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Removal of Heavy Metal Ions from Solutions Using Zeolites. III. Influence of Sodium Ion Concentration in the Liquid Phase on the Kinetics of Exchange Processes Between Cadmium Ions from Solution and Sodium Ions from Zeolite A

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ABSTRACT

Kinetics of exchange processes between the sodium ions from zeolite A and cadmium ions from solutions containing different contents of Na^+ ions was determined by measuring changes in the concentrations of cadmium and sodium ions in both zeolite and the liquid phase during the exchange processes. The exchange kinetics were analyzed in accordance

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with the kinetic model derived on the basis of the second-order forward reaction between the cadmium ions from solution and the sodium ions from zeolite A and on the second-order backward reaction between sodium ions from solution and cadmium ions from zeolite A. The equilibrium cadmium uptake on zeolite A decreases with increasing concentration of sodium ions in the liquid phase. Agreement between the measured exchange kinetics and the exchange kinetics calculated by numerical solutions of the model equations shows that the exchange process takes place in accordance with the proposed model.

Key Words: Zeolite A; Ion exchange; Sodium ions; Cadmium ions; Exchange kinetics.

INTRODUCTION

It is well known that heavy metals are very toxic elements and their discharge into receiving waters causes detrimental effects on human health and the environment.[1] One of the most toxic metals, cadmium, finds its way to water bodies through wastewaters from the following industries: metal plating cadmium–nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, and alloys.[2,3] The effects of acute cadmium poisoning in humans are very serious, among them are high blood pressure, kidney damage, and destruction of testicular tissue and red blood cells. Small amounts of Cd^{2+} ions are believed to be harmful to humans, having been associated with hypertensive diseases.[4] For this reason, there is a constant need to remove heavy metals, including cadmium, from industrial effluents and other wastewaters.

Different technologies for removal of heavy metals, such as chemical precipitation, electro-flotation, reverse osmosis, adsorption on activated carbon, and ion exchange, are described in literature.[5] Ion exchange seems to be an attractive method, especially when low-cost materials can be used as exchangers.[6] Although some of these methods may be more effective than ion exchange (e.g., the precipitation process leaves the waste solution with several parts per million of cadmium[7]), ion exchange is considered attractive because of the relative simplicity of its application.[8] Both natural[6,8–14] and synthetic[15–22] zeolites can be widely used as effective and/or selective cation exchangers.

Although natural zeolites are cheaper than synthetic ones and can be used directly in columns in crushed form, their exchange capacity considerably depends upon the content of zeolitic phase in the rock, the type of cation exchange form, and admixture character. This may cause serious difficulties in applications where the exchange process needs to be very well controlled. Besides, the use of natural zeolites is often limited to the countries that have their own deposits. An alternative is use of cheap synthetic zeolites, e.g., zeolite

4A, which is widely produced as a detergent builder and has defined chemical composition and high and constant cation-exchange capacity. Of course, the ion selectivity must also be considered in the choice of zeolite exchanger.

Our previous studies of the thermodynamics[21–23] and kinetics[23–25] of the exchange processes between heavy metal ions (Cd^{2+}, Pb^{2+}, and Zn^{2+}) from solutions and sodium ions from zeolite A have shown that: (i) the selectivity of zeolite A for cadmium ions is high, e.g., the separation factor $\alpha_{Cd} \approx 20$ in a wide range of equivalent cadmium ion fractions (0–0.8), total normality (0.02–0.1 $\mathrm{meq\,dm^{-3}}$), and temperature (20–60°C); (ii) the kinetic of the exchange process is governed by the second-order reaction of the cations from solution with the cations from zeolite; and (iii) the influence of the backward reaction (exchange of sodium ions from solution with heavy metal ions from zeolite) is negligible if an additional amount of Na^+ ions is not present in the system. Hence, all sodium ions from zeolite A may be exchanged with the heavy metal ions from solutions in "pure" systems,[21–25] e.g., in the absence of the additional amount of the competing exchangeable cations (e.g., Na^+). On the other hand, "pure" exchange systems appear very rarely in the purification practice; the presence of different competing cations is quite usual.[14,26–31] Since an increase in concentration of the competing cations results in a decrease of the cation binding capacity,[32] which may influence the exchange kinetics, our intention is to examine the influence of sodium ion concentration in the liquid phase on the exchange kinetics between cadmium ions from solution and sodium ions from zeolite A.

EXPERIMENTAL

Zeolite 4A (SILKEM, Kidričevo, Slovenia), which has the following oxide chemical composition: $1.087\ Na_2O \cdot Al_2O_3 \cdot 1.99\ SiO_2 \cdot 4.56\ H_2O$ and particle size in the range of 1.5–10 μm (with mean particle size of 4.5 μm),[23] was used as the cation exchanger. Before use, the zeolite was kept in a desiccator with saturated NaCl solution for 48 hr.

The $Cd(NO_3)_2 \cdot 4\ H_2O$ (Ventron, Germany) and $NaNO_3$ (Riedel de Haen A.G., Germany) were used for the preparation of the stock solution of cadmium nitrate and solutions of sodium nitrate, respectively. Distilled water was used as a solvent. The $Cd(NO_3)_2$ solutions and mixed $NaNO_3/Cd(NO_3)_2$ solutions were prepared by mixing appropriate volumes of the stock solutions of cadmium nitrate as well as sodium nitrate and cadmium nitrate, respectively, and distilled water.

