of the metal ion.

As a result of the polyfunctional character of humic acid, the number of charged sites per molecule can be large, if the functional groups are deprotonated. For humic acid molecules with a molecular mass of 10,000, about 50 deprotonable groups, mainly carboxylic, may be present on each molecule.[7-9] The resulting high charge density may evoke electrostatic binding of metal ions with humic acid in analogy to the "condensation" of metal ions onto linear polyanions.[10] Condensation of metal ions is a typical polyelectrolyte effect.

To investigate the effect of the macromolecular character of humic acid on the voltammetric response to the complexation with heavy metals and the polyelectrolyte effect on the heavy metal/humic acid interaction, the systems Cd,Pb,Zn/HA have been studied by normal pulse polarography (NPP). Solutions of humic acid at different degree of neutralization, and thus different charge density, have been titrated with heavy metal ions. The results have been compared to those for similar titrations into solutions of polyacrylic acid (PAA), a linear polycarboxylic acid.

In the polarographic experiments, any polyelectrolyte effect will be partially suppressed due to the presence of 1:1 salt as supporting electrolyte. Therefore, the same type of titrations into solutions of PAA and HA without supporting electrolyte have also been studied conductometrically.

MATERIALS AND METHODS

Humic acid (HA)

The humic acid solution was prepared from Fluka humic material (sample code 53680/191699116). The fraction soluble in the pH range 3–9 was used. It was dialysed against water using a Spectrapor membrane with a molecular mass cut-off of 3,500. The dialysed solution was treated with an ion exchanger of the type AG 50W-X4 from Bio-Rad to transfer the material into the acid form. The total number of deprotonable groups was determined by conductometric and potentiometric acid-base titrations. The concentration of deprotonable groups in the sample solutions used in the heavy metal ion titrations was $2.00\,\mathrm{mol.m^{-3}}$. This concentration corresponded to a DOC content of $0.2\,\mathrm{kg.m^{-3}}$. The intrinsic dissociation constant of the humic acid appeared to be $10^{-3.7}$ in $\mathrm{mol.dm^{-3}}$ units.

Polyacrylic acid (PAA)

The polyacrylic acid solutions were obtained from Polysciences. Two PAA samples were used, with an average molecular mass of 300,000 and 50,000 respectively. The total number of carboxylic groups was determined by conductometric and potentiometric acid-base titrations. The concentration carboxylic groups in the sample solutions used in the heavy metal ion titrations was $2.50\,\mathrm{mol.m^{-3}}$. The intrinsic dissociation constant of both PAA samples appeared to be

$10^{-4.72}$ in mol.dm^{-3} units. From literature data it was calculated that the diffusion coefficients of the PAA samples were *ca.* 0.9×10^{-7} cm^2.s^{-1} and 2.3×10^{-7} cm^2.s^{-1} of the high and low molecular mass versions respectively.[7,11,12]

Other reagents

All other reagents used were analytical grade. KOH was used for the (partial) neutralization of the polyacid solutions, and the acid-base titrations. KNO_3 was applied as supporting inert electrolyte, at a concentration of 50 mol.m^{-3}. Solutions of $Cd(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$ were used for the metal ion titrations. The diffusion coefficients of Cd^{2+}, Pb^{2+} and Zn^{2+} are all on the level of 10^{-5} cm^2.s^{-1}. Millipore Super-Q water was employed in all experiments. After degassing traces of CO_2, the water had a conductivity less than 0.5 μS.cm^{-1}.

Normal pulse polarography (NPP)

All polarograms were obtained with PAR Model 174A polarographic analyzers from EG&G. The NPP mode was employed for all sample solutions. An effective pulse period of 175 ms was applied in the polarographic measurements. Static mercury drop electrodes SMDE PAR Model 303 from EG&G were employed. A drop is formed within at most 0.2 s, whereas the drop period was maintained at 1 s. The drop size was about 1.4 mm^2. The SMDE was equipped with a Ag/AgCl,KCl$_{sat}$ reference electrode. The electrode block was modified to allow a pH microelectrode to be inserted into the solution. Purified nitrogen was used for deaeration and blanketing of the sample solutions.

Conductometry

The conductometric measurements were carried out with a conductometer WTW Model LF530. The conductometric cells used, WTW Model LTA01, equipped with blank platinum electrodes, had cell constants of 0.102 cm^{-1} and 0.109 cm^{-1}. Measurement of the pH was also performed simultaneously with the conductometric experiments in the course of the heavy metal ion titrations.

Procedure

Solutions of HA and PAA were partially neutralized to a certain degree of neutralization α_n. Aliquots of heavy metal ion solutions were pipetted into the polyacid solutions, and the normal pulse polarogram was recorded, or the conductivity measured. The pH values of all solutions were monitored to allow a calculation of the protons released in the course of the metal ion titrations, and the number of initially present deprotonated groups.

