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Studies of the Hydrous Niobium(V) Oxide Ion Exchanger. VI. Rate of the Isotopic Exchange of Strontium Ions between the Exchanger in the Sr^{2+} Form and Aqueous Solution

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The rate of the isotopic exchange of Sr^{2+} between hydrous niobium(V) oxide in the Sr^{2+} form and aqueous solution of strontium salts was determined radiochemically. The exchange rate was controlled by the diffusion of Sr^{2+} in the exchanger particles. The diffusion coefficients of Sr^{2+} and their activation energy changed with the pH in a solution equilibrated with exchangers. Under the conditions of constant pH, the diffusion coefficients were constant up to a certain concentration of Sr^{2+} (0.1 mol dm^{-3}, pH 7.5), wherefrom they began to increase. The results were considered in terms of the interaction between the ions and the ion-exchange sites by comparing them with the Na^+ isotopic exchange rate on this material.

An investigation of ion-exchange kinetics is very important for understanding the ion-exchange mechanism of hydrous metal oxides. In order to provide data that are useful for elucidating ion-exchange kinetics we undertook radiochemical experiments to measure the isotopic exchange rate of sodium ions between hydrous metal oxides and solutions.[1—3] The rate of the reaction cannot be understood in terms of a unified view, since the rate-controlling step differs from material to material. As for cations other than Na^+, a Co^{2+} isotopic exchange on hydrous tin(IV) oxide was studied, showing that the kinetic behavior is very complex and differs from a Na^+ isotopic exchange.[4] Further investigations should therefore be carried out for many kinds of the exchangers and counter cations in order to understand the ion-exchange kinetics of hydrous metal oxides.

This paper discusses the results of radiochemical experiments undertaken to measure the isotopic exchange rate of Sr^{2+} between a hydrous niobium(V) oxide exchanger in the Sr^{2+} form and aqueous solutions of strontium salts. The results are compared with the isotopic exchange rates of Na^+ on the exchanger, which has already been reported.[2]

Experimental

Preparation of the Exchanger in the Sr^{2+} Form Spiked with ^{85}Sr. The hydrous niobium(V) oxide prepared by a previously recommended method[5] was classified into four particle sizes using Japan Industrial Standard sieves; it was then converted to the H^+ form by treating it with a 0.1 mol dm^{-3} HCl solution. After being washed with water, the exchanger was air-dried and stored in a desiccator containing a saturated NH_4Cl solution (relative humidity, 79% at 25 °C). The reproducibility of the preparation was confirmed by examining the composition and Na^+-uptake curves (acid-base property). The average particle radius was estimated by approximating the particle shape by a sphere from the particle-size distribution measured in a 84.5 wt% glycerol solution using a Seishin Enterprise micron-photosizer (Model SKC-2000); the particle radii (r) were 164±7, 126±6, 87±1, and 57±4 μm. The exchanger in the H^+ form was then converted to the Sr^{2+} form by treating it with solutions having the same chemical composition as those used for the rate measurement. The exchanger was then labeled with ^{85}Sr by equilibrating it with a ^{85}Sr solution having the same chemical composition as the above-mentioned solution for longer than 2 d at room temperature. After being separated from the solution by filtration under suction, the exchanger was used for a rate measurement. The Sr^{2+} solutions used for these procedures were prepared by desired combinations of $SrCl_2$ and $Sr(OH)_2$–tris(hydroxymethyl)-methyl-2-aminoethanesulfonic acid (TES) or 2-morpholinoethanesulfonic acid (MES) buffer solutions. The presence of the buffer reagents was experimentally confirmed to affect neither the Sr^{2+} exchange capacity nor the reaction rate.

Stoichiometry of Ion-Exchange Reaction. The exchanger in the Sr^{2+} form (0.30 g) was immersed in 10 cm^3 of a 0.5 mol dm^{-3} HCl solution for 5 d. The amount of Sr^{2+} released was assayed by Zn–EDTA compleximetric titration using eriochrome black T as an indicator; the amount of H^+ consumed was determined by titration using a standard NaOH solution. The excess amount of Sr^{2+} ions taken up by the exchanger over the exchanged H^+ ions was evaluated based on the difference between these analytical values. Any difference larger than 0.02 mmol g^{-1} can be regarded as being significant, based on the experimental error in the chemical analysis. The stoichiometry of the exchange reaction between H^+ and Sr^{2+} ions was also confirmed in the reverse direction by immersing the exchanger in the H^+ form in a 0.1 mol dm^{-3} $SrCl_2$ solution at pH 7.2.

