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Determination of the Non-stoichiometry of Zeolite A

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Zeolite A was synthesized in the sodium form with the composition $Na_{12}(AlO_2 \cdot SiO_2)_{12}(NaAlO_2)_\delta \cdot nH_2O$, $0 \leqq \delta \leqq 1$. A new method was developed for the determination of the δ-value of the non-stoichiometric part in the product. It consists of repeated ion exchanges of zeolite with $TlNO_3$ (or $BaCl_2$), and determination of the residual amount of Na^+ in the zeolite as a function of the number of treatments. The K_δ/δ value was determined from a linear plot, where K_δ is a selectivity coefficient of the ion exchange reaction between Tl^+ (or Ba^{2+}) and Na^+ in the non-stoichiometric part. The K_δ value was taken from the observed K_δ/δ value, the δ-value being obtained by chemical analysis. The δ-value of a sample can be determined by introducing the K_δ-value into K_δ/δ. An approximate δ-value can be estimated from a break point of the curve, log(residual amount of Na^+) *vs.* the number of times of treatment.

Zeolite A was synthesized in the sodium form, having the composition $Na_{12}(AlO_2 \cdot SiO_2)_{12}(NaAlO_2)_\delta \cdot nH_2O$, with $0 \leqq \delta \leqq 1$.[1,2] The $(AlO_2 \cdot SiO_2)_{12}$ constitutes the framework of the crystal, twelve Na^+ undergoing ion exchange with other cations.[1–4] The non-stoichiometric part, $NaAlO_2$, abbreviated as the δ-part, is occluded in the β-cage of sodalite unit.[2,5] This model for the δ-part, however, has not been confirmed as yet by X-ray analysis, since the structural studies have usually been carried out with single crystals synthesized by Charnell's method,[6] which are said to contain no non-stoichiometric part.[7,8] On the other hand, most studies on ion exchange, thermal measurement, gas sorption, and catalysis are carried out with commercial zeolite (hydrothermally synthesized), and their non-stoichiometry cannot be ignored. The physical and chemical properties of zeolite A, which might be influenced by the δ-value are as follows. In entirely Ca-exchanged zeolite A, $(1+\delta)Ca^{2+}$ ions are located on the 8-membered oxygen ring,[9] Ca^{2+} acting as a highly active center for the isomerization reaction of 1-butene.[10] In (K,Zn)–A systems, discrepancy was found between the conclusions obtained by X-ray analysis[11] and ion exchange isotherm.[12] This was explained by a difference in δ-values of samples.[9] Recently Rees analyzed ion exchange isotherms on (Na,Ca)–A systems and found that there is considerable divergence in data obtained by different authors.[13] He suggested that such divergence is partly attributable to the difference in δ-values.[14]

It is desirable to work out a reliable method to determine the δ-value. The one proposed by Barrer and Meier is too laborious.[15] In the present paper new methods are proposed.

Experimental

Pretreatment. Commercial molecular sieves 4A powder (Shōwa-Unox Co., Lot No. 410713) was used as the starting material. The powder, which was passed through a 200-mesh sieve, contained some sodium hydroxide and iron oxide. In order to remove these impurities, the powder was shaken with a vibrator washer fifteen times in 0.2—0.02 mol dm^{-3} sodium acetate and then washed with distilled water three times. The residual iron impurity was less than 50 ppm as checked by spectrophotometry.

Chemical Analysis. The pretreated zeolite (*ca.* 0.6 g) was dehydrated at 400 °C in a vacuum of 10^{-3} Pa for 4 h and weighed *in situ* with a quartz spring balance. The sensitivity and sensibility of the balance were 0.5 mm/mg and 0.2 mg, respectively. The sample was dissolved in 2 mol dm^{-3} HCl with sodium impurity less than 0.65 ppm in 37% concentration. The amount of silicon, aluminum, and sodium in the dissolved solution was analyzed by gravimetry. Silicon was precipitated as silica, and the filtrate, free from silica, was analyzed. Aluminum and sodium were precipitated as complexes with oxine and zinc uranyl acetate, respectively, and weighed after filtration.[16]

