

Zinc-Calcium Exchange on Bentonite. Application of a Simple Three-Parameter Model

József Kónya,^a Noémi Nagy^a and Erik Högfeldt^{b,*}

^aIsotope Laboratory, Kossuth Lajos University, H-4010 Debrecen, Hungary and ^bDepartment of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

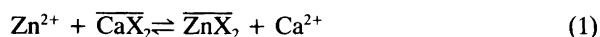
Kónya, J., Nagy, N. and Högfeldt, E., 1989. Zinc-Calcium Exchange on Bentonite. Application of a Simple Three-Parameter Model. – Acta Chem. Scand. 43: 612–614.

Recently, Konya and Nagy¹ showed that the sorption of zinc by calcium bentonite can be divided into ion exchange and adsorption of excess zinc. Data were acquired at 1, 20 and 40 °C, activity coefficients in the solid phase were estimated, and it was suggested that the deviations from ideality were mainly due to site heterogeneity.

In this paper the data in Ref. 1 are treated using the Högfeldt three-parameter model in order to find out how well this approach applies to the data of Konya and Nagy.¹

The model

Free energy. According to the model the equilibrium quotient (κ) for the reaction



(X = anion framework of bentonite)

can be fitted by the equation

$$\log \kappa = \log \kappa(1)\bar{x}^2 + \log \kappa(0)(1-\bar{x})^2 + 2\log \kappa_m \bar{x}(1-\bar{x}) \quad (2)$$

where \bar{x} is the equivalent fraction of zinc in the bentonite.

$\log \kappa$ depends on the nature of the neighbouring species. There are three kinds of neighbours (A-A, B-B and A-B) and thus three parameters. The parameters $\log \kappa(1)$ and $\log \kappa(0)$ correspond to the limiting values for $\bar{x} = 1$ and $\bar{x} = 0$ (i.e. only A-A or B-B). These limiting values can not be obtained by direct experiment, but they can be estimated by tracer methods. If these estimates do not agree with those of the model, site heterogeneity is implied. The parameter $\log \kappa_m$ corresponds to the mixed ionic forms (A-B). It is sufficient to assume that the amount of each kind is proportional to \bar{x}^2 , $(1-\bar{x})^2$ and $2\bar{x}(1-\bar{x})$; the proportionality factor can be included in the parameter.

In ion exchange work, data are often plotted against \bar{x} rather than \bar{x}^2 , etc. It is then useful to introduce the equation

$$\log \kappa = \log \kappa(1)\bar{x} + \log \kappa(0)(1-\bar{x}) + \bar{B}\bar{x}(1-\bar{x}) \quad (3)$$

The experimental data can be fitted to eqn. (3) using least-squares methods, giving the parameters $\log \kappa(0)$ and $\log \kappa(1)$ as well as the empirical constant \bar{B} . The parameter $\log \kappa_m$ is then obtained from

$$\log \kappa_m = \frac{1}{2}[\log \kappa(0) + \log \kappa(1) + \bar{B}] \quad (4)$$

The thermodynamic equilibrium constant, K , is obtained from

$$\log K = \int_0^1 \log \kappa(\bar{x}) d\bar{x} = \frac{1}{3}[\log \kappa(0) + \log \kappa(1) + \log \kappa_m] \quad (5)$$

Activity coefficients. Let us for simplicity assume that $\log \kappa$ as a function of \bar{x} can be approximated by a straight line, i.e. $\bar{B} = 0$ and thus

$$\log \kappa = a + b\bar{x} \quad (6)$$

where a and b are constants related to the parameters of the model. From

$$\log K = \log \kappa + \log f_{\text{Zn}} - \log f_{\text{Ca}} = a + b\bar{x} + \log f_{\text{Zn}} - \log f_{\text{Ca}} \quad (7)$$

and the Gibbs-Duhem equation

$$\bar{x}_{\text{Zn}} d \ln f_{\text{Zn}} + \bar{x}_{\text{Ca}} d \ln f_{\text{Ca}} = 0 \quad (p, T \text{ const}) \quad (8)$$

the following expressions are obtained for the activity coefficients:

$$\log f_{\text{Ca}} = \frac{1}{2}b\bar{x}^2, \quad \log f_{\text{Zn}} = \frac{1}{2}b(1-\bar{x})^2 \quad (9a, b)$$

The constant b is obtained from

$$b = \log \kappa(1) - \log \kappa(0) \quad (10)$$

Expressions (9a, b) are those for regular solutions, i.e. a straight line, eqn. (6), corresponds to a regular solution, a fact already noted by Kielland.² Typical examples of the use of the model are given in Refs. 3 and 4.

* To whom correspondence should be addressed.