RESULTS AND DISCUSSION

The normal pulse polarograms for both the Me/HA and the Me/PAA systems investigated, showed the usual shape and had well-defined limiting current plateaux. In some polarograms, for systems with high values of α_n and high metal/ligand ratio, a maximum appeared at the onset of the wave, indicating reactant adsorption.[13] From additional experiments with different pulse periods, Cottrell plots were constructed.[14] These plots of the normal pulse polarographic limiting current as a function of the square root of the reciprocal effective pulse period, appeared to be linear, with only a small intercept of the ordinate axis. These findings indicate that the limiting currents were diffusion controlled and not seriously affected by reactant adsorption. Thus, bulk parameters of the systems are reflected in the limiting currents.

Lability

In the Figures 1 and 2, the normal pulse polarographic limiting currents i_l are plotted as a function of the concentration of zinc nitrate for the systems Zn/HA and Zn/PAA respectively, at three different values of α_n. Additionally, the calibration graph is plotted. This graph refers to the corresponding zinc nitrate solutions without polyacid, in the presence of 50 mol.m^{-3} supporting electrolyte.

The i_l-plots for the metal/polyacid systems demonstrate that:

i) at low metal/ligand ratio, the slope is reduced as compared to the calibration graph, indicating binding of Zn^{2+};

ii) at high metal/ligand ratio, the slope approaches that of the calibration graph, suggesting that the maximum metal complexing capacity is approximately reached.

These trends may also be observed in voltammetric analyses of low molecular mass complexes.[15] Then, any reduction of the slope is generally attributed to the non- or quasi-lability of the complex involved. However, for all the systems in this study, the linearity of the Cottrell plots excludes quasi-lability.

In the course of the zinc ion titrations, the half-wave potential $E_{1/2}$ gradually shifted to more positive values, indicating polarographic lability of the Zn/HA and Zn/PAA complexes.

A confirmation of the lability of the Zn/HA,PAA systems could be obtained from titrations of ligand into zinc solutions: a definite plateau value for i_l is asymptotically reached.

For the Pb/HA and the Cd/HA,PAA systems, observations similar to those for the Zn/HA,PAA systems could be made with respect to the slope of the i_l-plots, the shift of $E_{1/2}$ and the occurrence of a

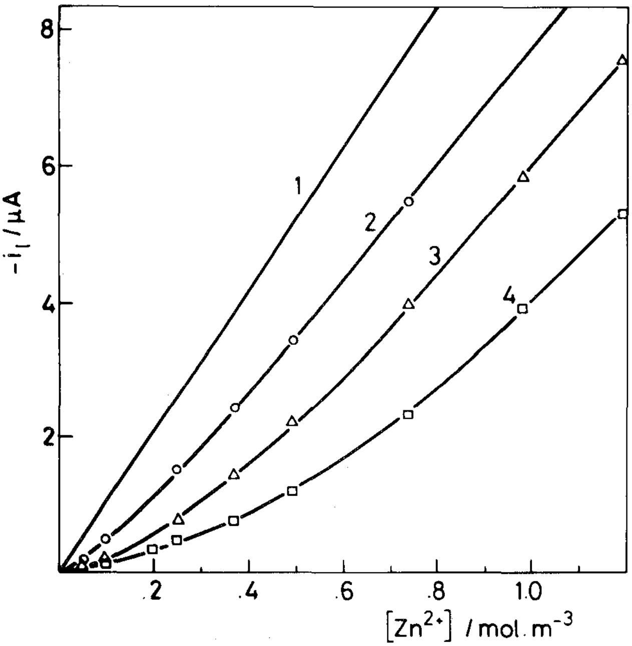

FIGURE 1 The limiting current for Zn/HA as a function of the amount of $Zn(NO_3)_2$; $[HA] = 2.00\ mol.m^{-3}$; $[KNO_3] = 50\ mol.m^{-3}$; 1, calibration; 2, $\alpha_n = 0.4$; 3, $\alpha_n = 0.6$; 4, $\alpha_n = 0.8$.

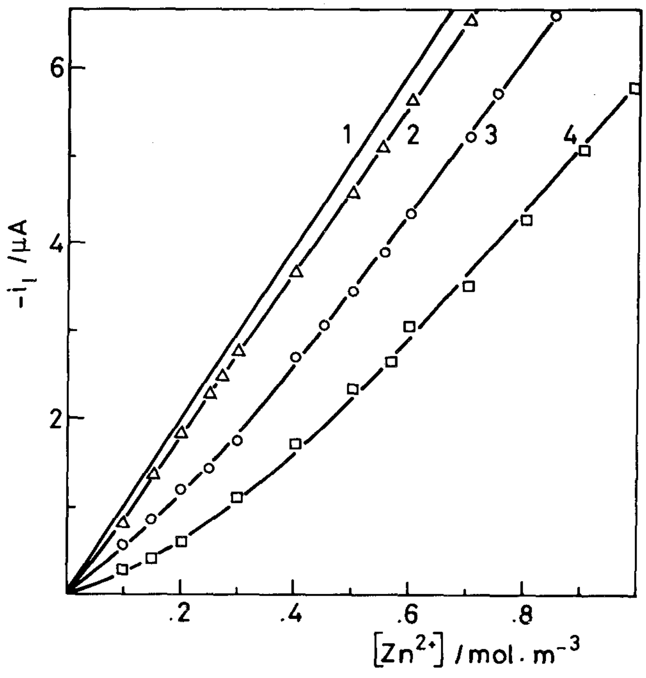

FIGURE 2 The limiting current for Zn/PAA as a function of the amount of $Zn(NO_3)_2$; [PAA] = 2.50 mol . m^{-3}; [KNO_3] = 50 mol . m^{-3}; 1, calibration; 2, $\alpha_n = 0.2$; 3, $\alpha_n = 0.4$; 4, $\alpha_n = 0.6$.

