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Study of lithium ion exchange by two synthetic zeolites: Kinetics and equilibrium

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Abstract

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We examined the exchange of univalent cations (Na⁺ and H⁺) retained on two commercially available synthetic zeolites with Li⁺ ions present in aqueous solutions in contact with the solids with a view to preparing effective controlled-release pharmaceutical forms. The studied zeolites were manufactured by Merck and featured channel diameters of 0.5 (Zeolite 5A, Ref. 1.05705.250, designated Z-05 in this work) and 1.0 nm (Zeolite 13X, Ref. 1.05703.250, designated Z-10 here). The XRD technique revealed that Z-05 possesses an LTA structure derived from that of sodalite and Z-10 a faujasite-type structure. Their exchange capacities were found to be 2.72 and 3.54 meq/g. The Z-Na + Li⁺/Z- $Li + Na^+$ and $Z-H + Li^+/Z-Li + H^+$ ion-exchange processes were found to be reversible and their kinetic laws to obey the equation (-dC/dt) = $k_a \cdot C^n \cdot (1-\theta) - (k_d \cdot \theta)$, with n = 1 for Z-10 and n = 2 for Z-05. Based on the equilibrium results, the overall processes involve one (with Z-05) or two single ion-exchange processes (with Z-10). In both cases, the equations that govern equilibrium are direct results of the kinetic laws. Thus, the first process-the one with only Z-05-involves the retention of Li⁺ cations at anionic sites on the outer surface of the solid and their access to the larger pores; the second process—which occurs with Z-10 only—involves the retention of lithium(I) cations within the zeolite channels. In both systems, the exchange with Li^+ (from the aqueous solution) is easier than that with H^+ ; this is consistent with our kinetic, equilibrium, and thermodynamic results.

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Keywords: Zeolites; Ion-exchange; Lithium; Kinetics; Adsorption; Equilibrium

1. Introduction

1.1. Zeolites

Zeolites are natural or synthetic crystalline aluminosilicates consisting of SiO₄ and AlO₄ tetrahedra [with (Si,Al)O₄ as the T primary units] connected via their vertices—by sharing an oxygen atom-that form three-dimensional networks with channels leading to the outside of the structure and accounting for roughly 50% of the solid volume (void intracrystal space). The different possible arrangements of the tetrahedra dictate the structure of the different types of zeolite, which include chan-

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nels of variable diameter (in the nanometer region) arranged in a regular manner that is identical for each structure type. This last feature has led to zeolites being classified as periodic porous materials [1].

Four or more primary T units connected to one another constitute secondary units or building blocks [2] that form rings with as many edges as (Si,Al)O₄ tetrahedra are connected. One of the most salient building blocks is probably sodalite [3], which is the parent structure for natural faujasite and synthetic zeolites of the X and Y types. Building blocks assemble to form various types of zeolites (seven are known at present). The way T units connect to one another is the criterion used to classify and designate zeolites [1,4], irrespective of chemical composition or the specific symmetry of the crystalline solid.

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Fig. 1. Z-10 structure (secondary unit of sodalite).

The secondary unit of sodalite (Fig. 1), the so-called T24 unit, consists of 24 T units that form a sort of truncated octahedron; the eight triangular sides of the octahedron become regular hexagons and the six vertices are replaced with as many square sides.

1.2. Pharmacological interest of lithium

In addition to its current uses in chemistry, technology, and battery manufacture, lithium is arousing increasing interest among biologists-it is believed to be an essential element for humans-and pharmacologists. Although most of the pharmacological uses of Li⁺ ions fall into the psychiatric domain, research aimed at its therapeutic introduction and utilization is growing steadily in areas as diverse as neurology [5], endocrinology [6], dermatology [7,8], immunotherapy [9], oncology [10,11], hematology [12], and nephrology [13]. In psychiatry, Li⁺ ions have been successfully used for years for a variety of purposes, particularly in the prevention and treatment of bipolar disorders [14-19], unipolar depression [20], and violent episodes caused by alcohol abuse [17].

