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Na^+/Cu^{2+} ion exchange equilibrium on Zeolite A: a thermodynamic study

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Abstract The ion exchange isotherms at 302 K for Na^+/Cu^{2+} and Cu^{2+}/Na^+ on zeolite A were determined for six total equivalent concentrations of the external solution, in the range 0.05–2.1 eq/L. Interpolated points from the curves fitted with different isotherms were used in the calculation of the selectivity coefficients. The activity coefficients in the external solution were calculated by means of the Pitzer model. Thermodynamic equilibrium constant values corresponding to different total concentrations of the external solution have been obtained investigating the reaction from both sides. The method of Gaines and Thomas, revised by Soldatov, based on the dependence of the normalized Kielland selectivity quotients on the copper ionic fraction in the zeolite was used in order to obtain the thermodynamic equilibrium constant value. The significance of the thermodynamic equilibrium constant and the reversibility of the process were analyzed, as well as the influence of the non-ideality of the zeolite and solution phases.

Keywords Ion exchange · Equilibrium constant · Adsorption isotherm · Zeolite A

List of symbols

a	Coefficient in isotherm equations, thermodynamic activity in solution
$\bar{a}$	Thermodynamic activity in zeolite
b	Coefficient in isotherm equations
c	Coefficient in isotherm equation (Keller)
f^{γ}	Debye–Hückel term, in the equation for the activity coefficient
m	Molality
r	R-squared coefficient
x	Ionic fraction in solution
$\bar{x}$	Ionic fraction in zeolite
z	Number of elementary charges of an ion
B	Second virial coefficient in the Debye equation for activity coeffiecients
C	Third virial coefficient in the Debye equation for activity coeffiecients
F	Test value for errors
K	Thermodynamic equilibrium constant
$\tilde{K}$	Corrected selectivity quotient
γ	Activity coefficient in solution
γ'	Activity coefficient in zeolite
ν	Number of ions in an electrolyte

Subscripts

a	Index for anion
c	Index for cation
i	Index for ion
M	A certain cation
X	A certain anion
$\pm$	Mean ionic

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1 Introduction

The aim of this work is to verify if the data obtained for the Cu^{2+}/Na^{+} and Na^{+}/Cu^{2+} ion exchange processes on zeolite A at various concentrations correspond to a real thermodynamic equilibrium. The symbol A, in this article designates a monovalent fragment of the zeolite A-type framework. In fact, this is a complex system, in which the ion exchange is not the only process. Hydrolysis of the zeolite, dealumination of the zeolite, water sorption and reactions in solution leading to several copper containing species can also take place simultaneously.

Systematic studies of this problem are scarce in the literature; most reports refer to low concentrations (0.1 N or less) with the reaction developing in only one direction (Tanaka et al. 2000; Kuronen et al. 2000; Altschuler et al. 2004; Boyd et al. 1974; Chen et al. 1990; de Barros et al. 2002; Heo et al. 1990; Valverde et al. 2001; Carmona et al. 2008; Borge et al. 1999; Sherry and Walton 1967; Miyata 1983). However some researchers e.g. de Lucas et al. (1993), (Barrer and Klinowski 1972, 1974a, 1974b; Barrer et al. 1966; 1968, 1969) and their co-workers have performed thermodynamic studies of the ion exchange, having in view multiple aspects: selectivity, reversibility, thermal effect, the influence of solution concentration and of the number of homogeneous groups of sites in the ion exchanger etc. The studies of Adams et al. (1997) investigated the Ca–Na equilibrium on zeolites in both directions while that of Tagami et al. (2001) was dealing with the thermodynamics of ion exchange of both NaY and CrY zeolites with Cr^{3+} and Na^{+}. A remarkable reversibility of the ion exchange process was observed in the case of univalent ions (Barrer and Klinowski 1972; Barrer et al. 1966) and in that of the Na–Ca pair (Adams et al. 1997). The maximum level of exchange reaches 100 % only for univalent cations, so that the equivalent ionic fractions should be normalized by dividing them through the maximum exchange attainable for the multivalent ion. (Valverde et al. 2001; Carmona et al. 2008; Barrer and Klinowski 1972; Sherry 1968; Barrer et al. 1973; Vansant and Uytterhoeven 1971) Singare et al. (2008a, 2008b; 2009; Lokhande et al. 2007; Lokhande et al. 2009) have investigated the ion exchange of univalent ions, both anions and cations, on resins, at very low concentrations and they have obtained values of the equilibrium constant at different total concentrations, in remarkable agreement, even without using corrections for the non-ideal behavior of the external solution and of the zeolite phase.

