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STANDARD GIBBS ENERGY CHANGES AND PARTICLE SIZE DISTRIBUTION FOR THE Na—Ca EXCHANGE EQUILIBRIUM IN THE MONTMORILLONITE—WATER SYSTEM

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The exchange reaction between the single charged Na *and the double charged* Ca *on the bentonite from Braňany has an endothermic character with* $\Delta G^\circ = -0.398$ *kJ/mol eq*. The selectivity coefficients are not constant within the entire occupation of the surface by exchange cations. This property is prevailingly due to the formation of tactoids. It has been found on the basis of the activity coefficients of the ions bound on the surface of montmorillonite that the adsorption energy depends on the character of the surface. The increase of selectivity for* Ca^{2+} *of mineral in an area where this cation is widely distributed on the surface is probably caused by the presence of active centres with unequal bond energy.*

INTRODUCTION

Some phenomena in the suspension of montmorillonite, such as colligative properties, viscosity, swelling etc., are influenced by the size of floccules. According to the theory of flocculation, the stability of lyophobic colloids mostly depends on the values of attraction and repulsion forces acting between the particles of the system. These forces are composed of the London—van der Waals attraction force, the magnitude of which is mainly practically independent of the electrolyte concentration, and of the repulsion force depending on the electrolyte type and concentration. This repulsion force is a direct result of the presence of electrostatic fields surrounding the colloid—size clay particles.

In order to understand the nature of the exchange reaction between the Na^+ and Ca^{2+} ions on the surface of montmorillonite and the influence of these cations on the flocculation of the suspension, standard Gibbs energy changes and the particle size distribution during an exchange reaction have been determined. Although the value of standard Gibbs energy change does not give direct information on the reaction mechanism, it is possible to use it to calculate the same value for a further cation exchange — in so far as a certain model of exchange reactions is assumed. The thermodynamics of Na—Ca exchange reactions on montmorillonite, and the influence of these cations on flocculation of the suspension have been subject of a number of studies [1—6]. It has been found that it is not possible to compare the thermodynamic data obtained for diverse minerals, as there exist hitherto unknown differences in the manifestations of the changes on the tetrahedra and octahedra, and therefore also imperceptible changes in the ΔG° values.

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*) The abbreviation "mol eq." (or "mmol eq.") used in this article means moles (or millimoles) of chemical equivalents (earlier designated as "eq." or "meq.").

EXPERIMENTAL

Bentonite from Braňany near Most in West Bohemia was used for the study. In an aqueous medium, the fraction of < 1 μm was separated. It contained 80 mass % montmorillonite, 10 mass % kaolinite, 2 mass % quartz, 2 mass % calcite, 3 mass % anatase and 3 mass % lepidocrocite. The cation exchange capacity of Li-montmorillonite was 85 mmol eq. /100 g, and the specific surface determined by the ethylene glycol monoethyl ether retention method was 630 $m^2 . g^{-1}$. The charge deficiency of the montmorillonite structure is due to the isomorphous substitution of Fe, Mn and Mg atoms for aluminium in octahedra (—0.473), and of aluminium for silicon in tetrahedra (—0.290), so that the following holds:

$$(Si_{7.710}\,Al_{0.290})\,(Al_{2.697}\,Fe^{3+}_{0.830}\,Fe^{2+}_{0.022}\,Mn_{0.010}\,Mg_{0.441})$$

$$(Mg_{0.311}\,Ca_{0.015}\,Na_{0.046}\,K_{0.066})\,0_{20}\,(OH)_4.$$

An higher Fe^{3+} content in the structure of montmorillonite has also been confirmed using the DTA method, according to the shift of the endothermic peak to 530 °C. The parameters of the montmorillonite structure from the X-ray analysis are $a_0 = 0.516_5$ nm, $b_0 = 0.895$ nm, $V = 443.6 \times 10^{-24}$ cm^3. The calculated density of the montmorillonite is 2.829 $g.cm^{-3}$. The structure parameters from the crystallochemical formula are $a_0 = 0.520$ nm, $b_0 = 0.901$ nm, $V = 450.0 \times \times 10^{-24}$ cm^3, the specific surface being 747 $m^2.g^{-1}$. The ideal parameter for a hexagonal network $b_{tetr} = 0.909$ nm, the rotational shift of the tetrahedra by an angle α of 10°08′. The theoretical value of the cation exchange capacity of the pure montmorillonite is 101 mmol eq. /100 g.

