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EQUILIBRIUM ION EXCHANGE METHOD: METHODOLOGY AT LOW IONIC STRENGTH AND COPPER(II) COMPLEXATION BY DISSOLVED ORGANIC MATTER IN A LEAF LITTER EXTRACT

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Summary—The equilibrium ion exchange method (EIM) is a powerful tool for the investigation of metal cation complexation by dissolved organic matter (DOM) in natural systems. Tests with different ion exchange resins demonstrated that under low ionic strength conditions (0.01 mol/kg) and in the presence of DOM, equilibration times of at least 24 h are required for experiments with Cu(II). The classical approach to the EIM was modified by using nonlinear reference adsorption isotherms in order to expand the method to a broader range of experimental conditions. For Cu(II) at low ionic strength (0.01 mol/kg), the reference isotherms between pH 4 and 6 were identical and were mathematically modeled in terms of Langmuir adsorption parameters. The EIM using nonlinear reference isotherms was validated between pH 4 and 6 by the correct determination of the stability constants for the complexes CuOxalate and $Cu(Oxalate)_2$. Then the method was used to quantitatively characterize the Cu(II) complexation behavior of DOM in an aqueous chestnut leaf litter extract between pH 4 and 6. In contrast to the classical approach to the EIM, data were analyzed by using plots $[Cu]_{bound}/[Cu]_{free}$ *vs.* $[Cu]_{bound}$. This allowed the determination of both, conditional stability constants and metal binding capacities for two different binding site classes. The logarithmic values of the stability constants were about 8 for the strong binding sites and 5.5–6 for the weak binding sites. The total Cu(II) binding capacity increased from 0.22 mol/(kg C) at pH 4 to 2.85 mol/(kg C) at pH 6.

The equilibrium ion exchange method (EIM) using strongly acidic cation exchange resins, as introduced by Schubert,[1,2] is one of the most suitable methods for the determination of conditional binding parameters for the complexation of metal cations by dissolved organic matter (DOM) in natural systems. The main advantage of the method is it is a real equilibrium method. Furthermore, it only requires the measurement of total metal concentrations, which generally is uncritical. In principle, there is also no limitation on the metal cations the method can be applied to.

In fact, the EIM has been widely used in studies of metal ion complexation by DOM from soil origin[3–15] and from natural waters.[16–18] In all these investigations essentially the classical approach to the EIM is used which is based on the initial work by Schubert[1] and the theoretical treatment by Calvin and Martell.[19] This approach, however, is restrictive in two respects.

First it is limited to experimental conditions that lead to linear or quasilinear reference adsorption isotherms. In this paper the EIM was expanded to a broader range of experimental conditions by using nonlinear reference isotherms. This permits, in particular, investigations at low ionic strength (⩽0.01 mol/kg) conditions characteristic for soil solutions and natural waters.

Second, data analysis by the classical approach allows the calculation of conditional stability constants only if the total ligand concentration is known. Thus far, either metal binding capacities separately determined by an independent method,[3,4,6,8,16] or the total acidity[9,18] or a concentration based on an average molecular weight[5,7,10,15] were used as total ligand concentrations. In this paper a different method of analysis of the experimental data was applied to determine both conditional stability

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constants for metal ion complexes of DOM and the metal binding capacities of DOM.

The new approach to the EIM is demonstrated for Cu(II) complexation by a chestnut leaf litter extract (LLE) at low ionic strength (0.01 mol/kg). Furthermore, experimental data are presented that provide a better insight into equilibration time under low ionic strength conditions.