A remarkable thermodynamic exchange equilibrium study is that of Ioannidis et al. (2000) who have used data at total electrolyte concentrations up to 0.5 N, using model parameters for the zeolite solid solution, derived independently of the equilibrium constant (Pabalan 1994).

Ferapontov et al. (2000, 2006) have investigated the ion exchange H^{+}/K^{+} on an acidic resin at total electrolyte concentrations up to 1 N and have obtained rather compatible values of the thermodynamic equilibrium constant for different concentrations (standard deviation ±23 %).

2 Experimental

The binder-free NaA zeolite was obtained from Soda Products Works Govora (Romania) and was purified by two consecutive treatments with 1 M sodium chloride solution (150 % excess). In both treatments, the solution was stirred during the first 3 h; after this period the two phases were left in contact without stirring for 24 h in the first treatment and for 4 days, in the second. The purified zeolite was washed with doubly distilled water and filtered off, dried at room temperature, and equilibrated to constant weight by saturation with water vapor for more than 2 weeks, in a desiccator with saturated solution of NH_4Cl. The elemental composition of the zeolite certified by the manufacturer is $Si/Al = 1.02 \pm 0.01$.

The copper form of the zeolite A was obtained from the purified NaA, by treating it with 1 M $CuSO_4$ solution (250 % excess), in freshly doubly distilled water. The sample was stirred for 2 h at room temperature and left in a closed vessel without stirring for 24 h. The solution was separated and the procedure was repeated twice, the last time the solid was in contact with the copper containing solution for 3 days. Finally the blue copper form of zeolite A was filtered and washed several times with doubly distilled water, until copper traces in the filtrates could no longer be detected, by wet chemical methods. The solid product was dried at room temperature and kept in a desiccator over a saturated aqueous solution of NH_4Cl, for 2 weeks, before use.

The total exchange capacity of the purified NaA product was measured, by replacing the Na^{+} ions with Ag^{+}, taking into account that Barrer and Meier (1959) showed that Ag^{+} ions can replace all Na^{+} ions in the unit cell of NaA zeolite even those occluded as $NaAlO_2$, in the sodalite cage. A known amount of zeolite saturated with water vapor (~0.2 g) was let in contact with 50 mL of 0.1 M standardized $AgNO_3$ solution for 1 week at room temperature, stored in darkness and stirred periodically. The Ag^{+} ion concentration in the solution in equilibrium with the zeolite was measured by titration in acidic media, with standardized 0.1 M NH_4SCN solution [$Fe(NH_4)_2(SO_4)_2 \cdot 12H_2O$ saturated solution as indicator]. The NaA ion exchange capacity was 5.82 ± 0.08 meq/g (99 % probability to find the value in this range, for a student distribution). The copper form of the zeolite A was analyzed in order to determine the Cu(II) content, as follows: a known amount of zeolite (around 0.1 g), saturated with water vapor was treated with 10 mL of 0.1 M standardized solution of disodium salt of ethylenediaminetetraacetic acid (EDTA) and stirred for 10 min at room temperature. The excess EDTA was titrated with standardized 0.1 M $Cu(NO_3)_2$ solution at pH 8 and murexid as indicator. A mean value of 5.58 ± 0.43 meq/g, representing almost 96 % of the ion exchange capacity of NaA was obtained.

The forward Na^+/Cu^{2+} and the reverse Cu^{2+}/Na^+ ion exchange isotherms on zeolite A were measured at six constant total equivalent concentrations of the external solution: 2.09, 0.980, 0.480, 0.247, 0.102 and 0.050 N.

A known amount of NaA or CuA_2 zeolite saturated with water vapor was added in a solution containing Na^+ and Cu^{2+} ions with known equivalent fractions, prepared by mixing isonormal solutions of $NaNO_3$ and $Cu(NO_3)_2$. The Cu^{2+} and Na^+ equivalent fraction varied from 0 to 1. The samples were kept for equilibration at 29 °C, in closed vessels without stirring, for at least 18 days. No precipitation was noticed.

At least two complexometric titrations with 0.1 or 0.02 M EDTA solution were done, for the analysis of the Cu^{2+} ions in all solutions in equilibrium with the zeolite. The density of the external solution was measured for each sample at equilibrium.

All reagents used in this work were analytical reagent grade.

3 Results and discussion

The ion exchange equilibrium:

$$\left(Cu^{2+}\right)_{soln}+2\left(Na^+\right)_{zeol}\leftrightarrows 2\left(Na^+\right)_{soln}+\left(Cu^{2+}\right)_{zeol} \tag{I}$$

was followed in both directions.

