

A STUDY OF THE SORPTION OF STRONTIUM IONS ON α -FeOOH

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The sorption of strontium ions on the solid-liquid interface of the α -FeOOH-0.1M-NaNO₃ system was studied over a wide concentration region of strontium ions and a constant concentration of sorbent so that $c_{rel} = c_{sorbent}/c_{sorbate}$ was 10^1-10^4 . The ΔG value of the sorption varies with c_{rel} and pH; it is as low as -32 kJ mol^{-1} at $c_{rel} = 10\ 000$ and pH 11 and increases to -18 kJ mol^{-1} at $c_{rel} = 10$ and pH 7.5. None of the conventional sorption equations can be applied to the studied system over the entire concentration region, but an equation of a different form is suggested for the description of this system.

The sorption of trace quantities on matter has been extensively studied, largely in conditions approaching the natural or prospective industrial systems. Thus the span of the variables was usually rather narrow and the sorption equations suggested differed appreciably and lacked general validity.

The aim of the present study of the Sr²⁺ ion-goethite sorption system was to gain a better insight into the phenomena occurring on the goethite-solution interface over a wide region of relative sorbent/sorbate concentrations and, based on the experimental data, to seek for relations applicable to the quantitative description of the sorption.

EXPERIMENTAL

The preparation and properties of the goethite used have been described¹. The substance was stored as suspension in redistilled water, in which form it was also used for the study.

The sorption of strontium was studied so that sodium and barium nitrate solutions and redistilled water were added to the suspension so that the ionic strength was 0.1, and the pH was then adjusted with nitric acid and sodium hydroxide (carbon dioxide-free). The sample was heated to boil and then thermostated under argon, and the pH was checked and readjusted if necessary. The time of contact, chosen based on kinetic experiments, was 24 h. After this time the pH and concentration of strontium ions were determined in the centrifugation supernatant.

The pH was measured with a GK 2402B combined electrode (Radiometer, Copenhagen) and an Acidimeter 325 (Druopta, Prague). Standard buffers were used for the pH and ionic strength calibration. The concentration of strontium was measured radiometrically by means of an ⁸⁵Sr tracer.

All chemicals were of reagent grade purity or better, and water was redistilled; Teflon vessels were employed. The temperature of samples was $23 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

The experimental data of the relative sorption of strontium ions on $\alpha\text{-FeOOH}$, *i.e.*, the ratio of the amount of sorbed substance to the total amount added (Z_i), for various $c_{rel} = c_{\text{sorbent}}/c_{\text{sorbate}}$ values are plotted in Fig. 1 in dependence on pH, and for selected pH, given in Table I. The data show that considerable sorption occurs even in the zero-point-of-charge range, pH (ZPC) ≈ 7.5 (ref.²). Table II gives the calculated surface concentrations Γ (amounts of strontium ions per unit interface area) and the corresponding degrees of coverage $\theta = \Gamma/\Gamma_{\text{max}}$, where the value of $6.64 \mu\text{mol m}^{-2}$ was used for Γ_{max} (ref.²). The ΔG values for the adsorption were calculated assuming the validity of the Stern–Graham equation,