THEORETICAL

Principle of the method

The principle of the EIM is summarized below focusing on the modifications made by the new approach. Further details on the conventional approach can be found elsewhere.[1,9,13,19,20]

The EIM is based on the idea that the concentration of a free metal ion, M_f, which is in equilibrium with metal ion bound by an organic ligand, M_b (equation 1a), can be determined via a competing ion exchange equilibrium (equation 1b).

$$\begin{array}{lllll} & \text{(a)} & \mathrm{L_f} & & \\ \mathrm{M_b} & \rightleftharpoons & & & \\ & & \mathrm{M_f} & \text{(b)} & \\ & & & \rightleftharpoons & \mathrm{M_R(s)} \\ & & \mathrm{R(s)} & & \end{array} \qquad (1)$$

In this equilibrium system, M_f includes all metal ion species in solution that do not involve the organic ligand, *i.e.* the aquoion M^{z+}, the hydroxo complexes $M(OH)_n^{(z-n)}$ and complexes with the anion of a background electrolyte. Similarly, L_f includes all organic ligand species that are not involved in the complexation of the metal ion M^{z+}. M_b includes all complexes of the metal ion with the organic ligand. R represents the binding site of a strongly acidic cation exchange resin with sulfonic acid functional groups and M_R the metal ion bound to it.

The first step is the quantitative characterization of the competing ion exchange equilibrium (equation 1b) which accomplished by recording a *reference* (adsorption) *isotherm* $(M)_R$ *vs.* $\{[M]_{sol} = [M]_f\}$ in a constant ionic background of an alkali ion G^+ at a resin which is initially saturated with G^+. Square brackets, *e.g.* [M] for M^{z+}, denote concentrations in solution, parentheses, *e.g.* (M) for M^{z+}, concentrations in the solid phase. For each titration point the metal concentration in solution, $[M]_{sol}$, is measured and the metal concentration at the resin, $(M)_R$, calculated by equation (2):

$$(M)_R = \frac{[M]_{add} - [M]_{sol}}{C_R}. \qquad (2)$$

$[M]_{add}$ is the initially added metal concentration, and C_R the concentration of the resin in the solution. The reference isotherm is nonlinear (Fig. 1). but can have a quasilinear part for [M] and $(M)_R$ being much smaller than [G] and $(G)_R$, respectively. The quasilinear part can be characterized quantitatively by a constant distribution coefficient ${}^cD_M$ as follows:

$$(M)_R = {}^cD_M[M]_f. \qquad (3)$$

In the conventional approach to the EIM the quasilinear part only is considered. If [G] is small, however, as it is at low ionic strength, and if the resin has a strong preference for M^{z+} over G^+, the quasilinear part of the reference isotherm can be small. One possibility for describing a nonlinear reference isotherm with L-type characteristics is the Langmuir model:[21]

$$(M)_R = \frac{R_t\,{}^cK_{RM}[M]_f}{1 + {}^cK_{RM}[M]_f}. \qquad (4)$$

Based on the linearized form of equation (4),

$$\frac{(M)_R}{[M]_f} = R_t\,{}^cK_{RM} - {}^cK_{RM}(M)_R, \qquad (5)$$

the Langmuir adsorption parameters, *i.e.* the conditional stability constant, ${}^cK_{RM}$, and the binding capacity of the resin, R_t, can be determined by linear regression analysis of a plot of ${}^cD_M = (M)_R/[M]_f$ *vs.* $(M)_R$.

In a second step, a *sample* (adsorption) *isotherm* $(M)_R$ *vs.* $\{[M]_{sol} = [M]_f + [M]_b\}$ is recorded in the presence of the organic ligand. For each titration point on the sample isotherm,

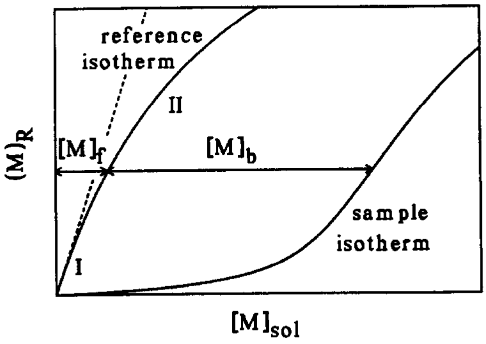

Fig. 1. Principle of the equilibrium ion exchange method; the reference isotherm is divided into a quasilinear part I (visualized by a straight line with the initial slope, – – –) and a nonlinear part II.

