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# Thermodynamics of the Exchange Processes between $K^+$, $Ca^{2+}$ and $Cr^{3+}$ in Zeolite NaA

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**Abstract.** In this paper it was analyzed the ion exchange isotherm of $K^+$, $Ca^{2+}$ and also $Cr^{3+}$ ions with NaA zeolites at three temperatures: 30, 45 and 60°C. The NaA isotherms were favorable for the metal cations studied. Differences in shape are due to the different influence of temperature in the interaction of the in-going cation with the zeolite framework. As a consequence, sites of different energies were used in the exchange process, which provided non linear Kielland plots. Equilibrium constant, standard free energy, enthalpy and enthopy changes were measured and tabulated. Equilibrium constant is directly proportional to the in-going ion charge. Concerning enthalpy, endothermic and exothermic exchanges were observed due to differences in the cation-framework interaction. The selectivity order based on the standard free energy over the entire temperature range was $K^+ < Cr^{3+} < Ca^{2+}$, a consequence of different ion exchange mechanisms. It was also noted that the entropy change increases with the polarizibility of the cations.

**Keywords:** zeolite A, ion exchange, isotherm, thermodynamic data, chromium

## 1. Introduction

One of the most important heavy metals is chromium which finds its way to bodies of water through wastewaters from iron and steel manufacturing, chrome leather tanning, chromium plating and others anthropogenic sources. The effluent from these industries may contain chromium at concentrations ranging from tenths to hundreds of mg/L that would endanger public health and the environment if discharged without adequate treatment. Particularly, the effects of acute chromium poisoning in humans are very serious, including lung cancer (Barros et al., 2001). According to the Brazilian law the upper limit of chromium trivalent in wastewaters is 0.5 mg/L (Barros, 2003). For this reason there is a constant need to remove chromium from industrial effluents. Heavy-metal ion exchange from this residual liquid phase is certainly an attractive option because it

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starts immediately after the contact of a heavy-metal solution with the ion exchanger.

Among the various available cation exchangers, zeolites meet the requirements of good selectivity and acceptable capacity. As the balancing cations are not rigidly fixed at specific locations within the hydrated unit cell, it is possible to effect exchange with external cations in solutions. Some parameters such as the hydration ratio of both co-ion and in-going ion as well as temperature and the three-dimensional zeolite framework highly influence the ion exchange mechanism.

Zeolite 4A has defined chemical composition and high and constant cation-exchange capacity. The aluminosilicate framework of zeolite A includes truncated octahedron ($\beta$-cage), which enclose a cavity with a free diameter of 6.6 Å. The center of the unit cell is a large cavity ($\alpha$-cage), which has a free diameter of 11.4 Å (Giannetto et al., 2000). Commercial exploitation of zeolites A as ion exchange has largely been limited to their use in water softening and their effectiveness in removing heavy metals from aqueous solution has not been properly assessed. A first step in direction of applying NaA as ion exchanger is to study the exchange behavior towards the cation of interest in equilibrium systems through isotherms.

In recent years an increasing number of studies have been made of the ion exchange properties of zeolite A with some heavy metal ions such as $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, as well as with hard cations such as $Ca^{2+}$ and $Mg^{2+}$ (Biškup and Subotić, 1998, 2000; Barri and Rees, 1980; Franklin and Townsend, 1985). The selectivity towards the in-going ion in zeolite A seems to be very dependent on temperature. An increase in equilibrium content with increasing temperature is a consequence of the reduction of the effective size of ions (Tagami et al., 2001) caused both 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 radius (Biškup and Subotić, 1998). This hydration effect may explain the fact that zeolite NaA has a huge preference towards $Ca^{2+}$ over $Mg^{2+}$ when the isotherms are obtained from solutions that contain the in-going cation ($Ca^{2+}$ or $Mg^{2+}$) and also the outgoing cation ($Na^+$)—Franklin and Townsend (1985). It suggests that the in-going ions occupy specific sites in the three dimensional framework according to their hydration coating. $Mg^{2+}$ ions may reside in the open eight-membered oxygen rings ($\alpha$ cages) where they can be hydrated with the maximum number of water molecules while $Ca^{2+}$ ions prefer the six-membered oxygen ring sites where they can be co-coordinated to the framework oxygens in the $\beta$ cages and also with the water molecules present in the $\alpha$ cages (Barri and Rees, 1980). Attempts to exchange the in-going ions with trivalent cations were unsuccessful (Breck, 1974) or partially successful in NaA (Wiers et al., 1982) but comparatively few papers dealing with chromium ion exchange in NaA have been published. In fact, chromium ions may be exchanged in a certain extent (Arroyo et al., 2000) in dynamic runs. In batch equilibrium system a partially successful selectivity are obtained (Wiers, 1982). On the other hand, the structure may exhibit an ion-sieve effect (Breck, 1974) due to the large hydrated ratio of $Cr^{3+}$ ions (4.61 Å—Nightingale, 1959). Therefore, only few cations may diffuse through the channels.

