

NaY and CrY zeolites ion exchange. Thermodynamics

Lucia Tagami¹, Onélia Aparecida Andreo dos Santos¹, Eduardo Falabella Sousa-Aguiar², Pedro Augusto Arroyo¹ and Maria Angélica Simões Dornellas de Barros^{1*}

¹Departamento de Engenharia Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, Paraná, Brasil. ²CENPES/PETROBRAS, Ilha do Fundão, Quadra 7, 21949-900, Rio de Janeiro, Brasil. *Author for correspondence. e-mail: angelica@deq.uem.br

ABSTRACT. Isotherm ion exchange of Y zeolite has been studied at different temperatures. The direct exchanges of chromium in NaY show a very high selectivity to the in-going Cr³⁺ ion. It was also shown that exchange increases with increasing temperature. On the other hand, the reverse isotherms in Cr-NaY are non-preferential process. In both cases Kielland plots and thermodynamic properties such as standard enthalpy of ion exchange (ΔH°), standard free energy of ion exchange (ΔG°), and standard entropy of ion exchange (ΔS°) were calculated. Thermodynamic properties show a favorable process for direct exchange. The reverse exchange process is less sensitive to the changes in temperature due to the high energy needed to replace 3Na⁺ by Cr³⁺ in the zeolitic phase.

Key words: Chromium, ion exchange, isotherm, Y zeolite, thermodynamic properties.

RESUMO. Troca iônica em zeólitas NaY e CrY. Termodinâmica. Isotermas de troca iônica de zeólita Y foram investigadas a diferentes temperaturas. As trocas diretas de cromo em NaY apresentaram uma grande seletividade ao Cr³⁺. Foi também observado que a troca é proporcional ao aumento da temperatura. Por outro lado, as trocas reversas em zeólitas Cr-NaY não são preferenciais. Em ambos os casos, os diagramas de Kielland bem como as propriedades termodinâmicas entalpia padrão (ΔH°), energia livre padrão (ΔG°) e entropia padrão (ΔS°) de troca iônica foram calculados. As propriedades termodinâmicas mostram um processo favorável para a troca direta. O processo reverso de troca é pouco sensível às mudanças de temperatura devido à alta energia necessária à substituição de 3Na⁺ por apenas um Cr³⁺ na zeólita.

Palavras-chave: Cromo, troca iônica, isoterma, zeólita Y, propriedades termodinâmicas.

Zeolites are crystalline aluminosilicates. Their physical structure is porous with interconnected cavities in which metal cations and water molecules are sited. The structure consists of SiO₄ and AlO₄⁻ tetrahedra arranged in such a way that each oxygen atom is shared between two tetrahedra. The framework has a negative charge of one at the site of each aluminum atom and is balanced by the exchangeable cation. Due to their cation exchange capacity, zeolites are widely used as sorbents, catalysts and cation exchangers. In zeolite Y cations are located in their supercage, sodalite and double hexagonal prisms. Supercages are able to accommodate many cations, even those with high hydrated radii, due to their aperture (7.4Å) and diameter (12.5Å). On the other hand, sodalite and hexagonal prisms have an aperture of 2.2 Å, being less favorable for ion exchanging, because of steric factors (Breck, 1984).

Cation exchange capacity (CEC) is directly related to the amount of aluminum present in the framework. Properties such as Si/Al ratio, specific to the cationic species in solution and the anionic associated to them, solvent, pH, and temperature must be observed for good exchange efficiency (Breck, 1984). High charges and small radii cations are preferred by zeolites of lower Si/Al ratio such as zeolite Y (Townsend, 1991). Few studies concerning heavy metal exchange isotherms in zeolite Y have been reported (Chen *et al.*, 1990; Keane, 1996). In all cases, it has been emphasized that the entering ions are preferably located in large cages such as supercages and sodalites. Exchange degree in such cages depends on the nature of each entering ion (Keane, 1994). The exchange of Na⁺ by La³⁺, for example, preferably occurs in the supercavities and only a few cations of lanthanum may get into the sodalite cage (Chen *et al.*, 1990). The La-NaY isotherms showed a very convexly upward curvature

