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Removal of Heavy-Metal Ions from Solutions by Means of Zeolites. II. Thermodynamics of the Exchange Processes Between Zinc and Lead Ions from Solutions and Sodium Ions from Zeolite A

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ABSTRACT

Relationships between the corrected selectivity coefficient, $K_C(\mathrm{Me})$ (Me = Zn, Pb), and fraction of the exchanged Me^{2+} ions in zeolite A, $f_{\mathrm{Me,Z}}$, were determined from the corresponding exchange isotherms. The exchange isotherms were obtained by measuring the equilibrium concentrations of sodium and Me^{2+} ions in both the solid and the liquid phase at constant total-ion concentrations and different temperatures in the range from 20°C to 60°C. Thermodynamic equilibrium constants, $K_a(\mathrm{Me})$, calculated from the corresponding Kielland's plots ($\ln K_C(\mathrm{Me})$ vs. $f_{\mathrm{Me,Z}}$ plots) were used for the calculation of the appropriate values of standard free energy, $\Delta G°(\mathrm{Me})$, standard enthalpy, $\Delta H°(\mathrm{Me})$, and standard entropy, $\Delta S°(\mathrm{Me})$.

Key Words. Zeolite A; Ion exchange; Sodium ions; Zinc ions; Lead ions; Exchange equilibrium; Thermodynamic data

INTRODUCTION

Lead is one of the most widely used nonferrous metals in manufacturing metal products, pigments, chemicals, and a variety of other products (1). Although classical lead poisoning has been well known for centuries, lead, one of the most useful metals, has been continuously used. Present-day distribu-

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tion in soil, glaciers, and water is simply the result of a continued and increasing addition to the environment, with an exponential surge following the industrial revolution (1). Lead is widely employed in the manufacture of storage batteries, antiknock gasoline additives, paint pigments, and glazes for ceramics, in addition to numerous metallic products (2). Humans may be contaminated by lead through the food chain, as many metals concentrate in plants and animals, especially fish (1, 2). Lead in particular turns out to be remarkably dangerous. The most prominent adverse effects of lead involve three organ systems: the nervous system (3, 4), the hematopoietic system (5, 6), and the kidneys (7, 8).

Waste containing zinc and its compounds arise from many industrial processes, particularly in metal plating and the manufacture of organic constituents, such as acrylic fiber, rayon, cellophane, and special synthetic rubbers. In general, the metal-plating industry tends to discharge wastewaters into municipal sewers, thereby generating potential problems with subsequent combined treatment (9). Since zinc is a normal component of many human, animal, and vegetable tissues, it is indispensable for the normal development and functioning of many organisms (10). However, larger amounts of zinc can cause symptoms such as neurosis and vomiting in humans (11).

Different technologies are described in the literature for removal of heavy metals, including lead and zinc. Removal of heavy-metal ions from wastewater is most often accomplished by precipitating hydrous oxides (12). Although this method is relatively simple and inexpensive, it does have the following disadvantages (12): (i) It generates a large volume of sludge that is both costly and hazardous to dispose of; (ii) at around 4°C, the precipitation layer in settling ponds undergoes an inversion; (iii) it may fail to sufficiently reduce heavy-metal content; and (iv) the metal values are not directly recovered.

On the other hand, both natural (3, 11–18) and synthetic (11, 19–24) zeolites can be widely used for this purpose. Although natural zeolites are cheaper than synthetic zeolites and can be directly used in columns in crushed form, their exchange capacity depends to a large extent on the content of zeolitic phase in the rock, the form of cation exchange, and the nature of other components contained in natural material. These may be reasons for serious difficulties in applications where the exchange process needs to be very well controlled. Additionally, the use of natural zeolites is often limited to countries having their own deposits. An alternative is the use of cheap synthetic zeolites, e.g., zeolite 4A, which is widely produced as a detergent builder, and has a defined chemical composition and high and constant cation-exchange capacity.

Because of the great importance of zeolite A as a substitute for phosphates in detergents and as an absorbent and efficient cation exchanger, ion exchange of different cations from solutions with sodium ions from zeolite A have been subjects of numerous investigations (25–39). Most of these investigations are related to thermodynamics (30, 32, 33, 35, 37) and kinetics (28, 29, 31, 34) of the exchange processes between Ca^{2+} and Mg^{2+} ions from solutions with Na^{+} ions from zeolite A. The exchange processes between sodium ions from zeolite A and different cations such as Ag^{+}, Tl^{+}, Sr^{2+}, Ba^{2+} (26), K^{+}, Li^{+}, Cu^{2+} (27), Cs^{+} (25, 36, 39), Cd^{2+} (40), and Zn^{2+} (41) from solutions have also been intensely studied. In spite of the great environmental impact of lead, the thermodynamics of the exchange process between Pb^{2+} from solutions and Na^{+} ions from zeolite A were not studied.

Hence, the objective here is to examine the thermodynamics of the exchange equilibrium in the system (Na^{+}, Pb^{2+})–solution + (Na^{+}, Pb^{2+})–zeolite A and different factors that influence the equilibrium and thus efficiency of removal of Pb^{2+} ions from solutions, using zeolite A as an exchanger. Although the thermodynamics of the exchange equilibrium in the system (Na^{+}, Zn^{2+})–solution + (Na^{+}, Zn^{2+})–zeolite A was already studied (42), it was investigated repeatedly under the conditions used in the study of the systems (Na^{+}, Pb^{2+})–solution + (Na^{+}, Pb^{2+})–zeolite A (this work) and (Na^{+}, Cd^{2+})–solution + (Na^{+}, Cd^{2+})–zeolite A (40). This enables a comparison of the exchange behavior of different heavy-metal cations (Zn^{2+}, Pb^{2+}) on particular samples of zeolite A under the same or similar conditions as well as exchange of the same cations (Zn^{2+}) on different samples of zeolite A under different conditions.