Table 1. Properties of the cation exchange resins used for the EIM (source: manufacturers)

	Serdolit CS 2	Bio Rex MSZ 50	Vydac 401SC
Basis	Amberlite IR 120, SDB*, cross-linking 8%	Dowex 50, SDB*, cross-linking 10%	Glass core with 1 *μm* layer of modified silica
Functional group	$-SO_3^-$	$-SO_3^-$	$-SO_3^-$
Grain size	100–200 *μm* (>90%)	600–700 *μm* (>99%)	30–40 *μm*
Dry capacity	4.4 *meq/g*	4.8–5 *meq/g*	0.1 *meq/g*

*Styrene-divinylbenzene copolymer.

the measured total equilibrium concentration in solution, $[M]_{sol}$, is related to $[M]_f$ via $(M)_R$ and the known reference isotherm parameters by equations (3) or (4). The concentration of organically bound M^{z+}, $[M]_b$, is obtained by mass balance. The relationship between $[M]_{sol}$, $[M]_f$, $[M]_b$ and $(M)_R$ is illustrated in Fig. 1.

Data analysis

In contrast to the conventional EIM, $[M]_f$ and $[M]_b$ from all the sample isotherm titration points were used for the quantitative characterization of the metal complexation equilibrium (equation 1a). For complexation by organic ligand mixtures in leaf litter extracts, the formation of 1:1 quasiparticle complexes ML was assumed.[22] The pH-dependent conditional stability constant, ${}^cK$, and the metal binding capacity of the ligand, L_t, are defined by

$$ {}^cK = \frac{[M]_b}{[M]_f[L]_f} = \frac{[M]_b}{[M]_f(L_t - [M]_b)}. \quad (6)$$

These binding parameters were deduced from a plot of $[M]_b/[M]_f$ *vs.* $[M]_b$. If the plot is linear, stability parameters for a single quasiparticle complex ML are obtained by linear regression analysis. If the plot is nonlinear, the stability parameter for two quasiparticle complexes M(L1) and M(L2) are determined by nonlinear regression analysis.[21]

EXPERIMENTAL

Ion exchange resins

Different cation exchange resins (analytical grade) were used: Serdolit CS2 (Serva), BioRex MSZ50 (Bio Rad), and Vydac 401SC (Machery & Nagel). Their properties are summarized in Table 1. The K^+ or Li^+-form of the Serdolit and the BioRex resins were prepared following standard procedures using 1*M* solutions of KOH or LiOH. For the Vydac 401SC, 1*M* KNO_3 or $LiNO_3$ were used because of the limited pH-stability of the silica surface layer. All resins were dried at 40°C and ambient pressure for 2 days and stored in a desiccator over silica gel.

Ligand solutions

Oxalate solutions were prepared from analytical grade oxalic acid in a concentration of 5 mmol/kg.

The water extraction of dried and finely ground chestnut (*Castanea sativa* L.) leaf litter from southern Switzerland was carried out as described elsewhere.[23] To obtain a clear water extract, the following filters were used in sequence: Schleicher & Schüll 589/1 (cellulose filter for coarse precipitates), 589/3 (cellulose filter for very fine precipitates), ME25 (mixed ester membrane filter, 0.45 μm). The filtrate with pH 4.2 ± 0.2 and dissolved organic carbon (DOC) content of 1477 ± 84 mg/kg was purified by passing through a column of strongly acidic cation exchange resin in H^+-form (Amberlite IR120, crosslinking 8%, grain size 525–650 μm).[24] By this procedure, the residual cations, which in the complexation studies could possibly compete with added Cu(II), could be completely removed with the exception of 2 μmol/kg Fe(III) and 40 μmol/kg Al(III). The DOC content of the purified extract was 1393 ± 84 mg/kg. Because of adsorption at the ion exchange resin, part of the DOM in the unpurified extract was lost during purification. Data characterizing the DOC of the unpurified and purified extract can be found elsewhere.[23,24] For the experiments, purified extract was used either fresh or freeze-dried.

Other reagents

Acids and $LiNO_3$ were 'suprapur'-quality (Merck). All other reagents were analytical or biochemical grade.