followed by a large plateau at 70% of the total exchange capacity, which agrees with the occupancy of the large cages only (Giannetto *et al.*, 2000). As charge and hydration radius of La^{3+} ($r_{\text{H}} = 4,52 \text{ \AA}$ - Nightingale, 1959) are similar to Cr^{3+} ($r_{\text{H}} = 4,61 \text{ \AA}$ - Nightingale, 1959), a plateau for Cr-NaY is expected at least for low temperatures. The Cr^{3+} ion, in spite of its high charge and small size ($0,64 \text{ \AA}$), has a strong tendency to undergo hydration. In fact, for the exchange with Cr^{3+} , Weckuysen *et al.* (1994) stated that these cations have a hexahydrated form $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and are preferably present in the supercavities of zeolites NaY. Custódio *et al.* (1998) reported a strong preference of chromium in NaY. Due to the presence of supercavities, NaY zeolite has a great affinity for ions Cr^{3+} . Hexagonal prisms may be possibly occupied only in very favorable thermodynamic conditions. Moreover, according to Chen *et al.* (1990), after 3-5 days of contact between zeolite and lanthanum solution the concentration was found to be constant. Therefore, such contact time should be used for Cr^{3+} isotherms. On the other hand, the reversibility of La-NaY ion exchange isotherm may be established at an equilibrium time about one week for each measurement at 25-65°C. This implies that reverse isotherm Na-CrY may not attain equilibrium before seven days. Such difference in contact time may indicate the difficulty of sites in exchanging trivalent cations for univalent ones in the reverse exchange.

It is also interesting to note that in zeolite Y very sharp non-linear Kielland plots ($\ln K_c$ versus normalized X_{AZ}) for heavy metals (Keane, 1994 and 1996). This feature is a consequence of site heterogeneity of the framework (Maes and Cremers, 1975). At low degrees of exchange, cations involved in the exchange are mobile, hydrated and not located on any specific sites. After most of the non-localized Na^+ ions in the supercages were replaced, the entering ions replaced the Na^+ ions located in less accessible cavities (Maes and Cremers, 1975), originating differences in the exchange energies, and consequently, in non-linear Kielland plots. Kielland data play an important role in the estimation of the standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) of ion exchange (Rupp, 1996). Negative standard free energy values indicate a favorable ion exchange process, whereas changes in enthalpy and entropy reflect the binding energies of the solvated cations in the zeolite lattice (Biškup and Subotić, 2000). Endothermic and exothermic processes as well as negative and positive entropy changes have already been observed in zeolites (Keane, 1994; Dyer and White, 1999), as a

consequence of the interaction of the in-going ions with the hydration sphere and with the zeolite framework (Barros *et al.*, 2001).

The present work aims at constructing direct and reverse ion exchange isotherms at different temperatures for Cr-NaY and Na-CrY systems, and to obtain the Kielland plots from these data. Thermodynamic properties may be determined from isotherms and Kielland plots using procedures described elsewhere (Barros *et al.*, 1997; Rupp, 1996). The thermodynamic investigation presented in this paper may contribute towards the application of zeolite Y in the removal of chromium ions from industrial wastewaters.

Material and methods

The parent zeolite was a NaY with unit cell molar composition in dry base $\text{Na}_{51}(\text{AlO}_2^-)_{51}(\text{SiO}_2)_{141}$, and Si/Al ratio of 2.8. The loss of ignition (LOI), or rather, the amount of water in the zeolite, was determined by the weight difference before and after calcination for 1 hr at 815°C.

All chemical composition of parent zeolites and analysis of exchanging ions content were carried out by atomic absorption spectrophotometry using a Varian model SpectrAA-10 Plus spectrophotometer.

Chromium zeolite treatment

In order to obtain, as far as possible, the homoionic chromium form, NaY sample was put under reflux with a chromium solution with twice the zeolite CEC concentration. The solid/liquid ratio in this experiment was fixed at 10%. After a period of 12h, the sample was filtered, washed exhaustively with deionised water at 80°C, and dried at 100°C overnight. This procedure was repeated three times.