EXPERIMENTAL

Zeolite 4A (SILKEM, Kidričevo, Slovenia), which has the oxide chemical composition $1.087\ Na_2O \cdot Al_2O_3 \cdot 1.99\ SiO_2 \cdot 4.56\ H_2O$ and a range of particle sizes between 1.5 and 10 μm (with mean particle size of 4.5 μm) was used as a cation exchanger in this study. Before use, the zeolite was kept in a desiccator with saturated NaCl solution for 48 h. Analytical grade $Pb(NO_3)_2$ (AnalaR), $Zn(NO_3)_2 \cdot 6\ H_2O$ (Kemika), and $NaNO_3$ (Riedel de Haen A.G.) were used for the preparation of the stock solution of lead nitrate (15g of Pb^{2+}/dm^3), zinc nitrate (10 g of Zn^{2+}/dm^3), and sodium nitrate (10 g of Na^{+}/dm^3), respectively. Distilled water was used as a solvent. Mixed $NaNO_3/Me(NO_3)_2$ (Me = Pb and/or Zn) solutions with different fractions of Na^{+} and Me^{2+} ions at constant equivalent cation concentrations were prepared by mixing appropriate volumes of the stock solutions of sodium nitrate and Me–nitrate, respectively, and distilled water. The pH of the mixed $NaNO_3/Zn(NO_3)_2$ solutions was approximately 5.3, and the pH of the mixed $NaNO_3/Pb(NO_3)_2$ was 4.3–4.8.

The equilibrium distribution of Na^{+} and Me^{2+} ions between the solid (zeolite A) and the liquid phase (solution) was determined as follows: An appropriate amount of zeolite 4A was added into an appropriate volume of the thermostated (20, 40, and/or 60°C), well-mixed solution containing appropriate amounts of Na^+ and Me^{2+} ions, so that total concentration of the exchangeable ions ($Na^+ + Me^{2+}$) in the batch was 0.1 geqv/dm^{-3}. The temperature of the system was maintained by a circulating water bath during the exchange process.

Suspension of the zeolite in solution was stirred for a predetermined time, $t_E(eq)$ ($\geq$ 3h), by a Teflon-coated magnetic bar ($\phi = 7$ mm, $l = 30$ mm) driven by a magnetic stirrer (stirring rate was 400 rpm). Thereafter, the suspension was centrifuged to separate the solid from the liquid phase. Three independent measurements were performed at each temperature.

The clear-liquid phase above the sediment (Na–Me-form of zeolite A) was used for measuring Na and Me concentrations and controlling the pH at different stages of the exchange process. Some of the sediments were used for measuring Na and Me contents in the solid phase.

Chemical composition of the starting zeolite 4A powder as well as of its Zn- and Pb-exchanged forms were determined as follows: A given amount of zeolite powder was calcined at 800°C for 2 h. The amount of water was calculated by the weight difference before and after calcination. A given amount of the calcined (waterless) sample was dissolved in 1 : 1 HCl solution. The solution was diluted with distilled water to the concentration ranges available for measuring the concentrations of sodium, zinc, lead, aluminium, and silicon by atomic absorption spectroscopy.

Some sediments separated from the suspension were washed with distilled water, dried at 105°C overnight, and kept in the desiccator with saturated NaCl for 48 h. Thereafter, the samples were dissolved in 1 : 1 HCl solution. The solutions were diluted with distilled water to the concentration ranges available for measuring the concentrations of sodium, lead, and zinc by atomic absorption spectroscopy.

The clear-liquid phases obtained after solid–liquid separation by centrifugation were diluted with distilled water to the concentration ranges available for measuring the concentrations of sodium, lead, and zinc by atomic absorption spectroscopy.

The exchange capacities $\Gamma_{A,Pb}$ and $\Gamma_{A,Zn}$ of zeolite A for Pb^{2+} and Zn^+ ions at 25°C were determined as follows: about 1 g of zeolite A was suspended in 200 mL zinc nitrate (8 g Zn^{2+}/dm^3) and/or lead nitrate (28 g Pb^{2+}/dm^3) solution, then the suspension was kept at 25°C under stirring for 24 h. Thereafter, zeolite A was separated from the solution by centrifugation. The procedure (dispersion in Me–nitrate solution, centrifugation) was repeated three times; after the last centrifugation the solid phase was redispersed in distilled water and centrifuged again. The procedure (dispersion in distilled water, centrifugation) was repeated until the liquid phase after centrifugation did not contain a measurable (by AAS) amount of Me (e.g., lead, zinc). The washed solid phase (Pb- or Zn-exchanged zeolite A) was dried at 105°C, overnight, and then kept in a desiccator with saturated NaCl solution. A given amount of the zeolite A was weighed, and then was dissolved in 1 : 1 HCl solution. The solution was diluted with distilled water to the concentration ranges available for measuring the concentrations of lead and/or zinc by atomic absorption spectroscopy. The exchange capacities $\Gamma_{A,Pb}$ = 394 mg Pb^{2+}/g of zeolite A and $\Gamma_{A,Zn}$ = 166 mg Zn^{2+}/g of zeolite A were calculated from the known mass of the dissolved zeolite and measured concentration of Zn in the solution.

Concentrations of sodium, lead, zinc, aluminum, and silicon in the solutions were measured by the Perkin-Elmer 3030B atomic absorption spectrometer.

