Reviews

Approaches to the study and description of metal cation binding on functional fragments of high-molecular weight substances in aqueous systems

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The main approaches to the study and description of equilibria of metal cation and proton binding by a high-molecular weight substance in aqueous systems were analyzed in the case of scarce information on binding sites. Almost all the approaches have substantial disadvantages, especially from the viewpoint of model verification, informativeness, and opportunities of meaningful interpretations of the results obtained. A specific approach to a combined estimation of both binding constants and concentrations of binding sites was recommended. This approach uses experimental data only on the degree of complex formation and makes it possible to enhance significantly the informativeness of research of the state of heavy metals and a high-molecular weight organic substance interacting with the heavy metals in natural waters.

Key words: metals, high-molecular weight substance, functional fragment, natural waters, equilibrium, effective constant.

A key problem of chemistry is the quantitative description of the state of a substance in aqueous systems. In particular, in the recent years many researchers often considered the detailed description of the so-called heavy metals (HM) in natural and technogenic aqueous systems, *i.e.*, identification and complex characterization of specific *chemical species*,[1] whose formation involves HM.[2—4] These studies are carried out in the framework of the solution of problems of environmental chemistry and/or chemical ecology. It is known that the most part of HM are transition (Hg, Cd, Cu, *etc.*) and p-metals (Pb, Sn, Bi, and others). Such a description for these metal ions is based on the theory and methods of studying stepwise complex formation.[5—9] At the same time, many aqueous systems (natural, technogenic, and technological) are multicomponent and contain, as a rule, both inorganic and organic (predominantly, high-molecular weight) substances. In addition, when analyzing HM dis-

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tributions over chemical species, one should take into account the presence of both the "solute" part in the investigated waters (therefore, the species in the solution composition, including colloidal species if necessary) and the suspended part of the substance (*i.e.*, species adsorbed and/or composing the suspended substance). In both cases, natural organic high-molecular weight substances are presently most poorly studied regarding their ability to bind HM ions. For these substances, often it is even impossible to distinguish distinctly the highly dispersed state (including colloid), surface phase state, or specific macromolecularly associated (but not colloidal) state in solution. However, in aqueous systems these are precisely the interactions between dissolved and suspended organic substances (DOS and SOS, respectively) that often play the key role in migration, bioaccessibility, toxicity, and other characteristics of HM.[10,11] At the same time, since both DOS and SOS themselves and their possible states are complex and diverse, it is often impossible to characterize these components even at a level of molar concentrations of binding sites, to say nothing of the modes of HM ion binding. Here it seems appropriate to mention that the term *binding site* can reasonably be related to such terms as *functional fragment* or *acceptor*. In the latter case, we only extend somewhat the idea of proton acceptors, which is already used in chemical literature. In the general case, the functional fragment playing the role of an acceptor of H^+ or M^{z+} can possess this function due to one or several electron-donor centers in its composition, as well as for other reasons. For instance, the pronounced specificity of alkaline and/or alkaline-earth metal cation binding to form complexes with organic substances of a certain type in solutions due to inclusion phenomena has been known long ago.[12] Similar binding types can be expected for microfragment ensembles in the composition of high-molecular weight substances in aqueous systems, and they manifest this binding types toward alkaline and alkaline-earth metals and also toward transition and p-metals. That is why, we use a broader term *functional fragment* in the specific context instead of the known concept of *functional group*.

The classical procedures of studying complex formation become inappropriate when information on the nature and concentration of binding sites is scarce or even absent. In the present world-wide research practice, two main routes of surmounting this obstacle can be emphasized. First, this is the very labor-consuming characterization of both natural binding components and their different synthetic analogs by a complex of methods. Nevertheless, even these results do not always provide reliable and sufficient information appropriate for the subsequent study of binding (in particular, of transition metal ions) on the beforehand comprehensively characterized high-molecular weight organic substances containing certain sets of functional groups. Second, this is a modification of the classical procedures of studying the complex formation of HM ions to describe their binding by acceptors of the unknown nature and concentration at any appropriate informative level using some restricted information on the state of these HM ions (for example, on *degrees of complex formation* $\Phi = C_M/[M^{z+}] = f(C_M)$, where C_M is the overall metal concentration, and $[M^{z+}]$ is the equilibrium concentration of the corresponding cation).[7] This description involves partially the characterization of macroensembles of functional fragments responsible for binding. Here the main attention is given to the experimental finding and mathematical analysis of different *auxiliary functions*,[5,7,9,13] whose parametrizations are consequences of transforms of equations of the laws of mass action and material balance taking into account restraints purposefully specified by the choice of the model and a complex of initial boundary conditions. Many researchers combine these two directions to this or another extent. In our opinion, the second method has several evident advantages over the first method. First, it allows one to obtain fruitful quantitative information escaping labor-consuming and artificial procedures for the independent characterization of unknown DOS and SOS. Second, this method makes it possible to study HM binding *in situ*, *i.e.*, directly in samples of natural waters without isolation and, as a consequence, without substantial distortions of the states of organic substances responsible for the desired characteristics. Naturally, since investigated objects are complex and uncertain, any method organizing research of this type increases sharply the role of analysis whether the proposed model is adequate to the whole experimental situation or not. This analysis includes both consequences from the error model and independent additional knowledge about this or similar systems. The role of the active approach to choosing procedures and complexes of conditions providing such possibilities is also substantial. Therefore, models for the description of the interaction of a high-molecular weight substance with HM ions in complex aqueous systems (which are often artificial, including technological ones, systems along with natural systems) should be, first, as simple as possible (*i.e.*, they should assume verification at the stage of checking adequacy) and, second, rather efficient and informal (in other words, appropriate for the description of a possibly wide class of systems, corresponding to the main statements of physical chemistry, and containing an informative sense of the used parameters, which can reproducibly be related to certain sets of initial boundary conditions). Emphasizing these aspects, we will examine approaches and models available presently from the world-wide research practice for the description of the interaction of a high-molecular weight substance with metal cations (M^{z+}) and protons (H^+) in aqueous systems.

Place and the subservient role of auxiliary functions in studies of the considered class

In terms of the modern approaches to the study of complex formation in solutions for determining the desired parameters (stoichiometry of chemical species, equilibrium constants), various auxiliary functions are widely used.[5,7,9,13] In some foreign sources,[6,8] they are named introduced functions or secondary concentration variables (unlike the primary variables C_X and [X], where C_X is the overall concentration of the X fragments, and [X] is the equilibrium concentration of the solvated X fragments). The main auxiliary functions have standard forms (especially at low amounts of the desired species and respective equilibrium constants) and have been described in detail to date.[5–9] These functions are informative at all stages of investigation. At first they are used to check a hypothesis on the number and stoichiometry of species of the *studied system*,[1,7,14] the absence of significant systematic errors, the presence of required equilibria, and the absence of a contribution from side processes to the material balance of the system and measured property. Then they are used to calculate the desired meaningful parameters of auxiliary functions. At the final stage, the experimental and calculated (from the determined constants) functions are compared and, correspondingly, one of the variants of the model is chosen using statistical goodness-of-fit tests.[13] It is shown[7,13,14] that the construction and use of nonclassical auxiliary functions are possible and fruitful for more complex systems (*e.g.*, for the formation of heteroligand complexes) or more complicated detailed composition—property interrelations, or when experimental data on the system are scarce.

Naturally, the above traditions affected the studies on the simulation of phenomena of cation binding by high-molecular weight substances. Therefore, when analyzing the corresponding works, we will give the main attention to problems of the meaning and informativeness of the auxiliary functions used by the authors by comparing them with classical examples.[5–9] Of course, the works cited in our review contain those oriented to the rejection of the use of auxiliary functions. We have already attempted[13] to analyze illusory concepts on the universal character of such procedures even in rather simple situations (for low-molecular weight substances). In this case, we are intending to apply the same principles. Naturally, the quantitative characterization of cation binding becomes much more difficult when independent information on concentrations of binding sites is lacking and that on the number of discernible types of these sites and their nature is scarce. This situation requires new nontrivial developments in respect of both informal aspects and formalizations.

We believe that the routes for enhancing informativeness can be elucidated by the above-proposed analysis of the approaches that already exist in the world to the simulation and quantitative characterization of phenomena of H^+ and M^{z+} cation binding on DOS and SOS (which are high-molecular weight substances, as a rule) in aqueous systems.