Kinetics of the exchange processes between Cd^{2+} ions from solution and Na^+ ions from zeolite 4A were measured as follows: 0.2 g of zeolite 4A was introduced into a reaction vessel containing 200 mL of a thermostated (25°C), well-mixed solution with appropriate amounts of Cd^{2+} ($\approx 4.5 \times 10^{-3}$ mol dm^{-3}) and Na^{+} ions (0–0.348 mol dm^{-3}). The temperature of the system was maintained by a circulatory water bath during the exchange process. The moment at which zeolite 4A was added to the solution was taken as the zero time ($t_E = 0$) of the exchange process. The reaction mixture (suspension of zeolite 4A in solution) was stirred by a Teflon-coated magnetic bar driven by a magnetic stirrer. At various times, t_E, of the exchange process, aliquots of the reaction mixture were drawn off the reaction vessel and centrifuged to separate the solid from the liquid phase in order to stop the exchange process. Aliquots of the clear liquid phase above the sediment (Na, Cd form of zeolite A) were diluted with distilled water to the concentration ranges appropriate for measuring the concentrations of sodium and cadmium by atomic absorption spectroscopy.

The sediments separated from the suspensions at various times t_E were washed with distilled water, dried at 105°C overnight, and kept in a desiccator with saturated NaCl solution for 48 hr. Thereafter, the samples were dissolved in a 1 : 1 HCl solution. The solutions were diluted with distilled water to the concentration ranges appropriate for measuring the concentrations of sodium and cadmium by atomic absorption spectroscopy.

Concentrations of sodium and cadmium in the solutions were measured by the Perkin–Elmer 3030B (USA) atomic absorption spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows changes in concentrations, $C_{Cd,s}$, of cadmium ions in zeolite A during the exchange of sodium ions from zeolite A with cadmium ions to the solutions having an approximately constant starting concentration ($C^0_{Cd,s} \approx 4.5 \times 10^{-3}$ mol dm^{-3}; see Table 1) of cadmium ions and different concentrations ($C^0_{Na,s} = 0$–0.348 mol dm^{-3}; see Table 1) of sodium ions. In all cases, the equilibrium exchange ($C_{Cd,z} = C_{Cd,z}$ (eq); plateau of the $C_{Cd,z}$ vs. t_E curves) was reached in less than $t_E = 25$ min (see Fig. 1), but the value of $C_{Cd,z}$(eq) decreases with increasing concentration $C^0_{Na,s}$ of the sodium ions in solution (see Figs. 1 and 2 and Table 1).

The overall exchange reaction of Na^{+} ion fixed in the zeolite (e.g., zeolite 4A) by divalent metallic cation Me^{2+} (e.g., $Me^{2+} = Cd^{2+}$) in the solution can be written:

$$Cd^{2+}(s) + 2Na^{+}(z) \underset{k_b}{\overset{k_f}{\rightleftarrows}} Cd^{2+}(z) + 2Na^{+}(s)$$

where k_f and k_b are rate constants of the forward and backward reactions, respectively, and the denotations (s) and (z) refer to the ions in solution and zeolite, respectively.

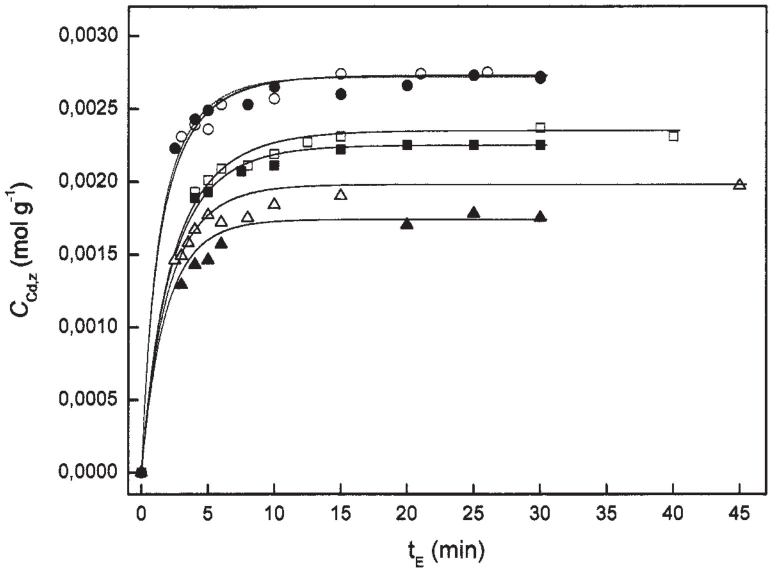

Figure 1. Kinetics of exchange between sodium ions from zeolite A and cadmium ions from solutions having nearly constant initial concentration of cadmium ions ($C^0_{\mathrm{Cd,s}} \approx 4.5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$; see Table 1) and different initial concentrations of sodium ions ($C^0_{\mathrm{Na,s}} = 0$ (○, ●), 0.0215 (□), 0.0471 (■), 0.087 (△), and 0.174 (▲) $\mathrm{mol\,dm^{-3}}$. Solid curve and symbol ○ represent the exchange kinetics with $C^0_{\mathrm{Cd,s}} = 4.27 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ and dashed curve and symbol ● represent the exchange kinetics with $C^0_{\mathrm{Cd,s}} = 4.46 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. Curves represent the concentration of cadmium ions in zeolite A ($C_{\mathrm{Cd,z}}$) vs. time of the exchange process (t_{E}) functions calculated by numerical solution of Eq. (5).