plateau value for i_l in the ligand titrations. For the Pb/HA system, the i_l-plots for three values of α_n are given in Figure 3. In the Pb/PAA system, flocculation occurred. The results for this system will not be considered.

The polarographic lability of the metal/polyacid systems implies that different metal species, "free" and "bound" metal ions, with unequal diffusion coefficients are present in the sample solutions. In such cases, the limiting current i_l can be expressed by:[16]

$$i_l = A \cdot \sqrt{\bar{D}} \cdot [\mathrm{Me}]_{\mathrm{total}} \qquad (1)$$

where A is a constant, $[\mathrm{Me}]_{\mathrm{total}}$ is the total concentration of heavy metal ions in the bulk, and $\bar{D}$ is the mean diffusion coefficient given

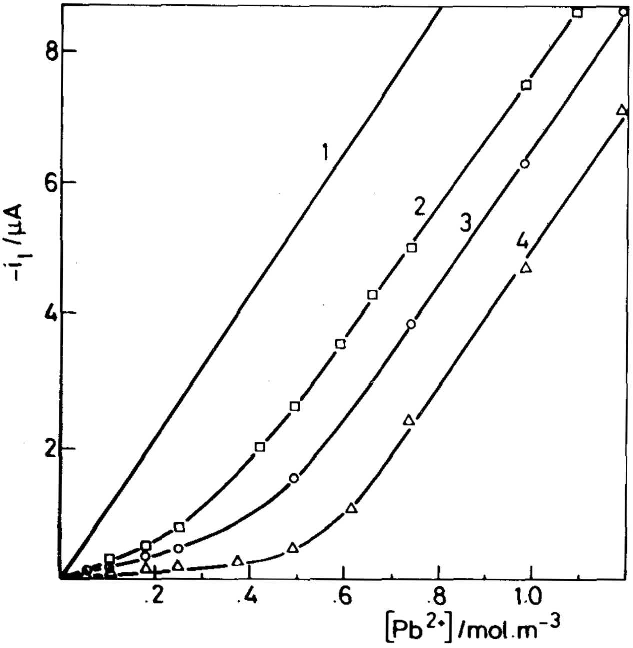

FIGURE 3 The limiting current for Pb/HA as a function of the amount of $Pb(NO_3)_2$; $[HA]=2.00\,mol.m^{-3}$; $[KNO_3]=50\,mol.m^{-3}$; 1, calibration; 2, $\alpha_n=0.2$; 3, $\alpha_n=0.4$; 4, $\alpha_n=0.6$.

by:

$$\bar{D}=D_{free}\cdot\frac{[Me]_{free}}{[Me]_{total}}+D_{bound}\cdot\frac{[Me]_{bound}}{[Me]_{total}}. \tag{2}$$

A detailed description of the operation of the mean diffusion coefficient in the normal pulse polarographic analysis of metal/polyelectrolyte systems will be published elsewhere.[17] It is noted here that the application of Eq. (1) and Eq. (2) is restricted to low metal/ligand ratio.[18]

The mean diffusion coefficient $\bar{D}$ can be determined by using the limiting currents given by the calibration graph i_{cal}:

$$\frac{i_l^2}{i_{cal}^2}=\frac{\bar{D}}{D_{free}}. \tag{3}$$

Application of Eq. (2) to the resulting values of $\bar{D}$ enables the calculation of the fractions "bound" and "free" metal ions, provided that the diffusion coefficient of the metal complex D_{bound} is known. Subsequently, binding constants for the complex formations can be calculated. The well-known method of DeFord–Hume[19] to calculate binding constants from the shifts of the half-wave potential can be employed to test the results.

Values of the diffusion coefficients of the PAA ligands could be calculated from literature data on the radii of gyration of the PAA coils by application of the Stokes–Einstein relation. Since the molecular mass of HA molecules may range from 1,000 to 100,000,[20] the radii of gyration may range from *ca.* 1 to 10 nm,[21–24] if HA behaves in solution as a spherical random coil.[21] An estimation of the average diffusion coefficient of the HA molecules in the sample solutions was established by determination of the plateau value for the limiting current for the ligand titrations. In the case of a large excess of ligand, virtually all metal ions will be bound, and the plateau value can be expressed by:

$$i_{l(\text{plateau})} = A \cdot \sqrt{D_{\text{bound}}} \cdot [\text{Me}]_{\text{total}}. \tag{4}$$

