Speciation and Lability of Zinc(II) in River Waters

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Dynamic voltammetric experiments on a number of European river water samples reveal the presence of labile zinc(II) complexes with stability constants in the range between $10^{6.4}$ and 10^7 M^{-1}. Theoretical reconstruction of the labilities on the basis of the elementary association/dissociation rate constants confirms the experimental findings. Taking into account (i) the differences in diffusion coefficients between free metal ions and metal complexes, and (ii) the lability of the complexes, the distribution of zinc-(II) over free metal and complexed species is found to be roughly 30% and 70%, respectively. Consequently the operational bioavailability of zinc(II), i.e., the flux of zinc(II) into an organism, is reduced to 30% if the actual interfacial uptake process is rate-determining. The reduction amounts to 50% if the diffusional supply of zinc(II) to the biointerphase is rate-determining.

Introduction

As recently outlined by Xue and Sigg (*1*), the speciation of zinc(II) in freshwater deserves thorough investigation. One of the arguments for this is based on the need for elucidation of the relationship between the bioavailability of zinc(II) and its speciation. Depending on the nature of the rate-determining step in the overall biouptake process, it may be the free zinc(II) ion activity or the total labile zinc(II) activity which is the biologically relevant parameter (*2*). Therefore it is of elementary importance to understand both the equilibrium speciation of zinc(II) and the labilities of its complexes. It should be stressed that complex species which are labile on the effective time scale of the biouptake process *are*, by definition, *bioavailable*. Whether such bioavailable complexes indeed contribute to the supply of zinc(II) to a surface which selectively takes up free Zn(II), is determined by the nature of the flux-determining step: If the transport through the supplying medium is flux-determining, labile complexes contribute, in a certain proportion to their mobilities; if the actual uptake of free zinc(II) at the very interface is flux-determining, then there is no zinc(II) activity gradient in the supplying medium and hence no driving force for the complexes to contribute (*3*).

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The present study is concerned with the speciation and the speciation dynamics of zinc(II) in river water. It intends to determine the equilibrium speciation as well as the labilities of the complex species in different European river water samples. For this purpose we are applying differential pulse voltammetry (DPV) and stripping voltammetry (SV), techniques which provide combined information on speciation and lability. The crucial variable in testing lability is the effective time scale of the technique, i.e., the pulse time in DPV and the stirring rate in SV. The distribution of zinc(II) over free and bound species is computed from the dependence of the voltammetric response on the ligand concentration, the so-called complexation curve. The results also permit an estimation of the theoretical bioavailability of zinc(II) in the samples studied, considering the two extreme cases outlined above.

Theory

The simplest mode of complexation between a free (hydrated) metal ion M and a ligand L can be described by

$$M + L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} ML \qquad (1)$$

where k_a and k_d are the association and dissociation rate constants of the complex (ML), respectively. The complexation equilibrium is characterized by the stability constant K:

$$K = \frac{c^*_{ML}}{c^*_M c^*_L} \qquad (2)$$

where c^*_M, c^*_L, and c^*_{ML} are the bulk concentrations of the free metal, the free ligand, and the complex, respectively. Under conditions of a sufficient excess of ligand ($c^*_L \gg c^*_M + c^*_{ML}$), the association reaction becomes quasi-monomolecular with rate constant k_a':

$$k_a c^*_L = k_a' \qquad (3a)$$

$$k_a'/k_d = K' = c^*_{ML}/c^*_M \qquad (3b)$$

The lability of a complex system, in an electrochemical cell or in a biouptake situation, is determined by its ability to maintain a fully diffusion-controlled flux of metal toward an interface which selectively takes up one of the species, usually M. Rigorous theory (*4*) shows that lability is only defined for systems where the complexation equilibria in the bulk are dynamic, i.e., systems obeying the condition that

$$k_a't, \, k_d t \gg 1 \qquad (4)$$

where t is the effective time scale. Fulfilment of eq 4 means that the metal M frequently changes from free M to the complex ML and vice versa on the time scale of consideration. It should be emphasized that condition 4 refers to the rate characteristics of a *volume* reaction. Applicability of eq 4 implies that equilibrium is achieved in the bulk of the system. Lability requires something more: supply of metal toward a species-selective interface should not be limited by the association/dissociation kinetics of the complex species involved. The pertaining criterion is conveniently expressed in terms of the ratio between the flux resulting from dissociation of the complex species (J_{kin}) and that resulting from pure diffusion (J_{dif}). This additional condition then reads