The resultant CrY zeolite had a unit cell molar composition in dry base $\text{Cr}_{15}\text{Na}_6(\text{AlO}_2^-)_{51}(\text{SiO}_2)_{141}$ with a Si/Al ratio of 2.8. Furthermore, the loss of ignition (LOI) was determined at 17.4%.

Direct ion exchange isotherm

The procedure used a constant mass of NaY zeolite in such a manner that the percentage of dried mass in the flasks was 0.5%. The initial chromium concentration (C_0) was not maintained constant and it was increased in order to reach higher X_{AZ} values. The pH of the chromium nitrate solution was measured for range 3.0 - 5.0, but the samples were not buffered during the experiments. The pH values lower than 2.5 were avoided because they could cause a dealumination of the zeolite framework (Breck, 1984). Erlenmeyer flasks were stirred

continuously for 3 days, since it had been previously concluded that this period would be sufficient for the equilibrium (Custódio *et al.*, 1998; Chen *et al.*, 1990). Three isotherms were obtained at 25°C, 40°C and 60°C.

Direct isotherm data were calculated by:

$$X_{AS} = \frac{C}{C_0} \quad (1)$$

$$X_{AZ} = \frac{(C_0 - C)}{CEC \text{ ms}} \quad (2)$$

where X_{AS} stands for the equivalent fraction of Cr^{3+} cation that remained in the solution, X_{AZ} stands for the equivalent fraction of the cation Cr^{3+} exchanged in the zeolite, C is the equilibrium concentration of Cr^{3+} in equivalents, C_0 is the initial Cr^{3+} concentration also in equivalents, and CEC refers to cation exchange capacity. For NaY CEC was determined as 3.90 meq/g by chemical analysis of the parent zeolite. Finally, ms is the dry mass of the solid.

Reverse ion exchange isotherm

Pretreated CrY zeolite was used to construct the reverse isotherms. Erlenmeyer flasks were stirred continuously for 8 days, since it had been previously concluded that this time would be sufficient for the equilibrium (Chen *et al.*, 1990). Reverse isotherms were obtained at three different temperatures: 30°C, 40°C and 60°C.

Reverse isotherm data were calculated by:

$$X_{AS} = \frac{C_0 - C}{C_0} \quad (3)$$

$$X_{AZ} = \frac{(CEC - C)}{CEC \text{ ms}} \quad (4)$$

where X_{AS} stands for the equivalent fraction of the Na^+ cation originally in the liquid phase that remains in the solution, X_{AZ} stands for the equivalent fraction of the cation Na^+ exchanged in the zeolite, C is the equilibrium concentration of Cr^{3+} , C_0 is the initial Na^+ concentration, and finally CEC refers to the cation exchange capacity that, in the case of CrY, has been determined as 3.75 meq/g by chemical analysis of the parent zeolite. The term ms refers to the dry mass of the solid.

In this ion exchange equilibrium a stoichiometric exchange was expected, which implies that the sodium equivalent content in the zeolite was the

same as that of the chromium in solution; therefore, the sodium ion exchanged from solution corresponds to the chromium equivalent content in the same solution.

The CrY samples were also analyzed by IR spectroscopy and compared with NaY to certify that no dealumination occurred during the pretreatment procedure. The IR spectra showed no significant deviation from those recorded for the parent zeolites, suggesting that zeolite crystallinity was retained after the exchange step. In fact, both NaY and CrY show no differences at all with regard to framework Si/Al ratio obtained from IR analysis. Moreover, the difference between 3.9 meq/g obtained for NaY and 3.75 meq/g obtained for CrY is negligible.

Kielland plots and thermodynamic properties

The Kielland constant is defined as:

$$Kc = \frac{X_{A(Z)}^{Z_B} X_{B(S)}^{Z_A}}{X_{B(Z)}^{Z_A} X_{A(S)}^{Z_B}} \left(\frac{\gamma_{B(S)}^{Z_A}}{\gamma_{A(S)}^{Z_B}} \right) \quad (5)$$

where $\gamma_{i(S)}$ are mean activity coefficients associated with molality. All activity coefficients in this investigation have been considered a unit. X_{BZ} and X_{BS} are the equivalent fractions of the out-going ion B in the zeolite and in solution, given as $1 - X_{AZ}$ and $1 - X_{AS}$ respectively.