It was found that the average diffusion coefficient of the HA molecules is about $5 \times 10^{-7}\,\text{cm}^2.\text{s}^{-1}$. This value corresponds to an average molecular mass of about 10,000.[22]

Polyelectrolyte effects

The i_l-plots of the systems investigated, of which some have been depicted in the Figures 1–3, reveal that the binding of the heavy metal ions to HA and PAA is strongly dependent on α_n. Three important observations can be made in this respect.

i) The higher α_n for a given metal/polyacid concentration ratio, the lower i_l. For Me/PAA systems, this observation is readily explained by the increase of the charge density of the polycarboxylic ligand upon neutralization, and is considered as a typical polyelectrolyte effect.[7,10,25,26]

ii) The metal complexing capacities are almost linearly dependent on α_n. At the "equivalence point" of the metal ion titrations, the amount of metal ions is somewhat less than half of the number of deprotonated groups. This observation suggests that primarily a charge compensation process occurs.

iii) Analogies between the i_l-plots for ME/PAA and Me/PAA are obvious.

It is widely assumed that the association of metal ions with HA predominantly occurs through the carboxylate groups.[27,28] A 1:1 binding (viz. 1 metal ion:1 carboxylate group) is generally assumed for the interactions Cd,Pb,Zn/HA and Cd,Zn/PAA.[7,29–33] These assumptions in combination with the observations described, strongly suggest that the metal binding to HA and PAA can schematically be expressed by (charges omitting):

$$\mathrm{Me} + \mathrm{A} \rightleftharpoons \mathrm{MeA} \tag{5}$$

where A represents a carboxylate group.

Conditional binding constants K_1 have been calculated for the Cd,Zn/PAA systems from polarographic data. Values of $\log K_1$ are given in Figure 4 as a function of the actual fractional ligand density, defined by:

$$\alpha_{\mathrm{eff}} = \frac{[\mathrm{COO^-}]_{\mathrm{free}}}{[\mathrm{COO^-}]_{\mathrm{free}} + [\mathrm{COOH}]} \tag{6}$$

where $[\mathrm{COO^-}]_{\mathrm{free}}$ is the concentration of free carboxylate groups, and [COOH] is the concentration carboxylic groups.

The data in Figure 4 represented by the closed symbols were calculated from i_l values applying the $\bar{D}$ method, whereas those represented by the open symbols were calculated from the shifts in $E_{1/2}$ applying the DeFord–Hume method. Although the values of $\log K_1$ using $E_{1/2}$ are slightly higher than those using $\bar{D}$, they confirm the applicability of the concept of a mean diffusion coefficient.

The curves for Cd,Zn/PAA in Figure 4 enable the following conclusions:

i) the dependence of $\log K_1$ on α_n is approximately linear;

ii) intrinsic values of K_1 (for $\alpha_{\mathrm{eff}} = 0$) are of the same order of magnitude of those for the binding of $\mathrm{Cd^{2+}}$ and $\mathrm{Zn^{2+}}$ to low molecular mass monocarboxylic acids.[7,34,35]