$(J_{kin})/(J_{dif}) \gg 1$. The appropriate derivation has been given by de Jong et al. (5) and yields a further condition. For the case of semiinfinite linear diffusion and quasi-monomolecular reaction kinetics, the extra condition reads

$$\Lambda_1 t^{1/2} \gg 1 \qquad (5a)$$

where Λ_1 is a basic lability parameter which appears as the relevant argument in the time-dependent flux expressions (4, 5)

$$\Lambda_1 = \frac{k_d^{1/2}(1 + \epsilon K')}{\epsilon^{3/2} K'(1 + K')^{1/2}} \qquad (5b)$$

where ϵ is the diffusion coefficient ratio D_{ML}/D_M. It should be noted that labile behavior of a complex system corresponds to the limiting situation where the association/dissociation kinetics are so fast that coupled diffusion of labile complexes and free metal ions results. Between labile behavior and inert behavior there is a transitional regime where the kinetics partly uncouple the diffusion of complex species. The problem has been analyzed in detail by de Jong et al. (4, 5). Within the frame of the present study, it is useful to consider the transformation of condition 5a into the equivalent expression for steady-state conditions, where the diffusion layer thickness δ takes the place of time t as the relevant variable.

Their basic relation is

$$t = \delta^2/\bar{D} \qquad (6)$$

where $\bar{D}$, the mean diffusion coefficient of M and ML, is given by

$$\bar{D} = \frac{c_M^*}{c_T^*}D_M + \frac{c_{ML}^*}{c_T^*}D_{ML} = D_M\frac{(1 + \epsilon K')}{(1 + K')} \qquad (7)$$

where c_T^* equals $c_M^* + c_{ML}^*$. Substituting eqs 6 and 7 into eq 5a, which is equivalent to comparing the kinetic flux (J_{kin}) to the steady-state diffusion-controlled flux (J_{dif}), yields the steady-state equivalent of condition 5a:

$$\Lambda_2 \delta \gg 1 \qquad (8a)$$

with

$$\Lambda_2 = \frac{k_d^{1/2}(1 + \epsilon K')^{1/2}}{D_{ML}^{1/2} \epsilon K'} \qquad (8b)$$

In the limiting case of $\epsilon K' \gg 1$ and $\epsilon \rightarrow 1$, condition 8a reduces to

$$\frac{k_d \delta}{k_a^{1/2} D_M^{1/2}} \gg 1 \qquad (9)$$

which is well-known as the Davison criterion (6). It should be noted that for many environmental complexes ϵ may be as low as 10^{-2} or 10^{-3} (7), so that $\epsilon K' \gg 1$ constitutes a quite restrictive condition. Hence it will be of practical value to consider eq 8 as the origin of eq 9.

Lability criteria can be tested experimentally, using eq 5 or 8 together with potential characteristics, and theoretically, starting from known values of the rate constants for metal complexation reactions. It has been demonstrated by Eigen (8) that the rates of metal complexation reactions in aqueous systems are governed by the rate of removal of a coordinated water molecule from the inner hydration shell. The corresponding dehydration rate constant k_{-w} is directly related to
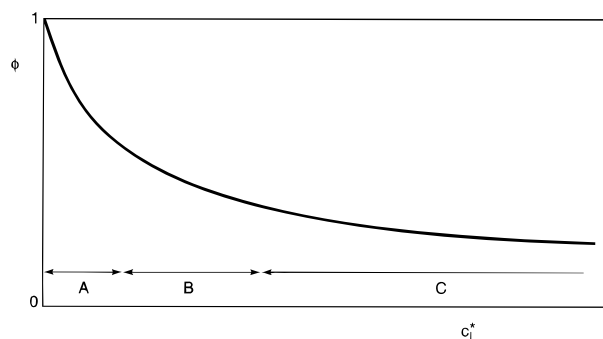

