

Isotherm equation of sorption of electrolyte solutions on solids: how to do heterogeneous surface from homogeneous one?

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Abstract

It is a rather common phenomenon in the literature, that the surface accumulation processes are treated by different isotherm equations without taking into account the mechanism of the sorption processes. In this paper, a model calculation is presented for homoivalent ion exchange process on energetically homogeneous surface. It reveals all incorrect conclusions which can be drawn in this way.

Keywords

Adsorption · competitive adsorption · ion exchange · isotherm equations · sorption mechanism

Acknowledgement

The paper is dedicated to the 10th anniversary of György Lajos Nagy's death.

1 Introduction

Recently, the interfacial reactions of contaminants and geological media, soils and rocks are intensively studied. The thermodynamic parameters of the interactions are determined in different ways. One of them is the application of sorption isotherms where the quantity sorbed on a solid surface (soil and rock) is studied as a function of the concentration of the solution (groundwater and soil solution). Sorbed quantity and sorption means the overall accumulated quantity, independently on the mechanism. The experimental data are interpreted by different isotherm models: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, etc. models. Some papers evaluate the sorption isotherms by several models simultaneously and found several models satisfactorily at the same time. For example, Langmuir and Freundlich models are applied for the same experimental results, e.g. [1]-[3]. The different models, however, are valid under different conditions and for certain sorption mechanisms. Obviously, it is non-sense if the models contradict each other. An illustrative example is the simultaneous application of Langmuir and Freundlich model. Langmuir model assumes an ideal homogeneous surface with no interaction between adsorbed particles. Freundlich isotherm, however, considers a heterogeneous surface, where the energy distribution (heat of adsorption) vs. coverage function is logarithmic. So, the energy distribution of the interface is different in the two models. Other discrepancy arises when different sorption mechanisms can be present. On rocks and soils adsorption, ion exchange and precipitation may occur simultaneously. Some types of precipitation take place because of the solved components, independent of the presence of the solid phase. Such a process, the hydrolysis of metal ions and the precipitation of hydroxides at high pH values can be mentioned. Some authors consider this process as adsorption and speak about adsorption edges as a function of pH. In this paper, the consequences of this treatment of sorption processes will be discussed. It will be shown also what kind of information can be obtained from the sorption isotherms. Only the sorption of electrolyte solution on solid surfaces is discussed.

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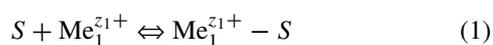
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2 Interfacial processes in solid/electrolyte solution systems

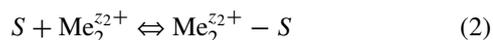
The interface can be thermodynamically treated by the Gibbs model [4, 5]. It uses a reference system where all extensive properties of the two bulk phases are unchanged divided by an imaginary Gibbs dividing plane. In a real interface the number of moles of each components, charge, entropy, energy can be either positive or negative compared to the reference system. These excess quantities can be defined as surface excess of the various extensive properties.

On the interface between a solid (including rocks and soils) and electrolyte solution the surface excess quantity/concentration of the dissolved components can be accumulated by different ways: adsorption, ion exchange and precipitation.

Adsorption is the increase in the concentration of a substance at the interface due to the operation of surface forces. For example, for the adsorption of the Me_1 cation with z_1+ charge:



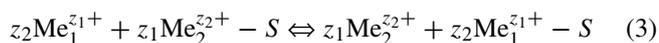
When two or more different substances are adsorbed, competitive adsorption occurs. In this case, Me_2 with z_2+ charges can adsorb, too:



S means the surface adsorption sites. Beside the adsorbed species, free surface sites of the adsorbents can also be present; namely the surface coverage (Θ) can be in the range of 0 to 1.

In aqueous solution competitive adsorption takes place in all cases, because water molecules cover the total surface of the solid. The water concentration, however, is usually much greater than the dissolved substances, so the change of water concentration can be neglected. In the thermodynamic equations, the parameters characterizing water are included into the other thermodynamic parameters. On the other hand, the properties of water molecules (e.g. electric permittivity) can change in the interfacial layer.

Ion exchange is the equivalent change of the ions on the surface to other ions. For example, the cation exchange can be described as:



where S means the surface, Me_1 and Me_2 are the cations with z_1+ and z_2+ charges. When $z_1+ = z_2+$, the ion exchange is homovalent, in other cases heterovalent. The anion exchange can be described by a similar equation.