Concerning industrial wastewater, together with chromium, other cations with different charges and consequently different energy of hydration are found. Particularly, in the case of tannery wastewater, $Ca^{2+}$ and $K^+$ ions have a significant concentration. Therefore, the purpose of this research was to test NaA zeolite for the ability to remove these metal ions and to investigate their exchange mechanism. In this paper the application of zeolite A in removing $Cr^{3+}$in comparison with $Ca^{2+}$ and $K^+$ ions from aqueous solution was examined at three different temperatures: 30, 45 and 60°C.

## 2. Materials and Methods

### 2.1. Materials

The starting zeolite was a very high crystalline NaA powder without binder, Advera 401, provided by PQ Corporation which has the unit cell composition $Na_{90}(AlO_2)_{90}(SiO_2)_{102}$ in dry basis, corresponding to a SAR of 2.27 and to a cation exchange capacity of 6.47 meq $g^{-1}$. In order to obtain, as far as possible, the homoionic sodium form, the zeolite, as received, was contacted four times with 1 mol $dm^{-3}$ solutions of NaCl at 60°C. The zeolite was then washed each time with 2 $dm^3$ of hot deionised water and oven-dried at 100°C.

All experiments were carried out with chloride salts of chromium, calcium and potassium. Chloride was chosen because its good solubility in aqueous environment. Moreover, chloride is a small anion and may have low influence in the diffusion process of the in-going cations towards the exchange sites. The reagent-grade

$CrCl_3{\cdot}9H_2O$, $CaCl_2{\cdot}2H_2O$ and KCl were mixed with deionised water to prepare 15 meq dm$^{-3}$ solutions for unicomponent ion exchange. The ion exchange reactions were carried out by weighting suitable quantities of NaA zeolite (0.01 g up to 2.00 g) in 35-mL glass flasks containing 20 g of the salt solution and letting the system equilibrate in water bath shaker at 30, 45 and 60°C as described in Barros et al. (2003a). Each experimental data was repeated twice or three times in order to assure reproducibility. After 4–7 days of contact time between zeolite and solution as previously observed as enough to attain equilibrium (Barros, 2003), the flasks were removed from the constant-temperature bath; the solid and solution phases in equilibrium were rapidly separated by filtration. The pH of the samples at all isothermal temperatures was measured but the solution was not buffered. This procedure was adopted in order to analyze the cations behavior in a real wastewater situation, that is, with variable pH. Anyway, there was no evidence of hydronium ion exchange or metal precipitation as pH varied in a narrow range, from 3 to 6.

The exchanging ions content in the fluid phase before and after the experiments was determined by atomic absorption spectrophotometry using a Varian SpectrAA10-Plus spectrometer.

### 2.2. *Methods*

The isotherm data were calculated by

$$X_{\mathrm{AS}} = \frac{C_A}{C_{O_A}} \quad \text{and} \quad X_{\mathrm{AZ}} = \frac{\left(C_{O_A} - C_A\right)}{CEC} \tag{1}$$

where $C_A$ stands for the final concentration of the cation $A$. $C_{O_A}$ stands for the initial concentration of the cation $A$ and *CEC* is the cation exchange capacity (Al equivalents present in zeolite sample). $X_{\mathrm{AZ}}$ and $X_{\mathrm{AS}}$ are the equivalent fractions of the in-going ion $A$ in the zeolite and in solution phase, respectively.

The selectivity quotient is defined as:

$$K_B^{\prime A} = \frac{X_{A(Z)}^{\mathrm{ZB}} X_{B(S)}^{\mathrm{ZA}}}{X_{B(Z)}^{\mathrm{ZA}} X_{A(S)}^{\mathrm{ZB}}} \left[\frac{\gamma_{B(S)}^{\mathrm{ZA}}}{\gamma_{A(S)}^{\mathrm{ZB}}}\right] \tag{2}$$

where $\gamma_{i(S)}$ are the mean activity coefficients associated with molality. $X_{\mathrm{BZ}}$ and $X_{\mathrm{BS}}$ are the equivalent fractions of the out-going ion $B$, both in the zeolite and in solution, given as $1 - X_{\mathrm{AZ}}$ and $1 - X_{\mathrm{AS}}$ respectively. *ZA* and *ZB* are the charge of the in-going ion $A$ and the out going ion $B$.

In order to obtain $K_B^{\prime A}$, as it could be seen in Eq. (2), the mean activity coefficients of individual strong electrolyte must also be known. This parameter in an aqueous solution may be obtained using the Meissner's method (Zemaitis et al., 1986). Values of $\gamma_{i(S)}$ of an individual strong electrolyte in an aqueous solution of two strong electrolytes composed by two cations and only one anion, as it is the case of single ion exchange, can be obtained in Meissner and Kusik (1972).