FIGURE 1. Sketch of the normalized current ϕ as a function of the ligand concentration c_L^* for a labile complex system. The regimes A, B, and C refer to regions of highest sensitivity to the parameters K, p, and ϵ, respectively.

the association rate constant k_a in the overall complexation reaction. The value for k_{-w} for zinc(II) has been found to be between 10^7 and $10^8\,s^{-1}$. From that it can be deduced that the association rate constant k_a for zinc(II) complexation reactions will be $O(10^8)\,M^{-1}\,s^{-1}$ (O denoting order of magnitude). For complexes with known stability K and known diffusion coefficient, we may thus calculate the lability parameters Λ_1 and Λ_2 and make theoretical predictions about labilities for given values of t and δ, respectively.

In the case of labile complexes and an excess of ligand the preelectrolysis current in a SV-measurement (I_{pre}) is proportional to the total metal concentration:

$$I_{pre} \propto \bar{D}^p c_T^* \qquad (10)$$

The value of the parameter p is determined by the type of mass transport during the preelectrolysis and generally has an effective value between $^1/_2$ and $^2/_3$ (9). Under conditions where the reoxidation current is independent of the complexing properties of the medium, the reoxidation peak current (I) in an SV measurement is linearly proportional to the metal concentration in the mercury drop (c_{M^o}). And this in turn, is proportional to the preelectrolysis current and duration (t_{pre}):

$$I \propto c_{M^o} \propto I_{pre} t_{pre} \qquad (11)$$

Combination of eqs 2, 7, 10, and 11 gives:

$$\phi = \left(\frac{\bar{D}}{D_M}\right)^p = \left(\frac{1 + \epsilon K c_L^*}{1 + K c_L^*}\right)^p \qquad (12)$$

where ϕ is the ratio between the reoxidation peak current for the system with complexing compounds and that for the reference system without these compounds. A plot of ϕ against the free ligand concentration will reflect the complexing properties of the system (Figure 1). As explained before (10), such a ϕ, c_L^* plot can be considered to be composed of three regions. Region A has the highest information content with respect to the stability K. For $p = ^1/_2$ the curve is most sensitive to K in the range around $K c_L^* \approx 2$ (9). The region B is most sensitive to the parameter p, and the diffusion coefficient ratio ϵ has its greatest influence in region C. Equation 12 shows that for $c_L^* \rightarrow \infty$, ϕ approaches ϵ^p. The current then becomes a constant with a value determined by the diffusion coefficient of the labile complex ML.

Materials and Methods

The water samples were collected from several European rivers and stored in the dark in acid-rinsed polyethene bottles

TABLE 1. pH, Concentration Dissolved Organic Carbon (DOC), Concentration Total Zinc $c^*_{Zn,T'}$, and Complexing Capacity (CC) in Some of the Studied River Samples (11)

sample[a]	pH	DOC, mmol L^{-1}	$c^*_{Zn,T'}$ μmol L^{-1}	CC, μmol L^{-1}
Eysden, NL	7.91	0.268	0.40	0.62
Keizersveer, NL	8.21	0.344	0.41	0.98
Geul, NL	8.27	0.268	4.76	<3.28[b]
Eindergatsloot, NL	7.25	0.353	1.80	1.54
Larjean, Sw	7.61	0.509	0.29	1.16
Hultabäcken1, Sw	6.95	0.808	0.33	2.64
Hultabäcken2, Sw	6.84	0.578	0.54	0.92
Lillan, Sw	7.19	0.528	0.20	0.26
Långemossen, Sw	5.94	1.405	0.28	0.66
Göta älv, Sw	7.32	0.332	0.41	0.55
Rio Major 1, Sp	8.08	2.120	0.09	0.44
Rio Major 2, Sp	8.16	0.134	0.37	0.67
Congost, Sp	8.30	0.362	0.42	2.41