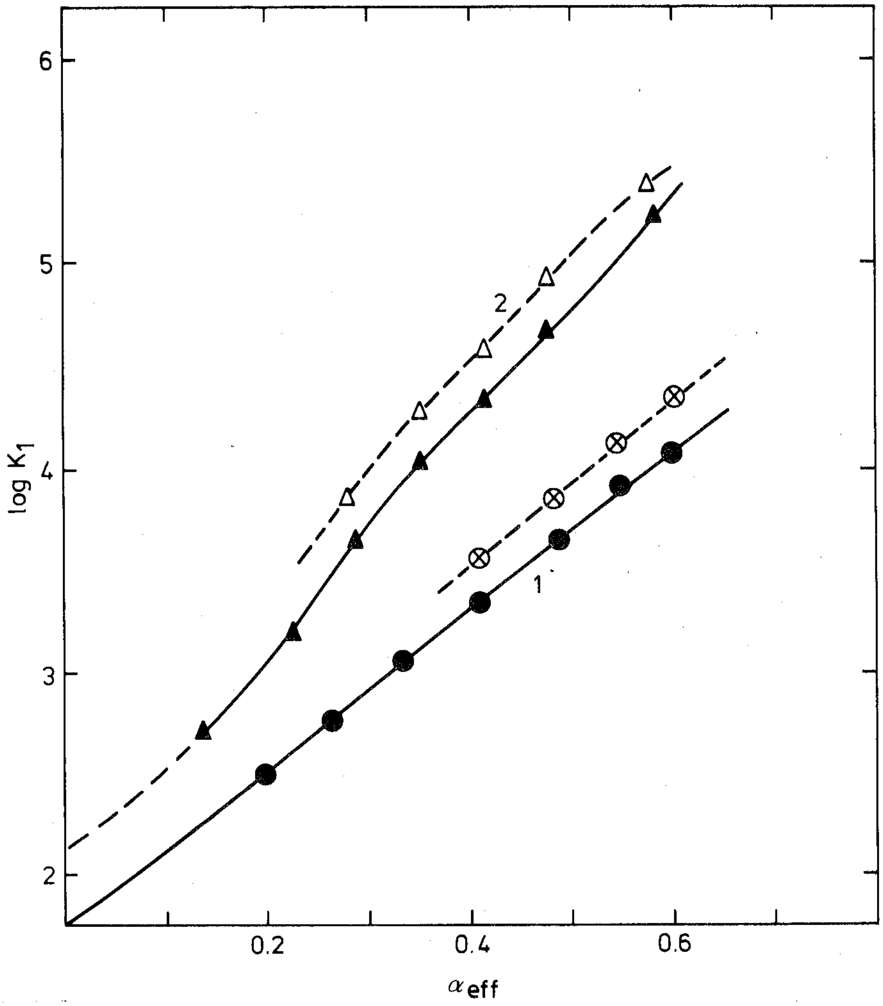

FIGURE 4 Dependence of $\log K_1$ on α_{eff} for Zn,Cd/PAA systems from polarographic data. $[KNO_3] = 50\,mol.m^{-3}$; closed symbols: from i_l-data; open symbols: from $E_{1/2}$-data; 1, Zn/PAA; 2, Cd/PAA.

These conclusions illustrate the polyelectrolyte effect on the binding of heavy metals to polycarboxylic acids: the polyionic field enhances the strength of the chemical interaction.[36]

In Figure 5, $\log K_1$ is plotted as a function of α_{eff} for the Cd,Pb,Zn/HA systems. It is clear that the conclusions reached for the Me/PAA systems are also applicable to Me/HA. Intrinsic values of $\log K_1$ for Cd,Pb,Zn/HA are 2.4, 3.8 and 2.5 respectively. These values are close to those for low molecular mass monocarboxylic acids.

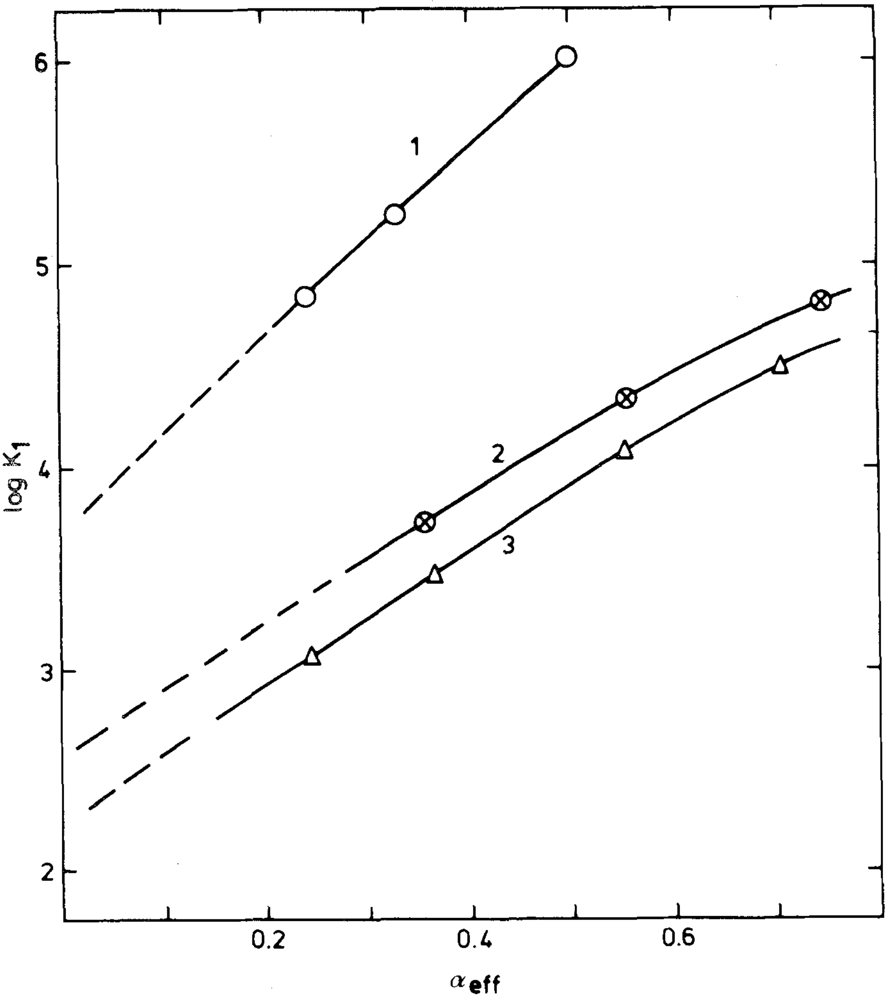

FIGURE 5 Dependence of $\log K_1$ on α_{eff} for Pb,Zn,Cd/HA systems from polarographic data. $[KNO_3] = 50\,mol.m^{-3}$; 1, Pb/HA; 2, Zn/HA; 3, Cd/HA.