To obtain the Kielland plots, normalized values of X_{AZ} (X_{AZ}') were used as suggested elsewhere (Barrer and Klinowski, 1972; Barros *et al.*, 1997).

The thermodynamic properties were calculated from isotherms data and Kielland plots, using the relationship listed below:

$$\ln K_A = (Z_B - Z_A) + 2.3025 \int_0^1 \log Kc dX_{A(Z)} \quad (6)$$

$$\Delta G^0 = \frac{-RT}{Z_A Z_B} \ln K_A \quad (7)$$

$$\frac{d \ln K_A}{dT} = \frac{\Delta H^0}{RT^2} \quad (8)$$

$$\Delta S^0 = \left(\frac{\Delta H^0 - \Delta G^0}{T} \right) \quad (9)$$

where K_A stands for constant equilibrium, Kc stands for Kielland constant, R stands for universal gas constant, T stands for absolute temperature, Z_A stands for charge of in-going ion, Z_B stands for charge of out-going ion, ΔH^0 stands for standard enthalpy of ion exchange, ΔG^0 stands for free energy

and finally ΔS° stands for the standard entropy of ion exchange.

The exchange isotherms data obtained under known conditions may be used for determining these thermodynamic properties. To determine the thermodynamic equilibrium constant, K_A , for the examined exchange processes, the integral on the right-hand side of Equation (6) was evaluated graphically as the area under the corresponding $\ln K_c$ vs X_{AZ} curves, denominated Kielland plots (Breck, 1984; Barrer, 1974).

Results and discussion

The direct isotherms are shown in Figure 1. One can observe a concavely upward curvature of the isotherms due to the very high preference of NaY for Cr^{3+} . Higher temperatures increase Cr^{3+} exchange; however, even at 60°C the ion exchange reaction fails to proceed to completion. As pH was not buffered, it was impossible to obtain values of X_{AS} closer to 1 without dealumination of the framework. One may also note that at 25°C an initial plateau occurs corresponding to X_{AZ} close to 0.7 that refers to Cr^{3+} exchanged only in the supercages (Breck, 1984). At 40°C, a higher loading ($X_{AZ} \approx 0.85$) is due to some Cr^{3+} located in sodalite cages and hexagonal prisms, besides supercages. At 60°C, X_{AZ} values almost reach the maximum value of 1 ($X_{AZ} \approx 0.95$), even at low X_{AS} values, indicating that most sites located in hexagonal prisms are also occupied. Results agree with those of Maes and Cremers (1975) who showed that in cases of complete exchange the ions occupied predominantly positions in the supercavities at the initial stage of the exchange reaction. The sites in the small cages (sodalite and hexagonal prisms) were taken at the very last stages of the exchange. Keane (1996) also observed that ion exchange in the fully hydrated unit cell was limited to the supercages and sodalites; nevertheless, upon temperature increase few trivalent cations were located in the small cages. When all supercages are filled, the Cr^{3+} cations diffuse into hexagonal prisms, causing an increasing degree of exchange.

The reverse exchange is therefore carried out directly on CrY samples. These back-exchanging isotherms are very concavely upward, as shown in Figure 2. This means a non-preference of the parent zeolite for the in-going Na^+ ion. Only a small amount of Cr^{3+} can be removed from the sites. A high initial sodium concentration, much more than the stoichiometric quantity, is necessary to replace some Cr^{3+} ions, even those located in the most

accessible sites in the supercages. In order to replace Cr^{3+} in the sodalite cages, these out-going cations have to increase their solvation coating when inhabiting these cavities (Breck, 1984), which is not a favorable process (Maes and Cremers, 1975). Furthermore, trivalent exchange is more efficient in neutralizing the framework charge in Y zeolites (Keane, 1996).

