Phase separation in hydrated LTA zeolite

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Abstract

The coexistence of two distinct phases, $[Li_{0.08}(NH_4)_{0.92}]$- and $[Li_{0.32}(NH_4)_{0.68}]$-A, was observed for a mixed crystal of $[Li_x(NH_4)_{1-x}]$-A of LTA (Linde type A) zeolite in the range of 0.08 < x < 0.32 at 295 K, where -A denotes the aluminosilicate framework of LTA containing water molecules. In contrast, for x < 0.08 and x > 0.32, a uniform monophase was observed for the mixed crystal. The coexistence of the separated phases was deduced from ion-exchange-isotherm measurements at 295 K and thermodynamic analyses. Spinodal and binodal curves were obtained. The monophasic and biphasic states were confirmed by powder X-ray diffraction. The excess Gibbs energy and the excess volume of $[Li_x(NH_4)_{1-x}]$-A were unsymmetrical with respect to x = 1/2. The Li ions favored specific ion-exchange sites. The preferential occupation of Li ions in the six-membered oxygen ring of $[Li_x(NH_4)_{1-x}]$-A was proved by Li-isotope measurements, and was demonstrated by *ab initio* molecular orbital calculations. The separation of two LTA-phases due to ordered Li-occupation within the six-membered oxygen rings is discussed.

Keywords: spinodal; ion-exchange thermodynamics; X-ray diffraction; isotopic effect; *ab initio* molecular orbital calculations

1. Introduction

The LTA (Linde type A) zeolite is a microporous crystal that is formed from aluminosilicate cages and ion-exchangeable cations with volatile water molecules[1]. The chemical formula of LTA is expressed as $M_{12/m}[(AlO_2)_{12}(SiO_2)_{12}] \cdot n\ H_2O$, where M represents the ion-exchangeable cations of charge m, and n varies from 20 to 30 (Hereafter the above formula is abbreviated as M-A). Aluminum and silicon atoms are alternately arranged through an oxygen atom forming oxygen-atom rings and cage structures (Fig. 1). These ring and cage structures of various LTA crystals were originally ascribed to be rigid. The lattice constant of a pseudo-cell (Pm3m) of LTA (Fig. 1) was nearly constant ($a = 1232\pm6$ pm)[2], independent of dehydration and

hydration, and was practically unaltered by complete or partial ion-exchange with various cations (Na, K, Cs, Tl, Ag, Mg, Ca, Sr,) [2,3]. However, the detailed X-ray studies revealed that LTA framework-angles are not strictly rigid. The appreciable changes in the framework angles (Si-O-Al), corresponding to the rotations of SiO_4 and AlO_4 unites, were observed upon the dehydration of several LTA zeolites (Tl-A [4], Na-A [5], K-A [6], and $Cs_{0.58}Na_{0.42}$-A [7]). The framework-angle-flexibility of zeolites is clearly described in a recent literature [8] to account for the mechanism of the structural phase transformation of Li-LSX (Li-faujasite with Si/Al = 1) at low temperature.

Significant short length of the cubic LTA pseudo-cell was observed for hydrated $[Li_{0.67}Na_{0.33}]$-A (a = 1204 pm) [9], dehydrated Li-A (a = 1210.5 pm) [2], and a molten salt contained $Li_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 9.8LiNO_3 \cdot 9.3 H_2O$ (a = 1207.5 pm) [10]. The internal molecules in the large cage did not resist the cell length to shrink from the normal size (a = 1232±6 pm). In the case of the hydrated LTA zeolites (Tl-A, Na-A, K-A, and $Cs_{0.58}Na_{0.42}$-A), the water molecules sustain the normal Si-O-Al angles and cell length [7]. The above hydrated $[Li_{0.67}Na_{0.33}]$-A showed the appreciable size reduction (the lattice constant: ca. −2%; the volume: ca. −8%). This suggests that the small size of Li ion strongly attracts the oxygen atoms with the rotations of AlO_4 and SiO_4 tetrahedra, and causes the shrinkage over the framework. A wide variation of Si-O-Al angles of the framework was confirmed in dehydrated $[Li_{0.75}Na_{0.25}]$- and dehydrated $[Li_{0.81}Na_{0.19}]$-A by X-ray and neutron diffraction [11]. The strong interaction between a Li ion and the oxygen atoms of the six-membered oxygen ring of hydrated Li-A was evident in infrared and Raman spectroscopy [12]. The rotation behavior of AlO_4 and SiO_4 tetrahedra of the six-membered oxygen ring of Li-X (faujasite) was clearly illustrated in a recent neutron diffraction study [8].