Most researchers assume that diffusion of exchangeable ions through the channel/void system of zeolites is the rate-determining step of the exchange process.[26,32–40]

Another, less popular, approach to the kinetics of ion exchange of zeolites assumes that zeolite is an open structure and that all cations in zeolite are instantaneously and simultaneously available for exchange with the cations from solution and thus that a chemical exchange is slow compared to any difusion process, i.e., the chemical exchange is the rate-determing mechanism.[8,23–26,29,41] Assuming that the kinetic order of chemical exchange is two with respect to the number ($Q_\infty - Q_{t_{\mathrm{E}}}$) of available sites for the exchange, Blanchard et al.[8] derived the kinetic equation:

$$\frac{-dQ_t}{dt_{\mathrm{E}}} = K(Q_\infty - Q_{t_{\mathrm{E}}})^2 \qquad (1)$$

Table 1. Initial concentrations of cadmium ions ($C^0_{\mathrm{Cd,s}}$) and of sodium ions ($C^0_{\mathrm{Na,s}}$) in solution and equilibrium concentrations of Cd^{2+} in zeolite A [$C_{\mathrm{Cd,z}}$(eq)], of Cd^{2+} ions in solution [$C_{\mathrm{Cd,s}}$(eq)], and of Na^+ ions in solution [$C_{\mathrm{Na,s}}$(eq)].

$C^0_{\mathrm{Cd,s}}$ (mol dm^{-3})	$C^0_{\mathrm{Na,s}}$ (mol dm^{-3})	$C_{\mathrm{Cd,z}}$(eq) (mol g^{-1})	$C_{\mathrm{Cd,s}}$(eq) (mol dm^{-3})	$C_{\mathrm{Na,s}}$(eq) (mol dm^{-3})
4.27×10^{-3}	0	2.73×10^{-3}	1.54×10^{-3}	5.46×10^{-3}
4.46×10^{-3}	0	2.71×10^{-3}	1.75×10^{-3}	5.42×10^{-3}
4.37×10^{-3}	2.15×10^{-2}	2.35×10^{-3}	2.02×10^{-3}	2.62×10^{-2}
4.50×10^{-3}	4.71×10^{-2}	2.25×10^{-3}	2.25×10^{-3}	5.16×10^{-2}
4.39×10^{-3}	8.70×10^{-2}	2.00×10^{-3}	2.39×10^{-3}	9.10×10^{-2}
4.58×10^{-3}	1.74×10^{-1}	1.80×10^{-3}	2.78×10^{-3}	1.77×10^{-1}

where $Q_\infty = Q^0_{\mathrm{Me,z}}$ is the exchange capacity of zeolite for cations Me^{n+}, $Q_{t_\mathrm{E}} = C_{\mathrm{Me,z}}$ is the concentration of cations Me^{n+} in zeolite at $t_\mathrm{E} > 0$, and K is the rate constant. Since integration of Eq. (3) gives

$$\frac{1}{(Q_\infty - Q_{t_\mathrm{E}})} - \alpha = K t_\mathrm{E} \tag{2}$$

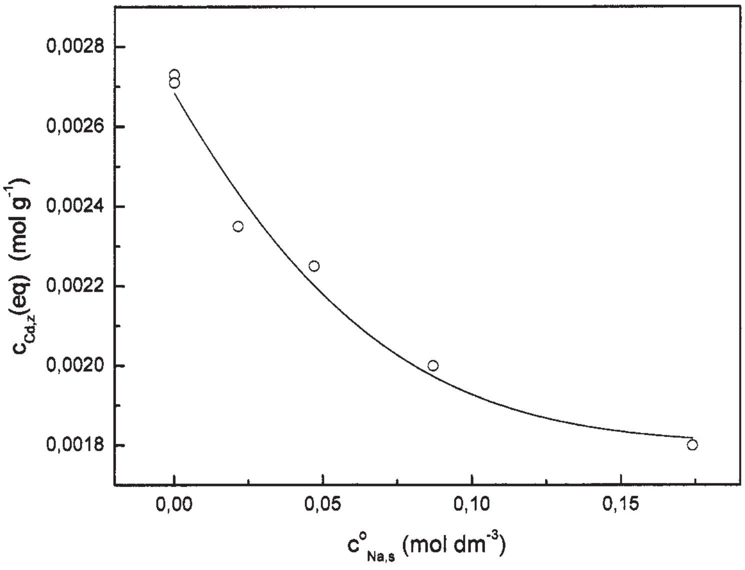

Figure 2. Influence of the initial concentration of sodium ions in the liquid phase ($C^0_{\mathrm{Na,s}}$) on the equilibrium uptake ($C_{\mathrm{Cd,z}}$(eq)).