The experimental Na^+/Cu^{2+} and Cu^{2+}/Na^+ ion exchange isotherms on zeolite A at 302 K and different total equivalent concentrations of the external solution are shown in Fig. 1. The equivalent ionic fractions at equilibrium were calculated from the variation of the copper concentration in the external solution, normalized in the solid phase to the maximum loading, and in the solution phase to the total equivalent concentration. The isotherms indicate the high selectivity of the zeolite type A for Cu^{2+} ions, and the increase of the selectivity with the decrease in the concentration of the external solution. This behavior supports the electroselectivity effect due to the Donnan potential which acts with a greater force on an ion with higher charge and which increases with the dilution of the external solution (Ziyath et al. 2011). It can be observed that for concentrations of the external solution higher than 0.5 eq/L, the Na^+/Cu^{2+} ion exchange equilibrium is not reversible, while for low concentration it can be considered as an almost reversible process.

Several adsorption isotherms (Langmuir, Freundlich, Sips, Tóth, Unilan, Keller-Staudt-Tóth and Dubinin–Radushkevich) were tested to fit the normalized experimental points (Ziyath et al. 2011). The equations of four selected isotherms are given in Table 1, while Table 2 shows the data referring to the curve fit. The data for the highest total concentration of the external solution (2.09 N) could not be fitted with any isotherm (Fig. 1). The ion exchange equilibrium at high concentrations of Cu^{2+} in the external solution looks like coming from two processes: one characteristic to lower Cu^{2+} concentrations in the zeolite, the other to high ones. This is probably due to the partial dealumination of the bond network at low pH values, associated with high Cu^{2+} concentrations. Dealumination diminishes the affinity of the zeolite for transition metal ions. (Tagami et al. 2001).

High R-squared coefficient and *F* test values have been obtained in most cases. It is observed that the best correlation accuracy is obtained at high concentrations with Freundlich isotherm, at medium concentrations with Tóth and Sips isotherms and at the lowest concentration with Unilan. Tóth and Sips isotherms yield for 0.05 N very high R-squared coefficient and *F* test values too,

For lower total concentrations, points corresponding to the reverse reaction are properly described by the same isotherm as those for the forward one. This confirms that in such conditions the reaction shows a certain reversibility and hence obtaining of the thermodynamic equilibrium constant and of the standard Gibbs energy of ion exchange is justifiable (Adams et al. 1997).

The parameters of two isotherms (Sips and Toth) were fitted with high R-squared coefficients, by means of quadratic equations (coeff. $= aN^2+bN+c$) as functions of the total concentration. The parameters of these equations are given in Table 3. The isotherms for 0.05 N calculated with coefficients obtained with the above equation and data of Table 3 differ from those calculated by means of coefficients from Table 2, by >3 %, as a mean. This relative insensitivity of the isotherms at very low concentrations is due to the high selectivity of zeolite A for Cu^{2+} (Helfferich 1995), so that quasi-saturation is reached at small ion fractions of this ion.

Interpolated points from the fitted isotherms were used in the calculation of the corrected selectivity quotients:

$$\tilde{K}=\frac{\bar{x}_{Cu}}{\bar{x}_{Na}^2}\cdot\frac{m_{Na}^2\ \gamma_{\pm}^2(NaNO_3)}{m_{Cu}\ \gamma_{\pm}(Cu(NO_3)_2)} \tag{1}$$

Mean ionic activity coefficients of the external solution were calculated by means of the Pitzer (Pitzer and Kim 1974) model :

Fig. 1 Experimental and fitted Na^+/Cu^{2+} and Cu^{2+}/Na^+ ion exchange isotherms on zeolite A at 302 K