It is concluded that there is strong evidence for a polyelectrolyte effect in the interaction of Cd^{2+}, Pb^{2+} and Zn^{2+} with humic acid. Although the occurrence of a polyelectrolyte effect for Me/HA has been suggested by other authors,[37-40] the large variation of binding constants of Me/HA with experimental condition is often predominantly attributed to the effect of the heterofunctionality of the HA samples.[41-43]

The presence of KNO_3 as supporting electrolyte in the polarographic experiments will suppress the polyelectrolyte effect because of competitive binding of K^+ ions present in excess. Thus, generally, the typical polyelectrolyte effects will be more pronouncedly manifest in Me/polyacid systems without inert salt. Therefore conductometric heavy metal ion titrations into 1:1 salt-free polyacid solutions have been carried out, following the same procedures as in the polarographic experiments. The data are represented as the conductivity excess $\Delta\varkappa_T$ which expresses the change of the conductivity $\varkappa$ with heavy metal ion addition into a blank solution (no polyacid present), minus the change of $\varkappa$ with heavy metal ion addition into the polyacid containing sample solution:

$$\Delta\varkappa_T = \varkappa(\text{Me in blank}) - [\varkappa(\text{sample with Me}) - \varkappa(\text{sample without Me})]. \tag{7}$$

The representation of the data as $\Delta\varkappa_T$ readily visualizes any binding of heavy metal ions. If no heavy metal binding would occur, the initial value $\Delta\varkappa_T = 0$ would remain unchanged in the course of the titration. If only heavy metal binding would occur, $\Delta\varkappa_T$ will have a positive value. If as a result of heavy metal binding other cations, such as K^+ or H^+, would be released, negative contributions are incorporated in $\Delta\varkappa_T$.

In Figure 6 the conductivity excess is plotted for Cd/PAA. Initially the slope of the $\Delta\varkappa_T$-curve is positive, indicating binding of Cd^{2+}. From the value of the slope it can be calculated[7] that virtually all of the Cd^{2+} ions are initially bound. From the three curves at different α_n it is clear that the slope is strongly reduced at the stage which roughly corresponds with charge compensation, i.e. when the concentration of Cd^{2+} ions is about half that of the carboxylate groups. From the change of the pH in the course of the metal ion titration, it is concluded that after this "equivalence point" protons are released upon further addition of Cd^{2+}. The corresponding pH curves are given in Figure 7. In this figure, the concentration released protons is also pictured. The data in the Figures 6 and 7 allow the following conclusions:

i) Up to charge compensation, the binding of Cd^{2+} to PAA is nearly complete in 1:1 salt-free solutions;

ii) Beyond charge compensation, further binding of Cd^{2+} to PAA is weak and accompanied by some release of protons.

For the system Pb/HA similar curves for the conductivity excess and the corresponding proton release are given in the Figures 8 and 9. From the trends in these curves, strong analogies between the Me/HA and the Me/PAA systems emerge. The binding of Pb^{2+} to HA is nearly complete at the point of charge compensation. If the deprotonated groups on the humic acid ligand have been saturated with heavy metal ions, another type of binding process occurs upon further addition of heavy metal ions. This process can schematically be described by (charges omitting):

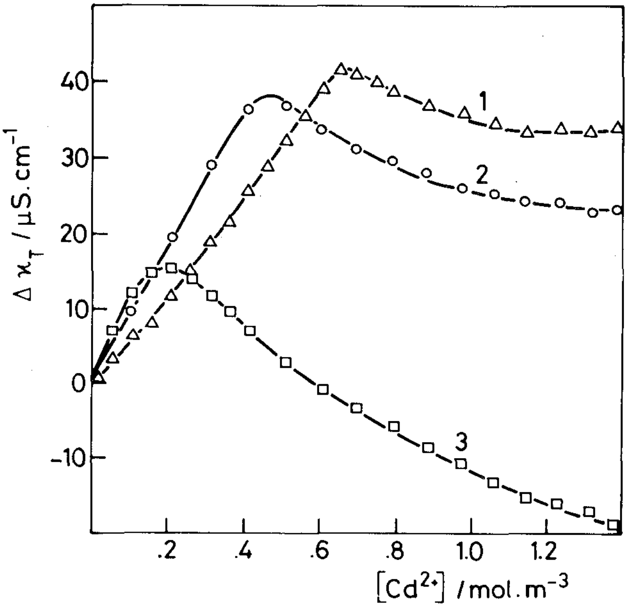

FIGURE 6 The conductivity excess $\Delta\varkappa_T$ versus the concentration $Cd(NO_3)_2$. $[PAA] = 2.50\ mol.m^{-3}$; 1, $\alpha_n = 0.6$; 2, $\alpha_n = 0.4$; 3, $\alpha_n = 0.2$.