Glassware

Most glassware and plasticware were soaked for at least 24 h in HNO_3 (20% v/v). For the silicon sealing rings of the filter holders 0.1*M*

HNO_3 was used. Soaking in HNO_3 was followed by thorough rinsing with distilled water. Membrane filters were soaked in distilled water for 24 h, rinsed and then stored up to two days in fresh distilled water at 4°C.

Apparatus

A combination of Mettler DK10,11,12 and 13 together with an Orion Ross electrode 81-02 served as pH-meter and endpoint-titrator. DOC was measured with a Shimadzu TOC500 after acidification of the sample and expulsion of inorganic carbon by purging with N_2. Total metal concentrations were measured on the following instruments: flame atomic absorption spectrometry on an Instrumentation Laboratory IL951 and a Philips PU9200, electrothermal atomic absorption spectrometry on an Instrumentation Laboratory IL555 with aerosol injection unit FASTAC IL254 and a Philips PU9390 with automatic sampling system PU9380. Pyrolytically coated graphite tubes and a temperature program that included an ashing step for the destruction of DOM were used with all electrothermal atomic absorption measurements.

Procedure for recording reference and sample isotherms

Fifty milligrams of Serdolit CS 2 resin in Li^+-form was placed in a 50 ml low density polyethylene bottle. About 20 g of 0.01 mol/kg $LiNO_3$ was added. The pH was adjusted to the desired value by adding small amounts of dilute LiOH or HNO_3 while stirring continuously with a magnetic stirring bar. An aliquot of $Cu(NO_3)_2$ stock solution with Cu concentration of 10, 100 or 1000 mg/kg was added using gravimetrically calibrated piston-type pipettes while continuously adjusting the pH. Then, 0.01 mol/kg $LiNO_3$ was added to make up to a total liquid mass of 25 g (reference isotherms) or 24.5 g (sample isotherms). The suspensions were equilibrated in closed bottles for at least 1 h at 25°C under continuous stirring at a rate of about 300 r.p.m. (multiple magnetic stirring plate 'Variomag', placed in a thermostatted waterbath). In the case of sample isotherms, 0.5 g of oxalate solution or chestnut LLE were now added under continuous pH-adjustment. The suspensions were equilibrated for 20 h as described above, while periodically checking and adjusting pH. Then stirring was stopped and suspended resin particles were allowed to settle down. An aliquot of about 5 ml of the equilibrated solution, which also contained remaining resin particles, was sampled with a polyethylene syringe and filtrated through a 0.45 μm membrane filter (Schleicher & Schüll ME25) placed in a polycarbonate filterholder with a silicon sealing-ring. The first ml of the filtrate was discarded. The rest of the filtrate was acidified to 0.1% (v/v) HNO_3 and its total Cu content measured by either flame or electrothermal atomic absorption spectrometry.

Determination of minimum equilibration times

Experiments to determine minimum equilibration times (MET) were performed at pH 6 with the three ion exchange resins described in Table 1. The procedure above was modified as follows: (a) concentration of the resin, C_R, was either 20 or 100 mg in 50 g solution; (b) equilibration time was 48 h; (c) aliquots of 2 ml of the solution were periodically sampled for analysis without filtration; (d) apart from Li^+, K^+ was used as counterion G^+.

RESULTS AND DISCUSSION

Minimum equilibration times

The time needed to reach a constant total metal concentration in solution (minimum equilibration time, MET) is a prerequisite for the application of the EIM. The influence of different experimental conditions on the MET for Cu(II) adsorption to three ion exchange resins at pH 6 and low ionic strength ($I = 0.01$ mol/kg) is shown in Table 2.

The experiments without organic ligand are discussed first. The longest MET of up to 48 h were found for the resin BioRex MSZ50, a macroporous resin with large grains, narrow size distribution and large exchange capacity (Table 1). In contrast to this result, many researchers report MET of 1–3 h for experiments with resins that have characteristics similar to the BioRex MSZ 50.[2,4,5,10,13,27] The shortest MET of less than 2 h were observed for the film-exchanger Vydac 401SC with very small grains, narrow size distribution and small capacity. The MET for Serdolit CS2, a macroporous resin with small grains, wide size distribution and large capacity, were in between. The comparison of the results for the different resins shows an increase of MET with increasing grain size and a much shorter MET for the film-exchanger than for the two macroporous resins. This is consistent with diffusion as the rate-controlling process of ion exchange.[25]

Table 2. Exchange kinetic of Cu(II) at different cation exchange resins (pH 6, $I = 0.01$ mol/kg, stirring rate ≈ 300 r.p.m.)