Treatments based on lithium salts must be strictly controlled, as high concentrations of Li⁺ ions can be severely toxic to the kidneys. Also, Li⁺ can have variably severe side effects [21], so it is counterindicated for pregnant women, lactating mothers, and children under 12, as well as in patients allergic to Li⁺ ions or having leukemia, CNS disorders (epilepsy or Parkinson's disease), cardiac insufficiency, Addison's disease (renal insufficiency boosts lithium toxicity), diabetes, hypothyroidism, myasthenia gravis, or dehydration symptoms. The doses and administration patterns of lithium salts (of which Li₂CO₃ is the most widely used at present) must be strictly controlled to maintain effective serum levels while avoiding reaching toxic limits. This would be easily achieved if a Li⁺ controlled release form similar to those existing for other pharmaceuticals [22] could be developed.

We believe some lithium zeolites may be effective raw materials for the preparation of controlled release oral pharmaceutical forms. Obviously, this hypothesis must be confirmed with experimental data about the nature and extent of interactions between Li⁺ ions and anionic sites in zeolites; this entails 54 examining the reversible cation-exchange processes that occur in $Z-M^{I}/Li^{+}$ and $Z-M^{II}/Li^{+}$ (Li⁺ adsorption) processes, as 55 56 well as in Z-Li^I/M⁺ and Z-Li^I/M²⁺ (Li⁺ desorption or release) 57 processes.

2. Experimental

We have studied two synthetic zeolites commercially avail-60 able from Merck. According to the manufacturer, zeolite 5A 61 (Ref. 1.05705.250) consists of calcium aluminosilicate and 62 has a channel diameter of 0.5 nm, whereas zeolite 13X 63 (Ref. 1-05703.250) consists of sodium aluminosilicate and pos-64 sesses a faujasite-type structure and channels that are 1.0 nm in 65 diameter. We shall henceforward use Z-05 and Z-10 to desig-66 nate the two zeolites. Both were obtained as spheres 2 mm in 67 diameter. Because the exchange capacity was not among the 68 specifications supplied by Merck, it was determined using the 69 method of Fernández del Barrio [23], which provided a value 70 of 3.54 meq/g for Z-10 and 2.72 meq/g for Z-05. 71

To confirm the specifications supplied by Merck about the 72 structure of the two commercially available zeolites, we used 73 a Phillips PW 1700 instrument to record XRD patterns for 74 powdered samples, using CuK_{α} radiation and a graphite sec-75 ondary monochromator. Two series of digital recordings were 76 obtained: one of the general type $(12 \text{ min}/2\theta = 80^\circ)$ and the 77 other of the static type (8 s per $0.02^{\circ} 2\theta$). 78

The commercial zeolites were used to prepare the corre-79 sponding acid and sodium forms of Z-05, both of which were 80 81 to be examined in this work. Sodium Z-05 was obtained from the commercial calcium zeolite, using the method of Fernández 82 del Barrio [23]: an amount of the commercial solid was placed 83 in a glass column through which a 1 M sodium chloride solu-84 tion was passed at a rate of 1 ml/min (the total amount passed 85 was five times greater than that theoretically needed to effect 86 the exchange of calcium ions with sodium ions); the percolate 87 was checked to contain no Ca^{2+} . Subsequently, sodium Z-05 88 was rinsed with bidistilled water to the absence of chloride ions 89 and dried at 120 °C to constant weight. 90

The ammonium forms of Z-05 and Z-10 were obtained simi-91 larly to the sodium zeolite, using 1 M ammonium nitrate instead 92 of NaCl. The resulting solids were heated at 300 °C for 2 h to 93 obtain the corresponding acid forms. Aqueous LiCl solutions 94 were made from Merck pro-analysis lithium chloride, using 95 bidistilled, deionized water.

