Ion Exchange Experiments with Zeolite A

Marc Meyer and Gion Calzaferri

Department of Chemistry and Biochemistry,
University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

Lab Documentation

Instructor Notes

Equipment used in our lab

Voltmeter:	Unicam model 9460 ion-selective voltmeter
Working electrode:	Unicam model IS-Ag Ag^+-selective electrode
Reference electrode:	Metrohm model 6.0726.100 double junction Ag/AgCl electrode Inner Filling: 3 M KCl Outer Filling: 3 M $NaNO_3$
Thermostat:	Required precision: at least 0.1°C

CAS Registry Numbers

Zeolite Na-A / Linde Type A zeolite:	N/A
Silver nitrate, $AgNO_3$:	007761-88-8
Sodium nitrate, $NaNO_3$:	007631-99-4

Hazards

$AgNO_3$ is corrosive and environmentally hazardous. Use safety glasses and dispose waste solution appropriately.
No further potential hazards or safety warnings.

Instructions for Students

Goal

In this experiment you perform an ion exchange using zeolite Na-A as the exchanger and silver ions as the exchanging species. You will see how to determine the thermodynamic equilibrium constant as well as the thermodynamic quantities $\Delta G_T^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of the ion exchange.

Problem

Perform the ion exchange at three different temperatures between 20°C and 50°C. At each temperature first measure a calibration curve for the Ag^+-selective electrode. Promptly afterwards, measure the ion exchange through stepwise addition of silver nitrate solution to a suspension of zeolite Na-A in sodium nitrate solution. Determine the thermodynamic equilibrium constant as well as the free energy, the enthalpy and the entropy of the ion exchange using the Mathcad worksheet ‘Evaluation.mcd’.

Theory

Zeolite A: Zeolites are among the most frequently used host materials for host-guest systems. They are able to accommodate various kinds of guests, from gases and small molecules like water (what makes them widely used dehumidifiers) up to large molecules such as polycyclic aromatic hydrocarbons and even polymers. Their spatial constitution is characterized by internal cavities and channels. Depending on the type of zeolite, these differ in number, size, shape and arrangement. The guests are normally adsorbed to the framework of the zeolite. A different adsorptivity of varying guests makes zeolites efficient molecular sieves for otherwise hardly separable species such as m-xylene and p-xylene. Furthermore, for each aluminum atom replacing a framework silicon atom, charge compensation is required. This is accomplished by charge-compensating cations incorporated in the zeolite. They can partly and sometimes completely be exchanged for cations of the surrounding solution, establishing aluminum-containing zeolites as ion exchangers, e.g. for water softening. Further applications include their use as catalysts or nanoreactors. A more recent development is their application as a host for the construction of new materials for imaging techniques, dye lasers of extremely small size, probes in biological systems and photonic devices. The preparation of many of these materials involves ion exchange processes, and the unique features of such host-guest systems depend on factors such as the type of host, the type of the guest(s) and the distribution of the guest particles in the host. *(1-3)* Classical zeolites are crystalline aluminosilicates, built up of [SiO_4] and [AlO_4] tetrahedra. In zeolite A, these units strictly alternate, yielding a 1:1 ratio of Si and Al. The units are linked via oxygen bridges, resulting in a three-dimensional framework of corner-sharing tetrahedra. Two kinds of structural sub-units are formed, a larger and a smaller one. They consist of 48 and 24 tetrahedra and are denoted as α-cage and β-cage, respectively. Zeolite A can be imagined as being built up by octahedrally assembled α- or β-cages, eight β-cages forming one crystallographic unit cell. *(4)* Pluth and Smith have determined the locations of the charge-compensating sodium ions in dehydrated zeolite Na-A: *(5)* There are three sets of equivalent occupied cation sites. One set contains eight sodium ions per β-cage in so-called six-ring positions. One set contains three ions in eight-ring positions. The last set contains only a single ion in a four-ring position. In total, there are 12 sodium ions per β-cage. Figure 1a) shows an assembly of eight β-cages with the mentioned cation positions:

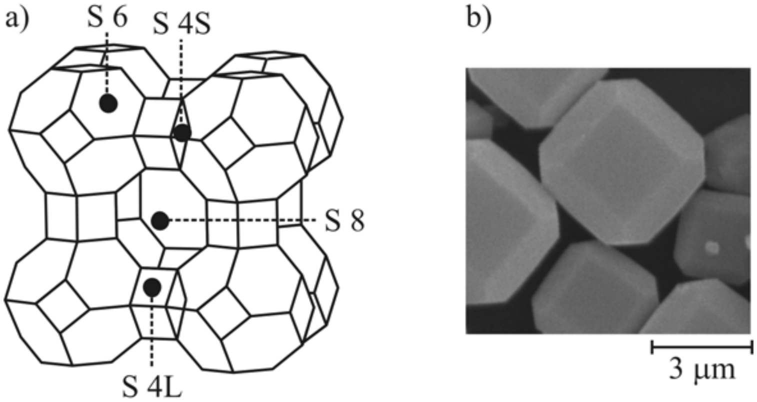

Figure 1: a) Scheme of the framework of zeolite A: assembly of eight β-cages with the crystallographically identified cation sites: S 6 and S 8: 6-ring and 8-ring positions, respectively. S 4S and S 4L: 4-ring positions, whereof only S 4L is occupied in zeolite Na-A. b) SEM image of typical zeolite A crystals.

The SEM picture in Figure 1b) visualizes typical zeolite A crystals, their shape reflecting the cubic build-up of the framework. More detailed structural information on zeolites can be found in refs *(6-7)*. Zeolite A was first synthesized by Breck. *(8-9)* Recent synthetic developments have been reported in ref. *(10)*.

Ion exchange isotherms: Exchange isotherms are a common way to depict ion exchange reactions. These are plots of the equivalent fraction of the exchanging species in the exchanger versus its equivalent fraction in the solution, measured under equilibrium conditions and at constant temperature. Given an ionic species, its equivalent amount of substance, also called the number of equivalents, is the amount of substance, weighted by the charge of one ion. Consequently, the equivalent fraction of ionic species A in an environment is the ratio of the number of equivalents of A in the environment and the total number of equivalents of all ionic species under consideration in the environment. Thus, in the special case of an ion exchange reaction, with ions of species A exchanging ions of species B in a host H, the equivalent fraction of A in the host, H_A, is:

$$\mathrm{H_A} = \frac{\text{Number of equivalents of A in the host}}{\text{Total number of equivalents of A and B in the host}} \tag{1}$$

If a and b are the charges of the ions A and B, respectively, then the equivalent fraction of A in the solution, $\mathrm{S_A}$, is:

$$\mathrm{S_A} = \frac{a \cdot [\mathrm{A}]}{a \cdot [\mathrm{A}] + b \cdot [\mathrm{B}]} \tag{2}$$

Figure 2 shows measured isotherms for the Na^+ vs. Ag^+ exchange in zeolite Na-A at different temperatures as plots of the equivalent fraction of the silver ions in the zeolite $(\mathrm{H_{Ag}})$ versus the one of the silver ions in solution $(\mathrm{S_{Ag}})$:

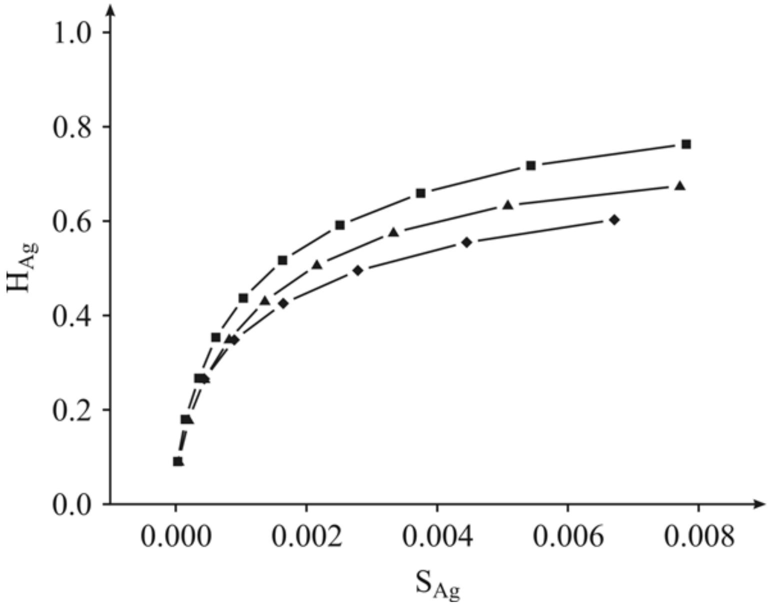

Figure 2: Ion exchange isotherms for the Na^+ vs. Ag^+ exchange at 25°C (boxes), 35°C (up-pointing triangles) and 45°C (diamonds).

$\mathrm{S_{Ag}}$ and $\mathrm{H_{Ag}}$ are calculated from measured quantities according to the following formulae:

$$\mathrm{S_{Ag}} = \frac{\left[\mathrm{Ag^+}\right]_s}{\left[\mathrm{Ag^+}\right]_s + \left[\mathrm{Na^+}\right]_s} \tag{3}$$

$$\mathrm{H_{Ag}} = \frac{n^0_{\mathrm{Ag}_s^+} - n_{\mathrm{Ag}_s^+}}{\frac{m_{zeol} \cdot n_{box}}{M_\beta}} \tag{4}$$

$\left[\mathrm{Ag^+}\right]_s$ is the measured concentration of silver in solution, $\left[\mathrm{Na^+}\right]_s$ is the calculated concentration of sodium in solution. $n^0_{\mathrm{Ag}_s^+}$ is the amount of silver in solution in absence of zeolite in moles, $n_{\mathrm{Ag}_s^+}$ is the amount of silver in solution in presence of zeolite after establishment of the ion exchange equilibrium, m_{zeol} is the mass of zeolite in grams, M_β is the molar mass of one β-cage of zeolite Na-A including the intracrystalline water in grams per mole, and $n_{box} = 12$ is the maximum number of exchangeable monovalent cations per β-cage. Thus, the numerator of (4) is the amount of exchanged silver in moles, while the denominator of (4) is the amount of monovalent cation sites of zeolite A in moles.

Data fitting: The evaluation method presented here is described in full detail in ref. *(11)*. It is based on a statistical particle distribution and exchange theory described in ref. *(12)*. In zeolite A every β-cage includes 12 monovalent cation sites. While not all sites within a β-cage are equivalent, the situation in every β-cage is equal. Hence, the ion exchange is described with the β-cage as the smallest chemical unit. Consequently, a system of 12 individual exchange reactions has to be considered:

$$\begin{array}{cccc} \mathrm{ZB}_{12} + \mathrm{A} & \rightleftarrows & \mathrm{ZAB}_{11} + \mathrm{B} & K_1 \\ \mathrm{ZAB}_{11} + \mathrm{A} & \rightleftarrows & \mathrm{ZA}_2\mathrm{B}_{10} + \mathrm{B} & K_2 \\ \mathrm{ZA}_2\mathrm{B}_{10} + \mathrm{A} & \rightleftarrows & \mathrm{ZA}_3\mathrm{B}_9 + \mathrm{B} & K_3 \\ \vdots & & \vdots & \vdots \\ \mathrm{ZA}_{11}\mathrm{B} + \mathrm{A} & \rightleftarrows & \mathrm{ZA}_{12} + \mathrm{B} & K_{12} \end{array} \tag{5}$$

Here, Z symbolizes a β-cage of zeolite A, while A and B symbolize the charge compensating cations (A: exchanging species; B: species being exchanged). The K_i are the rational selectivity coefficients (concentration quotients) of the individual exchange reactions. We have shown in ref. *(12)* that these coefficients are, for sufficiently large systems, related to the exchange isotherm via

$$K_r = K_1 \frac{13 - r}{12r} \quad r = 1,\ 2,\ \ldots,\ 12 \tag{6}$$

and

$$\mathrm{H_A} = \frac{K_1 \cdot \mathrm{S_A}}{\left(K_1 - 12\right)\mathrm{S_A} + 12} \tag{7}$$