Methods

After the substitution of the exchange cations by sodium, the bentonite from Braňany was peptized, and the < 1 μm fraction was separated by centrifugation and decantation [7]. The reserve suspension contained 3 mass % of the fine fraction of bentonite. The Ca-montmorillonite was prepared from Na-montmorillonite in a similar way [7]. The basal distance (d_{001}) of the montmorillonite was determined using the X-ray diffraction method from the preparates made by sedimentation from 3 mass % suspension, and by subsequent drying at 20 °C and 35 mass % relative humidity.

In order to perceive the course of the exchange reaction, homoionic montmorillonite in the Na- or Ca-form was weighed into small polyethylene vessels containing 50 ml of a mixed solution NaCl and $CaCl_2$, these components being present in various ratios, but always at an equal total concentration (in mol eq. per litre). The exchange reaction was carried out at 25 ± 0.2 °C, the total concentration of the solution being 0.01, 0.005 and 0.002 mol eq. per litre, and pH 7.0. The suspension was agitated with a high-speed electric mixer and then shaken continuously for one week. After this time, both phases were separated by centrifugation at $G = 2400$ (1—3 h), the temperature being kept constant all the time. In the solution, the respective contents of both cations were analyzed; the content of the cations bound by the solid phase was determined by a three times repeated extraction of 30 ml CH_3COONH_4 the concentration of which was 1 $mol.l^{-1}$, and also by their determination.

The exchange reaction was carried out for:
2 Na-montmorillonite + Ca^{2+} → Ca-montmorillonite + 2 Na^+ and for
Ca-montmorillonite + 2 Na^+ → 2 Na-montmorillonite + Ca^{2+}

Both these exchange reactions were performed in order to reveal whether during this exchange hysteresis phenomena occur. The values and graphs are given for an average isotherm in which the equilibrium was investigated from both directions.

CALCULATION

The number of single platelets in tactoid in a diluted suspension of montmorillonite has been determined by measuring the viscosity of the suspension using a flow viscosimeter. For anisometric particles the relation between the relative viscosity (η_{rel}) and the total volume fraction of the particles of the dispersion proportion (Θ) is expressed by the equation:

$$\eta_{\text{rel}} - 1 = k \, . \, \Theta. \tag{1}$$

According to Simha [8] the proportionality constant k depends on the relation of the long axis (a) to the short one (b) of the tactoid, the form of which is a disc-ellipsoid:

$$k = \frac{4}{3} \frac{a/b}{\text{arctg}\,(a/b)} \, . \tag{2}$$

This equation holds for $a/b > 10$ which is fulfielled in the systems studied. Li-montmorillonite was used as reference sample, in which it was found that in suspensions the single clay platelets are separated from one another. This was also confirmed by X-ray analysis.

Table I shows the experimentally found and calculated values of the relative size of tactoids of montmorillonite with varying ratio of adsorbed Na^+ and Ca^{2+} ions. The symbols n, V, S and m mean the average number of the platelets of montmorillonite in a tactoid, the volume of the tactoid, its surface and mass, respectively.

The thermodynamic equilibrium constant of the reaction

$$2\ \text{Na-montmorillonite} + Ca^{2+} \rightleftarrows \text{Ca-montmorillonite} + 2Na^+ \tag{3}$$

has a form:

$$K = \frac{\bar{a}_{Ca^{2+}}\, a^2_{Na^+}}{\bar{a}^2_{Na^+}\, a_{Ca^{2+}}} = \frac{N_{Ca^{2+}} \cdot (m_{Na^+})^2 \cdot \gamma^2_{Na^+} \cdot f_{Ca^{2+}}}{N^2_{Na^+} \cdot m_{Ca^{2+}} \cdot \gamma_{Ca^{2+}} \cdot f^2_{Na^+}} = K_c \frac{f_{Ca^{2+}}}{f^2_{Na^+}} \, . \tag{4}$$

In this equation refers $\bar{a}$ and a activities of the cations adsorbed on the montmorillonite surface, and of the cations in an equilibrium solution, respectively; m means the molalities of the cations in an equilibrium silution; N is an equivalent fractions of moles of the ions which are bound on the surface of the mineral; γ and f are activity coefficients of the cations in solution and on the mineral surface, respectively.