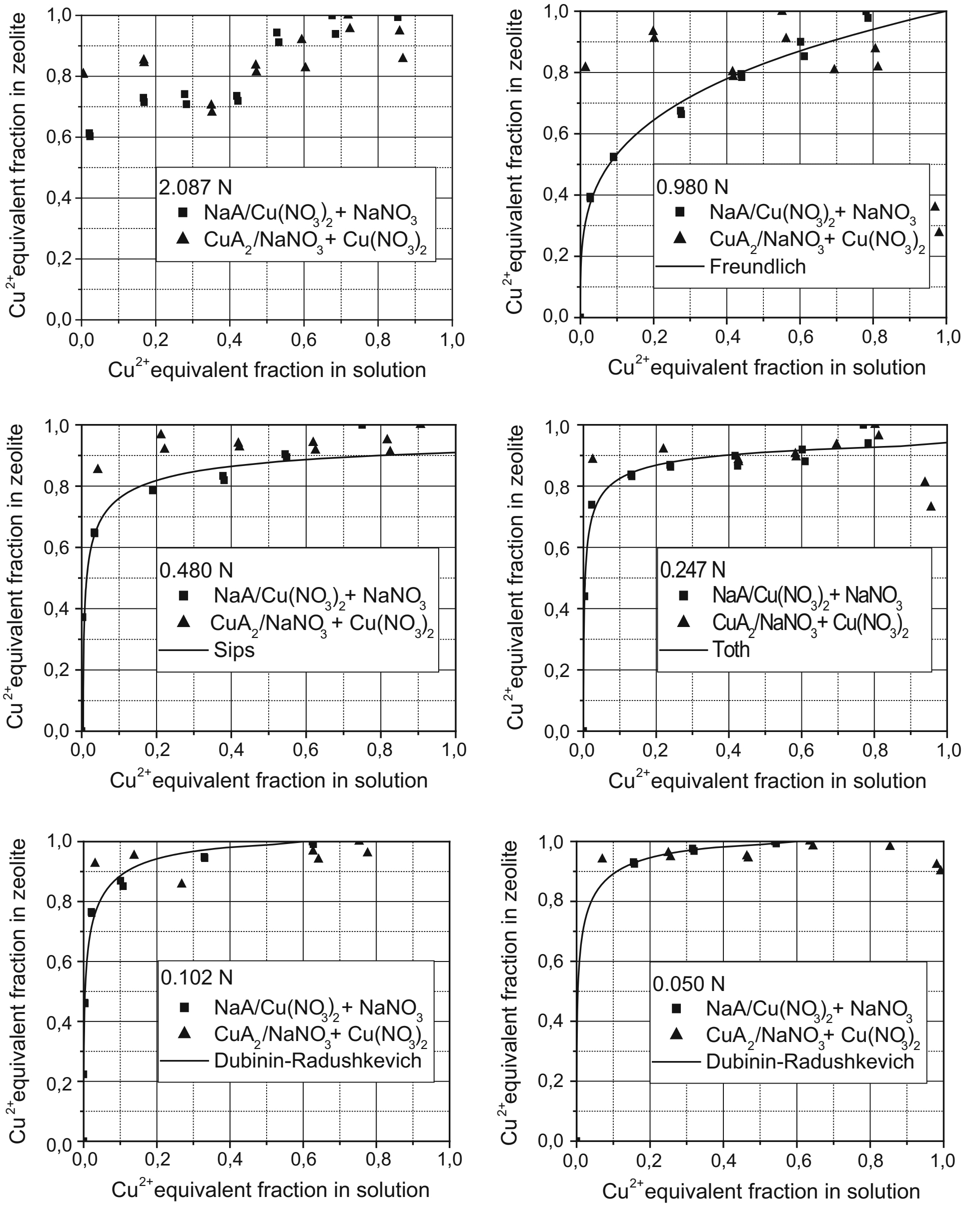

Table 1 The equations of used isotherms

Name	Equation
Freundlich	$\bar{x}_i = a_F \cdot x_i^{b_F}$
Sips	$\bar{x}_i = \frac{(a_S \cdot x_i)^{1/b_S}}{1+(a_S \cdot x_i)^{1/b_S}}$
Toth	$\bar{x}_i = \frac{a_T \cdot x_i}{\left[1+(a_T \cdot x_i)^{b_T}\right]^{1/b_T}}$
Unilan	$\bar{x}_i = \frac{1}{2a_U}\ln\left(\frac{1+b_U \cdot x_i \cdot \exp(a_U)}{1+b_U \cdot x_i \cdot \exp(-a_U)}\right)$

$$\begin{aligned}\ln\gamma_\pm = {} & |z_+z_-|f^\gamma + (2v_M/v)\sum_a m_a\left[B_{Ma} + \left(\sum mz\right)C_{Ma}\right] \\ & + (2v_X/v)\sum_c m_c\left[B_{cX} + \left(\sum mz\right)C_{cX}\right] \\ & + \sum_c\sum_a m_c m_a\left[|z_+z_-|B'_{ca} + (2v_M z_M/v)C_{ca}\right]\end{aligned} \tag{2}$$

The thermodynamic equilibrium constant, defined by Eq. (3) was calculated with data corresponding to different

Table 2 The parameters of the fitted isotherms and the goodness parameters of the fit

