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The pH Titration Study of Lithium Ion Adsorption on λ-MnO_2

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The pH titration curves of λ-MnO_2 showed apparently dibasic acid character toward Li^+ ions, but a monobasic acid character toward Na^+, K^+, Rb^+, and Cs^+ ions. The adsorptive capacities of alkali metal ions increased in the order; K^+, Rb^+, $Cs^+ < Na^+ \ll Li^+$ at pH 10. Overall equilibrium constants were calculated by a simplified Gaines-Thomas equation from the titration curves based on the ion-exchange mechanism. Thermodynamic data were derived for the system of (0.1-M LiCl+LiOH)(1 M=1 mol dm^{-3}) at different temperatures. Effects of ionic strength and adsorption temperature on the lithium ion adsorptivity were studied using (LiCl+LiOH) and (KCl+LiOH) solutions.

Ion-sieve type manganese oxides show excellent selectivities for certain ions or group of ions.[1-7] They are prepared by a crystallization of manganese hydroxide containing metal ions, followed by a topotactic extraction of the metal ions with mineral acid. Their adsorptive properties depend on the kind of metal ions introduced as precursors into the manganese hydroxide.[2,6] When lithium and magnesium ions were used as introducing ions, the manganese oxides obtained show a remarkably high selectivity for lithium ions.[6,7] Their lithium-selective properties are closely related to the formation of such spinel-type materials as $LiMn_2O_4$ and $MgMn_2O_4$ during thermal crystallization while being prepared.

Recently, Hunter prepared spinel-type manganese oxide (λ-MnO_2) by extracting lithium from pure $LiMn_2O_4$ with acid.[8] Because of its uniform character, λ-MnO_2 is very suitable as a model compound for a fundamental study of the ion-sieve effect for metal ions extracted from the aqueous phase. In a previous paper, its adsorptive properties for various metal ions showed a remarkably high selectivity for lithium ions in a range above pH 2.5.[9] The metal-ion uptake at pH 10 reached about 5 meq·g^{-1} for lithium ions but less than 0.2 meq·g^{-1} for potassium and cesium ions. The distribution coefficients (K_d's) of metal ions at pH 4 were in the order $Na^+ < K^+ < Rb^+ < Cs^+ \ll Li^+$ for alkali metal-, $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ for alkaline earth metal-, and $Ni^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+}$ for transition metal-ions. These results are readily explained if we recognize that the tetrahedral vacant sites in λ-MnO_2 are too narrow for metal ions other than lithium to enter. The only species which can enter these sites are H^+ and dehydrated Li^+ ions.

The present paper describes a pH titration study on λ-MnO_2 for alkali metal ions. The selectivity constants and overall thermodynamic constant were evaluated from the titration data based on the ion-exchange model. Acid-base properties have been investigated for different types of manganese oxides from electrochemical[10,11] and geochemical[12-14] interests and for the fundamental study of the adsorption phenomena.[15,16]

Experimental

Ion-Exchange Material and Characterization. The λ-MnO_2 used was the same as that described in a preceding paper.[8] It was prepared by the acid treatment of $LiMn_2O_4$ with a 1-M HNO_3 solution. The lithium content of the acid-treated sample was 0.12 meq·g^{-1}, indicating that more than 97% of the lithium was extracted from the $LiMn_2O_4$ by the acid treatment. A powdered X-ray diffraction analysis showed λ-MnO_2 of a spinel type structure with an 0.800-nm lattice constant on a cubic unit cell.

pH Titration Curve. A weighed amount (0.100 g) of the λ-MnO_2 was immersed into a mixed solution (10 cm^3) of (MCl+MOH) (M=Li, Na, K, Rb, Cs) in varying ratios with intermittent shaking at 25 °C. The concentration of MCl was adjusted to 0.1 M. After shaking for 3 weeks, the pH of the supernatant solution was determined in a decarbonated atmosphere. The kinetic study showed that three weeks were sufficient to attain a constant pH value. The metal ion concentration in the supernatant solution was determined by atomic absorption spectrometry. The metal ion uptake by λ-MnO_2 was evaluated from the difference between the initial and equilibrium concentrations of the metal ion in the solution or from determining metal ions after dissolving metal ion-adsorbed λ-MnO_2 with a mixed solution of concentrated HNO_3 and HCl. The chloride ion uptake was determined by ion chromatography after dissolving the λ-MnO_2 with a mixed solution of H_2O_2 and H_2SO_4.

