PHYSICO-CHEMICAL MODELLING OF THE SORPTION REACTIVITY OF TRUE TRACE COLLOIDS

E. V. POLYAKOV*)

Institute of Solid State Chemistry, UD RAS, 620219 Ekaterinburg, Russia

YU. V. EGOROV

Ural State Technical University – UPI, 620002 Ekaterinburg, Russia

G. N. ILVES

Institute of Solid State Chemistry, UD RAS, 620219 Ekaterinburg, Russia

Physico-chemical model of trace hydrolyzed element adsorption by H-form of ion-exchange resin is considered. The model implies the existence of both ionic forms and trace hydroxide colloids in aqueous phase and predicts two sharp maxima separated by a plateau on the adsorption diagram. It is shown that complicated adsorption profile arises as a result of superposition of the trace hydroxide colloid formation/dissolution by-processes accompanied by irreversible ageing of the colloid.

1 Introduction

The authors of [1] considered the thermodynamic model of ion-exchange adsorption of trace hydrolysed element M^{z+} in the system in which stoichiometric trace hydroxide colloid $M(OH)_z nH_2O$ can be formed by this trace element. This model is based on the analysis of experimental adsorption data in the form of the equation (1)

$$\bar{\varepsilon} = \frac{M_s}{M^{tot} - M_s} \tag{1}$$

$$M^{tot} = M_l^{tot} + M_s = M_l + M_c + M_s$$

in which M^{tot} is the total mass of trace element in the system; M_l is the mass of trace element in the form of ions and molecules in aqueous phase, M_c is the mass the trace element in the form of hydroxide colloid and the term M_s denotes the mass of adsorbed trace element in the phase of the ion-exchange resin. The model implies assumptions in accord with which only positively charged and molecular forms of the given trace element can be adsorbed by the ion-exchanger, and various forms of trace element are in equilibrium depending on pH. Adsorption proceeds in agreement with the mass action law [2] and can be expressed by the following equation

$$\bar{\varepsilon} = \frac{[m]\sum_i^z \bar{k}_i b_i}{CN \sum_i b_i h^{(z-1)}} . \tag{2}$$

Eq.(2) describes equilibrium adsorption system in which aqueous phase is not saturated relative to the trace hydroxide colloid of the element. On the other hand in the state of adsorption system in which the supersaturated solution with trace hydroxide colloid arises, the overall distribution coefficient $\bar{\varepsilon}$ should be expressed by the Eq.(3) instead of Eq.(2) [1]:

$$\bar{\varepsilon} = \frac{\eta K_s K_w^{-z}}{C^{tot} - \eta K_s K_w^{-z}} = const. \tag{3}$$

$$\eta = [m]\sum_i^z k_i[H]_s^{z-i} b_{i,} \bar{k}_i = k_i [H]_s^{(z-i)} \text{ ,} [m] = m/V, C^{tot}/V$$

where k_i is exchange constant for hydroxo-complex of the composition $M(OH)_i^{(z-i)+}$, $[H]_s$ is adsorption capacity of H-form of the ion-exchange resin which is supposed to be equal to the initial ion-exchange capacity in the case of trace elements adsorption, $b_i$is overall stability constant of the hydroxo-complex $M(OH)_i^{(z-i)+}$, m is the mass of resin and V is the volume of aqueous phase in adsorption experiment, K_s is solubility product of the colloidal form of trace element, h is the concentration of hydrogen ions in aqueous phase and CN is coordination number of the element chosen.