Precipitation has different types. The first one occurs when the concentration of some components reaches the value of solubility product, the solution becomes oversaturated and a new solid phase precipitates independently in the presence of a solid surface. When, however, a solid phase is originally present, the precipitate is formed on it, thus the total composition of the solid phase changes. When the precipitation forms colloid particles,

especially in diluted solutions, they can be adsorbed on the solid, if it is present. This process is treated by the theory of colloid adsorption, the so-called DLVO theory [6, 7].

The second form of precipitation is surface precipitation, which requires the presence of solid phase. In this case there are three possibilities. One of them is when the precipitate is formed in a monomolecular layer. The second possibility is co-precipitation, when a component in low concentration co-precipitates with another component in high concentration if it can be built into the crystal lattice. In this case the thickness can be higher than monolayer. The third case is when heteronucleation takes place on certain places of the solid directed by chemical forces, and discrete colloid particles are formed.

The ion exchange and precipitation are frequently considered as adsorption, and the surface excess concentration vs. solution concentration function is described by adsorption isotherms. It is not correct because the processes are principally different: adsorption is directed by the decrease of surface energy. The main feature of the adsorption is that the adsorbed particles occupy the free sites of the interface. Ion exchange, however, is a competitive process on an already covered surface. Therefore, considering the ion exchange, there are no free sites on the surface, the surface coverage is always equal to 1. Precipitation, including colloid formation, is governed by the composition of the liquid phase, the crystal structure (co-precipitation) or primary chemical forces.

Therefore, when studying interfacial reactions, it must always be determined what the mechanism of the interfacial reaction is. Also, the dominant processes responsible for the surface excess concentration must be identified. If this is not done and the resultant process is evaluated without knowing it, in conventional ways, incorrect thermodynamical data are obtained. The concepts of the adsorption, ion exchange and surface precipitation have to be clearly distinguished, as done previously. When the character of the process can be neglected, only the surface accumulation is considered, we can speak about *sorption*, including all of the surface processes. In this case, only a phenomenological description can be given, no thermodynamics can be applied. In this paper, the consequences of the neglecting of sorption mechanism will be presented.

3 Quantitative treatment of solid/solution interfacial processes by isotherm equations

3.1 Adsorption isotherms

The interfacial processes can be correctly treated by Gibbs sorption isotherm. In solid surfaces, however, Gibbs isotherm equation cannot be applied because only the excess surface concentration can be measured directly, the surface tension cannot. Instead, other adsorption equations are applied; some of them contain some thermodynamic approaches, others are empirical or semi-empirical. One of the most widespread isotherms is the Langmuir equation, which was derived for the adsorption of gas molecules on planar surfaces [8]. It has four basic assumptions

for the adsorption [9]:

- 1 The adsorption takes place on the free sites of the adsorbent.
- 2 One adsorption site can adsorb one molecule; at most monolayer coverage is present.
- 3 The adsorption sites have the same energy (homogeneous surface), no interaction is between the adsorbed molecules. It means that the adsorption energy is independent on coverage.
- 4 There is adsorption equilibrium between the phases.

These assumptions are very strict and usually fulfilled neither in solid/gas nor solid/liquid systems. In practice, however, the Langmuir isotherm frequently describes the adsorption function quite well. For the adsorption of a dissolved substance:

$$a = z \frac{bc}{1 + bc} \quad (4)$$

where a is the excess adsorbed amount per unit mass of the adsorbent, z is the number of surface sites (that is the maximum adsorption capacity), c is the concentration of the adsorptive in the equilibrium solution, b is the parameter characterizing the adsorption energy.

In case of the adsorption of the dissolved substance (solid/liquid interface) the reciprocal amount of b can be used ($K = 1/b$). The surface coverage of the adsorbed substances (Θ) can be defined as $\Theta = a/z$.

By equivalent mathematical transformations, Langmuir equation can be expressed in linear forms.

$$\frac{c}{a} = \frac{1}{z} (c + K) \quad (5)$$

The c/a vs. c function is plotted here, the slope is $1/z$, the intercept is K/z . This linear form is fairly suitable for the determination of the maximum adsorption capacity, since it is calculated from the slope. The dimension of K is a concentration dimension, in an agreement with the dimension of c .

Among the four assumptions of Langmuir adsorption equation No. 3 is the most critical. It assumes that the surface is homogeneous and there are no interactions between the adsorbed particles. On multi-component adsorbents, as rocks and soils, the surface is heterogeneous, so the adsorption energy may depend on the coverage. In addition, at great coverage values, the adsorbed particles may have interactions. In some lucky cases, the two effects are compensated, and the adsorption isotherm can be described by the Langmuir equation: Eq. (5) gives a linear plot. In certain cases, the adsorption isotherm can be approached by different energy or site affinity distribution functions [10]-[13].