$$\Gamma = 2rc \exp(-\Delta G/RT), \quad (1)$$

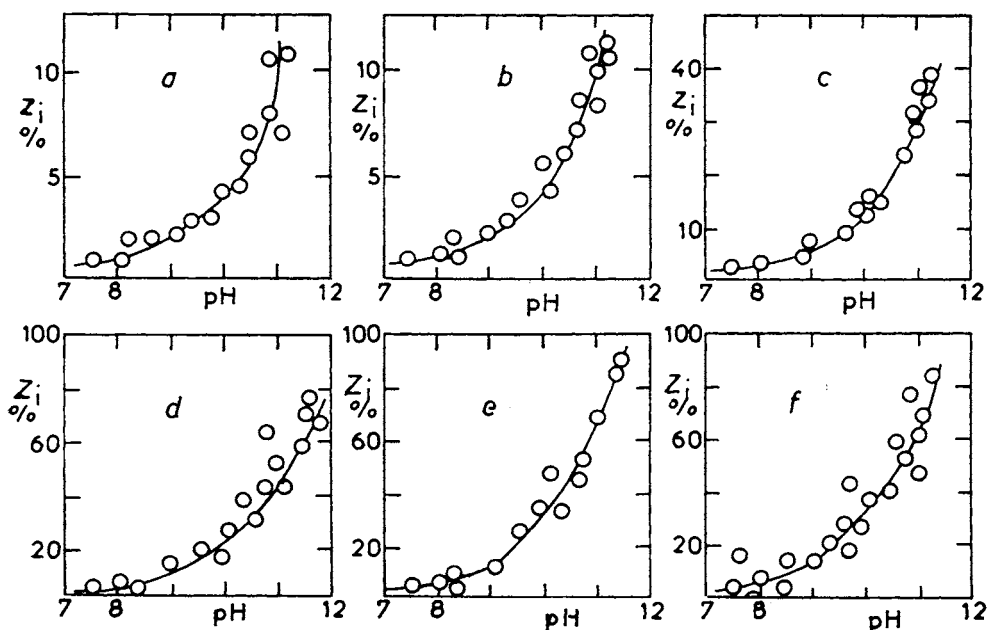


FIG. 1

Dependence of relative sorption of strontium ions Z_i (%) on pH at $c_{rel} = 10$ (a), 100 (b), 300 (c), 1 000 (d), 3 000 (e), and 10 000 (f)

TABLE I
Dependence of the relative sorption of Sr^{2+} ions on the relative concentration and pH

c_{rel}	$Z_i, \%$				
	pH 7.5	pH 8	pH 9	pH 10	pH 11
10	1.0	1.3	2.1	3.9	9.5
100	1.1	1.4	2.1	4.0	9.6
300	1.9	2.5	5.7	10.4	28.1
1 000	3.6	4.9	9.3	22.8	45.9
3 000	4.2	5.7	11.6	32.4	68.0
10 000	4.7	5.7	11.6	35.2	68.3

TABLE II
Dependence of the surface concentration of Sr^{2+} ions Γ (nmol m^{-2}) and the relative degree of coverage Θ (%) on the relative concentration and pH

c_{rel}	pH 7.5		pH 8		pH 9		pH 10		pH 11	
	Γ	Θ	Γ	Θ	Γ	Θ	Γ	Θ	Γ	Θ
10	349.9	5.3	513.4	7.7	829.3	12.5	1540.1	23.2	3451.1	56.5
100	43.4	0.65	55.3	0.83	82.9	1.25	158.0	2.38	379.1	5.71
300	25.0	0.38	32.9	0.50	75.0	1.13	136.9	2.06	369.9	5.57
1 000	14.2	0.21	19.3	0.29	36.7	0.55	90.0	1.36	181.3	2.73
3 000	5.5	0.08	7.5	0.11	15.3	0.23	42.6	0.64	89.5	1.35
10 000	1.9	0.03	2.3	0.03	4.6	0.07	13.9	0.21	27.0	0.41

TABLE III
Dependence of the adsorption ΔG on the relative concentration and pH

c_{rel}	$\Delta G, -\text{kJ mol}^{-1}$				
	pH 7.5	pH 8	pH 9	pH 10	pH 11
10	18.4	19.0	20.3	21.8	24.2
100	18.6	19.2	20.3	21.9	24.2
300	20.0	20.7	22.8	24.4	27.4
1 000	21.6	22.4	24.1	26.7	29.3
3 000	22.0	22.8	24.7	27.9	31.6
10 000	22.3	22.8	24.7	28.2	31.6

where r is the radius of the Sr^{2+} ion (113 pm), c is the equilibrium concentration and T is the absolute temperature. The calculated values, for various c_{rel} and pH, are given in Table III and plotted against the degree of coverage in Fig. 2; they are lowest in the region of low degrees of coverage, hence, only a small fraction of sorbate ions bonds to the active surface groups by the strongest bonding. The ΔG values also

