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Ion exchange isotherms in solid: electrolyte solution systems

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Abstract It is shown show that the ion exchange isotherms and the law of mass action are equivalent, the c/a versus c functions can be derived from the law of mass action (c and a: the concentration of ions in ion exchanger and solution, respectively). The equations are applied for cation exchange processes of bentonite clay (cobalt, manganese, mercury ions with calcium-bentonite; strontium ions with sodium-bentonite; cesium ions with lanthanide bentonite; lutetium ion with calcium-bentonite). The linear or non-linear shape of the isotherms does not prove the heterogeneity of the ion exchanger or the interaction among the sorbed cations.

Keywords Bentonite · Heterovalent exchange · Homovalent exchange · Ion exchange isotherm · Law of mass action

Introduction

The correct thermodynamic description of the ion exchange processes between a solution and the surface of solid ion exchangers is very problematic because the quantities characterizing the process mostly depend on the molar fraction of the ions on the surface. This fact is treated by different ways in the models describing the ion exchange. The first approach was proposed by [1] using the law of mass action. The general features of the additional models are described briefly [2].

1. The models applying the law of mass action [3–11] introduce the term of surface activity coefficient.
2. The models where the ion exchange processes included into the surface complexation models, take into account the surface electric work, e.g. [2, 12–16].
3. Those that use competitive ion exchange isotherm equations consider heterogeneous surface characterized by an energy distribution function [17–20].

All models, however, have the same deficiency, namely the concentrations in the solid ion exchanger and solution can be measured experimentally, however, the surface activity coefficients, the surface electric work as well as the energy distribution function can only be estimated. It means that the models are adapted to the experimental data and the best-fitted model is used, thus the selected model has no thermodynamically significant meaning [21].

Despite of their deficiencies, the models mentioned tend to evaluate the ion exchange processes by thermodynamically correct ways. For this reason, the results of the different authors can be compared if a given model is systematically used.

However, there are many papers in the literature which totally neglect the mechanism of the ion exchange process, apply formal adsorption isotherms, calculate meaningless isotherm constants and thermodynamic parameters; then utilize them in the prognosis of sorption, desorption, isolation, leaching, migration, etc. processes, e.g. [22–27]. The main goal of this paper is to illustrate that the evaluation of the ion exchange processes by adsorption isotherm models leads to incorrect results.

As mentioned previously, the adsorption isotherms are used in many papers neglecting the sorption mechanism,

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and the differences between adsorption and ion exchange, namely adsorption is defined as the increase in the concentration of a substance at the interface due to the operation of surface forces, while ion exchange is the equivalent change of the ions on the surface to other ions [2]. The motivation of the application of the adsorption isotherms is that both ion adsorption and exchange result in the increase of surface excess concentration of the ions. However, in case of ion adsorption, the net charge of the surface changes, while in case of ion exchange this remains constant. In our previous the papers, the misleading information obtained by the formal applications of adsorption isotherms is studied using a simple mathematical model of homovalent ion exchange on homogeneous surface [28, 29]. It was demonstrated that the curved (nonlinear) shape and regression values of the adsorption isotherm (c/a vs c plots) models give correct information neither on the surface heterogeneity nor the interactions among the sorbed species. As a result of the formal application of the sorption isotherms neglecting the sorption mechanism, the utilization of the isotherm constants in thermodynamic calculations and prognosis of sorption processes is not adequate.

In our previous papers mentioned above, we made principle calculations without any experimental results. In this paper, real ion exchange systems are studied and the exchange processes are evaluated by correct ion exchange isotherms. Firstly, the ion exchange isotherm equations will be derived from the law of mass action both for homovalent and heterovalent ion exchange reactions. Then, the ion exchange isotherms will be applied for cation exchange in bentonite clay rock.

Bentonite rocks are frequently used as natural and engineering barriers in waste disposals and environmental protection [2, 30, 31], but this is a suitably model substance in theoretical studies too. The main mineral component of bentonite rocks is montmorillonite, a swelling aluminosilicate clay mineral. Montmorillonite has a permanent negative layer charge which is compensated by exchangeable cations in the interlayer space [2, 30]. In our studies, calcium- and sodium-bentonite is applied, that is bivalent calcium ions and monovalent sodium ions, respectively, are in the interlayer space. For illustrating the homovalent ion exchange isotherms, the bivalent calcium ions are exchanged to other bivalent cations (cobalt, manganese, and mercury). The application of the heterovalent cation exchange isotherms, the exchange between monovalent and bivalent cations (sodium and strontium ions), bivalent and trivalent cations (calcium and lutetium cations) are studied. In addition, trivalent cation exchanged bentonites (praseodymium-, neodymium-, and dysprosium-bentonite) are prepared from calcium-bentonite and using them the

exchange of monovalent and trivalent cations (cesium and lanthanide cations) are studied.

It is important to note that the main goal of the paper is not the study of cation exchange on bentonite. For this reason, we will qualitatively compare our data to the literature data, however, there are many thermodynamic quantities describing the cation exchange on bentonite (except lanthanide cations) e.g. [8, 32–36] and we also showed our results and the experimental conditions in detail in other papers [2, 37–40]. The results of the exchange with lanthanide bentonites are new; they will be published in another paper for all lanthanide cations.