[a] Abbreviation: NL, Netherlands; Sw, Sweden; Sp, Spain. [b] Uncertain.
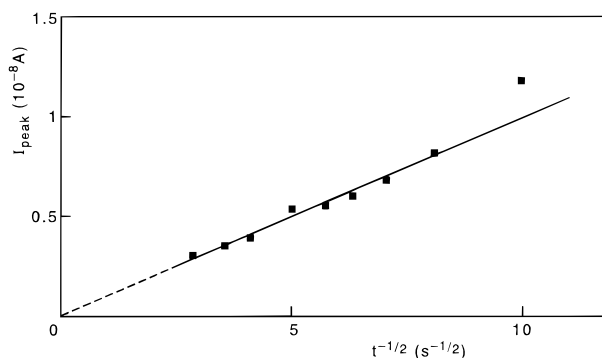

FIGURE 2. Cottrell plot of DPV peak currents for different values of the pulse duration t for the sample Eindergatsloot. The linear behavior illustrates the diffusion-controlled character of the current.

at a temperature of 4 °C. The pH, the concentration of dissolved organic carbon (DOC), the total zinc concentration, and the complexing capacity were measured in a preceding investigation (11). Complexing capacities had been determined by titration with zinc(II), taking into account the bound zinc(II) in the original sample, and are set equal to ligand concentration. A selection of the results of these measurements is given in Table 1.

For the speciation measurements of zinc, samples were put into acid-rinsed polyethene bottles. These bottles were transported immediately to the laboratory of Inorganic Chemistry of the RIVM (The Netherlands) for the analyses of zinc speciation and for the physical and chemical characterization within 24 h after sampling. The samples were not filtered because this study was partly aimed at bioavailability characteristics of the full sample. For details, the reader is referred to a preceding technical report (11) and a forthcoming paper on the environmental aspects (12).

Voltammetric measurements were performed using a Metrohm VA stand 663 controlled by an Autolab PSTAT 10 potentiostat with a digital DIO48 input/output module from Eco Chemie. The working electrode was a static mercury drop electrode (SMDE) with a surface area of 0.52 mm². The reference and counter electrodes were Ag/AgCl/3 M KCl and glassy carbon, respectively. Considering the possible interferences due to zinc(II) adsorption on the cell wall, we used a regular glass cell (13) and developed a special measurement procedure (see below). Before measurements, the solutions were stirred and purged with nitrogen for at least 5 min. All experiments were performed at room temperature.

Lability was tested with DPV and SV measurements. In DPV the pulse time was varied between 0.01 and 0.12 s, the pulse height was 0.06 V and the time between the pulses 0.5 s. Measurements at pulse times of 10 ms or less may suffer from capacitive currents. In SV, the stirring rate was varied between 500 and 3,000 rpm in the lability tests, and kept constant at 1000 rpm in the complexation curve measurements. The deposition time was 60 s and the deposition potential was −1.2 V. Adsorption of humic components does not occur at this relatively negative potential (14). The stripping was performed in the differential pulse mode (DPASV). The equilibration time, the pulse height, the pulse time, and the time between pulses were 20 s, 0.05 V, 0.05 s and 0.2 s, respectively.

The stability K was determined from the dependency of ϕ on c^*_L, i.e., the complexation curves (see eq 12). The ligand concentration was varied by way of dilution of the river

samples. The present set of river water samples is characterized by ligand concentrations at the level of 1 μM and metal-to-ligand concentration ratios which in some cases are quite appreciable (see Table 1). Therefore, the useful range of c^*_L values is rather limited. Nevertheless, for most of the samples we obtained K values which were reproducible within 0.2 log units. The pH of the solutions was kept constant at the natural pH of the river water by using TRIS buffer, which has no complexing effects on the zinc ions (13). KNO$_3$ is added to a concentration of 0.01 M as a supporting electrolyte; its influence on the effective K through modification of the activity coefficients remains well within 0.1 log unit. Specific data for a number of complexes of zinc(II) with commercial humic acids samples also show an average modification of less than 0.1 log unit on changing the ionic strength from 0.01 to 0.02 M (15).