Recently, a study using chromatography has suggested the coexistence of two distinct solid phases in $[Li_x(NH_4)_{1-x}]$-A [13]. The biphasic behavior were qualitatively deduced form the phase rule and the pseudo-selectivity-coefficient. In addition to this thermodynamic analysis, structural evaluation for the two phases will be important. In the phase separation of (Na_xSr_{1-x})-X,

the distinct two solid-phases of $(Na_{0.29}Sr_{0.71})$- and $(Na_{0.13}Sr_{0.87})$-X were proved by X-ray diffraction [14]. Relocation of Na and Sr cations in the crystal sites was suggested for the phase separation mechanism.

For the mechanism of the phase separation of $[Li_x(NH_4)_{1-x}]$-A, the cooperative distortion of the six-membered oxygen rings caused by Li occupation may be an origin. The zeolite framework shows flexibility in a certain extent; however phase-separation phenomena have been unusual in almost all zeolites. Therefore the definite confirmation of the phase separation of $[Li_x(NH_4)_{1-x}]$-A and the corresponding framework flexibility are the subjects of the present investigation.

The phase-separation thermodynamics of $[Li_x(NH_4)_{1-x}]$-A was studied using ion-exchange equilibrium experiments. The separated phases and the lattice-flexibility were directly clarified through powder X-ray diffraction measurements. The positions of the Li^+ and NH_4^+ ions within the zeolite were hypothesized by thermodynamics and by Li isotopic measurements. *Ab initio* molecular orbital calculations were also carried out to interpret the experimental isotopic results and to support the hypothetical Li-sites.

2. Experimental

2. 1. Ion exchange

Experiments utilized homogeneous fine powder (ca. 10 μm) of NH_4-A, which was prepared from Na-A (Tosoh) by ion-exchange [13]. At the final process of the ion-exchange, to remove the excess amount of NH_3 within the column voids, a dilute solution (ca. 40 mM) of NH_4NO_3 at pH 8 prepared by mixing acid (HNO_3) and base (NH_3) was fed onto a $[Na_x(NH_4)_{1-x}]$-A column until every Na ion was replaced with NH_4^+ ions.

The prepared NH_4-A hydrated powder and a solution of $LiNO_3$ at pH 8 made from LiOH and HNO_3 were mixed at room temperature (295 ± 1 K). Ion-exchange equilibrium between $[Li_x(NH_4)_{1-x}]$-A and $LiNO_3$ or NH_4NO_3 solutions was attained by the procedures listed in Table 1.

In the case of Entry 3, a mixed crystal of $[Li_x(NH_4)_{1-x}]$-A was obtained by the single ion-exchange between

certain amounts of NH_4-A and of $LiNO_3$ solution. To reach different points of equilibrium within an isotherm, various quantities of zeolites and solutions were used.

For Entries 1 and 2, filtered $[Li_x(NH_4)_{1-x}]$-A was remixed with a new solution of $LiNO_3$. The remix processes were repeated until a large value of x was attained. In the case of Entry 2, the number of initial samples (NH_4-A) was seven. Each sample was ion-exchanged with different numbers of repetitive remixing. Entry 4 is a reverse procedure.

In every experiment, the ionic strength of the aqueous solution was maintained as almost constant, thus minimizing the changes in the activity coefficients of the cations in the aqueous solution due to ion exchange. A shaking time of one hour was deemed sufficient for attaining equilibrium.

For Entries 2 and 3, the concentration of Li ([Li]), and NH_4 ($[NH_4]$) were determined for both phases after every filtration. Zeolite solids were dissolved in HNO_3 for the measurements. For Entries 1 and 4, [Li] and $[NH_4]$ were determined for every filtered solution, and only on the zeolite solid after the final filtration. A flame emission spectrometer (Shimadzu AA650) and an ammonia-selective-electrode (TOA Electronics Ltd. IM-55G) were used to measure [Li] and $[NH_4]$, respectively. All chemicals used in the experiments were reagent grade.