Theory: cation exchange processes on solid/electrolyte solution interfaces

The equilibrium of ion exchange processes is usually evaluated by sorption isotherms or on the basis of the law of mass action. Mostly, the so-called "linearized" sorption isotherms are used, i.e., the distribution ratios of the ions between the solution and solid ion exchanger is plotted as a function of the equilibrium concentration of that ion; c/a versus c plots are constructed. Now, we will show that the two methods, ion exchange isotherms and the law of mass action are equivalent, the c/a versus c functions can be derived from the law of mass action.

The general equation of a cation exchange between Me_A cation with z_{A^+} charge (in the solution) and Me_B cation with z_{B^+} charge (on the solid surface) can be expressed as:

$$z_B Me_A^{z_{A^+}} + z_A Me_B^{z_{B^+}} - S \rightleftharpoons z_A Me_B^{z_{B^+}} + z_B Me_A^{z_{A^+}} - S \quad (1)$$
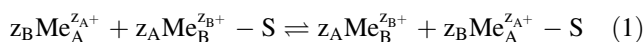
where S means the exchange sites of the solid. In case of $z_{A^+} = z_{B^+}$, the ion exchange is homovalent, in other cases heterovalent.

The equilibrium constant ($K_{B,A}$) of the reaction (Eq. 1) is:

$$K_{B,A} = \frac{a_A^{z_B} c_B^{z_A}}{a_B^{z_A} c_A^{z_B}} \quad (2)$$

where a's and c's mean the concentrations (activities) of the ions in mols on the solid and in the solution, respectively. The correct thermodynamic treatment of the exchange equilibrium applies the activities of the ions both in solution and solid. In diluted solution, the activities and concentrations of the ions can be considered to be equal. The activities of the ions in the solid surface, however, are very problematic, they cannot be determined experimentally. For this reason, in this paper we use the concentrations both in the solution and solid. The c/a versus c functions for homovalent and heterovalent exchanges can be derived from Eq. 2 as discussed in Appendix.

In this paper, different cation exchange processes will be evaluated by the equations in Table 1 derived in Appendix.

Experimental

Cation exchange experiments were made on calcium-bentonite (Istenmezeje, Hungary) and sodium-bentonite (Valea Chioarului, Romanian) clay rocks. The mineral compositions were determined by X-ray diffraction (intensity of the basal reflection) and thermoanalytical (weight loss upon heating) data. Cation exchange capacity was determined by ammonium acetate method [41] (Table 2).

The equilibrium of the cation exchange processes was studied in the systems as listed below:

Homovalent exchanges:

– The exchange of cobalt(II) and calcium(II) ions on calcium-bentonite (Istenmezeje, sedimented) [2, 40],
– The exchange of manganese(II) and calcium(II) ions on calcium-bentonite (Istenmezeje, sedimented) [2, 37],
– The exchange of mercury(II) and calcium(II) ions on calcium-bentonite (Istenmezeje, sedimented) [38].

Heterovalent exchanges:

– The exchange of strontium(II) and sodium(I) ions on sodium-bentonite (Valea Chioarului),

– The exchange of cesium(I) and rare earth (Pr(III), Nd(III), Dy(III)) cations on Pr(III)-, Nd(III)-, and Dy(III)-bentonite produced from calcium-bentonite (Istenmezeje, natural),
– The exchange of lutetium(III) and calcium(II) ions on calcium-bentonite (Istenmezeje, sedimented).

The rare earth (REE)-bentonites were prepared from REE-oxides as follows. The oxides of REEs (the oxides of Pr, Nd, Dy) were dissolved in concentrated HCl. The excess of HCl was evaporated; the remaining chloride of REEs was dissolved in water. REEs were precipitated in their carbonate form using ammonium carbonate. After filtering, the REE-carbonates were dissolved in known amount of 0.1 mol dm^{-3} HClO$_4$ solution. This REE-perchlorate solution (pH 5–5.5, cca. 0.05 mol dm^{-3}) was used in the ion exchange procedure. 4 g Ca-bentonite (Istenmezeje, natural) was suspended in 20 cm^3 of the resulting REE-perchlorate solution. The suspension was stirred for 4–5 h at room temperature, then filtered on cellulose nitrate membrane filter with 0.45 μm pore size (Sartorius). The bentonite was suspended again in 20 cm^3 solution of the same REE-perchlorate, and the cycle started again. Altogether the ion-exchange procedure was carried out three times. After the three exchanges, no more rare earth cations were taken up by bentonite under the experimental conditions. At the end of the preparation, the REE-bentonite was

Table 1 c/a versus c functions of homo and heterovalent ion exchanges derived from the law of mass action

Homovalent ion exchange

$$\frac{c_A}{a_A} = \frac{1}{\zeta}\left(c_A + \frac{c_B}{K_{B,A}}\right) \quad (10) \qquad\qquad \frac{c_B}{a_B} = \frac{1}{\zeta}\left(c_B + K_{B,A}c_A\right) = \frac{1}{\zeta}\left(c_B + \frac{c_A}{K_{A,B}}\right) \quad (12)$$