Activation Analysis. Residual amounts of sodium, in ion exchanged Tl–A, Ba–A, and Sr–A zeolite, were determined by neutron activation analysis. Dehydrated samples weighed were irradiated in a TRIGA MARK II REACTOR of Rikkyo (St. Paul's) University for 1—5 h. After a cooling time of 20 h, 1368.4 and 2753.6 keV γ-rays from ^{24}Na in the sample were measured with a γ-ray spectrometer (CANBERRA Ge(Li)-4K-PHA). The absolute amount of ^{24}Na in the sample was determined by comparison with a standard sample. Dehydrated Na_{12}–A zeolite was used as a standard since neutrons are absorbed and reflected by it in a way similar to that of the sample concerned. The sodium content of the standard was determined by chemical analysis.[16]

Results

Chemical Analysis. Results of the chemical analysis of Na–A are given in Table 1. The δ-value was determined from the ratio [Si]/[Al] but not from [Si]/[Na]. When zeolite A is washed a certain amount of Na^+'s is replaced by proton,[17–19] and hence the ratio [Si]/[Na] cannot be used as a means to determine the δ-value. The unfavorable proton exchange is estimated to be 0.5 protons per unit cell from the ratio [Na]/[Al] (Table 1), since [Na]/[Al] would have been unity if no hydrolysis took place.† The observed value for the ratio [Si]/[Al] is 0.988±0.05, giving $\delta = 0.15 \pm 0.05$.

Ion Exchange. (a) Na_{12}–A zeolite (2 g) was subjected to ion exchange in 30 ml of a 0.2 mol dm^{-3} $TlNO_3$ or $BaCl_2$ solution at 82±2 °C. (b) The same amount of zeolite was treated in 50 ml of a 0.05 mol dm^{-3} $BaCl_2$, $SrCl_2$, or $TlNO_3$ solution at 82±2 °C.

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† The decrease in the total sum of the components resulted from both partial hydrolysis and incomplete dehydration. No analysis of protons and water was carried out. The residual amount of H_2O molecules is estimated to be *ca.* 2 molecules per unit cell.

Table 1. Results of the chemical analysis of Na-A

No.	Dehydrated zeolite wt / mg	SiO_2 wt%	Al_2O_3[a)] wt%	Na_2O[b)] wt%	Total wt%	[Si]/[Al] $=\delta/(12+\delta)$	δ
1	644.7	41.82	—	—	—	—	—
2	561.4	41.86	36.02	—	—	0.986	0.17
3	642.5	41.66	35.78	—	—	0.988	0.15
4	660.5	—	35.82	21.0	—	—	—
5	693.6	41.74	35.86	20.8	98.4	0.988	0.15
Ave.		41.77±0.11	35.87±0.14	20.9±0.3	98.5±0.4	0.988±0.005	0.15±0.05

a) The weight of Al_2O_3 was calculated from that of $Al(C_9H_6ON)_3$. The conversion factor is 0.1109. b) The weight of Na_2O was calculated by multipling the weight of $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ by 0.01495.

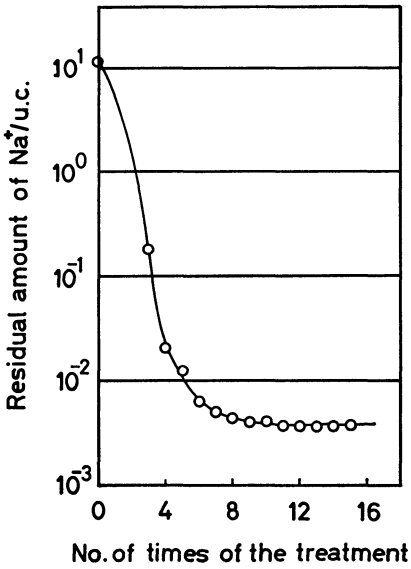

Fig. 1. Residual amount of Na^+ per unit cell in Tl-exchanged zeolites *vs.* the number of times of the treatment.