Main models and methods for the description and study of cation binding on acceptors composing a high-molecular weight substance

Electrostatic models were historically among the first models for the quantitative description of cation states in solutions of high-molecular weight substances, *i.e.*, models of H^+ or M^{z+} cation binding on these or other functional fragments (A*, L*). In particular, for acid-base equilibria involving the so-called polyelectrolytes, these models were developed already in the 1940—50s.[15–17] The key ideas are the concepts on the constant (K_a) and degree of dissociation (α_{dis}). In the previous section we presented reasons for which the aforementioned and other models will be considered in the context of their resemblance and difference with classical formalizations, which are accepted in the area of description of the stepwise dissociation of polybasic acids and stepwise complex formation on metal ions, *i.e.*, processes involving low-molecular weight chemical species. The equations describing the equilibrium, laws of mass action and material balance, and degree of dissociation in the case of monobasic acid (low-molecular weight substance) have the form

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-, \qquad (1)$$

$$K_a = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}], \qquad (2)$$

$$C_A = [\mathrm{A}^-] + [\mathrm{HA}], \qquad (3)$$

$$\alpha_{dis} = [\mathrm{A}^-]/C_A = [\mathrm{A}^-]/([\mathrm{A}^-] + [\mathrm{HA}]), \qquad (4)$$

where $[\mathrm{H}^+]$, $[\mathrm{A}^-]$, [HA], and C_A are the equilibrium and total (analytical) molar concentrations of the corresponding components. Naturally, to estimate the K_a value in this simple case, one of the auxiliary functions can be used. The following form is often used in this area of research:

$$\mathrm{pH} = \mathrm{p}K_a + \log[\alpha_{dis}/(1 - \alpha_{dis})]. \qquad (5)$$

Using this equation, K_a is determined from the experimental plots $\alpha_{dis} = f(\mathrm{pH})$. We will also use equilibrium constants of formation that are inverse to values of the K_a type for convenience of applying developments from the area of stepwise complex formation. In these cases, α_{dis} can be replaced by the fraction (α) of the A-type sites occupied by protons (or ligands L in the case of their stepwise binding with M). For the one-step process, inverse to that described by Eq. (1), we have

$$\alpha = [\mathrm{HA}]/C_A.$$

Let us introduce the discrete α' value as the degree of filling of sites accessible for binding in a particular species of the empirical component A, and in the above-considered case α' can take only two values: 0 (in A^-) and 1 (in HA). For some several (n) steps of H^+ binding, for example, by the anionic acid residue A^{n-}, we obtain a set of the corresponding expressions of the law of mass action for equilibria of the type

$$H_{i-1}A + H^+ \rightleftharpoons H_iA, \tag{6}$$
$$K_i = [H_iA]/([H_{i-1}A] \cdot [H^+]),$$

$i = 1—n$.

Information on charges of component species (including those in the so-called electrostatic models) is demanded only to interpret more deeply the empirically observed effects (changes in constants and other parameters of the model) from the viewpoint of the microlevel. Therefore, here we do not present charges on all species, except protons, for simplicity, although we remember that they exist and the reactions should be equalized by charge as well. The fraction of sites occupied by protons for system (6) is determined by the inequality

$$\alpha = \sum_{i=0}^{i=n}(i \cdot [H_iA])/(n \cdot C_A). \tag{7}$$

It is obvious that

$$\alpha = \sum_{i=0}^{i=n}[(i/n) \cdot \alpha_i],$$

where α_i is a magnitude that is known as the fraction of the ith species in the description of stepwise protonation or complex formation. Naturally, the discrete α' value for a given n depends only on i, and, *e.g.*, at $n = 2$ for three subsets of the species set containing A^{2-} (A^{2-}, HA^-, H_2A), and, hence, it equals 0, 0.5, and 1. In the general case, there are $n + 1$ values that are equal to i/n for i from 0 to n, which can be reflected by the formula

$$\alpha'_i = i/n.$$

For equilibria of the type (6) at A = M and H = L, K_i (constants of steps) often differ from each other only in the statistical factor value (isocharge substitution[5,7b])

$$f_i = [n - (i - 1)]/i,$$

similarly to that considered by Bjerrum[5] as the universal form for taking into account changes in the ratio of the occupied sites to free sites in the first coordination sphere for stepwise complex formation. As known, this situation is also possible for stepwise protonation with the same piecemeal proton-accepting fragments of the polybasic acid residue, when they are considerably remote inside the corresponding molecule. This type of protonation was the first to be considered in the world scientific literature, and only later the same concept was applied to analysis of stepwise complex formation phenomena. Thus, an idea appears of the *average constant*[5] (K) of binding species of the type H^+ (or L) on A^{n-} (or M)

$$K_i = f_i \cdot K = \{[n - (i - 1)]/i\} \cdot K.$$

For stepwise protonation at any regularity of K_i changing along the i series from 1 to n, one can introduce a more general concept about the *effective equilibrium constant* (K^*) of *piecemeal binding* of protons on ensembles of accepting A* sites ($C_{A^*} = n \cdot C_A$)

$$H^+ + A^* \rightleftharpoons HA^*. \tag{8}$$

Then from Eqs (6) and (7), we formally obtain an analog of expression (5)

$$pH = \log K^* - \log[\alpha/(1 - \alpha)], \tag{9}$$

but the $\log K^*$ value for the majority of particular systems will be any specific locally restricted function of α (pH). If the ratio of the K_i values is determined only by the statistical factor, then, taking into account that

$$K \cdot [H^+] = \{i/[n - (i - 1)]\} \cdot [H_iA]/[H_{i-1}A] \tag{10}$$

for each i, we find $K^* = K$. Therefore, it is impossible to distinguish the n-step binding from the objectively one-step binding by the experimental pH-metric study of these systems in the absence of independent information on the C_A (C_{A^*}) value and the nature of A (A*).[5] It should be emphasized that α, α'_i, and α_i differ in both content and magnitude, and α is only some empirically determined $((C_H - [H^+])/C_{A^*})$ characteristic of the state of the whole macroensemble of H_iA species. At the same time, to interpret empirically the observed dependences of the $\log K^* = f(pH, \alpha)$ type at the microlevel, for example, from the viewpoint of Coulomb interactions of occupied and free sites in H_iA, α'_i (fractions of occupied sites in particular acid residues, *i.e.*, in H_iA) and α_i can become necessary. In the cases when n are high, the α value is often implicitly equalized to some α'_i from the set, assuming, most likely, that the corresponding species prevails among all other species. In the framework of the model considered (only statistical factors are responsible for differences in K_i), the correspondence between α and α'_i of the species predominant in the material balance of the system at specified α can easily be found. The result shows no simple correspondence between α and the level of prevailing of the set of species with i in the vicinity of $\alpha \cdot n$ either for high n.

An approach similar to that reflected by Eq. (9) can be used, which is usually done, to describe the state of high-molecular weight components (in particular, polyelectrolytes) and when the substance binding the cations considered forms a separate phase; in other words, for the description of sorption from solution or ion-exchange equilibria. In the latter cases, the specific content of the law of mass action differs from the traditional sense (for low-molecular weight substances), although constants of the corresponding equilibria are determined by the formally similar equations

$$K^* = \alpha_{\mathrm{occ}}/\{(1 - \alpha_{\mathrm{occ}}) \cdot [\mathrm{M}^{z+}]\}, \qquad (11)$$

where α_{occ} is the fraction of occupied sites (on the surface or in the bulk of the sorbent and "globules" of a polyelectrolyte or high-molecular weight substance).

