Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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**To cite this Article** Biškup, Biserka and Subotić, Boris(1998) 'Removal of Heavy Metal Ions from Solutions by Means of Zeolites. I. Thermodynamics of the Exchange Processes between Cadmium Ions from Solution and Sodium Ions from Zeolite A', Separation Science and Technology, 33: 4, 449 — 466

**To link to this Article: DOI:** 10.1080/01496399808544990

**URL:** http://dx.doi.org/10.1080/01496399808544990

SEPARATION SCIENCE AND TECHNOLOGY, 33(4), pp. 449–466, 1998

# Removal of Heavy Metal Ions from Solutions by Means of Zeolites. I. Thermodynamics of the Exchange Processes between Cadmium Ions from Solution and Sodium Ions from Zeolite A

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## ABSTRACT

Relationships between corrected selectivity coefficient ($K_C$) and fraction of the exchanged cadmium ions in zeolite A ($f_{Cd,Z}$) were determined from data obtained by measuring the concentrations of sodium and cadmium ions in both the solid and the liquid phase at equilibrium of the exchange processes between cadmium ions from solution and sodium ions from zeolite A at different total ion concentrations and different temperatures. Thermodynamic equilibrium constants ($K_a$) calculated from the corresponding Kielland's plots ($K_C$ vs $f_{Cd,Z}$ plots) were used for the calculation of the appropriate values of standard free energy ($\Delta G°$) standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$). The influence of the degree of exchange on the activity coefficients of sodium and cadmium ions in zeolite is also considered.

*Key Words.* Zeolite A; Ion exchange; Sodium ions; Cadmium ions; Exchange equilibrium; Thermodynamic data

## INTRODUCTION

One of unique properties of zeolite molecular sieves is their ability to exchange cations, M, which are located at specific sites in the channel-cage system of zeolites, by various cations from solutions (1–3). Cation exchange of zeolites is used routinely in modifying the properties of zeolite

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products in adsorption and catalysis (4–6), e.g., use of potassium-exchanged zeolite A (3A) in drying and removal of carbon dioxide from natural gas and drying of cracked gas, use of calcium-exchanged zeolite A (5A) in separation of *n*-paraffins from petroleum fractions and in separation of oxygen from air, use of noble metals- and lanthanide-exchanged zeolites X and Y as FCC catalysts, use of Cu- and Ce-exchanged ZSM-5 and mordenite as catalysts for $NO_x$ reduction in mobile engine exhaust (7, 8), etc. In addition, ion-exchange of zeolites can be used to modify zeolite properties in order to prepare new types of conductors, semiconductors (9), visual display units (10), dielectric gas sensors (11), and catalysts (12). In addition, cation-exchange of zeolites is widely used in the nuclear industry (long-term storage of long-lived radioisotopes of cesium and strontium; preparation of curium-247 by irradiation of lanthanides or trivalent actinides into X or Y zeolites) (13), agriculture (soil improvement by addition of zeolites exchanged by fertilizer-type cations such as $NH_4^+$ and $K^+$ and micronutrients-type cations such as $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$, $Zn^{2+}$) (14), laundry detergent industry (water softening by the exchange of $Na^+$ ions from zeolite 4A with $Ca^{2+}$ and $Mg^{2+}$ ions from washing water, and thus the preferred alternative to phosphates as builders) (15, 16), and environmental protection (the removal and recovery of heavy metal ions; wastewater purification by removal of ammonia and ammonium ions from aqueous effluents) (17, 18).

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 (18). One of the most important toxic metals, cadmium, finds its way to bodies of water through wastewaters from metal plating industries and the manufacture of cadmium-nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, and alloys (19, 20). The effects of acute cadmium poisoning in humans are very serious, among which 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 man, having been associated with hypertensive diseases (21). For this reason there is a constant need to remove heavy metals, including cadmium, from industrial effluents and other wastewaters.

Different technologies are described in the literature for the removal of heavy metals, including cadmium, such as chemical precipitation, electroflotation, reverse osmosis, adsorption on activated carbon, and ion exchange (22). Ion exchange seems to be an attractive method especially when low cost materials can be used as exchangers (17). Although some of these methods may be under given conditions more effective than ion exchange [e.g. the precipitation process leaves the waste solution with several ppm of cadmium (23)], ion exchange is considered attractive because of the relative simplicity of application (24). Both natural and synthetic zeolites can be widely used for this purpose (17, 18, 25–27). Although natural zeolites are cheaper than the synthetic ones and can be used directly in columns in crushed form, their exchange capacity depends considerably upon the zeolitic phase content in the rock, the type of cation exchange form, and the admixture character. This may be a reason for serious difficulties in applications where the exchange process needs to be strongly controlled. Besides, the use of natural zeolites is often limited to countries having their own deposits. An alternative is the use of chip synthetic zeolites, e.g., zeolite 4A widely produced as a detergent builder, that have defined chemical composition and high and constant cation-exchange capacity. Hence, our intention is to examine different factors which determine the efficiency of removal of different heavy metal ions ($Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, and $Zn^{2+}$) from solutions, using some synthetic zeolites (mainly zeolite 4A) as cation exchangers in discontinuous (batch) and continuous (filtration) exchange processes. In this, the first work of this series, thermodynamics of exchange equilibrium in the system ($Na^+$,$Cd^{2+}$)-solution + ($Na^+$,$Cd^{2+}$)-zeolite A is studied.

## EXPERIMENTAL

Zeolite 4A (SILKEM, Kidričevo, Slovenia), which has the oxide chemical composition $1.087Na_2O \cdot Al_2O_3 \cdot 1.99SiO_2 \cdot 4.56H_2O$ and a particle size ranged between 1.5 and 10 μm (with a mean particle size of 4.5 μm), was used as a cation exchanger. The zeolite was kept in a desiccator with saturated NaCl solution for 48 hours before use. $Cd(NO_3)_2 \cdot 4\ H_2O$ (Ventron) and $NaNO_3$ (Riedel de Haen A.G.) were used for the preparation of the stock solution of cadmium nitrate (5 g of $Cd^{2+}/dm^3$) and sodium nitrate (10 g of $Na^+/dm^3$), respectively. Distilled water was used as the solvent. Mixed $NaNO_3/Cd(NO_3)_2$ solutions having different fractions of sodium and cadmium ions at constant equivalent cation concentrations were prepared by mixing appropriate volumes of the stock solutions of sodium nitrate and cadmium nitrate, respectively, and distilled water. The pH of the mixed solutions was ca. 4.4.