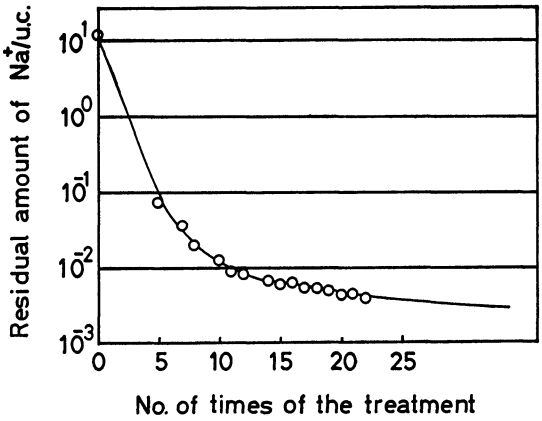

Fig. 2. Residual amount of Na^+ per unit cell in Ba-exchanged zeolites *vs.* the number of times of the treatment.

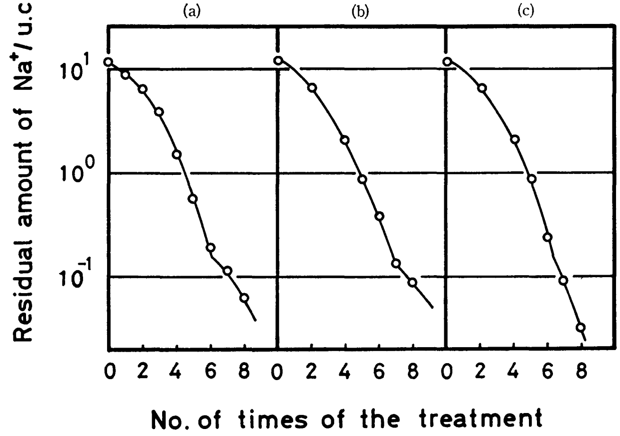

Fig. 3. Residual amount of Na^+ per unit cell in zeolites ion exchanged with dilute solutions.
a): Ba-exchanged zeolite, b): Sr-exchanged zeolite, c): Tl-exchanged zeolite.

After equilibration the zeolite and the solution were separated, the zeolite being subjected to the same treatment. The process was repeated. We prepared samples subjected to the treatment 1, 2,……ν-times. The residual amount of sodium in the sample treated n-times, $[Na]_n$, was determined by activation analysis. The value for log $[Na]_n$, thus determined, is plotted against n, the number of times of treatment (Figs. 1—3).

Analysis and Discussion

Determination of the Selectivity Coefficient. After repetition of ion exchange, all Na^+ ions on easily exchangeable sites (normal site) are replaced by the ion exchanging cations. Further exchange deals with the Na^+ ions on the δ-site. However, the amount of sodium includes the contribution from a nuclear side-reaction $^{27}Al(n,\alpha)^{24}Na$. This is negligibly small in the initial part of the curves (Figs. 1 and 2) but significant in the final part. The contribution corresponds to a spurious 1.83×10^{-3} Na per unit cell.[20)] Subtracting this we obtain the curves for the residual amount (Figs. 4 and 5).

Let us analyze the curve (Fig. 4) by means of the equation

$$[Na]_n = \frac{[Na]_{n-1}}{1+m'(Tl)_s K_\delta(Na,Tl)/\delta} + \frac{m'(Tl)_s K_\delta(Na,Tl)[Na]_\infty/\delta}{1+m'(Tl)_s K_\delta(Na,Tl)/\delta}, \qquad (1)$$

where $[Na]_n$ and $[Na]_\infty$ denote the residual amount of sodium after repetition of treatment n-times and infinite number of times, respectively, $K_\delta(Na,Tl)$ the

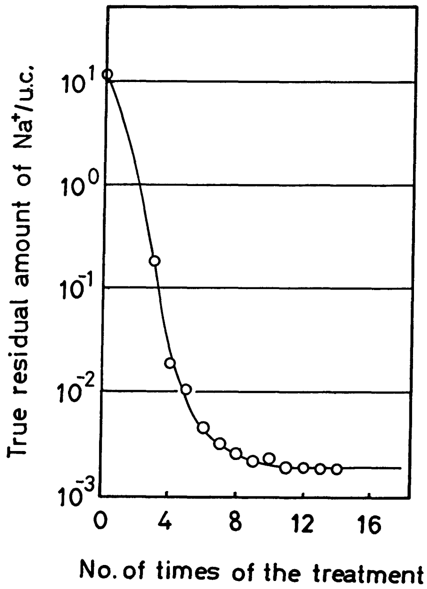

Fig. 4. True residual amount of Na^+ per unit cell in Tl-exchanged zeolites *vs.* the number of times of the treatment.