RESULTS AND DISCUSSION

The Na^+–Me^{2+} ion-exchange reaction in zeolite A may be written as

$$Me^{2+}(L) + 2\,Na^+(Z) \Leftrightarrow Me^{2+}(Z) + 2Na^+(L)$$

where $Me^{2+} = Pb^{2+}$ and/or Zn^{2+}, and the denotations (L) and (Z) refer to the ions in solution and zeolite A, respectively. The correlated corrected selectivity coefficient, K_C(Me), for the Na^+–Me^{2+} exchange, can be defined as (33, 37, 43, 44):

$$K_C(\mathrm{Me}) = 2N\cdot(\gamma_{\mathrm{Na(Me)L}})^4\cdot f_{\mathrm{Me,Z}}\cdot(f_{\mathrm{Na,L}})^2/(\gamma_{\mathrm{Me(Na)L}})^3\cdot(f_{\mathrm{Na,Z}})^2\cdot f_{\mathrm{Me,L}} \quad (1)$$

where $f_{\mathrm{Me,Z}} = 2m_{\mathrm{Me,Z}}/(m_{\mathrm{Na,Z}} + 2m_{\mathrm{Me,Z}})$ and $f_{\mathrm{Na,Z}} = 1 - f_{\mathrm{Me,Z}} = m_{\mathrm{Na,Z}}/(m_{\mathrm{Na,Z}} + 2m_{\mathrm{Me,Z}})$ are the equivalent cation fractions of Me^{2+} and Na^+ in the zeolite phase, and $f_{\mathrm{Na,L}} = m_{\mathrm{Na,L}}/(m_{\mathrm{Na,L}} + 2m_{\mathrm{Me,L}})$ and $f_{\mathrm{Me,L}} = 2m_{\mathrm{Me,L}}/(m_{\mathrm{Na,L}} + 2m_{\mathrm{Me,L}})$ are equivalent cation fractions of Na^+ and Me^{2+} in solution. Here, $m_{\mathrm{Me,L}}$ and $m_{\mathrm{Na,L}}$ are the molalities of Me^{2+} and Na^+ ions in the solution phase, $\gamma_{\mathrm{Na(Me)L}}$ is the activity coefficient of $NaNO_3$ in a binary mixture with $Me(NO_3)_2$, $\gamma_{\mathrm{Me(Na)L}}$ is the activity coefficient of $Me(NO_3)_2$ in a binary mixture with $NaNO_3$ (45), and N is total normality of the equilibrium-solution phase. Based on earlier experiences that the corrected selectivity coefficient, K_C(Me) is independent of the solution normality in the range 0.01 to 0.1 N (40, 46), the total normality of the equilibrium-solution phase was not varied. Instead, the thermodynamic data relevant for the exchange processes between Zn^{2+} and Pb^{2+} ions from solutions and Na^+ ions from zeolite A were determined from the distribution of Na^+ and Me^{2+} (e.g., Zn^{2+}, Pb^{2+}) ions between solution and zeolite at the exchange equilibrium established at constant total-ions concentration ($N = 0.1$ geqv/dm^3) and different exchange temperatures (20, 40, and 60°C).

Figure 1 shows the equilibrium isotherms of the exchange processes between Zn^{2+} (a) and Pb^{2+} ions (b) from solutions and Na^+ ions from zeolite A at 20°C (○), 40°C (□), and 60°C (△), and total normality, $N = 0.1$ geqv/dm^3, represented as the plots of equivalent heavy-metal-ion fractions, $f_{Me,Z}$, in zeolite A against the heavy-metal-ion fractions, $f_{Me,L}$, in solutions. Experimental values of $f_{Me,Z}$ (symbols) represent average values calculated from the data obtained in three independent experiments (see Experimental). While the