2. 2. X-ray measurements

X-ray diffraction patterns from hydrated $[Li_x(NH_4)_{1-x}]$-A powders were measured in $5° < 2\theta < 50°$, using a Cu-K_α source and diffractmeter (Rigaku Denki Co. model 2012). For determination of the lattice constant, a small amount of Si powder was mixed with the hydrated zeolite sample as an internal standard for the correction of diffraction angles. The X-ray samples were separately prepared following similar method as for Entries 1 and 4. For preparation of the samples with high-x values (x > 0.7), a column process was employed. Ion chromatography (Shimadzu HIC-6A) was used for the determination of x.

2. 3. Isotopic measurements

Lithium isotopic concentration ratios in solutions, $([^7Li]/[^6Li])_{aq}$, and in solids, $([^7Li]/[^6Li])_{solid}$, were measured for Entries 2 and 3, using a thermal ionization mass spectrometer (Finnigan MAT 262). Lithium ions in the zeolite solids were extracted with NH_4NO_3. Residual NH_4NO_3 in the extract solution was removed by heating. Moderate heating processes had minimal effects on the $[^7Li]/[^6Li]$ values [13]. Samples of $LiNO_3$ with a small addition of $Ca(NO_3)_2$ were used for the isotopic measurements. The separation factor, $\alpha = ([^7Li]/[^6Li])_{aq}/([^7Li]/[^6Li])_{solid}$, was determined as a function of x.

2. 4. Ab initio methods

The lithium isotope separation by ion exchange is a quantum effect of molecular vibrations. The partition function product ($Q = q_{trans}q_{rot}q_{vib}$) ratio of the isotopic substitution ($Q(^7Li) / Q(^6Li)$) is simply expressed by normal mode frequencies and vibrational partition functions [15-17]. Accordingly, the lithium isotope separation factor (α) is defined using the frequencies and isotopic shifts of Li oscillations in both phases at room temperature [13].

$$K = \frac{Q_S(^6Li)\,Q_W(^7Li)}{Q_S(^7Li)\,Q_W(^6Li)} = \alpha \approx 1 + \frac{1}{12}\left(\frac{hc}{kT}\right)^2 \delta \qquad (1)$$

$$\delta = \sum_{\substack{normal \\ modes}} \nu(W)_{av}\Delta\nu(W) - \sum_{\substack{normal \\ modes}} \nu(S)_{av}\Delta\nu(S)$$

$$(2)$$

$$= \sum_{\substack{Li\ oscil. \\ modes}} \nu_{Li}(W)_{av}\Delta\nu_{Li}(W) - \sum_{\substack{Li\ oscil. \\ modes}} \nu_{Li}(S)_{av}\Delta\nu_{Li}(S)$$

In the above expressions, W and S denote water and solid phase, respectively, and av denotes the average wave number for the oscillation of lithium isotopes: $\nu_{Li}(X)_{av} = [\nu_{^7Li}(X) + \nu_{^6Li}(X)]/2$, where X = W or S. The wave number shifts for isotopic substitution ($\Delta\nu_{Li}$) are defined as positive. The notations of h, c, k, and

T are the Planck constant, the speed of light, the Boltzmann constant, and temperature, respectively.

The frequencies for the normal modes involving the lithium oscillation were evaluated using *ab initio* molecular orbital calculations (Gaussian 94 [18]). Four model molecules, $[LiOH_2][H_3SiOAlH_3]$, $[Li(OH_2)_2][H_3SiOAlH_3]$, $[LiOH_2][H_3SiOAlH_2OSiH_3]$, and $[Li(OH_2)_2][H_3SiOAlH_2OSiH_3]$, which represent the local atomic arrangement around the Li ion standing on the eight-membered oxygen ring, were utilized in the present study. Previously calculated results [13] were used for the lithium tetrahydrate ion and a ring-molecule ion which represent the Li ion in aqueous solution and the local atomic arrangement around the Li ion of the six-membered oxygen ring, respectively.

In the *ab initio* calculations, molecular geometry optimization and vibrational frequency determination were performed under the Hartree-Fock self-consistent field using the 6-31+G* basis set functions. The vibrational frequencies were corrected by multiplying 0.8929 as a scale factor to take the electron correlation effect into account [19].