The kinetic law for each studied process was established 97 from the results obtained in two test series aimed at calculat-98 ing the partial order of the process in the dissolved lithium 99 concentration and the specific rate of lithium absorption for 100 the zeolite, respectively. The experimental procedure used was 101 very similar in both cases: an amount of 0.5 g of zeolite and 102 100 ml of an aqueous LiCl solution of known concentration 103 were placed in a 250-ml glass flask furnished with a threaded 104 stopper and stirred at 150 rpm in a Gallenkamp apparatus at a 105 temperature constant to within ± 0.1 °C for a preset time, after 106 which the dissolved Li⁺ concentration was determined by us-107 ing a Perkin-Elmer 1100B spectrophotometer at $\lambda = 670.8$ nm. 108 In one test series, T = 20 °C and five LiCl solutions of concen-109 trations ranging from 7.0×10^{-4} to 2.0×10^{-3} M were used; 110 in the other, working temperatures of 10, 20, 30, 40, or 50 °C 111 and a 1.2×10^{-3} M LiCl solution were employed. 112

The equilibrium data needed to run the corresponding ion-113 exchange isotherms (at 10, 20, 30, and 40 °C, in addition to 114 R. Navarrete-Casas et al. / Journal of Colloid and Interface Science ••• (••••) •••-•••

50 °C with the sodium samples) were obtained by following a procedure similar to that described in the previous paragraph; an amount of 1.00 g of solid and 100 ml of aqueous LiCl solutions at concentrations over the range 7.2×10^{-4} – 1.44×10^{-1} M were used, the two phases being maintained in contact for 7 days (i.e., for much longer than the equilibrium time).

3. Results and discussion

3.1. Structures of the zeolites

Based on the XRD patterns obtained, zeolite Z-10 consists of T24 units such as those depicted in Fig. 1 that connect to one another via hexagonal rings to form chains such as those of Fig. 2. The chains in turn form a faujasite-type structure (Fig. 3) with a large channel (0.74×0.74 nm) bounded by the ring formed by 12 tetrahedra belonging to 6 T24 units. Each channel is connected to other identical ones along the three spatial dimensions to form a three-dimensional network. The crystallographic data also revealed that Z-10 possesses a cubic structure belonging to the *Fd3m* (No. 227) space group, and that dimensions of the unit cell are dictated by the magnitude of parameter a_0 (2.47 nm).

Z-05 was assigned a Lynde Type A (LTA) structure derived from sodalite; T4 units are connected via cube sides, which are oriented in the [100] direction (Figs. 4 and 5) and form T4 double rings. The resulting solid is a cubic network of *Pm3m* symmetry with an edge length of ca. 1.22 nm that encompasses a primary network (P) of T8 channels 0.41×0.41 nm in size connected to one another in three symmetric directions (viz. those of the [100] sides). Z-05 also belongs to the cubic sys-



Fig. 3. Z-10 structure (faujasite-type structure).

tem, Fm3c space group, with unit cell dimension $a_0 = 2.48$ nm. The space group and unit cell dimension for the spatial pseudonetwork is $a_0 = 1.24$ nm.

 Ca^{2+} ions are not completely displaced by Na⁺ ions, as the peaks for Ca^{2+} ions in the sample remain in the XRD patterns, albeit slightly displaced to the right, as can be seen in Fig. 6.

3.2. Ion-exchange processes

The exchange of Na^+ or H^+ ions in the zeolites by Li^+ ions in solution can be represented by the equation

$$S-B + A \to S-A + B, \tag{1}$$

which can be assigned the kinetic law of Navarrete-Guijosa et al. [24],

$$-\left(\frac{\mathrm{d}C}{\mathrm{d}t}\right) = k_{\mathrm{a}} \cdot C^{n_{1}} \cdot (1-\theta)^{n_{2}} - k_{\mathrm{d}} \cdot \theta^{n_{3}}$$
$$= k_{\mathrm{a}} \cdot C^{n} \cdot (1-\theta) - k_{\mathrm{d}} \cdot \theta, \qquad (2)$$

where n_1 , n_2 , and n_3 are partial reaction orders of the process in *C*, $(1 - \theta)$, and θ , respectively (in our systems, $n_2 = n_3 = 1$ and $n_1 = n$); k_a is specific rate of adsorption of Li⁺ ions by the solid; k_d —specific rate of desorption of Li⁺ ions; θ —fraction of anionic sites in the exchanger occupied by Li⁺ ions; and $(1 - \theta)$ —fraction of anionic sites in the exchanger occupied by Na⁺ or H⁺ ions.



Fig. 4. Z-05 structure (Lynde-type A).



Fig. 5. Z-05 structure (Lynde-type A).