Isotherm	0.980 N	0.480 N	0.247 N	0.102 N	0.050 N
Freundlich					
r^2	0.9923	0.9864	0.9691	0.9496	0.9991
F	1276	581	345	155	5709
a_F	1.0005	0.9934	0.9892	1.0876	1.0500
b_F	0.2729	0.1462	0.1073	0.1327	0.07047
Sips					
r^2	0.9567	0.9812	0.9863	0.9967	0.9997
F	221	419	790	204	18653
a_S	15.54	107.1	208.4	374.6	29.54
b_S	1.405	2.020	1.984	1.680	0.6009
Toth					
r^2	0.9532	0.9792	0.9870	0.9955	0.9997
F	204	376	836	204	18852
a_T	36.53	1210	1676	1851	20.84
b_T	0.6582	0.4378	0.4632	0.5346	1.6893
Unilan					
r^2	0.9380	0.9414	0.9795	0.9893	0.9999
F	151	128	525	2176	36816
a_U	0.9641	0.9361	0.9514	0.9759	1.0130
b_U	17.66	146.8	239.9	240.5	68.59

Table 3 Parameter values of equations for the dependence of coefficients of Sips and Toth isotherms on the total concentration

Coefficient	a	b	c	r^2
a_S	641.2	−1084.3	464.45	0.9833
b_S	−2.5178	2.3721	1.494	0.9788
a_T	−787.86	−1233.6	1999.9	0.9993
b_T	0.8012	−0.723	0.5976	0.9988

total concentrations of the external solution, by using the method of Gaines and Thomas (1953) revised by Soldatov (1995) based on the dependence of the normalized Kielland selectivity quotients, on the copper ionic fraction of the zeolite (Eq. 4, see Fig. 2). This method suggested first by Ekedahl et al. (1950) overcomes the lack of experimental data of activity coefficients in the solid phase and requires equilibrium data at the limits of the concentration range that must be obtained by extrapolation.

$$K = \frac{\bar{x}_{Cu}\,\gamma'_{Cu}}{\bar{x}^2_{Na}\,\gamma'^2_{Na}} \cdot \frac{m^2_{Na}\,\gamma^2_{\pm}(\mathrm{NaNO_3})}{m_{Cu}\,\gamma_{\pm}(\mathrm{Cu(NO_3)_2})} \qquad (3)$$

$$\ln K = z_{Na} - z_{Cu} + \int_0^1 \ln \tilde{K}\,\mathrm{d}\bar{x}_{Cu} \qquad (4)$$

An alternative method which allows the calculation of the thermodynamic equilibrium constant was used by Ioannidis et al. (2000) which involves the Wilson equation (Wilson 1964) for correlating the activity coefficients of the solid solution. Similar approaches using Wilson's equation have been also used by other authors including (Valverde et al. 2001; Carmona et al. 2008; Pabalan 1994; Smith and Woodburn 1978). A different possibility to overcome the problem of the activity coefficients in the solid phase was used by Ruvarac and Petkovic (1988, 1993) based on the existence of an inflexion point in the dependence (written here for our system) $\log {}^{a_{Cu}}/{}_{a^2_{Na}} = f(\bar{a}_{Cu})$.

The shape of the Kieland plots is very sensitive to the form of the isotherm, even in the case when different isotherms fitted the entry data with high R-squared values. The values of the selectivity quotient show a faster decrease with the ionic fraction of Cu^{2+}, at high total normalities, than for low ones. A faster decrease is generally observed at the limits of the ionic fraction range (see Fig. 2). The integration from zero to unity of the corrected selectivity coefficient versus the copper ionic fraction in zeolite, in Eq. (4) is strongly dependent on the mathematical form of the isotherm, especially toward zero and unity ionic fractions. (Adolphs and Setzer 1996).

The analysis of the thermodynamic equilibrium constants for sodium ion exchange with copper ion in zeolite A at 302 K and different total equivalent concentrations given in Table 4 reveals that the equilibrium constants have values differing by a maximum factor of almost 2, for different total concentrations, in the case of Sips isotherm, while for those resulting from the Tóth isotherm, the relative departure from the mean is only 8.23 % (2.27 % for ΔG^0).

More important discrepancies are observed at high concentrations. The equilibrium constant at 0.98 N, calculated based on the Freundlich isotherm amounts only 51.6. A different process, which becomes evident for the 2.1 N solution, including probably dealumination, is already present in some extent at this concentration too.

The thermodynamic equilibrium constants were obtained with neglecting of the variation of the water content and water activity within the zeolite framework, and also neglecting the electrolyte sorption/desorption accompanying the ion exchange process.