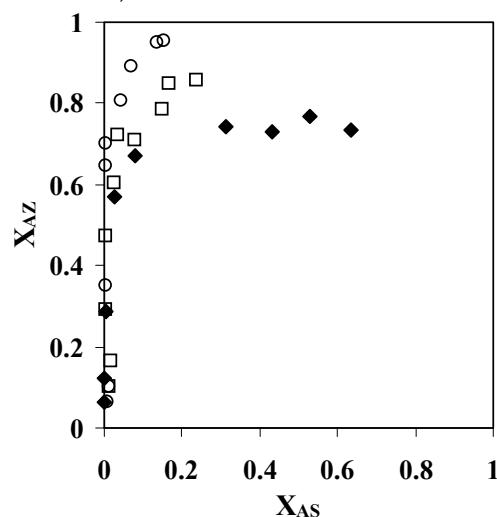


Figure 1. Direct exchange isotherms at (◆) 25°C, (□) 45°C and (○) 60°C

Figure 2 shows that temperature had a small influence in reverse Na-CrY ion exchange process. It may also be observed that higher chromium contents ($X_{AZ} \approx 0.4$) are reached only with very concentrated Na^+ aqueous solution ($X_{AS} > 0.99$). Therefore, it may be concluded that the influence of sodium concentration in the solution is really important. Indeed, Belincanta *et al.* (1999) showed that very high concentrations, such as 2.0 Mol/L of Na^+ , were necessary to replace all Cr^{3+} cations in the dynamic regeneration of NaY zeolite in a fixed bed column after total saturation with 15 mg/L of Cr^{3+} solution. Less concentrated sodium solutions were not able to regenerate the sites located in the small cages, mainly in the hexagonal prisms. As a consequence, a progressive accumulation of chromium ions was reported, thus decreasing the total exchange capacity of NaY zeolite.

Representative Kielland plots are shown in Figures 3 and 4, wherein the selectivity of the zeolite phase for the in-going cations is illustrated as a function of increasing exchange. Direct exchange Kielland plots shown in Figure 3 agree with NaY exchange behavior towards trivalent cations (Chen *et al.*, 1990; Custódio *et al.*, 1998; Keane, 1996). The very significant curvature observed with increasing

loading indicates pronounced site heterogeneity in Y zeolite (Chen *et al.*, 1990). As the temperature increased, the Kielland plots seem to have more pronounced curvature. Consequently, some Cr^{3+} may have entered the small cages, probably where the less thermodynamic favorable sites are located. This is in agreement with the isotherms behavior as chromium content reached 95% of the cation exchange capacity of zeolite Y.

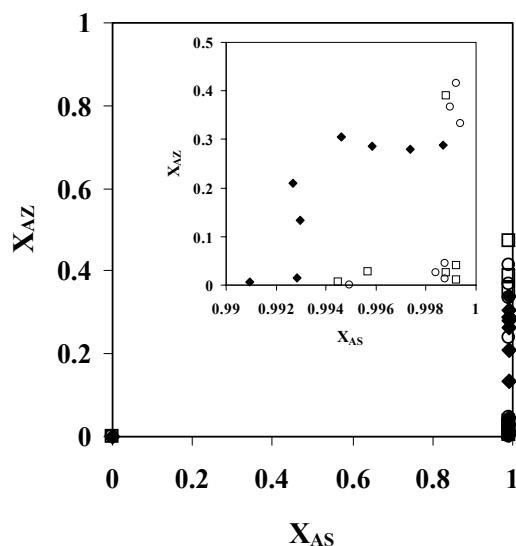


Figure 2. Reverse isotherms at (◆) 30°C, (□) 40°C and (○) 60°C. - Inset: detail of reverse isotherms

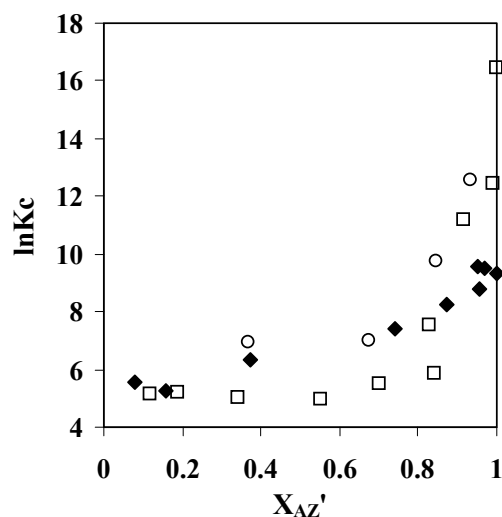


Figure 3. Kielland plots for direct isotherms at (◆) 25°C, (□) 40°C and (○) 60°C

In the case of Kielland plots of the reverse isotherms presented in Figure 4, the most striking