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Fig. 6. XRD data for Z-05-Na/Li+

Based on the previous equation, the initial rate of the process is given by

$$-\mathrm{d}C/\mathrm{d}t)_0 = k_\mathrm{a} \cdot C^n,\tag{3}$$

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 $\ln(-\mathrm{d}C/\mathrm{d}t)_0 = \ln k_\mathrm{a} + n \cdot \ln C.$ (4)

Equation (4) was used to calculate the corresponding n values from the results obtained in the first series. By integration of Eq. (2) at n = 1 and n = 2, respectively, using the equilibrium state, for which the assumption was made [24] that

$$\theta = (C_0 - C) / (C_0 - C_e), \tag{5}$$

we can obtain for n = 1:

$$C = \frac{C_0 + k_a \cdot C_e \cdot t}{1 + k_a \cdot t}$$

and for n = 2:

$$\ln \frac{C - C_{\rm e}}{C + C_{\rm e}} + \frac{2C_{\rm e}}{C - C_{\rm e}} = \ln \frac{C_0 - C_{\rm e}}{C_0 + C_{\rm e}} + \frac{2C_{\rm e}}{C_0 - C_{\rm e}} + \frac{4 \cdot C_{\rm e}^2 \cdot k_{\rm a}}{C_0 - C_{\rm e}}t.$$
(7)

The n values were checked by fitting the experimental results to Eqs. (6) and (7). The same fitting allowed us to calculate k_a from the experimental results of the second test series. Based on Eq. (2), at equilibrium,

$$\theta = \frac{n^{\rm s}}{n_{\rm e}^{\rm s}} = \frac{K_{\rm kin} \cdot C_{\rm e}}{1 + K_{\rm kin} \cdot C_{\rm e}} \tag{8}$$

and

$$\frac{C^{\rm n}}{n^{\rm s}} = \frac{1}{K_{\rm kin} \cdot n_{\rm e}^{\rm s}} + \frac{C_{\rm e}}{n_{\rm e}^{\rm s}},\tag{9}$$

where $\boldsymbol{\theta}$ is fraction of anionic sites in the exchanger occupied by Li^+ ions; C_e —molar concentration of lithium ions in the dissolved phase under equilibrium conditions; n^{s} —amount (mol) of lithium retained per gram of zeolite; n^s_e—exchange capacity of the zeolite relative to Li⁺ ion under the working conditions; and $K_{\rm kin}$ —kinetic equilibrium constant (= $k_{\rm a}/k_{\rm d}$).

54 Consequently, the equilibrium isotherms must conform to 55 Eq. (8), so their fitting to Eq. (9) should allow one to calcu-56 late n_e^s and K_{kin} . The thermodynamic equilibrium constant K 57 for each studied process was calculated using the method of Gaines and Thomas [25],

$$\ln K = (Z_{\rm B} - Z_{\rm A}) + \int_{0}^{1} (\ln K_{\rm s}) dN_{\rm A}, \qquad (10)$$

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where K is thermodynamic equilibrium constant; K_s —coefficient of selectivity; $(Z_B - Z_A)$ —difference in the charges of the ions that are interchanged; and N_A —equivalent fraction of the ion A in the bosom of the changer.

3.2.1. Kinetics

The experimental results obtained for the Z-Na/Li⁺ systems are shown in the form of C vs t plots in Figs. 7 and 8. The data in Figs. 7a and 8a were subjected to the differential method of Valenzuela-Calahorro [26] to determine the initial rates, which were much lower for Z-05 than for Z-10. Taking into account that the data used to calculate $-(dC/dt)_0$ corresponded to extremely short times, at which the diffusion of Li⁺ inside the zeolite channels could hardly have begun, the decreased initial rates of Z-05 may be related to the smaller size of its channels. A plot of initial rates in the form of Eq. (4) provided the *n* values given in Table 1.