The following reaction equations are often put in correspondence with these equilibria:

$$\mathrm{H}^{+}{}_{\mathrm{solv}}\ (\text{or } \mathrm{M}^{z+}{}_{\mathrm{solv}}) + \overline{\mathrm{A}^*} \rightleftharpoons \overline{\mathrm{HA}^*}\ (\text{or } \overline{\mathrm{MA}^*}), \qquad (12)$$

where $\mathrm{H}^{+}{}_{\mathrm{solv}}$ (or $\mathrm{M}^{z+}{}_{\mathrm{solv}}$) are protons (or metal ions) in the solution bulk, and $\overline{\mathrm{A}^*}$ and $\overline{\mathrm{HA}^*}$ (or $\overline{\mathrm{MA}^*}$) are free and occupied binding sites (fragments of the A* type) in the composition of the ion-exchange resin, macromolecule, or macromolecular ensemble that withdraws protons (or metal ions). Therefore, α_{occ} concerns the fraction of occupied A* fragments, whose total amounts are usually normed to the unit of surface (adsorption), weight (sorption), weight or volume (adsorption), or to the statistical average molecule or globule (for high-molecular weight substances). However, these amounts can also be normed to the unit volume of a solution containing a certain amount of the considered sorbent or high-molecular weight substance, which was introduced or present in the solution due to the pre-history of the discussed samples of natural waters, regardless of its final (but reproducible!) state (true solution, globules, colloidal or suspended species, or a simply vigorously stirred precipitate). In addition, the term *binding* designates in this context, in fact, objectively complex (and often different) arrays of real transformations involving solvent molecules and ions that form the medium. All these facts require special attention to sets of the initial and boundary conditions for the investigated systems to provide their reproducibility and satisfactorily unchanged K^* values or such changes in K^* with the α_{occ} increase that can be identified and described in meaningful terms (see, *e.g.*, Ref. 18).

In the case of polyelectrolytes (and any high-molecular weight compounds), many researchers long since implicitly considered functional groups or, in the general case, functional fragments of the same chemical nature as an analog of some *detailed component*[1] A*. Unfortunately, the corresponding studies contain no analysis for this consideration at least at the level presented above, *i.e.*, in the terms of α, α_i, α'_i, α_{occ}, K_i, K, f_i, and K^*.

It should be emphasized that the specific content of an idea of the functional fragment of a high-molecular weight substance designed by A* is not identical to either the concept on the set of low-molecular weight acid residues $\mathrm{H}_i\mathrm{A}$, or the concept of the A* fragment in the composition of a molecule of acid residues of a low-molecular weight polybasic acid, although dependences of the $\alpha = f(\mathrm{pH})$ type are formally described in the same terms. For instance, the known[17] semiempirical equation

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + k \cdot \log[\alpha_{\mathrm{dis}}/(1 - \alpha_{\mathrm{dis}})] \qquad (13)$$

is rather popular for polyelectrolytes. However, it cannot be compared to Eqs (5) and (9) for low-molecular weight analogs ($\mathrm{H}_i\mathrm{A}$) in the terms of the model described by Eqs (8)—(10) for the only reason: the fitting parameter k differs from 1. The latter was usually attributed to the electrostatic effect. However, it seems evident that the whole sum of factors having a significant effect on K_i is responsible for the difference of k from 1. For this reason, most likely, the development and improvement of electrostatic models for the description of acid-base properties of macromolecules (polyelectrolytes) were reduced mainly to more detailed interpretations of the $\alpha_{\mathrm{dis}} = f(\mathrm{pH}$, ionic medium) dependences when the set of empirically estimated parameters included those, whose meaning is close to the microlevel (see, *e.g.*, Refs 19 and 20)

$$\alpha_{\mathrm{dis}} = f(\mathrm{pH}, I\{\overline{K_{\mathrm{a}i}}, R, n\}), \qquad (14)$$

where I is the ionic strength of the solution, $\overline{K_{\mathrm{a}i}}$ is some restricted set of dissociation constants $K_{\mathrm{a}i}$ (for functional groups of the ith type), R is the radius of the sphere corresponding to a particular (statistical average) macromolecule), and n is the number of functional groups in the macromolecule. Model (14) has earlier[19] been applied to the description of acid-base equilibria of river fulvic acids. The following model was found for the latter: macromolecules with the average molecular weight $M \approx 1000$ Da, $n = 6$, and $R = 6.4$ Å. Only three types of functional groups were distinguished and characterized: $\mathrm{p}K_{\mathrm{a}1} = 2.4\pm0.1$, $\mathrm{p}K_{\mathrm{a}2} = 3.6\pm0.1$, and $\mathrm{p}K_{\mathrm{a}3} = 5.6\pm0.1$ (25 °C and $I = 0.1$ mol L^{-1}).

In the domestic scientific practice, electrostatic models are also used mainly for treating semiempirical dependences, such as (13), or other variants of parametrization of empirical relations $\alpha_{\mathrm{dis}} = f(\mathrm{pH}$, ionic medium). For example, the acid properties of phosphate cation-exchange resins are described[21] by the model of equilibria of dissociation of a polyelectrolyte with two types of functional groups according to Eq. (13), although the interaction with the Sc^{3+} cations was further presented as standard complex formation. The authors of Ref. 22 described acid-base equilibria involving silica-grafted amine functional groups of oligoethyleneamines by equations of the (9) and (11) type with additional fitting coefficients for the formal regression description of logK^* as a function of I and α_{occ}. Evidently, the presented[22] a_{ij} coefficients

$$\log K^* = a_{00} + a_{10}\cdot\alpha_{\text{occ}} + a_{01}\cdot\sqrt{I} + a_{11}\cdot\sqrt{I}\cdot\alpha_{\text{occ}} + a_{20}\cdot\alpha_{\text{occ}}^2 + a_{21}\cdot\sqrt{I}\cdot\alpha_{\text{occ}}^2 \quad (15)$$

are fitting only formally and quite inappropriate for informal interpretations. In addition, according to the presented estimates of the a_{ij} coefficients, some of them are statistical nulls (for instance, for tetraethylenepentamine $a_{11} = 7.7\pm6.2$, $a_{21} = -7.2\pm6.1$, and $a_{20} = 5.1\pm3.7$ at room temperature). Thus, the authors baselessly used the extended set of fitting parameters, although their number should be restricted in the case, excluding statistical nulls and attaining the residual dispersion values at a level estimated by the independent error model.[23]

Evidently, even for a successful selection of parameters of the models described by Eqs (13)—(15) and others, *i.e.*, for the adequate description of each particular experiment, the further extension of these parameters to other objects or even other states of the same objects (the nature and concentration of macromolecules and cations, acidity, ionic medium, temperature) requires additional substantiations, which are not presented, as a rule, and, probably, do not exist at all.

In our opinion, the most reasonable approach to the description and study of the binding of low-molecular weight components (H^+ and M^{z+} ions) by macromolecules in solution is the *conventional* representation of macroensembles of functional groups and, in the general case, functional fragments of the same type as some *detailed component*.[1] The functional fragment of the same type is considered to be any of *piecemeal binding sites* of the H^+ or M^{z+} ions, whose macroensemble is characterized by certain binding constant. Of course, this does not exclude, in the general case, some regular (quantitatively parametrizable) variability of concentration constants of this type (*i.e.*, effective constants) at different total concentrations of a high-molecular weight substance and degrees of filling of the corresponding macroensemble of fragments with the H^+ and/or M^{z+} ions, if this variability can empirically be revealed and informally interpreted when sufficient information is accumulated. Of course, the term *binding* should not be treated literally. That is why, perhaps, *proton acceptors* rather than *binders* are often discussed. In fact, a much more complicated phenomenon is always implied, which involves both solvent molecules and ions of the supporting electrolyte, and the binding of the cations considered (for instance, M^{z+}) can be the substitution of protons or any other cations saturating the investigated array of *acceptors* under the conditions of the so-called constant medium (including constant pH, *etc.*). Naturally, the functional fragment can be both a certain functional group or any their combination and some fragment in the composition of a macromolecule of a specific macromolecular associate capable of binding due to the inclusion phenomenon. One should take into account the influence of consequences of the intrinsic binding process on a possibility of division of the fragments into discernible macroensembles. Note that this method can be used to describe the cases when a high-molecular weight substance can become similar to a particular phase extracting components from solution onto its surface and/or into the bulk. An idea that ensembles of functional groups are responsible for empirically determined parameters of H^+ and M^{z+} binding on macromolecular ensembles has previously[24—30] been advanced in different forms. However, the published specific accomplishments of this idea usually contain no fundamental substantiations and possibilities for testing whether the models are adequate (or even their non-adequate character is obvious) and the inclusion of the error model into analysis.