In the case of lithium ion adsorption, the effects of ionic strength and adsorption temperature were examined in (KCl+LiOH) and (LiCl+LiOH) systems in addition to the above titration.

Apparatus. X-Ray diffraction analysis was carried out with a Rigaku Denki X-ray diffractometer (model Rad II) using Ni filtered Cu $K\alpha$ radiation(graphite monochrometer). A Perkin-Elmer atomic absorption spectrophotometer (model 403) was employed for atomic absorption spectrometry and a Horiba M8s pH meter for pH measurement. A Dionex Ion Chromatograph apparatus (model 10) was used for ion chromatography.

Reagents. All the chemicals were of an analytical grade from Wako Pure Chemical Ind. Ltd., except for RbCl, RbOH, and CsOH which were obtained from Merck Ltd. These were used without further purification.

Results and Discussion

pH Titration Curves. The pH titration curves and pH dependences of metal ion uptakes are shown in Fig. 1. A remarkable difference was obtained between a (LiCl+LiOH) system and the other metal salt systems on the pH titration curve. The pH titration curve in the (LiCl+LiOH) system (Fig. 1, top right) showed a dibasic acid charactor. The apparent capacity of Li^+ was found to be about 5 meq·g^{-1} on the pH titration curve. The supernatant solutions at pH>8 had a slightly purplish color due to the presence of a small amount of Mn(VII) ions. Their concentration was less than 5×10^{-4} M by atomic absorption spectrometry. Smaller differences than the Li-system were observed between the pH titration curves for the other systems and for the blank experiment. A small apparent capacity of 0.2 meq·g^{-1} was obtained even on the system of (NaCl+NaOH). The supernatant solutions were colorless over the pH ranges studied.

The apparent capacities determined by metal ion uptakes were nearly equal to those obtained by the differences between the blank run and each titration curve (Fig. 1(B)). This suggests that the metal ion adsorption proceeds by an ion-exchange mechanism. The apparent adsorptive capacity increased in the order: Na, K, Rb, Cs≪Li at pH values below 7. The affinity order changed to K, Rb, Cs<Na≪Li above pH 7, probably due to the large steric effect for large unhydrated cations (K, Rb, Cs) at higher pH. The chloride ion uptakes were found to be less than 0.01 meq·g^{-1} over the pH range studied. The affinity orders in the present study showed large differences from those on other types of manganese oxides. For example, cryptomelane-type hydrous manganese(IV) oxide(CRYMO) shows the affinity orders; Li< Na<Cs<Rb<K at pH 2 and Cs<Rb<Na<Li<K at pH 10,[16] and the layered hydrous manganese oxide ($H_4Mn_9O_{18}\cdot7H_2O$) Li<Na<K at pH<4 and K< Na<Li at pH>5.[5]

The difference in the affinity order between λ-MnO_2 and CRYMO can well be understood based on the difference in crystal structure. Cryptomelane-type manganese oxide has [2×2] tunnels of edge-shared MnO_6 octahedra.[17] Tsuji and Abe have pointed out that these [2×2] tunnels are very suitable to fix the metal ions with an effective ionic radius of 0.14 nm (K^+, Rb^+, Ba^{2+}).[4] Our result agrees in showing that the manganese oxides with [2×2] tunnels have high selectivities for Rb^+ and K^+ ions.[6] The λ-MnO_2 in H^+ form can be derived from the spinel structure of $LiMn_2O_4$.[18] The cubic $LiMn_2O_4$ spinel (lattice parameter a_0) contains eight formula units and has its close-packed array of

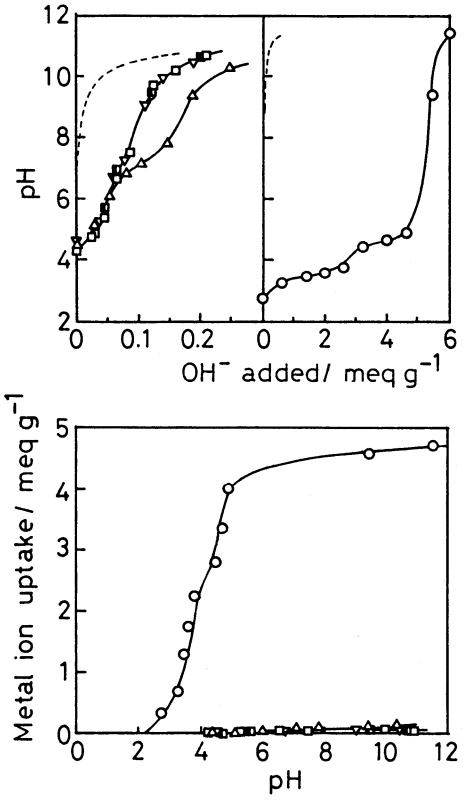

Fig. 1. pH titration curves of λ-MnO_2 by various bases and the pH dependences of metal ion uptake. λ-MnO_2: 0.100 g, soln: (0.1-M MCl+MOH) (M=Li(○), Na(△), K(□), Rb(▽), and Cs(■)), total vol. of soln: 10 cm³, temp: 25 °C. The dotted lines describe blank titrations.