Measurement of the Isotopic Exchange Rate. Rate measurements were performed in a nitrogen atmosphere using the same apparatus as described earlier.[6] The rate was measured in a solution having the same composition as that used for converting the exchanger to the Sr^{2+} form; otherwise, the ion-exchange reaction would occur between H^+ and Sr^{2+} ions, since the ion-exchange capacity for Sr^{2+} strongly depends on both the pH and the concentration of the solution. A 0.1 gram portion of the sample was placed in a cage and immersed in 200 cm^3 of a solution of the desired composition while the cage was being rotated. The frequency of rotation was kept constant at 1300 min^{-1}. This was reasonable, since the exchange rate was empirically confirmed to be independent of the frequency between 1000 and 1300 min^{-1}, indicating efficient agitation of the solution. The frequency of revolution was measured with a Yokogawa

(Model 2607) phototachometer. The solution had been adjusted in advance to a constant temperature within ±0.1 °C. Aliquots of the solution (0.2 cm^3) were taken out at appropriate time intervals in order to measure the radioactivity with a well-type NaI(Tl)-scintillation counter (Aroka Model ARC-361). The time of contact of the exchanger with the solution was taken as the elapsed time between immersing the cage and withdrawing an aliquot of the solution. The fractional attainment of equilibrium, $F=Q_t/Q_\infty$ was calculated from these results; here, Q_t is the total radioactivity of the solution at time t and Q_∞ at $t=\infty$. Q_∞ was calculated using $Q_\infty=Q_iM/(M+m)$, where Q_i is the initial total radioactivity of the exchanger; m and M are the total amounts of Sr^{2+} in the exchanger and in the solution, respectively. Although the rate was measured using a batch method, the infinite solution-volume approximation was closely obeyed under the present experimental conditions; the ratio of the total amount of Sr^{2+} in the exchanger to that in solution was less than 0.02, unless otherwise noted.

Results and Discussion

As has been previously reported,[2)] hydrous niobium (V) oxide has a large fractional pore volume (0.5) and the diameter of a large majority of the pores is around 2.3 nm, which is larger than the diameter of hydrated Sr^{2+} ions (repoted to be 1.9 nm[7)]). Since the pores, functioning as the main paths of the ions, occupy a large fraction of the total volume, the particles of hydrous niobium(V) oxide can be regarded as being homogeneous from the standpoint of kinetics.

Figure 1 shows the uptake curves for Na^+ and Sr^{2+}. The presence of buffer reagents (MES and TES) had no effect on the uptake of Sr^{2+}. The ion-exchange capacity was higher for Sr^{2+} than for Na^+ ions. Furthermore, the exchange sites interact much more strongly with Sr^{2+} than with Na^+, as is obvious from the isotherm of the exchange reaction between Sr^{2+} on the exchanger and Na^+ in the solutions (Fig. 2). It is considered that the larger positive charge on Sr^{2+}, which is localized more closely to the sites than Na^+, enhances the dissociation of neighboring sites, resulting in a larger ion-exchange capacity for Sr^{2+} than for Na^+. Table 1 shows the stoichiometry of the exchange reaction between H^+ and Sr^{2+} in the form of $\Delta[Sr^{2+}]_{ex}$, which means the amount of Sr^{2+} ions sorbed on the exchanger excess over the exchanged H^+ ions. We can see that the equivalency of the exchange is broken at a higher Sr^{2+} loading of the exchanger; that is, the amount of Sr^{2+} taken up is in excess over the exchanged H^+ ions beyond certain Sr^{2+} concentrations in solutions.