As a result of preliminary investigations of the above mentioned model [1] it has become evident that the overall mathematical form of adsorption isotherm should have peculiar points owing to the phase transition of adsorbing trace element. In particular, in every such point both Eqs. (2) and (3) are valid simultaneously and the numeric values of adsorption immediately up to (S_-) and after the point (S_+) can be expressed by Eq.(4)

$$\delta = \frac{S_+}{S_-} = \frac{K_s K_w^{-z}}{h^{-z}[M^{z+}]} = \frac{[M^{z+}]_c}{[M^{z+}]}, S = \frac{M_s}{M^{tot}} \tag{4}$$

in which $[M^{z+}]$ and $[M^{z+}]_c$ are concentrations of simple cations of trace element in homogeneous aqueous phase and the phase saturated with trace hydroxide colloid, respectively. The investigation has shown that for the totally equilibrated system the parameter $\delta = 1$. But if such a system is formed in non-equilibrium conditions when $[M^{z+}] > [M^{z+}]_c$ one can expect that parameter δ in Eq.(4) will be less than unity. The well known process of trace colloid ageing may be responsible for the lower value of the term $[M^{z+}]_c$ in Eq.(4).

The goal of this work was to investigate, by means of numerical simulation the effect of phase transition phenomena on the profile of trace hydrolysed element adsorption isotherm for the adsorption systems in which true hydroxide colloids can arise as a result of some ageing process.

2 Experimental

Numerical simulation of trace element adsorption processes was based on Eqs (1) – (4) and the following ion-exchange equilibria

$$(z-i)H_s^+ + M(OH)_{i,s}^{z-i} + (z-i)H^+ \tag{5}$$

where the terms with index "s" correspond to the phase of ion-exchange resin. It was assumed that only those of trace element concentrations will be analyzed that fit the conditions of Henry law [2-4]. Following characteristics of the trace element chosen were selected – $z = +2$, $i = 0 - 4$, $CN = 4$. Numerical values of the overall stability constants of the hydroxo-complex $M(OH)_i^{(z-i)+}$ were specially selected to cover all the regions of pH on the diagram, Fig. 1. Regression analysis of experimental data [2-5] was carried out with the help of the programmes TableCurve for Win., v. 1.10 and Statistica/w 5.0. The tabulated thermodynamic data were taken from [6].

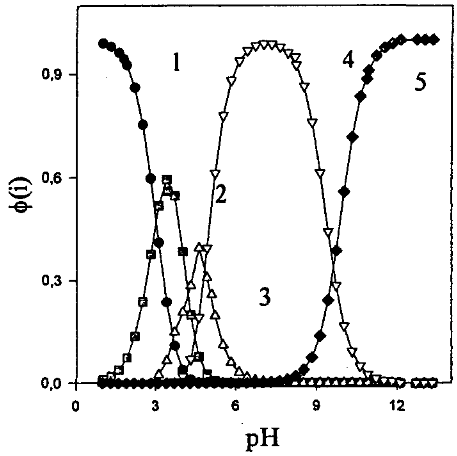

Fig. 1. Predominance-area diagram for the selected model system of trace element hydroxo-complexes as a function of pH. Lines: 1- M^{2+}; 2 – $M(OH)^+$; 3 – $M(OH)_2^0$; 4 – $M(OH)_3^-$; 5 – $M(OH)_4^{2-}$.

3 Results and discussion

According to the accepted model Eqs (1) – (3) determine the pH region within which trace colloidal hydroxide precipitation occurs, i.e., the inequality $[M^{z+}] > [M^{z+}]_c$ is valid (see Fig. 2). Outside this region the mass balance equation for the trace element leads to the conclusion that

$$[M^{z+}] = \frac{C^{tot}}{(\sum_{0}^{CN} b_i h^{-z} + [m]\sum \bar{K}_i b_i h^{z+})} \tag{6}$$

and within the region the equation

$$[M^{z+}]_c = K_s K_w^{-z} h^z < [M^{z+}] \tag{7}$$

is valid. Reversible equilibrium transition of adsorption system from the state denoted by Eq.(6) to the state denoted by Eq.(7) gives smooth profile of the overall isotherm of adsorption (Fig. 3, curve 1). Nevertheless, the more realistic and frequently met is the scenario when trace colloid formation is accompanied by its ageing, i.e. variation of the size, phase composition, the sign and value of the surface charge. One can suppose that this process is governed by some time-depending solubility product $K^{age}(\gamma)$ and it should decrease the solubility of the colloid to a lower level at which the following relation (8)