Since zinc(II) adsorbs at the cell wall at a pH higher than 6 (13), we designed a special procedure to deal with this problem. Before measuring a complexation curve, the cell was filled with the sample solution and kept overnight. The solution was then replaced by fresh sample, and the measurement series was carried out. Immediately after completing the experiment, the solution was transferred to another, acid-rinsed, cell. By addition of HNO$_3$ the pH was then lowered to about 4. At this pH adsorption of zinc(II) to the cell components and complexation by the natural ligands are negligible (13, 16, 17). The SV signal of this acidified solution therefore yields the total zinc(II) concentration. This corresponds with the *total concentration of zinc(II) in solution* in the original measuring situation, which is thus measured a posteriori.

Results and Discussion

Labilities. Lability tests were performed with DPV and SV. The DPV peak currents (*I*) generally showed a linear dependence on $t^{-1/2}$ which is typical for a diffusion-controlled electrode process. An example of an experimentally obtained *I*, $t^{-1/2}$ plot, a so-called Cottrell plot, is given in Figure 2. For all samples, the DPV peak potential was shifted toward more negative values with respect to the ligand-free reference. Averaged values of the shift varied from 8 to 26 mV. The combination of a linear Cottrell plot and a systematic shift of the characteristic potential shows that the zinc(II) complexes involved are voltammetrically labile. The SV data support these findings. The SV voltammograms showed regular shapes, without signs of adsorption and ligand saturation effects (14). For a number of samples, the SV peak current is linearly dependent on the square root of the stirring rate, as it should be for a diffusion-controlled process. A more detailed analysis of the SV data is given elsewhere (12).

Complexation Curves. Some examples of experimentally obtained plots of ϕ vs c^*_L are shown in Figure 3. Each
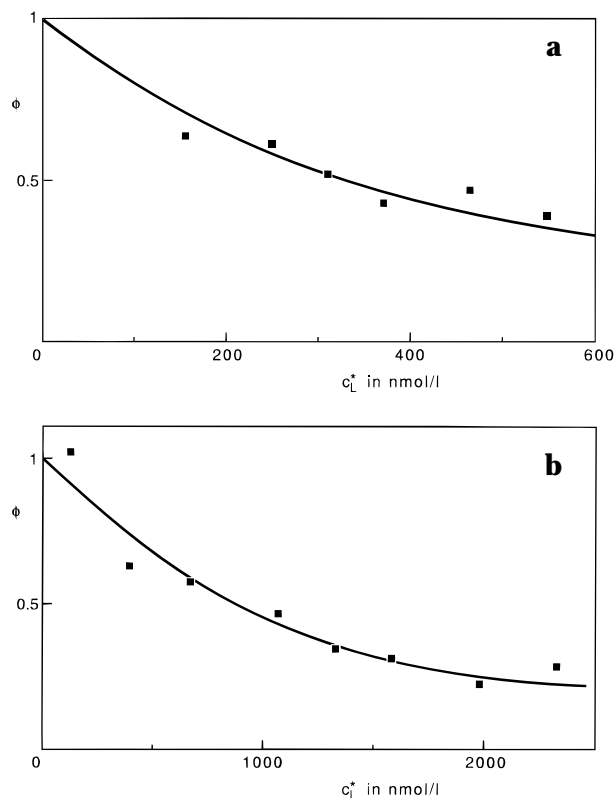
FIGURE 3. Complexation curves for the samples Eysden (a) and Hultabäcken-1 (b). Analysis is based on application of eq 12 and the stability constant K is mainly derived from the initial decay (compare Figure 1).

TABLE 2. Values Found for the Zinc(II) Complex Stability (log K), the Corresponding Fraction of Free Zinc(II), and the Resulting ϕ for Different European River Waters

sample	log K	free zinc(II)/total zinc(II)	θ
Hultabäcken1	6.5	0.12	0.10
Hultabäcken2	6.6	0.33	0.25
Larjean	6.4	0.28	0.14
Långemossen	6.6	0.39	0.18
Keizersveer	6.7	0.24	0.22
Eysden	7.0	0.28	0.28
Lillan	7.0	0.45	0.24