The equilibrium distribution of $Na^+$ and $Cd^{2+}$ 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 a thermostated (20, 40, and/or 60°C), well-mixed solution containing appropriate amounts of $Na^+$ and $Cd^{2+}$ ions, so that the total concentration of the exchangeable ions ($Na^+ + Cd^{2+}$) in the batch was 0.02, 0.05, or 0.1 $meqv \cdot dm^{-3}$. The temperature of the system was maintained by a circulatory water bath during the exchange process. A suspension of zeolite in solution was stirred for a predetermined time, $t_E$(eq) ($\geq$ 3 hours), by a Teflon-coated magnetic bar ($\phi$ = 7 mm, $l$ = 30 mm) driven by a magnetic stirrer (stirring rate = 400 rpm). Thereafter, the suspension was centrifuged to stop the exchange process (for kinetic experiments) and to separate the solid from the liquid phase. The clear liquid phase above the sediment (Na,Cd-form of zeolite A) was used for measuring Na and Cd concentrations and controlling the pH at different stages of the exchange process. Some of the sediments were used for measuring Na and Cd contents in the solid phase. The equilibrium time, $t_E$(eq), of the exchange process was determined by sampling, phase separation, and measuring the Na and Cd concentrations in the liquid phase at various stages of the exchange process (from $t_E$ = 0.5 minute to $t_E$ = 1500 minutes).

The chemical composition of the starting zeolite 4A powder was determined as follows: A given amount of the starting zeolite 4A powder was calcined at 800°C for 2 hours. 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 a 1:1 HCl solution The solution was diluted with distilled water to the concentration ranges available for measuring the concentrations of sodium, aluminum, and silicon by atomic absorption spectroscopy.

Some of sediments separated from the suspension at $t_E \geq t_E$(eq) were washed with distilled water, dried at 105°C overnight, and kept in a desiccator with saturated NaCl for 48 hours. Thereafter the samples were dissolved in a 1:1 HCl solution. The solutions were diluted with distilled water to the concentration ranges available for measuring the concentrations of sodium and cadmium 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 and cadmium by atomic absorption spectroscopy.

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

## RESULTS AND DISCUSSION

Figure 1 shows the kinetics of exchange of $Cd^{2+}$ ions from solutions initially containing 500 mg $Cd^{2+}$ ions [= $(C_{Cd})_O$] and 0 (□) or 4000 (○) mg $Na^+$ ions [= $(C_{Na})_O$] per dm$^3$ of the solution with $Na^+$ ions from zeolite 4A at 20°C. In both cases the concentration of the suspension was 1 g of zeolite A per dm$^3$. The equilibrium exchange capacity, $(Cd_Z)_{eq}$ = 280 mg of $Cd^{2+}$ ions per gram of zeolite A for $(C_{Na})_O$ = 0 and $(Cd_Z)_{eq}$

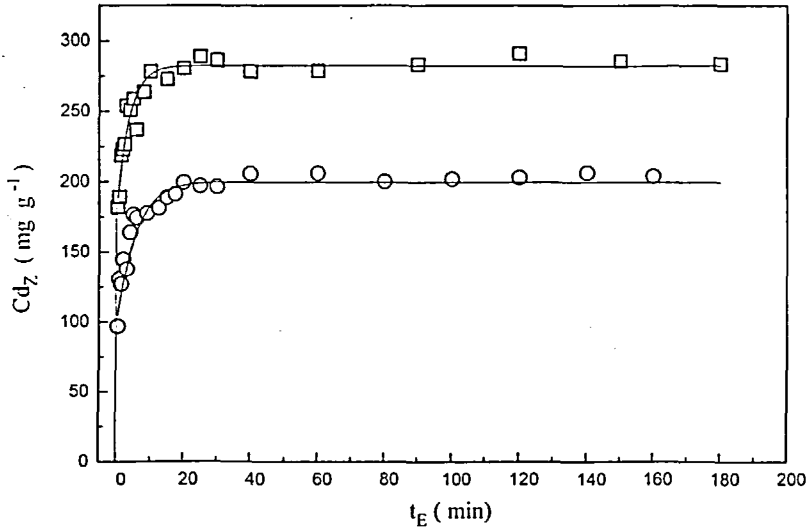

FIG. 1 Kinetics of exchange of $Cd^{2+}$ ions from solutions initially containing 500 mg $Cd^{2+}$ ions [= $(C_{Cd})_O$] and 0 (□) or 4000 (○) mg $Na^+$ ions [= $(C_{Na})_O$] per dm$^3$ of the solution with $Na^+$ ions from zeolite 4A at 20°C $Cd_Z$ is the cadmium exchange capacity (mg of $Cd^{2+}$ ions per gram of zeolite A), and $t_E$ is time of the exchange.

= 200 mg of $Cd^{2+}$ ions per gram of zeolite A for $(C_{Na})_O$ = 4000 mg/dm$^3$, was attained in less than 30 minutes (see Fig. 1), and thereafter the values of $Cd_Z = (Cd_Z)_{eq}$ were kept constant for at least 1500 minutes when the last samplings were done. Hence, the equilibrium distribution of $Na^+$ and $Cd^{2+}$ ions between the solid (zeolite A) and the liquid phase may be determined for any exchange time, $t_E$, longer than 30 minutes. For reason of dependability, the exchange isotherms in this work were constructed from the data relevant to $t_E$ = 180 minutes. The pH of the suspensions gradually increased from ca. 4.4 (starting solutions) to ca. 6 (at equilibrium) during the exchange processes.