3. Results

3. 1. Ion-exchange equilibrium

Molar fraction of Li in solution (y), plotted as a function of that in zeolite (x), is shown in Fig. 2 (ion-exchange isotherm). With forward and reverse ion-exchanges, the plot exhibited hysteresis, in which two plateaus of different heights were observed in the range of 0.1 < x < 0.3. In the range of x > 0.3, the isotherm was independent of the experimental procedures given in Table 1.

The selectivity coefficient ($k_{Li/NH4}$) of the ion-exchange between Li^+ and NH_4^+ is defined [20] as

$$k_{Li/NH4} = \frac{x(1-y)}{(1-x)y} \tag{3}$$

The logarithmic selectivity-coefficient ($\ln k_{Li/NH4}$) was plotted, as shown in Fig. 3. A fifth order polynomial, expressed as

$$\ln k_{Li/NH4} = \sum_{n=0}^{5} a_n x^n$$

$$(4),$$

$$= -1.52 - 15.4\ x + 201\ x^2 - 677\ x^3 + 870\ x^4 - 387\ x^5$$

was fitted on the $\ln k_{Li/NH4}$ data (Fig. 3). The polynomials up to the second, third, fourth, and higher than seventh order did not agree with the observed $\ln k_{Li/NH_4}$ variation.

Equation (3) can express the isotherm with the alternate form.

$$y = \frac{x}{x + k_{Li/NH_4}(1 - x)} \qquad (5)$$

An isotherm, calculated from Eqs. (4) and (5), is shown in Fig. 2. The calculated isotherm exhibited a sinusoidal behavior against the plateaus of the experimental data. The sinusoidal peak and trough corresponded to the hysteresis of the plateau heights. In the ranges of $0 < x < 0.03$ and $0.86 < x < 1$, calculated $k_{Li/NH4}$ values of Eq. (4) showed good extrapolations in the isotherm.

3. 2. X-ray diffraction

In the ranges of $x < 0.1$ and $x > 0.3$, the X-ray diffraction peaks from a hydrated powder of $[Li_x(NH_4)_{1-x}]$-A showed one-to-one correspondence to those from a hydrated powder of Na-A. The isostructual peaks indicated that $[Li_x(NH_4)_{1-x}]$-A formed a solid solution.

In the range of $0.1 < x < 0.3$, several diffraction peaks were split into doublets. Typical doublets are displayed in Fig. 4. With increasing values of x, the peak intensity of lower angles decreased, while that of higher angles increased. The doublet peak structure and its intensity variation are attributable to the coexistence of two distinct solid-phases.

The cubic lattice constant (a) of $[Li_x(NH_4)_{1-x}]$-A was determined with the space group Pm3m adapted the pseudo-cell.

(In the pseudo-cell, Al and Si atoms are indistinguishable, whereas in the true-cell, the atoms show alternation. The space group of the true-cell is $Fm\bar{3}c$ [21-23], in which the lattice constant of the pseudo-cell is doubled.) For NH_4-A, a = 1235 $\pm$3 pm was obtained. A plot of a as a function of x is shown in Fig. 5. For 0.1 < x < 0.3, two types of a values were determined for each of the two distinct phases; their almost constant a values were consistent with that of the mixture of the two phases. For x > 0.3, as x increased, lower a values were obtained, which was attributable to the formation of the solid solution. For x = 0.92, a = 1204 pm was obtained. The volume reduction of $[Li_x(NH_4)_{1-x}]$-A was also observed qualitatively in the contraction of column height during the chromatographic ion-exchange.

3. 3. *Isotopic separation factor*

As shown in Fig. 6, the plot of the separation factor (α) for the lithium isotopes resembles a pseudo-α determined from column experiments [13]. In the range of 0.04 < x < 0.32, high α values were obtained (α = 1.017$\pm$0.003), whereas in the higher filling range of 0.56 < x < 0.71, low α values were obtained (α = 1.010$\pm$0.003). Both the estimated error intervals of the above α values are the 95% confidence limits of the t-distribution. The above two types of α are distinguishable in the statistics. The extent of the deviation of α is attributable to the isotopic fractionation occurring in the thermal ionization source of mass spectrometer [24-26]. The high α values in the range of 0.04 < x < 0.32 are attributable to the zeolite sites where the excess amount of ^6Li ions is left behind by the ion exchange with aqueous solutions that contain enriched ^7Li with strong hydration [13]. The low α values in the range of 0.56 < x < 0.71 indicate that the Li ions are distributed over the other ion-exchangeable sites that prefer ^7Li.