feature concerns a smooth curvature when compared to direct Kielland plot. There is no temperature dependence from 30°C up to 60°C. This is due to the location and energy of the sites that are different from the ones used in the direct exchange. The increase in $\ln Kc$ values may be attributed to the progressive weakening of the ion-dipole interaction between the sodium ion and the solvent dipoles and the consequent increased sodium ion mobility (Keane, 1995) in the CrY zeolite. A low exchange degree resulted since only part of the cations Cr^{3+} located in the less energetically sites in the supercages could be exchanged. In the hydrated unit cell, the indigenous Cr^{3+} ions interact with the aluminosilicate framework to a greater extent than Na^+ ions, with a result that the Cr^{3+} ions are more resistant to exchange.

It was possible to calculate the thermodynamic properties for both direct and reverse exchange systems from the Kielland plots and equations 6 to 9. These data are presented in Table 1 and Table 2, respectively.

From Table 1 one may observe that all ΔG° values for the direct isotherms are negative, indicating that the three systems reached a more stable energy level after ion exchange. Such results agree with the favorable curvature in the isotherms (Figure 1) and was already expected since $\Delta G^\circ < 0$ had been previously reported for other trivalent cations (Keane, 1996; Chen *et al.*, 1990). Concerning the ΔH° values, it is observed that at 25°C the reaction is exothermic and at 40°C and 60°C the exchanges are endothermic. At 25°C the ion exchange in NaY zeolites is exothermic because Cr^{3+} ions can maintain their hydration and mobility in the supercages (Weckuysen *et al.*, 1994). At 40 and 60°C, the ion exchange is endothermic because some energy must be supplied to the cation as it undergoes dehydration to occupy the less accessible sites located in the small cages (Radak and Gal, 1973). Particularly at 60°C the highest endothermic process has been reported, characteristic of a severe water stripping, possibly originating from almost complete chromium loading in the hexagonal prisms ($X_{AZ} \approx 1$ from Figure 1).

The entropy, similar to enthalpy, reflects the changes to ion hydration, which occurs during the exchange reaction. For a closed but not isolated system, like the flasks where the experimental points were obtained, entropy may decrease since the surroundings have a gain in this property. Therefore, negative entropy change of ion exchange process is possible, while already reported in zeolite

systems (Maes and Cremers, 1975; Keane, 1994). At 25°C the entropy change for direct isotherm is negative, which suggests that release of water from the tightly bound hydration sphere of sodium contributes to the ion exchange process as it moves from solid to solution phase (Dyer and Zubair, 1998). At higher temperatures the replacement of a less polarizing ion from the fluid phase (Cr^{3+}) originates a decrease of order with increasing temperatures, and consequently, an increase in entropy changes.

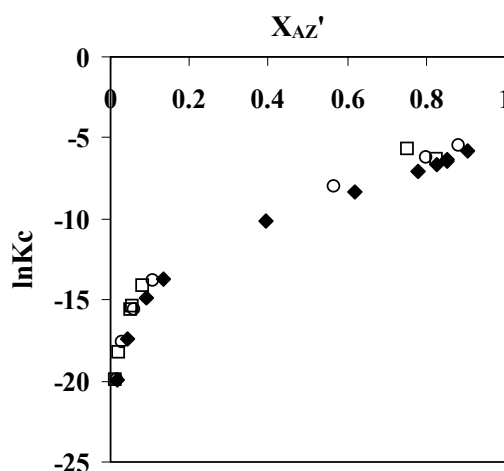


Figure 4. Kielland plots for reverse isotherms at (◆) 30°C, (□) 40°C and (○) 60°C