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

$$Cd^{2+}(s) + 2Na^+(z) \Leftrightarrow Cd^{2+} + 2Na^+(s)$$

where the notations (s) and (z) refer to the ions in solution and zeolite A, respectively. The selectivity coefficient, $K$, can be defined for the $Na^+$–$Cd^{2+}$ exchange as (28)

$$K = f_{Cd,Z} \cdot (m_{Na,L})^2/(f_{Na,Z})^2 \cdot m_{Cd,L} \qquad (1)$$

where $f_{Cd,Z} = (Cd_Z)_{eq}/[(Cd_Z)_{eq} + (Na_Z)_{eq}]$ and $f_{Na,Z} = 1 - f_{Cd,Z} = (Na_Z)_{eq}/[(Cd_Z)_{eq} + (Na_Z)_{eq}]$ are the equivalent cation fractions of $Cd^{2+}$ and $Na^+$ in the zeolite phase and $m_{Cd,L}$ and $m_{Na,L}$ are the molalities of $Cd(NO_3)_2$ and $NaNO_3$ salts in the solution phase, respectively. However, Eq. (1) is valid only for very low concentrations of ions in solution, i.e., when the ionic activity coefficients are 1, and for most or real cases the corrected selectivity coefficient, $K_C$, can be calculated as (29, 30)

$$K_C = K\cdot\Gamma = (\gamma_{Na,L})^4\cdot f_{Cd,Z}\cdot(m_{Na,L})^2/(\gamma_{Cd,L})^3\cdot(f_{Na,Z})^2\cdot m_{Cd,L} \qquad (2)$$

where $K_C$ is the corrected selectivity coefficient, $\gamma_{Na,L}$ and $\gamma_{Cd,L}$ are activity coefficients of $NaNO_3$ and $Cd(NO_3)_2$, respectively, in the mixed $[NaNO_3 + Cd(NO_3)_2]$ solution phase, and, according to Fletcher and Townsend (31), $\Gamma = (\gamma_{Na,L})^4/(\gamma_{Cd,L})^3$. Since exchange isotherms are always represented in terms of the equivalent cation fractions in the zeolite phase against the equivalent cation fraction in solution, i.e., $f_{Na,L} = m_{Na,L}/(m_{Na,L} + 2m_{Cd,L})$ and $f_{Cd,L} = 2m_{Cd,L}/(m_{Na,L} + 2m_{Cd,L})$, the corrected selectivity coefficient, $K_C$, can be expressed as (32)

$$K_C = 2N\cdot(\gamma_{Na,L})^4\cdot f_{Cd,Z}\cdot(f_{Na,L})^2/(\gamma_{Cd,L})^3\cdot(f_{Na,Z})^2\cdot f_{Cd,L} \qquad (3)$$

where $N$ is total normality of the equilibrium solution phase.

Figure 2 shows the equilibrium isotherms of the exchange processes between $Cd^{2+}$ ions from solutions and $Na^+$ ions from zeolite A at 20°C and total normality, $N = 0.02$ geqv/dm$^3$ (Δ), $N = 0.05$ geqv/dm$^3$ (□), and $N = 0.1$ geqv/dm$^3$ (○), represented as the plots of equivalent cadmium ion fractions, $f_{Cd,Z}$, in zeolite A against the cadmium ion fractions, $f_{Cd,L}$, in solutions. Figure 3 shows the equilibrium isotherms at 20°C (○), 40°C (□), and 60°C (Δ) for total normality, $N = 0.1$ geqv/dm$^3$. All the isotherms are of type C (33), i.e., the entering ion shows a selectivity reverse to the increasing fraction in the zeolite, resulting in "sigmoidal"-shape isotherms (see Figs. 2 and 3). The values of "plateau"-$f_{Cd,Z}$ slightly increase with increase of both the total normality, $N$, and temperature of the exchange process. The increase in equilibrium cadmium content with increasing exchange temperature is a consequence of the effects appearing at higher temperatures (34, 35), i.e., an increase of the diffusion coefficient due to the reduction of the effective size of ions caused by a decrease of the ion hydration shell and a reduction of the limitation for diffusion in the inner part of the pore system arising from a decrease in the effective ionic radius.

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, $K_C$ (see Eq. 3), thermodynamic equilibrium constant, $K_a$, activation energy of the exchange process, stan-

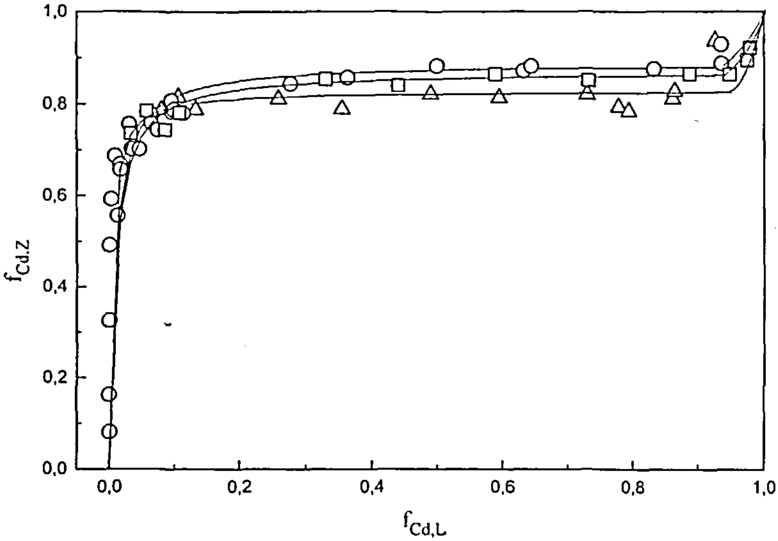

FIG. 2 Equilibrium isotherms of the exchange processes between $Cd^{2+}$ ions from solutions and $Na^+$ ions from zeolite A at 20°C and total normality, $N = 0.02$ geqv/dm$^3$ (△), $N = 0.05$ geqv/dm$^3$ (□), and $N = 0.1$ geqv/dm$^3$ (○), represented as the plots of equivalent cadmium ion fractions, $f_{Cd,Z}$, in zeolite A against the cadmium ion fractions, $f_{Cd,L}$, in solutions.