Heterovalent ion exchange

Mono and bivalent ions	Number of exchange sites for monovalent ion	$\frac{c_1}{a_1} = \frac{1}{\zeta_{mono}}\left(c_1 + \frac{2}{K_{2,1}}\frac{a_1c_2}{c_1}\right)$ (27)	$\frac{c_2}{a_2} = \frac{1}{\zeta_{mono}}\left(2c_2 + \frac{1}{K_{1,2}}\frac{c_1^2}{(\zeta_{mono}-2a_2)}\right)$ (22)
	Number of exchange sites expressed for bivalent ion	$\frac{c_1}{a_1} = \frac{1}{\zeta_{bi}}\left(\frac{1}{2}c_1 + \frac{1}{K_{2,1}}\frac{a_1c_2}{c_1}\right)$ (32)	$\frac{c_2}{a_2} = \frac{1}{\zeta_{bi}}\left(c_2 + \frac{1}{K_{1,2}}\frac{c_1^2}{2^2\times(\zeta_{bi}-a_2)}\right)$ (31)
Mono- and trivalent ions	Number of exchange sites for monovalent ion	$\frac{c_1}{a_1} = \frac{1}{\zeta_{mono}}\left(c_1 + \frac{3}{K_{3,1}}\frac{a_1^2c_3}{c_1^2}\right)$ (33)	$\frac{c_3}{a_3} = \frac{1}{\zeta_{mono}}\left(3c_3 + \frac{1}{K_{1,3}}\frac{c_1^3}{[\zeta_{mono}-3a_3]^2}\right)$ (34)
	Number of exchange sites expressed for trivalent ion	$\frac{c_1}{a_1} = \frac{1}{\zeta_{tri}}\left(\frac{1}{3}c_1 + \frac{1}{K_{3,1}}\frac{a_1^2c_3}{c_1^2}\right)$ (35)	$\frac{c_3}{a_3} = \frac{1}{\zeta_{tri}}\left(c_3 + \frac{1}{K_{1,3}}\frac{c_1^3}{3^3[\zeta_{tri}-a_3]^2}\right)$ (36)
Bi- and trivalent ions	Number of exchange sites for monovalent ion	$\frac{c_2}{a_2} = \frac{1}{\zeta_{mono}}\left(2c_2 + \frac{3^2}{K_{3,2}}\times\frac{a_2^2c_3^2}{[\zeta_{mono}-2a_2]c_2^2}\right)$ (37)	$\frac{c_3}{a_3} = \frac{1}{\zeta_{mono}}\left(3c_3 + \frac{2^3}{K_{2,3}}\frac{a_3c_2^3}{[\zeta_{mono}-3a_3]^2c_3}\right)$ (38)
	Number of exchange sites expressed for bivalent ion	$\frac{c_2}{a_2} = \frac{1}{\zeta_{bi}}\left(c_2 + \frac{1.5^2}{K_{3,2}}\times\frac{a_2^2c_3^2}{[\zeta_{bi}-a_2]c_2^2}\right)$ (39)	$\frac{c_3}{a_3} = \frac{1}{\zeta_{bi}}\left(1.5c_3 + \frac{1}{K_{2,3}}\frac{a_3c_2^3}{[\zeta_{bi}-1.5a_3]^2c_3}\right)$ (40)
	Number of exchange sites expressed for trivalent ion	$\frac{c_2}{a_2} = \frac{1}{\zeta_{tri}}\left(\frac{2}{3}c_2 + \frac{1}{K_{3,2}}\times\frac{a_2^2c_3^2}{[\zeta_{tri}-\frac{2}{3}a_2]c_2^2}\right)$ (41)	$\frac{c_3}{a_3} = \frac{1}{\zeta_{tri}}\left(c_3 + \frac{1}{K_{2,3}}\frac{\frac{2^3}{3}a_3c_2^3}{[\zeta_{tri}-a_3]^2c_3}\right)$ (42)

For the homovalent ion exchange, the concentrations are expressed in moles, the two columns contain the distribution of the A and B ions, as a function of the solution concentration of A and B, respectively. For the heterovalent ion exchanges, the concentrations can be expressed for the ions with different valencies (2nd column). The 3rd and 4th columns contain the distribution of the A and B ions, as a function of the solution concentration of A and B, respectively

Table 2 Mineral composition and cation exchange capacity of bentonite rocks (m/m%)

Sample	Montmorillonite	Illite	Kaolinite	Kalifeldspar	Amorphous	Crystobalite + opal CT	Zeolite	Calcite	Quartz	CEC (meq/g)
Ca-bentonite (Istenmezeje (HU), sedimented)	91		3		1			5	tr	1.04
Ca-bentonite (Istenmezeje (HU), natural)	71	8	3			12		2	4	0.81
Na-bentonite [Valea Chioarului (RO)]	48	8		10	5	25	4			0.61

washed with water, air-dried and powdered in an agate mortar.