The basic idea of the evaluation method is to fit the value of K_1 so that the measured isotherm is optimally simulated by relation (7). K_2 to K_{12} are determined by K_1 through (6), and the overall rational selectivity coefficient of the system of coupled exchange reactions is then given by

$$K_{tot} = \prod_{r=1}^{12} K_r \tag{8}$$

Through the fit, the rational selectivity coefficients are corrected by the unknown activity coefficients. Hence, K_{tot} corresponds to the thermodynamic equilibrium constant. The values of K_{tot} for different temperatures can finally be used to calculate the standard quantities $\Delta G_T^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of the exchange reaction:

$$\Delta G_T^{\ominus} = -RT \ln K_{tot} \tag{9}$$

$$\Delta H^{\ominus} = -R \frac{d \ln K_{tot}}{d \frac{1}{T}} \tag{10}$$

$$\Delta S^{\ominus} = \frac{\Delta H^{\ominus} - \Delta G_T^{\ominus}}{T} \tag{11}$$

These quantities refer to 1 mole of β-cages. For $\Delta S^{\ominus}$ the mean for the individual temperatures is taken.

A complication is that formulae (6) and (7) only hold for equivalent cation sites. However, not all cation sites within a β-cage of zeolite A are pairwise equivalent. But as there are sets of equivalent cation sites, this problem can be solved: Since ions in equivalent positions can be assumed to be exchanged consecutively, K_1 to K_{12} can be split into groups, each group corresponding to the exchange of one set of equivalent cations. This grouping is done based on structural arguments and by assuming an exchange sequence of the cations. Then one fits a separate value of K_1 for each group. This value determines the coefficients of its group via (6). (Note that (6) fully holds within a set of equivalent cation sites.) Again, K_{tot} is then given through (8). Since the consecutive exchange of the cations of an equivalent set of cation sites corresponds to one segment of the isotherm, the described procedure can be understood as a segmental simulation of the measured isotherm. Technically, this segmental fitting is performed using a continuous piecewise fitting function which, in the simplified case of only two sets of equivalent cation sites in a β-cage would have the following form:

$$\mathrm{H}_{\mathrm{Ag},sim}\left(\mathrm{S}_{\mathrm{Ag}}\right) = \begin{cases} \mathrm{H}_{\mathrm{Ag},1}\left(\mathrm{S}_{\mathrm{Ag}}\right) & 0 \le \mathrm{S}_{\mathrm{Ag}} \le x \\ \mathrm{H}_{\mathrm{Ag},2}\left(\mathrm{S}_{\mathrm{Ag}}\right) - \mathrm{H}_{\mathrm{Ag},2}(x) + \mathrm{H}_{\mathrm{Ag},1}(x) & x < \mathrm{S}_{\mathrm{Ag}} \le 1 \end{cases} \tag{12}$$

Here, the following relations have been used:

$$\mathrm{H}_{\mathrm{Ag},i}\left(\mathrm{S}_{\mathrm{Ag}}\right)=\frac{K_{1,i}\cdot \mathrm{S}_{\mathrm{Ag}}}{\left(K_{1,i}-12\right)\mathrm{S}_{\mathrm{Ag}}+12} \tag{13}$$