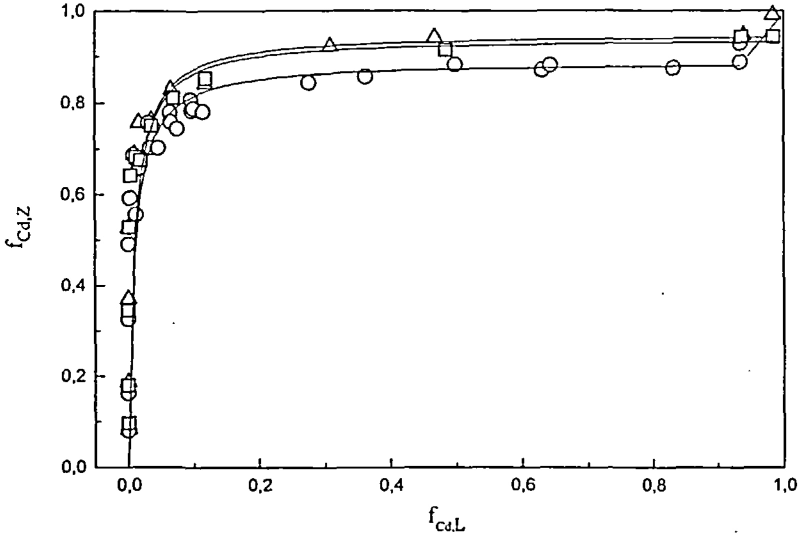

FIG. 3 Equilibrium isotherms of the exchange processes between $Cd^{2+}$ ions from solutions and $Na^+$ ions from zeolite A at 20°C (○), 40°C (□), and 60°C (△) for total normality, $N = 0.1$ geqv/dm$^3$, represented as the plots of equivalent cadmium ion fractions, $f_{Cd,Z}$, in zeolite A against the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

dard free energy, and standard enthalpy and standard entropy of the exchange process. The thermodynamic equilibrium constant, $K_a$, of the exchange process is a function of both the selectivity coefficient, $K_C$, and activity coefficients, $\gamma_{Cd,Z}$, of cadmium and, $\gamma_{Na,Z}$, of sodium ions, respectively, in the zeolite phase, and may be expressed as (28, 32)

$$K_a = 2N\cdot\gamma_{Cd,Z}\cdot(\gamma_{Na,L})^4\cdot f_{Cd,Z}\cdot(f_{Na,L})^2/(\gamma_{Na,Z})^2 \cdot(\gamma_{Cd,L})^3\cdot(f_{Na,Z})^2\cdot f_{Cd,L} = K_C\cdot\gamma_{Cd,Z}/(\gamma_{Na,Z})^2 \qquad (4)$$

Because the determination of the activity coefficients, $\gamma_{Cd,Z}$ of cadmium and $\gamma_{Na,Z}$ of sodium ions, respectively, in the zeolite phase is dubious, further thermodynamic treatment (29) gives for $K_a$

$$\ln K_a = (Z_{Cd} - Z_{Na}) + \int \ln K_C\cdot df_{Cd,Z} = -1 + \int \ln K_c\cdot df_{Cd,Z} \qquad (5)$$

where $Z_{Cd} = 2$ and $Z_{Na} = 1$ are the valences of cadmium and sodium ions, respectively. To determine the thermodynamic equilibrium constant, $K_a$, for the examined exchange processes, the integral on the right-hand side of Eq. (5) was evaluated graphically as the area under the corresponding $\ln K_C$ vs $f_{Cd,Z}$ curves (see Figs. 4 and 5). The corresponding values of $K_C$ were calculated by Eq. (3) using the experimentally determined fractions $f_{Cd,Z}$, $f_{Cd,L}$, $f_{Na,Z}$, and $f_{Na,L}$ and the values of the activity coefficients $\gamma_{Na(Cd),L}$ of $NaNO_3$ in a binary mixture with $Cd(NO)_2$ and $\gamma_{Cd(Na),L}$ of $Cd(NO_3)_2$ in a binary mixture with $NaNO_3$ calculated by Gleckauf's equations (32, 36), i.e.,

$$\log \gamma_{Na(Cd),L} = \log \gamma_{Na,L} - (m_{Cd,L}/4I) \times \{8 \log \gamma_{Na,L} - 4.5 \log \gamma_{Cd,L} - [0.5/(1 + I^{1/2})]\} \qquad (6)$$

$$\log \gamma_{Cd(Na),L} = \log \gamma_{Cd,L} - (m_{Na,L}/4I) \times \{\log \gamma_{Na,L} - 2.667 \log \gamma_{Na,L} - [0.333/(1 + I^{1/2})]\} \qquad (7)$$

where the ionic strength, $I$, was calculated as (32)

$$I = 0.5 \sum m_i z_i^2 = m_{Na,L} + m_{Cd,L} \qquad (8)$$

The activity coefficients $\gamma_{Na,L}$ for pure $NaNO_3$ solutions and $\gamma_{Cd,L}$ for pure $Cd(NO_3)_2$ solutions, respectively, were used from the corresponding literature (37, 38). The values of $\ln K_a$, calculated for three different temperatures (293, 313, and 333 K) by Eq. (5) and the corresponding $\ln K_C$ vs $f_{Cd,Z}$ curves (see Figs. 4 and 5) are listed in Table 1. The activation