The REE concentration of REE-bentonites was determined by an energy dispersive X-ray fluorescence system. The parts of the system were: radioactive source (185 MBq ^{241}Am), Si(Li) detector with 20 mm^2 surface, 3.5 mm evaporated layer, Canberra DSA 1000 digital spectrum analyzer, Canberra Genie 2000 3.0 spectroscopy software.

The sorption experiments were done by the conventional batch technique.

Accurately weighted bentonite samples were suspended 20.0 cm^3 of double distilled water, and the pH was adjusted by adding 0.1 mol/dm^3 perchloric acid solutions. The experimental conditions are summarized in Table 3.

During the cobalt(II) ion—calcium-bentonite, manganese(II) ion—calcium-bentonite, and mercury(II) ion—calcium-bentonite cation exchange, calcium-bentonite labeled with ^{45}Ca isotope was applied, the production of which is discussed elsewhere (e.g. [39]). By measuring the radioactivity of ^{45}Ca isotope, the quantity of the calcium ions leaving the bentonite can be measured.

The suspensions were stirred at constant speed (1440 rpm) for 60 min to reach the solubility equilibrium between the bentonite and the solution. It was checked by conductivity measurements. Then solutions of cation perchlorate were added to the suspension. The cations were labeled with radioactive isotopes (supplied by Institute of Isotopes Co., Ltd. Budapest, Hungary) (Table 4), except lutetium, which concentration in bentonite was determined by X-ray fluorescence analysis as discussed previously. The suspensions were stirred at additional 120 min at 1440 rpm. As experimentally checked by previous kinetic studies, this time is enough to reach equilibrium. The liquid and solid phases were separated with a membrane filter (0.45 μm pore size). The pH was measured before and after filtration, and the difference of pH was <0.06. pH was measured by Metrohm 654 pH meter with combined glass electrode (Catalog number 6.0220.100).

It is important to note that the concentration of the solution was <0.001 mol dm^{-3} that is the concentration and activity of the cations was practically the same. For this reason, the ionic strength was not adjusted because we did not want to complicate the cation exchange by a third cation. In addition, the great concentration of a support electrolyte could change the surface of the bentonite significantly [11]. In this way, the experimental uncertainties are lower.

Table 3 Conditions of sorption experiments

Exchanging ion	Sorbent	Mass of sorbent (mg)	Volume of solution (cm^3)	pH of suspension	Temperature (°C)
Cobalt(II)	Ca-bentonite	10	20	6.5	33
Manganese(II)	Ca-bentonite	50	20	6.6	20
Mercury(II)	Ca-bentonite	100	20	2.76	25
Strontium(II)	Na-bentonite	10	20	7	25
Cesium(I)	Pr(III)-, Nd(III)-, Dy(III)-bentonite	50	20	6.5	25
Lutetium(III)	Ca-bentonite	100	20	5.5	25

Table 4 Radiophysical properties of tracers

Isotope	Half-life	Type and energy of decay for measurement
^{60}Co	5.27 years	Gamma 1.173 MeV
		Gamma 1.333 MeV
^{54}Mn	312.3 days	Gamma 0.835 MeV
^{203}Hg	46.6 days	Gamma 0.279 MeV
^{45}Ca	164 days	Beta. $E_{max} = 0.254$ MeV
^{90}Sr (^{90}Y)	28.79 years	Beta. $E_{max} = 0.546$ MeV (^{90}Sr) and 2.280 MeV (^{90}Y)
^{137}Cs (^{137m}Ba)	30.17 years	Beta. $E_{max} = 0.514$ MeV (^{137}Cs)
		Gamma 0.662 MeV (^{137m}Ba)

The equilibrium distribution of the exchanging cations was determined using the radioactive tracers. The beta activities of the solution as well as the gamma activities of both the solutions and solid were measured. The decay type and energies are listed in Table 4. The activities of ^{90}Sr–^{90}Y as well as ^{137}Cs–^{137m}Ba parent–daughter pairs were measured after reaching secular equilibrium (1 month and half an hour, respectively).

The beta-activities were measured by a Wallac 1409 liquid scintillation counter. The composition of the scintillator was as follows: 4.0 g 2,5-diphenyl-oxazol (PPO), 257 cm^3 Triton-X 100, 37 cm^3 ethylene glycol, 106 cm^3 ethanol, diluted to 1000 cm^3 with xylene. 1 cm^3 solution was added to 4 cm^3 scintillation cocktail. The gamma activities were measured by a NaI(Tl) scintillation crystal.
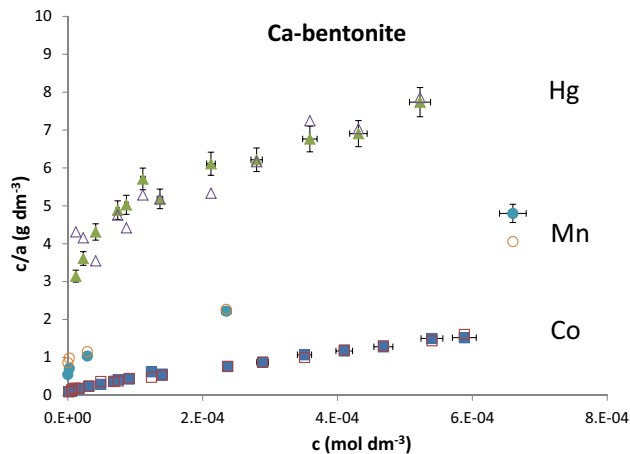
The experiments were done at room temperature (25 °C), except manganese(II) (20 °C) and cobalt ions (33 °C) and open-air atmosphere and repeated three times.