Resin	G^{+}*	$C_R = 0.4$† without ligand	$C_R = 2$† without ligand	$C_R = 2$† with CLLE‡
		minimum equilibration time (MET) (hr)		
Serdolit CS 2	K^+	24–(≥48)	4–24	
	Li^+	7–24	5–6	24
BioRex MSZ 50	K^+	≥48	≥48	
	Li^+	24–(≥48)	24	
Vydac 401SC	K^+	<2	<2	
	Li^+	<2	<2	24

*Counterion.

†Concentration of the resin in the solution, g resin/(kg solution).

‡CLLE: Chestnut leaf litter extract.

For the two macroporous resins, influence of the resin concentration, C_R, and the type of the counterion G^+ on the MET was observed (Table 2). Shorter MET for higher resin concentrations can be understood on the basis of diffusion.[25] The influence of the type of G^+, shown for K^+ and Li^+, is probably due to the low ionic strength conditions: at the beginning of the exchange process, [Cu] is not much smaller than [G]. For $[Cu] \ll [G]$, the exchange rate should depend on the mobility of Cu^{2+} only, according to the minority rule deduced from the Nernst–Planck equation.[26] The MET in the experiments with Li^+ are shorter than with K^+, suggesting that the mobility of the counterion in the resin macropores is governed by the radius of the nonhydrated ion. This result is in good accordance with earlier investigations on alkaliion mobility in highly crosslinked resins.[25]

The discrepancy between the results with the BioRex MSZ50 in this study and results with similar resins in earlier studies (see above) can be explained by different experimental conditions. Both the resin concentration ($C_R = 8$–20 g/kg) and the ionic strength ($I = 0.1$–$1M$) were much higher in the previous studies[2,4,5,10,13,27] than in this work (Table 2). The influence of C_R on MET was experimentally shown in this research (see above). Longer MET at lower ionic strength can theoretically be explained for macroporous resins as follows. The ratio $(Cu)_R/[Cu]$ for a given [Cu] increases with decreasing ionic strength. Thus, less accessible sites in the macropores become involved in the ion exchange, diffusion paths are longer and ion mobility is reduced.

The influence of DOM in a chestnut leaf litter extract (LLE) on the MET for Cu(II) adsorption was studied in further experiments with the film-exchanger Vydac 401SC and the macroporous resin Serdolit CS2. In the presence of LLE (DOC = 26 mg/kg), with Li^+ as counterion and at a resin concentration $C_R = 2$ g/kg, the MET was 24 h for both resins, an increase by a factor four and 12, respectively, when compared to the results in the absence of LLE. This finding can be interpreted as follows. Immediately after the addition of the LLE, fast reaction of Cu(II) with the ligands in the extract leads to high complex concentrations corresponding to the degree to which the ion exchange equilibrium has been established. The relatively slow establishment of the ion exchange equilibrium thereafter can be either reaction or diffusion controlled.[26] This means that the rate-controlling step is either the dissociation of the Cu(II)–LLE complexes or their diffusion into the resin pores. The difficulty of fulvic acid complex penetration into resin pores is discussed by Buffle.[20] The result of this study, however, *i.e.* the same MET for the macroporous resin and the film-exchanger, suggests slow dissociation of Cu(II) complexes with macromolecules in the LLE as the rate-controlling process.

Reference isotherms Cu(II)–*Serdolit CS2 and validation of the EIM*

The procedure for recording reference isotherms and sample isotherms, as described in the Experimental section, was based on the results presented in the previous chapter. The advantage of using the macroporous resin Serdolit CS2 instead of the film-exchanger Vydac 401SC is the larger exchange capacity of the Serdolit CS2.