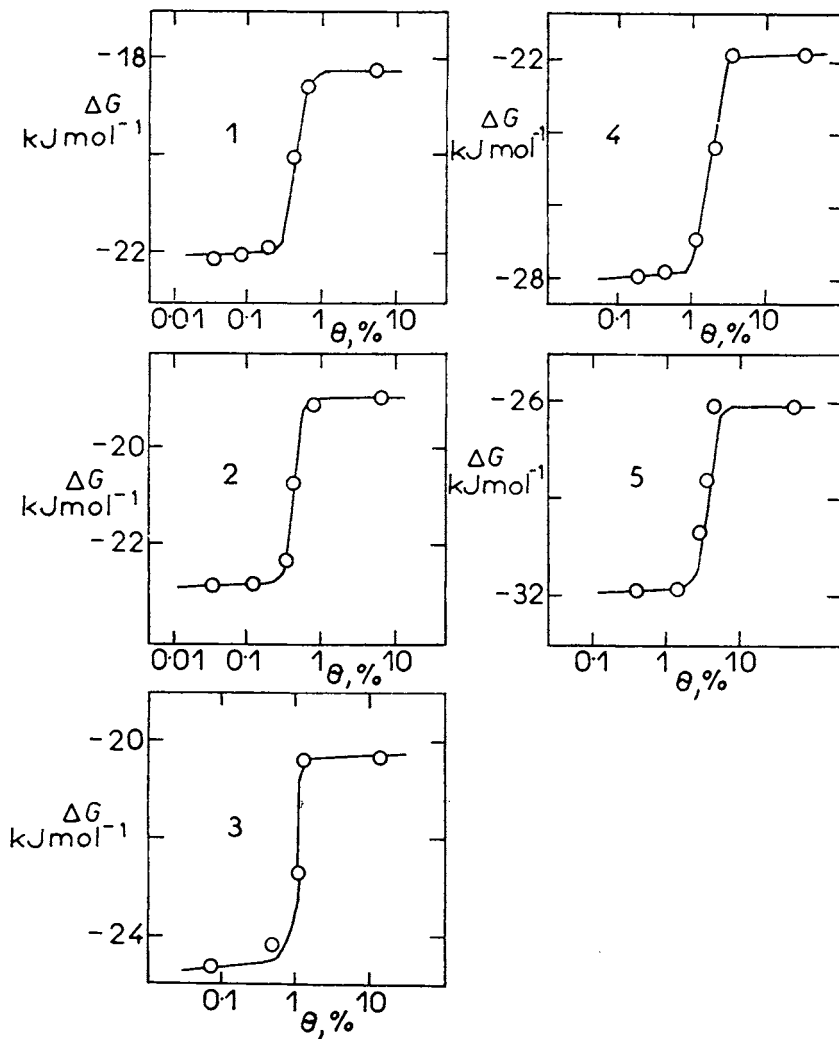


FIG. 2
Dependence of ΔG on degree of coverage θ (%). pH: 1.7-5, 2.8, 3.9, 4.10, 5.11

indicate the occurrence of relatively strong bonding forces at high pH, as compared, e.g., to the value of $-11.3 \text{ kJ mol}^{-1}$ found by Huang and Stumm³ for the $\text{Sr}^{2+} - \gamma\text{-Al}_2\text{O}_3$ system at high c_{rel} . As the degree of coverage increase, however, ΔG rises rapidly. This rise takes place in the degree of coverage range of tenths to units per cent, in dependence on pH. This increase is followed by a region where ΔG in dependence on θ is approximately constant; this character is the same for the various pH within the pH region examined. It turns out that in the system studied, ΔG attains at least two different values (Fig. 2), the lower corresponding to low degrees of coverage.

Fig. 2 also shows that none of the conventional isotherms can be applied to the entire concentration region. There can be several reasons for this. Most important will be the *a priori* difference between the sorption centres. It is well known that the surfaces of crystalline substances have many discontinuities, resulting from surface defects of various kind. Even the different planes of an ideal crystal can include sorption centres with different affinities. Using IR spectrometry, Parfitt and coworkers⁴, for instance, identified three different types of bonding OH groups on the surface of goethite.

The well-known fact that Coulomb interactions between the surface of sorbent and the sorbate decrease as the positive charge increases on the sorption, on the other hand, does not seem to be responsible for the shape of the $\Delta G = f(\theta)$ dependence, because the rapid increase in ΔG occurs at low degrees of coverage, where the sorbed molecules are far apart. The contribution of this effect to the total adsorption energy has been estimated by Benjamin and Leckie⁵ for the system of suspension of hydrated iron(III) oxide-metal and found very low.

Some authors seek the cause of the deviation from the Langmuir sorption law in the possibility that several ions of sorbate may bond to one sorption centre⁶. This, however, again cannot account for the observed sorption behaviour at low degrees of coverage. This behaviour can also be hardly due to any other negatively acting interaction between the sorbed ions because such an interaction could only appear if the ions were close to one another. At the low degrees of coverage where the rapid change in ΔG is observed, a sorbed ion is beyond the reach of chemical interaction with another, sorbed before; actually, while the diameter of the strontium ion is about 0.2 nm and the diameter of the hydrated strontium ion is about 0.9 nm, there is one sorbed molecule per tens, or perhaps hundreds, nm^2 in the region where the rapid change in ΔG appears. Thus it is the hypothesis of the sorbent surface consisting of several types of sorption centres, exhibiting different affinities for the sorbate ions, that remains as the most likely explanation of the effect under study.