Presently, the main model of M^{z+} (H^+) binding with DOS and SOS of natural waters and, more widely, with any high-molecular weight reagents is accepted to be an analog of the classical metal—ligand complex formation with the 1 : 1 stoichiometry

$$\mathrm{M} + \mathrm{L}^* \rightleftharpoons \mathrm{ML}^*, \quad (16)$$

where the buffer capacity (C_{L^*}) of the reactant with respect to this M^{z+} and effective binding constant (K^*) are determined. In essence, hereinafter we simply re-designate the binding sites with A* (see Eqs (8) and (12)) for L*. Since the nature of the L* and ML* reagents is complex and often poorly known, the specific informal sense of the estimated K^* and C_{L^*} parameters remains unrevealed, which is correctly mentioned by many authors (see, *e.g.*, Refs 29—31). Therefore, the modern research practice even has no single opinion on the interpretation of the nature of the L* reagent: whether the piecemeal binding of M on L* should be referred to a particular macromolecule or to a certain functional group, or some site, which does not necessarily coincide, in the general case, with the functional group of any type.

For instance, when the binding of several HM ions (Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}) with components of river water (the water samples were titrated with solutions of metal salts, and $[M^{2+}]$ was potentiometrically determined) was studied,[32] $C_{\mathrm{L}^*} = [\mathrm{M}_{\text{bind}}]_{\text{sat}}$ ($[\mathrm{M}_{\text{bind}}]_{\text{sat}}$ is the saturated equilibrium concentration of the bound metal cation) was accepted to avoid the use of such unknown values as C_{L^*} and [L*], and the following expression is used to calculate the constant:

$$K^* = [\mathrm{M}_{\text{bind}}]/[\mathrm{M}^{2+}]^2$$

under equilibrium conditions, *i.e.*, at $[\mathrm{M}_{\text{bind}}]/(C_{\mathrm{M}})^2 \approx$ const. The description in terms of *piecemeal binding sites*

M^{z+} is thus taken as the basis (see equilibrium (16)). However, the $[M_{bind}]/[M^{2+}]^2$ values calculated by the presented initial data turned out to be inconstant, and we failed to determine the regions of fulfillment of the condition $[M_{bind}]/(C_M)^2 \approx$ const. Note that the equality $[L^*] = [M^{2+}]$ could not be accepted, because the investigated system cannot be considered as consisting of only one *initial component*[1] ML*. This was possible when the condition $C_M = C_{L^*}$ is fulfilled in the region of solution compositions used for the calculation of K^* by the proposed formula, while it was not fulfilled according to Ref. 32. Thus, the data[32] on K^* are not correct estimates of the desired parameter. In fact, only estimates of the lower boundaries of C_{L^*} found as $C_{L^*} \geq [M_{bind}]$ at maximum C_M values can be appropriate for further comparison and use. Analysis of the initial data of this work in the form of dependences $\Phi - 1 = f(C_M)$ showed that in the studied interval of C_M the values of the $\Phi - 1$ function are low and approximately constant and individual C_{L^*} and K^* parameters cannot be estimated rigidly (for example, for Hg^{2+} at C_M = 0.25—10 mg L^{-1} ((1.25—49.8)$\cdot 10^{-6}$ mol L^{-1}) in sample *2* $\Phi - 1 = 3.6\pm0.2$, and in sample *1* it is 4.1±0.4). From this it is clear that $C_{L^*} \geq 4 \cdot 10^{-5}$ mol L^{-1}, while the authors of the work[31] on the desirable parameters reported the following: $C_{L^*} = 2.0 \cdot 10^{-5}$ mol L^{-1}, $K^* = (1.25\pm0.46) \cdot 10^6$.

A species of the L* reagent is often accepted to be either a statistical average macromolecule,[33—38] or the reagent is not detailed at all but the estimate of M^{z+} binding is normed to the analytical content of an organic substance in the system expressed in g L^{-1} or (g of C) L^{-1}.[36,39,40] The analytical molar concentrations C_{L^*} (L* implies the statistical average macromolecule) are usually determined by the molecular-weight distribution of DOS[33,34,41—43] consisting mainly of humic acids (HA), which is estimated by ultrafiltration[35,37,38] or chromatography.[33,34,36,41—43] For instance, the stoichiometry of metal binding with HA was concluded[43] from the angular coefficient of the experimental dependence of $\log\Phi$ (ionometry) or $\log C_M$ (solubility) on $\log C_{L^*}$ at $C_{L^*} \gg C_M$, although it is basically impossible, in these cases, to understand whether the binding stoichiometry M : L* = 1 : 1 is provided by a macromolecule, any functional group of the macromolecule, or any certain set of functional groups with polydentate coordination of one metal ion. In addition, when the *n*-fold underestimated concentration of the binding component is taken for these calculations, then the resulting effective constant will also be *n*-fold overestimated. Probably, this takes place in the case described in the work[43] accepting $C_{L^*} = C_{HA}$, although the reagent is, most likely, a macroensemble of functional groups, which are $n \gg 1$ per macromolecule. Let us clarify this point by writing expressions for the law of mass action by Eq. (16) and the auxiliary function $\Phi - 1$ revealed on the basis of this law and material balance

$$K^* = [ML^*]/[M][L^*], \quad (17)$$

$$\Phi - 1 = (C_M/[M]) - 1 = [ML^*]/[M], \quad (18)$$

$$\log(\Phi - 1) = \log([ML^*]/[M]) = \log K^* + \log[L^*]. \quad (19)$$

Indeed, if $C_{L^*} \gg C_M$ (*i.e.*, when the contribution of the ML* species to the material balance of the L* ligand can be neglected) and a significant contribution of protonated ligand species to its material balance is absent or the ratio of the protonated and deprotonated species is constant for M binding (note that these restrictions were not formulated by the authors), we have $C_{L^*} \approx [L^*]$ and the linear dependence of $\log(\Phi - 1)$ on $\log C_{L^*}$ is

$$\log(\Phi - 1) \approx \log K^* + \log C_{L^*}. \quad (20)$$

Here $\log K^*$ is the intercept, and the unity coefficient at the term $\log C_{L^*}$ is taken as the basis to conclude that the binding stoichiometry is M : L* = 1 : 1. However, when the *n*-fold value (compared to the true value) $C_{L^*}' = C_{L^*}/n$ is taken as the concentration of functional fragments binding M by Eq. (16), then instead of (19) we have

$$\log(\Phi - 1) = \log K^* + \log(C_{L^*}' \cdot n) = \log K^* + \log n + \log C_{L^*}' = \\ = \log(K^* \cdot n) + \log C_{L^*}', \quad (21)$$

i.e., in the function $\log(\Phi - 1) = f(\log C_{L^*}')$ we find $\log K^{*\prime} = \log(K^* \cdot n)$ as the intercept.

The complexes with M : L* = 1 : 1 and 1 : 2 were found,[36] where L* are HA isolated from coal and peat with average molecular weights of 4700 and 5000 Da, and M is the transition metal (Zn and Cd). One more error characteristic of many other ecologists (see, *e.g.*, Refs 21 and 39) appeared in this work: the use of non-integer $\bar{n}$ coefficients as exponents to [L*] in equations of the law of mass action. Of course, the average ligand numbers

$$\bar{n} = (C_L - [L^*])/C_M$$

depend monotonically on [L*], but only stoichiometric coefficients should be placed in exponents to equilibrium concentrations of chemical species in correctly formed sets of equations of the law of mass action.[1,44] It is not surprising that the constants calculated by the same authors[36] using the Froneus method and the model of formation of the ML* and ML^*_2 complexes differ significantly from those found using non-integer $\bar{n}$ values in expressions of the law of mass action.

The K^* values estimated only in one composition point for each complex,[21,37] *i.e.*, without variation of the concentration of M or L*, are often presented, which worsens strongly the informativeness of these parametrizations for the investigated binding phenomena. The authors of the work[37] used ultrafiltration after the separation of a mixture of humic substances of natural waters with radioactive-labeled ^{65}Zn into four fractions (by the nominally molecular weight cut-off) and found the binding Zn : L* = 1 : 1, where L* are macromolecules of humic substances with an average molecular weight of 5000, 50 000, and 200 000 Da. Naturally, there are no grounds to take thus obtained ratios of concentrations of HM ions and macromolecules for binding ($[\mathrm{M_{bind}}]/[\mathrm{M}]\cdot[\mathrm{L^*}]$) as constants in any more or less wide interval of C_{M} or C_{DOS}.