The reference isotherms for Cu(II) adsorption to Serdolit CS2 at pH 4, 5 and 6 were the same within experimental error. The data for the three pH-values were, therefore, combined for mathematical analysis (Table 3). The shape of the combined reference isotherm is nonlinear

Table 3. Reference isotherm Cu(II)–Serdolit CS 2, pH 4–6

$(\mathrm{Cu})_\mathrm{R}$ (*mol/kg*)	$[\mathrm{Cu}]_\mathrm{f}$ (*μmol/kg*) Measured ± *s**	Calculated (see text)
0.0079	0.039 ± 0.011	0.021
0.039	0.14 ± 0.02	0.11
0.079	0.21 ± 0.07	0.22
0.158	0.50 ± 0.02	0.48
0.237	0.79 ± 0.04	0.78
0.315	1.19 ± 0.06	1.13
0.394	1.46 ± 0.16	1.55
0.473	2.57 ± 0.37	2.08
0.630	3.43 ± 0.20	3.59
0.788	5.77 ± 0.28	6.45

*Mean and standard deviation for two to five measurements.

(Fig. 2), generally of the L-type[21] and, therefore, can be described by the Langmuir equation (equation 4). The Langmuir adsorption parameters, ${}^{c}K_{\mathrm{RM}}$ and R_t, were determined by linear regression analysis of the linear part of the plot ${}^{c}D_\mathrm{M}$ *vs.* $(\mathrm{Cu})_\mathrm{R}$ (Fig. 3), which is a sensitive representation of the adsorption isotherm (Fig. 2).

Free Cu concentrations calculated with these parameters were compared with the experimental values (Table 3). The difference between the measured and calculated $[\mathrm{Cu}]_\mathrm{f}$ at very low $[\mathrm{Cu}]_\mathrm{sol}$ is indicative of a departure from the Langmuir-type adsorption behavior. This departure is clearly seen in the plot of ${}^{c}D_\mathrm{M}$ *vs.* $(\mathrm{Cu})_\mathrm{R}$ (Fig. 3). The two data points at the lowest Cu concentrations are not lying on the line obtained by fitting of the other data points. Because of the departure from the Langmuir-type adsorption behavior, the adsorption isotherm (Fig. 2) can be described as an S-type[21] in the range of low $[\mathrm{Cu}]_\mathrm{f}$. The S-shape can be caused by the presence of Cu(II) ligands in low concentration. Most likely these ligands are dissolved organic substances washed out of the ion exchange resin. A similar explanation was given for S-type adsorption of Cu(II) by soils.[21] With this assumption, the measured isotherm represents the sum of the free Cu concentration, $[\mathrm{Cu}]_\mathrm{f}$, and the concentration of Cu bound by resin-derived organic ligands (ROL), [CuROL]. The influence of the ROL was estimated by fitting the S-shaped isotherm under the assumption of competition between Cu(II) adsorption to the ion exchange resin characterized by Langmuir adsorption parameters, and formation of a 1:1 Cu(II) complex with the ROL characterized by a stability constant ${}^{c}K_{\mathrm{ROL}}$ and a binding capacity ROL_t. A good fit was obtained with $\log {}^{c}K_{\mathrm{ROL}} = 8$ and $\mathrm{ROL}_\mathrm{t} = 3 \times 10^{-8}$ mol/kg and the same values for ${}^{c}K_{\mathrm{RM}}$ and R_t, as they were derived from the plot ${}^{c}D_\mathrm{M}$ *vs.* $(\mathrm{Cu})_\mathrm{R}$ (Fig. 3) without considering ROL.

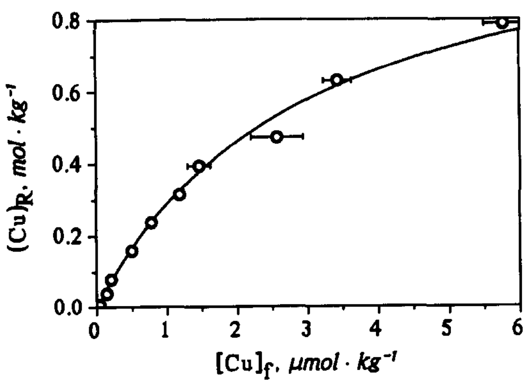

Fig. 2. Reference isotherm Cu(II)—Serdolit CS 2, pH 4–6. The measured values as well as an isotherm calculated with the parameters obtained from the linear part of the plot ${}^{c}D_\mathrm{M}$ *vs.* $(\mathrm{Cu})_\mathrm{R}$ (Fig. 3) are shown.