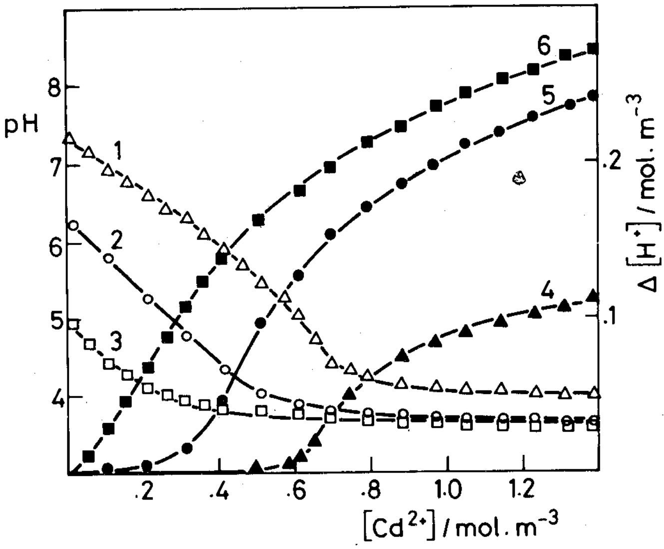

FIGURE 7 The concentration of released protons, and the pH versus the concentration $Cd(NO_3)_2$. $[PAA]=2.50\,mol.m^{-3}$; $\alpha_n=0.6$ (1,4); $\alpha_n=0.4$ (2,5); $\alpha_n=0.2$ (3,6).

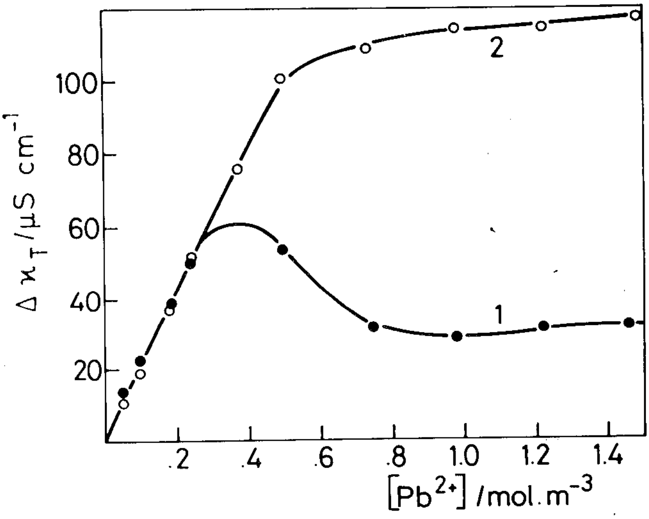

FIGURE 8 The conductivity excess $\Delta\varkappa_T$ versus the concentration $Pb(NO_3)_2$. $[HA]=2.00\,mol.m^{-3}$; 1, $\alpha_n=0.4$; 2, $\alpha_n=0.6$.

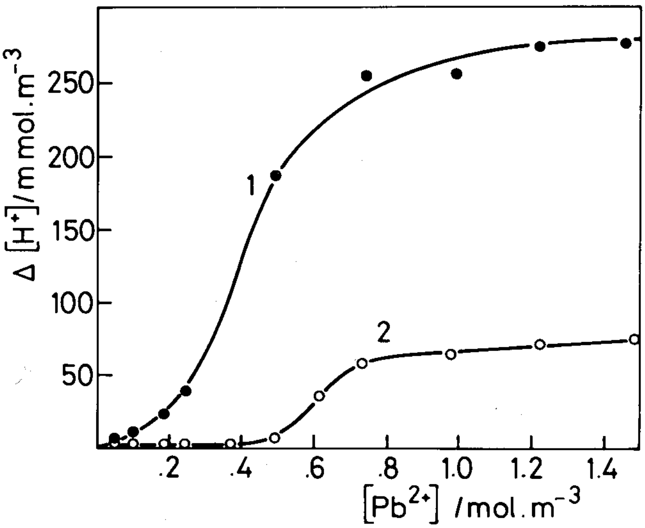

FIGURE 9 The concentration of released protons versus the concentration $Pb(NO_3)_2$; $[HA] = 2.00\ mol.m^{-3}$; 1, $\alpha_n = 0.4$; 2, $\alpha_n = 0.6$.

$$Me + HA \rightleftharpoons MeA + H. \tag{8}$$

The importance of the binding process described by Eq. (8) decreases for the Me/HA systems in the series $Pb > Zn \geq Cd$, which corroborates with the corresponding values of the intrinsic binding constants.

The conductometric data confirm the conclusion that a strong analogy exists between the binding of heavy metals with humic acid and their binding with polyelectrolytes.

CONCLUSIONS

The systems Cd,Pb,Zn/HA are polarographically labile. The binding of Cd^{2+}, Pb^{2+} and Zn^{2+} to humic acid is quite similar to the binding of these heavy metals to homofunctional polycarboxylic acids.

The results show that in the electrochemical analysis of environmental samples containing heavy metals in interaction with organic matter, a mean diffusion coefficient may be operative controlling the voltammetric current. Experimentally determined binding constants may describe the charge density of the humic acid rather than the chemical binding strength.