Table 1. Thermodynamic properties for direct isotherms

Temperature (°C)	ΔG° (kJ/eq)	ΔH° (kJ/eq)	ΔS° (kJ/eq.K)
25	-35.65	-2313.10	-0.6857
40	-30.12	80.00	0.3517
60	-48.76	610.99	1.9803

In the case of reverse ion exchange, the thermodynamic properties are presented in Table 2. One may observe that all ΔG° values are positive and thus indicating that the processes at the three different temperatures studied are unfavorable. Furthermore, these ΔG° values are numerically very similar, in agreement with the unfavorable isotherms (Figure 2) and with the Kielland plots too (Figure 4), where the curves are almost superposed. Therefore, these very close values also show that the reverse process is less sensitive to temperature changes.

Table 2. Thermodynamic properties for reverse isotherms

Temperature (°C)	ΔG° (kJ/eq)	ΔH° (kJ/eq)	ΔS° (kJ/eq.K)
30	19.88	10.54	0.0282
40	17.56	47.21	0.0947
60	18.98	-94.21	-0.3398

Concerning the standard enthalpy of reverse ion exchange, it has been observed that at 30°C and 40°C the processes are endothermic. At 60°C the reaction proceeds exothermically, indicating that Cr^{3+} cations can re-coordinate their solvation coating through the energy provided by the system. The standard entropy of reverse exchange shows a slight decrease with increasing temperature, indicating a very low influence of this factor in the ion exchange. The entropy change at 60°C is negative, probably due to the hydration of the out-going ion, which originated an increase of order in the system.

Conclusion

The data presented in this paper indicate the following conclusions:

- Direct isotherms are very convexly upward; this indicates that NaY are selective to Cr^{3+} over the entire temperature range. CrY zeolite is also selective to chromium ions and the reverse isotherms are unfavorable;
- The direct exchange of sodium for chromium ions occurs in all cages. On the other hand, possibly only the sites located in the supercages have their balancing cations exchanged in the reverse isotherms;
- The direct exchange is favorable over the entire temperature range, whereas the reverse exchange is totally unfavorable;
- The direct ion exchange is exothermic when Cr^{3+} preserves its hydration sphere in the supercages, and endothermic when the ion dehydrates to occupy less accessible sites. In reverse isotherms the enthalpy is positive for low temperatures and negative at 60°C, indicating that the out-going ion could re-coordinate its hydration sphere;
- The entropy of the direct isotherms increases with the replacement of Cr^{3+} ions from the fluid phase for sodium ions. The entropy of the reverse isotherms is slightly influenced by the ion exchange process.

Nomenclature

- CEC - cation exchange capacity (meq/g)
 C - equilibrium concentration of cation in equivalents
 Co - initial cation concentration in equivalents
 K_A - thermodynamic equilibrium constant
 K_C - Kielland constant
 R - universal gas constant (8.314J/molK)
 T - absolute temperature (K)
 X_{AS} - equivalent fraction of in-going cation -

- originally in the liquid that remains in the solution after equilibrium
- X_{AZ} - equivalent fraction of in-going cation exchanged in the zeolite
- X_{AZ}' - normalized equivalent fraction of in-going cation exchanged in the zeolite
- Z_A - charge of in-going cation
- Z_B - charge of out-going cation
- ΔH° - standard enthalpy of ion exchange (kJ/eq)
- ΔG° - standard free energy of ion exchange (kJ/eq)
- ΔS° - standard entropy of ion exchange (kJ/eqK)