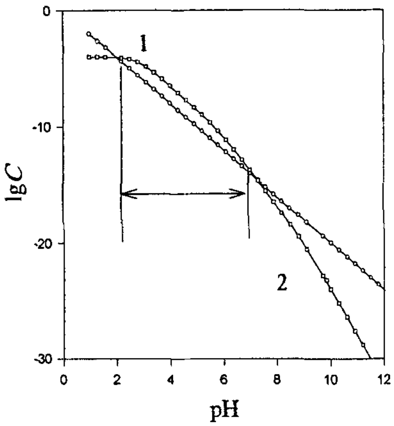

Fig. 2. Plots of equilibrium concentration of simple aqua-ion $M^{2+}(C)$ as a function of pH in super-(1) and sub-saturated solutions (2). Marked by the arrow is the region of trace hydroxide $M(OH)_2\, n H_2O$ formation.

Рис.3.

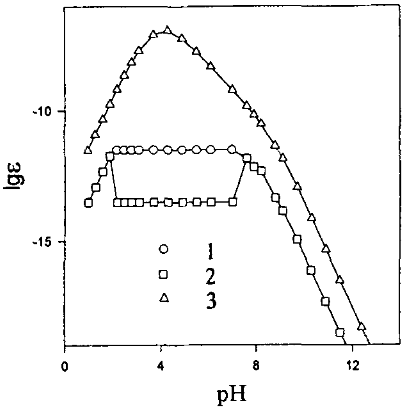

Fig. 3. Calculated overall adsorption isotherms for the model trace element according to the Fig. 1. Lines: 1 – $K_s = K^{age}(\gamma)$ in Eq. (3), [m] = 600 a. u.; 2 – $K_s < K^{age}(\gamma)$, [m]=600 a.u.; 3 – $K_s < K^{age}(\gamma)$, [m] = 60000 a.u.

$$[M^{z+}]_c^{age} = K_s^{age}(\tau) K_w^{-z} < [M^{z+}]_c < [M^{z+}] \tag{8}$$

is valid.

The variable $K^{age}(\gamma)$ characterizes the solubility of quasi-stable colloidal hydroxide by the time of ageing γ. In the case that the model considers the processes of formation and ageing of non-equilibrium colloid phase the thermodynamic term K_s in Eqs (4) and

(7) should be substituted by time-depending solubility product variable $K^{age}(\gamma)$. For the ageing-time depending adsorption process Eq.(4) is transformed into Eq.(9)

$$\delta = \frac{S_+}{S_-} = \frac{K_s^{age}(\tau)K_w^{-z}}{h^{-z}[M^{z+}]} = \frac{[M^{z+}]_c^{age}}{[M^{z+}]} \qquad (9)$$

which shows, together with Eq.(8), that parameter δ should be less than unity if the time of adsorption experiment is comparable with the time of ageing. This conclusion is conformed by numerical simulation of the adsorption profile for the distribution coefficient as a function of pH within the framework of Eqs (6)-(9) (cf. Fig. 3, curve 2). The corresponding isotherm reveals two characteristic narrow maxima one of which coincides with the pH formation of trace colloid in acid region and the other one coincides with the pH dissolving of amphoteric colloidal hydroxide. The results of the numeric analysis of the distribution coefficient change as a function of mass to volume ratio [m] have shown that the considered ageing phenomenon can lead to rupture on the adsorption profile owing to the dissolving of colloidal hydroxide by the excess of resin (cf. Fig. 4).