3. 4. *Ab initio calculation*

Calculated separation factors for the Li-isotope exchange between a lithium tetrahydrate molecule and an ion-exchanger model molecule are summarized in Table 2.

Geometries of the model molecules are shown in Fig. 7. The model molecule of the six-membered oxygen ring resulted in an α value greater than 1; in contrast, molecules of the eight-membered oxygen ring resulted in α values equal to or less than 1. These results suggest that the six- and the eight-membered oxygen ring favor ^{6}Li and ^{7}Li, respectively.

The frequencies of lithium oscillation were high in the model molecules of the eight-membered oxygen ring; whereas the frequencies were low in the model molecule of the six-membered oxygen ring. At the center of the six-membered oxygen ring, Coulombic forces acting on the lithium ion were counterbalanced by the symmetrical oxygen arrangement. The pore diameter of the six-membered oxygen ring (220 pm), which exceeds the effective ionic diameter of lithium ion (118-184 pm [27]), is a principal factor of the ^{6}Li preference of the ring [13].

4. Discussion

4. 1. Phase rule

Both plateaus of the ion-exchange isotherm of the forward and reverse ion-exchange processes for $0.1 < x < 0.3$ are attributable to a biphasic solid following the phase rule [13, 20]. Two solid phases and one liquid phase (p = 3), which are in an ion-exchange equilibrium (r = 1) in the present five-component mixture (c = 5: $LiNO_3$, NH_4NO_3, Li-A, NH_4-A, and H_2O), suggest that the degree of freedom is one (f = c – p – r = 1), under constant temperature and pressure (variation of x was allowed in the zeolite phase, whereas y was fixed in the aqueous phase). The hysteresis of the plateau heights in forward and reverse ion-exchanges clearly indicates phase transition. Similar isotherms showing hysteresis were found in other systems of phase transitions [14, 20, 28, 29].

4. 2. Mixing energy

Phase transition from a uniform monophasic to a biphasic solid can be studied using the molar Gibbs energy of mixing ($\Delta_{mix}G_m = \Delta_{mix}G/(\bar{n}_{Li} + \bar{n}_{NH4})$), which consists of ideal mixing

$(\Delta_{mix}G_m^I)$ and the excess molar Gibbs energy $(G_m^E = G^E / (\overline{n}_{Li} + \overline{n}_{NH4}))$,

$$\Delta_{mix}G_m = \Delta_{mix}G_m^I + G_m^E$$

(6),

$$= RT[x \ln x + (1 - x) \ln (1 - x)] + G_m^E$$

where R and T are the gas constant and the temperature of system, respectively, and $\overline{n}_{Li}$ and $\overline{n}_{NH4}$ denote the amount of Li^+ and NH_4^+ ions in the solid, respectively.

    At high temperatures, the value of $\Delta_{mix}G_m$ is dominated by the ideal mixing term of Eq. (6), indicating that the solid phase is uniform. At low temperatures, G_m^E is not negligible, and the solid may separate into two phases. In a uniform solid phase, $\partial^2\Delta_{mix}G_m/\partial x^2$ is positive, whereas in a separated solid-phase, $\partial^2\Delta_{mix}G_m / \partial x^2$ is negative. The stability limit of the uniform phase is $\partial^2\Delta_{mix}G_m / \partial x^2 = 0$. At critical temperature (T_c), the critical composition (x_c) is the solution of the next equation.

$$\frac{\partial^2\Delta_{mix}G_m}{\partial x^2} = \frac{RT}{x(1 - x)} + \frac{\partial^2 G_m^E}{\partial x^2} = 0$$

(7)

In symmetrical mixtures [30], the critical composition is $x_c = 1 / 2$, whereas in unsymmetrical mixtures [30], the critical composition depends on the shape of G_m^E. The compositions of x_{c1} and x_{c2} of the two distinct phases below T_c are the solutions of Eq. (7).