The thermodynamic equilibrium constant for ion exchange reaction was estimated from the Kielland plots ($\log K_B^{\prime A}$ versus $X_{\mathrm{AZ}}$) using the equation:

$$\ln K_A = (ZB - ZA) + 2.3025 \int_0^1 \log K_B^{\prime A} dX_{A(Z)} \tag{3}$$

The standard enthalpy of exchange $(\Delta H^0)$ was estimated from the temperature dependence of $K_A$ (Van't Hoff equation) by plotting log $K_A$ against reciprocal temperature to give a line of gradient $-\Delta H^0/R$ according to

$$\frac{d \ln K_A}{dT} = \frac{\Delta H^0}{RT^2} \tag{4}$$

The standard free energy of exchange was determined from the equation

$$\Delta G^0 = \frac{-RT}{Z_A Z_B} \ln K_A \tag{5}$$

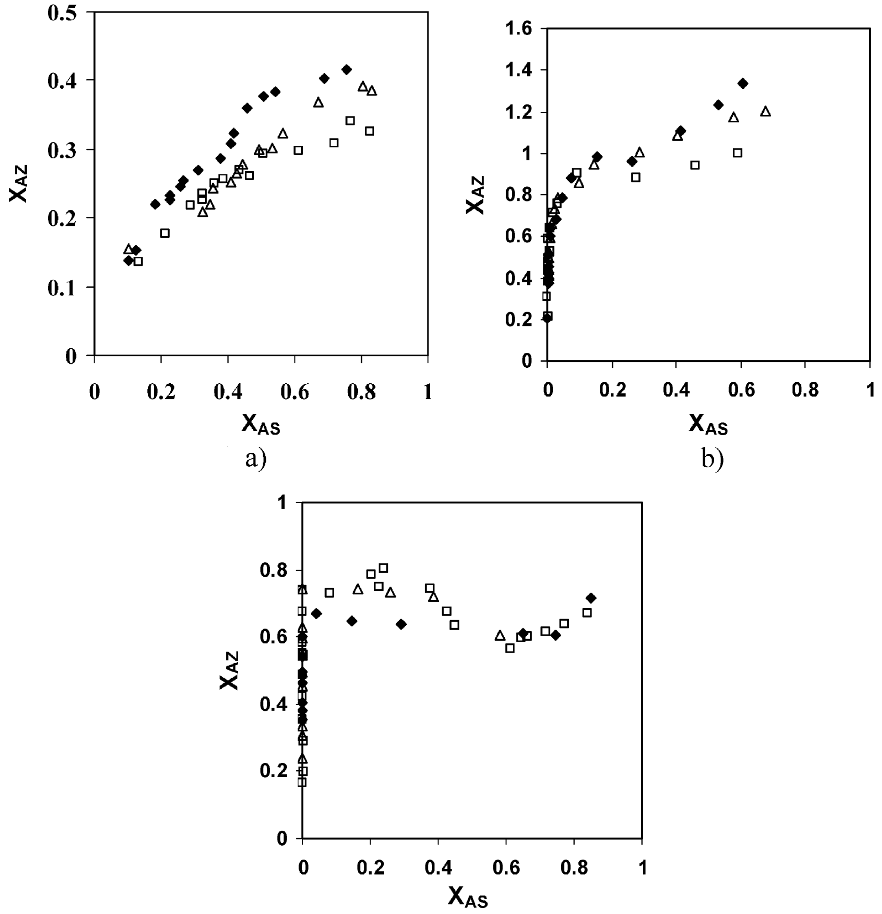
where $R$ is the ideal gas constant and $T$ is the absolute temperature.

The standard entropy of the exchange processes, $\Delta S^0$, was calculated in the usual way:

$$\Delta S^0 = \left[\frac{\Delta H^0 - \Delta G^0}{T}\right] \tag{6}$$

using the previously calculated values of $\Delta H^0$ and $\Delta G^0$.

In cases of incomplete exchange, a normalization procedure is required in which the experimental $X_{\mathrm{AZ}}$ values are multiplied by a normalization factor $f = 1/X_{\mathrm{AZ}}^{\max}$, where $X_{\mathrm{AZ}}^{\max}$ represents the maximum observed exchange level (Barrer and Klinowski, 1972). In order to calculate $K_B^{\prime A}$, all $X_{\mathrm{AZ}}$ experimental values were normalized.



a)

b)

c)

*Figure 1.* Ion exchanging isotherms in NaA for (a) $K^+$, (b) $Ca^{2+}$ and (c) $Cr^{3+}$ at (♦) 30°C, (□) 45°C and (△) 60°C.

## 3. Results and Discussion

The ion exchange isotherms generated during the exchange of the parent zeolite are shown in Fig. 1(a)–(c) for the cations $K^+$, $Ca^{2+}$ and $Cr^{3+}$ respectively. Different convexly upward curvatures can be seen as a consequence of different degrees of exchange caused by nature, size and charge of the cations, temperature of the system and cation-framework interaction. The isotherms for the K-NaA system (Fig. 1(a)) are almost straight lines. They show a kind of unselective form with tendencies of selectivity for the leaving cation $Na^+$ as the straight lines seem to have slopes smaller than 45°. This finding is in total agreement with Breck (1974), where the selectivity of zeolite A towards sodium is slightly greater than towards potassium ions. Besides the univalent charge, the hydration energies of both cations are very close to each other ($\Delta H_K^{\text{hidr}} = -72.6$ kcal/g ion, $\Delta H_{Na}^{\text{hidr}} = -89.6$ kcal/g ion, Cotton and Wilkensen, 1988), which means that both cations may compete to the same sites, originating the unselective form of the isotherms. It is also interesting to note that an increase in temperature favors a decrease in the potassium content in the solid phase, which is just the opposite phenomenon when the system K-NaX was considered with the same experimental conditions (Barros et al., 2003b). It indicates that, although both zeolites have almost the same Si/Al ratio, the ion exchange mechanism is also strongly influenced by the three dimensional framework of the zeolite. High convexly upward isotherms are observed when the Ca-NaA system was considered in Fig. 1(b).