The selectivity coefficient K_c has been derived from the relation:

$$K_c = \frac{N_{Ca^{2+}} \cdot (m_{Na^+})^2 \cdot \gamma^2_{Na^+}}{N^2_{Na^+} \cdot m_{Ca^{2+}} \cdot \gamma_{Ca^{2+}}} = K'_c \cdot \frac{\gamma^2_{Na^+}}{\gamma_{Ca^{2+}}} \, . \tag{5}$$

The concentrations of the ions in solution and those bound on montmorillonite were ascertained experimentally. The ratio of the solution phase activity coefficients is calculated using the Debye—Hückel extended equation (taking as the distance of closest approach for Na 0.4 nm and for Ca 0.6 nm) [9]. Applying the Gibbs—Duhem equation [10] to the ion exchange for the

$$2\ \text{Na-montmorillonite} + \text{Ca}^{2+} \rightleftarrows \text{Ca-montmorillonite} + 2\ \text{Na}^+$$

reaction, it is possible to obtain the thermodynamic equilibrium constant from K_C found for a finite total concentration of the electrolyte from the formula:

$$\ln K = \int_L (\ln K_c \,.\, \mathrm{d}N_{\mathrm{Na}} - 2\, n_w \,.\, d\ln a_w) + \ln \frac{f_{\mathrm{Ca}}(a)}{f^2_{\mathrm{Na}}(b)} - 1\,, \tag{6}$$

where n_w is the number of moles of water in the surface of the montmorillonite, and a_w is the activity of the imbibed water which due to the identical standard state in both phases is equal to the activity of the water in the equilibrium solution; L is an integration path going from a standard initial state of a pure homoionic Na-montmorillonite to the standard final state of a pure Ca-montmorillonite.

The first integral in equation (6) takes into consideration the dependence of selectivity coefficients on montmorillonite composition. The second and third term refers to the variations in the water sorption by the montmorillonite. The term "—1" means that the divalent Ca substituted for monovalent Na ion. The activity coefficients f at a and b (the third term in eq. 6) has been derived [10] from the relation:

$$\ln f_{\mathrm{Ca}}(a) = 2 \int_{a_w=1}^{a_w(a)} (V_{\mathrm{Ca}}/\tau - n_w) \,.\, d\ln a_w \,. \tag{7}$$

in which V_{Ca} is the equivalent volume of pure Ca-montmorillonite, τ is the molar volume of the water vapor. An entirely similar expression holds for $f_{\mathrm{Na}}(b)$. The V_{Ca}/τ and V_{Na}/τ terms are comparatively small compared to n_w terms for the montmorillonite.

Combining expressions (6) and (7) and neglecting V_{Ca}/τ and V_{Na}/τ terms, the calculation of the thermodynamic eguilibrium constant of the reaction requires for finite total concentration of an equilibrium solution a knowledge of the activity variation of the water and of the ratios of the activity coefficients in the mixed solution during the ion exchange. Furthermore, the application of the thermodynamic method requires a perfect reversibility of the exchange reaction. At a finite total concentration of the electrolyte, we often find an exchange irreversibility during which it appears that with decreasing ionic strength of the solution this irreversibility drops to zero if the electrolyte concentration is a zero also. The increase of the reaction irreversibility may be expected mainly in the area of occupation of the active centres of the montmorillonite where the preference for a certain exchange cation has decreased. But in this area the aggregation of particles strongly increases.

After extrapolation of the stoichiometric equilibrium coefficients K_c' to the zero ionic strength of the solution, the term for the water activity may be neglected and the thermodynamic equilibrium constant may be calculated by integration of the equation of the selectivity coefficient (fig. 2):

$$\ln K \simeq \int_0^1 \ln K_c \,.\, \mathrm{d}N_{\mathrm{Na}} - 1\,. \tag{8}$$

The composition of the exchanger phase is expressed so that $N_{Na} + N_{Ca} = 1$, the equilibrium constant can be written as

$$\ln K \simeq \int_0^1 \ln K_c \, . \, dN_{Ca} - 1 \, . \tag{9}$$

The values of the activity coefficients of Na and Ca were calculated for the ions bound on montmorillonite (fig. 3):

$$\ln f^2_{Na} = N_{Ca} + N_{Ca} \ln K_c - \int_0^{N_{Ca}} \ln K_c \, . \, dN_{Ca} \tag{10}$$

$$\ln f_{Ca} = -N_{Na} - N_{Na} \ln K_c + \int_{N_{Ca}}^{1} \ln K_c \, . \, dN_{Ca} \, . \tag{11}$$