4. 3. Sinusoidal isotherm and phase separation

When the aqueous solution is dilute, the logarithmic selectivity coefficient is expressed by the logarithmic thermodynamic equilibrium constant (ln K) and the logarithmic activity coefficient ratio of the cations in the solid.

$$\ln k_{Li / NH_4} = \ln K - \ln(\frac{\overline{f}_{Li}}{\overline{f}_{NH4}})$$

(8)

(The activity coefficient ratio of the cations in the aqueous solution was neglected.) The activity coefficient ratio of the cations in the solid is related to the non-ideal cation-mixing trough the excess Gibbs energy of mixing.

$$RT \ln \left(\frac{\bar{f}_{Li}}{\bar{f}_{NH4}}\right) = \frac{\partial G^E}{\partial \bar{n}_{Li}} - \frac{\partial G^E}{\partial \bar{n}_{NH4}} = \frac{\partial G^E_m}{\partial x} \qquad (9)$$

Solution of the phase stability limit ($\partial^2 \Delta_{mix} G_m / \partial x^2 = 0$) using

$$\frac{\partial^2 \Delta_{mix} G_m}{\partial x^2} = RT\left[\frac{1}{x(1-x)} - \frac{\partial \ln k_{Li/NH4}}{\partial x}\right] = \left[\frac{RT}{y(1-y)}\right]\frac{dy}{dx} = 0 \qquad (10)$$

gives x_{c1} and x_{c2}, which correspond to the x positions at the maximum and minimum of the isotherm, respectively.

The sinusoidal isotherm of Fig. 2 indicates that dy/dx is zero at $x_{c1}=0.12$ and $x_{c2}=0.24$, and is negative between x_{c1} and x_{c2}. These indicate that the monophasic solid separates into two immiscible phases inside the x_{c1}-x_{c2} range.

4. 4. Spinodal [31]

The constant value of ln K of Eq. (8) can be deduced from the integration of $\ln k_{Li/NH4}$ under the condition of a pure compound boundary ($G^E_m = 0$ at x = 0 and 1).

$$\ln K = \int_0^1 \ln k_{Li/NH4} dx - \frac{1}{RT}[G^E_m]_0^1 = \int_0^1 \ln k_{Li/NH4} dx \qquad (11)$$

The logarithmic thermodynamic equilibrium constant was evaluated as $\ln K = \sum_{n=0}^{5} [a_n / (n+1)] = -2.0$. The value of G^E_m as the function of x was calculated from the $\ln k_{Li/NH4}$ data using Eqs. (8) and (9). The last polynomial term of

$$G_m^E = RT \int_0^x [\ln K - \ln k_{Li/NH4}] dx$$

$$= RT[x(1-x)(\sum_{m=1}^{5} \frac{a_m}{m+1}(\sum_{n=0}^{m-1} x^n))] \tag{12}$$

$$= RT[x(1-x)(\sum_{n=0}^{4} b_n x^n)]$$

is equivalent to the Guggenheim expression of G_m^E [30]. The calculated G_m^E / RT curve at 295 K is depicted in Fig. 8 along with the ideal $(\Delta_{mix}G_m^I / RT)$ and the whole $(\Delta_{mix}G_m / RT)$ mixing curves. The stability condition of $\partial^2(\Delta_{mix}G_m / RT) / \partial x^2$ is also shown in the figure.

The temperature dependence of the stability condition curve was calculated under the assumption that the excess Gibbs energy does not include an entropy term, or is enthalpic $(\partial G_m^E / \partial T = -S_m^E = 0; G_m^E = \Delta_{mix}H_m)$. The temperature dependence of the phase stability limits (a spinodal curve) were calculated (Fig. 9), and T_c was evaluated at 405 K. The high value of T_c implies that the spinodal decomposition of $[Li_x(NH_4)_{1-x}]$-A by ion-exchange occurs at ordinary temperatures.

The isotherms at several temperatures are also displayed in Fig. 9. At T_c, the sinusoidal behavior of the isotherm was not observed. The sinusoidal isotherm below T_c is indicative of phase separation due to the excess Gibbs energy. Above T_c, the isotherm was monotonous variation. The Gibbs function is dominated by the ideal mixing effect.