Results

Because of experimental difficulties the experimental data show a large scatter. For that reason the data treatment has been applied to a representative selection. It was found that the data could be fitted by straight lines, i.e. $\bar{B} = 0$ at all three temperatures. This is shown in Figs. 1–3, where $\log \kappa$ is plotted against \bar{x} at each temperature. This gives only two parameters to study as functions of temperature, $\log \kappa(0)$ and $\log \kappa(1)$. It was found that $\log \kappa(1)$ was practically independent of temperature, giving

$$\log \kappa(1) = -2.03 \pm 0.03 \quad (11a)$$

while $\log \kappa(0)$ as a function of $1/T$ gave

$$\log \kappa(0) = 1.06 - 372/T \quad (11b)$$

According to eqns. (4) and (5) with $\bar{B} = 0$

$$\log \kappa_m = \log K = \frac{1}{2}[\log \kappa(0) + \log \kappa(1)] \quad (12)$$

Table gives the parameters obtained from eqns. (11a, b) and (12) together with the standard deviation in $\log \kappa$, $s(\log \kappa)$.

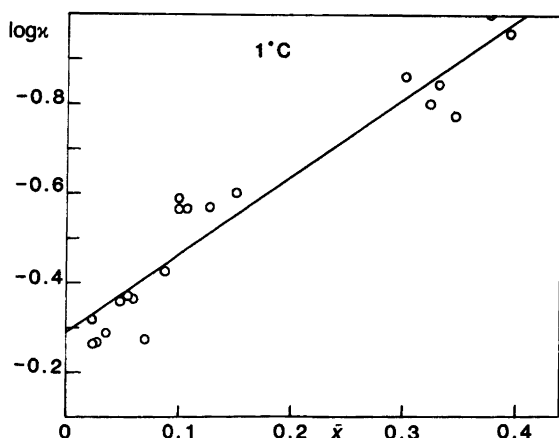


Fig. 1. $\log \kappa$ plotted against $\bar{x} = \bar{x}_{Zn}$ at $T = 1^\circ\text{C}$.

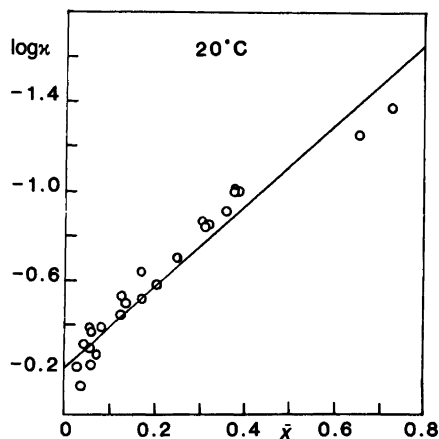


Fig. 2. $\log \kappa$ plotted against $\bar{x} = \bar{x}_{Zn}$ at $T = 20^\circ\text{C}$.

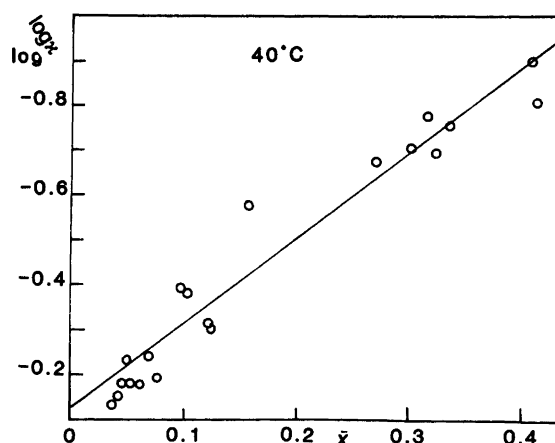


Fig. 3. $\log \kappa$ plotted against $\bar{x} = \bar{x}_{Zn}$ at $T = 40^\circ\text{C}$.

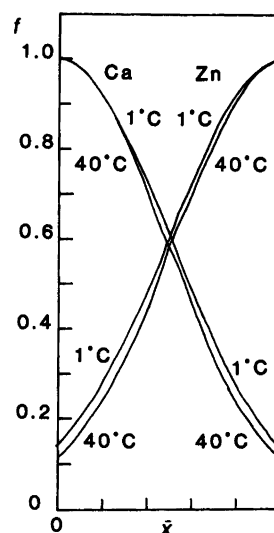


Fig. 4. f_{Ca} and f_{Zn} plotted against $\bar{x} = \bar{x}_{Zn}$ at 1°C and 40°C .

In Fig. 4, f_{Ca} and f_{Zn} are plotted against \bar{x}_{Zn} for the temperatures 1° and 40°C . The temperature dependence of the activity coefficients in the bentonite phase is thus rather small.

Concluding remarks

For most data in the literature treated so far by the model, the standard deviation is about ± 0.03 to about ± 0.04 (using decadic logarithms).

Table 1. Parameters obtained from eqns. (11a, b) and (12).

$T/^\circ\text{C}$	$\log \kappa(0)$	$\log \kappa(1)$	$\log \kappa_m = \log K$	$s(\log \kappa)$
1	-0.2(9)	-2.0(3)	-1.1(6)	± 0.08
20	-0.2(1)	-2.0(3)	-1.1(2)	± 0.09
40	-0.1(3)	-2.0(3)	-1.0(8)	± 0.07

SHORT COMMUNICATION

In view of the low concentrations used and the corrections made for adsorption, it can be concluded that the data are consistent with the model, which can be used as a first approximation. Site heterogeneity cannot be ruled out, and part of the variation in $\log \kappa$ may be due to this effect.

References

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