By substitution of K'_c for K_c in calculating the thermodynamic equilibrium constant in equation (9) for the total concentration of the solution 0.01 mol eq./l, the difference between ΔG° ascertained in this way and ΔG° found for a zero ionic strength of the solution was 0.097 kJ . mol^{-1}.

RESULTS AND DISCUSION

Fig. 1 shows the exchange isotherms of the replacement of Na$^+$ by Ca^{2+} as the dependence of the equivalent fractions of moles of Na$^+$ ions bound by montmorillonite (N_{Na}) on the equivalent fractions of moles of Na$^+$ ions which remained in the solution after having attained the exchange equilibrium (X_{Na}). As it may be expected on the basis of a consideration of the Donnan equilibrium of a di-mono-

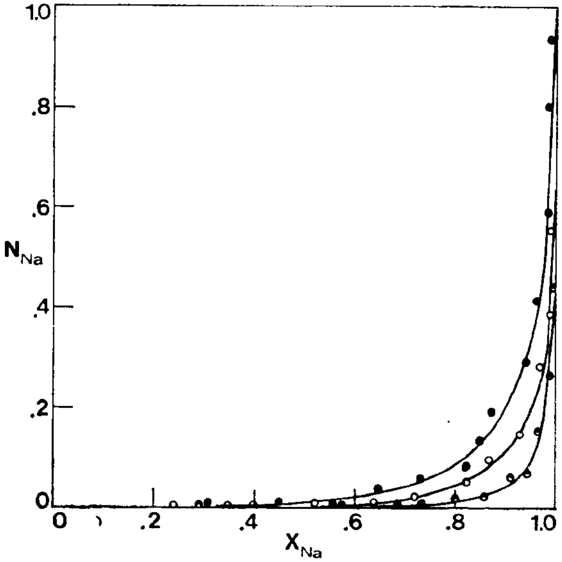

Fig. 1. Exchange isotherms for the substitution of calcium for sodium. Total concentration of the solution from top to bottom: 0.01, 0.005 and 0.002 moles of chemical equivalents in a litre of the solution. Temperature 25 ± 0.2 °C, pH 7.0.

valent ion exchange, montmorillonite strongly prefers to bind Ca^{2+}. However, the selectivity coefficiet K_c is not constant in the whole range of the occupation of the centres on the montmorillonite surface by Ca^{2+} ions, but varies in dependence on the Ca^{2+} content in the solution (fig. 2). Up to an approximately 50%-occupation of the mineral's surface by Ca^{2+} ions, the change of the selectivity coefficients is not very great. But a notable change takes place when Ca^{2+} ions on the surface of the mineral begin to prevail over the amount of Na^+ ions. A characteristic feature of this change consists in the considerable selectivity of montmorillonite for Ca^{2+} at the Ca-rich end of the exchange isotherms. This phenomenon is clearly percentible in fig. 2, and is probably due to a fairly great aggregation change of the single platelets of montmorillonite (comp. fig. 2 with table I).

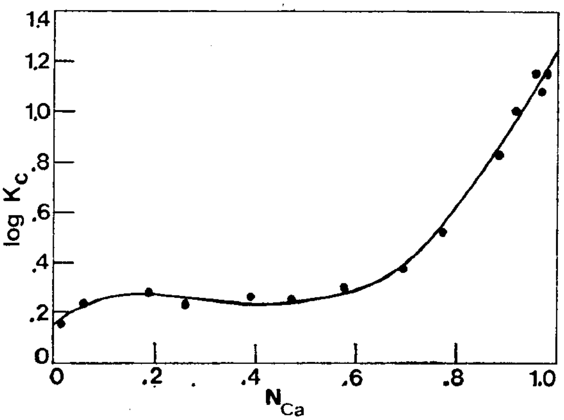

Fig. 2. Logarithm K_c for reaction (3) against the equivalent fraction of moles of chemical equivalents of calcium.