Fig. 1 Homovalent exchange: c/a versus c plots for the exchange of mercury(II), manganese(II), and cobalt(II) ions on Ca-bentonite (Istenmezeje, sedimented). The *filled* and *empty signs* refer to the experimental and calculated (Eq. 10) points, respectively
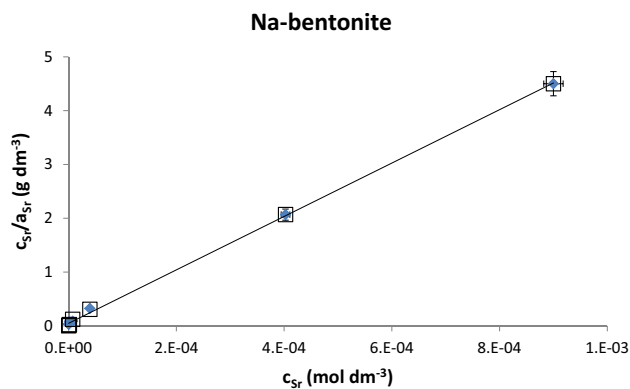
Results and discussion

The cation exchange isotherms that is the c/a versus c plots are shown in Figs. 1, 2, 3 and 4.

As seen in Figs. 1, 2, 3 and 4, the shape of the c/a versus c plots is rather variable: both linear (Figs. 2, 4) and curved (Figs. 1, 3) shapes can be found. The homovalent cation exchange should be expected to be the simplest; however, all plots are more or less curved (Fig. 1). Similarly, some heterovalent exchange studies result in curved c/a versus c plots (monovalent–trivalent ion exchanges, Fig. 3; The error bars are included in this figure (similarly to the other ones), but they are so small that they cannot be seen because of the signs). On the other hand, other heterovalent exchange systems (bivalent–monovalent and trivalent–bivalent exchanges, Figs. 2, 4) show linear c/a versus c plots.

As mentioned in Introduction, in a previous paper a theoretical example has been shown and concluded that the shape of the c/a versus c plots provide no information on the surface heterogeneity or the interactions among the sorbed species [29]. The same conclusions can be drawn in

Fig. 2 Heterovalent exchange of monovalent and bivalent cations: c/a versus c plots for the exchange of strontium(II) ions on Na-bentonite (Valea Chioarului). The *filled* and *empty signs* refer to the experimental and calculated (Eq. 31) points, respectively

practical ion exchange systems, too. As usual in the literature, the c/a versus c plots can be evaluated isotherm equations [25, 26]. The most popular is the formal application of the Langmuir adsorption isotherm (Eq. 43)
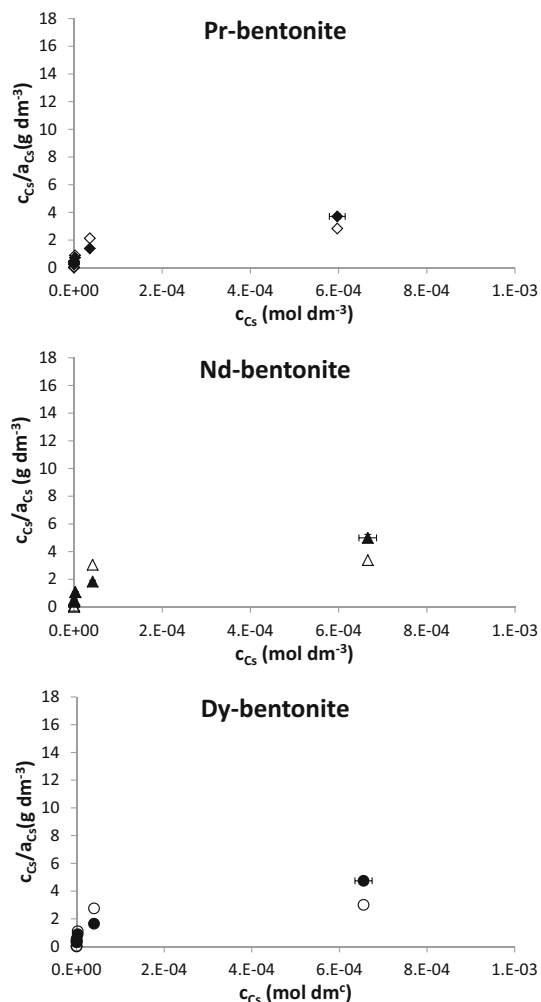
Fig. 3 Heterovalent exchange of monovalent and trivalent cations: c/a versus c plots for the exchange of cesium(I) ions on Pr-, Nd-, and Dy-bentonite (prepared form Ca-bentonite, Istenmezeje natural). The *filled* and *empty signs* refer to the experimental and calculated (Eq. 35) points, respectively