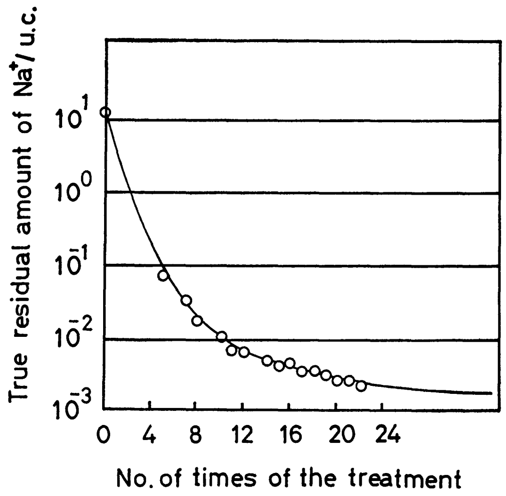

Fig. 5. True residual amount of Na^+ per unit cell in Ba-exchanged zeolites *vs.* the number of the times of the treatment.

selectivity coefficient of the ion exchange reaction between Tl^+ and Na^+ on δ-site, $m'(\mathrm{Tl})_s$ the amount of Tl^+, in mole, contained in the exchanging solution initially loaded. The derivation of Eq. 1 is given in the Appendix. Figure 4 gives the value of $[\mathrm{Na}]_\infty$:

$$[\mathrm{Na}]_\infty = 1.90\times10^{-3}\mathrm{Na^+/u.c.}$$

When $[\mathrm{Na}]_n$ is plotted against $[\mathrm{Na}]_{n-1}$, we have a straight line (Fig. 6). The line crosses a line having a slope of unity at $[\mathrm{Na}]_\infty(=1.90\times10^{-3})$. The straight line is represented by

$$[\mathrm{Na}]_n = 0.53[\mathrm{Na}]_{n-1} + 9.0\times10^{-4}. \qquad (2)$$

Comparing Eqs. 1 and 2, we get

$$K_\delta(\mathrm{Na,Tl}) = 0.89\ \delta/m'(\mathrm{Tl})_s.$$

Introducing the experimental value $m'(\mathrm{Tl})_s=6.67$, we have

$$K_\delta(\mathrm{Na,Tl}) = 0.13\delta.$$

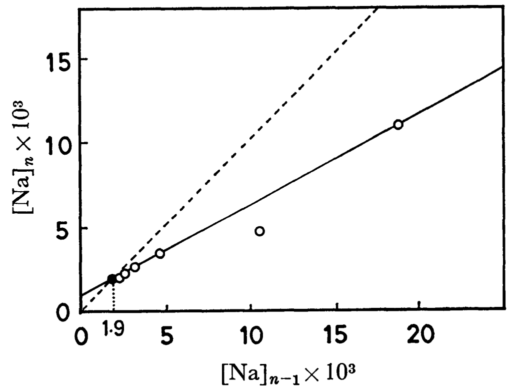

Fig. 6. Plots of $[\mathrm{Na}]_n$ *vs.* $[\mathrm{Na}]_{n-1}$ for (Na,Tl)-A system. The solid line is a most probable line to the plotts and the broken line is that of unity slope.

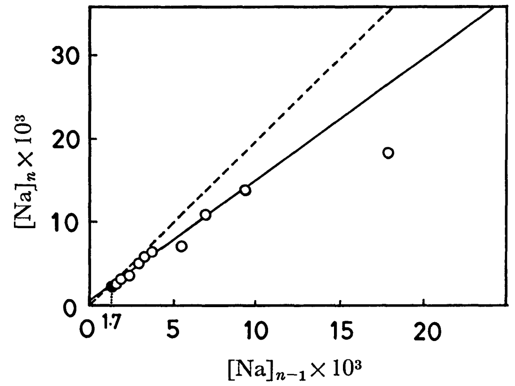

Fig. 7. Plots of $[\mathrm{Na}]_n$ *vs.* $[\mathrm{Na}]_{n-1}$ for (Na,Ba)-A system. Broken line is that of unity slope.