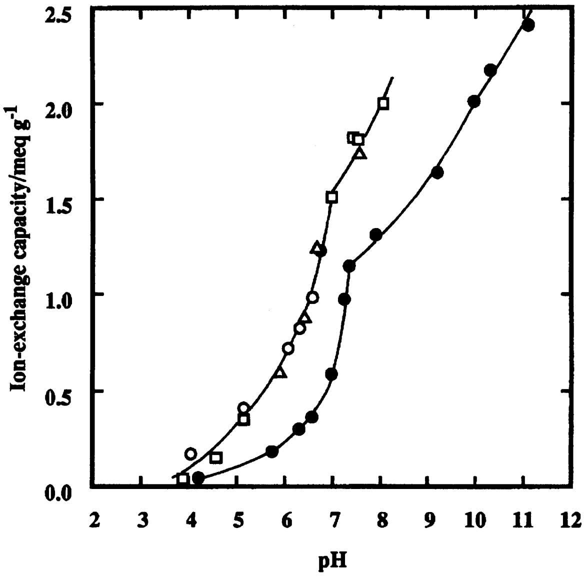

Fig. 1. Uptake curves for Na^+ and Sr^{2+} ions. m (exchanger amount)/V (solution volume) = 0.10 g/15 cm^3. The initial concentration of cations: 0.10 mol dm^{-3}. ●: NaCl–NaOH; ○: $SrCl_2$–$Sr(OH)_2$; △: $SrCl_2$–MES–$Sr(OH)_2$; □: $SrCl_2$–TES–$Sr(OH)_2$.

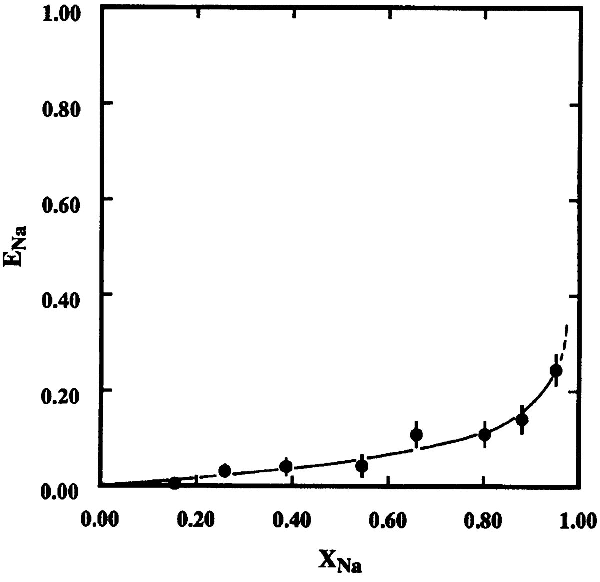

Fig. 2. Ion-exchange isotherm of the hydrous Nb^V oxide (Na^+/Sr^{2+} system). Exchanger, 0.050 g Sr^{2+}-form; Solution, 5 cm^3; Metal ion concentration, 0.1 mol dm^{-3}; pH=7.5±0.1. E_{Na}: Equivalent ionic fraction of Na^+ in the exchanger. X_{Na}: Equivalent ionic fraction of Na^+ in the solution.

When the isotopic exchange rate is controlled by the diffusion of ions in homogeneous spherical exchangers immersed in a well-stirred solution of approximately infinite volume (particle diffusion), the fractional attainment of equilibrium (F) can be obtained by solving the following equation:[8)]

$$F=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-Bn^2t), \qquad (1)$$

where

$$B=\pi^2\ D/r^2, \qquad (2)$$

D is the diffusion coefficient of the ions in the exchanger, and r the radius of the particles. When F is less than about 0.85, the Bt values can be calculated to a fairly good approximation from the measured values of F by

Table 1. Stoichiometry and D Value of Sr^{2+}/H^+ Exchange Reaction in Various Sr^{2+} Solutions

	pH 6.5			pH 7.5		
$[Sr^{2+}]_{sol}$ a) / mol dm^{-3}	$[Sr^{2+}]_{ex}$ b) / mmol g^{-1}	$\Delta[Sr^{2+}]_{ex}$ c) / mmol g^{-1}	D / $m^2\ s^{-1}$	$[Sr^{2+}]_{ex}$ b) / mmol g^{-1}	$\Delta[Sr^{2+}]_{ex}$ c) / mmol g^{-1}	D / $m^2\ s^{-1}$
0.05	—	—	—	0.770	0	8.6×10^{-13}
0.10	0.458	0	2.6×10^{-12}	0.819	0	8.7×10^{-13}
0.20	0.561	0	2.7×10^{-12}	0.882	0.08	1.4×10^{-12}
0.50	0.717	0.07	4.1×10^{-12}	1.016	0.13	2.2×10^{-12}

a): Sr^{2+}-concentration in the solutions. b): Sr^{2+}-exchange capacity. c): The amount of Sr^{2+} ions sorbed on the exchanger excess over the exchanged H^+ ions.

using the following equation derived by Reichenberg:9)

$$Bt = 2\pi - \frac{\pi^2}{3}F - 2\pi\left(1 - \frac{\pi}{3}F\right)^{1/2}. \qquad (3)$$

In this case, a plot of Bt against t gives a straight line passing through the point of origin.