$$x=\frac{60}{7K_{1,1}+60} \tag{14}$$

$\mathrm{H}_{\mathrm{Ag},i}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ are isotherm functions, based on (7), one for each value of i, i.e. one for each set of equivalent cation sites. If, for example, the first group of equivalent cation sites consists of 5 and the second group of 7 sites, then $\mathrm{H}_{\mathrm{Ag},1}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ describes the exchange of the first 5, $\mathrm{H}_{\mathrm{Ag},2}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ the exchange of the remaining 7 cations in a β-cage. Hence, $\mathrm{H}_{\mathrm{Ag},1}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ is associated with K_1 to K_5, $\mathrm{H}_{\mathrm{Ag},2}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ with K_6 to K_{12}. As a consequence, $\mathrm{H}_{\mathrm{Ag},1}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ simulates the isotherm up to an exchange degree of $5/12$ and $\mathrm{H}_{\mathrm{Ag},2}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ from there up to full exchange. The definition of $\mathrm{H}_{\mathrm{Ag},sim}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ reflects this: $\mathrm{H}_{\mathrm{Ag},sim}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ equals $\mathrm{H}_{\mathrm{Ag},1}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ up to $\mathrm{S}_{\mathrm{Ag}}=x$; the definition of x in (14) is such that $\mathrm{H}_{\mathrm{Ag},sim}\left(x\right)=5/12$. Starting there, $\mathrm{H}_{\mathrm{Ag},2}\left(\mathrm{S}_{\mathrm{Ag}}\right)$ comes into operation; the corresponding segment of the simulated isotherm is connected continuously to the first segment what can be seen by letting S_{Ag} be x on both lines of (12).

The simplified case described here with only two sets of equivalent cation sites does not correspond to the situation in zeolite Na-A. In fact, there the best fits result if 5 sets of equivalent cation sites are assumed; the corresponding sets of selectivity coefficients are $\left\{K_1\right\}$, $\left\{K_2,K_3,K_4\right\}$, $\left\{K_5\right\}$, $\left\{K_6,K_7\right\}$ and $\left\{K_8,\ldots,K_{12}\right\}$. The corresponding piecewise fitting function, which is lengthy but simply a logical expansion of (12), is included in the evaluation worksheet 'Evaluation.mcd'. The non-linear least-squares fit is performed using Mathcad *(13)* in conjunction with the Levenberg-Marquardt minimization algorithm. *(14)* Fit quality criteria are the mean squared error and the plot of the residuals. Table 1 summarizes the results of the fits for the isotherms presented in Figure 2:

	25°C	35°C	45°C
$\ln K_{tot}$	65.4	59.2	54.3
$\Delta G_T^{\ominus}$ / kJ mol^{-1}	−162	−152	−144
$\Delta H^{\ominus}$ / kJ mol^{-1}		-438 ± 22	
$\Delta S^{\ominus}$ / J mol^{-1} K^{-1}		-925 ± 41	

Table 1: Fitting results for the Na^+ vs. Ag^+ exchange in zeolite Na-A. $\Delta G_T^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ refer to 1 mole of β-cages.

Figure 3 presents the measured and the simulated isotherms:

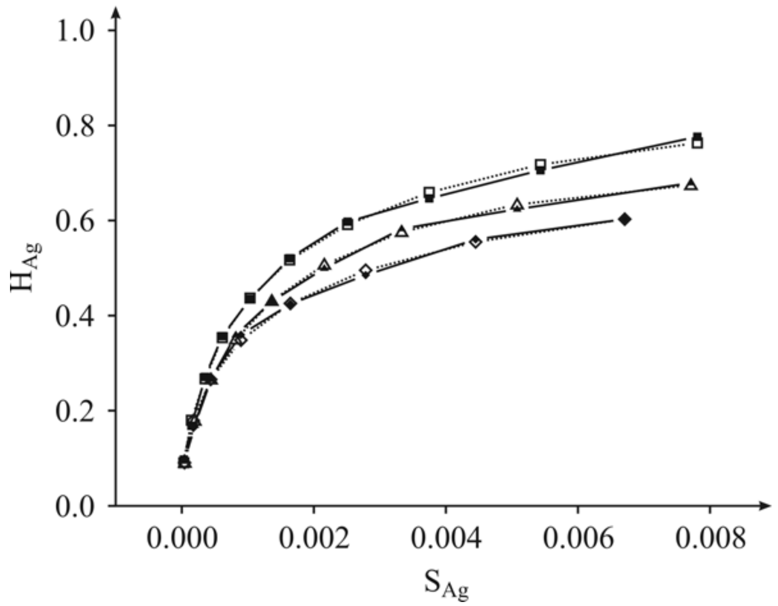

Figure 3: Measured (dotted lines, unfilled symbols) and fitted (continuous lines, filled symbols) ion exchange isotherms of the Na^+ vs. Ag^+ exchange in zeolite Na-A at 25°C (boxes), 35°C (triangles) and 45°C (diamonds).