If we use the δ-value obtained by chemical analysis, the value for $K_\delta(\mathrm{Na,Tl})$ is determined as

$$K_\delta(\mathrm{Na,Tl}) = (2.0\pm0.4)\times10^{-2}. \qquad (3)$$

Similar analysis can be carried out for a (Na,Ba)-A system by use of the equation

$$[\mathrm{Na}]_n = \frac{[\mathrm{Na}]_{n-1}}{1+\frac{m'(\mathrm{Ba})_s}{\delta}\sqrt{\frac{2K_\delta(\mathrm{Na,Ba})}{T_n}}} + \frac{[\mathrm{Na}]_\infty\frac{m'(\mathrm{Ba})_s}{\delta}\sqrt{\frac{2K_\delta(\mathrm{Na,Ba})}{T_n}}}{1+\frac{m'(\mathrm{Ba})_s}{\delta}\sqrt{\frac{2K_\delta(\mathrm{Na,Ba})}{T_n}}} \qquad (1')$$

where $K_\delta(\mathrm{Na,Ba})$ is the selectivity coefficient of the ion exchange reaction between Ba^{2+} and Na^+ on the δ-site and T_n the total normality of the solution. From Fig. 5, $[\mathrm{Na}]_\infty$ was chosen for the (Na,Ba)-A as

$$[\mathrm{Na}]_\infty = 1.7\times10^{-3}\ \mathrm{Na^+/u.c.}$$

Plots of $[\mathrm{Na}]_n$ *vs.* $[\mathrm{Na}]_{n-1}$ for the system are shown in Fig. 7. A straight line for the plots, passing through the point $[\mathrm{Na}]_\infty$, is represented by

$$[\mathrm{Na}]_n = 0.77[\mathrm{Na}]_{n-1}+3.9\times10^{-4}. \qquad (2')$$

From Eqs. 1′ and 2′, we obtain

$$K_\delta(\mathrm{Na,Ba}) = 4.5\times10^{-2}\,\delta^2T_n/m'(\mathrm{Ba})_s.$$

Since $m'(\mathrm{Ba})_s=3.33$ and $T_n=0.20$, we have

$$K_\delta(\mathrm{Na,Ba}) = 8.0\times10^{-4}\,\delta^2.$$

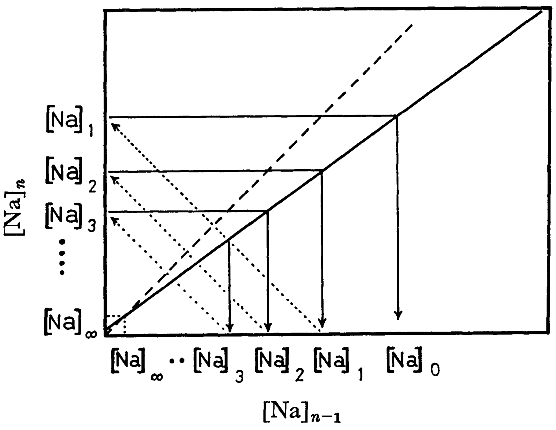

Fig. 8. Schematic diagram which shows a procedure to obtain $[\mathrm{Na}]_0$ by using $[\mathrm{Na}]_n$-$[\mathrm{Na}]_{n-1}$ plotts.

By use of the δ-value determined by chemical analysis, $K_\delta(\mathrm{Na,Ba})$ is calculated as

$$K_\delta(\mathrm{Na,Ba}) = (1.8\pm0.4)\times10^{-5}.$$

Determination of the δ-Value. *Use of Eq. 1*: For the sake of brevity, let us discuss the case of Tl-exchanges.