chemical exchange is characterized by a linear relationship between $(Q_\infty - Q_{t_\mathrm{E}})$ and t_E. On the other hand, Boyd et al.[32] and later, Varon and Rieman[42] concluded that the plots $-\log(1 - Q_{t_\mathrm{E}}/Q_\infty)$ vs. t_E should be linear if the chemical reaction is the rate-determining step, i.e.,

$$-\log\left(1 - \frac{Q_{t_\mathrm{E}}}{Q_\infty}\right) = Kt_\mathrm{E} \tag{3}$$

Although diffusion as a controlling mechanism of exchange on zeolites is widely accepted, the diffusion equation is strictly valid only for exchange of cations from solution having the same charge and diffusion coefficient as the cations in monodispersed spherical particles of zolite.[36,42] Most real systems do not satisfy these conditions. Moreover, the diffusion coefficient changes its value with the extent of the exchange process.[42] On the other hand, simplification of the original equation, e.g., $F = Q_{t_\mathrm{E}}/Q_\infty = k\ (t_\mathrm{E})^{1/2}$, restricts the analysis of experimental data either to a low extent of the exchange ($F \leq 0.05$) or very short exchange time.[36] In addition, diffusion of ions in the channel/void system of zeolite is only one part of the entire process of replacement of the ions positioned at specific sites in the zeolite framework with the ions from solution. This makes any analysis of the exchange process using the diffusion equation very uncertain. In this context, although it cannot be strictly evaluated, an assumption that the exchange process between Na^+ ions from zeolite A and Cd^{2+} ions from solution is slow compared to any diffusion process in zeolite particles is quite reasonable. In addition, the second-order reaction exchange model has no limitation with respect to particle size and shape,[43] and thus the simplified relationships between t and F, derived on the basis of this model [see Eqs. (2) and (3)], are valid for most of or even the entire exchange process. Hence, the linear relationship between t and $[1/(Q_\infty - Q_{t_\mathrm{E}})]$ (correlation factor $R = 0.9913$; see Fig. 3) and t and $-\log(1 - Q_\infty/Q_{t_\mathrm{E}})$ ($R = 0.984$; see Fig. 4), respectively, during nearly the entire exchange process ($C^0_{\mathrm{Na,s}} = 0$) indicates that the second order is the most apparent rate-determining step of the exchange process.

Based on the assumption that the kinetics of exchange of Na^+ ions from the zeolite by Cd^{2+} ions in the solution of a constant batch volume can be defined as a second-order reaction,

$$\frac{dC_\mathrm{Cd,z}}{dt_\mathrm{E}} = k_\mathrm{f}(Q^0_\mathrm{Cd,z} - C_\mathrm{Cd,z})a_\mathrm{Cd,s} - k_\mathrm{b}C_\mathrm{Cd,z}a_\mathrm{Na,s} \tag{4}$$

where $Q^0_{\mathrm{Cd},z}$ is the exchange capacity of zeolite A for Cd^{2+} ions (maximum amount of Cd^{2+} ions that may be exchanged by Na^+ ions from the unit mass of zeolite 4A ($Q^0_{\mathrm{Cd},z} = 2.74 \times 10^{-3}\ \mathrm{mol\ g^{-1}}$); $C_\mathrm{Cd,z}$ is the concentration of Cd^{2+} ions in zeolite A at $t_\mathrm{E} > 0$; $a_\mathrm{Cd,s} = \gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}} C_\mathrm{Cd,s}$, $C_\mathrm{Cd,s} = C_{\mathrm{Cd(NO_3)_2}} = C^0_\mathrm{Cd,s} - C_{\mathrm{Cd},z}$ is the molar

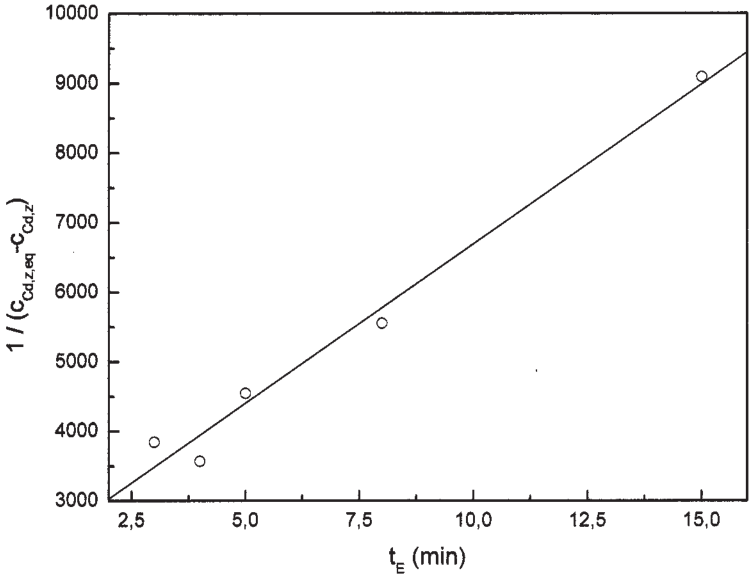

Figure 3. Dependence of $[1/(Q_\infty - Q_{t_E})] = [1/(C_{Cd,z}(eq) - C_{Cd,z})]$ on t_E for the exchange process between cadmium ions from solution ($C^0_{Na,s} = 0$, $C^0_{Cd,s} = 4.46 \times 10^{-3}$ mol dm^{-3}) and sodium ions from zeolite A.