For the quantitative treatment of equilibria in sorption systems including hydrated oxides, the sorption surface concentrations of sorbate T are related to its concentration in solution in terms of various isotherms, which, however, are usually applicable over relatively narrow regions only, Fig. 3 shows the experimental ΔG vs c_{rel} plot.

It is clear at first glance that the conventional Langmuir isotherm can only be used in regions where c_{rel} is either very low or very high. On the other hand, it is noteworthy that this plot resembles that for the Fermi-Dirac statistical quantum distribution; this suggests that the results can be described by the equation

$$(\Delta G - \Delta G_{\infty})/(\Delta G_0 - \Delta G_{\infty}) = 1/\{1 + \exp [(\log c_{rel} - \log c_{crit})/A]\}, \quad (2)$$

where ΔG_0 and ΔG_{∞} are the ΔG values for $c_{rel} \rightarrow 0$ and $c_{rel} \rightarrow \infty$, respectively, and c_{crit} and A are pH-dependent parameters. This equation was transformed into the linear form by logarithmization, and the c_{crit} and A values were calculated by

TABLE IV

Values of parameters A , c_{crit} , ΔG_0 , and ΔG_{∞} in Eq. (2) in dependence on pH

pH	A	$\log c_{crit}$	ΔG_0 kJ mol ⁻¹	ΔG_{∞} kJ mol ⁻¹
7.5	0.18	2.53	18.5	22.2
8	0.18	2.53	19.1	22.8
9	0.17	2.53	20.3	24.7
10	0.16	2.57	21.9	28.0
11	0.13	2.63	24.2	31.6

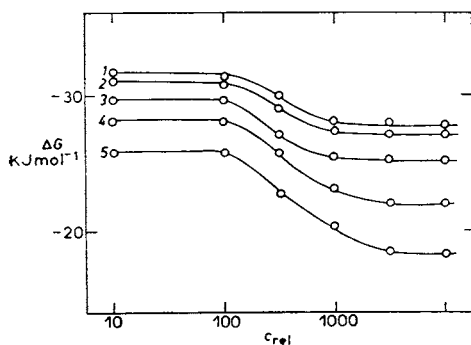


FIG. 3

Dependence of ΔG on relative concentration c_{rel} . pH: 1.75, 2.8, 3.9, 4.10, 5.11

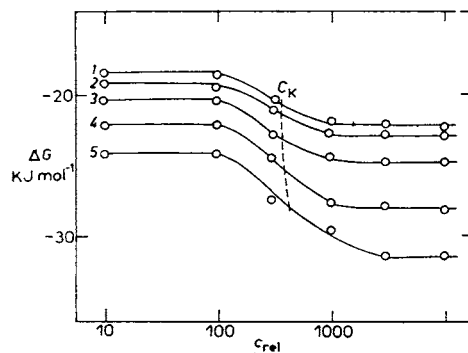


FIG. 4

Fit of the suggested function for ΔG to experimental data. pH: 1.75, 2.8, 3.9, 4.10, 5.11. c_K means c_{crit}

the least squares method as the straight line parameters; the corresponding plot is shown in Fig. 4. The ΔG_0 and ΔG_∞ values derived from Fig. 3, along with the calculated c_{crit} and A values, are given in Table IV.

Fig. 4 demonstrates that Eq. (2) fits the experimental data well. Thus, introducing the quantity

$$D = 2r \exp \left\{ -1/RT [\Delta G_\infty + (\Delta G_0 - \Delta G_\infty) / \exp \{ (\log c_{\text{rel}} - \log c_{\text{crit}}) / A + 1 \}] \right\}, \quad (3)$$

we can write the isotherm sought in the form

$$\Gamma = c_{\text{in}} D / (1 + DS_x), \quad (4)$$

where Γ , the surface concentration of Sr^{2+} ions, is in mol m^{-2} , c_{in} is the input (analytical) concentration of Sr^{2+} ions, in mol m^{-3} , and S_x is the surface area concentration (in $\text{m}^2 \text{ per m}^3$, hence, m^{-1}).

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