4. 5. Binodal [31]

The chemical potentials, μ_{Li} and μ_{NH4}, are defined as

$$\mu_{Li} = \frac{\partial \Delta_{mix}G}{\partial n_{Li}} = RT \ln x + G_m^E + (1-x)\frac{\partial G_m^E}{\partial x} \tag{13}$$

$$\mu_{NH4} = \frac{\partial \Delta_{mix}G}{\partial \bar{n}_{NH4}} = RT \ln(1 - x) + G_m^E - x \frac{\partial G_m^E}{\partial x} \qquad (14)$$

When the two phases of the solid are separated and equilibrated at the range of x_{e1} - x_{e2}, the two phases have equal μ values ($\mu_{Li}(x_{e1}) = \mu_{Li}(x_{e2})$ and $\mu_{NH4}(x_{e1}) = \mu_{NH4}(x_{e2})$). In such case, $\mu_{Li}(x_{e1}) - \mu_{NH4}(x_{e1})$ and $\mu_{Li}(x_{e2}) - \mu_{NH4}(x_{e2})$ are equal. The slope of the $\Delta_{mix}G_m$ curve ($\partial \Delta_{mix}G_m / \partial x$), which is equal to $\mu_{Li}(x) - \mu_{NH4}(x)$, should be invariant over the equilibrium range ($x_{e1} < x < x_{e2}$).

$$\frac{\partial \Delta_{mix}G_m}{\partial x} = \mu_{Li} - \mu_{NH4} = RT[\ln K + \ln \frac{y}{1 - y}] \qquad (15)$$

The constancy of y at the measured points of isotherm (x_{e1}-x_{e2} range) indicates that the two phases of the solid are in mutual equilibrium.

With forward ion-exchanges, y was constant for $0.08 < x < 0.34$, whereas in reverse ion-exchanges, y was constant in $0.05 < x < 0.25$. The phases of $x_{e1} = 0.08 \approx x_{c1}$ and of $x_{e2} = 0.34$ were in equilibrium in the forward ion-exchanges, while in the reverse ion-exchanges, the phases of $x_{e1} = 0.05$ and of $x_{e2} = 0.25 \approx x_{c2}$ were in equilibrium. The hysteresis behavior can be explained as the spinodal decomposition of $x_{c1} = 0.12$ and $x_{c2} = 0.24$ causing the phase separation with forward and with reverse ion-exchanges, respectively.

Temperature dependence of the phase boundary (a binodal curve) was determined from the temperature dependence of the calculated isotherms (Fig. 9).

4. 6. Excess volume

From the value of the lattice constant, the molar volume of $[Li_x(NH_4)_{1-x}]$-A (V_m) was calculated as

$$V_m = \frac{V}{(\bar{n}_{Li} + \bar{n}_{NH4})} = \frac{a^3}{12} N_A \qquad (16),$$

where V is the volume of $[Li_x(NH_4)_{1-x}]$-A, and N_A is Avogadro

constant. A polynomial of the sixth order was fitted on the variation of the volume (Fig. 10). The polynomials of the second, third, fourth, and higher than seventh order did not agree with the experimental variation.

$$V_m = \sum_{n=0}^{6} c_n x^n$$

(17)

$$= -239x^6 + 845x^5 - 1151x^4 + 750x^3 - 228x^2 + 15.4x + 94.4$$

The molar volume V_m of $[Li_x(NH_4)_{1-x}]$-A includes the molar volumes $V_{m,Li}$ of Li-A (87.5 cm^3) and $V_{m,NH4}$ of NH_4-A (94.4 cm^3), and the excess molar volume V_m^E.

$$V_m = x\ V_{m,Li} + (1 - x)\ V_{m,NH4} + V_m^E \tag{18}$$

The V_m^E values were calculated using from Eq. (17), and were plotted, as shown in Fig. 11.

The value of V_m^E can also be defined by G_m^E.

$$V_m^E = \frac{\partial G_m^E}{\partial P} = RT[x(1-x)\ (\sum_{n=0}^{4} \frac{\partial b_n}{\partial p} x^n)] \tag{19}$$

Both V_m^E and G_m^E, expressed by the sixth order polynomials, were unsymmetrical around x = 1/2. The mixture of $[Li_x(NH_4)_{1-x}]$-A can thus be classified as an unsymmetrical mixture; interchange of x and 1-x causes different G_m^E and V_m^E, indicating that Li^+ and NH_4^+ favor specific sites in the solid.