particular point represents the average value as resulting from two measurements. Most of the curves show the expected decrease of ϕ with increasing c_L^*, simply reflecting the increased complexation of zinc(II) with increasing ligand concentration. In few cases, the decrease of ϕ remained within the experimental error (about 10%) so that the stability constant K could not be determined. In all the other cases, the measured change of ϕ with c_L^* was sufficient to compute a finite value of K. Note that, as explained before, the initial portion of the complexation curve has the highest information content on K. As can be read from Table 1, there are several samples for which the ligand concentration c_L^* is not much larger than the zinc(II) concentration. In these cases the theoretical condition of excess ligand over metal is not very well obeyed. Therefore we have applied an iterative computational procedure, based on the calculation of the real free ligand concentration c_L^*, to obtain the most reliable values for K. The procedure calculates a first estimate of K on the basis of the total ligand concentration $c_{L,t}^*$, then computes the corresponding c_L^*, recalculates K, etc. The iteration modified the log K values by about 0.1 unit for the relatively high metal-to-ligand ratio samples, and by less for the others, in agreement with similar findings for model systems (18). Table 2 shows the resulting K values, together with the corresponding ratios between free zinc(II) and total zinc(II). We note that these values for K are in line with the potential shifts observed in the DPV experiments. These yield (less accurate) log K values between 6 and 7.

Theory prescribes that for labile systems ϕ should approach ϵ^p for infinite c_L^*. However, none of the complexation curves reaches the expected plateau for large c_L^*. Only the curve for the sample Hultabäcken-1 shows some tendency to level off. On the basis of this curve, we made a very rough estimate, and nothing more than that, of the diffusion coefficient ratio ϵ. For p between $^1/_2$ and $^2/_3$, ϵ takes values

around 5×10^{-2}. For our present purposes, it is not necessary to have more quantitative information on ϵ. It was already shown (10), and once more verified in our computations, that the influence of ϵ on the resulting K is small; a change of ϵ by a factor of 2 yields a change in log K of less than 0.1 unit. Further inspection of eq 12 clarifies why the complexation curves do not reach the plateau of ϵ^p. The relevant condition for that is $\epsilon Kc_L^* \gg 1$, whereas for the samples studied, with $\epsilon = O(10^{-1})$, $K = O(10^6$ to $10^7)$ M^{-1} and $c_L^* = O(10^{-6})$ M, ϵKc_L^* does not even reach unity.

Reconstruction of Labilities. The experimental finding of labile behavior can be confirmed if the lability criteria 5 and 8 appear to be satisfied. This can be checked on the basis of the literature value for the (inner shell) dehydration rate constant k_{-w} of the $Zn(H_2O)_n^{2+}$ ion. Eigen (8) reported a value of $O(10^7$ to $10^8)$ s^{-1} for k_{-w}. If we combine this value with the value of $O(1$ to $10)$ M^{-1} for the equilibrium constant of the fast preceding step in the complexation mechanism (19), an effective association rate constant k_a of $O(10^8)$ M^{-1} s^{-1} results. Thus for zinc(II) complexes with a K of $10^{6.5}$ M^{-1} the dissociation rate constant k_d is $O(10$ to $10^2)$ s^{-1}. For an effective time scale t of $O(10^{-1})$ s the complex system is just dynamic (compare eq 4) and for $\epsilon = O(10^{-1})$ and $c_L^* = O(10^{-6})$ M we obtain for the dynamic lability criterion parameter

$$\Lambda_1 t^{1/2} = O(10 \text{ to } 10^2)$$

For a usual δ of about 5 μm the steady-state equivalent eq 8 comes to

$$\Lambda_2 \delta = O(10^2)$$

which confirms the experimental observation that the zinc-(II) complexes in this study are labile for the experimental time scales employed. In passing, we note that application of criterion 9 leads to erroneous results, since $\epsilon K'$ does not obey the condition of being much larger than unity.