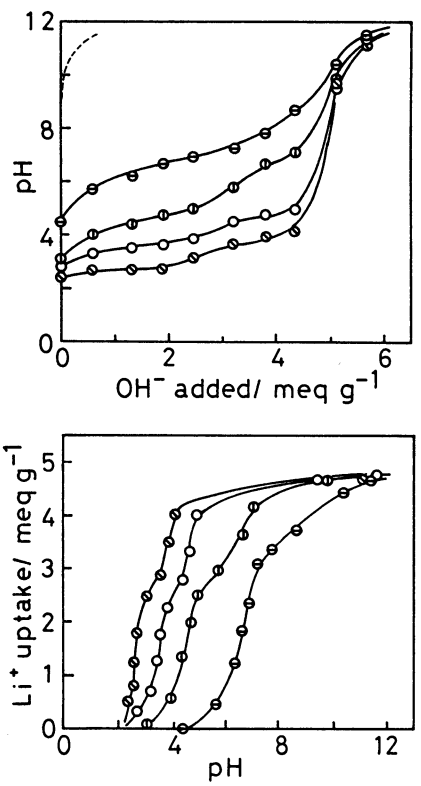

Fig. 2. pH titration curves of λ-MnO_2 toward lithium ions and the pH dependences of lithium ion uptakes. λ-MnO_2: 0.100 g, soln: (LiCl+LiOH) (concn of LiCl: 0 M(⊖), 0.01 M(Φ), 0.1 M(○), 1 M(⊘)), total vol. of soln: 10 cm³, temp: 25 °C.

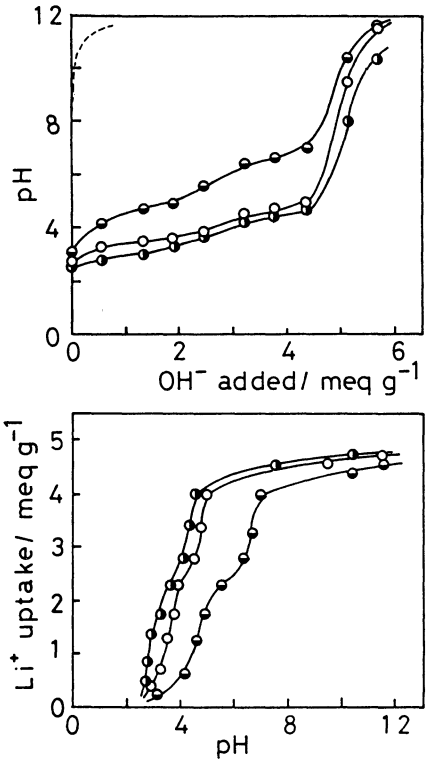

Fig. 3. pH titration curves in (0.1-M LiCl+LiOH) solution and the pH dependences of lithium ion uptakes. The experimental conditions are the same as those in Fig. 2 except for adsorption temperature. Temp: 10°C(◒), 25°C(○), 40°C(◑).

oxygens located at the 32e positions of the space group $Fd3m(O_h^7)$.[19] The Mn^{3+} and Mn^{4+} ions occupy half the octahedral sites, and the Li^+ ions an eighth of the tetrahedral sites. The acid treatment of $LiMn_2O_4$ causes the removal of nearly all of the lithium from the tetrahedral sites while maintaining a spinel structure.[8] Therefore, λ-MnO_2 has a structure that is related to spinel but with vacant tetrahedral sites. Since the size of the vacant sites is markedly smaller than the width of the [2×2] tunnels, it is reasonable to consider that the vacant sites are too narrow to hold the alkali metal ions except lithium even in a dehydrated state. Therefore, the pH titration curves for Na^+, K^+, Rb^+, and Cs^+ ions suggests that the ion-exchange reactions proceed only at the surface of the λ-MnO_2 particles.