4. 7. Lithium sites

The unit cell volume of $[Li_x(NH_4)_{1-x}]$-A was effectively reduced in the range of 0 < x < 0.33; 50% of the total reduction at x = 0.33 was attributable to the formation of $[Li_{0.33}(NH_4)_{0.67}]$-A phase by the spinodal decomposition. The ion-exchange insertion

of Li ions into $[Li_{0.08}(NH_4)_{0.92}]$-A lattice was responsible for the main reduction of the size of the LTA cages. If a Li ion is positioned at the center of the six-membered oxygen ring, the Li cation attracts the ring oxygen through the Coulombic interaction [8, 11], whereas if the Li ion is located at the edge of the eight-membered oxygen ring, the Li ion is unable to reduce the ring diameter.

An X-ray study [9] and a sorption experiment [32] revealed that the Li ions fully occupied the six-membered oxygen rings in $[Li_{0.67}Na_{0.33}]$-A. (Hydrated LTA zeolite has ion-exchangeable sites within the six- and the eight-membered oxgen rings [2]. Cation occupancy for the six-membered oxygen rings is 8 / 12 = 0.67. The authors assume that cation occupancy for the eight-membered oxgen rings at hydrated state is 4 /12 = 0.33 according to the literature [2].) Theoretical [33] and spectroscopic [12] studies also suggest that the six-membered oxygen rings possess a strong affinity for the Li ions.

The G_m^E/RT curve showed negative in the whole range of x (Fig. 8). The negative values of G^E are favorable to mixing of Li^+ and NH_4^+ ions over the ion-exchange sites of LTA zeolite.

In conclusion, the occupation of Li ions in the two separated zeolite-phases inside the spinodal can be considered as both: (i) one Li ion occupies the six-membered oxygen ring, and (ii) Li^+ and NH_4^+ ions alternatively occupy the six-membered oxygen rings of the internal large cage of the pseudo-cell. (The two distinct phases of (i) and (ii) mix inside the spinodal.) The manner of the occupancy is shown in Fig. 12.

4. 8. Isotopic separation factor

For lithium isotope separations with the six- and eight-membered oxygen rings, elemental isotope separation factors K(6r) and K(8r) are expressed as

$$K(6r) = \frac{[^6Li(6r)][^7Li(aq)]}{[^7Li(6r)][^6Li(aq)]} = 1 + \delta(6r) \qquad (20)$$

and

$$K(8r) = \frac{[^6Li(8r)][^7Li(aq)]}{[^7Li(8r)][^6Li(aq)]} = 1 + \delta(8r) \tag{21},$$

where 6r, 8r, and aq denote the six- and eight-membered oxygen rings, and aqueous solution, respectively. The values for $\delta(6)$ $\delta(8)$ are minimal.

The isotopic separation factor (α) is defined by the amount of lithium isotopes in both phases.

$$\alpha = \frac{\dfrac{n_{7Li}(aq)}{n_{6Li}(aq)}}{\dfrac{n_{7Li}(6r) + n_{7Li}(8r)}{n_{6Li}(6r) + n_{6Li}(8r)}} = \frac{\dfrac{[^7Li(aq)]}{[^6Li(aq)]}}{\dfrac{[^7Li(6r)] + [^7Li(8r)]}{[^6Li(6r)] + [^6Li(8r)]}}$$

$$= K(6r) - [K(6r) - K(8r)]\left(\frac{z}{1+z}\right) \tag{22}$$

$$\approx 1 + \delta(6r) - [\delta(6r) - \delta(8r)]\left(\frac{z}{1+z}\right)$$

Moreover, α can be decomposed [34] by the above elemental factors as a function of concentration ratio of $z = [^7Li(8r)]/[^7Li(6r)]$.
When the preferential occupation of lithium ions occurs in the six-membered oxygen ring, as described in the preceding section, z is in the range of $0 \le z \le 1/2$. Furthermore, z can be replaced by $z' = [Li(8r)]/[Li(6r)]$, approximately.

A fitting curve of Eq. (22) as a function of z' is shown in Fig. 6, in which K(6r)=1.017 and K(8r)=0.991 were obtained. Experimentally determined K(6r) > 1 and K(8r) < 1 were consistent with the *ab initio* results.

In lower filling (x < 0.33), the horizontal fitting line ($z' \equiv 0$) indicated that the Li ions did not occupy the eight-membered rings. Reduction of the α value in higher filling (x > 0.33) is attributable to occupation of Li ions in the eight-membered oxygen rings via formation of a continuous solid solution. The spinodal decomposition was a result of the preferential occupation of Li ions in the six-membered oxygen rings, showing the constancy of high α values for x < 0.33.

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