Fig. 4 Heterovalent exchange of trivalent and bivalent cations: c/a versus c plots for the exchange of lutetium(III) ions on Ca-bentonite (Istenmezeje natural). The *filled* and *empty signs* refer to the experimental and calculated (Eq. 40) points, respectively
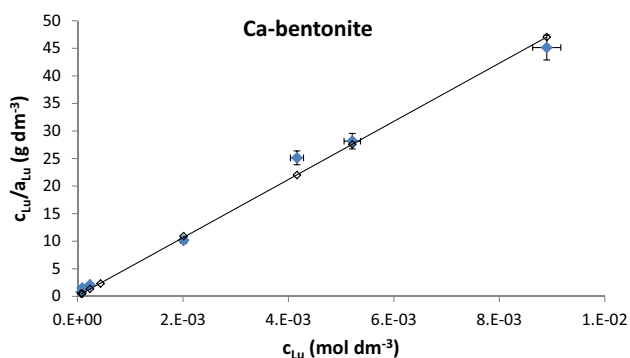
derived for the adsorption of one adsorptive on a perfectly homogeneous surface.

$$\frac{c}{a} = \frac{1}{z}(c + K_L) \tag{43}$$

where c is the equilibrium concentration of the solution, 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), K_L is the parameter characterizing the adsorption energy. According to Eq. 43, c/a versus c plot is linear if the exchange sites are energetically homogeneous. Using the Langmuir isotherm equation, the number of exchange sites and the parameter characterizing the sorption energy are determined from the slope and the intercept of the c/a versus c plot. If the plot is not linear, surface heterogeneity is supposed. The widespread procedure is that linear portions are separated; the slopes and the intercepts are determined and related to the different homogeneous portions of the exchange sites.

However, there are no connections between the non-linearity of the c/a versus c plot and heterogeneity of the exchange sites. As mentioned previously, our experimental plots may be both linear and non-linear (Figs. 1, 2, 3, 4). The c/a versus c plots in the ion exchange systems of cations and bentonite, can be evaluated by the ion exchange isotherm equations in Table 1. The isotherm parameters are summarized in Table 5.

As seen in Table 5, both linear and non-linear/curved c/a versus c plots can be evaluated by the ion exchange isotherm equations derived from the law of mass action (Eq. 2). Neither the surface heterogeneity of the ion exchanger nor the interaction among ions in the ion exchanger phase needs to be supposed.

The number of exchange sites can well be calculated from the ion exchange isotherm equations (Tables 1, 5) provided, of course, correct isotherm equation is used. The homovalent exchanges (mercury, manganese and cobalt ions) show different numbers of exchange sites caused by the pH values of the systems (Table 3). In order to avoid the hydrolysis of the ions, lower pH values are applied in case of mercury ions (pH 2.76). At low pH values, the hydrogen ions can also neutralize the negative layer charge of montmorillonite. The affinity of hydrogen ions to the layer charge is much larger than that of the other cations studied here [40]; thus the exchange sites neutralized by hydrogen ions does not take place in the cation exchange of the metal ions. Thus, only the exchange of calcium and mercury cations on the exchange sites not occupied by hydrogen ions is considered showing by the less ζ value.

The K parameters (equilibrium constants), however, have rather high standard deviations, thus at most the relative preference of the cations can be compared. The high

Table 5 The isotherm parameters of cation exchange processes calculated by ion exchange isotherm equations in Table 1 (4th column)

	pH of suspension	K	ζ_{mono} (mol/g)	Eq	Preferred ion
Co–Ca	6.5	0.64 ± 0.12	$9.3E{-}04 \pm 3.9E{-}5$	10	Co
Mn–Ca	6.6	0.85 ± 0.15	$6.2E{-}04 \pm 3.9E{-}5$	10	Mn
Hg–Ca	2.76	1.02 ± 0.36	$4.2E{-}04 \pm 6.0E{-}6$	10	$\sim$
Sr–Na	7	0.89 ± 0.38	$9.9E{-}04 \pm 1.0E{-}4$	31	Sr
Cs–Pr	6.5	37.7 ± 7.8	$6.0E{-}04 \pm 8.0E{-}6$	35	Pr
Cs–Nd	6.5	108.8 ± 29.4	$6.3E{-}04 \pm 1.5E{-}6$	35	Nd
Cs–Dy	6.5	69.5 ± 20.9	$5.7E{-}04 \pm 1.2E{-}5$	35	Dy
Lu–Ca	5.5	0.01 ± 0.01	$8.5E{-}04 \pm 1.3E{-}5$	40	Lu

standard deviation is caused isotherm equations. The equations in Table 1 show that the shape of the c/a versus c plots are determined by the ratio of the two parameters in the parenthesis of the right side of the equation. The first member is always the equilibrium concentration of a cation in the solution (or this value is multiplied by a number characterizing the valencies), the second member, however, is a complex quantity, which contains the equilibrium constant and the concentration of the ions in the solid and solution, on the powers determined by the stoichiometry of the ion exchange reaction. If the numerical values of the two members are within the same order of magnitude, the c/a versus c plot will be non-linear. If the value of the second member is much less than the equilibrium concentration, the plot will be linear. The linearity and non-linearity depends on the concentration range studied, so we can find linear portions in c/a versus c plot taken up in a wide concentration range.