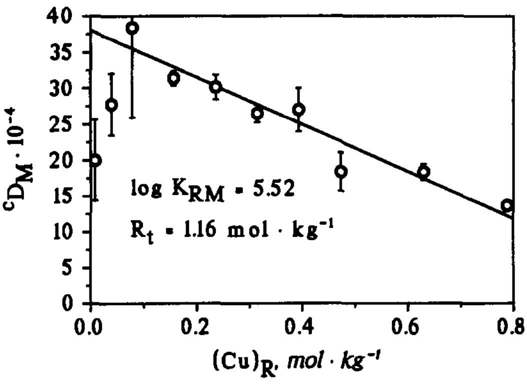

Fig. 3. Reference isotherm Cu(II)–Serdolit CS 2, pH 4–6; plot of the distribution coefficient ${}^{c}D_\mathrm{M}$ *vs.* $(\mathrm{Cu})_\mathrm{R}$; errors were obtained by propagation of the error for $[\mathrm{Cu}]_\mathrm{f}$ (Table 3); the adsorption parameters determined by linear regression of the data for $(\mathrm{Cu})_\mathrm{R} \geqslant 0.079$ mol/kg are indicated.

It can be concluded that the influence of ROL is small. For the characterization of the reference isotherm, the existence of these organic substances can be neglected. When recording sample isotherms, however, small $[\mathrm{Cu}]_\mathrm{b}$ have to be corrected for [CuROL].

The EIM using nonlinear reference isotherms was validated by recording sample isotherms with oxalate (Ox) as ligand at pH 4, 5 and 6. Stability constants for the complexes CuOx and CuOx_2 were determined by nonlinear regression analysis of the isotherms, $(\mathrm{Cu})_\mathrm{R}$ *vs.* $[\mathrm{Cu}]_\mathrm{sol}$. Side-reaction coefficients for the reaction of Cu(II) with OH^{-}[28] and NO_3^{-},[29] and for the protonation of the ligand[29] were incorporated in the analysis. The values obtained at three pH-values

Table 4. Cu(II) complexation by oxalate at $I = 0.01$ mol/kg: conditional stability constants for the complexes CuOx and $CuOx_2$

	Equilibrium ion exchange (this work)			Potentiometry, polarography[29]	
	pH 4	pH 5	pH 6	$I = 0$	$I = 0.01$*
log K_{CuOx}	6.19	6.15	6.11	6.23	5.87
log K_{CuOx_2}	10.38	10.44	10.02	10.27	9.91

*By transformation of the '$I = 0$' values,[29] using activity coefficients calculated with the Davies equation.

agreed well with those from the literature (Table 4).

Cu(II) *complexation by DOM in an aqueous chestnut leaf litter extract*

The complexation of Cu(II) by the chestnut LLE was studied in the pH-range 4–6 under conditions likely to be found in soil solutions. The ligand concentration in the extract was 26 mg DOC/kg. The range of $[Cu]_f$ from 0.02 to 6 μmol/kg, well characterized by the reference isotherm (Fig. 2), corresponded to total concentrations in solution, $[Cu]_{sol}$, from 0.24 to 9.9 μmol/kg at pH 4, from 0.68 to 17 μmol/kg at pH 5, and from 3.6 to 69 μmol/kg at pH 6.

All plots of $[Cu]_b/[Cu]_f$ *vs.* $[Cu]_b$ were nonlinear (Fig. 4). They were modeled by nonlinear regression analysis with conditional stability constants, ^cK, and binding capacities, L_t, for two 1:1 quasiparticle complexes, Cu(L1) and Cu(L2) (Table 5). At all pH-values the more stable quasiparticle complex, Cu(L1), had a log $^cK \approx 8$. The corresponding class of binding sites provided 4–5% of the total measured binding capacity. For the less stable quasiparticle complex, Cu(L2), log $^cK \approx 5.5$ was found at pH 4 and 5 and log $^cK \approx 6$ was obtained at pH 6. The corresponding class of binding sites represented the major part of the total measured binding capacity.