This ion exchange behavior was already expected as NaA zeolite is generally used in water softening where its prime purpose is to replace $Ca^{2+}$ and also $Mg^{2+}$ ions present in hard water. It is well known that NaA zeolite has a great affinity to $Ca^{2+}$ (Barri and Ress, 1980). Moreover, a temperature-dependent sigmoid shape of isotherms with inflexion point close to $X_{AZ} = 1$ is obtained indicating that some effort should be done to diffuse some ions into unfavorable sites. It is also worth to note some over exchanged values ($X_{AZ} > 1$), that means an amount of calcium in the zeolite after exchange greater than the amount of sodium lost during the exchange process. Hence, the ratio of total divalent metal to aluminum was everywhere higher than theory. Such phenomenon is probably due to some multilayer adsorption and it becomes increasingly significant as the monolayer, which corresponds to the ion-exchange reaction, becomes more and more crowded, that means an appreciable affinity towards the in-going cation. A densely occupied monolayer will act in some degree as an extension of the zeolite, and will be able to attract further cations from the solution phase. Therefore, the unfavorable sites mentioned are related to the sites located in the monolayer originating an ion-exchange adsorption. The occurrence of this kind of phenomenon in zeolite ion exchange isotherms was already seen (Shibata and Seff, 1997; Wiers et al., 1982) indicating that $X_{AZ}$ values greater than 1 are possible to occur and the hypothesis of experimental errors should be completed discarded. Precipitation of $Ca(OH)_{2(S)}$ was not a reasonable explanation due to the high solubility of the calcium hydroxide in an aqueous environment. The isotherm behavior, presented in the Ca-NaA system, is qualitatively similar to the isotherms previously reported (Franklin and Townsend, 1985). Quantitatively differences were already expected since the ion exchange solution had, besides the in-going cation $Ca^{2+}$, the out-going cation $Na^+$in the reported paper, and the content of this solution influences the exchange behavior (Giannetto et al., 2000). The Cr-NaA isotherms (Fig. 1(c)) exhibit an initial steep slope followed by a sigmoidal profile. This behavior was unexpected but repeated experiments confirmed such a trend discarding the hypothesis of experimental errors. Unusual isotherm profiles were already reported in divalent exchange in NaX zeolite (Sherry, 1968). Therefore, isotherms that do not fit Breck's classification (Breck, 1974) seem to happen. The shape of the Cr-NaA isotherms can be attributed to changes in pH and consequently in the in-going chromium species (Richard and Bourg, 1991) as the ion exchange solution was not buffered. It must be emphasized that pH reached the minimum value of 3.0, indicating that dealumination of the zeolite may be neglected. Furthermore, the exchange process is operating under diffusion limitations, where the progress of exchange is controlled by the diffusion of the large hydrated cation $Cr^{3+}$ (4.61 Å—Nightingale, 1959) within the crystal structure. The effect of the aqueous environment on ion migration is pronounced in zeolites (Keane, 1998), mainly in zeolite A due to its small apertures of 4.2 Å of the $\alpha$-cages and 2.2 Å of the $\beta$-cages. It must be reminded that $Cr^{3+}$ ion has also very high hydration energy ($\Delta H_{Cr}^{hidr} = -1005.5$ kcal/g-ion—Cotton and Wilkensen, 1988) and the strength of the hydration coating is an important factor in the water stripping process, and consequently, in the ion exchange reaction. It is noteworthy that the progress of exchange is not enhanced as the exchange temperature is increased from 30 to 60°C. Possibly an increment of 30 degrees Celsius is not enough to overcome the ion-sieve effect and all isotherms terminated in an average equivalent fraction of $X_{AZ} = 0.67$, which is diagnostic of occupancy of the large cavities only (Giannetto et al., 2000). Therefore, it seems that $Cr^{3+}$ ions prefer to be located in the sites of the $\alpha$-cages, probably due to the possibility of coordination with the framework oxygens and the water molecules. It is outstanding that the rather pronounced differences in behavior of Ca-NaA and Cr-NaA isotherms are unexpected in view of close hydration radii ($r_{Ca^{2+}}^{hidr} = 4.12$ Å, $r_{Cr^{3+}}^{hidr} = 4.61$ Å—Nightingale, 1959). The ionic radii of $Cr^{3+}$ are even smaller than the $Ca^{2+}$ ones, which might indicate, in an erroneous conclusion, that chromium ions would be better accomodated in the sites of $\beta$ and also $\alpha$-cages. It seems that the hydration coating of the cations has a great contribution in the marked differences of the ion exchange isotherms. The energy of hydration of $Cr^{3+}$ ions is higher by a factor up to 3 (Cotton and Wilkensen, 1988) and probably partial water stripping, necessary of the accomodation in the $\beta$-cages, may be thermodynamically unfavorable due its high value.