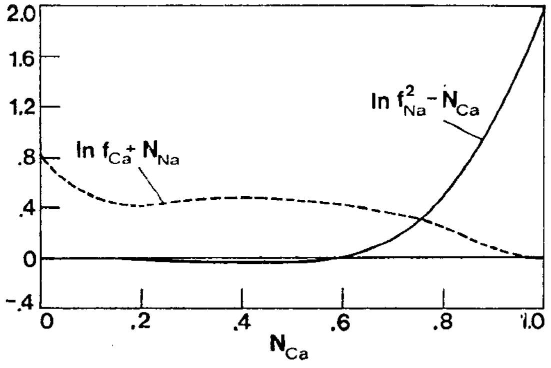

Fig. 3. Change of the activity coefficients f of Ca^{2+} and Na^+ ions bound on the surface of the Braňany montmorillonite as function of equivalent fractions of moles of the calcium equivalents. The horizontal straight line indicates their ideal value.

The value of standard Gibbs energy changes of reaction (3) was calculated from the thermodynamic equilibrium constant in which the ion concentration in an equilibrium solution are expressed as molalities:

$$\Delta G^\circ = -RT \ln \mathrm{K} = -0.398 \text{ kJ/mol eq.} \tag{12}$$

The course of the activity coefficients f_{Ca} and f_{Na} in dependence on the amount of the adsorbed Ca^{2+} on the surface of montmorillonite derived from equations (10) and (11) is shown in fig. 3.

By calculating ΔG° for reaction (3) according to the Ericksson equation [13] at a different concentration of the exchange solution, and by extrapolating K_c to zero ionic strength [14] the magnitude of the purely coulombic term ($\Delta G^\circ_{\mathrm{coul}}$) in the standard Gibbs energy change [15] has been found. The linear relation (fig. 4) between $\Delta G^\circ_{\mathrm{coul}}$ and the logarithm charge density on the surface of montmorillonite ($\ln \Gamma$) has been obtained (for $c_0 \rightarrow 0$):

$$\Delta G^\circ_{\mathrm{coul}} = RT\left(1 - \ln\frac{\Gamma\sqrt{\beta}}{2}\right) \tag{13}$$

or

$$\ln K_{\mathrm{coul}} = \left(\ln\frac{\sqrt{\beta}}{2} - 1\right) + \ln \Gamma. \tag{14}$$

The symbol Γ is the charge density on the surface of montmorillonite ($\Gamma = 1.35 \times 10^{-7}$ mol eq./cm^2), β is the double layer constant (at 25 °C, $\beta = 1.06 \times 10^{15}$ cm/mmol eq.). By this calculation K_{coul} and $\Delta G^\circ_{\mathrm{coul}}$ were obtained for the exchange reaction (3): $K_{\mathrm{coul}} = 0.808$, and $\Delta G^\circ_{\mathrm{coul}} = 0.527$ kJ/mol eq. By comparison with the experimentally obtained value of the standard Gibbs energy change, it has been found that the value of the non-coulombic component is -0.925 kJ/mol eq.

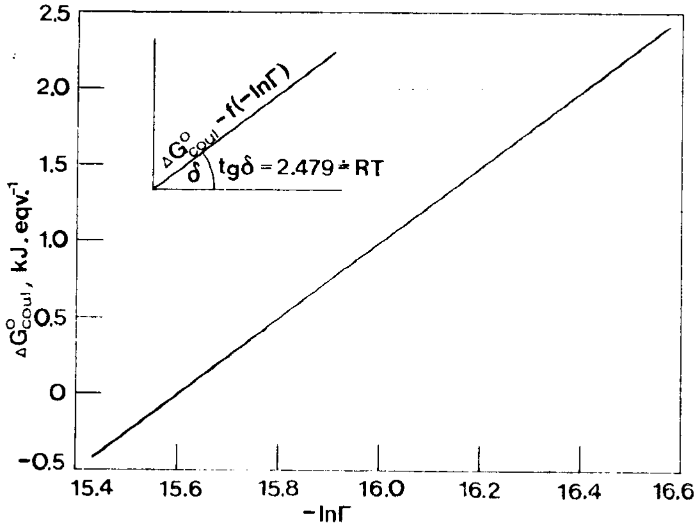

Fig. 4. Dependence of $\Delta G^\circ_{\mathrm{coul}}$ on the logarithm of the surface charge density upon the surface of the mineral.