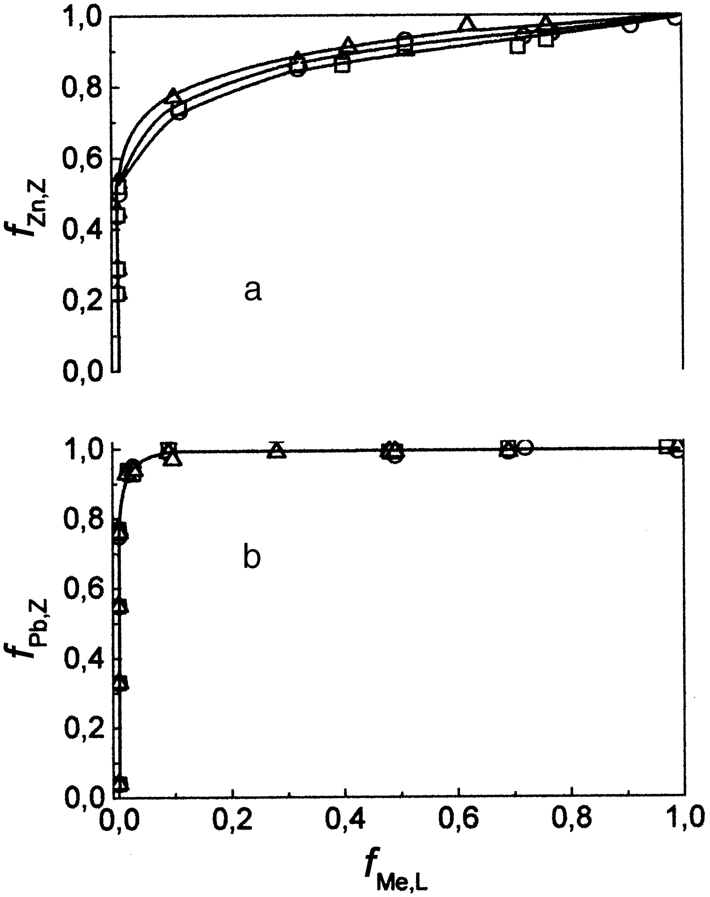

FIG. 1 Equilibrium isotherms of the exchange processes between Zn^{2+} (1a) and Pb^{2+} (1b) ions from solutions and Na^+ ions from zeolite A at 20°C (○), 40°C (□), and 60°C (△) and total normality, $N = 0.1$ geqv/dm^3. Plots are represented as equivalent cadmium ion fractions, $f_{Me,Z}$, in zeolite A against the Me^{2+} ion fractions, $f_{Me,L}$, in solutions (Me = Zn; Fig. 1a and Me = Pb; Fig. 1b).

value of $f_{Zn,Z}$ gradually increases with $f_{Zn,L}$ (see Fig. 1a), the value $f_{Pb,Z} \cong 1$ is reached for $f_{Pb,L} \cong 0.1$ (see Fig. 1b). This indicates that affinity of zeolite A to Pb^{2+} ions is considerably higher than the affinity to Zn^{2+} ions under similar conditions ($N = 0.1$ geq dm^{-3}, $T = 20$–60°C). In contrast to an observable influence of temperature on the equilibrium of the exchange process between Cd^{2+} (40) and Zn^{2+} (see Fig. 1a) ions from solutions and Na^+ ions from zeolite A, the exchange temperature does not affect the equilibrium of the exchange process between Pb^{2+} ions from solutions and Na^+ ions from zeolite A (see Fig. 1b). The increase in equilibrium zinc content with increasing exchange temperature is a consequence of the effects appearing at higher temperatures (47, 48). The increase of temperature increases diffusion coefficients of ions due to the reduction of their effective size caused by a decrease of ion hydration shells. In this way, the increase of the exchange temperature reduces the limitation for diffusion in the inner part of the pore system of zeolite. On the other hand, it seems that these effects are neglected in the case of the exchange process between Pb^{2+} ions from solutions and Na^+ ions from zeolite A.

The exchange isotherms data obtained under known exchange conditions (total normality, N, temperature of the exchange process) can be used for determining the thermodynamic values of the exchange process, such as corrected selectivity coefficient, K_c(Me) [see Eq. (1)], thermodynamic equilibrium constant, K_a(Me), difference in activation energy of the exchange process, ΔE_a(Me), standard free energy, standard enthalpy, and standard entropy of the exchange process. The thermodynamic equilibrium constant, K_a(Me), of the exchange process is a function of both the selectivity coefficient, K_c(Me), and equivalent cation fraction of the Me^{2+} ions, and may be expressed as (43)

$$\begin{aligned} \ln K_a(\mathrm{Me}) &= (z_{Na} - z_{Me}) + \int \ln K_C(\mathrm{Me}) \cdot df_{Me,Z} \\ &= -1 + \int \ln K_C(\mathrm{Me}) \cdot df_{Me,Z} \qquad (2) \end{aligned}$$

where $z_{Me} = 2$ and $z_{Na} = 1$ are valences of Me^{2+} and Na^+ ions. To determine the thermodynamic equilibrium constant, K_a(Me), for the examined exchange processes, the integral on the right-hand side of Eq. (2) was evaluated graphically as the area under the corresponding $\ln K_C$(Me) vs. $f_{Me,Z}$ curves (see Fig. 2). The corresponding values of K_C(Me) were calculated by Eq. (1) using the experimentally determined fractions $f_{Me,Z}$, $f_{Me,L}$, $f_{Na,Z}$, and $f_{Na,L}$ and the values of the activity coefficients, $\gamma_{Na(Me),L}$, of $NaNO_3$ in a binary mixture with $Me(NO)_2$ and, $\gamma_{Me(Na),L}$, of $Me(NO_3)_2$ in a binary mixture with $NaNO_3$ calculated by Glueckauf's equations (37, 49), as explained previously (40). The activity coefficients, $\gamma_{Na,L}$ for pure $NaNO_3$ solutions and, $\gamma_{Me,L}$ for pure $Pb(NO_3)_2$ and $Zn(NO_3)_2$ solutions, respectively, were used from the corresponding literature (50–52). The values of $\ln K_a$(Me), calculated for three dif-