The pH Titration Curves in (LiCl+LiOH) Solutions. Figure 2 illustrates the pH titration curves in (LiCl+LiOH) solutions with different LiCl concetrations. The pH titration curve shifts to lower pH range with increasing LiCl concentration. Figure 3 showed that the titration curve shifted to lower pH range with increasing adsorption temperature in the system of the (0.1-M LiCl+LiOH). The maximum lithium ion uptake can be estimated to be 4.75 meq·g^{-1} from Figs. 2 and 3, which is somewhat smaller than the value that is expected from the chemical formula of $LiMn_2O_4$ (5.7 meq·g^{-1}).

The previous paper indicated that the lattice constant (a_0) of the spinel structure increased by adsorption of lithium ions.[9] A similar tendency was also observed in the present study. The a_0 value calculated from the d_{111} peak of the X-ray diffraction pattern is plotted against $\overline{X}_{Li}$ ($\overline{X}_{Li}$ in Fig. 4: Equivalent fraction of lithium ions in λ-MnO_2=lithium ion uptake/ maximum lithium ion uptake). There was a difference in a_0 vs. $\overline{X}_{Li}$ curves between $\overline{X}_{Li}<0.5$ and $\overline{X}_{Li}>0.5$. The curve was sigmoidal at $\overline{X}_{Li}<0.5$ with steep slope around $\overline{X}_{Li}=0.25$. The a_0 value increased gradualy with increasing $\overline{X}_{Li}$ in a range of $\overline{X}_{Li}>0.5$. The lithium ion uptake vs. pH curves (Fig. 2) showed a pH rise at the boundary of the two curves ($\overline{X}_{Li}=0.5$). These results suggest that the mode of the insertion reaction of lithium ions differed slightly between $\overline{X}_{Li}<0.5$ and $\overline{X}_{Li}>0.5$. The presence of a stable $Li_{0.5}Mn_2O_4$ species has been observed in the case of the electrochemical removal of lithium from $LiMn_2O_4$; the removal of lithium proceeds easily to $Li_{0.5}Mn_2O_4$ but further electrochemical extraction becomes more difficult.[19]

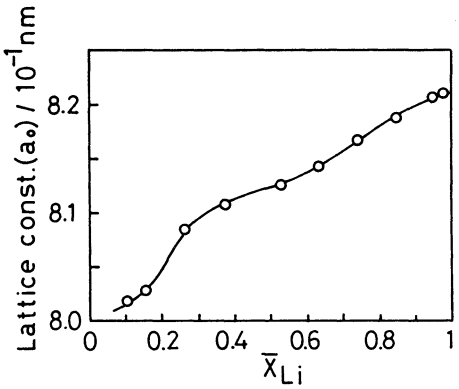

Fig. 4. Lattice constant of spinel structure as a function of $\overline{X}_{Li}$. Ion-exchanged λ-MnO_2 are obtained from (1-M LiCl+LiOH) solution at 25°C.

The pH Titration Curves in (KCl+LiOH) Solutions. Figure 5 illustrates pH titration curves in (KCl+LiOH) solutions with different KCl concentrations. The pH titration curve and the lithium ion uptake curve were scarcely influenced by the addition of KCl in a range below pH 7. This indicates that the sites for lithium ion adsorption are very specific and are scarcely influenced by the presence of potassium ions. In the range above pH 7, the pH titration curve showed a tendency to shift to lower pH values by the addition of KCl, and the lithium ion uptake to increase. The increase of the lithium ion uptake may not be due to a Li^+-K^+ exchange, because the lithium ion uptake decreases with KCl concentration in the case of competing exchange between lithium and potassium ions. The pH titration curves suggest that the λ-MnO_2 has negative charge at pH>5. Therefore, both the decrease of the pH value and the increase of the lithium ion uptake may be due to a decrease of the negative potential at the surface of λ-MnO_2 by the addition of KCl. The decrease of pH with increasing