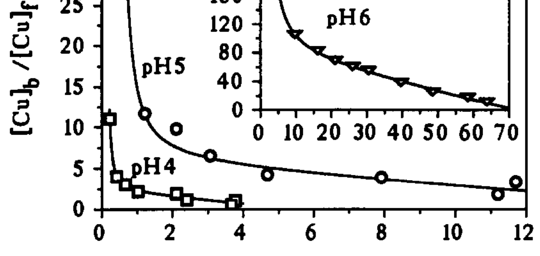

Fig. 4. Cu(II) complexation by DOM in a chestnut leaf litter extract, pH 4–6; the experimental values and their fit with the model parameters as shown in Table 5 are given.

The conditional stability constant and the binding capacity at pH 6 for the less stable quasiparticle complex, Cu(L2), agreed well with binding parameters (log $^cK = 5.8$, $L_t = 2.5$ mol/(kg C) found for the chestnut LLE by a bioassay.[30]

The dramatic increase of the binding capacities for the two binding site classes with pH by more than one order of magnitude (Table 5) can be explained by conformation changes of macromolecules leading to better accessibility of potential binding sites.[31]

The conditional binding parameters can be discussed in terms of molecular structure. This approach, however, has to be considered with reservation because the binding parameters were determined as interdependent fitting parameters in a nonlinear regression analysis. Considering magnitude and pH-dependence of the conditional stability constants, quasiparticle complex Cu(L1) is best compared with Cu(II) complexes of long-chain saturated aliphatic amino acids like lysine[29] and quasiparticle complex Cu(L2) with Cu(II) complexes of saturated aliphatic carboxylic acids like oxalic acid.[29] The ratio between the Cu binding capacities of the strongly complexing binding site and the weaker binding site was about 1:20 at pH 6. This ratio is similar to the ratio between the N content of the chestnut LLE of 0.7 mol/(kg C) and its carboxylate content of 10 mol/(kg C).[23] This comparison supports the assignments of

Table 5. Cu(II) complexation by DOM in a chestnut leaf litter extract at $I = 0.01$ mol/kg; conditional binding parameters determined by the EIM

	Quasiparticle complex Cu(L1)		Quasiparticle complex Cu(L2)	
pH	log ^cK	L_t [*mol/(kg C)*]	log ^cK	L_t [*mol/(kg C)*]
4	8.35	0.0084	5.59	0.21
5	8.34	0.026	5.49	0.69
6	8.19	0.132	6.06	2.72

the stability constants to different classes of organic ligands made above.

CONCLUSIONS

Investigation of the EIM for Cu(II) at low ionic strength (0.01 mol/kg) leads to the following conclusions: in the presence of DOM, a minimum equilibration time of 24 h is required. Nonlinear reference isotherms can be used over a wide range of Cu concentrations in the resin, when mathematically modeled in terms of Langmuir adsorption parameters. A restriction to the quasilinear part is not necessary. Using nonlinear reference isotherms and mathematical analysis of plots $[Cu]_b/[Cu]_f$ *vs.* $[Cu]_b$, the Cu(II) complexation behavior of DOM in aqueous leaf litter extracts between pH 4 and 6 and at low ionic strength can quantitatively be characterized in terms of conditional stability constants and binding capacities over a wide range of Cu/ligand ratios. A separate determination or estimation of the total binding capacity by another method is not necessary.

The new approach of using nonlinear reference isotherms and analyzing the sample isotherms in terms of free and bound metal concentrations makes the EIM a versatile method for the investigation of metal ion complexation reactions with mixtures of natural organic ligands. The classical and the new approach to the EIM, however, have the same limitation that specific interactions between the DOM and the resin cannot be taken into account and, therefore, can lead to erroneous results.

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