Representative Kielland plots, shown in Fig. 2, were constructed to all isotherms through the selectivity coefficient. All $\gamma_{i(S)}$ for the solutions composed by two cations (the in-going and the out-going cations) and only one ion (chloride) were calculated as described in Section 2. In Ca-NaA system, all overexchanged values presented in the isotherm were neglected to the calculous of the selectivity quotient and consequently to the

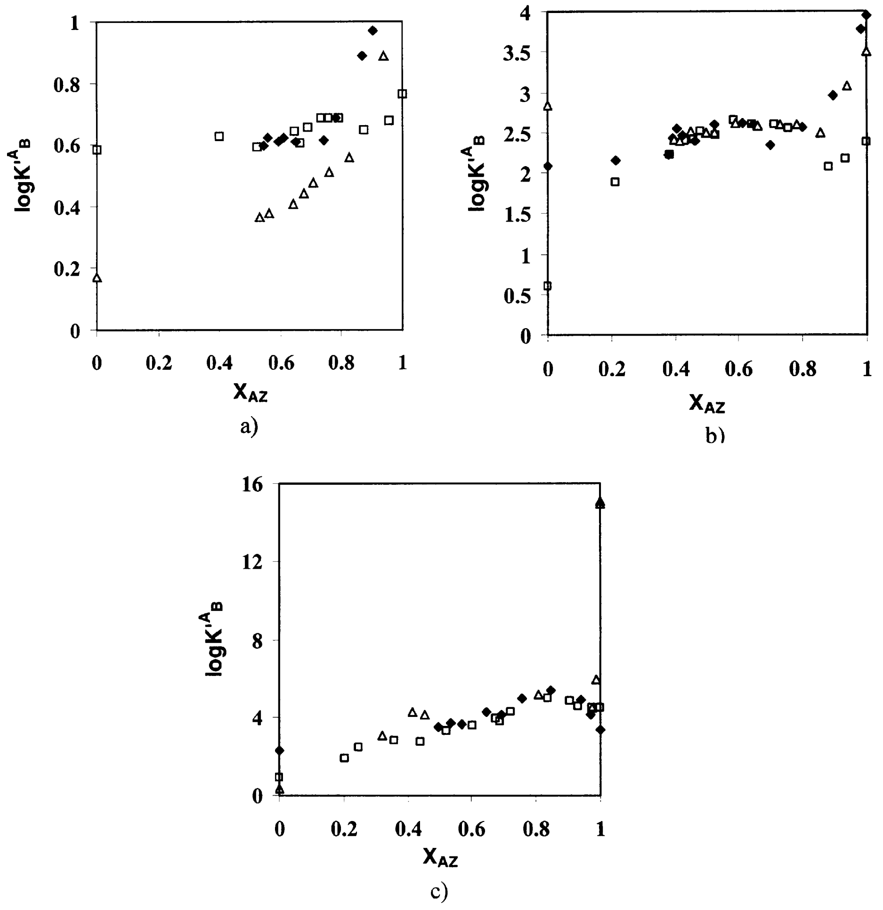


*Figure 2.* Kielland plots in NaA zeolite for (a) $K^+$, (b) $Ca^{2+}$ and (c) $Cr^{3+}$ at (♦) 30°C, (□) 45°C and (Δ) 60°C.

Kielland plots. The very non-linear plots was observed for all systems are a consequence of distinct groups of exchange sites participating in the ion exchange reaction as expected. Concerning the Kielland plots, it is observed that the ion exchange mechanism depends on the cationic in-going species and on the temperature as well. The Kielland plots related to the K-NaA isotherms show almost straight lines, which means that the majority of the sites that participate of the ion exchange reaction may have the same energy. The Kielland plots for Ca-NaA system show a pronounced non-linear shape for all temperatures studied. This behavior is in total agreement with the occupancy of different exchange sites located in all cages as observed in the isotherms. On the other hand, the Kielland plots for Cr-NaA system are non-linear and less pronounced than the plots obtained for Ca-NaA exchanges, due to the predominance of exchange in sites located only in the $\alpha$-cages as already explained.

A thermodynamic analysis of the Kielland plots yielded the parameters given in Table 1. The thermodynamic equilibrium constant, $K_A$, presents huge differences in the ion exchange of the in-going cations analysed. In the K-NaA system it is possible to note small $K_A$ values if compared to the other in-going cations, possibly due to the small affinity of NaA towards potassium. It is also noted a decrease in $K_A$ values with increasing temperature, which indicates a progressive selectivity towards the out-going ion $Na^+$. The exchange of NaA with $Ca^{2+}$ is accompained by large values of the thermodynamic equilibrium constant, which is in agreement with the high affinity already shown in Fig. 1(b). A decrease in $K_A$ values is observed at 45°C probably as a consequence of the complex interaction of the hydrated $Ca^{2+}$ ions with the ion exchange sites. If the results are compared to the ones shown in Barri and Rees (1980) it is possible to observe that $K_A$ values reported earlier are much lower. Once more this is

*Table 1.* Thermodynamic data on ion exchange at different temperatures.