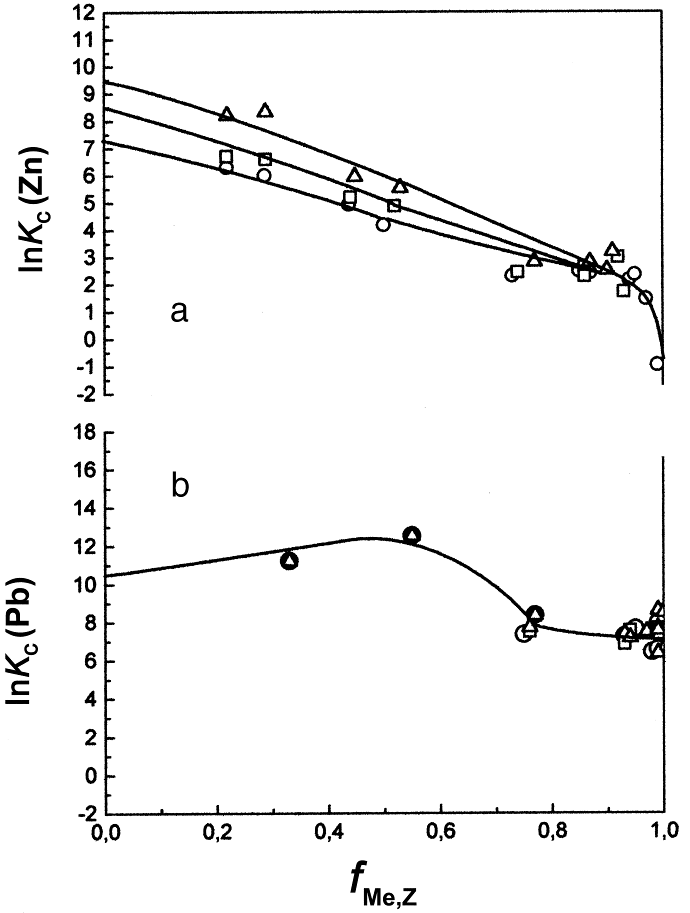

FIG. 2 Kielland plots of the equilibrium exchange processes between Me^{2+} ions from solutions (Me = Zn; Fig. 2a and Me = Pb; Fig. 2b) and Na^+ ions from zeolite A at 20°C (○), 40°C (□), and 60°C (△) and total normality, $N = 0.1$ geqv/dm^3.

ferent temperatures (293 K, 313 K, and 333 K) by Eq. (2) and the corresponding lnK_c(Me) vs. $f_{Me,Z}$ curves (see Fig. 2) are listed in Tables 1 and 2.

Differences in activation energies of the exchange processes, ΔE_a(Zn) = 6.58 kJ/geqv^{-1} and ΔE_a(Pb) = 0, were calculated from the linear relationship between lnK_a(Me) and $1/T$ (Arrhenius plot where T is thermodynamic temperature; see Fig. 3) by the relation (53):

$$\ln[K_a(\mathrm{Me})_2/K_a(\mathrm{Me})_1] = -(\Delta E_a/R)[1/T(2) - 1/T(1)] \qquad (3)$$

TABLE 1
Thermodynamic Data on the Ion-Exchange $Zn^{2+}(L) + 2\ Na^{+}(Z) \Leftrightarrow Zn^{2+}(Z) + 2Na^{+}(L)$ at Different Temperatures

Exchange temperature, T (K)	Thermodynamic equilibrium constant, $K_a(Zn)$	Standard free energy, $\Delta G°(Zn)$ (kJ/geqv)	Standard enthalpy, $\Delta H°(Zn)$ (kJ/geqv)	Standard entropy, $\Delta S°(Zn)$ (kJ/geqv·K)
293	3.44	−1.50	6.58	0.0275
313	4.60	−1.99	6.58	0.0273
333	6.52	−2.60	6.58	0.0275

where $K_a(Me)_1$ and $K_a(Me)_2$ are the values of the thermodynamic equilibrium constant that correspond to the exchange temperatures $T(1)$ and $T(2)$, $R = 8.314$ J/K · mol is the gas constant, and $\Delta E_a = E_{af} - E_{ab}$ is the difference of the activation energies of forward (E_{af}) and backward (E_{ab}) directions of the exchange process (54, 55).

The standard free energies, $\Delta G°(Me)$, of the exchange processes at different temperatures were calculated by the relation (56):

$$\Delta G°(Me) = [-RT/(z_{Na}\ z_{Me})]\ \ln K_a(Me) \tag{4}$$

using the corresponding values of thermodynamic equilibrium constants, $K_a(Me)$ (see Tables 1 and 2). The values of $\Delta G°(Me)$ that correspond to different exchange temperatures are listed in Tables 1 and 2.

The standard enthalpy, $\Delta H°(Me)$, may be calculated by the values of both thermodynamic equilibrium constant, $K_a(Me)$, and standard free energy, $\Delta G°(Me)$ (42, 57), i.e.,

$$\Delta H°(Me) = \{-R/(z_{Na}\ z_{Me})\}\ \{\delta[\ln K_a(Me)]/\delta(1/T)\} \tag{5}$$

$$\Delta H°(Me) = \{\delta[\Delta G°(Me)/T]/\delta(1/T)\} \tag{6}$$

TABLE 2
Thermodynamic Data on the Ion-Exchange $Pb^{2+}(L) + 2\ Na^{+}(Z) \Leftrightarrow Pb^{2+}(Z) + 2Na^{+}(L)$ at Different Temperatures

Exchange temperature, T (K)	Thermodynamic equilibrium constant, $K_a(Pb)$	Standard free energy, $\Delta G°(Pb)$ (kJ/geqv)	Standard enthalpy, $\Delta H°(Pb)$ (kJ/geqv)	Standard entropy, $\Delta S°(Pb)$ (kJ/geqv·K)
293	72.60	−5.22	0.00024	0.0178
313	72.60	−5.58	0.00024	0.0178
333	72.60	−5.93	0.00024	0.0178