For the same reasons (complex and uncertain nature and concentration of the binding component), the dependences $[\mathrm{Cd_{bind}}]/[\mathrm{Cd^{2+}}] = f(\mathrm{pH}, C_{\mathrm{HA}})$ were studied[39] to describe the cadmium(II) binding by the titration of solutions of the known HA preparations with solutions of $\mathrm{Cd^{2+}}$ salts. The idea to use only easily experimentally accessible values C_{M}, $[\mathrm{M}^{z+}]$, pH, and C_{HA} (in g L^{-1}) is worth of attention, but the parametrization of the cadmium binding on the HA preparations was carried out only in the "black-box" variant

$$[\mathrm{Cd_{bind}}]/[\mathrm{Cd^{2+}}] = a + b\cdot C_{\mathrm{HA}}{}^{0.64}/[\mathrm{H^+}]^{0.20}.$$

Further, the state of $\mathrm{Cd^{II}}$ in natural waters was quantitatively estimated on the basis of these and published data on the complex formation of cadmium with inorganic components ($\mathrm{OH^-}$, $\mathrm{HCO_3{}^-}$, $\mathrm{Cl^-}$, $\mathrm{SO_4{}^{2-}}$). However, the results of the "black-box" parameterizations are hardly appropriate for aqueous systems of different compositions and, correspondingly, with a different state of even the same HA.

Nevertheless, many authors declare a quite reasonable idea about L* as one certain type of functional groups in the composition of the considered macromolecular ensemble. However, rules for including such ideas into the corresponding quantitative descriptions of M^{z+} bindings are much worse realized. For instance, it was validly accepted[29] that in an aqueous solution the $\mathrm{Hg^{2+}}$ cation in the 1 : 1 stoichiometry is bound not by the HA molecule but by some site ($\mathrm{S^{2-}}$), which is one or several functional groups in its composition. The overall stoichiometry of the precipitated mercury humate (HgHA) was estimated, and its IR spectrum was recorded. Its comparison with the spectrum of humate in the H form suggested mercury binding by the carboxyl groups. However, when the authors attempted to estimate the effective equilibrium constant of $\mathrm{Hg^{2+}}$ binding on $\mathrm{S^{2-}}$ in solutions, they identified, in fact, basically different objects ($\mathrm{S^{2-}}$ and $\mathrm{H_2S}$, HgS and HgHA).

Note that the greatest efforts of the most part of researchers were aimed at developing mathematical aspects of the physicochemical description of M^{z+} ($\mathrm{H^+}$) binding with DOS and SOS of natural waters and, more widely, with any high-molecular weight reagents. In this case, they often advance, on the one hand, too flexible (with respect to assumed stoichiometries) formal models ignoring correspondence of their meaning to the sum of physicochemical knowledge about complex formation phenomena in solutions and, on the other hand, a complex of procedures on the standardization of the nature and states of reagents designated as L* is unappreciated, taking into account consequences of the fact that these standards cannot be made absolutely rigid.

Among the works on the mathematical processing of results of ionometric titration of natural waters, we can emphasize the study,[31] the publication of which stimulated many researchers[38,45] to use the so-called Ruzic method. In that work, the authors considered variants of linearization of titration curves for several types of *investigated systems*[1]: {M, L, ML}, {M, $\mathrm{L_{(1)}}$, $\mathrm{L_{(2)}}$, $\mathrm{ML_{(1)}}$, $\mathrm{ML_{(2)}}$}, {$\mathrm{M_{(1)}}$, $\mathrm{M_{(2)}}$, L, $\mathrm{M_{(1)}L}$, $\mathrm{M_{(2)}L}$}, and {M, L, $\mathrm{M}_a\mathrm{L}_b$}, which are oriented to the combined estimation of both the effective constants ($K_{(i)}{}^*$) and concentrations of binding sites ($C_{\mathrm{L}_{(i)}{}^*}$). In addition, the influence of the ratios of the desired parameters $K_{(i)}{}^*$ and $C_{\mathrm{L}_{(i)}{}^*}$ on the shape of titration curves was analyzed. Based on the results of this analysis, the authors recommended how to plan studies of this class. Note that the most constructive point in author´s development is the idea about the combined estimation of $K_{(i)}{}^*$ and $C_{\mathrm{L}_{(i)}{}^*}$. The procedure of determination of the desired parameters is based on the analysis of the function

$$[\mathrm{M}]/(C_{\mathrm{M}} - [\mathrm{M}]) = f([\mathrm{M}]). \qquad (22)$$

In the simplest system (one ML complex and unchanged C_{L^*} and K^*), function (22) is linear with respect to the argument

$$[\mathrm{M}]/(C_{\mathrm{M}} - [\mathrm{M}]) = 1/C_{\mathrm{L}^*}\cdot[\mathrm{M}] + 1/(K^*\cdot C_{\mathrm{L}^*}). \qquad (23)$$

Dependence (22) is nonlinear in a system with two types of ligands, and the whole curve is recommended to be divided into two regions: at high C_{M}, the total capacity ($C_{\mathrm{L}_{(1)}{}^*} + C_{\mathrm{L}_{(2)}{}^*}$) and the effective constant

$$K_{(i)}{}^* = (C_{\mathrm{L}_{(1)}{}^*} + C_{\mathrm{L}_{(2)}{}^*})/(C_{\mathrm{L}_{(1)}{}^*}/K_{(1)}{}^* + C_{\mathrm{L}_{(2)}{}^*}/K_{(2)}{}^*)$$

can be determined, and then, at low C_{M}, one can find separately $K_{(1)}{}^*$, $K_{(2)}{}^*$, $C_{\mathrm{L}_{(1)}{}^*}$, and $C_{\mathrm{L}_{(2)}{}^*}$. Unfortunately, a possibility of the objective and, hence, parametrized variability of K^* with an increase in C_{M} and [M] was not considered. Nevertheless, precisely this situation is quite probable for a high-molecular weight substance during titration, which is mentioned by many researchers during the potentiometric study of polyelectrolytes (a change in $\mathrm{p}K_{\mathrm{a}}$ with a change in the degree of dissociation α).[16,17] Naturally, in these cases, dependence (22) is not linear either. In our opinion, the most substantial disadvantages of the Ruzic method can be listed as follows:

(1) it is implicitly accepted for the least-squares data processing that the argument (here [M]) is exact; however, this is often not true (especially at low [M] values,

taking into account that this parameter is usually determined potentiometrically using ion-selective electrodes);

(2) when several types of binding (sorts of the $L_{(i)}{}^*$ ligands) and/or inconstant K^* appear during titration, functional dependence (22) becomes very complicated for the analysis, which uses independent knowledge on the error model and is aimed at both determining the binding parameters ($K_{(i)}{}^*$, $C_{L_{(i)}{}^*}$) and checking whether the model is adequate to the experimental conditions.

Thus, despite the very fruitful idea on using only the data on the state of the metal ions themselves in the $\{C_M, [M]\}$ species, its accomplishment by the author is far from perfection. The proposed procedure[31] is insufficiently oriented to the inclusion of consequences from the error model into the processing and interpretation of the results and, finally, it predicts a binding model restricted by the simplest variant, which is often violated in solutions of high-molecular weight substances, including those in natural waters.

The so-called Scatchard method[24] has become abundant since the 1960s: the method of linearization of titration curves of solutions of high-molecular weight compounds with solutions of metal salts (or salts of strong acids) in the case of appearance of one or more types of binding sites. The method provides the estimation of constants only. These models also assume binding in the stoichiometry $M : L_{(i)} = 1 : 1$, where $L_{(i)}$ is the functional group of the *i*th type ($i = 1$—k). To calculate the binding parameters, the following function is recommended:

$$\nu = (C_M - [M])/C_L,$$

i.e., in fact, the degree of site filling, which is an averaged (over $C_{L_{(i)}}$) degree of filling

$$\nu_i = [ML_{(i)}]/C_{L_{(i)}}$$

for each type of sites ($\nu = \Sigma(\nu_i \cdot C_{L_{(i)}})/\Sigma C_{L_{(i)}}$). The author suggests to analyze the $\nu/[M]$ functions of ν, *i.e.*, applies the Leden method known in the theory of complex formation (see, *e.g.*, Ref. 8). For the same type of sites ($k = 1$), we have a simple linear dependence