Interpretation of the Results

The exchange isotherms are best fitted with the first set consisting of one, the second set consisting of three equivalent cation sites. The choice of the subsequent sets can be varied somewhat without strongly influencing the quality of the fit. This exchange sequence can be interpreted when we recall that there are three sets of equivalent cation sites in zeolite Na-A: 8 6-ring sites, 3 8-ring sites and 1 4-ring site. It is thus an obvious conclusion that in zeolite Na-A first the 4-ring sodium ion is exchanged for silver, followed by the three 8-ring ions, while the eight 6-ring ions are exchanged only at last. This interpretation is verified by spectroscopic observations: On dehydration in vacuum at room temperature zeolite $Ag^+_xNa^+_{12-x}$-A turns yellow already at very low silver loadings ($x < 0.2$). *(15)* Because only 4-ring coordinated silver ions yield transitions in the visible, while 6-ring and 8-ring coordinated Ag^+ ions are responsible for transitions in the UV, this observation shows that indeed, first the Na^+ ion in the 4-membered ring is be exchanged for Ag^+. Because the absorption bands of the 8-ring coordinated Ag^+ ions emerge when $x > 1$, one can also verify that the three 8-ring Na^+ ions are exchanged immediately after the 4-ring Na^+. *(15,16)*

The loss of entropy due to the silver ions leaving the solution and entering the zeolite exceeds the increase of entropy due to the sodium ions leaving the zeolite and entering the solution. This explains the negative $\Delta S^{\ominus}$ value occurring in the ion exchange, see Table 1.

Laboratory Instructions

The ion exchange isotherms are obtained by measuring the voltage in a suspension of zeolite Na-A after addition of different amounts of $AgNO_3$ solution. The zeolite should have been stored under ambient, i.e. not water-free conditions.

Equipment: The experiments are carried out using a glass vessel with a water jacket, the latter being connected to a thermostatic water circulator, and two electrodes connected to an ion-selective voltmeter: An Ag^+-selective electrode and a double junction Ag/AgCl electrode serve as working and reference electrode, respectively. The experimental setup is outlined in Figure 4:

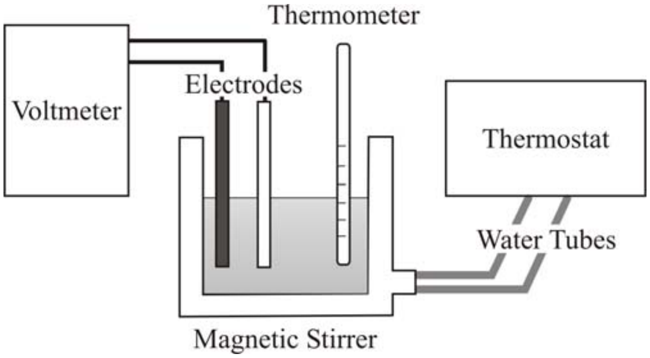

Figure 4: Experimental setup.

Experimental Procedure: The ion exchange is performed at three different temperatures between 20°C and 50°C. The temperature is set by a thermostat with a precision of at least 0.1°C. Establishment of the thermal equilibrium in the suspension is controlled with a thermometer, dipped in the solution. The vessel is wrapped in aluminum foil preventing photoreduction of Ag^+ and helping to keep the temperature constant. For every temperature a calibration curve for the Ag^+ selective electrode is measured: $NaNO_3$ solution (0.1 M, 100 ml) is filled into the double-walled vessel and heated up to the desired temperature. Then, 4 µl of $AgNO_3$ solution (0.1 M) are added while constantly stirring, the voltage being recorded right afterwards. This step is repeated several times using the following volumes of $AgNO_3$ solution:

Measurement #	Added Volume of $AgNO_3$ 0.1 M	Total Volume of $AgNO_3$ 0.1 M
1-5	4 µl	4 µl - 20 µl
6-9	20 µl	40 µl – 100 µl
10-16	100 µl	200 µl – 800 µl
17-19	500 µl	1300 µl - 2300 µl

Table 2: Portions of $AgNO_3$ solution added when the calibration curve is measured, and the resulting total volume of $AgNO_3$ solution.