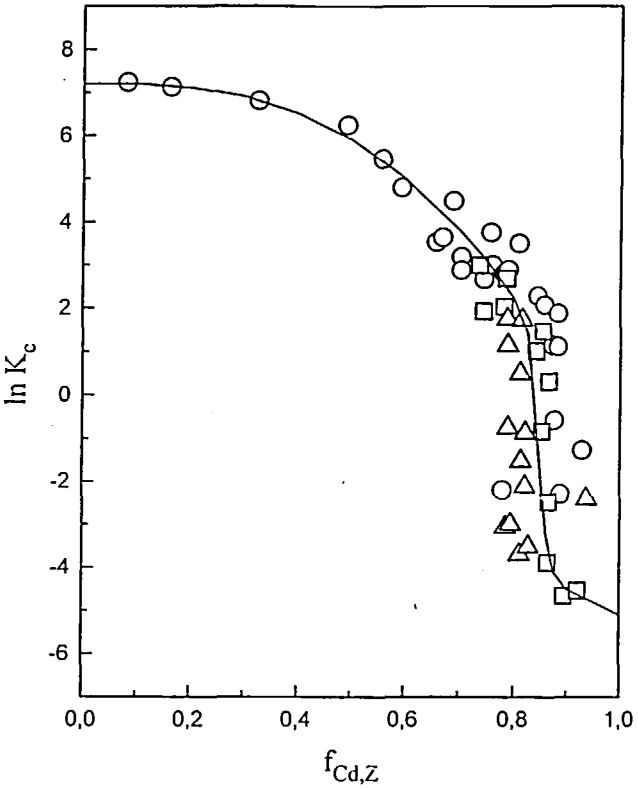

FIG. 4 Kielland plots (logarithm of the corrected selectivity coefficient, ln $K_C$ vs equivalent fraction of cadmium ions in zeolite A, $f_{Cd,Z}$) of the equilibrium exchange processes between $Cd^{2+}$ ions from solutions and $Na^+$ ions from zeolite A at 20°C and total normality, $N$ = 0.02 geqv/dm³ (△), $N$ = 0.05 geqv/dm³ (□), and $N$ = 0.1 geqv/dm³ (○).

energy of the exchange process, $E_a = 17.18$ kJ·geqv$^{-1}$ was calculated from the linear relationship between ln $K_a$ and $1/T$ (Arrhenius plot where $T$ is the thermodynamic temperature; see Fig. 6) by the relation (39)

$$\ln[K_a(2)/K_a(1)] = -(E_a/R)[1/T(2) - 1/T(1)] \qquad (9)$$

where $K_a(1)$ and $K_a(2)$ are the values of the thermodynamic equilibrium constants that correspond to the exchange temperatures $T(1)$ and $T(2)$, and $R = 8.314$ J·K$^{-1}$·mol$^{-1}$ is the gas constant.

Although it should be particularly noted that the activity coefficients $\gamma_{Cd,Z}$ and, $\gamma_{Na,Z}$ of cadmium and sodium ions in the zeolite phase do not have the character of individual ion activity coefficients but refer to the

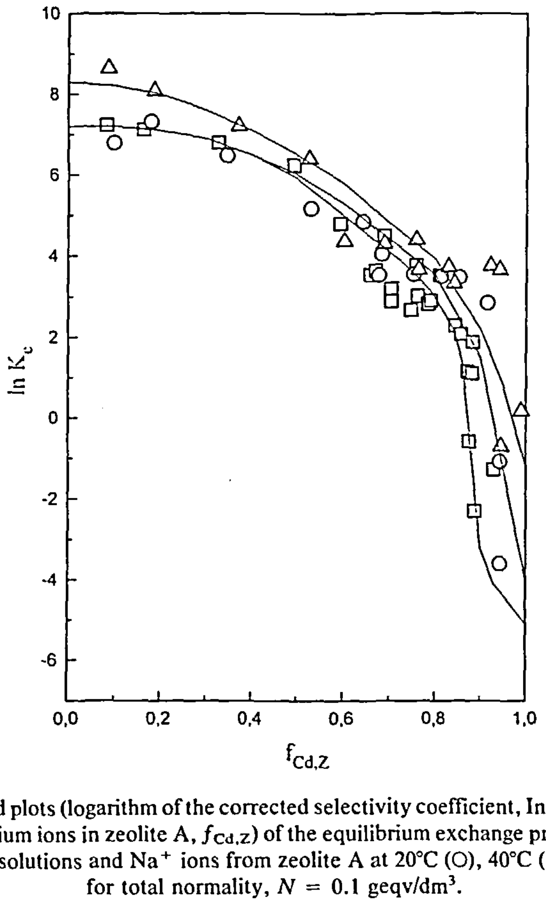

FIG. 5 Kielland plots (logarithm of the corrected selectivity coefficient, ln $K_C$ vs equivalent fraction of cadmium ions in zeolite A, $f_{Cd,Z}$) of the equilibrium exchange processes between $Cd^{2+}$ ions from solutions and $Na^+$ ions from zeolite A at 20°C (○), 40°C (□), and 60°C (△) for total normality, $N$ = 0.1 geqv/dm$^3$.

TABLE 1
Thermodynamic Data on the Ion-Exchange $Cd^{2+}(s) + 2Na^+(z) \Leftrightarrow Cd^{2+}(z) + 2Na^+(s)$ at Different Temperatures

| Exchange temperature, $T$ (K) | Thermodynamic equilibrium constant, $K_a$ | Standard free energy, $\Delta G°$ (kJ·geqv$^{-1}$) | Standard enthalpy, $\Delta H°$ (kJ·geqv$^{-1}$) | Standard entropy, $\Delta S°$ (kJ·geqv$^{-1}$·K$^{-1}$) |
|---|---|---|---|---|
| 293 | 21.89 | −3.76 | 17.18 | 0.0715 |
| 313 | 54.60 | −4.06 | 17.18 | 0.0715 |
| 333 | 119.10 | −6.62 | 17.18 | 0.0715 |