concentration of cadmium ions in the solution at $t_E > 0$; and $a_{Na,s} = \gamma^{NaNO_3}_{Cd(NO_3)_2} C_{Na,s}$ and $C_{Na,s} = C_{NaNO_3} = C^0_{Na,s} + C'_{Na,s}$ is the molar concentration of Na^+ ions in the solution at $t_E > 0$, where $C^{\,0}_{Na,s} = C^{\,0}_{NaNO_3}$ is the initial (at $t_E = 0$) molar concentration of Na^+ ions in solution. Since an increase in the concentration $C'_{Na,s}$ of Na^+ ions in solution is the consequence of the exchange process between the Na^+ ions from the zeolite and the Cd^{2+} ions from the solution, the concentration $C'_{Na,s}$ may be expressed as: $C'_{Na,s} = 2C_{Cd,z}$, and thus $a'_{Na,s} = 2\gamma^{NaNO_3}_{Cd(NO_3)_2} C_{Cd,z}$. The values, $Q^0_{Cd,z}$, $C_{Cd,z}$, $C^0_{Cd,s}$, $C_{Na,s}$, $C'_{Na,s}$, and $C^0_{Na,s}$ represent moles of the corresponding cations (Na^+, Cd^{2+}) in the system (1 g of zeolite A in a dm^3 of suspension). At equilibrium (the end of the exchange process),

$$\frac{dC_{Cd,z}}{dt_E} = 0 \tag{5}$$

and thus,

$$k_b = \frac{k_f \left[Q^0_{Cd,z} - C_{Cd,z}(eq)\right] \gamma^{Cd(NO_2)_2}_{NaNO_3} \left[C^0_{Cd,s} - C_{Cd,z}(eq)\right]}{C_{Cd,z}(eq)\, \gamma^{NaNO_3}_{Cd(NO_3)_2} \left[2C_{Cd,z}(eq) + C^0_{Na,s}\right]} \tag{6}$$

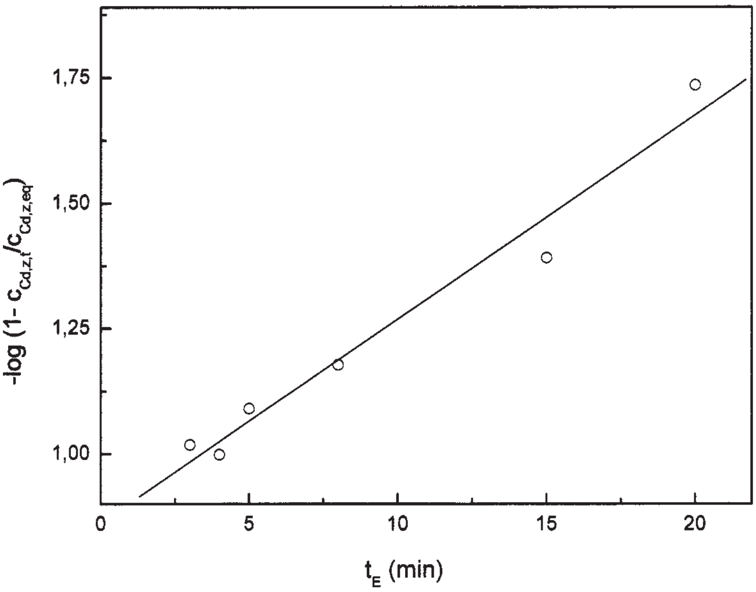

Figure 4. Dependence of $-\log(1 - Q_{t_E}/Q_\infty) = -\log(1 - C_{\mathrm{Cd,z}}(\mathrm{eq}))$ on t_E for the exchange process between cadmium ions from solution ($C^0_{\mathrm{Na,s}} = 0$, $C^0_{\mathrm{Cd,s}} = 4.46 \times 10^{-3}$ mol dm^{-3}) and sodium ions from zeolite A.

where $C_{\mathrm{Cd,z}}(\mathrm{eq})$ is concentration (in mol g^{-1}) of Cd^{2+} ions in zeolite A at the end of the exchange process.