Introducing Eq. 3 into Eq. 1, we get

$$[\mathrm{Na}]_n = \frac{[\mathrm{Na}]_{n-1}}{1+2.0\times10^{-2}\,m'(\mathrm{Tl})_\mathrm{s}/\delta} + \frac{2.0\times10^{-2}m'(\mathrm{Tl})_\mathrm{s}[\mathrm{Na}]_\infty/\delta}{1+2.0\times10^{-2}\,m'(\mathrm{Tl})_\mathrm{s}/\delta}. \tag{4}$$

When the same experiments are carried out with an unknown sample, values for $[\mathrm{Na}]_n$, $[\mathrm{Na}]_{n+1}$ *etc.* being measured, its δ-value is determined by means of Eq. 4.

Approximate Methods: The principle of the method is schematically given in Fig. 8. The value for $[\mathrm{Na}]_{\nu-1}$ is given from $[\mathrm{Na}]_\nu$. The final value for $[\mathrm{Na}]_0$ is obtained by repeating the procedure. According to Eq. 1, the $[\mathrm{Na}]_0$ value corresponds to the initial amount of sodium in the δ-part. In the present case, we have

$$\delta = 0.12\pm0.05,$$

in agreement with the result of the chemical analysis.

Empirical Methods: When Na–A zeolite is treated with a dilute solution, we obtain curves as shown in Fig. 3. Break points in the curves roughly correspond to the point where easy exchange stops and hard exchange starts. The δ-value is determined from the break as follows.

$\delta = 0.16\pm0.02$ in $\mathrm{BaCl_2}$ solution

$\delta = 0.14\pm0.02$ in $\mathrm{SrCl_2}$ solution

and

$\delta = 0.15\pm0.04$ in $\mathrm{TlNO_3}$ solution.

These values agree with those given by chemical analysis, in spite of the crude procedure.

Conclusion

As compared with the method of Barrer and Meier, the present method is efficient.

Systems (Na,Tl)–A and (Na,Ba)–A were used for determination of the δ-value; the former seems superior. Determination of the $[\mathrm{Na}]_\infty$ value is easier in (Na, Tl)–A. In the empirical method, systems (Na,Ba)–A and (Na,Sr)–A are superior to system (Na,Tl)–A since $\mathrm{Na^+}$ on the δ-site is not easily replaced by $\mathrm{Ba^{2+}}$ or $\mathrm{Sr^{2+}}$, a sharp break appearing in the curve of $\log[\mathrm{Na}]_n$ *vs.* n.

$\mathrm{Tl^+}$ and $\mathrm{Ba^{2+}}$ do not seem to enter into the δ-part.[15,21] However, the present results show that this is not the case. As for $\mathrm{Sr^{2+}}$, Sherry and Walton concluded that it enters into the δ-part,[21] in line with the present results.

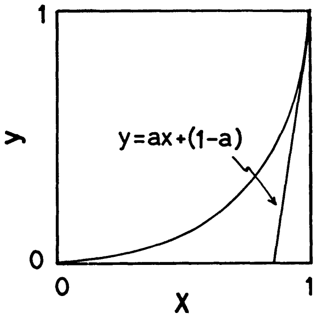

Fig. 9. Ion exchange isotherm for the δ-site. x and y are equivalent cation fractions in a solution and on the δ-site, respectively. Solid line is an asymptote.

Appendix

An ion exchange isotherm for the δ-site has a form shown in Fig. 9, where x and y are equivalent cation fractions in a solution and on the δ-site, respectively.[15] In the case of (Na,Tl)–A system, they are defined by

$$x = \frac{m(\mathrm{Tl})_\mathrm{s}}{m(\mathrm{Tl})_\mathrm{s}+m(\mathrm{Na})_\mathrm{s}} \tag{5}$$

and

$$y = \frac{m(\mathrm{Tl})_\delta}{m(\mathrm{Tl})_\delta+m(\mathrm{Na})_\delta}, \tag{6}$$