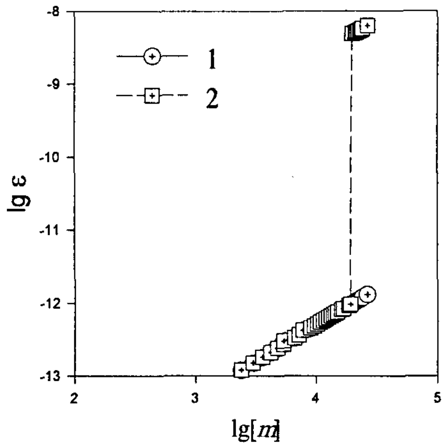

Fig. 4. Diagram of calculated distribution coefficient in Eqs. (2), (3) as a function of mass to volume ratio [m]. Lines (see Fig. 3): 1 – pH=1; 2 – pH=3.

Graphical results of Pu(IV) adsorption by glass surface [5, p. 105] can be considered as a typical example of ageing-time dependent adsorption profile. In accordance with these data, the experimental dependence of adsorption coefficient (this term is proportional to S in Eq.(4), [3]) on pH in the experiments carried out in aged solutions of Pu(IV) reveals a narrow maximum followed by a smooth horizontal right part at pH>5 (Fig. 5, curve 1). In contrast, freshly prepared solutions of Pu(IV) in the same adsorption system give a "dome-like" shape of isotherm with two weak maxima, one of which coincides with the position of the maximum in aged solutions and the other is separated by a horizontal segment and lies in the region of pH = 7,5 (Fig. 5, curve

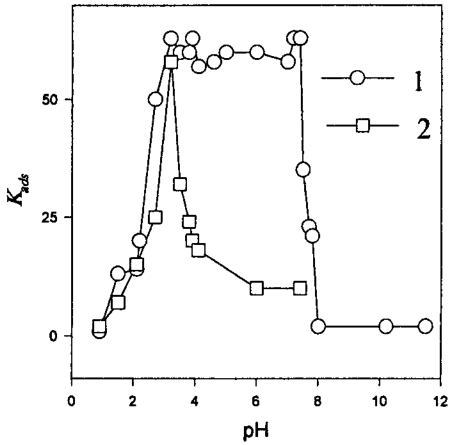

Fig. 5. Adsorption coefficient of Pu(IV) as a function of pH, [5]; Lines: 1 – time of ageing 5 h; 2 – time of ageing 24 h.

2). The general character of this dependence is identical with the shape of adsorption isotherm of colloidal hydroxide under ageing, Fig. 3, curve 2. Taking into account the similarity of dependence of the adsorption coefficient and the molar fraction of Pu(IV) deposited at centrifugation from pH, the author of [5] makes a conclusion about adsorption nature of plutonium colloid state. This inference, however, does not contradict the true trace colloids formation model discussed above and Starik's viewpoint on the true hydroxide colloid state of plutonium at pH = 3 – 4 [3] assuming that the adsorption colloid emerges by the heteronucleaton mechanism of trace quantities of plutonium hydroxide forming on the surface of a foreign phase nuclei [4, p. 68]. The resulting disperse phase will have the properties of both the true trace colloid and pseudocolloid. The mechanism of heteronucleation is advantageous for Gibbs energy of the trace hydroxide phase forming on the surface of "the carrier", and may cause an additional decrease in curvature radius of hydroxide phase islands as compared with the bulk colloid of the same phase. If we consider the ageing of this sorption colloid as the process of lateral growth accompanied by a decrease in surface curvature of particles of the growing plutonium hydroxide phase on the surface of the carrier phase and by diminishing of their solubility, the following facts become clear: the decrease in reversibility of plutonium adsorption by glass under pH conditions of true hydroxide phase formation beginning [5, p. 105] brought about by a reduction of its solubility with the time of exposure of the system [3, 5] and appearance of sharp maxima on the boundaries of pH region of pseudocolloid existence. In our opinion, this explanation makes possible to withdraw the objection of the thermodynamic character regarding the possibility of formation of sparingly soluble stoichiometric compounds in the form on trace colloids as well as to describe sorption phenomena using solubility product K_s or a certain effective value $K^{age}(\gamma)$ characterizing the phase solubility at a given ageing stage [2-5].