$$\nu/[M] = K_{(1)} - K_{(1)} \cdot \nu. \qquad (24)$$

For two and more types of sites ($k > 1$), the whole curve $\nu/[M] = f(\nu)$ is proposed to be described by one equation and to simultaneously find the $2k - 1$ parameters or to divide the curve into linear regions and determine $K_{(i)}$ and $n_i = C_{L_{(i)}}/C_L$ successively (beginning from the maximum slope) in each region, further calculating ν' corrected taking into account the contribution of preceding $\{K_{(i)}, n_i\}$. The multisite Scatchard model was used, for instance, to describe[46] the Cd^{II} binding by polycysteine groups grafted on the porous glass (SH groups, four types of binding sites were found). Note that both the authors of the method and their followers[47] use the fairly correct (for some particular cases) approach for $k > 1$. The n_1 and $K_{(1)}$ values are estimated from the equation

$$\nu/[M] = K_{(1)}n_1 - K_{(1)}\nu$$

in the first region. To determine the binding parameters of the second and further types of sites, they recommend the forms

$$\nu'/[M] = (\nu - n_1)/[M] = f(\nu'),$$

$$\nu''/[M] = (\nu - n_1 - n_2)/[M] = f(\nu''),$$

etc. for each subsequent distinguished linear region, where $n_i = C_{L_{(i)}}/C_L$. In fact, according to the proposed form $\nu'/[M] = f(\nu')$, for $k = 2$ we obtain

$$\nu'/[M] \approx K_{(2)}n_2 - K_{(2)}\nu' \qquad (25)$$

or

$$(\nu - n_1)/[M] \approx K_{(2)}n_2 - K_{(2)}(\nu - n_1). \qquad (26)$$

The approximate equality sign means that $[ML_{(1)}] \approx C_{L_{(1)}}$ is accepted in the second region, *i.e.*, almost all $L_{(1)}$ sites have already been occupied by the M metal. Of course, such an inaccuracy is not always appropriate, as well as ignoring the influence of some contribution from $ML_{(2)}$ to the material balance when n_1 and $K_{(1)}$ are determined in the first region. However, the influence of the above-mentioned inaccuracies can sharply be decreased, in many cases, by some iteration procedure. Thus, the demand for independent knowledge of C_L remains to be one the principal restrictions of the proposed procedure, and precisely this value is unknown beforehand in practice.

An independent determination of C_{L^*} is also necessary in the Cheam method.[48] Here the K^* constant of equilibrium (16) is calculated in each titration point, *i.e.*, for each pair of the C_M and [M] values. This variant was used in the work[47] in addition to the Scatchard method to show that the determined K^* values are conventional for the competitive binding of Cu^{2+} and H^+ in solutions of fulvic acids. The C_{L^*} value for copper(II) binding was accepted to be equal to a half of the $C_{L^*(H^+)}$ value for H^+ binding ($C_{L^*} = C_{L^*(H^+)}/2$). The $[Cu^{2+}]$ and $[H^+]$ values were measured directly, and the concentrations of other species were calculated from the material balance equations taking into account that the relations $C_{Cu} = [Cu^{2+}] + [CuL^*]$ and $[H_2L_2] \approx [L^*]$ are fulfilled. As a result, the hyperbolic dependences of the desired $K^* = [CuL^*]/([Cu^{2+}][L^*])$ on the $[CuL^*]/C_{L^*}$ ratio (*i.e.*, in fact, on the degree of site filling) were found at pH 4.0, 5.0, and 6.0. The obtained estimates of K^* do not coincide[47] with the results of processing of the same data by the Scatchard method. However, no hypotheses were advanced to explain such a discrepancy and the inconstant character of the K^* found.

Another direction supported by many studies on the simulation of metal states in solutions of high-molecular weight substances (including DOS of natural waters) is presented by the so-called models of continuous ligand distribution (see, *e.g.*, Ref. 49). These models restrict the consideration by the simplest variant of the binding stoichiometry $M : L_{(i)} = 1 : 1$, where $L_{(i)}$ is some fragment of a high-molecular weight substance designated by the term *ligand* in the contexts. Then the concentrations of such ligands C_i are assumed at any $\Sigma_i C_i = C_L$ = const to be continuously distributed over the corresponding binding constants $K_{(i)}$ (unimodal, bimodal, and other distributions). The normal (Gaussian) distribution is usually accepted

$$C_i/C_L = 1/[\sigma(2\pi)^{1/2}]\exp[-1/2(\mu - pK_{(i)})^2/\sigma^2]dpK, \quad (27)$$

where C_i/C_L is the fraction of ligands for which $pK = \mu \pm \sigma$. The latter incorrect assertion is also met in other works. However, it follows from expression (27) that C_i/C_L is the fraction of ligands for which the constant lies in some interval, for instance, $pK_{(i)} \le pK < pK_{(i)} + dpK$. Note that the question about the role of choosing the position of the $pK_{(i)}$ points inside the $\Delta pK_{(i)}$ intervals and the values of the $\Delta pK_{(i)}$ intervals is not discussed in the works of this direction (probably, the importance of this problem is not realized), when numerical approximations based on Eq. (27) of the experimentally available dependences are related to the error model. These models were one of the first to be used for the description of potentiometric titration of humic substances[50] and later[51—53] for the description of the interaction of these substances with HM ions. These models have previously[30] been used to describe the binding of low-molecular weight anions with proteins[54] and gas adsorption on the catalytic surface.[55] This approach is most completely and clearly described in the review[30] and is being used to date by many foreign researchers (see, *e.g.*, Refs 30, 56, and 57).

In the framework of these models for the same type of ligands (for numerical approximations based on differential form (27)), two parameters are estimated: μ and σ. In the case of two types, an additional parameter, *viz.*, the fraction of one of the site types $\theta = C_1/C_L$, *etc.*, is used along with $\mu_{1,2}$ and $\sigma_{1,2}$. To verify the adequacy of the model (comparison with experimental data), the Scatchard form is used

$$\nu = \Sigma(\nu_i C_i)/\Sigma C_i = (C_M - [M])/C_L, \quad (28)$$

which surely needs to use the independently found C_L value, which is the total ligand concentration. It should be noted that in all considered works almost no attention is paid to methods of error estimation in such parametrizations, while the parameters themselves and their errors are often presented with the explicitly overestimated number of significant digits. For example, the authors[30] used the model presented by Eqs (27) and (28) to describe the binding of the H^+ and Cu^{2+} cations in solutions of river humic substances at 25 °C and I = 0.1 mol L^{-1} and found and reported the following parameters: $\mu_1 = 3.62 \pm 2.31$ (!), $\mu_2 = 12.3 \pm 1.68$, $\theta_1 = 0.48$ at the pH from 3 to 11 (for H^+) and $\mu = 4.15$, $\sigma = 1.20$ (with an accuracy to hundredths!) at pH 5 and pCu from 6.5 to 4.0 (for Cu^{2+}). At the same time, the significant discrepancies of ν_{calc} and ν_{exp} (>5%) in the regions of the highest titrant concentrations (pH 3.0—3.5, pCu ≈ 4.0) were ascribed (without any consideration of the error model) to the C_i* distribution type that differs from form (27) (*i.e.*, non-Gaussian distribution).

In the last decade, these models are used by several researchers[58—60] in our country mainly for protolytic equilibria of polyelectrolytes. Following the authors of the study,[57] this approach is named integral p*K* spectroscopy and is not related to the above-listed studies. Models of this type named the density function method were also developed (perhaps, independently or not, at least without citation and discussion of the relation with the aforementioned works) by other researchers.[61] After development, the density function method is used[62,63] for the description of both equilibria in mixtures of several acids (bases) and acid-base equilibria in solutions of proteins (high-molecular weight components), binding of cations (H^+, Mg^{2+}, Cd^{2+}) in solutions of humic and fulvic acids, and H^+ sorption by different solid phases (microporous glass, manganese dioxide, silica—anionic polysaccharide (alginic acid) and $Ti(OH)_4$(sol)—protein systems).