where $m(\mathrm{Tl})_\mathrm{s}$ and $m(\mathrm{Tl})_\delta$ denote the amount of $\mathrm{Tl^+}$ in mole unit in the solution and on the δ-site, respectively. In the final range of the exchange, the most part of the δ-site has been occupied by $\mathrm{Tl^+}$ and the final part of the exchange isotherm might converge to an asymptote

$$y = ax + (1-a). \tag{7}$$

Consider the case in which one mole of zeolite is repeatedly treated with a solution having a certain composition. The solution initially contains $m'(\mathrm{Tl})_\mathrm{s}$ mole of $\mathrm{Tl^+}$ ion and $r\cdot m'(\mathrm{Tl})_\mathrm{s}$ of trace impurity $\mathrm{Na^+}$ ion, where r denotes the proportion of the amount of $\mathrm{Na^+}$ to that of $\mathrm{Tl^+}$. From Eqs. 5, 6 and the material balance, we have

$$(1+r)m'(\mathrm{Tl})_\mathrm{s}x = m(\mathrm{Tl})_\mathrm{s},$$

$$\delta y = m(\mathrm{Tl})_\delta,$$

and

$$(1+r)m'(\mathrm{Tl})_\mathrm{s}x + \delta y = m(\mathrm{Tl})_\mathrm{t}, \tag{8}$$

where $m(\mathrm{Tl})_\mathrm{t}$ is the total amount of $\mathrm{Tl^+}$ in the system. From Eqs. 7 and 8, we obtain

$$1-y = \frac{\delta+(1+r)m'(\mathrm{Tl})_\mathrm{s}-m(\mathrm{Tl})_\mathrm{t}}{\delta+(1+r)m'(\mathrm{Tl})_\mathrm{s}/a}.$$

After ion exchange n-times, we get

$$1-y_{\rm n} = \frac{\delta+(1+r)m'(\mathrm{Tl})_{\rm s}-m(\mathrm{Tl})_{\rm t,n}}{\delta+(1+r)m'(\mathrm{Tl})_{\rm s}/a}. \tag{9}$$

From the material balance we have

$$m(\mathrm{Tl})_{{\rm t},n} = \delta y_{n-1} + m'(\mathrm{Tl})_{\rm s}.$$

Introducing this into Eq. 9, we get

$$\begin{aligned}1-y_{\rm n} &= \frac{\delta(1-y_{\rm n-1})}{\delta+(1+r)m'(\mathrm{Tl})_{\rm s}/a}+\frac{r\cdot m'(\mathrm{Tl})_{\rm s}}{\delta+(1+r)m'(\mathrm{Tl})_{\rm s}/a}\\ &\approx \frac{\delta(1-y_{\rm n-1})}{\delta+m'(\mathrm{Tl})_{\rm s}/a}+\frac{r\cdot m'(\mathrm{Tl})_{\rm s}}{\delta+m'(\mathrm{Tl})_{\rm s}/a},\end{aligned} \tag{10}$$

where the equation was simplified by the condition $r \ll 1$. In the present experiments, the residual amount of sodium per unit cell, $[\mathrm{Na}]_n$, is measured as a function of n, and is given by

$$[\mathrm{Na}]_n = \delta(1-y_n).$$

Thus Eq. 10 becomes

$$[\mathrm{Na}]_{\rm n} = \frac{[\mathrm{Na}]_{\rm n-1}}{1+m'(\mathrm{Tl})_{\rm s}/a\delta}+\frac{r\cdot m'(\mathrm{Tl})_{\rm s}}{1+m'(\mathrm{Tl})_{\rm s}/a\delta}. \tag{11}$$

By repetition of ion exchange, $[\mathrm{Na}]_n$ decreases, converging to a definite value:

$$\lim_{n\to\infty}\frac{[\mathrm{Na}]_n}{[\mathrm{Na}]_{n-1}} = 1.$$

Combining the above two equation, we get

$$[\mathrm{Na}]_\infty = a\delta r,$$

where $[\mathrm{Na}]_\infty$ is the converged value and determined from the flat part of the curve in Fig. 5. Thus, the unknown parameter r is eliminated from Eq. 11, and we have

$$[\mathrm{Na}]_n = \frac{[\mathrm{Na}]_{n-1}}{1+m'(\mathrm{Tl})_{\rm s}/a\delta}+\frac{m'(\mathrm{Tl})_{\rm s}[\mathrm{Na}]_\infty/a\delta}{1+m'(\mathrm{Tl})_{\rm s}/a\delta}. \tag{12}$$

This shows that when $[\mathrm{Na}]_n$ is plotted against $[\mathrm{Na}]_{n-1}$, we get a straight line which crosses at $[\mathrm{Na}]_\infty$ with a line having a slope of unity.