When two or more substance can be adsorbed on a surface, competitive isotherms are applied. The substances are adsorbed on the free sites of the surface (Θ_{free}) and desorbed from the covered sites (Θ_1 or Θ_2). In adsorption equilibrium, the rate of adsorption and desorption are equal:

$$(1 - \Theta_1 - \Theta_2)b_1c_1 = \Theta_1 \quad (6.a)$$

and

$$(1 - \Theta_1 - \Theta_2)b_2c_2 = \Theta_2 \quad (6.b)$$

The surface coverage of the substances can be expressed from (6) as:

$$\frac{\Theta_1}{\Theta_2} = \frac{c_1b_1}{c_2b_2} = \frac{c_1K_2}{c_2K_1} \quad (7)$$

By expressing Θ_2 from Eq. (7) and substituted into Eq. (6.a) we obtain:

$$(1 - \Theta_1 - \frac{\Theta_1b_2c_2}{b_1c_1})b_1c_1 = \Theta_1 \quad (8)$$

After equivalent mathematical transformation of Eq. (8):

$$\Theta_1 = \frac{b_1c_1}{1 + b_1c_1 + b_2c_2} = \frac{\frac{1}{K_1}c_1}{1 + \frac{1}{K_1}c_1 + \frac{1}{K_2}c_2} \quad (9)$$

Using that $\Theta_1 = a_1/z$:

$$a_1 = z \frac{b_1c_1}{1 + b_1c_1 + b_2c_2} = z \frac{\frac{1}{K_1}c_1}{1 + \frac{1}{K_1}c_1 + \frac{1}{K_2}c_2} \quad (10)$$

By the equivalent mathematical transformation of Eq. (10) we obtain:

$$\frac{c_1}{a_1} = \frac{1}{z} \left(c_1 + K_1 + \frac{K_1}{K_2}c_2 \right) \quad (11)$$

Similar equation can be described for the component 2.

As seen from Eq. (11), the c_1/a_1 vs. c_1 function is not linear because a composite amount containing the K 's of both adsorbed component and the concentration of the other component is present, instead of K constant in Eq. (5).

It is important to note that for adsorption process:

$$\Theta_1 + \Theta_2 + \Theta_{\text{free}} = 1 \quad (12)$$

4 Ion exchange isotherm for homovalent ion exchange

When ion exchange Eq. (3) can also take place on the solid, the surface accumulation by ion exchange can be described by isotherm equation. In case of ion exchange, the surface coverage is always equal to 1, that is $\Theta_{\text{free}} = 0$:

$$\Theta_1 + \Theta_2 = 1 \quad (13)$$

Eq. 12 similarly to Eqs. (1)-(3), expresses the important difference between the adsorption and ion exchange: adsorption takes place on the free sites, while ion exchange takes place on the covered sites of the surface. For homovalent exchange, using that $\Theta_1 = \frac{a_1}{\zeta}$ and $\Theta_2 = \frac{a_2}{\zeta}$, where ζ is the number of exchanged sites and a_1 and a_2 are the amounts of the ions on the solid:

$$\zeta = a_1 + a_2 \quad (14)$$

Considering Eqs. (13) or (14), from Eq. (7) we obtain:

$$\frac{\Theta_1}{\Theta_2} = \frac{a_1}{a_2} = \frac{a_1}{\zeta - a_1} = \frac{c_1K_2}{c_2K_1} \quad (15)$$

The reciprocal of Eq. (15):

$$\frac{\zeta - a_1}{a_1} = \frac{\zeta}{a_1} - 1 = \frac{c_2 K_1}{c_1 K_2} \quad (16)$$

or

$$\frac{\zeta}{a_1} = 1 + \frac{c_2 K_1}{c_1 K_2} \quad (17)$$

$$\frac{c_1}{a_1} = \frac{1}{\zeta} \left(c_1 + \frac{K_1 c_2}{K_2} \right) \quad (18)$$

Similar equation can be written for the exchanged cation (Me_2). In Eqs. (14)-(18), the number of exchange sites is signed by ζ , just to differentiate the adsorption and ion exchange sites. As comparing the adsorption Eq. (11) and ion exchange isotherms Eq. (18), we can see that one parameter (K_1) is absent in the right side of the ion exchange isotherms. This ion exchange isotherm equation has been applied by [10, 12]-[16].