It should be noted that some formal statements of such models can be obtained from the analysis of differential forms of dependences of the type $C_M - [M] = f(\log[M])$ plotted for both one-step complex formation at n sorts of independent ligands ($M : L_{(i)} = 1 : 1$) and multistep complex formation (ML_i, $i = 1—n$). Nevertheless, this genetic interrelation is not emphasized (and, most likely, even is not realized) in any of the listed works. Thus, consequences of generalizations, which can be related to differential mathematical transforms of some auxiliary functions on the basis of simple, in essence, equations of the laws of mass action and material balance for the simplest physicochemical models of complex formation, are interpreted quite invalidly, in our opinion, by both the authors of the method and their followers as a new informal model of M binding, *viz.*, the model of continuous ligand distribution. Of course, we cannot agree with this interpretation of differentially transformed known empirical functions. The latter themselves, naturally, are informative, which determines the satisfactory (in particular respects and cases) description of experiments even in such nonrigid and, in addition, incorrectly treated forms. This correspondence is based on the following fact. When concentration intervals of the development of piecemeal binding on independent ligands of the *i*th type (or complexation—protonation steps) are separated, the maximum of the $(d\alpha/d\log[M])$ derivative in the log[M] coordinate coincides with $-\log K_{(i)}$ (or $-\log K_i$). In our opinion, in the works considered above and many other studies, the over-indulgence of some mathematical aspects of simulation, which is often one-sided as well, is accompanied by ignoring of important physicochemical restraints.

Another variant of simulation, where some mathematical aspects prevail, is presented in the study[64]: here the macromolecular nature of the ligand is taken into account using the combinatorial analysis of the acceptor (M) distributions over active sites (Z_i) of the polyligand. The accepted restraints of the model are described: all acceptors are independent, any stoichiometry $M : Z_i = a : b$ (a, b are integers) is possible; macromolecules can be "cross-linked" by the M atoms as bridges. To decrease the number of desired parameters of the model, the authors recommend to express the general complex formation constants through characteristic binding constants of M on active sites to form $M—Z_i$, which undoubtedly seems reasonable. The further isolation of subcomponents of the $M—Z_i$ type serves, evidently, as a transition to another level of specification of the *initial system*.[1,14] It seems unreasonable, in our opinion, to attribute equilibrium constants of some *level of specification*[1] to true thermodynamic constants and those of another level to imaginary constants. This is, in fact, a result of denial of the intrinsic possibility to specify a system at different levels.

In the already mentioned work,[64] the model was applied to describe the extraction of Hg^{2+} from an aqueous solution of HNO_3—AcOH acids to the organic phase by macromolecular polyazacrown ether (its molecule contains 11 active sites). The authors found seven (!) variants of Hg^{2+} addition to the crown ether, one of which leads to the cross-linking of two macromolecules, and determined all binding constants (the values are presented with an accuracy to hundredths of logarithmic unit). In our opinion, this is the too flexible formal model (in other words, the model is based on the nonverifiably deep specification of the system). Naturally, this approach provides an adequate description of experimental data for many rather complex systems, but the corresponding parameters will be, most likely, formally fitting and inappropriate for other systems. Some significant and objectively existing factors, such as the influence of the degree of site filling on the binding constants, are ignored in this model.

Many other domestic works, including reviews, are devoted to predominantly mathematical aspects of equilibria simulation involving high-molecular weight components (this is often accompanied by a substantial underestimation of the physicochemical aspects). For instance, three types of the already mentioned models have been considered[49]: electrostatic, with a continuous range of constants, and discrete. As a result, the latter, which are also named chemical, were recommended as the most constructive. In these models, the specifics of binding by high-molecular weight components is taken into account in the form of an unusual stoichiometry of complexes ($M : A = a : b$, $H : A = a : b$, where A are functional groups of the macromolecule). In fact, the authors[27,49] only select a set of chemical species and the corresponding equilibria constants for the most smooth description (the minimum of the sum of squared discrepancies) of results of potentiometric experiment (usually being the titration of a solution based on a high-molecular weight component with a solution of a strong acid or metal salt with the measurement of the pH and/or pM). In this case, the physicochemical sense and the content of the found parameters are secondary or are not discussed at all. In our opinion, the discovery of superfluous and missing of objectively existing chemical species are thus possible (without the comprehensive analysis of the adequacy of the model). It is not surprising that the constants of the equilibria found depend incorrectly on the ionic strength of the solution. At the same time, the results of an additional experiment (the change in the viscosity and electric conductivity of alkaline solutions of polyacrylamidoxime upon the addition of metal salts) are insufficiently informative to conclude that the chosen model is adequate. These results only allow one to identify the formation of mixed complexes $M(OH)_nA_x$ ($n \geq 1$; however, nothing is known about the x value), while the set itself of the really existing species and the respective constants can differ significantly (and even dramatically) from that proposed by the authors.

The same authors used the chemical models to describe the acid-base and complexation properties of sorbents,[65,66] namely, chemically modified silicas, *i.e.*, SiO_2(sol) phases with grafted functional groups. Other authors[67—69] thus described the properties of fibrous sorbents of the high-molecular nature. Although researchers have already realized that the corresponding functional groups should be considered as a reagent, a single approach to the standardization of the main parameters of the state of the reagent (for example, its concentration) is lacking. For instance, the reagent concentration is expressed both in moles per liter of solution[65,66] and moles per gram of sorbent.[67—69] In this case, the resulting equilibrium constants[65,66] depend incorrectly on the ionic strength (even after the correction for the involvement of components of the salt background in complex formation was applied). For the most smooth description of the experiment, the authors have to introduce hypothetical, in our opinion, equilibria of homoconjugation between grafted functional groups.

Similar models were applied[70] to the description of vanadium sorption on chemically modified silicas with carboxyl functional groups. The development was named the mathematical simulation and more explicitly manifested the often met and already mentioned exaggeration of some mathematical aspects in the simulation of physicochemical phenomena. The authors assert that this method makes it possible to calculate stepwise equilibrium constants of any complexity without any restraints. However, the matter is that the role of independent objective restraints introduced in the form of the initial informal model increases sharply for studying complex equilibria. The mathematical simulation itself cannot solve problems on the objective state of reagents. In fact, the authors[70] used both some restraints (for example, the concentrations of functional groups and ML* complexes were expressed in moles per gram of sorbent, the concentrations of species in solution were expressed in moles per liter of solution, the concentrations of functional groups were specified, *etc.*) and comparison of results of different experimental methods (pH-metry and interphase metal distribution, as well as ESR spectroscopy to confirm vanadium(IV) coordination on the sorbent surface) in their complex study, where the mathematical simulation was only a part of the work.

To describe the acid-base and complexation properties of sorbents (usually they are the same chemically modified silicas), one more class of models is being developed and used. These are models of fixed and statistically polydentate sites.[25,26] In this case, several (n) grafted sites $\overline{\mathrm{R}}$ (or functional groups) are considered as one n-dentate ligand (interacting with a metal), and each site can add at most one proton. The equilibria basis can be written as follows:

$$\mathrm{M}^{z+} + \overline{\mathrm{R}}_n \overset{\beta_n}{\rightleftharpoons} \overline{\mathrm{MR}_n}, \qquad (29)$$

$$\mathrm{H}^{+} + \overline{\mathrm{H}_{i-1}\mathrm{R}_n} \overset{K_{in}}{\rightleftharpoons} \overline{\mathrm{H}_i\mathrm{R}_n}, \qquad (30)$$

where $i = 0$—n.

Species fixed on the solid phase surface of chemically modified silicas are marked above with line and the charge values are omitted. Concentrations of the fixed species are expressed in moles per gram of modified silica, and those of the species in solution are expressed in moles per liter of solution. In the model of fixed polydentate sites, the whole surface containing $C_{\mathrm{R}}{}^{\mathrm{s}}$ sites is divided into $C_{\mathrm{R}}{}^{\mathrm{s}}/n$ regions, each of which contains one n-dentate ligand $\overline{\mathrm{R}}_n$. In the model of statistically polydentate sites, for a specified site distribution, the number of groups of n sites $\overline{\mathrm{R}}$ (each of them is the n-dentate ligand $\overline{\mathrm{R}}_n$) is calculated, and the additional parameter χ_n is introduced, which is equal to the number of sites $\overline{\mathrm{R}}$ capable of forming the $\overline{\mathrm{R}}_n$ ligand together with the given ligand for binding with M. Although the n value is theoretically unrestricted, the authors believe[25,26] that almost no cases with $n > 4$ were found and, therefore, the number of variants for further analysis is restricted in the framework of this model too. In addition, the K_{in} values were taken equal for different i and n and independent, as β_n, of the degree of filling of binding sites by both protons and metal ions.