If in the calculation of $\Delta G^{\circ}_{\text{coul}}$ the influence of broken bonds on the surface of montmorillonite is not considered, we may assume that the differences between the experimentally determined value ΔG° and the same quantity determined according to the electric double layer theory may be due to polarization effects. In fig. 4 it may be seen that such effects would roughly amount to —2.48 kJ/mol. The polarizability effects depend directly on the solvation changes of the exchange cations placed in the interlayer spaces of the Braňany montmorillonite as it clearly follows from the comparison of the value of the logarithm K_e with the change of the interlayer distance (comp. fig. 2 and fig. 5).

Table I shows the size variations of tactoids depending on the occupation of the exchange centres of montmorillonite by Ca^{2+} ions. In an aqueous medium tactoids form in such a way that single platelets of montmorillonite sit by their basal plates on each other. The length of the long axis of the particle (parameter *a*) is equal in Na-montmorillonite and Ca-montmorillonite as well as for the montmorillonite displaying different ratios of adsorbed Na^+ to Ca^{2+}. Only the thickness of the tactoid (parameter *b*) increases with rising Ca^{2+} ions amount on the surface of montmorillonite. But Ca-montmorillonite occurs as tactoids composed of 6 platelets. The thickness of such a tactoid is eleven times the thickness of a single platelet because of the water layer between the platelets. It has been found by the X-ray diffraction method that in Ca-montmorillonite the thickness of the water layers is approx. the same as that of a single platelet (~ 1.9 nm). Together with the change of the size of the tactoids, the value of K_c occurs in nearly the same N_{Ca} area. During the interaction of Na^+ with Ca-montmorillonite, Na^+ ions concentrate on the outer surface of a tactoid, whereas Ca^{2+} ions concentrate within a tactoid (i.e. in the interlayer space) [16]. This is well evidenced by X-ray data. With increasing Ca^{2+} content in montmorillonite the value d_{001} rises due to high solvation of this cation in the interlayer spaces (fig. 5). By the effect of ethylene glycol (EGL) montmorillonite swells so strongly that the difference between the *EGL* complex of Na-montmorillonite as well as that of Ca-montmorillonite is very small. The change of d_{001} for the Na- and Ca-forms of montmorillonite also supports the opi-

Table I

Structural data for tactoids of montmorillonite in aqueous suspension with various contents of adsorbed Na^+ and Ca^{2+} ions

Parametr	Content of adsorbed ions on the montmorillonite							
	100 % Na	10 % Ca 90 % Na	30 % Ca 70 % Na	50 % Ca 50 % Na	60 % Ca 40 % Na	80 % Ca 20 % Na	90 % Ca 10 % Na	100 % Ca
k	126	125	101	93	82	29	27	17
a/b	148.4	147.3	119.0	109.6	96.6	34.2	31.8	20.0
n	1.2	1.3	1.4	1.5	1.6	3.7	4.0	6.0
b, nm	4.25	4.28	5.30	5.76	6.53	18.50	19.86	31.58
V, 10^{-6} μm^3	5.96	6.04	9.27	10.94	14.07	112.9	130.11	328.98
S, μm^2	0.377	0.380	0.470	0.510	0.578	1.618	1.735	2.728
m, 10^{-18} g	14.09	15.04	20.77	23.63	29.79	229.75	259.43	642.49

nion that during the interaction between Ca^{2+} and Na-montmorillonite, first the interlayer spaces are occupied by Ca^{2+}, and only when the amount of Ca^{2+} ions is high enough are Na^+ ions on the surface of tactoids replaced. When the outer surface of a tactoid carries a fairly large number of Na^+ ions the preference of the surface for these ions strongly decreases. From Table I it also may be concluded that a change of the size of tactoids does not occur before 60 % of the adsorbed Na^+ are replaced by Ca^{2+} ions. For this reason it cannot be expected that mixing of both exchange cations on the mineral could take place earlier than when this substitution is attained.