It is general in the literature that the adsorption and ion exchange are evaluated by a *linearized* isotherm Eq. (5), neglecting the competitive character of the sorption processes. The number of active sites (z or ζ) and the K isotherm parameter characteristic of the sorption affinities are determined from the slope and the intercept of the plot. However, the isotherms are usually not linear. The divergence from the linearity is interpreted by surface heterogeneity and the interactions between the particles of the sorbed substances. The isotherms are divided into linear portions, and different z/ζ and K values are determined for the linear portions. When we carefully study the isotherms, we can see that this way of treatment is not suitable for competitive interfacial processes, including competitive adsorption and ion exchange. As seen from Eqs. (11) and (18), the isotherms cannot be linear because the concentration of competing substance is also in the equation, which is a variable quantity.

To illustrate the effect of the competing substance, the results of model calculations are shown in Fig. 1 in case of homovalent ion exchange ($z_1+ = z_2+$). Consider a system with the different parameters: the mass of the sorbent is 1 g, the volume of the solution is 1 dm^3 , the number of ion exchange is 10^{-3} mol/g . Let the ratio of K_1/K_2 be 0.1, 1, 10, respectively. The concentration of the competing ion (c_2) in Eq. (18) is calculated from the sorbed quantity (a_1). Since 1 g and 1 dm^3 are used in the model calculation, and the ion exchange is homovalent, the numerical value of c_2 and a_1 are equal ($c_2 = a_1$).

As seen in Fig. 1, the plot of the isotherms is usually not linear. The shape of the plot is determined by the ratios of K_1/K_2 and c_2 . During the model calculations, the surface heterogeneity and the interactions of the ions are neglected, after all, the shape of the isotherm is curved. If there is any surface heterogeneity or interaction between the sorbed ions, it cannot be concluded from the isotherm.

Let us see the conclusions of the usual linear evaluation Eq. (5) in detail on the example of the plot with $K_1/K_2=10$ in Fig. 1. As seen in Fig. 2, three linear portions can be divided.

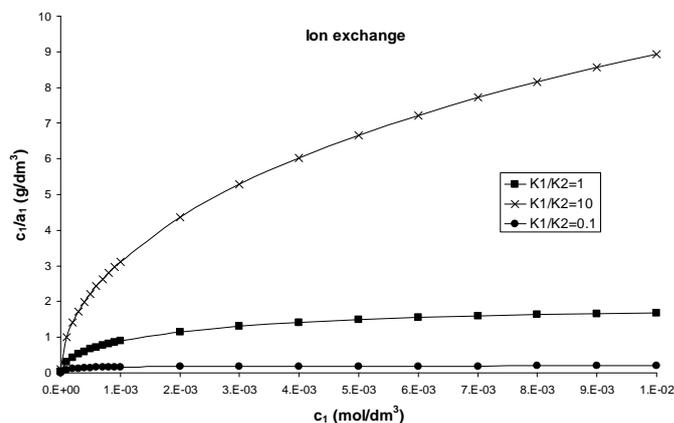


Fig. 1. c_1/a_1 vs. c_1 function of the homovalent ion exchange (Eq. (18)). Input parameters: $m=1 \text{ g}$, $V=1 \text{ dm}^3$, $\zeta=10^{-3} \text{ mol/g}$, $K_1/K_2=0.1, 1, 10$, respectively, $c_2 = a_1$

The slope and intercept of the linear portions, the number of exchange sites and “ K ” isotherms parameters, as well as the input parameters of the model are listed in Table 1.

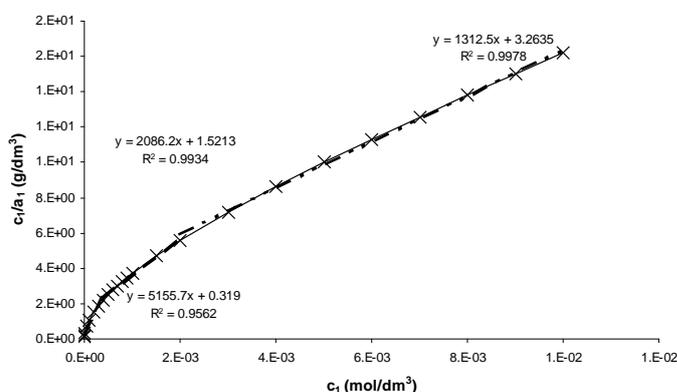


Fig. 2. The linear portions of c_1/a_1 vs. c_1 function of the homovalent ion exchange Eq. (5). Input parameters: $m=1 \text{ g}$, $V=1 \text{ dm}^3$, $\zeta=10^{-3} \text{ mol/g}$, $K_1/K_2=10$. $c_2 = a_1$.