The values n = 1 (Z-10-Na/Li⁺ system) and n = 2 (Z-05-Na/Li⁺ system) shown in Table 1 were confirmed by fitting the experimental data to Eqs. (6) and (7), respectively, thus defining the solid lines in the above-mentioned figures. These equations were also used to fit the experimental results of Figs. 7a and 8b, respectively, in order to calculate the specific rate (k_a) values shown in Table 2, which also include the values for the thermodynamic activation functions for the ion-exchange process as calculated by fitting the k_a/T values to

$$k = \frac{RT}{Nh} \cdot e^{(\Delta S^*/R)} \cdot e^{-(\Delta H^*/RT)},$$
(11)

from which it follows that

$$\ln\frac{k}{T} = \ln\frac{R}{Nh} + \frac{\Delta S^*}{R} - \frac{\Delta H}{R} \cdot \frac{1}{T},$$
(12)

where R is gas constant, N—Avogadro's number, h—Planck's constant, and T—temperature (K).

Equation (11) was derived under the assumption that the ion-exchange process occurred permanently in the transition state [26].

Obviously, Li⁺ ions present in hydrated form in solution 112 must lose at least part of the water molecules in their coordi-113 nation spheres in order to be able to penetrate into the zeolite 114

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Fig. 7. *C*-*t* isotherms for the Z-05-Na_(solid)/Li⁺_(aq) system: (a) $T = 20^{\circ}$ C, (b) $C_0 = \text{const.}$

33 Table 1

Initial rates and partial order of the process in the dissolved Li⁺ concentration for the Z-05-Na/Li⁺ and Z-10-Na/Li⁺ systems (T = 20 °C)

Zeolite	$\begin{array}{c} C_0 \times 10^4 \\ (\text{mol/L}) \end{array}$	$\begin{array}{c} -(\mathrm{d}C/\mathrm{d}t)_0 \\ \times 10^6 \end{array}$	$n = n_1$	<i>R</i> ²
Z-05-Na	7.21	0.36	2	0.999
	10.1	0.70		
	12.3	0.99		
	20.9	3.0		
Z-10-Na	7.50	1.8	1	0.980
	9.81	2.1		
	12.3	3.0		
	18.8	4.8		

channels (the radius of Li⁺, 0.06 nm, increases to 0.382 nm
upon hydration [27]).

As can be seen from Table 2, in both Z-Na + $Li^+ \rightarrow Z$ - $Li + Na^+$ processes, k_a increases with increasing temperature, as is usually the case. Also, k_a is greater for Z-05 than for Z-10, which suggests that the adverse influence on k_a (i.e. restricted diffusion) is much stronger with Z-10, which pos-sesses a three-dimensional network of interconnected channels. In Z-05, neighboring voids are not identical in size, which can restrict the access of Li⁺ ions to the inside of the solid; as a result, Li⁺ ions could only reach, in a rapid manner, positions



Fig. 8. C-t isotherms for the Z-10-Na_(solid)/Li⁺_(aq) system: (a) T = 20 °C, (b) $C_0 = \text{const.}$

inside the channels lying very close to the outer surface of each particle, but not the exchange sites located on the inside.

In principle, this is a plausible hypothesis, particularly at short diffusion times (first few points in the *C*-*t* isotherms); at long enough times, however, diffusion must progress further inside the particles, via the zeolite channels, so the ease of diffusion must increase with increasing channel diameter and hence be easier in Z-10. As can be seen from Table 2, both the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) are very similar for the two Z-Na/Li⁺ systems studied; this is unsurprising, as these thermodynamic activation functions depend on the chemical nature of the anionic sites (similar in Z-05 and Z-10) and the exchanged cation (Li⁺ in both cases).

As stated previously, the retention of lithium(I) ions in the zeolite channels must be governed to a great extent by diffusion. To obtain relevant information in this respect, we used the approximate method of Carman and Haul [28], which provides qualitative data from which a rough estimate of the influence of diffusion on the rate of the process can be derived. Fig. 9 shows the diffusion coefficient (*D*) values obtained by applying this method to the experimental kinetic data. As can be seen, consistent with the initial assumption, the ease of diffusion increased with increasing diameter of the zeolite channels and temperature and decreased with increasing adsorption of Li^+ ions.