| Cation | $T$ (°C) | $K_A$ | $\Delta G^0$ (kJ/equiv) | $\Delta H^0$ (kJ/equiv) | $\Delta S^0$ (kJ/equiv K) |
|---|---|---|---|---|---|
| $K^+$ | 30 | 4.7 | −3.899 | 26.94 | 0.102 |
| | 45 | 4.2 | −3.825 | 9.500 | 0.041 |
| | 60 | 2.6 | −2.667 | −11.71 | −0.027 |
| $Ca^{2+}$ | 30 | 114 | −5.969 | −115.3 | −0.361 |
| | 45 | 49.1 | −5.147 | −13.45 | −0.0261 |
| | 60 | 163 | −7.049 | 109.7 | 0.351 |
| $Cr^{3+}$ | 30 | 653 | −5.443 | −140.6 | −0.446 |
| | 45 | 197 | −4.657 | −18.66 | −0.044 |
| | 60 | 688 | −6.029 | 128.89 | 0.405 |

due to the ion exchange solution used. The presence of $Na^+$ ions in the initial solution may displace the equilibrium towards sodium in the solid phase, decreasing the equilibrium constant for calcium ions. Considering the Cr-NaA system it is observed, through the high values of thermodynamic equilibrium constant that NaA has really a wild preference towards $Cr^{3+}$ maybe due to the trivalent charge of this cation that gives rise to a strong interaction with the framework. Actually, it seems that $K_A$ is directly proportional to the charge of the in-going ion as it increases when K-NaA, Ca-NaA and Cr-NaA systems are analyzed at the same temperature. $K_A$ is not linear proportional with temperature in Cr-NaA ion exchange but it may be explained through the complex interaction with the sites in the three dimensional structure. Considering the $\Delta G^0$ values given in Table 1 it is possible to observe in all systems a negative free energy change over the entire temperature range. The exchange of K-NaA is less thermodynamically favorable than the other systems. This fact was already expected since the isotherms fitted to almost straight lines and no large affinity was present in the equilibrium constant. An increase in temperature rendered the K-NaA processes less favorable possibly due to the weak cation-framework interaction. From a consideration of $\Delta G^0$ values of Ca-NaA ion exchange one can observe that, as it could be expected, the system is more stable than the previous case due to the "comfortable" accomodation of the in-going ions in the $\beta$-cages (Barri and Rees, 1980). A small decrease in stability is observed at 45°C but it does not endanger the high selectivity towards calcium. A comparison of $\Delta G^0$ values of Ca-NaA system, generated in this work, with those reported previously (Barri and Rees, 1980; Franklin and Townsend, 1985) for the exchange temperature close to 30°C, reveals that the values of this thermodynamic property reported here are higher by a factor of up to 3. The deviation in the presented $\Delta G^0$ values from the published data may be ascribed, at least inpart, to differences in $K_A$ which, in turn, are due to the different content of the ion exchange solution as already mentioned. The Cr-NaA system also present a high selectivity, maybe due to the exchange of the sodium ions located in the $\alpha$-cages for $Cr^{3+}$. Temperature influence in Cr-NaA system is also not directly proportional to $\Delta G^0$ values and the complex interaction between tha in-going cation and the framework is again a reasonable explanation.