Figure 3 shows the effect of particle size on the rate in a 0.1 mol dm^{-3} Sr^{2+} solution, indicating that the plot agreed well with this expectation for any particle size. As is shown in Fig. 4, B, thus obtained, was inversely proportional to the square of the particle radius, as expected from Eq. 2. The isotopic exchange rate is, therefore, controlled by the diffusion of Sr^{2+} in the exchanger particles.

The same is true in solutions with varing pH and Sr^{2+} concentration, as is shown in Figs. 5 and 6. Table 1 also gives the D values evaluated from the slopes of the lines on these figures by means of Eq. 2. The D values are constant up to a certain concentration of Sr^{2+}, wherefrom they begin to increase, and depend on the pH of the solutions. This behavior is different from that of Na^+ isotopic exchange.

As has been previously reported,2) the rate of the Na^+ isotopic exchange rate on the hydrous niobium (V) oxdie is independent of both the pH and Na^+ concentration in solutions. The diffusion coefficient of Na^+ in the exchanger (1.4×10^{-11} $m^2\ s^{-1}$) was higher by one order of magnitude than that of Sr^{2+} and constant over a wide conditions ($6.6 < pH < 11$, $[Na^+] > 0.1$ mol dm^{-3}). The difference in the isotopic exchange rate between Sr^{2+} and Na^+ cannot be understood by simply considering the size of two ions; both ions may not differ markedly from each other in the degree of interaction with the pore walls, since the size of hydrated ions (Sr^{2+} (1.9 nm) and Na^+ (1.6 nm)7)) is smaller than the pores and is not largely different from each other. We, therefore, must consider the difference in the interaction of these ions with the ion-exchange sites. As described earlier, Sr^{2+} ions interact much more strongly with dissociated sites in the exchanger than do Na^+ ions. Hence, it may be considered that Sr^{2+} ions are localized more closely

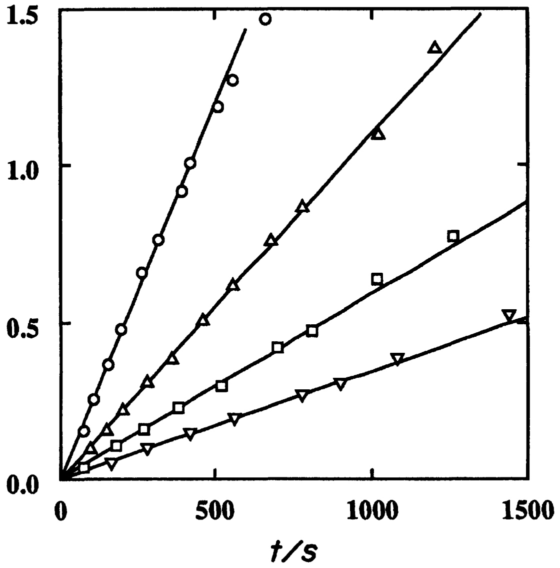

Fig. 3. Effect of particle size on the isotopic exchange rates (Bt–t plot). Temperature, 5 °C; 0.1 mol dm^{-3} Sr^{2+}-solution; pH, 7.5. Particle radius/μm, ▽: 164±7; □: 126±6; △: 87±1; ○: 57±4.