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Table 2	
Specific rates and thermodynamic activation functions f	for Z-05-Na/Li ⁺ and Z-

S.C. ^a	<i>Т</i> (°С)	Order (<i>n</i>)	$\begin{array}{c} C_0 \times 10^3 \\ (\text{mol/L}) \end{array}$	$k_a{}^b \times 10^3$	<i>R</i> ²	ΔH^{*c} (kJ/mol)	ΔS^{*d} (J/ (K mol))	<i>R</i> ²
Z-05-Na	10	2	1.17	466.4	0.986	27.9	-0.15	0.99
	20			799.5	0.962			
	30			1184.0	0.991			
	40			1767.0	0.983			
Z-10-Na	10	1	1.32	1.5	0.997	30.1	-0.19	0.95
	20			3.1	0.997			
	30			4.3	0.998			
	40			5.8	0.999			

^a S.C.—solid cation exchanger.

^b k_a —specific rate of adsorption of dissolved Li⁺ ions by the solid.

 ΔH^* —enthalpy of activation of the exchange process.

^d ΔS^* —entropy of activation of the exchange process.



Fig. 9. Variation of the diffusion coefficient as a function of time for the Z-05-Na/Li⁺ (a) and Z-10-Na/Li⁺ systems (b).

3.2.2. Equilibrium

The experimental equilibrium results for the ion-exchange processes in the Z-05-Na/Li⁺, Z-05-H/Li⁺, Z-10-Na/Li⁺, and



Fig. 10. Equilibrium isotherms for the Z-05-Na/Li⁺ (a) and Z-05-H/Li⁺ systems (b).

Z-10-H/Li⁺ systems found at 10, 20, 30, 40, and 50 $^{\circ}$ C were used to construct n^{s} vs (C/C_{0}) plots that allowed the isotherms in Figs. 10 and 11 to be obtained. At first sight, these ion-exchange isotherms are of the S type in the classification of Giles et al. [29]; also, the curves for the Z-Na/Li⁺ systems are better defined than those for the Z-H/Li⁺ systems and Li⁺ ad-sorption starts at lower (C/C_0) ratios in the former. In any case, none exhibits the well-defined plateau that Giles et al. [29] re-late to the exchange capacity of the solid. The isotherms also reveal that Li⁺ adsorption seemingly involves a single process in the Z-05-Na/Li⁺ system [see Eq. (1)] and two in the Z-10-Na/Li⁺ system. Finally, the isotherms for Z-05-H/Li⁺ and Z-10-H/Li⁺ obtained under the operating conditions used are not well defined enough for reliable conclusions to be drawn from their mere visual inspection, so we had to fit the experi-mental data of Figs. 10 and 11 to Eq. (8) by plotting them in accordance with Eq. (9), using n = 2 for the isotherms of Z-05-Na/Li⁺ and Z-05-H/Li⁺, and n = 1 for those of Z-10-Na/Li⁺ and Z-10-H/Li⁺. The results of the fitting are summarized in Table 3.

The isotherms for the Z-05-Na/Li⁺ and Z-05-H/Li⁺ systems (Fig. 10) conform to a continuous function of the form

$$n^{s} = \frac{K_{\text{kin}} \cdot n_{\text{e}}^{s} \cdot C^{2}}{1 + K_{\text{kin}} \cdot C^{2}},$$
(13) ¹¹³
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Table 3

Fitting of the equilibrium results to Eq. (9)



Solid	Segment	<i>Т</i> (°С)	R^2	$n_{\rm e}^{\rm s} \times 10^4$ (mol/g)	<i>K</i> kin
Z-05-Na	1	10	0.999	3.9	25582
(n = 2)		20	0.999	4.6	16181
		30	0.999	5.3	9366
		40	0.998	6.0	6463
		50	0.998	7.2	4731
Z-05-H	1	10	0.999	2.5	1918
(n = 2)		20	0.999	2.6	2667
		30	0.999	2.8	4323
		40	0.999	3.0	12705
Z-10-Na	1	10	0.998	2.80	813
(n = 1)		20	0.995	3.20	644
		30	0.999	3.70	486
		40	0.981	4.10	367
		50	0.993	4.40	302
	2	10	0.998	13.8	33
		20	0.978	15.7	35
		30	0.997	16.3	36
		40	0.991	16.4	38
		50	0.982	17.1	39
Z-10-H	1	10	0.989	1.70	211
(n = 1)		20	0.995	2.30	172
		30	0.999	3.70	121
		40	0.993	11.1	49

Note. The *n* value used in the equation is given under the exchanger name.