References

- BARRER, R.M. Isomorphous replacement by ion exchange: Some equilibrium aspects. *Bull. Soc. Fr. Minéral. Cristallogr.*, v. 97, p. 89-100, 1974.
- BARRER, R.M.; KLINOWSKI, J. Ion exchange involving several groups of homogeneous sites. *J. Chem. Soc. Faraday Trans. I.*, Cambridge, v. 68, p. 73-87, 1972.
- BARROS, M.A.S.D. *et al.* Ion exchange mechanism of Cr^{3+} on naturally occurring Clinoptilolite. *Braz. J. Chem. Eng.*, São Paulo, v. 14, p. 3, 233-241, 1997.
- BARROS, M.A.S.D. *et al.* Multicomponent ion exchange isotherms in NaX Zeolite, *ENPROMER 2001*, Santa Fe - Argentina, Proc., v. I, p. 559-564, 2001.
- BELINCANTA, J. *et al.* Estudo da regenerabilidade de zeólitas NaY na troca iônica dinâmica Cr^{3+} . *ENPROMER*, 2, Florianópolis, 1999. *Cd-Rom...* Florianópolis: 1999. 5 p.
- BIŠKUP, B.; SUBO TIĆ, B. 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. *Sep. Sci. Technol.*, New York, v. 35, n. 14, p. 2311-2326, 2000.
- BRECK, D.W. *Zeolite Molecular Sieve*. Malabar-FL: Robert E. Krieger Publishing Company, 1984.
- CHEN, S.H. *et al.* Lanthanum-NaY zeolite exchange. 1. Thermodynamics and Thermochemistry. *Ind. Eng. Chem. Res.*, v. 29, p. 2020-2023, 1990.
- CUSTÓDIO, D.C. *et al.* Análise do comportamento de troca catiônica de íons Cr^{3+} em zeólitas NaY, ENCUESTRO LATINOAMERICANO DE INGENIERÍA QUÍMICA, 2, Antofagasta, 1998. *Anais...* Antofagasta, 1998, p. 294-301.
- DYER, A.; ZUBAIR, M. Ion exchange in chabazite¹. *Microporous and Mesoporous Materials*, Amsterdam, v. 22, p. 135-150, 1998.
- DYER, A.; WHITE, K. J. Cation diffusion in the natural zeolite clinoptilolite. *Thermochimica Acta*, Amsterdam, v. 340-341, p. 341-348, 1999.
- GIANNETTO, G. *et al.* (Ed.). *Zeólitas características, propiedades y aplicaciones industriales*. Caracas: Ed. Innovación Tecnológica - Facultad de Ingeniería - UCV, 2000.
- KEANE, M.A. Role of the alkali metal Co-cation in the ion exchange of Y zeolites I. Alkali Metal and Nickel ion-exchange equilibria. *Microporous Materials*, Norwalk, v. 3, p. 93-108, 1994.
- KEANE, M.A. The role of the alkali metal Co-cation in the ion exchange of Y zeolites II. Copper ion exchange equilibria. *Microporous Materials*, Norwalk, v. 3, p. 385-394, 1995.
- KEANE, M.A. The role of the alkali metal Co-cation in the ion exchange of Y zeolites IV. Cerium Ion Exchange Equilibria. *Microporous Materials*, Norwalk, v. 7, p. 51-59, 1996.
- MAES, A.; CREMERS, A. Ion exchange of synthetic zeolite X and Y with Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} Ions. *J. Chem. Soc. Faraday Trans. I*, Cambridge, v. 71, p. 265-277, 1975.
- NIGHTINGALE, Jr. E.R. Phenomenological theory of ion solvation. Effective radii of hydrated ions. *J. Phys. Chem.*, Washington D.C., v. 63, p. 1381-1387, 1959.
- RUPP, M.T.C. *Utilização de zeólitas no tratamento de efluentes inorgânicos*. Tese (Doutorado) - COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 1996.
- RADAK, V.M.; GAL, I.J. Ion-exchange equilibria of Co^{++} , Zn^{++} and Cd^{++} on Y-Zeolite and heats of immersion of ion-exchanged Y forms In: INTERNATIONAL CONFERENCE ON MOLECULAR SIEVES, 3, 1973, Zurick, *Proceedings...* Zurick, 1973, p. 201-205.
- TOWNSEND, R.P. Ion exchange in zeolites. In: FLANIGEN, E.M.; JANSON, J.C. (Ed.). *Studies in surface and science catalysis*. Amsterdam: Elsevier, v. 58, 1991, p. 359-390.
- WECKHUYSSEN, B.M. *et al.* A Quantitative diffuse reflectance spectroscopy study of Chromium - containing zeolites. *Zeolites*, Amsterdam, v. 14, p. 450-457, 1994.

Received on October 08, 2001.

Accepted on November 19, 2001.