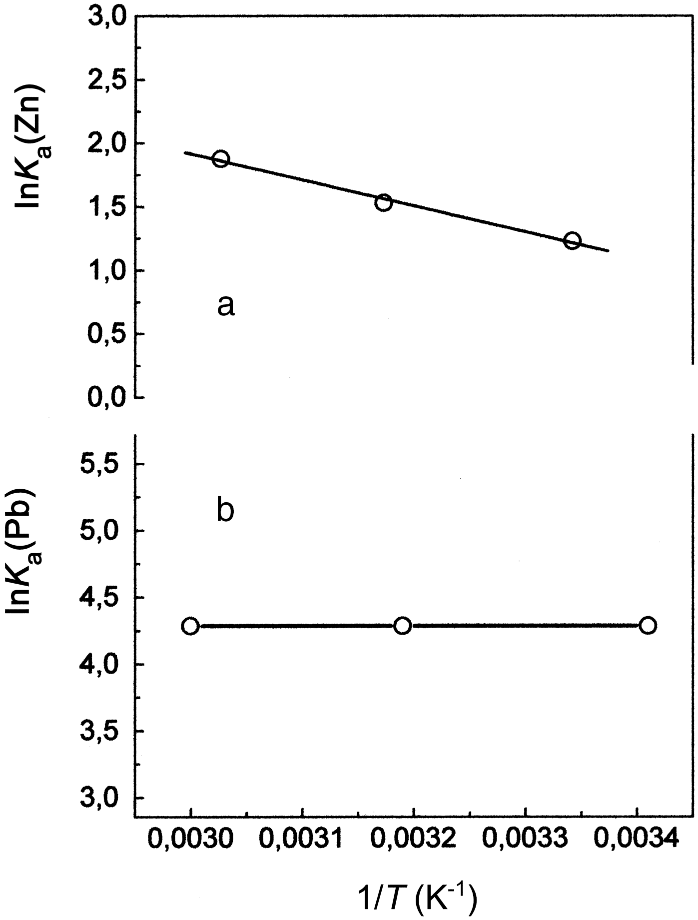

FIG. 3 Logarithms of the thermodynamic equilibrium constants, K_a(Zn) (3a) and K_a(Pb) (3b), which correspond to the exchange processes in the temperature range between $T = 293$ K and $T = 333$ K, plotted against $1/T$.

The linear relationship between ln K_a(Me) vs. $1/T$, i.e.,

$$\Delta H°(\mathrm{Me}) = [-R\,(z_{\mathrm{Na}}\, z_{\mathrm{Me}})]\, S_{\mathrm{I}}(\mathrm{Me}) \tag{7}$$

where $S_I(\mathrm{Me}) = [\ln K_a(\mathrm{Me})_2 - \ln K_a(\mathrm{Me})_1] / [1/T(2) - 1/T(1)]$ is the slope of the lnK_a(Me) vs. $1/T$ straight line in Fig. 3. The constancy of S_I(Me) indicates that the standard enthalpy, $\Delta H°$(Me), of the exchange processes does not depend on the exchange temperature in the temperature range from $T = 293$ K to $T = 333$ K (see Tables 1 and 2). Since $S_I(\mathrm{Pb}) = 0$ (see Fig. 3b) the value

$\Delta H°(\mathrm{Pb}) = 0.00024$ kJ/geqv, calculated by Eq. (6) is used as the relevant value. The positive value of standard enthalpy (see Tables 1 and 2) and thus the endothermicity of the exchange process is in accordance with the finding that when divalent ions enter the crystals, $\Delta H°(\mathrm{Me})$ will be positive when $2r_{\mathrm{Na}} > r_{\mathrm{Me}}$ (58), i.e., $2r_{\mathrm{Na}} > r_{\mathrm{Zn}}$ and $2r_{\mathrm{Na}} > r_{\mathrm{Pb}}$ where $r_{\mathrm{Na}} = 0.097$ nm is the ionic radius of Na^+ ion, $r_{\mathrm{Zn}} = 0.074$ nm is the ionic radius of Zn^{2+} ion, and $r_{\mathrm{Pb}} = 0.12$ nm is the ionic radius of Pb^{2+} ion (59). By the same principle, the absolute value of enthalpy, $|\ \Delta H°(\mathrm{Me})\ |$, decreases with decreasing absolute value of $r_{\mathrm{Na}} - r_{\mathrm{Me}}$ (for univalent Me ions) and $2r_{\mathrm{Na}} - r_{\mathrm{Me}}$ (for divalent Me ions) (58). Hence, the relationship $\Delta H°\ (\mathrm{Zn}) > \Delta H°(\mathrm{Pb})$ (see Tables 1 and 2) was expected, because $2r_{\mathrm{Na}} - r_{\mathrm{Zn}} = 1.2 > 2r_{\mathrm{Na}} - r_{\mathrm{Pb}} = 0.74$. A great difference between $\Delta H°(\mathrm{Zn})$ and $\Delta H°(\mathrm{Pb})$ (see Tables 1 and 2) may be explained by the difference in hydration numbers of Zn^{2+} and Pb^{2+} ions in solution on the one hand and the difference in hydration numbers of the ions in solution and zeolite A on the other hand. Namely, Zn^{2+} ions contain 10–12.5 water molecules in the inner hydration shell in water solution (60) and 4.83 water molecules in zeolite A (6 Zn^{2+} + 28 $\mathrm{H_2O}$ per unit cell) (42). On the other hand, Pb^{2+} ions contain 4–7.5 water molecules in water solution (60) and 4.67 water molecules in zeolite A (6 Pb^{2+} + 29 $\mathrm{H_2O}$ per unit cell). This means that 5–8 water molecules per one Zn^{2+} ion and 0–3 water molecules per one Pb^{2+} ion must be stripped from the inner hydration shells of the ions during their exchange with Na^+ ions from zeolite A. Hence, a higher value of the enthalpy change for Zn^{2+} exchange relative to the Pb^{2+} exchange is attributed to the higher energy needed for the reduction of the hydration shell of Zn^{2+} ions than Pb^{2+} ions. Since the difference in activation energy $\Delta E_{\mathrm{a}}(\mathrm{Me})$ is the same as the standard enthalpy, i.e., $\Delta E_{\mathrm{a}}(\mathrm{Me}) = \Delta H°(\mathrm{Me})$ for a constant volume of the system (54, 55), a great difference between $\Delta E_{\mathrm{a}}\ (\mathrm{Zn}) = 6.58$ kJ/geqv and $\Delta E_{\mathrm{a}}\ (\mathrm{Pb}) \cong 0$, may be explained in the same way as the difference between $\Delta H°(\mathrm{Zn})$ and $\Delta H°(\mathrm{Pb})$.