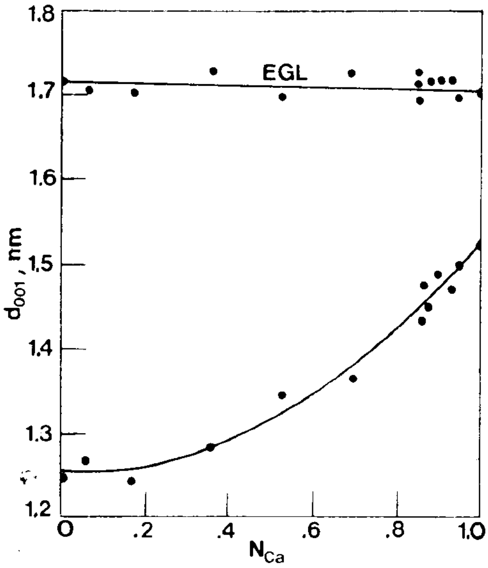

Fig. 5. Change of d_{001} of the Braňany montmorillonite in dependence on the amount of adsorbed Na^+ ions. EGL indicates the samples saturated with ethylene glycol.

Study of the size of tactoids has shown that the Na^+ content being higher than 50 % the greater part of montmorillonite platelets are separated from one another, and that the behaviour of such a suspension approaches that of a Na-montmorillonite suspension. As most Na^+ ions are concentrated on the surface of the tactoids, these ions determine the magnitude of the ionic strength between two neighbouring tactoids. If during the exchange reaction the Ca^{2+} content on the surface of the mineral rises over 60 %, the size of the tactoids strongly increase. In such tactoids the distance between the single platelets has been ascertained by the X-ray method to be only 0.9 nm. The dimensionless potential midway the platelets is no longer zero as was the case of the Na-montmorillonite (see Ericksson's equation [13]).

From the above facts it follows that for the Braňany bentonite suspension that all Ca^{2+} ions are not necessarily replaced by Na^+. The distance between the single platelets strongly increases when more that 40 % of Ca^{2+} ions are replaced by Na^+ ions. During the increasing Na^+ amount on the montmorillonite surface the separation of the platelets from one another becomes finished, so that finally the single tactoids are composed on the average of 1.2 plate (three-layer unit) if a homoionic Na-montmorillonite is involved. The outer surface, whose surface-charge density is less than that of the edges of the particles in adsorbing prefers Na^+ ions. The higher the number of particles separated from one another, the more intensely will the montmorillonite prefer the bond of sodium to that of calcium.

CONCLUSION

The exchange reaction between the Na^+ and Ca^{2+} on the montmorillonite, provoked by the charge originated due to isomorphous substitutions in the structure is perfectly reversible. This reaction may therefore be described by thermodynamic quantities. By substitution of Ca^{2+} ions for Na^+ ones the platelets of montmorillonite aggregate, and tactoids of different thicknesses arise. The aggregation occurs by stacking of the platelets (which by their basal planes sit on one another) in the direction of the crystallographic axis *c*. The ordering of the tactoids in the flocules depends on the type and concentration of the surrounding electrolyte. The change of the size of the tactoids is probably responsible for the change of the values of the selectivity coefficients.

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STANDARDNÍ ZMĚNA GIBBSOVY ENERGIE A DISTRIBUCE ČÁSTIC PODLE VELIKOSTI PRO Na—Ca VÝMĚNNOU ROVNOVÁHU V SYSTÉMU MONTMORILLONIT—VODA

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Výměnná reakce mezi Na^+ a Ca^{2+} na bentonitu z Braňan je endotermická s $\Delta G^\circ = -0{,}398$ kJ/mol ekv. Selektivitní koeficienty nejsou v celém rozsahu obsazení povrchu výměnnými kationty konstantní. Tato vlastnost je v převážné míře způsobena tvorbou taktoidů. Z aktivitních koeficientů pro ionty vázané na povrchu montmorillonitu bylo zjištěno, že energie adsorpce výměnných kationtů závisí na složení povrchu. Zvýšená selektivita minerálu pro Ca^{2+} v oblasti vysokého obsazení povrchu tímto kationtem je pravděpodobně způsobena přítomností aktivních center o nestejné energii vazby.