Table. 1. Calculated values of the coefficients in Eq. (17). The data taken from [4] and [5].

Estimated values, a.u.	Author [4]	Authors [5]
a_0	$(4,7 \pm 3.8)10^{-3}$	$(6,9 \pm 5,9)10^{-3}$
a_1	$(1,5 \pm 0,8)10^{-3}$	$(8,3 \pm 3,3)10^{-4}$
a_2	$(5,8 \pm 1,2)10^{-9}$	$(5,7 \pm 1,4)10^{-9}$
r^2	0,946	0,933
F	91,7	44,0
S_x	0,21	0,10

r^2 is squared correlation coefficient; F is the Fisher' criterion; S_x is the standard error.

The conclusions made are confirmed by the results of numerical analysis of adsorption and ultrafiltration of Fe(III) with concentration about 10-7 mol $L^{-1}1$ taken from independent data [4] and [5]. According to these works, the isotherms of Fe(III) adsorption by glass has a similar dome-like shape with two maxima an pH ~5 and ~10. The maxima are separated by a flat segment, Fig. 6.

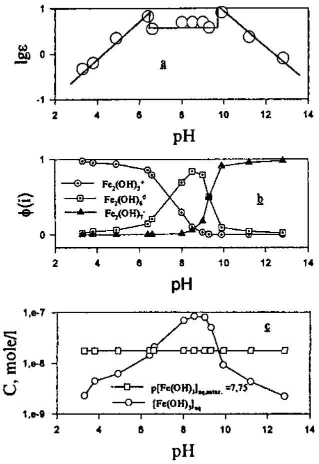

Fig. 6. Experimental isotherm of Fe(III) adsorption by glass-walls [5], (a); Calculated diagram of Fe(III) hydroxo-complexes in the investigated system, (b); comparative diagram of the molecular complex $Fe(OH)_3{}^0$ concentration in adsorption system and in the solutions saturated with amorphous ferric hydroxide as a function of pH, (c). 6<pH<10 is the region of supposed heteronucleation process, C^{tot} ~10-7 mol L^{-1}.

Based on the trace colloidal hydroxide model, the adsorption process outside these maxima is determined by distribution of ionic forms of iron between the surface of glass and aqueous phase according ion-exchange mechanism. That is why the characteristics of the sorbate state in this pH region should be similar irrespective of the experimental procedure employed. Within the region pH = 5 – 10 [5, p. 186], the iron forms prevail which are irreversibly adsorbed by foreign impurities (pseudocolloids).

The explanation of the data [4, 5] on the trace iron adsorption in the framework of the thermodynamic model is grounded on the calculation of the $Fe(OH)_3{}^0$ molecular complex concentration in the solution saturated relative to the amorphous ferric hydroxide of the $FeOOH_{amorph}$ composition. The constant of heterogeneous reaction (10)

$$FeOOh_{amorph} + H_2O = Fe^{3-} + 3OH^- \tag{10}$$

K_s for zero ionic strength is equal to $pK_s = 39,5$ [6]. The overall hydrolysis constant

$$Fe^{3+} + 3OH = Fe(OH)_3^0 \tag{11}$$

for the same conditions is $\lg\beta_3 = 30$, whence the molecular complex concentration in the saturated solution is $[Fe(OH)_3{}^0] = 1,8.10^{-8}$ mol L^{-1}. It is an order of magnitude smaller than the total iron concentration in the experiments [5]. This fact testifies to the possibility of the amorphous hydroxide phase formation in the conditions when this complex prevails. Colloidal silicon hydroxide can play the role of the "foreign carrier" sustaining the origin and growth of $FeOOH_{amorph}$. In this case the position of the horizontal segment on the adsorption isotherm coinciding with the pH region of colloidal hydroxide existence will be determined by the value of $K^{age}(\gamma)$, i.e. it will depend upon the time of adsorption system exposure. It is evident that outside the region of hydroxide stability this term does not affects the formal adsorption parameters.