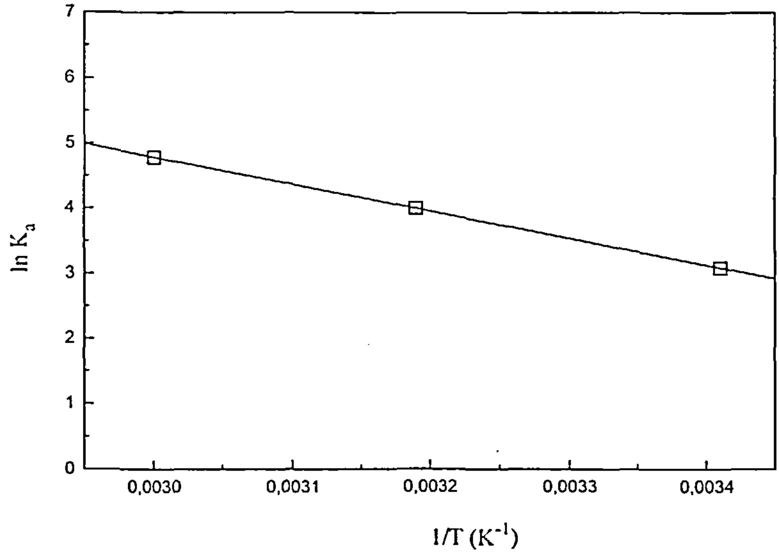

FIG. 6 Logarithms of the thermodynamic equilibrium constants, $K_a$, that correspond to the exchange processes in the temperature range between $T$ = 293 K and $T$ = 333 K, plotted against $1/T$.

combination of the ions with the exchanger in a definite composition of the whole mass (29), their values for various fractions, $f_{\mathrm{Cd,Z}}$, may be calculated using the Gibbs–Duhem equation after the method of Gaines and Thomas (29, 40):

$$\ln \gamma_{\mathrm{Cd,Z}} = f_{\mathrm{Na,Z}} (Z_{\mathrm{Na}} - Z_{\mathrm{Cd}}) - \ln K_C (1 - f_{\mathrm{Cd,Z}}) + \int \ln K_C \cdot df_{\mathrm{Cd,Z}} \tag{10}$$

$$\ln (\gamma_{\mathrm{Na,Z}})^2 = f_{\mathrm{Cd,Z}} (Z_{\mathrm{Cd}} - Z_{\mathrm{Na}}) + f_{\mathrm{Cd,Z}} \ln K_C - \int \ln K_C \cdot df_{\mathrm{Cd,Z}} \tag{11}$$

Figure 7 shows the change of activity coefficients $\gamma_{\mathrm{Cd,Z}}$, and, $\gamma_{\mathrm{Na,Z}}$ calculated by Eqs. (10) and (11), respectively, as functions of the fractions, $f_{\mathrm{Cd,Z}}$, relevant for equilibrium states of the exchange processes at 293 K (Fig. 7A), 313 K (Fig. 7B), and 333 K (Fig. 7C). In contrast to the decrease of the activity coefficients of a given type of ions with the increase of

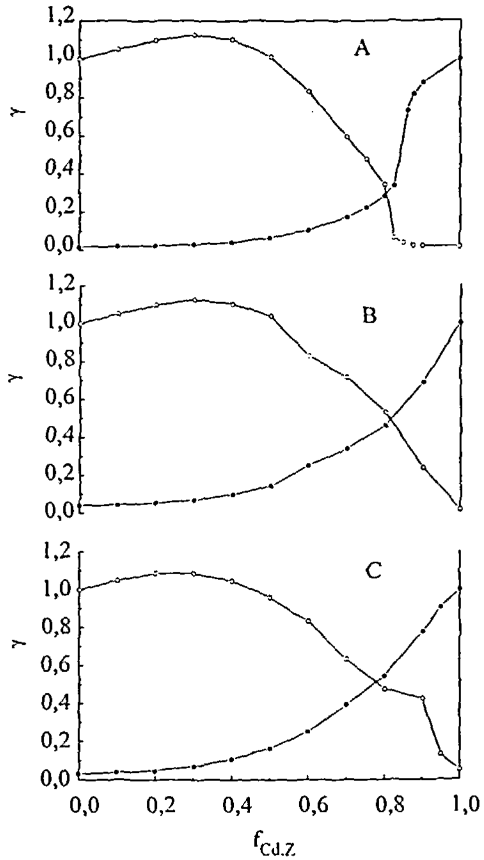

FIG. 7 Activity coefficients of cadmium ions, $\gamma_{Cd,Z}$ (●), and sodium ions, $\gamma_{Na,Z}$ (○), in zeolite A plotted as functions of the equivalent fractions of cadmium ions in zeolite A, $f_{Cd,Z}$, relevant for equilibrium states of the exchange processes at 293 K (A), 313 K (B), and 333 K (C).

their concentration in solution (37, 38), the activity coefficient, $\gamma_{Cd,Z}$, of cadmium ions increases with the increase of their "concentration" in zeolite and reaches the value $\gamma_{Cd,Z} = 1$ for $f_{Cd,Z} \approx 1$. On the other hand, the value of $\gamma_{Na,Z}$ slightly increases with the increase of $f_{Cd,Z}$ ($\gamma_{Na,Z} \approx 1$ for $f_{Cd,Z} = 0$), reaches a maximum ($\gamma_{Na,Z} = 1.09$–$1.13$) for $f_{Cd,Z} = 0.3$, and then sharply decreases with the increase of $f_{Cd,Z}$. The temperature of the exchange process slightly influences the changes in $\gamma_{Na,Z}$ and $\gamma_{Cd,Z}$ (the rate of increase of $\gamma_{Cd,Z}$ with the increase of $f_{Cd,Z}$ slightly increases with the increasing exchange temperature, see Fig. 7). The seemingly unusual relations between the activity coefficients $\gamma_{Na,Z}$ and $\gamma_{Cd,Z}$ and $f_{Cd,Z}$ (the increase of the value of the activity coefficient with the increase of ion "concentration" in zeolite; see Fig. 7) are, however, in accordance with previously reported results (40–42).