References

1. T. M. Florence and G. E. Batley, *CRC Crit. Rev. Anal. Chem.* **9,** 219 (1980).
2. H. W. Nürnberg, *Anal. Chim. Acta* **164,** 1 (1984).
3. R. Ernst, H. E. Allen and K. H. Mancy, *Water Res.* **9,** 969 (1975).
4. T. M. Florence, *Talanta* **29,** 345 (1982).
5. W. Davison and M. Whitfield, *J. Electroanal. Chem.* **75,** 763 (1977).
6. D. P. H. Laxen and R. M. Harrison, *Water Res.* **15,** 1053 (1981).
7. R. F. M. J. Cleven, Thesis, Agricultural University, Wageningen (1984).
8. B. Brady and G. K. Pagenkopf, *Can. J. Chem.* **56,** 2331 (1978).
9. F. H. Frimmel, *Z. Wasser Abwasser Forsch.* **14,** 7 (1981).
10. G. S. Manning, *Ann. Rev. Phys. Chem.* **23,** 117 (1972).
11. J. Brandrup and E. H. Immergut (eds.), *Polymer Handbook* (Interscience Publishers, New York, 1965).
12. J. H. Baxendale, S. Bywater and M. G. Evans, *J. Polymer Sci.* **1,** 237 (1946).
13. H. P. van Leeuwen, *Anal. Chem.* **51,** 1322 (1979).
14. H. P. van Leeuwen, *Anal. Chem. Symp. Series* **2,** 383 (1980).
15. K. W. Hanck and J. W. Dillard, *Anal. Chim. Acta* **89,** 329 (1977).
16. D. R. Crow, *Polarography of Metal Complexes* (Academic Press, London, 1969).
17. R. F. M. J. Cleven, H. G. de Jong and H. P. van Leeuwen, *J. Electroanal. Chem.*, in press.
18. H. P. van Leeuwen, *Sci. Total Env.*, in press.
19. D. D. DeFord and D. N. Hume, *J. Amer. Chem. Soc.* **73,** 5321 (1951).
20. E. L. Piret, R. G. White, H. C. Walther and A. J. Madden, *Sci. Proc. Dublin Soc.* **A-1,** 69 (1960).
21. K. Ghosh and M. Schnitzer, *Soil Sci. Soc. Amer. J.* **45,** 89 (1981).
22. E. M. Thurman, R. L. Wershaw and D. J. Pinckney, *Org. Geochem.* **4,** 27 (1982).
23. M. S. Varney, R. F. C. Mantoura, M. Whitfield, D. R. Turner and J. P. Riley, *IMER-Manuscript No. 487* (Inst. Marine Env. Res., Plymouth, 1981).
24. W. Flaig, H. Beutelspacher and E. Rietz, in: *Soil Components*, Vol. I (J. E. Gieseking, ed.) (Springer-Verlag, Berlin, 1975), p. 1.
25. J. A. Marinsky, *Coord. Chem. Rev.* **19,** 125 (1976).
26. M. Mandel and J. C. Leyte, *J. Polymer Sci.* **A-2,** 2883 (1964).
27. H. Kerndorff and M. Schnitzer, *Geochim. Cosmochim. Acta* **44,** 1701 (1980).
28. P. Vinkler, B. Lakatos and J. Meisel, *Geoderma* **15,** 231 (1976).
29. J. Buffle, F.-L. Greter and W. Haerdi, *Anal. Chem.* **49,** 216 (1977).
30. R. A. Saar and J. H. Weber, *Can. J. Chem.* **57,** 1263 (1979).
31. M. Adhikari, G. Chakrabarti and G. Hazra, *Agrochimia* **12,** 134 (1977).
32. C. Whitworth and G. K. Pagenkopf, *J. Inorg. Nucl. Chem.* **41,** 317 (1979).
33. C. Travers and J. A. Marinsky, *J. Polymer Sci.: Symp. Series* **47,** 285 (1974).

34. L. G. Sillen and A. E. Martell, *Stability Constants of Metal Complexes,* Special Publication No. 17 (The Chemical Society, London, 1964).
35. D. W. Archer and C. B. Monk, *J. Chem. Soc.* 3117 (1964).
36. M. Guéron and G. Weisbuch, *Biopolymers* **19,** 353 (1980).
37. J. Buffle, A. Tessier and W. Haerdi, in: *Complexation of Trace Metals in Natural Waters* (C. J. M. Kramer and J. C. Duinker, eds.) (Martinus Nijhoff/Dr. W. Junk Publishers, The Hague, 1984), pp. 301–315.
38. J. A. Marinsky, A. Wolf and K. Bunzl. *Talanta* **27,** 461 (1980).
39. K. L. Nash and G. R. Choppin, *J. Inorg. Nucl. Chem.* **42,** 1045 (1980).
40. J. R. Tuschall and P. L. Brezonik, in: *Complexation of Trace Metals in Natural Waters* (C. J. M. Kramer and J. C. Duinker, eds.) (Martinus Nijhoff/Dr. W. Junk Publishers, The Hague, 1984), pp. 83–94.
41. D. S. Gamble, A. W. Underdown and C. H. Langford, *Anal. Chem.* **52,** 1901 (1980).
42. H. Davis and C. J. B. Mott, *J. Soil Sci.* **32,** 379 (1981).
43. A. M. Posner, *J. Soil Sci.* **17,** 65 (1966).