As seen in Fig. 2 and Table 1, the surface of the ion exchanger seems to be heterogeneous with three different exchange sites. The number of exchange sites, however, does not provide the input parameter. Furthermore, the values of “ K ” are meaningless because they contain a variable amount, the concentration of the competing ion. For this reason, any conclusions, thermodynamic parameters estimated from the data obtained the linear portions have no real physical or chemical meaning, even if the regression of the estimation is very good ($R^2 > 0.99$). For the correct evaluation of a sorption isotherm, the competition and the mechanism (ion exchange or adsorption) have to be taken into account.

As mentioned in Introduction, the experimental data of sorption are frequently evaluated using Freundlich isotherm as well, and this isotherm is found to be satisfactory beside Langmuir isotherm. The surface and solution concentration data (a_1 and c_1) obtained in our model are plotted according to Freundlich isotherm (Fig. 3):

Tab. 1. The estimated parameters of isotherms on Fig. 2 and the input parameters

Range of c_1 (mol/dm ³)	Slope (g/mol)	Intercept (g/dm ³)	R ²	ζ (mol/g)	Estimated „K” of the linear portions (mol/dm ³)
1.0E-06-4.0E-04	5155.7	0.319	0.9562	1.9E-04	6.2E-05
3.0E-04-2.0E-03	2086.2	1.5213	0.9934	4.8E-04	7.3E-04
1.0E-03-1.0E-02	1312.5	3.2635	0.9978	7.6E-04	2.5E-03
Input parameter				1.0E-03	10*c ₂

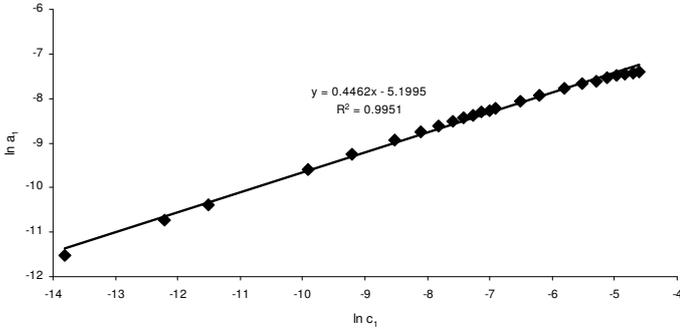


Fig. 3. Freundlich isotherm obtained from the data of homovalent ion exchange Eq. (19). Input parameters: $m=1\text{g}$, $V=1\text{dm}^3$, $\zeta=10^{-3}\text{mol/g}$, $K_1/K_2=10$. $c_2 = a_1$.

$$\ln a_1 = \ln k_F + \frac{1}{n} \ln c_1 \quad (19)$$

As seen in Fig. 3, the data can be described by Freundlich isotherm, too. The conditions of our model, however, do not satisfy the conditions of Freundlich isotherm; namely Freundlich isotherm considers a heterogeneous surface, but our model investigates homogeneous surface.

Beside the exchange isotherm, the ion exchange can be quantitatively described by the law of mass action, i.e. the equilibrium constant or selectivity coefficients of the ion exchange can be given. For the most convenient description of the equilibrium constant of the homovalent exchange (K_e), the activity coefficients of the ions both on the surface and in the solution are neglected, the equilibrium constant of a homovalent exchange can be expressed as:

$$K_e = \frac{a_1 c_2}{c_1 a_2} \quad (20)$$

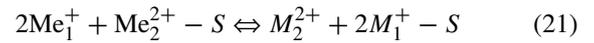
Eq. (20) is equivalent with Eq. (15), assuming that $K_e = K_2/K_1$. Therefore, the two treatments of ion exchange reactions are equivalent: exchange isotherm equations can be transformed to the ones that used the law of mass action.

The neglecting of the activity coefficients in the description of Eq. (20) is usual for example in the surface complexation models, but it is not absolutely correct thermodynamically [17].