These processes could be important at high concentration of the external solution, but a larger effect could be produced by the change in the nature of the binary ion exchange system which occurs if the nature of the zeolite phase and/or of the solution phase is modified at different total equivalent concentrations of the external solution. The type A zeolite is hydrolytically unstable in even mildly acid pH, and removal of aluminum from the framework will readily occur. (Townsend 1991) The copper ion

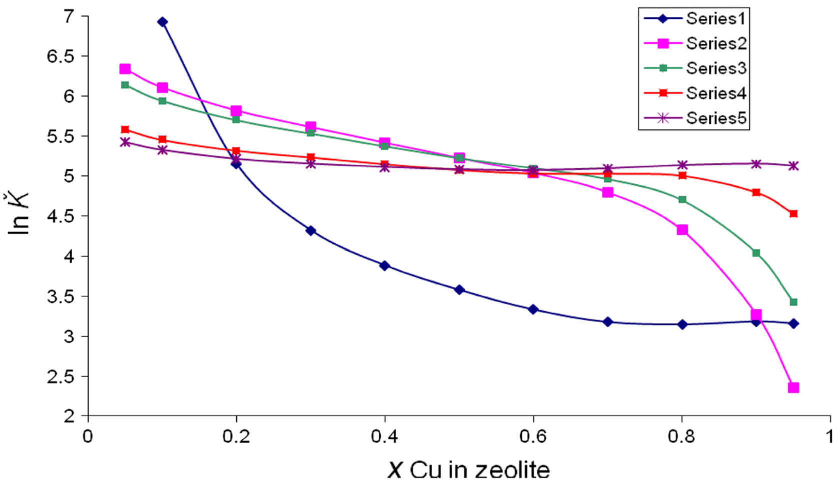

Fig. 2 Kielland plot for the ion exchange equilibrium at various total concentrations of the solution. Data series: 1—0.98 N, 2—0.48 N, 3—247 N, 4—0.102 N, 5—0.050 N

Table 4 The thermodynamic equilibrium constant, K, and the standard Gibbs free energy, ΔG^0, at 302 K, for Na^+/Cu^{2+} ion exchange on zeolite A

Isotherm	Conc. (eq/L)	K	$-\Delta G^0$ (kJ/eq)
Sips	0.480	116	5.972
	0.247	135	6.154
	0.102	77.2	5.456
	0.050	135	6.157
	Average	115.8 ± 27.2	5.94 ± 0.33
Toth	0.480	96.9	5.742
	0.247	108.1	5.879
	0.102	89.4	5.570
	0.050	94.0	5.703
	Average	97.1 ± 8.0	5.72 ± 0.13

speciation in aqueous solution even in the presence of nitrate ligands (which are known as weak ligands) transforms the binary ion exchange system into a multicomponent one (Do 1998).

In order to evaluate speciation in the external aqueous solution of copper(II) nitrate, the hydrolysis reaction of copper(II) aquaion and the reactions of formation of 1:1 and 1:2 complexes with the anionic ligand were taken into account:

$$Cu^{2+} + H_2O \Leftrightarrow CuOH^+ + H^+ \tag{II}$$

$$Cu^{2+} + NO_3^- \Leftrightarrow CuNO_3^+ \tag{III}$$

$$Cu^{2+} + 2NO_3^- \Leftrightarrow Cu(NO_3)_2(aq) \tag{IV}$$

The concentrations at equilibrium of the hydrated copper hydroxo ion $CuOH^+$, and of the complexes $CuNO_3{}^+$ and $Cu(NO_3)_2(aq)$ were obtained by solving the following system of equations containing the thermodynamic constants K_{II}, K_{III} and K_{IV} (Eqs. 5–7) and the corresponding material balance equations for copper and nitrate ions (Eqs. 8, 9):

$$K_{II} = \frac{[CuOH^+]\,[H^+]}{[Cu^{2+}]} \tag{5}$$

$$K_{III} = \frac{[CuNO_3^+]}{[Cu^{2+}]\,[NO_3^-]} \tag{6}$$

$$K_{IV} = \frac{[Cu(NO_3)_2]}{[Cu^{2+}]\,[NO_3^-]^2} \tag{7}$$

$$\begin{aligned}[Cu^{2+}]_{total} &= [Cu^{2+}] + [CuOH^+] + [CuNO_3^+] \\ &\quad + [Cu(NO_3)_2] \\ &= C\end{aligned} \tag{8}$$

$$[NO_3^-]_{total} = [NO_3^-] + [CuNO_3^+] + 2[Cu(NO_3)_2] = 2C \tag{9}$$

The square brackets denote the equilibrium concentrations of the corresponding species, and C the molar concentration of the $Cu(NO_3)_2$ solution. The values of thermodynamic constants taken in computations were $K_{II} = 3.164 \cdot 10^{-8}$, $K_{III} = 3.162$ and $K_{IV} = 0.3981$ (Assessment Model for Environmental Systems: Version 4.0 User's Manual 1999). The concentration values of various species in solution at a pH between 2 and 9, for several concentrations of $Cu(NO_3)_2$ are given in Table 5.