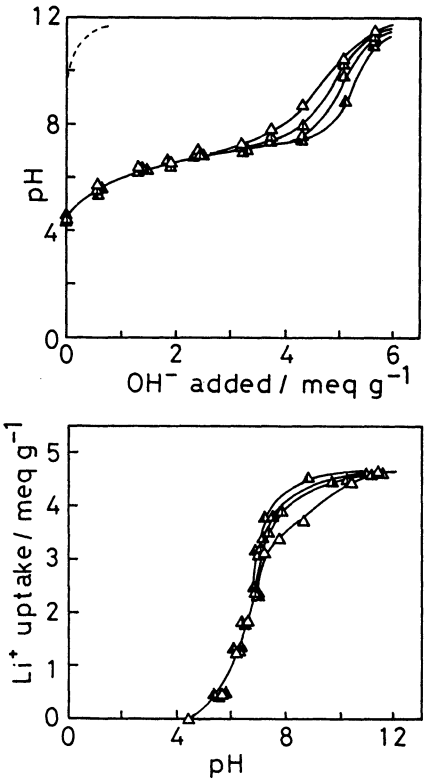

Fig. 5. pH titration curves in (KCl+LiOH) solutions and the pH dependences of lithium ion uptakes. The experimental conditions are the same as those in Fig. 2 except for KCl concentration. KCl concn: 0 M(△), 0.03 M(▲), 0.1 M(▲), and 1 M(▲).

salt concentration usually occurs in aqueous phase for negatively charged metal oxides owing to a decrease of the surface negative charge.[14,20]

Analysis Based on the Model of Ion-Exchange Reaction. The pH titration data can be analyzed on the basis of the ion-exchange mechanism as follows,

$$\bar{H}^+ + M^+ \rightleftarrows \bar{M}^+ + H^+ \quad (1)$$

where bar refers to H^+ or M^+ in λ-MnO_2 and M^+ is monovalent alkali metal ions. The equilibrium constant, K, of the above reaction is defined as,

$$K=[a_H(\bar{f}_M\bar{X}_M)]/[a_M(\bar{f}_H\bar{X}_H)]=K_C(\bar{f}_M/\bar{f}_H) \quad (2)$$

where a_H and a_M are activities of protons and metal ions in solution, respectively, $\bar{X}_H$ and $\bar{X}_M$ are the equivalent fractions of H^+ and M^+ in the λ-MnO_2, respectively, and $\bar{f}_H$ and $\bar{f}_M$ are the activity coefficients of H^+ and M^+ in the λ-MnO_2 phase, respectively. K_c is the selectivity constant including the activity coefficient of the metal ions in solution. It can be evaluated from the pH titration data as follows,

$$\begin{aligned} pK_C=-\log K_C &= -\log[(a_H\bar{X}_M)/(a_M\bar{X}_H)] \\ &= pH-\log[\bar{X}_M/(1-\bar{X}_M)]+\log a_M. \end{aligned} \quad (3)$$

In the case of a uni-univalent ion-exchange system, the contribution of the activity coefficient term in aqueous solution does not deviate seriously even over a temperature range from 283 to 313 K. Therefore, Eq. 3 can be related to the concentration term of metal ions (C_M) of Eq. 4,

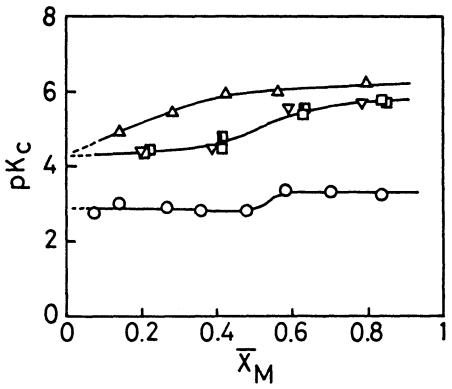

Fig. 6. pK_c vs. $\bar{X}_M$ plots calculated from Fig. 1. The symbols are the same as those in Fig. 1.

$$pK_C \doteqdot pH-\log[\bar{X}_M/(1-\bar{X}_M)]+\log C_M. \quad (4)$$

The K value and standard free energy change ($\Delta G°$) can be evaluated by using the simplified treatment of the Gaines-Thomas equation, assuming that the change of water content in the exchanger and the entrance of anion from the solution phase are negligible,[21]

$$pK = -\log K = \int_0^1 pK_C\, d\bar{X}_M \quad (5)$$

$$\Delta G° = (2.303\,RT)\,pK \quad (6)$$

pK_c vs. $\bar{X}_M$ Plots. Figure 6 illustrates a plot of pK_c vs. $\bar{X}_M$ in (MCl+MOH) system using Eq. 4. The maximum uptakes ($\bar{X}_M$ =1) of the metal ions were estimated as 4.75 meq·g^{-1} for Li^+, 0.18 meq·g^{-1} for Na^+, and 0.10 meq·g^{-1} for K^+, Rb^+, and Cs^+, respectively. The pK_c value was nearly constant (2.9) for Li^+/H^+ exchanges in the range below $\bar{X}_{Li}<0.5$ while it increased to 3.4 at $\bar{X}_{Li}>0.5$. This indicates the presence of two types of adsorption sites with slightly different affinities for lithium ions. The pK_c values showed a tendency to increase with increasing $\bar{X}_M$ for the other M^+/H^+ exchanges, probably due to an increase of negative surface charge with $\bar{X}_M$. The selectivity constant at $\bar{X}_M$=0 (pK_0) could be estimated by extrapolating pK_c value to $\bar{X}_M$=0 (Table 1).