From a consideration of $\Delta G^0$ values the affinity sequence $K^+ < Cr^{3+} < Ca^{2+}$ is stablished for 30, 45 and 60°C. It is interesting to note that, at a first glance, the selectivity of a zeolite towards the in-going cations should be proportional to the charge of the cation. According to this line of thinking, all zeolites would prefer trivalent cations instead of uni or divalent ones. Therefore, cations with higher charges would better balance the negative network provided by aluminum tetrahedra. But ion exchange behavior of zeolites depends upon the nature of the cation species and also charge and hydration energy besides zeolite framework. The interaction of such properties and not a single factor makes the affinity sequence of each zeolite structure. The enthalpy effect were also estimated from the temperature dependence of $K_A$ as described earlier. The changes in enthalpy reflect the binding energies of the solvated cations in the zeolite lattice. The restricted nature of the intracrystalline environment imposes large changes in the hydration state of the in-going ions. The enthalpy changes associated with K-NaA at 30 and 45°C are positive (endothermic), whereas at 60°C they are exothermic. It seems that at 30 and 45°C the replacement of $Na^+$ with $K^+$ in the zeolite phase is accompained by a net enthalpy gain as the hydrated in-going cation sheds its hydration coating and potassium ions are, in effect, solvated by framework oxygens. As temperature increases the interaction with the framework is changed, some energy is released and the enthalpy reaction becomes negative. Calcium exchange with zeolite A is accompained by an exothermic process at 30 and 45°C and an endothermic one at 60°C. In the first case, the negative enthalpy may reflect the favorable accomodation of the ions in the zeolite cages due to the relative facility of $Ca^{2+}$ ion in losing its hydration coating. At 60°C all sites already exchanged provided conditions to have really dense sites, requiring energy to promote an endothermic process. The Cr-NaA system seems to present the behavior observed in Ca-NaA system. At 30and 45°C the $Cr^{3+}$ ions are favorable exchanged in the $\beta$-cages releasing some energy to the environment. At 60°C the ion exchange is also favorable, however, to reach the most stable condition some energy must be required to water stripping of the $Cr^{3+}$ ions densely located in the sites of $\beta$-cages. The entropy, as it occurs with enthalpy, reflect the changes to ion hydration which happen during the exchange reaction. The entropy of all systems analyzed may be considered as consisting of two contributions, one, $\Delta S^0(_L)$, from the aqueous phase and the other, $\Delta S^0(_S)$, from the zeolite phase. Hence, $\Delta S^0 = \Delta S^0(_L) + \Delta S^0(_S)$. Such an effect is not as important in the intersticial environment of the zeolite crystal, $\Delta S^0(_S)$, because of the smaller amounts of water present (Biškup and Subotić, 1998). Therefore, only changes in the solution phase will be analyzed here. For a closed but not isolated system, as the flasks where the experimental points were obtained, the entropy may decrease since the surroundings have a gain in this property. Therefore, negative entropy change of ion exchange process is possible to occur and was already reported in zeolite systems (Maes and Cremers, 1975; Keane, 1994; Tagami et al., 2001). In K-NaA system, the entropy decreases as temperature increases and negative values are seen at 60°C. Such numerical result may be explained through the polarizibility of ions $Na^+$ and $K^+$. The replacement of $K^+$ ions by $Na^+$ ions causes an increase in order in the solution phase (Keane, 1994). $Na^+$ ions are more polarizing than $K^+$ and hence they cause more ordering of the water molecules in aqueous solution. Just the opposite happens with Ca-NaA and Cr-NaA systems as it was observed a direct proportionality between temperature of the system and entropy change. In these systems there is a replacement of a less polarizing ion ($Ca^{2+}$ or $Cr^{3+}$) originating a decrease in order with increasing temperatures, and consequently, an increase in entropy changes. At 30 and 45°C the entropy changes are negative to Ca-NaA and Cr-NaA system. It seems that at these temperatures, the ions already exchanged in the zeolites may preserve their hydration coating, removing some water molecules from the solution phase. At 60°C, more entering cations may be considered dehydrated, releasing some water molecules to the solution phase in order to solvate sodium ions. Such phenomenon creates a desorder in the aqueous system, which provides positive entropy change.

Considering the results obtained in Table 1, it may be stated that the uptake of the toxic heavy metal chromium in a real wastewater containing calcium would be diminished because both cations have similar thermodynamic behavior. On the other hand, presence of $K^+$ ions may not alter significantly the removal of the heavy metal cation. The zeolite NaA, more selective to chromium and potassium, would not compete with $Cr^{3+}$ ions to same sites.

## 4. Conclusion

The data presented in this paper support the following conclusions:

(1) In K-NaA, Ca-NaA and Cr-NaA systems, differences in the ion exchange mechanisms are caused by the in-going cation-framework interaction. Charge, size and hydration energy influences the exchange behavior. $K^+$ and $Cr^{3+}$ ions may be located in the $\alpha$-cages. $Ca^{2+}$ ions are located preferentially in the $\beta$-cages but as ion exchange proceeds, all sites are gradually exchanged.

(2) The strongest cation-framework interaction occurs with $Cr^{3+}$ ion although it is not the most selective one due to steric problems experienced in the zeolite sites.

(3) The affinity sequence $K^+ < Cr^{3+} < Ca^{2+}$ is established for over the entire temperature range. It means that, concerning the single ion exchange mechanism only, if the uptake of chromium ions from an industrial effluent that also contains calcium ions is considered, the zeolite NaA will not work successfully. The removal of the divalent ion will occur preferentially. On the other hand, the presence of potassium ions may not cause a significant decrease in the chromium uptake.

## Nomenclature

| | |
|---|---|
| CEC | Cation exchange capacity of the zeolite sample (meq) |
| $C_A$ | Final concentration of the in-going ion A (meq/L) |
| $C_{O_A}$ | Initial concentration of the in-going ion A (meq/L) |
| $K_A$ | Thermodynamic equilibrium constant |

| | |
|---|---|
| $K'^A_B$ | Selectivity quotient |
| $R$ | Ideal gas constant (8.314 J/molK) |
| $T$ | Absolute temperature (K) |
| $X_{\mathrm{AS}}$ | Equivalent fraction of the in-going ion A in the solution phase |
| $X_{\mathrm{AZ}}$ | Equivalent fraction of the in-going ion A in the zeolite phase |
| $X_{\mathrm{AZ}}^{\max}$ | Maximum $X_{\mathrm{AZ}}$ value |
| $X_{\mathrm{BS}}$ | Equivalent fraction of the out-going ion B in the solution phase |
| $X_{\mathrm{BZ}}$ | Equivalent fraction of the out-going ion B in the zeolite phase |
| $z\mathrm{A}$ | Charge of the in-going ion A |
| $z\mathrm{B}$ | Charge of the out-going ion BA |
| $\gamma_{A(S)}$ | Mean activity coefficient associated with molality of cation A |
| $\gamma_{B(S)}$ | Mean activity coefficient associated with molality of cation B |
| $\Delta H^0$ | Standard enthalpy of exchange (kJ/equiv) |
| $\Delta G^0$ | Standard free energy of exchange (kJ/equiv) |
| $\Delta S^0$ | Standard entropy of exchange (kJ/equiv·K) |
| $\Delta S^0({}_L)$ | Standard entropy of exchange from the aqueous phase (kJ/equiv·K) |
| $\Delta S^0({}_S)$ | Standard entropy of exchange from the zeolite phase (kJ/equiv·K) |

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## References

Arroyo, P.A., M.A.S.D. Barros, M.V. Querino, I.A. Ferreira Jr., and E.F. Sousa-Aguiar, "Troca multicomponente dinâmica em sistemas zeolíticos," Revista Tecnológica, Special Ed., 31–38 (2000).