5 Ion exchange isotherm for heterovalent exchange

The transformation of the equilibrium (or selectivity) constants and the ion exchange isotherms can easily be made only for homovalent ion exchange because the ion exchange

isotherms usually do not take into consideration the heterovalent character of the ion exchange. This causes additional serious problems in the evaluation of isotherm parameters. It is shown for the exchange of monovalent and divalent cations:



In this exchange process the number of exchange sites can be expressed for the monovalent ions as follows:

$$\zeta_{\text{mono}} = a_1 + 2a_2 \quad (22)$$

To construct the c/a vs. c function (similarly to Eq. (18), the equilibrium constant of the reaction in Eq. (21) is described. The surface concentration of the ions can be expressed by surface fractions, using again that $\Theta_1 = \frac{a_1}{\zeta}$ and $\Theta_2 = \frac{a_2}{\zeta}$:

$$\begin{aligned} K_e &= \frac{c_2 \left(\frac{a_1}{\zeta_{\text{mono}}} \right)^2}{c_1^2 \frac{a_2}{\zeta_{\text{mono}}}} \\ &= \frac{1}{\zeta_{\text{mono}}} \frac{c_2 a_1^2}{c_1^2 a_2} = \frac{1}{\zeta_{\text{mono}}} \frac{c_2 a_1^2}{c_1^2 \frac{\zeta_{\text{mono}} - a_1}{2}} = \frac{2}{\zeta_{\text{mono}}} \frac{c_2 a_1^2}{c_1^2 (\zeta_{\text{mono}} - a_1)} \end{aligned} \quad (23)$$

By equivalent mathematical transformation of Eq. 23 we obtain:

$$\frac{a_1^2}{\zeta_{\text{mono}} - a_1} = K_e \zeta_{\text{mono}} \frac{c_1^2}{2c_2} \quad (24)$$

The reciprocal of Eq. (24) is as follows:

$$\frac{\zeta_{\text{mono}} - a_1}{a_1^2} = \frac{\zeta_{\text{mono}}}{a_1^2} - \frac{1}{a_1} = \frac{2}{K_e \zeta_{\text{mono}}} \frac{c_2}{c_1^2} \quad (25)$$

From here

$$\frac{\zeta_{\text{mono}}}{a_1^2} c_1 = \frac{c_1}{a_1} + \frac{2}{K_e \zeta_{\text{mono}}} \frac{c_2}{c_1} \quad (26)$$

Divided by ζ_{mono} :

$$\frac{c_1}{a_1^2} = \frac{1}{\zeta_{\text{mono}}} \left(\frac{c_1}{a_1} + \frac{2}{K_e \zeta_{\text{mono}}} \frac{c_2}{c_1} \right) \quad (27)$$

then multiplied by a_1 :

$$\frac{c_1}{a_1} = \frac{1}{\zeta_{\text{mono}}} \left(c_1 + \frac{2}{K_e \zeta_{\text{mono}}} \frac{a_1 c_2}{c_1} \right) \quad (28)$$

Similar isotherm equation can be derived for the divalent cation, expresses ζ for the divalent cation:

$$\frac{c_2}{a_2} = \frac{1}{\zeta_{di}} \left(c_2 + \frac{K_e c_1^2}{2 a_1} \right) \quad (29)$$

Eqs. (28) and (29) can be plotted as a c/a vs. c function. As seen, the second member in the parenthesis of the right side of Eqs. 28 and 29 are more complex quantities than in case of homo-valent exchange, containing variable quantities, namely the concentrations of both ions in the solution and the sorbed quantity of the exchanging ion, as well. So, when evaluating c/a vs. c function by the ion exchange isotherm, the “intercept” depends on a lot of parameters, so give no information on the energy distribution of the surface.

6 Conclusions

If we study the accumulation of a substance on a surface, the first important thing is to explore the mechanism of the sorption process. The experimental data can be interpreted correctly by isotherm or other thermodynamic equations only when the mechanism is known and the applied treatment corresponds to this mechanism. If not, the thermodynamic parameters will be not correct, the isotherm equation will give fault values for the number of surface sites and the parameter characteristic for the sorption energy. Furthermore, a homogeneous surface can be seen to be heterogeneous just because of the application of an inadequate model. Obviously, there are heterogeneous surfaces, but the curved shape of a badly applied isotherm provides no information about the heterogeneity.

In order to study the energy distribution of surface sites, the thermodynamic equations, including isotherms, have to be selected according to the sorption mechanism. All variable quantities have to be determined which are involved in the applied model (e.g. concentration of the competing substances in all phases: in liquid and solid including the interface). These quantities have to be treated as independent variable during the estimation of the sorption parameters. This treatment can be combined with the methods for the determination of the energy distribution functions.

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