Fig. 11. Equilibrium isotherms for the Z-10-Na/Li⁺ (a) and Z-10-H/Li⁺ systems (b).

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which confirms that the process is second-order (n = 2) in C 33 (the Li⁺ ion concentration) and suggests that the overall ion-34 exchange process involves a single process of the type defined 35 by Eq. (1), so the exchange of cations can hardly alter, in a sub-36 37 stantial manner, the ability of Li⁺ cations to access the inside of 38 the zeolite channels, the porosity of the exchanger, or the behav-39 ior of Li⁺ ions. The exchange capacity referred to Li⁺ under the 40 operating conditions used, n_e^s (Table 3), which was calculated 41 from equilibrium data, is much lower than the value for Z-05 42 as determined with the method of Fernández del Barrio [23], 43 2.72 meq/g; this is unsurprising given the differences between 44 the two methods. Thus, n_e^s increased with increasing tempera-45 ture, which suggests that the ion-exchange process is strongly 46 influenced by the diffusion of cations along the zeolite chan-47 nels and that, as expected, diffusivity increases with increasing 48 temperature. As can also be seen from Table 3, the n_e^s values 49 obtained for Z-05-Na are much greater than those for Z-05-H, 50 which suggests that Na⁺ ions are more easily exchanged with 51 Li⁺ ions by the solid than are H⁺ ions; this is consistent with 52 the results for other ion-exchange processes [30]. This hypoth-53 esis is confirmed by the fact that Li⁺ adsorption starts at higher 54 C/C_0 ratios in Z-05-H and by the $K_{\rm kin}$ values obtained, which 55 56 reveal that the process is exothermal in Z-05-Na/Li⁺ but en-57 dothermal in Z-05-H/Li⁺.

Unlike the previous ones, the isotherms for the Z-10-Na/Li⁺ system suggest that the overall ion-exchange process involves two individual processes, each of which conforms to the following equation:

$$n^{\rm s} = \frac{K_{\rm kin} \cdot n_{\rm e}^{\rm s} \cdot C}{1 + K_{\rm kin} \cdot C}.$$
(14)

This is consistent with the fact that the process is first-order (n = 1) in the Li⁺ concentration (C). As is usually the case in this situation, K_{kin} is much smaller for the second adsorption or ion-exchange individual process [31]. This involves a higher net energy expense, so much so that the first process may be exothermal and the second endothermal [32], as in this work. As previously stated for Z-05, the exchange of H⁺ ions with Li⁺ in Z-10-H is more difficult than that of Na⁺ ions; in this zeolite, the exchange starts at higher C/C_0 ratios—so much so that we could not obtain enough experimental data to hypothesize whether the overall process involves one or two individual processes.

The origin of the two individual, probably consecutive, ionexchange processes in the Z-10-Na/Li⁺—the second of which 106 starts before the first has finished-is difficult to identify. In 107 any case, a comparison of the n_e^s values calculated for the first 108 segment of the isotherms for Z-10-Na and Z-10-H with those 109 for Z-05-with provision for their differences in structure and 110 channel morphology-suggests that the first process involves 111 the adsorption of Li⁺ ions in the outermost, readily accessi-112 ble voids of the solid-where Li⁺ ions may even be partially 113 hydrated-and that the second occurs at inner exchange sites 114

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that can only be reached, diffusively, by virtually dehydrated lithium(I) ions-the energy required influences the overall energy balance and results in the second individual process being endothermal.

5 The exchange of H^+ ions with Li^+ ions in Z-10 also appears 6 to occur to a lesser extent and less readily than that of Na⁺ ions initially retained by the exchanger. In the Z-10-H/Li⁺ system, 8 the process is apparently exothermal.

The kinetic equilibrium constant, K_{kin} , is known to have 9 some practical value, but no thermodynamic value, so it lacks 10 11 thermodynamic significance and cannot be used for predic-12 tive purposes; also, it can only be used for comparison when 13 the equilibrium processes concerned involve the same system 14 and/or conform to an identical equation [e.g., (9)] and with the 15 same *n* value—which is not the case with Z-05 and Z-10.