In our opinion, this model can be a satisfactory approximation only when the ionic medium is constant and the "load" is small.[18] However, it seems hardly correct to consider $K_{(i)}$ as independent of i in these cases as well. When the load with respect to H^+ approaches unity, the model can sharply be simplified accepting that only the process

$$\mathrm{M}^{z+} + \overline{\mathrm{H}_z\mathrm{R}_n} \rightleftharpoons \overline{\mathrm{MR}_n} + z\,\mathrm{H}^+$$

is significant in the balance.

Proposed approach

Analysis of the main approaches to the study and description of the binding of metal cations (in particular, HM cations) and protons on functional fragments of a high-molecular weight substance in aqueous (including natural) systems allows us to conclude the following.

First, the most part of presently available approaches and models require independent information on the nature and concentration of binding sites (acceptors). It is rather difficult and labor-consuming to obtain these data, and the results are not always sufficient for the standard use of the classical procedures for studying complex formation. Such novelties as models of continuous ligand distribution (pK spectroscopy) reducing to poorly substantiated parametrizations of some differential forms from the known auxiliary functions are hardly worth of attention. In addition, "fanciers" of these models ascribe the interpretation model to binding equilibria (for example, the normal ligand distribution over binding constants), while this model is quite inadequate to the regularities found in the area of complex formation phenomena.

Second, the virtually single method for determining the parameters of metal binding on acceptors with the unknown nature and concentration only from the data on C_{M} and [M], which are usually available in the framework of the modern ionometry, was proposed[31] by Ruzic. The intrinsic idea to identify the presence of HM ion acceptors and characterize them in part (concentration, equilibrium constant of binding) on the basis of only ionometric titration data is worth of attention. However, the real procedure proposed by the author of this idea is efficient only in the case of one type of sites with an unchanged binding constant and low errors of [M] determination. Both conditions are rarely obey simultaneously for studying the HM states in natural waters. In particular, for these systems, one should use information in the region of rather low equlibrium concentrations of M^{z+}, in which the error of their ionometric determination increases sharply and becomes difficult to estimate. Nevertheless, many researchers have used the Ruzic procedure long ago without giving proper attention to consequences of its limited nature. In the best case, this leads to rather rough estimates of the binding parameters, whereas the worst situation provides inappropriate or at least poorly appropriate results for further extrapolations and informal generalizations.

Third, presently performed quantitative parametrizations of HM ion binding by a high-molecular weight substance in solutions are often fairly exact for the adequate description of the really observed local empirical pattern (directly for the samples themselves under conditions of their investigation) but are inappropriate for extrapolations (this concerns conditions, in particular, concentrations of HM and binding components and the more so, the nature of binding compounds). For example, discrete formal models unrestricted by dimensions, for instance, the so-called chemical models, are fraught with the formal discovery of non-existing species and parameters of the corresponding equilibria, which are most adequate (in the narrow mathematical sense, often only by the minimum of the sum of squared discrepancies) only to data of experimental conditions and, therefore, they have no informal physicochemical sense and are inappropriate for any extrapolations.

Thus, the situation is substantially far from perfection because of complex independent procedures for the characterization of binding components and, as a consequence, drastic deficient of these data and also imperfect approaches, which are rational in essence (the Ruzic[31] and Scatchard[24] methods) and were proposed and are widely used to avoid this disadvantage. Therefore, the problem to select and improve parametrization procedures of auxiliary functions to enhance their informativeness in studying and describing HM ion binding by high-molecular weight substances in solution remains urgent.

We propose an approach to the solution of this problem that is oriented to the modification of the classical procedures, which have well recommended themselves in studying complex formation. Presently, we restrict ourselves by the improvement of possibilities to extract information from data on the degree of complex formation function ($\Phi = C_M/[M]$). This choice is caused by three factors. First, many ecological chemists used (long ago and widely) quite available data on degrees of complex formation, which are obtained by ionometric titrations of water samples.[31,32,39,71] Second, following Ruzic,[31] researchers began to use these data to extend knowledge on the DOS and SOS themselves, which are responsible for the ionometrically detected pattern of HM ion binding. Third, urgency of data of this type is much higher than their quality, although all prerequisites to improve substantially the corresponding technologies are available.

Since we have to determine $[M^{z+}]$ in the region of ultimately low (for ionometry) C_M concentrations, first of all we considered problems of obtaining valid data on the degrees of complex formation themselves in these regions: $[M] = f(C_M)$.[72,73] Some difficulties in the area of potentiometry with ion-selective electrodes, which is widely used in chemical ecology to characterize the HM states, can be named "the problem of stability and right of extension" of calibration parameters. It is known that a special processing, especially in the region of low concentrations C_M and/or [M], is always needed for the metrological substantiation of conditions providing the stability of calibration parameters of specific electrode systems based on ion-selective electrodes and the right of their extension to investigated systems. To achieve an appropriate and, most important, controlled informativeness of ionometric data, we propose the methodology of increment movement from the calibration systems to the investigated samples of natural waters, *i.e.*, successive complication in the series of related systems studied by available electrodes: calibration system → reference system → model system → natural water sample followed by the use of the comprehensive comparative analysis of the results.

Although the regression estimation of the $1/K^* \cdot C_{L^*}$ and $1/C_{L^*}$ parameters by linear equation (23) provides characteristics with the desired informal sense in simple cases (if the considered interval of experimental conditions objectively corresponds to a sharp predomination of species related by equilibrium (16) in the material balance of the system at unchanged C_{L^*} and K^* values and correctly measured [M]), this estimation is poorly appropriate for both the analysis of consequences of possible random and systematic errors (for example, in the determination of [M]) and for revealing and diagnostics of reasons for deviations in the behavior of the investigated system from a simple behavior. Our approach and related procedures are oriented to the possible elimination of the above-listed disadvantages.[72—74] Analyzing the data (C_M, [M]), we propose to use the auxiliary function

$$\Phi - 1 = (C_M - [M])/[M] = \sum_i (K_{(i)}^* \cdot [L_{(i)}^*]). \qquad (31)$$

The additivity of the right part of Eq. (31) has a specific informal sense: $K_{(i)}^*$ is the effective constant of equilibrium (16) for the *i*th site of the discernible sites (functional fragments of DOS and/or SOS) of HM piecemeal binding, and $[L_{(i)}^*]$ is the equilibrium concentration of this type of sites. When one term is predominates in Eq. (31), *i.e.*, when only one type of functional fragments responsible for binding is distinctly manifested, we obtain the following linear form:

$$\Phi - 1 = K^* \cdot C_{L^*} - K^* \cdot (C_M - [M]), \qquad (32)$$

where C_{L^*} is the overall concentration of functional fragments. In the absence of substantial complications from random and systematic errors and when only the contribution from equilibrium (16) with unchanged C_{L^*} and K^* really predominates in the material balance of the system, the regression analysis by both Eqs (23) and (32) can give only insignificant differences in the results. In all other cases, which really prevail in practice, the procedures of analysis and processing of ionometric data on the basis of the auxiliary function described by Eq. (31) with linearization of the type (32) are considerably better than the Ruzic method, because they make it possible to consider independent information on both the error model in the initial data (C_M, [M]) and a possible objective inconstancy of C_{L*} and K* during ionometric titrations (an increase in C_M), as well as a possible commensurability of contributions from two and more numbers of varieties of functional fragments.

Our choice is quite regular in the light of the subservient role of the auxiliary functions and the sense of the related effective parameters.[13] It should be emphasized only that the conventional character of such parameters, which is often substantially beyond the commonly accepted standards, is secondary, while their efficiency having a sense of efficacy in these or other respects plays the main role. For instance, in the framework of constructive accomplishment of concepts of physicochemical decompositions and the role of the auxiliary functions, the effective parameters become a facility for the accumulation of reproducible and verified new quantitative knowledge in spite of the fact that their meaning is unknown. In addition, this knowledge is appropriate for certain extrapolations, generalizations, and deepening of informal interpretations.

The approach and procedures have already been approved on the model systems[73,74] and used to estimate the binding of the Cd^{2+}, Cu^{2+}, and Pb^{2+} cations on functional fragments of high-molecular weight DOS of natural waters.[73] Note that the same data are, in fact, some quantitative information on the DOS and SOS *in situ*. The latter is especially urgent under modern conditions, because other variants of studying DOS and SOS *in situ* remain to be very labor-consuming and have no reliable instrumental and methodical basis.

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