The activity coefficients of $\mathrm{NaNO_3}$ in a binary mixture with $\mathrm{Cd(NO_3)_2}$, $\gamma^{\mathrm{NaNO_3}}_{\mathrm{Cd(NO_3)_2}}$ and activity coefficients of $\mathrm{Cd(NO_3)_2}$ in a binary mixture with $\mathrm{NaNO_3}$, $\gamma^{\mathrm{Cd(NO_3)_2}}_{\mathrm{NaNO_3}}$ may be calculated by the Glueckauf equations:[44,45]

$$\log \gamma^{\mathrm{NaNO_3}}_{\mathrm{Cd(NO_3)_2}} = \log \gamma_{\mathrm{NaNO_3,s}} - \frac{C_{\mathrm{Cd,s}}}{4I} \times \left[K_1 \log \gamma_{\mathrm{NaNO_3,s}} - K_2 \log \gamma_{\mathrm{Cd(NO_3)_2,s}} - \frac{K_3}{(1+I)} \right] \tag{7}$$

$$\log \gamma^{\mathrm{Cd(NO_3)_2}}_{\mathrm{NaNO_3}} = \log \gamma_{\mathrm{Cd(NO_3)_{2,s}}} - \frac{C_{\mathrm{Na,s}}}{4I} \times \left[K_4 \log \gamma_{\mathrm{Cd(NO_3)_2,s}} - K_5 \log \gamma_{\mathrm{NaNO_3,s}} - \frac{K_6}{(1+I)} \right] \tag{8}$$

where $\gamma_{\mathrm{Cd(NO_3)_2}}$ is the activity coefficient of cadmium nitrate in the cadmium nitrate solution having the concentration $C_{\mathrm{Cd,s}}$;[46] $\gamma_{\mathrm{NaNO_{3,s}}}$ is the activity coefficient of sodium nitrate in the sodium nitrate solution having the concentration $C_{\mathrm{Na,s}}$;[45] and $I = 3C_{\mathrm{Cd,s}} + C_{\mathrm{Na,s}}$ is the ionic strength of the mixed solution. The constants K_1–K_6 were calculated as[44,45]

$$K_1 = |z_{\mathrm{Cd}}|(2|z_{\mathrm{Cd}}| - |z_{\mathrm{Na}}| + |z_{\mathrm{NO_3}}|) = 8$$

$$K_2 = |z_{\mathrm{Na}}|\frac{(|z_{\mathrm{Cd}}| + |z_{\mathrm{NO_3}}|)^2}{(|z_{\mathrm{Na}}| + |z_{\mathrm{NO_3}}|)} = 4.5$$

$$K_3 = 0.5|z_{\mathrm{Na}}||z_{\mathrm{Cd}}||z_{\mathrm{NO_3}}|\frac{(|z_{\mathrm{Na}}| - |z_{\mathrm{Cd}}|)^2}{(|z_{\mathrm{Na}}| + |z_{\mathrm{NO_3}}|)} = 0.5$$

$$K_4 = |z_{\mathrm{Na}}|(2|z_{\mathrm{Na}}| - |z_{\mathrm{Cd}}| + |z_{\mathrm{NO_3}}|) = 1$$

$$K_5 = |z_{\mathrm{Cd}}|\frac{(|z_{\mathrm{Na}}| + |z_{\mathrm{NO_3}}|)^2}{(|z_{\mathrm{Cd}}| + |z_{\mathrm{NO_3}}|)} = 2.667$$

$$K_6 = 0.5|z_{\mathrm{Cd}}||z_{\mathrm{Na}}||z_{\mathrm{NO_3}}|\frac{(|z_{\mathrm{Cd}}| - |z_{\mathrm{Na}}|)^2}{(|z_{\mathrm{Cd}}| + |z_{\mathrm{NO_3}}|)} = 0.333$$

where $|z_{\mathrm{Na}}| = 1$, $|z_{\mathrm{Cd}}| = 2$, and $|Z_{\mathrm{NO_3}}| = 1$ are the absolute values of the charges of Na^+, Cd^{2+}, and $\mathrm{NO_3^-}$ ions.

An analysis of the change in the activity coefficients $\gamma_{\mathrm{Cd(NO_3)_2}}^{\mathrm{NaNO_3}}$ and $\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}}$ during the exchange process showed that the values of $\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}}$ and $\gamma_{\mathrm{Cd(NO_3)_2}}^{\mathrm{NaNO_3}}$ are almost constant during the exchange process (see Table 2 as an example) but considerably decrease with increasing concentration $C_{\mathrm{Cd,s}}^0$ (see Table 3). Hence, the values of $\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}}$ and $C_{\mathrm{Na,s}}^0$ in Table 3 represent their average, i.e., $\gamma_{\mathrm{Cd(NO_3)_2}}^{\mathrm{NaNO_3}} = [\sum_{i=1}^{n}(\gamma_{\mathrm{Cd(NO_3)_2}}^{\mathrm{NaNO_3}})_i]/n$ and $\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}} = [\sum_{i=1}^{n}(\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}})]/n$, where n is the number of the measuring/ calculation for each kinetics (see Table 2).