The standard entropy, $\Delta S°(\mathrm{Me})$, of the exchange processes was calculated in the usual way (61):

$$\Delta S°(\mathrm{Me}) = [\Delta H°(\mathrm{Me}) - \Delta G°(\mathrm{Me})]/T \qquad (8)$$

using the previously calculated values of $\Delta H°(\mathrm{Me})$ and $\Delta G°(\mathrm{Me})$ listed (see Tables 1 and 2). The values of $\Delta S°(\mathrm{Me})$ do not depend on the exchange temperature, T (see Tables 1 and 2). The values of $\Delta S°(\mathrm{Me})$ obtained from the slopes, $S_{\mathrm{II}}(\mathrm{Me})$, of the $\Delta G°(\mathrm{Me})$ vs. T straight line (see Fig. 4) are somewhat lower than the values calculated by eq. (6), i.e., $\Delta S°(\mathrm{Zn}) = -\delta\Delta G°(\mathrm{Zn})/\delta T = S_{\mathrm{II}}(\mathrm{Zn}) = 0.02305$ kJ/geqv·K and $\Delta S°(\mathrm{Pb}) = -\delta\Delta G°(\mathrm{Pb})/\delta T = S_{\mathrm{II}}(\mathrm{Pb}) = 0.0156$ kJ/geqv·K. In accordance with previous studies (26, 42) the observed increase in the entropy of the system (see Tables 1 and 2) may be considered as consisting of two contributions, one, $\Delta S°(\mathrm{Me})_{\mathrm{Z}}$, from zeolite phase and an-

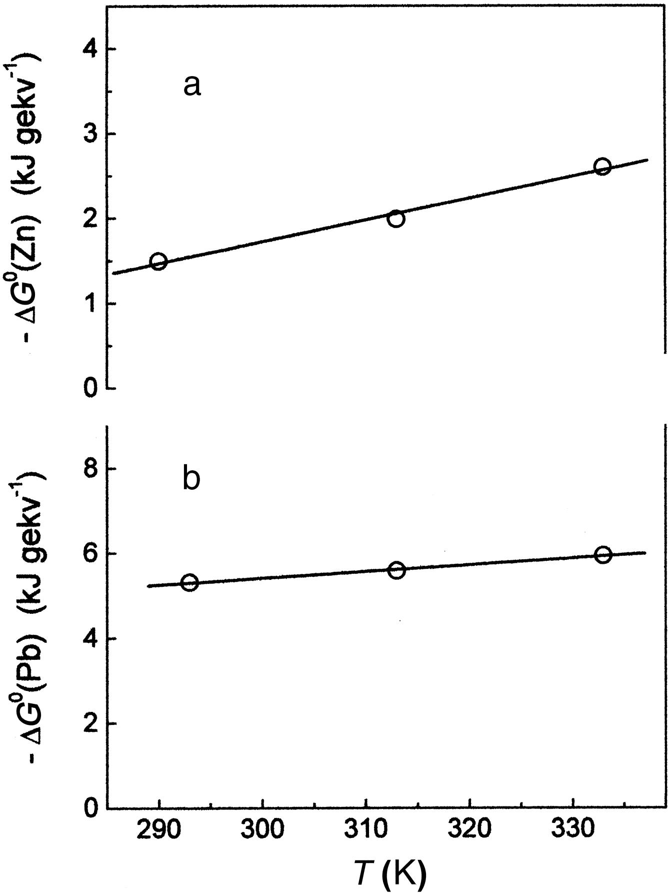

FIG. 4 The values of $\Delta G°(\mathrm{Zn})$ (4a) and $\Delta G°(\mathrm{Pb})$ (4b), which correspond to the equilibrium of the exchange processes in the temperature range between $T = 293$ K and $T = 333$ K plotted against the exchange temperature T.

other, $\Delta S°(\mathrm{Me})_L$, from the aqueous phase. The increase in $\Delta S°(\mathrm{Me})_Z$ is mainly caused by increase of “free” water in the cavities of zeolite during the exchange of Me^{2+} ions from solution with Na^+ ions from zeolite A. For example, zinc-exchanged zeolite A contains 29 water molecules per unit cell (18 molecules of “structured” water and 11 molecules of “free” water) and original Na-form of zeolite A contains 27 molecules of water per unit cell (18 molecules of “structured” water and 9 molecules of “free” water) (42), and thus the zinc-exchanged zeolite A has an excess of “free” water $[\Delta H_2O(\mathrm{Na,Zn}) = 2]$. On the other hand, based on chemical analysis, lead-exchanged zeolite A contains 28 water molecules per unit cell (18 molecules of "structured" water and 10 molecules of "free" water), and original Na-form of zeolite A contains 27 molecules of water per unit cell (18 molecules of "structured" water and 9 molecules of "free" water) (42), and thus $\Delta H_2O(Na,Pb) = 1$. Since $\Delta S°(Me)_Z/\Delta H_2O(Na,Me) \cong$ constant $= k$, (42), $\Delta S°(Zn)_Z = 2k > \Delta S°(Pb)_Z = k$. The values $\Delta S°(Zn)_L = 11.0$ e.u. and $\Delta S°(Pb)_L = -2.5$ e.u. were calculated from Rossinsky's tables of ionic entropies of hydration (62). Since $\Delta S°(Pb)_Z < \Delta S°(Zn)_Z$ and $\Delta S°(Pb)_L < \Delta S°(Zn)_L$, the relationship $\Delta S°(Pb) < \Delta S°(Zn)$ (see Tables 1 and 2) is logical.