The slope of straight line in Eq. 7, a, is related to a selectivity coefficient of the exchange reaction on the δ-site. The selectivity coefficient for the (Na,Tl)-A system, $K_\delta(\mathrm{Na,Tl})$, is given by

$$K_\delta(\mathrm{Na,Tl}) = \frac{Na_{\rm s}\cdot Tl_\delta}{Tl_{\rm s}\cdot Na_\delta},$$

where $Tl_{\rm s}$ and Tl_δ denote the equivalent cation fractions of Tl^+ in the solution and on the δ-site, respectively. Such an equation was found to hold for the exchange reaction on the δ-site.[13,15] Introducing Eqs. 5 and 6 into the above equation, we have

$$K_\delta(\mathrm{Na,Tl}) = \frac{(1-x)y}{x(1-y)}.$$

Since $a = (\mathrm{d}y/\mathrm{d}x)_{x=1}$, we get

$$a = \frac{1}{K_\delta(\mathrm{Na,Tl})}.$$

Eliminating the parameter a from this equation and Eq. 12, we obtain

$$\begin{aligned}[\mathrm{Na}]_n &= \frac{[\mathrm{Na}]_{n-1}}{1+m'(\mathrm{Tl})_{\rm s}K_\delta(\mathrm{Na,Tl})/\delta}\\ &+\frac{m'(\mathrm{Tl})_{\rm s}K_\delta(\mathrm{Na,Tl})[\mathrm{Na}]_\infty/\delta}{1+m'(\mathrm{Tl})_{\rm s}K_\delta(\mathrm{Na,Tl})/\delta}.\end{aligned} \tag{13}$$

This is the fundamental equation in the present analysis and is reduced to Eq. 1 when numerical values determined experimentally are introduced.

As for the (Na,Ba)-A system, minor changes should be introduced as

$$[\mathrm{Na}]_n = \frac{[\mathrm{Na}]_{n-1}}{1+2m'(\mathrm{Ba})_{\rm s}/a\delta}+\frac{2m'(\mathrm{Ba})_{\rm s}[\mathrm{Na}]_\infty/a\delta}{1+2m'(\mathrm{Ba})_{\rm s}/a\delta} \tag{12'}$$

and

$$K_\delta(\mathrm{Na,Ba}) = \frac{2Ba_\delta\cdot(Na_{\rm s})^2}{(Na_\delta)^2\cdot Ba_{\rm s}}\cdot T_{\rm n},$$

where Ba_δ means the equivalent cation fraction of Ba^{2+} on the δ-site, $Ba_{\rm s}$ that in the solution and $T_{\rm n}$ a total normality of the solution. Thus, we have

$$a = \sqrt{\frac{2T_{\rm n}}{K_\delta(\mathrm{Na,Ba})}}$$

and

$$\begin{aligned}[\mathrm{Na}]_n &= \frac{[\mathrm{Na}]_{n-1}}{1+\dfrac{m'(\mathrm{Ba})_{\rm s}}{\delta}\sqrt{\dfrac{2K_\delta(\mathrm{Na,Ba})}{T_{\rm n}}}}\\ &+\frac{[\mathrm{Na}]_\infty\cdot\dfrac{m'(\mathrm{Ba})_{\rm s}}{\delta}\sqrt{\dfrac{2K_\delta(\mathrm{Na,Ba})}{T_{\rm n}}}}{1+\dfrac{m'(\mathrm{Ba})_{\rm s}}{\delta}\sqrt{\dfrac{2\mathrm{K}_\delta(\mathrm{Na,Ba})}{T_{\rm n}}}}.\end{aligned} \tag{13'}$$

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