Figure 7 illustrates the pK_c vs. $\bar{X}_{Li}$ plots in (LiCl+LiOH) and (KCl+LiOH) solutions. The pK_0 values were nearly equal (2.9—3.2) regardless of the salt species and salt concentration (Table 1). In the range above $\bar{X}_{Li}>0.5$, the pK_c value showed a tendency to decrease with increasing salt concentration. Since the decrease of pK_c in the (KCl+LiOH) system corresponds to the decrease of the pH with KCl concentration, the decrease may be partly due to the decrease of surface negative potential by the addition of neutral salt.

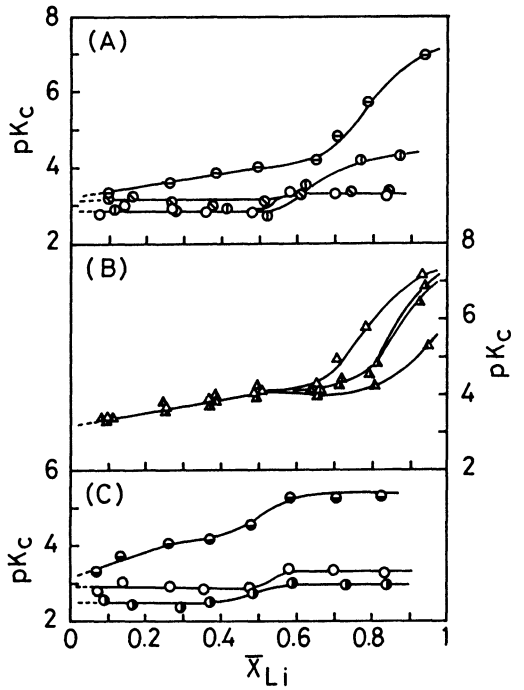

Fig. 7. pK_c vs. $\bar{X}_{Li}$ plots. Figures 8(A), 8(B), and 8(C) are calculated from Figs. 2, 5, and 3, respectively. The symbols are the same as those in the corresponding figures.

Table 1. Values of pK_0, pK, and $\Delta G°$ for λ-MnO_2

System	Concentration of added salt / mol dm^{-3}	T / °C	pK_0	pK	$\Delta G°$ / 10^3J mol^{-1}
LiCl+LiOH	0	25	3.23	4.53	25.9
	0.01	25	2.96	3.40	19.4
	0.1	25	2.91	3.13	17.9
	0.1	10	3.08	4.64	26.5
	0.1	40	2.58	2.74	16.4
	1	25	3.11	3.24	18.5
KCl+LiOH	0.03	25		4.33	24.7
	0.1	25	3.23	4.29	24.5
	1	25		4.01	22.8
NaCl+NaOH	0.1	25	4.2	5.8	33
KCl+KOH	0.1	25	4.2	5.1	29
RbCl+RbOH	0.1	25	4.2	5.1	29
CsCl+CsOH	0.1	25	4.2	5.1	29

Calculation of Equilibrium Constant. The pK values calculated using Eq. 5 and the $\Delta G°$ values are given in Table 1. The $\Delta G°$ value for Li^+/H^+ exchange showed tendencies to decrease with salt concentration and to decrease with adsorption temperature. The standard enthalpy and entropy changes ($\Delta H°$ and $\Delta S°$) at 298 K could be evaluated from the temperature dependence of $\Delta G°$ by the usual method. The $\Delta H°$ value, estimated with least square method, was 120 kJ per mole of lithium and a corresponding $\Delta S°$ 300 J K^{-1} mol^{-1}. Both of the $\Delta H°$ and $\Delta S°$ values were positive and were larger than those of Li^+/H^+ exchanges on another type of inorganic ion exchangers.[22,23] The positive $\Delta G°$ values may possibly arise from the increase of the volume of the unit cell and of water transfer to the aqueous solution from the exchanger with increasing adsorption of lithium ions at the tetrahedral vacant sites. Further study may be needed to determine the alternative contribution for $\Delta S°$ in this system.

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