It is interesting to note that the simple homovalent exchange always shows non-linear c/a versus c plot if the affinity of the ions to the exchanger phase is similar ($K \sim 1$) because the concentration of the A and B ions in the solution (c_A and c_B) continuously changes and depends on each other. As increasing the concentration of A ion in the solution (c_A), A ions exchange more and more B ion from the solid ion exchanger phase; and the concentration of B ions in the solution (c_B) increases.

The authors do not neglect the possibility of a heterogeneous exchanger or the interaction among the sorbed species; however, this is not proved alone by the shape of the isotherms.

In case of montmorillonite, the ions are bound in the interlayer space by electrostatic forces: the negative layer charge is neutralized by cations. Since the range of the electrostatic forces is long, the heterogeneity of the exchange sites can hardly be imagined.

Independently off the uncertainties of the determination of K's, our values are in a fairly good agreement with the literature data for homovalent and monovalent-bivalent exchanges (e.g. [8]).

Conclusion

As emphasized in Introduction, the some authors in the literature believe that the different adsorption isotherm equations are suitable for the correct evaluation of heterogeneous ion exchange processes, and the isotherm constants can be applied in thermodynamic calculations. This is not true because there is a basic difference between the adsorption and ion exchange: the main aspect of adsorption is the decrease of the surface energy and for this reason the adsorption occurs on the empty sites of the surface. This is valid even during the binary adsorption when the adsorbed components can exchange with each other after the first contact until the energetically preferential distribution is achieved. The ion exchange, however, means the equivalent exchange of the ions with the same charge; this means that the process takes place on the surface sites which are already occupied by ions. As a result, the adsorption of one component is possible on an "empty" surface, the ion exchange, however, is always a competitive process. For this reason, the mathematical formulas of the adsorption and ion exchange processes are different by two reasons: the first one is the mentioned competition of the ions. The second one is the range of the coverage: in case of adsorption the coverage can spread from zero to one; in case of ion exchange the coverage is always equal to 1 [28, 29].

In this paper, we derived the ion exchange isotherms of different homovalent and heterovalent ion exchanges and used them for the evaluation of cation exchange processes on bentonite clay rocks. The isotherm parameters, the number of exchange sites as well as the equilibrium constants of the cation exchange were determined. The number of exchange sites could be determined with high accuracy; the standard deviation of the equilibrium constants of the cation exchange is rather great, thus only the relative preference of the ions can be stated.

It is also shown that the linear or non-linear/curved shape of the isotherms does not prove the heterogeneity of the ion exchanger or the interaction among the sorbed

cations. As mentioned previously, the authors do not neglect the possibility of a heterogeneous exchanger or the interaction among the sorbed species; however, this is not proved alone by the shape of the isotherms.

Appendix

Homovalent exchange

In case of homovalent exchange, all exponents in Eq. 2 are equal to 1. Thus,

$$K_{B,A} = \frac{a_A c_B}{a_B c_A} \tag{3}$$

In the ion exchange processes, all exchange sites are always occupied by the ions, that is, the cation exchange capacity, or by the term used in the sorption isotherm, the number of exchange sites (ζ) is the sum of the concentration of the ions on the solid (a_A and a_B):

$$\zeta = a_A + a_B \tag{4}$$

From here,

$$a_B = \zeta - a_A \tag{5}$$

By substituting Eq. 5 into Eq. 3:

$$K_{B,A} = \frac{a_A c_B}{(\zeta - a_A) c_A} \tag{6}$$

$$\frac{(\zeta - a_A)}{a_A} = \frac{c_B}{K_{B,A} c_A} = \frac{\zeta}{a_A} - 1 \tag{7}$$

$$\frac{\zeta}{a_A} = 1 + \frac{c_B}{K_{B,A} c_A} \tag{8}$$

$$\frac{c_A \zeta}{a_A} = c_A + \frac{c_B}{K_{B,A}} \tag{9}$$

$$\frac{c_A}{a_A} = \frac{1}{\zeta}\left(c_A + \frac{c_B}{K_{B,A}}\right) \tag{10}$$

Equation 10 is equal to the homovalent ion exchange isotherm derived [29] where

$$K_{B,A} = \frac{K_B}{K_A} \tag{11}$$

where K_A and K_B are the parameter characterizing the Gibbs energy of the ions.

The differences between the homovalent ion exchange isotherm equation (Eq. 10), the simple and competitive Langmuir adsorption isotherms were discussed in detail in [29].

Similar equation can be described for the B ion:

$$\frac{c_B}{a_B} = \frac{1}{\zeta}\left(c_B + K_{B,A} c_A\right) = \frac{1}{\zeta}\left(c_B + \frac{c_A}{K_{A,B}}\right) \tag{12}$$

Heterovalent exchange: the exchange of monovalent and bivalent ions

Firstly, let's assume a monovalent ion exchanger and exchange the monovalent ions to bivalent ones:

$$2Me_1 - S + Me_2^{2+} = Me_2 - S + 2Me_1^+ \tag{13}$$
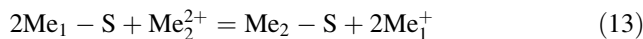
The indexes 1 and 2 mean the valences of the ions. The equilibrium constant of the process (Eq. 13) is:

$$K_{1,2} = \frac{a_2 c_1^2}{a_1^2 c_2} \tag{14}$$

where the index 1, 2 means that monovalent ions are exchanged to bivalent ions.