The standard free energies, $\Delta G°$, of the exchange processes at different temperatures were calculated by the relation (40)

$$\Delta G° = [-RT/(Z_{Na}Z_{Cd})] \ln K_a \tag{12}$$

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

The standard enthalpy, $\Delta H°$, may be calculated by using the values of both the thermodynamic equilibrium constant, $K_a$, and the standard free energy, $\Delta G°$ (43, 44), i.e.,

$$\Delta H° = [-R/(Z_{Na}Z_{Cd})] [\delta(\ln K_a)/\delta(1/T)] \tag{13}$$

$$\Delta H° = [\delta(\Delta G°/T)/\delta\,(1/T)] \tag{14}$$

The linear relationship between ln $K_a$ and $1/T$ (see Fig. 6) and between $\Delta G°/T$ and $1/T$ (Fig. 8), respectively, indicates that the standard enthalpy

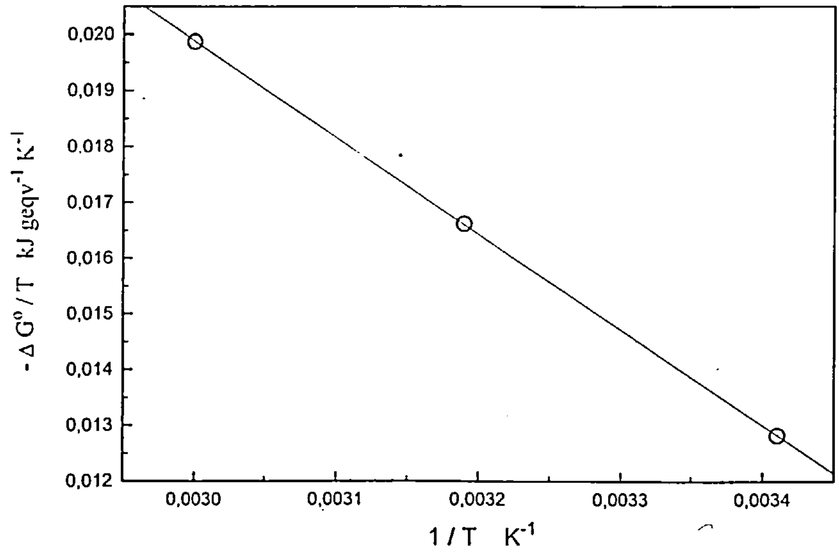

FIG. 8 The values of $\Delta G°/T$ that correspond to the equilibrium of the exchange processes in the temperature range between $T$ = 293 K and $T$ = 333 K plotted against $1/T$.

of the exchange process does not depend on the exchange temperature in the temperature range from $T = 293$ K to $T = 333$ K. Hence,

$$\Delta H^\circ = [-R/(Z_{Na}Z_{Cd})]\, S_I = S_{II} \tag{15}$$

where $S_I = [\ln K_a(2) - \ln K_a(1)]/[1/T(2) - 1/T(1)]$ is the slope of the ln $K_a$ vs $1/T$ straight line in Fig. 7(A) and $S_{II} = [(\Delta G^\circ/T)_2 - (\Delta G^\circ/T)_1/[1/T(2) - 1/T(1)]$ is the slope of the $\Delta G^\circ/T$ vs $1/T$ straight line in Fig. 7(B). The $\Delta H^\circ$ values calculated by using the Eq. (15), numerical values of the slopes $S_I$ and $S_{II}$, are almost the same, i.e., $\Delta H^\circ = [-R/(Z_{Na}Z_{Cd})]\, S_I = 17.19$ kJ·geqv$^{-1}$ and $\Delta H^\circ = S_{II} = 17.18$ kJ·geqv$^{-1}$. Hence, the standard enthalpy of the exchange process in the temperature range between $T = 293$ K and $T = 333$ K is the average value of the standard enthalpies calculated by the two methods described, i.e., $\Delta H^\circ = 17.185$ kJ·geqv$^{-1}$.

The standard entropy, $\Delta S^\circ$, of the exchange processes was calculated in the usual way (42):

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \tag{16}$$

using the previously calculated values of $\Delta H^\circ$ and $\Delta G^\circ$ listed (see Table 1). The values of $\Delta S^\circ$ do not depend on the exchange temperature, $T$ (see Table 1). The same value $\Delta S^\circ$ was obtained from the slope, $S_{III}$, of the $\Delta G^\circ$ vs $T$ straight line (see Fig. 9), i.e., $\Delta S^\circ = -\delta\Delta G^\circ/\delta T = S_{III} = 0.0715$ kJ·geqv$^{-1}$·K$^{-1}$.

The positive value of standard enthalpy (see Table 1), and thus the endothermicity of the exchange process, is in accordance with the finding that when a divalent ion enters the crystals, $\Delta H^\circ$ will be positive when $2r_{Na} > r_A$ (45), i.e., $2r_{Na} > r_{Cd}$ where $r_{Na} = 0.097$ nm is the ionic radius of the $Na^+$ ion and $r_{Cd} = 0.097$ nm is the ionic radius of the $Cd^{2+}$ ion (46). The observed increase in the entropy of the system (see Table 1) may be considered as consisting of two contributions, one, $\Delta S^\circ(L)$, from the aqueous phase and the other, $\Delta S^\circ(S)$, from the zeolite phase (47). The replacement of one $Cd^{2+}$ ion by two $Na^+$ ions in the aqueous phase frees water molecules and thereby increases the entropy of the solution phase for $Cd^{2+}$ because the $Cd^{2+}$ is more hydrated than two $Na^+$ (44). On the other hand, since cadmium-exchanged zeolite A contains 30 water molecules per unit cell (18 molecules of "structured" water and 12 of "free" water) and the original Na-form of zeolite A contains 27 molecules of water per unit cell (18 molecules of "structured" water and 9 of "free" water) (44), the positive value of the change in standard entropy $\Delta S^\circ(S)$ can be attributed to the increase of the content of "free" water in the cavities of Cd-exchanged zeolite A with respect to the original Na-form of zeolite A (44, 47). Hence, $\Delta S^\circ = \Delta S^\circ(L) + \Delta S^\circ(S)$. It may be assumed that $\Delta S^\circ(S) > \Delta S^\circ(L)$.