Finally, since both $\Delta H°(Me)$ and $\Delta S°(Me)$ are positive for both Zn^{2+} and Pb^{2+}, $T\Delta S°(Me) > \Delta H°(Me)$ (see the data in Tables 1 and 2), $\Delta G°(Me)$ must be negative, i.e., $\Delta G°(Me) = \Delta H°(Me) - T\Delta S°(Me)$ [see Eq. (8)]. The expected negative values of $\Delta G°(Me)$ were confirmed (see Tables 1 and 2) by its calculation using Eq. (4) and corresponding values of K_a. The decrease of $\Delta G°$ with the exchange temperature, T, can be formally explained by the increase of $T\Delta S°(Me)$ [see Eq. (8)]. In a physical sense the negative value of $\Delta G°(Me)$ and its decrease with the increasing exchange temperature is connected with the higher affinity of zeolite A to Zn^{2+} and Pb^{2+} ions, respectively, than to Na^+ ions, and thus with the change of thermodynamic stability of the zeolite A framework during the exchange process (46). Hence, the relationship $|\Delta G°(Pb)| > |\Delta G°(Zn)|$ (see Tables 1 and 2) is in accordance with the higher affinity of zeolite A to Pb^{2+} ions than to Zn^{2+} ions.

CONCLUSIONS

Thermodynamic data relevant for the exchange processes between Me^{2+} ions (Me = Zn, Pb) from solutions and Na^+ ions from zeolite A were determined from the distribution of Na^+ and Me^{2+} ions between solution and zeolite at the exchange equilibrium established at constant total-ions concentrations and different exchange temperatures. For all examined cases, the exchange equilibrium was established in less than 30 min.

The value of the thermodynamic equilibrium constant, $K_a(Pb)$ does not depend on temperature T. Consequently, the difference in activation energy $\Delta E_a(Pb)$ of the $Pb^{2+}(L) + 2\,Na^+(Z) \Leftrightarrow Pb^{2+}(Z) + 2Na^+(L)$ exchange process is 0 in the range from $T = 298$ K to $T = 333$ K. On the other hand, from the linear relationship between $\ln K_a(Zn)$ and $1/T$ it was calculated that the difference in activation energy, $\Delta E_a(Zn)$, of the $Zn^{2+}(L) + 2\,Na^+(Z) \Leftrightarrow Zn^{2+}(Z) + 2Na^+(L)$ exchange process is 6.58 kJ/geqv in the temperature range from $T = 298$ K to $T = 333$ K.

The thermodynamic equilibrium constant, $K_a(Zn) = 3.44$ at 20°C, is in good agreement with the value $K_a(Zn) = 3.56$ measured at 25°C (42). On the other hand, the values $\Delta H°(Zn)$ and $\Delta S°(Zn)$ listed in Table 1 are about 2–3 times lower than the previously published values of $\Delta H°(Zn)$ and $\Delta S°(Zn)$.

The differences are probably caused by different temperature ranges of the exchange processes [20°C–60°C in this work and 5°C–45°C in the previous study (42)].

Zeolite A exhibits higher affinity for ions from solution (Zn^{2+}, Pb^{2+}) than for host Na^+ ions of zeolite NaA, as is indicated by the appropriate exchange isotherms (Fig. 1) and highly corrected selectivity coefficients of Zn^{2+} (Fig. 2a) and Pb^{2+} exchange (Fig. 2b). Comparison of the corrected selectivity coefficients $K_c(\mathrm{Pb}) = 3.6 \times 10^4$ and $K_c(\mathrm{Zn}) = 1.4 \times 10^3$ at 20°C, $K_c(\mathrm{Zn}) = 4.9 \times 10^3$ at 40°C, and $K_c(\mathrm{Zn}) = 1.3 \times 10^4$ for $f_{\mathrm{Me,Z}} = 0$, indicates that the affinity of zeolite A is considerably higher for Pb^{2+} ions than for Zn^{2+} ions. In contrast to a gradual decrease of the corrected selectivity coefficient, $K_c(\mathrm{Zn})$, with increased fraction, $f_{\mathrm{Zn,Z}}$, of Zn^{2+} ions in zeolite A (Fig. 2a), the selectivity coeficient, $K_c(\mathrm{Pb})$, increases from $f_{\mathrm{Pb,Z}} = 0$ ($K_c(\mathrm{Pb}) = 3.6 \times 10^4$) to $f_{\mathrm{Pb,Z}} = 0.5$ ($K_c(\mathrm{Pb}) = 2.1 \times 10^5$), then decreases from $f_{\mathrm{Pb,Z}} = 0.5$ to $f_{\mathrm{Pb,Z}} = 0.8$, and thereafter keeps constant ($K_c(\mathrm{Pb}) = 1.8 \times 10^3$) up to $f_{\mathrm{Pb,Z}} = 1$.

The values of the selectivity-corrected coefficients indicate that Zn^{2+} ions, and especially Pb^{2+} ions may be effectively removed from solutions, even at high values of $f_{\mathrm{Me,Z}}$ [$K_c(\mathrm{Zn}) = 12$ for $f_{\mathrm{Zn,Z}} = 0.8$; $K_c(\mathrm{Pb}) \cong 1.1 \times 10^3$ for $f_{\mathrm{Pb,Z}} = 0.8 - 1$], by means of zeolite NaA.

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