Promptly after recording the calibration curve, the ion exchange is performed: Zeolite Na-A (100 mg, exactly weighed) is slurried in $NaNO_3$ solution (0.1 M, 100 ml) in the double-walled vessel. The isotherms are measured in 0.1 M aqueous $NaNO_3$ in order to keep the ionic strength constant and to avoid any hydrolysis of the zeolite. The suspension is heated up to the desired temperature while vigorously stirring permanently in order to prevent deposition of the zeolite. After the thermal equilibrium has established at the calibration temperature, $AgNO_3$ solution (0.1 M, 500 μl) is added and the suspension is vigorously stirred for 5 minutes until the exchange equilibrium has established and the voltage can be recorded. This step is repeated eleven times yielding 12 data points.

Evaluation: The Mathcad worksheet ‘Evaluation.mcd’ plots the ion exchange isotherm and performs the evaluation which yields the thermodynamic quantities of the ion exchange.

Hazards: $AgNO_3$ is corrosive and environmentally hazardous. Use safety glasses and dispose waste solution appropriately.

Literature

1. *Handbook of Zeolite Science and Technology*; Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; Marcel Dekker, Inc.: New York, 2003
2. *Host-Guest-Systems Based on Nanoporous Crystals*; Laeri, F., Schüth, F., Simon, U., Wark, M., Eds.; WILEY-VCH: Weinheim, 2003
3. Calzaferri, G.; Leiggener, C.; Glaus, S.; Schürch, D.; Kuge, K. *Chem. Soc. Rev.*, **2003**, *32*, 29-37
4. Breck, D. W. *Zeolite Molecular Sieves*, J. Wiley & Sons: New York, **1974**
5. Pluth, J. J.; Smith, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 4704-4708
6. Olson, D.; Meier, W. M.; Baerlocher, Ch. *Atlas of Zeolite Framework Types*, 5th Rev.; Elsevier Science Pub Co: Amsterdam, 2001
7. Treacy, M. M. J.; Higgins, J. B. *Collection of Simulated Xrd Powder Patterns for Zeolites*, 4th Rev.; Elsevier Science Pub Co: Amsterdam, 2001
8. Breck, D. W.; Eversole, W. G.; Milton, R. M.; Reed, T. B.; Thomas, T. L. *J. Am. Chem. Soc.* **1956**, *78*, 5963-5971
9. Reed, T. B.; Breck, D. W. *J. Am. Chem. Soc.* **1956**, *78*, 5972-5977
10. Lainé, P.; Seifert, R.; Giovanoli, R.; Calzaferri, G. *New J. Chem.* **1997**, *21*, 453-460
11. Meyer, M.; Leiggener, C.; Calzaferri, G. *ChemPhysChem*, **2005**, *6*, 1071-1080
12. Meyer, M.; Currao, A.; Calzaferri, G. *ChemPhysChem*, **2005**, *6*, 2167-2178
13. *Mathcad*, a complete solution for performing advanced calculations and preparing publication-quality technical documents..; Mathsoft Engineering & Education, Inc.: http://www.mathsoft.com, **2002**
14. Marquardt, D. W. *J. Soc. Industr. Appl. Math.* **1963**, *11*, 431-441
15. Seifert, R.; Kunzmann, A.; Calzaferri, G. *Angew. Chem. Int. Ed.* **1998**, *37*, 1521-1524
16. Seifert, R.; Rytz, R.; Calzaferri, G. *J. Phys. Chem. A* **2000**, *104*, 7473-7483
17. Leiggener C.; Calzaferri G. *Chem. Eur .J.* **2005**, *11*, 7191.