Obr. 1. Izoterma iontové výměny sodíku vápníkem. Celková koncentrace roztoku od shora dolů: 0,01, 0,005 a 0,002 moly chemických ekvivalentů v litru roztoku. Teplota 25 ± 0,2 °C, pH 7,0.

Obr. 2. Logaritmus K_c pro reakci (3) proti zlomku molů chemických ekvivalentů.

Obr. 3. Změna aktivitních koeficientů f iontů Ca^{2+} *a* Na^+ *vázaných na povrchu montmorillonitu z Braňan jako funkce zlomku molů chemických ekvivalentů vápníku. Horizontální přímka udává ideální hodnotu.*

Obr. 4. Závislost velikosti ΔG°_{coul} na logaritmu hustoty náboje na povrchu minerálu.

Obr. 5. Změna d_{001} montmorillonitu z Braňan v závislosti na množství adsorbovaného Na^+. *EGL označuje vzorky nasycené etylenglykolem.*

СТАНДАРТНОЕ ИЗМЕНЕНИЕ ЭНЕРГИИ ГИББСА И РАСПРЕДЕЛЕНИЕ ЧАСТИЦ В ЗАВИСИМОСТИ ОТ ИХ КРУПНОСТИ ДЛЯ Na—Ca ОБМЕННОГО РАВНОВЕСИЯ В СИСТЕМЕ МОНТМОРИЛЛОНИТ—ВОДА

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Реакция обмена между Na^+ и Ca^{2+} на бентоните из Бранян является эндотермической с $\Delta G^\circ = -0{,}398$ кдж/моль экв. Селективные коэффициенты в полном объеме занятия поверхности обменными катионами оказываются неконстантными. Это свойство вызвано большей частью образованием тактоидов. Из коэффициентов активности для ионов, связанных на поверхности монтмориллонита, установлено, что энергия адсорбции обменных катионов зависит от состава поверхности. Повышенная селективность минерала для Ca^{2+} в области высокой занятости поверхности этим катионом, по всей вероятности, вызвана наличием активных центров с неодинаковой энергией связи.

Рис. 1. Изотерма ионного обмена натрия кальцием. Суммарная концентрация раствора сверху вниз: 0,01, 0,005 и 0,002 моль химических эквивалентов в литре раствора. Температура 25 ± 0,2 °C, pH 7,0.

Рис. 2. Логарифм K_c для реакции (3) против мольной доли химических эквивалентов.

Рис. 3. Изменение коэффициентов активности f ионов Ca^{2+} *и* Na^+, *связанных на поверхности монтмориллонита из Бранян, как функция мольных долей химических эквивалентов кальция. Горизонтальная линия указывает идеальное значение.*

Рис. 4. Зависимость величины $\Delta G^{0}_{\text{дюйм}}$ от логарифма плотности заряда на поверхности минерала.

Рис. 5. Изменение d_{001} монтмориллонита из Бранян в зависимости от количества поглощенного Na^+. EGL *обозначает образцы, насыщенные этиленгликолем.*

AKUMULÁTORY S KERAMICKÝM ELEKTROLYTEM PRO ELEKTROMOBILY z hlediska dnešního stavu techniky se pro řešení elektrifikace osobní silniční dopravy považuje za nejnadějnější použití akumulárorů síra—sodík s pevným elektrolytem z keramického βAl_2O_3. Akumulátor pracuje při teplotě 300 °C, kdy anoda i katoda jsou v kapalném stavu, elektrolyt je na rozdíl od běžných galvanických článků tvořen pevnou fází.

Akumulátor tohoto typu pojme až pětinásobné množství energie na kilogram hmotnosti ve srovnání s běžným olověným akumulátorem. Na jeho vývoji pracuje řada zahraničních firem. Zdá se, že zatím nejlepších výsledků dosahují v NSR, kde vyvinuli prototyp elektromobilu s názvem Volkswagen Golf, který má akční radius na jedno nabití asi 150 km při rychlosti 90 km/h a jeho provoz je lacinější než s benzínovým motorem. „Tankování" se provádí prostým zapojením do elektrické rozvodné sítě. Zdá se, že hlavní problémy, s kterými se současný vývoj potýká, je prodloužení životnosti článků a ovšem i stále ještě značná hmotnost a objem baterie, která u zmíněného západoněmeckého prototypu zaplňuje celý zavazadlový prostor.

Pospíšil