Barrer, R.M. and J. Klinowski, "Influence of Charge Density on Ion-exchange Properties of Zeolites," *J. Chem. Soc. Faraday Trans. I*, **68**, 1956–1963 (1972).

Barri, S.A.I. and L.V.C. Rees, "Binary and Ternary Cation Exchange in Zeolites," *J. of Chromatography*, **201**, 21–34 (1980).

Barros, M.A.S.D., P.A. Arroyo, E.F. Sousa-Aguiar, and P.A. García, *Problemas Ambientais com Soluções Catalíticas. I. O cromo no processamento de peles*. Ed. CYTED, Madrid-Spain, 2001.

Barros, M.A.S.D., Avaliação do Mecanismo de Troca Iônica de Cromo em Sistemas Zeolíticos. Doctorate Thesis, PEQ/UEM, Maringá-Brazil, 2003.

Barros, M.A.S.D., P.A. Arroyo, C.R.G. Tavares, and E.F. Sousa-Aguiar, "Multicomponent Ion Exchange Isotherms in NaA Zeolite," *Chemical Engineering Transactions*, **3**, 1375–1381 (2003a).

Barros, M.A.S.D., I.F. Araújo Jr, P.A. Arroyo, E.F.S. Aguiar, and C.R.G. Tavares, "Multicomponent Ion Exchange Isotherms in NaX Zeolite," *Latin American Applied Research*, **33**, 339–344 (2003b).

Biškup, B. and B. Subotić, "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," *Sep. Sci. and Technol.*, **33**(4), 449–466 (1998).

Biškup, B. and B. Subotić, "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. and Tech.*, **35**(14), 2311–2326 (2000).

Breck, D.W., *Zeolite Molecular Sieves*, Robert E. Krieger Publishing Company, Malabar-FL-USA, 1974.

Cotton, F.A. and G. Wilkensen, *Advanced Inorganic Chemistry*, 5th ed., John Wiley & Sons, USA, 1988.

Franklin, K.R. and R. Townsend, "Multicomponent Ion Exchange in Zeolites," *J. Chem. Soc. Faraday Trans. I.*, **81**, 1071–1086 (1985).

Giannetto, G., A. Montes, and G. Rodriguez, *Zeolitas Características, Propiedades y Aplicaciones Industriales*, Ed. Innovación Tecnológica, Facultad de Ingeniería, UCV, Caracas, Venezuela, 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*, **3**, 93–108 (1994).

Keane, M.A., "The Removal of Copper and Nickel from Aqueous Solution using Y Zeolite ion Exchangers," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **138**, 11–20 (1998).

Maes, A. and A. Cremers, "Ion Exchange of sybthetic Zeolite X and Y with $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ Ions," *J. Chem. Soc. Farad. Trans. I.*, **71**, 265–274 (1975).

Meissner, H.P. and C.L. Kusik, "Activity Coefficients of Strong Electrolytes in Multicomponent Aqueous Solutions," *AIChE J.*, **18**(2), 294–298 (1972).

Nightingale Jr., E.R., "Phenomenological Theory of Ion Solvation Effective Radii of Hydrated Ions," *J. Phys. Chem.*, **63**, 1381–1387 (1959).

Richard, F.C. and A.C.M. Bourg, "Aqueous Geochemistry of Chromium: A Review," *Wat. Res.*, **25**(7), 807–816 (1991).

Sherry, H., "The Ion-Exchange Properties of Zeolites. IV. Alkaline Earth Ion Exchange in Synthethic Zeolites Linde X and Y," *The J. Phys. Chem.*, **72**(12), 4086–4094 (1968).

Shibata, W. and K. Seff, "$Pb^{2+}$ Exchange Isotherms for Zeolite Na-X at pH 5, 6, and 7," *Zeolites*, **19**, 87–89 (1997).

Tagami, L., O.A.A. Santos, E.F. Sousa-Aguiar, P.A. Arroyo, and M.A.S.D. Barros, "NaY and CrY Zeolites Ion Exchange. Thermodynamics," *Acta Scientiarum*, **23**(6), 1351–1357 (2001).

Wiers, B.H., R.J. Grosse, and W.A. Cilley, "Divalent and Trivalent Ion Exchange with Zeolite A," *Environ. Sci. Technol.*, **16**, 617–624 (1982).

Zemaitis, J.F., D.M. Clark, D.M.M. Rafal, and N.C. Scrivner, *Handbook of Aqueous Electrolyte Thermodynamics*, DPIR, New York-USA, 1986.