Discussion of the Zinc(II) Speciation and Bioavailability. As shown by Table 2, the stability constants of the zinc(II) complexes in this study are in the range between $10^{6.4}$ and 10^7 M^{-1}. The uncertainties in these values, due to experimental error and uncertainty concerning the value of ϵ, are ± 0.3 log units. For the samples of a few locations we did not find a significant decrease of ϕ with increasing c_L^*. Since for these samples the zinc(II)-to-ligand ratios were not particularly high, they apparently contain weaker complexes. The large majority of samples, however, show log K values in the range between 6.4 and 7.0, and this indicates a fair extent of similarity among these different locations. Our log K values are substantially higher than the 5.0 to 5.5 found by similar methods for commercial humic acid complexes at comparable pH values and metal-to-ligand ratios (14, 15, 20). More comparable to our results are the stabilities that can be deduced from Xue and Sigg's data (1) on lake water samples. From the *DOC* values, the ligand concentration c_L^* in these samples can be estimated to be near 10^{-5} M. Since the

fractions of free zinc(II) were found to be less than 10%, it follows that log K is above 6 for the lake waters studied.

It should also be mentioned that the measurement procedure implies differences between the original water sample and the measured solution with respect to the degree of zinc(II) coverage θ of the ligands. The importance of the point derives from the degree of (chemical) heterogeneity of the zinc(II) binding ligands. The coverage θ is given by

$$\theta = \frac{[\text{zinc(II)}_{\text{bound}}]}{[\text{total available ligand}]} \qquad (13)$$

and it is affected by dissociation effects upon dilution and by loss of zinc(II) due to adsorption (see section on Materials and Methods for details). Both effects lower θ. We calculated the values of θ in the measuring solution and found it to vary between 0.05 and 0.20 from one sample to another. Within one complexation curve the variation of θ is even less. For the original water samples, θ varies roughly between 0.1 and 0.3. So the operational mean K values for the river waters may be expected to be somewhat lower than the K values reported above. Our data suggest that the differences are small, but more extensive experiments would be necessary to definitely resolve the point. It could be envisaged to study in more detail the behavior of K as a function of θ in order to develop a more comprehensive physicochemical picture of the zinc(II) complexation. For this purpose it would be necessary to isolate and concentrate the ligands, so that full complexation curves and a more differentiated analysis of ϕ become accessible. This would also permit a reasonably accurate determination of the diffusion coefficients of the zinc(II) complexes and rule out possible interferences from competing cations originating from the sample.

For the river water samples considered, roughly some 30% of the zinc(II) is present as the free ion, 70% being present in the form of zinc(II) complexes which are labile on the voltammetric time scale. If we consider the bioavailability of zinc(II) in these samples we distinguish the two limiting cases outlined before. The first one is the situation where transport of zinc(II) in the solution limits the rate of uptake by the organism. Then, since the effective time scales in pulsed voltammetry and biouptake situations are generally fairly comparable (21), the coupled diffusion of free and complexed zinc(II) is flux-determining. For a diffusion coefficient ratio ϵ of $O(10^{-1})$ this means that the flux of zinc-(II) is reduced by about 50% as compared to the situation without complexes. This number follows from substitution of the mean diffusion coefficient (see eq 7) for the case where 70% of the zinc(II) is complexed, into the steady-state flux eq 12. In the other limit where the actual uptake of zinc(II) at the interface is flux-determining (and the zinc(II) complexes are neither lipophilic (22) nor subject to accidental uptake via membrane permeases (23)), the flux is just related to the concentration of free zinc(II) which is about 30% in comparison with the reference case without complexes. It may be anticipated that these figures will be drastically different for ions such as Cu(II) and Pb(II).

List of Symbols

c_i^*	bulk concentration of i
δ	diffusion layer thickness
D_i	diffusion coefficient of i
$\bar{D}$	mean diffusion coefficient, eq 7
ϵ	D_M/D_ML
I	current
J	flux
K	stability constant, eq 2
k_a	association rate constant, eq 1
k_a'	$k_\text{a}\,c_\text{L}^*$
k_d	dissociation rate constant, eq 1
Λ_1	lability parameter, eq 5b
Λ_2	lability parameter, eq 8b
p	power of D in steady-state flux expression
ϕ	current ratio, eq 12
t	time
θ	degree of occupation of ligands by zinc(II)

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