It may be noted that at pH 5–7 the main species are Cu^{2+} and $CuNO_3{}^+$. The molar fraction of Cu^{2+} increases and the molar fraction of $CuNO_3{}^+$ decreases with decreasing total concentration. The concentration of $CuOH^+$ is negligible at pH 5, but increases at pH 7, and is higher at low total concentrations of $Cu(NO_3)_2$. The concentration of the neutral species $Cu(NO_3)_2(aq)$ becomes significant only for concentrated solutions of copper nitrate. During the ion exchange process the correlated equilibria I–III shift and the total amount of copper(II) transferred at equilibrium in the zeolite phase depends on the species stability in

Table 5 Molar fraction of copper species formed in aqueous solution of $Cu(NO_3)_2$ of various concentrations at different pH values, at 298 K

pH	3	4	5	6	7	8	9
$Cu(NO_3)_2$ 0.490 M							
Cu^{2+}	0.320	0.320	0.320	0.316	0.283	0.146	0.0277
$CuOH^+$	1.02×10^{-5}	1.02×10^{-4}	1.02×10^{-3}	0.0101	0.0900	0.464	0.881
$CuNO_3{}^+$	0.630	0.630	0.630	0.625	0.580	0.356	0.0815
$Cu(NO_3)_2$(aq)	0.0494	0.0494	0.0494	0.0492	0.0474	0.0346	0.00955
$Cu(NO_3)_2$ 0.24 M							
Cu^{2+}	0.466	0.466	0.466	0.458	0.398	0.179	0.0291
$CuOH^+$	1.49×10^{-5}	1.49×10^{-4}	1.48×10^{-3}	1.46×10^{-2}	0.127	0.571	0.925
$CuNO_3{}^+$	0.511	0.511	0.511	0.505	0.454	0.237	0.043
$Cu(NO_3)_2$(aq)	0.0223	0.0223	0.0223	0.0221	0.0207	0.0124	0.00254
$Cu(NO_3)_2$ 0.12 M							
Cu^{2+}	0.610	0.609	0.608	0.597	0.505	0.203	0.0297
$CuOH^+$	1.94×10^{-5}	1.94×10^{-4}	1.94×10^{-3}	1.90×10^{-2}	0.161	0.646	0.947
$CuNO_3{}^+$	0.381	0.381	0.380	0.375	0.326	0.146	0.0229
$Cu(NO_3)_2$(aq)	9.48×10^{-3}	9.48×10^{-3}	9.46×10^{-3}	9.36×10^{-3}	8.41×10^{-3}	4.20×10^{-3}	7.05×10^{-4}
$Cu(NO_3)_2$ 0.051 M							
Cu^{2+}	0.776	0.776	0.774	0.756	0.619	0.222	0.0302
$CuOH^+$	2.47×10^{-5}	2.47×10^{-4}	$2.46{\cdot}10^{-3}$	2.41×10^{-2}	0.197	0.708	0.960
$CuNO_3{}^+$	0.222	0.222	0.221	0.217	0.181	0.0692	0.00968
$Cu(NO_3)_2$(aq)	2.53×10^{-3}	2.52×10^{-3}	2.51×10^{-3}	2.48×10^{-3}	2.11×10^{-3}	8.57×10^{-4}	1.24×10^{-4}
$Cu(NO_3)_2$ 0.025 M							
Cu^{2+}	0.871	0.870	0.868	0.847	0.681	0.230	0.0303
$CuOH^+$	2.77×10^{-5}	2.77×10^{-4}	2.76×10^{-3}	2.70×10^{-2}	0.217	0.734	0.965
$CuNO_3{}^+$	0.129	0.129	0.128	0.125	0.102	0.0358	0.00478
$Cu(NO_3)_2$(aq)	7.57×10^{-4}	7.57×10^{-4}	7.55×10^{-4}	7.39×10^{-4}	6.09×10^{-4}	2.21×10^{-4}	3.00×10^{-5}

aqueous solution, on the total copper(II) concentration and possibly on the zeolite selectivity for these species.