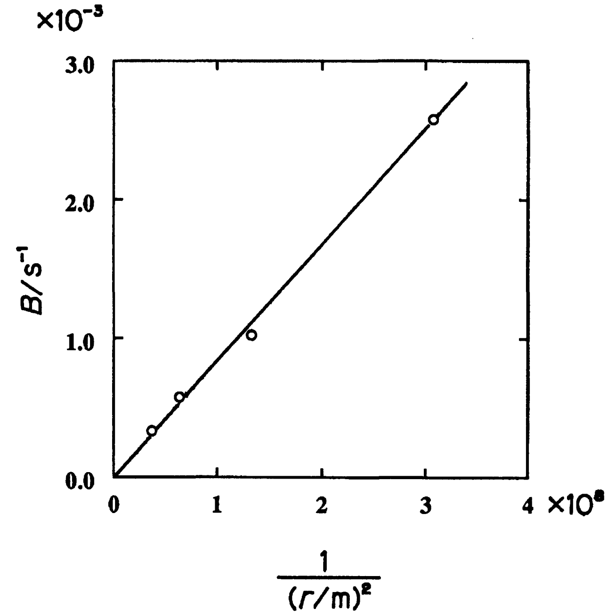

Fig. 4. Relation between particle radius (r) and B.

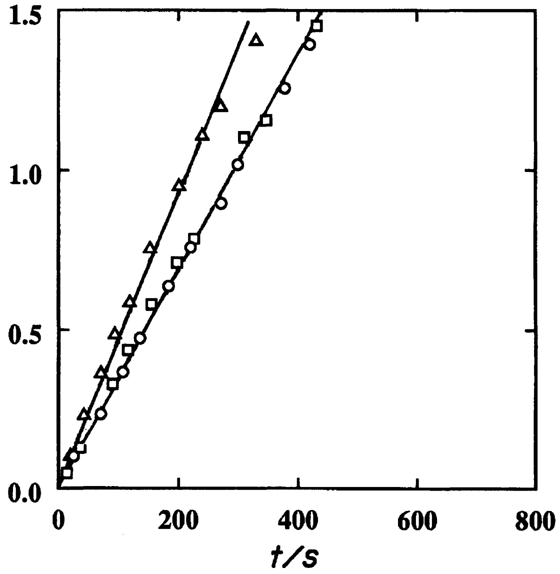

Fig. 5. Effect of Sr^{2+} concentration on the isotopic exchange rates (pH 6.5). Particle radius, 87±1 μm; Temperature, 5.0 °C; Sr^{2+} concentration/mol dm^{-3}, ○: 0.10; □: 0.20; △: 0.50.

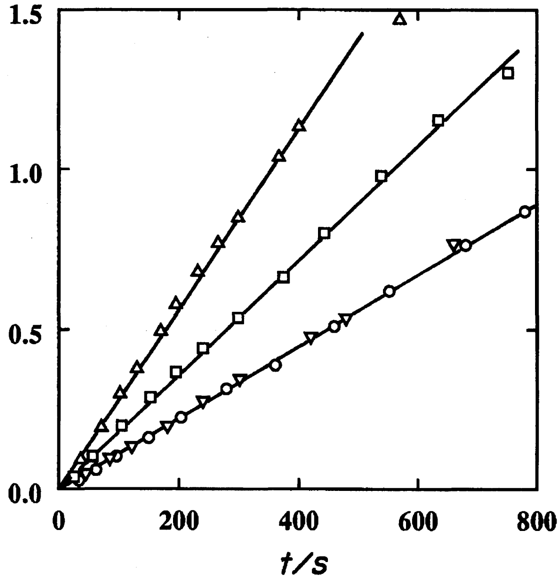

Fig. 6. Effect of Sr^{2+} concentration on the isotopic exchange rates (pH 7.5). Particle radius, 87±1 μm; Temperature, 5.0 °C; Sr^{2+} concentration/mol dm^{-3}, ▽: 0.05; ○: 0.10; □: 0.20; △: 0.50.

to the sites than Na^+, whose degree increases with the degree of site dissociation. This is the reason why the mobility of Sr^{2+} is smaller than that of Na^+, and is susceptible to any change in the pH of the solution.

The comparison of D and $\Delta[Sr^{2+}]_{ex}$ in Table 1 suggests a strong correlation between them; D increased with the Sr^{2+} concentration with the range where the exchanger took up an excess amount of Sr^{2+} over the exchanged H^+; it remained unchanged with the concentration with the range where the equivalence of the exchange held. The strong interaction of Sr^{2+} with anionic exchange sites makes such activity small, which facilitates the uptake of anions with Sr^{2+} into the exchanger phase (electrolyte sorption). The Sr^{2+} ions taken up by this mean are those sorbed in excess over the exchanged H^+ ions, and increase with pH due to the stronger interaction of Sr^{2+} ions at higher pH. The existence of mobile anions, thus introduced, relaxes any localized electrostatic interaction between cations and fixed anionic sites, and then accelerates the transport of cations. The degree of electrolyte sorption on the exchanger increases with the concentration of the electrolyte in bulk solution, resulting in a large increase of the exchange rates with the Sr^{2+} concentration. In 0.1 mol dm^{-3} Sr^{2+} solutions, where the electrolyte sorption was negligible, D decreased with increasing pH. Since the dissociation of exchange sites is enhanced with pH, Sr^{2+} ions should interact with larger numbers of the sites during diffusion throughout the exchanger, which reduces the mobility of ions.