16 The thermodynamic equilibrium constant, K, for each indi-17 vidual ion-exchange process was calculated using Eq. (10) [25] and a procedure described in a previous paper [24]. The results 18 are summarized in Table 4, which also includes the enthalpies 19 and entropies of the corresponding processes as calculated by 20 21 fitting the K values to the following equation:

$$\ln K = (\Delta S^{\circ}/R) - (\Delta H^{\circ}/R) \cdot (1/T).$$
(15)

24 The table also shows the corresponding ΔG values calculated 25 from them (Table 4).

26 The largest K values were provided by Li^+ exchange in 27 the Z-05-Na zeolites and the first individual process in Z-10-28 Na; the fact that both processes are exothermal and exoentropic 29 suggests that lithium(I) ions may be adsorbed as $[Li^{I}(H_{2}O)_{x}]^{+}$, 30

Table 4

32 Thermodynamic equilibrium constants and thermodynamic functions for the 33 ion-exchange processes

Calid	Stan of the	т	v	p 2	A 110	A Cº (L/	A.C.
Solid	isotherm	$(^{\circ}C)$	Λ	Λ	ΔH (kI/mol)	(K mol))	(kI/mol)
7-05-Na	Only 1	10	124 21	0 070	_74.7	-224.7	-11.04
2-05-1 v a	Only I	20	39.31	0.777	-/4./	-224.7	-8.80
		30	9.03				-6.55
		40	5.48				-4.30
		50	2.52				-2.06
Z-05-H	Only 1	10	1.23	0.965	4.3	16.7	-0.47
	•	20	1.29				-0.63
		30	1.35				-0.80
		40	1.47				-0.97
	1	10	640 71	0.094	55 1	120.9	15 50
	1	20	280.04	0.964	-55.1	-139.8	-13.30
		20	569.94 140.61				-14.10
		30 40	65 27				-12.70
		40 50	45.11				-9.90
7 10 No	2	10	2 72	0.017	20	21.6	2.20
Z-10-Na	Z	10	2.72	0.917	3.8	21.0	-2.50
		20	2.75				-2.51
		30 40	2.94				-2.75
		40 50	2 22				-2.94
		50	5.52				-5.10
Z-10-H	Only 1	10	1.57	0.988	-13.0	-42.1	-1.11
		20	1.35				-0.69
		30	1.14				-0.27
		40	0.92				0.15

with x > 0, at active sites on the surface—most likely at the out-58 ermost sites in the zeolite channels, as hypothesized earlier. The 59 increased retention capacity of Z-10 may be directly related to 60 the increased diameter of its channels. This may also be the ori-61 gin of Li⁺ ions retained by Z-05 possessing fewer degrees of 62 freedom (viz., a lower ΔS° value) and forming stronger bonds 63 (lower ΔH° values) than Z-10. 64

Unlike the first individual ion-exchange process in the Z-10-Na/Li⁺ system, the second is endothermal and endoentropic. This suggests that Li⁺ ions are retained at active sites inside the channels that form the three-dimensional network connected 68 with the outside. In order to reach them, $[Li^{I}(H_{2}O)_{x}]^{+}$ cations 69 from the aqueous solutions must previously undergo extensive or even complete dehydration. The amount of energy required for the dehydration and the increase in entropy involved in the release of coordinated water molecules may be the origin of the ΔH° and ΔS° values obtained.

4. Conclusions

The thermodynamic probability of lithium(I) being adsorbed onto the Z-H/Li⁺ systems is very low ($\Delta G = -1.1 \text{ kJ/mol}$). The ΔG values obtained for the Z-05-H/Li⁺ and Z-10-H/Li⁺ systems are very similar, even though the process is endothermal and endoentropic in the former, and exothermal and exoentropic in the latter-there is an obvious compensation effect. In any case, hydrogen ions are much less likely and easy to exchange with lithium(I) than are Na⁺ ions.

From the foregoing it follows that the reversible replacement of the Na⁺ ions in Z-10 with Li⁺ ions in an aqueous solution in contact with it is easier on account of its more open porous structure and the larger diameter of its channels. This, together with its higher effective exchange capacity, suggests that it may be more useful than Z-05 with a view to obtaining lithium raw materials for use in the preparation of lithium(I) release forms.

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