In order to evaluate the model of the exchange kinetics expressed by Eq. (4), the value of k_{b} was substituted by the right-hand side of Eq. (6) and then the values of constant k_{f} for the corresponding values of $Q_{\mathrm{Cd},z}^0$, $C_{\mathrm{Cd},s}^0$, $C_{\mathrm{Na},s}^0$, $\mathrm{C_{Na,s}(eq)}$, $C_{\mathrm{Cd,z}}(\mathrm{eq})$, $C_{\mathrm{Cd,s}}(\mathrm{eq})$, $\gamma_{\mathrm{Cd(NO_3)_2}}^{\mathrm{NaNO_3}}$, and $\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}}$, listed in Tables 1 and 3, were calculated by an iterative numerical solution of Eq. (4), using a fourth-order Runge–Kutta method. Then the appropriate values of the constant k_{b} were calculated using Eq. (6), using the corresponding values of $Q_{\mathrm{Cd},z}^0$, $C_{\mathrm{Cd,s}}^0$, $C_{\mathrm{Na,s}}^0$, $C_{\mathrm{Cd,z}}(\mathrm{eq})$, $\gamma_{\mathrm{Cd(NO_3)_2}}^{\mathrm{NaNO_3}}$, and $\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}}$ and the values of k_{f} calculated as described above. The appropriate numerical values of the constants k_{f} and k_{b} as well as the standard deviations of k_{f} are listed in Table 4.

The curves in Fig. 1 represent the changes of $C_{\mathrm{Cd,z}}$ with t_{E}, calculated by numerical solutions of Eq. (4) using the appropriate values of the constants $Q_{\mathrm{Cd},z}^0$, $C_{\mathrm{Cd,s}}^0$, $C_{\mathrm{Cd,z}}(\mathrm{eq})$, and $C_{\mathrm{Na,s}}^0$ (Table 1) $\gamma_{\mathrm{Cd(NO_3)_2}}^{\mathrm{NaNO_3}}$, and $\gamma_{\mathrm{NaNO_3}}^{\mathrm{Cd(NO_3)_2}}$ (Table 3); k_{f} and k_{b} (Table 4). The results presented in Fig. 1 show that the

Table 2. Values of the ionic strength, *I*, and activity coefficients $\gamma_{Cd(NO_3)_2}$, γ_{NaNO_3}, $\gamma_{NaNO_3}^{Cd(NO_3)_2}$, and $\gamma_{Cd(NO_3)_2}^{NaNO_3}$ at different stages of the exchange process of Cd^{2+} ions from solution with Na^+ ions from zeolite A. $C_{Cd,s}^0 = 4.5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $C_{Na,s}^2 = 4.71 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$.

i	t_E (min)	I_i (mol dm^{-3})	$(\gamma_{Cd(NO_3)2})_i^a$	$(\gamma_{NaNO_3})_i^b$	$(\gamma_{Cd(NO_3)_2}^{NaNO_3})_i^c$	$(\gamma_{NaNO_3}^{Cd(NO_3)_2})_i^d$
1	0	0.0606	0.970	0.830	0.859	0.912
2	0.5	0.0600	0.974	0.828	0.850	0.910
3	1	0.0593	0.974	0.824	0.845	0.907
4	1.5	0.0591	0.974	0.824	0.844	0.906
5	2	0.0590	0.974	0.824	0.843	0.906
6	2.5	0.0589	0.974	0.824	0.843	0.906
7	3	0.0588	0.974	0.824	0.842	0.905
8	4	0.0587	0.974	0.824	0.842	0.905
9	5	0.0585	0.980	0.824	0.841	0.905
10	7.5	0.0585	0.980	0.824	0.840	0.908
11	10	0.0585	0.980	0.824	0.840	0.908
12	15	0.0583	0.980	0.822	0.837	0.906
13	20	0.0584	0.980	0.822	0.837	0.906
14	25	0.0584	0.980	0.822	0.837	0.906
15	30	0.0585	0.980	0.822	0.837	0.906
16	60	0.0583	0.980	0.822	0.837	0.906
17	80	0.0583	0.980	0.822	0.837	0.906
18	100	0.0583	0.980	0.822	0.837	0.906
19	125	0.0582	0.980	0.822	0.837	0.906
20	140	0.0584	0.980	0.822	0.837	0.906
21	160	0.0584	0.980	0.822	0.837	0.906
22	180	0.0583	0.980	0.822	0.837	0.906
	Averages:	0.0587	0.980	0.823	0.841	0.907

[a] From Ref.[46].
[b] From Ref.[47].
[c] Calculated using Eq. (7).
[d] Calculated using Eq. (8).

agreement between the calculated (curves) and measured (symbols) $C_{Cd,z}$ vs. t_E functions are very well for all the exchange kinetics examined, what is evident from the values of standard deviations (see Table 4). This indicates that the process of exchange between Na^+ ions from zeolite A and Cd^{2+} ions from solution takes place in accordance with the proposed model (second-order reaction)[8,24,25,29,41] and that the kinetics of the exchange process may be described by Eq. (4). Considerably faster forward reaction (exchange of Cd^{2+} ions from solution with Na^+ ions from zeolite A) relative to the backward reaction (exchange of Na^+ ions from solution with Cd^{2+} ions from

Table 3. Initial concentrations of cadmium ions ($C^0_{\mathrm{Cd,s}}$) and of sodium ions ($C^0_{\mathrm{Na,s}}$) in solution and the average values of the activity coefficients $\gamma^{\mathrm{NaNO_3}}_{\mathrm{Cd(NO_3)_2}}$ and $\gamma^{\mathrm{Cd(NO_3)_2}}_{\mathrm{NaNO_3}}$.