The effect of temperature on the isotopic exchange rate was studied in a 0.1 mol dm^{-3} Sr^{2+} solution of pH 6.5 or 7.5. When ln D was plotted against $1/T$, a good linearity was obtained (Fig. 7). From the Arrhenius equation, $D=D_0\exp(-E_a/RT)$, the activation energy, E_a, and the constant, D_0, were determined (Table 2). The activation energy for Sr^{2+} diffusion in hydrous niobium(V) oxide increased slightly with pH, but was similar to that for Na^+ diffusion in the oxide. The similarity of E_a for the diffusion among these ions is reported for a strongly acidic ion-exchange resin.[10] This analogy suggests that, when cations are not bound chemically to ion-exchange sites, the activation process of the diffusion does not show any pronounced dependence on the strength of the electrostatic interaction

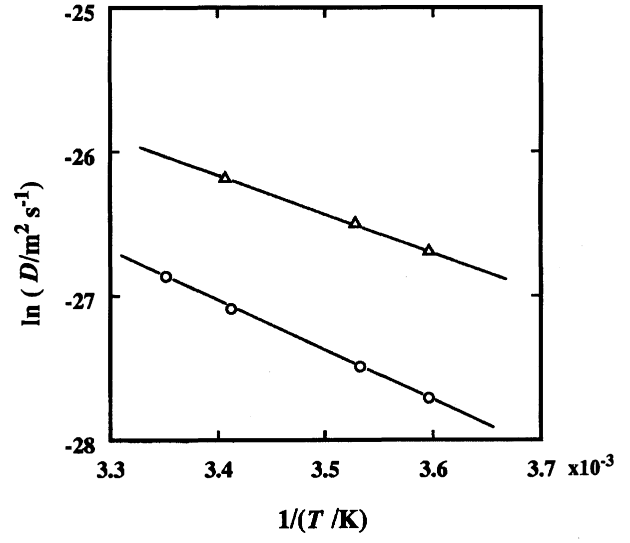

Fig. 7. Arrhenius plots of Sr^{2+} diffusion coefficients in the exchanger. Particle radius, 126±6 μm; 0.1 mol dm^{-3} Sr^{2+}-solution; pH, △: 6.5; ○: 7.5.

Table 2. E_a and D_0 for the Diffusion of Sr^{2+} and Na^+

Exchanger	Diffusing ion	E_a kJ mol^{-1}	D_0 m^2 s^{-1}	Reference
Hydrous	Sr^{2+} [a)]	22±4	2.2×10^{-7}	This work
Nb^V	Sr^{2+} [b)]	29±4	3.6×10^{-8}	This work
Oxide	Na^+ [c)]	27±4	2.3×10^{-6}	2
Sulfonated				
Polystyrene-type	Sr^{2+}	23.7	4.3×10^{-7}	10
Cation-exchanger[d)]	Na^+	20.7	3.4×10^{-6}	10

a) In 0.1 mol dm^{-3} Sr^{2+} solution of pH 6.5. b) In 0.1 mol dm^{-3} Sr^{2+} solution of pH 7.5. c) In 0.1 mol dm^{-3} Na^+ solution of pH 11. d) Divinylbenzene content, 4%.

between cations and anionic exchange sites. The D_0 for Sr^{2+} diffusion is, therefore, very small as compared with Na^+ diffusion, indicating that a strong electrostatic interaction between cations and exchange sites decreases the average distance between equilibrium positions in the diffusion process of the cations. The increase of E_a and the decrease of D_0 in a higher pH region, respectively, may be ascribed to an increase of the localized electrostatic interaction and to a decrease of the distance between the equilibrium positions in the diffusion process due to an increased density of the dissociated sites in the exchanger phase.

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