The number of exchange sites (ζ) can be expressed both for the monovalent and bivalent ions. For monovalent ions (ζ_{mono}):

$$\zeta_{mono} = a_1 + 2a_2 \tag{15}$$

$$a_1 = \zeta_{mono} - 2a_2 \tag{16}$$

Equation 16 can be substituted into Eq. 14, we obtain:

$$K_{1,2} = \frac{a_2 c_1^2}{(\zeta_{mono} - 2a_2)^2 c_2} \tag{17}$$

and from here

$$1 = \frac{1}{K_{1,2}} \times \frac{a_2 c_1^2}{(\zeta_{mono} - 2a_2)^2 c_2} \tag{18}$$

We make some equivalent mathematical transformations (Eqs. 19–21):

$$\frac{\zeta_{mono} - 2a_2}{a_2} = \frac{\zeta_{mono}}{a_2} - 2 = \frac{1}{K_{1,2}} \times \frac{c_1^2}{(\zeta_{mono} - 2a_2) c_2} \tag{19}$$

$$c_2\left(\frac{\zeta_{mono}}{a_2} - 2\right) = \frac{1}{K_{1,2}} \frac{c_1^2}{(\zeta_{mono} - 2a_2)} \tag{20}$$

$$\zeta_{mono} \frac{c_2}{a_2} = 2c_2 + \frac{1}{K_{1,2}} \times \frac{c_1^2}{(\zeta_{mono} - 2a_2)} \tag{21}$$

Finally, we obtain a c_2/a_2 versus c_2 function (Eq. 22):
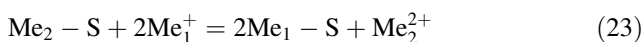
$$\frac{c_2}{a_2} = \frac{1}{\zeta_{mono}}\left(2c_2 + \frac{1}{K_{1,2}} \frac{c_1^2}{(\zeta_{mono} - 2a_2)}\right) \tag{22}$$

Formally, Eq. 22 is a sorption isotherm for the bivalent ions in a monovalent-bivalent ion exchange process.

Similar equation can be also derived for the monovalent ions. In order to do this, consider the reverse reaction of

Eq. 13 when bivalent ions are exchanged to monovalent ions:

$$Me_2 - S + 2Me_1^+ = 2Me_1 - S + Me_2^{2+} \tag{23}$$

The equilibrium constant of Eq. 23 is:

$$K_{2,1} = \frac{c_2 a_1^2}{c_1^2 a_2} = \frac{1}{K_{1,2}} \tag{24}$$

Equation 24 expresses that the equilibrium constants ($K_{1,2}$ and $K_{2,1}$) are reciprocal to each other.

From Eq. 15, we can express a_2:

$$a_2 = \frac{\zeta_{mono} - a_1}{2} \tag{25}$$

By substituting Eq. 25 into Eq. 24, we obtain:

$$K_{2,1} = \frac{c_2 a_1^2}{c_1^2 \frac{\zeta_{mono} - a_1}{2}} \tag{26}$$

Equation 26 is transformed as Eq. 17 (details in Eqs. 18–21):

$$\frac{c_1}{a_1} = \frac{1}{\zeta_{mono}} \left(c_1 + \frac{2}{K_{2,1}} \frac{c_2 a_1}{c_1} \right) \tag{27}$$

As mentioned previously in this paragraph, the number of exchange sites can be expressed to bivalent ions (ζ_{bi}) as follows:

$$\zeta_{bi} = \frac{a_1}{2} + a_2 \tag{28}$$

From here the concentration of the ion in the solid ion exchanger are:

$$a_1 = 2(\zeta_{bi} - a_2) \tag{29}$$

$$a_2 = \zeta_{bi} - \frac{a_1}{2} \tag{30}$$

By substituting Eqs. 29 and 30 into Eqs. 17 and 24, respectively, and after similar mathematical transformations, we obtain the c_2/a_2 versus c_2 functions:

$$\frac{c_2}{a_2} = \frac{1}{\zeta_{bi}} \left(c_2 + \frac{1}{K_{1,2}} \frac{c_1^2}{2^2 \times (\zeta_{bi} - a_2)} \right) \tag{31}$$

$$\frac{c_1}{a_1} = \frac{1}{\zeta_{bi}} \left(\frac{1}{2} c_1 + \frac{1}{K_{2,1}} \frac{a_1 c_2}{c_1} \right) \tag{32}$$

Similarly, the reaction equations and equilibrium constants of monovalent and trivalent, bivalent and trivalent ions, respectively, can be described. The number of exchange sites can be expressed all for the mono, bi and trivalent cations; and from here the c/a versus c functions can be derived. These functions are summarized in Table 1.

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