The activity coefficients, in the zeolite phase, were calculated, using the equations recommended by authors Ekedahl et al. (1950):

$$\ln \gamma'_{Na} = \frac{1}{z_{Na} z_{Cu}} \int_{\tilde{K}(\bar{x}_{Cu}=0)}^{\tilde{K}} \bar{x}_{Cu} \, \mathrm{d} \ln \tilde{K} \tag{10}$$

$$\ln \gamma'_{Cu} = \frac{1}{z_{Na} z_{Cu}} \int_{\tilde{K}(\bar{x}_{Na}=0)}^{\tilde{K}} \bar{x}_{Na} \, \mathrm{d} \ln \tilde{K} \tag{10'}$$

Their values, calculated with data resulting from the Tóth isotherm, for each value of the total concentration (excepting 0.98 N, where the Freundlich isotherm was used) are given under the form of polynomial equations, whose parameters are shown in Table 6.

$$\gamma' = A \bar{x}^4_{Cu} + B \bar{x}^3_{Cu} + C \bar{x}^2_{Cu} + D \bar{x}_{Cu} + E \tag{11}$$

At low total concentrations (0.05, 0.1 N), the activity coefficients of the ions in the zeolite have usually values close to unity, which never go below 0.8 and beyond 1.02. The value of the activity coefficient of the copper ion generally decreases with the increase of the total ion concentration, as well as with the decrease of the ionic fraction of this ion, except for low total concentrations, where the activity coefficient is very close to unity for $x_{Cu} > 0.2$. The values of the activity coefficient of the sodium ion are generally lower than those of the copper ion, at the same normality and they decrease as well with the decrease of the ionic fraction of this ion, except for the lowest total concentrations, where their value is close to unity. Again, the values of the activity coefficient of the sodium ion decrease with the increase of the total ion concentration.

4 Conclusions

The ion exchange Cu-Na on type A zeolite does not behave fully as a true thermodynamic equilibrium, at least at concentrations of the external solution exceeding 0.5 N. Reasonable thermodynamic values could only be obtained over a limited range of concentration due to the complexity

Table 6 Parameters of Eq. (11), for the activity coefficients of ions in the zeolite phase

Conc. (Eq./L)	*A*	*B*	*C*	*D*	*E*	R^2
Na^+						
0.980	−0.7834	1.9917	−2.0768	1.4088	1.0039	0.9977
0.480	−1.9843	2.0635	−0.8731	0.0737	1.0012	0.9988
0.247	−3.9656	5.6993	−2.7285	0.2410	0.9958	0.9990
0.102	−4.0211	6.8004	−3.3822	0.4655	0.9915	0.9250
0.050	−0.2895	0.7722	−0.47050	0.0103	0.9993	0.9911
Cu^{2+}						
0.980	−0.1841	1.4366	−4.0663	3.4554	0.0028	0.9933
0.480	−1.1878	3.3087	−3.0655	1.5195	0.4273	0.9992
0.247	−0.9963	2.9566	−3.0071	1.5329	0.5141	0.9982
0.102	−0.7854	2.3597	−2.4637	1.0123	0.8747	0.9766
0.050	−0.6396	1.8724	−2.0616	0.9934	0.8339	0.9983

of the system. The reversibility of the process seems to be only partial, the reverse reaction is probably under strong kinetic control at large concentrations of Cu^{2+}, that is, the equilibrium state is reached only after very long periods of time, in these conditions.

A relative agreement between the values of the thermodynamic equilibrium constant, for different total concentrations, is obtained when an isotherm which provides a good data fit and which is yielding an appropriate shape of the Kielland plot (e.g. Toth) is used. This indicates that the concept of chemical equilibrium constant can be properly used even by approximating the system to a binary one, at low and moderate total ion concentrations, as it may be seen from Table 4.

The Na^+/Cu^{2+} ion exchange on zeolite type A is not a process taking place in a two solute system, but involving a multicomponent solution with varying composition. The value of the thermodynamic equilibrium constant obtained from experimental data at a given total concentration of the external solution for an ion exchange system considered as binary could be influenced by the heavy metal ion speciation in the external solution even in the presence of weak ligands as nitrate. The selection of ions as the reactants from the external solution and NaA and CuA_2 as the components of the solid phase, together with the corrections for the non-ideal behavior in the two phases yield a thermodynamic constant describing the actual multicomponent system. This constant cannot be used to predict the behavior of Na^+/Cu^{2+} ion exchange equilibrium on zeolite A at a total concentration of the order of 1 N and higher, due to the influence of simultaneous processes mentioned above (Rida et al. 2012).

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