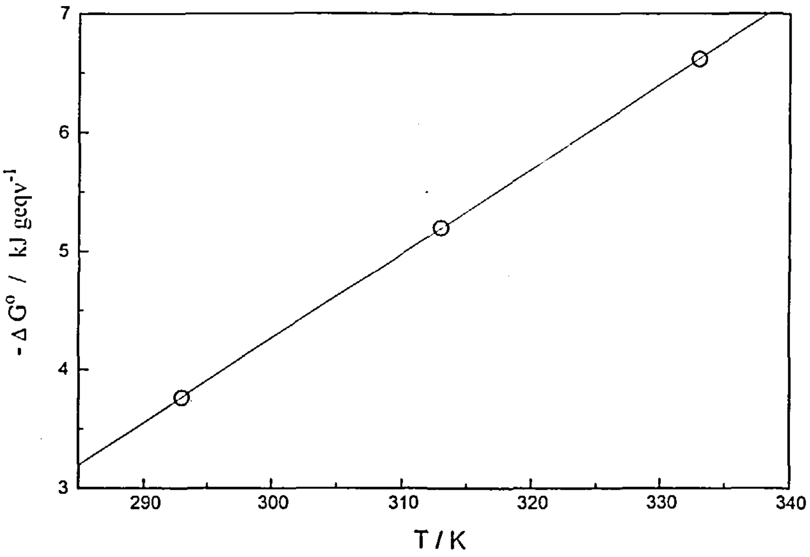

FIG. 9 The values of $\Delta G^\circ$ that correspond to the equilibrium of the exchange processes in the temperature range between $T = 293$ K and $T = 333$ K plotted against the exchange temperature $T$.

Finally, since both $\Delta H^\circ$ and $\Delta S^\circ$ are positive and $T\Delta S^\circ > \Delta H^\circ$ (see the data in Table 1), $\Delta G^\circ$ must be negative, i.e., $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (see Eq. 16). The expected negative values of $\Delta G^\circ$ were confirmed (see Table 1) by its calculation using Eq. (12) and the corresponding values of $K_a$. The decrease of $\Delta G^\circ$ with the exchange temperature, $T$, can be formally explained by the increase of $T\Delta S^\circ$ (see Eq. 16), but in a physical sense the negative value of $\Delta G^\circ$ and its decrease with the increasing exchange temperature is connected with the higher afinity of zeolite A to $Cd^{2+}$ ions than to $Na^+$ ions, and thus with the change in the thermodynamic stability of the zeolite A framework during the exchange process (48).

## CONCLUSIONS

Thermodynamic data relevant for the exchange processes between $Cd^{2+}$ ions from solutions and $Na^+$ ions from zeolite A are determined from the distribution of $Na^+$ and $Cd^{2+}$ ions between solution and zeolite at the exchange equilibrium established at different total ions concentrations and different exchange temperatures. For all the cases examined, the exchange equilibrium has been established in less than 30 minutes.

Equilibrium isotherms ($f_{\mathrm{Cd,Z}}$ vs $f_{\mathrm{Cd,L}}$ plots) are of type C ("sigmoidal"-shape isotherms), which means that the entering $\mathrm{Cd}^{2+}$ ion shows a selectivity that is the reverse of its increasing fraction in the zeolite.

Kielland plots of the exchange processes (logarithm of the corrected selectivity coefficients, ln $K_{\mathrm{C}}$, calculated from the exchange isotherms plotted against $f_{\mathrm{Cd,Z}}$) are independent on the total solution normality at constant temperature (293 K), which is in agreement with previously published results (49). The consequence is that the thermodynamic equilibrium constant $K_{\mathrm{a}}$, calculated from the Kielland plots, is independent on the solution normality in the range from 0.02 to 0.1 geqv·dm$^{-3}$. On the other hand, the value of $K_{\mathrm{a}}$ increases with the temperature of the exchange process, so that ln $K_{\mathrm{a}}$ is a linear function of $1/T$. From the linear relationship between ln $K_{\mathrm{a}}$ and $1/T$ it was calculated that the activation energy $E_{\mathrm{a}}$ of the exchange process is 17.18 kJ·geqv$^{-1}$ in the temperature range from $T = 298$ K to $T = 333$ K.

Standard free energy $\Delta G°$, standard enthalpy $\Delta H°$, and standard entropy $\Delta S°$ for the exchange processes at 293, 313, and 333 K were calculated by the appropriate thermodynamic relations and known numerical values of thermodynamic equilibrium constant $K_{\mathrm{a}}$.

Positive values of the standard enthalpy $\Delta H°$ follows from the fact that $2r_{\mathrm{Na}} > r_{\mathrm{Cd}}$ (46), and indicate that the exchange process is endothermic. The standard enthalpy, $\Delta H° = 8.563$ k·eqv$^{-1}$, is independent of the exchange temperature in the range from $T = 293$ to $T = 333$ K.

The increase in the entropy of the system may be considered as consisting of two contributions; one, $\Delta H°(\mathrm{L})$, from the aqueous phase and the other, $\Delta H°(\mathrm{S})$, from the zeolite phase, i.e., $\Delta S° = \Delta S°(\mathrm{L}) + \Delta S°(\mathrm{S})$. It may be assumed that an increase of $\Delta H°(\mathrm{S})$ caused by the increase of content of "free" water in the cavities of Cd-exchanged zeolite A with respect to the original Na-form of zeolite A is considerably higher than the increase of $\Delta H°(\mathrm{L})$ caused by the free water molecules in the liquid phase, i.e., $\Delta S°(\mathrm{S}) > \Delta S°(\mathrm{L})$.

The decrease of $\Delta G°$ with the exchange temperature $T$ can be formally explained by the increase of $T\Delta S°$ (see Eq. 16), but in a physical sense the negative value of $\Delta G°$ and its decrease with the increasing exchange temperature is connected with the higher affinity of zeolite A to $\mathrm{Cd}^{2+}$ ions than to $\mathrm{Na}^{+}$ ions, and thus with the change of the thermodynamic stability of the zeolite A framework during the exchange process (48)

The reported thermodynamic data will be used in further work for the prediction of the distribution of cadmium and sodium ions between zeolite and solution at equilibrium, and thus for the prediction of the efficiency of the removal of cadmium ions from solutions under given conditions of the $Cd^{2+}(s) + 2\ Na^{+}(z) \Leftrightarrow Cd^{2+}(z) + 2Na^{+}(s)$ exchange processes.

## ACKNOWLEDGMENT

This work was supported by the Ministry of Science and Technology of the Republic of Croatia.

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*Received by editor April 30, 1997*
*Revision received July 1997*