The regression analysis of data [4] and [5] carried out by us with the use of Eq.(3) showed that outside the pH=5-10 region the isotherms are described in both cases by the model for ion-exchange sorption of cationic and molecular forms which are connected by hydrolytic reactions

$$Fe(OH)_{2,5}^{0,5} + 0,5OH^- = Fe(OH)_3^0 , \quad K_1 \tag{12}$$

$$Fe(OH)_3^0 + 0,5OH^- = Fe(OH)_{3,3}^{0,5-} , \quad K_2 \tag{13}$$

where

$$K_1 = \frac{[Fe(OH)_3^0]}{[Fe(OH)_{2,5}^{0,5+}]\ [OH]^{0,5}} ; \; K_2 = \frac{[Fe(OH)_{3,5}^{0,5-}]}{[Fe(OH)_3^0]\ [OH]^{0,5}} \tag{14}$$

are stepwise hydrolysis constants. The relationship between these constants and the stability constants in Eqs (2),(3) is given by Eq. (15)

$$K_1 = b_1 \cdot K_w^{-0,5} ; \; K_2 \cdot K_1 = b_2 \cdot K_w^{-1} \tag{15}$$

The adsorption reaction of these complexes are described by Eqs (5), (6) with indices i=j/2, where j=0,1,2 for the complexes of the composition $Fe(OH)_{2,5}{}^{0,5+}$, $Fe(OH)_3{}^0$ and $Fe(OH)_{3,5}{}^{0,5-}$ respectively. In accordance with the condition of hydroxo-complexes adsorption by weakly acidic ion-exchanger (on the assumption that its capacity is independent of pH) the isotherm (2) takes the form

$$\bar{\varepsilon} = \frac{[m]\sum_{j}^{2} \bar{k}_j\, b_j}{\sum_{j}^{3} b_j\, h^{(z-j/2)}} = \frac{a_0}{10^{-0,5pH} + a_1 + a_2 10^{0,5pH}} \tag{16}$$

where z = +0,5 is the formal charge of the basic form of the complex and

$$a_0 = [m]\,(\bar{k}_0 + \bar{k}_1 b_1)\,; \quad a_1 = b_1\,; \quad a_2 = b_2\,. \tag{17}$$

The results of regression analysis are presented in the Table. These data confirm the hypothesis that the chemical state of ferric hydroxo-complexes is independent on the adsorption technique employed if colloidal hydroxide is absent in the aqueous phase. The complexes found correspond to the ions of the type $Fe_2(OH)_2^{4+}$ [7] though their composition and predominance region fit the non-equilibrium character of the considered adsorption system [5], and conforms the known low rate polymerization processes in diluted solutions [8]. Nevertheless, comparing the concentration of the molecular complex calculated from the data of the Table with the concentration of these molecules expected in accordance with Eqs. (10), (11) one can see that the pH region of super-saturated solutions (Fig. 6c) coincides with the region of maxima on the adsorption isotherm (Fig. 6a).

Thus, the reviewed data do not contradict to the viewpoint in accordance with which the heteronucleation and ageing of trace colloids play significant role in the processes of trace elements adsorption. The use of this point of view makes possible to reconcile the known contradictions in the interpretation of adsorption experiments brought about by alternative character of analysis of these phenomena – within the framework of true or adsorption origin of trace colloids. More scrupulous and expanded theoretical and experimental investigations are needed for deeper understanding of adsorption phenomena in the trace element systems. In particular, we are planning in future to apply for these purposes a relatively new and convenient class of inorganic ferrocyanides [9]. This investigation is conducted under auspices of the RFBR, Russia, proj. No. 98-03-32543a.

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