$C^0_{\mathrm{Cd,s}}$ (mol dm^{-3})	$C^0_{\mathrm{Na,s}}$ (mol dm^{-3})	$\gamma^{\mathrm{NaNO_3}}_{\mathrm{Cd(NO_3)_2}}$	$\gamma^{\mathrm{Cd(NO_3)_2}}_{\mathrm{NaNO_3}}$
4.27×10^{-3}	0	0.990	0.978
4.46×10^{-3}	0	0.991	0.976
4.37×10^{-3}	2.15×10^{-2}	0.892	0.931
4.50×10^{-3}	4.71×10^{-2}	0.841	0.906
4.39×10^{-3}	8.70×10^{-2}	0.787	0.874
4.58×10^{-3}	1.74×10^{-1}	0.726	0.835

zeolite A), i.e., $k_f/k_b \approx 10^4$, is in accordance with the finding that the affinity of zeolite A for cadmium ions is considerably higher than the affinity for the host sodium ions.[21]

As expected from formal chemical and reaction reasons, numerical values of both constants k_f and k_b do not change considerably with the concentration of $NaNO_3$ ($C_{\mathrm{NaNO_3}} = 0.0215$–$0.174$ mol dm^{-3}) added in the system. This is, together with fairly good agreement between measured and calculated kinetics (see Fig. 1), an additional argument that the exchange between Na^+ ions from zeolite A and Cd^{2+} ions from solution takes place by the second-order reaction. On the other hand, a decrease of both the values k_f and k_b in the systems containing $NaNO_3$ relative to the "pure" system may be explained by specific cation–anion interactions.[48,49] Namely, it is well known that Cd^{2+} ions tend to form $CdNO_3^+$ complex in the presence of NO_3^- ions,[48,49] e.g., 5.5×10^{-3} M solution of $Cd(NO_3)_2$ solution contains about 93% of Cd^{2+} ions and about 7% of $CdNO_3^+$ ions. Hence, it can be assumed that an increase in the concentration of

Table 4. Initial concentrations, of cadmium ions ($C^0_{\mathrm{Cd,s}}$) and of sodium ions ($C^0_{\mathrm{Na,s}}$) in solution, values of the rate constants of the forward reaction (k_f), of the backward reaction (k_b), and the standard deviation [$\Delta(k_f)$].

$C^0_{\mathrm{Cd,s}}$ (mol dm^{-3})	$C^0_{\mathrm{Na,s}}$ (mol dm^{-3})	k_f (mol^{-1} min^{-1})	$\Delta(k_f)$	k_b (mol^{-1} min^{-1})
4.27×10^{-3}	0	2.007×10^2	2.086×10^{-5}	3.79×10^{-4}
4.27×10^{-3}	0	2.007×10^2	2.761×10^{-5}	4.24×10^{-4}
4.37×10^{-3}	2.15×10^{-2}	1.068×10^2	1.564×10^{-5}	1.95×10^{-2}
4.50×10^{-3}	4.71×10^{-2}	1.071×10^2	2.267×10^{-5}	1.18×10^{-2}
4.39×10^{-3}	8.70×10^{-2}	1.061×10^2	1.953×10^{-5}	1.14×10^{-2}
4.58×10^{-3}	1.74×10^{-1}	0.995×10^2	3.975×10^{-5}	0.8×10^{-2}

NO_3^- ions caused by addition of $NaNO_3$ in the system increases the amount of $CdNO_3^+$ complex in the solution. Assuming that the rate of exchange between Na^+ ions from zeolite A and $CdNO_3^+$ ions from solution is slower than the rate of exchange between Na^+ ions form zeolite A and Cd^{2+} ions from solution, an increase in the concentration of $CdNO_3^+$ ions relative to the concentration of Cd^{2+} ions would decrease the rate of the overall exchange process. However, the influence of nitrate ions on the relative concentration of $CdNO_3^+$ complex, and thus on the overall exchange kinetics, cannot be evaluated on the basis of the present experimental data, and thus this objective will be investigated in our future work.

CONCLUSION

An analysis of the exchange processes between the sodium ions from zeolite A (1 g/dm^3) and cadmium ions from the solutions ($C^0_{Cd,s} \approx 4.5 \times 10^{-3}$ mol dm^{-3}) containing different contents of Na^+ ions ($C^0_{Na,s} = 0$–0.348 mol dm^{-3}) at 25°C have shown that the overall exchange process may be described by two second-order processes: the forward reaction between the cadmium ions from solution and sodium ions from zeolite A and the backward reaction between sodium ions from solution and cadmium ions from zeolite A. Invariability of the rate constants k_f and k_b with the concentration of $NaNO_3$ added to the systems confirms this conclusion. A considerably higher rate of the forward reaction relative to the backward reaction ($k_f \gg k_b$) is the consequence of the higher affinity of zeolite A to Cd^{2+} ions from solution than the host sodium ions. The decrease in values of both constants k_f and k_b in the systems containing $NaNO_3$ relative to the “pure” systems can be explained by the formation of $CdNO_3^+$ ions in the presence of NO_3^- ions. As expected, the equilibrium uptake, $C_{Cd,z}(eq)$, decreases with increasing concentration of $NaNO_3$ added in the systems.

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