

## Cation Movements in Dehydrated (Ca,Na)-A Zeolites

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Dielectric properties of dehydrated  $\text{Ca}_x\text{Na}_{11.8-2x}\text{-A}$  zeolites with  $x = 1.9, 3.1,$  and  $3.9$  were studied. In all compositions, two overlapping loss peaks were observed and variations of magnitudes of the losses with  $x$  were investigated. The magnitude of the peak observed at a lower frequency decreased with increasing  $x$  and the dependence of the magnitude upon  $x$  was almost the same as that of a loss expected for a  $\text{Na}^+$  jump from an 8-ring site to a 4-ring site. Hence the loss was assigned to the 8-4 jump of  $\text{Na}^+$ . A frequency factor for the jump was determined and a dependence of the factor upon  $x$  was studied. Another loss peak observed at the higher frequency side increased with increasing  $x$  and was attributed to a jump of  $\text{Ca}^{2+}$ . © 1990 Academic Press, Inc.

### Introduction

Zeolite A is synthesized in a sodium form and is converted to various cation forms through ion-exchange reaction. Cations are distributed over three kinds of sites, sites near an 8-, 6-, or 4-membered oxygen ring (1, 2). The cations are moving near the sites, and their movements affect adsorptive properties and reactivities of the zeolite at higher temperature (3-5). Thus it is important to study the cation movements in order to understand the properties of zeolite at higher temperature.

Dielectric measurements are useful for investigation of the movements of cations in zeolites. In previous papers (6, 7), dielectric properties of  $\text{Ca}_1\text{Na}_{10}\text{-A}$  and  $\text{Na}_{11}\text{-ZK4}$  zeolites (zeolite ZK4 is isostructural with zeolite A (8)) were studied and it was shown that if the zeolite contains both  $\text{Na}^+$ 's on the 8-ring sites and vacancies on the 4-ring sites, the  $\text{Na}^+$  jumps to the 4-ring site (8-4

jump). The zeolite of  $\text{Ca}_x\text{Na}_{12-2x}\text{-A}$  with  $1 < x < 4$  contains both  $\text{Na}^+$ 's and vacant sites (1), and thus the 8-4 jump is expected to be observed in the zeolite. If the jump is observed in the zeolite, effects of  $\text{Ca}^{2+}$  upon former occupants  $\text{Na}^+$ 's will be examined. Takaishi and co-workers (3, 4) predicted that movements of the 8-ring cation are affected by divalent cations introduced into the zeolite and that frequencies of vibration of the cation decrease with increasing content of divalent cation. The predictions may be confirmed by our dielectric measurements.

In the  $\text{Ca}_1\text{Na}_{10}\text{-A}$  zeolite, jumps of  $\text{Ca}^{2+}$  were not observed (7). This does not necessarily mean that there are no jumps of  $\text{Ca}^{2+}$  in the temperature and frequency ranges studied. Jumps may be observed in the zeolite of higher content of  $\text{Ca}^{2+}$ .

### Experimental

A commercial 4A zeolite, whose composition per unit cell is  $\text{Na}_{11.8}(\text{AlO}_2)_{11.8}$

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$(\text{SiO}_2)_{12.2}n\text{H}_2\text{O} ((\text{AlO}_2)_{11.8}(\text{SiO}_2)_{12.2}n\text{H}_2\text{O}$  will be abbreviated -A) was ion-exchanged with  $0.1 \text{ mole dm}^{-3}$  solution of  $(\text{CH}_3\text{COO})_2\text{Ca}$  at  $353 \pm 0.5 \text{ K}$  for 3 days, and the cation composition,  $\text{Ca}_x\text{Na}_{11.8-2x}\text{-A}$ , after ion-exchange was determined by EDTA titration of the ion-exchange solution and material balance. The ion-exchange isotherm obtained is in good agreement with that obtained under the same conditions by Takaishi *et al.* (1). The compositions used for the dielectric measurements are  $x = 1.9$ , 3.1, and 3.9.

Powdered zeolite was pressed at a pressure of  $8.8 \times 10^7 \text{ Pa}$  ( $900 \text{ kg cm}^{-2}$ ). The sample disk was outgassed in a vacuum system at room temperature and then gently heated. The sample was heated, at intervals, at a temperature above  $473 \text{ K}$  in flowing oxygen gas at a pressure of  $10^{-3} \text{ Pa}$  introduced through a variable leak valve. At the final stage, the sample was heated at  $723 \text{ K}$  for 1 day under a pressure of  $4 \times 10^{-5} \text{ Pa}$ .

Dielectric constants ( $\epsilon^* = \epsilon' - i\epsilon''$ ) were measured as functions of frequency  $f$  and temperature  $T$ , in the ranges of  $30\text{--}2 \times 10^6 \text{ Hz}$  and  $405\text{--}715 \text{ K}$ , respectively. We do not require the absolute value of the dielectric constant and did not make the correction for the packing density of the sample disk. The vacuum system and apparatus used in dielectric measurements are the same as in the previous paper (9).

## Results

Spectra of loss tangent,  $\tan \delta$ , for three compositions show essentially the same pattern, that is, a peakless loss in the lower frequency region and two overlapping loss peaks in the higher region, as illustrated in Fig. 1. The peakless loss increases remarkably with decreasing frequency. The loss peak at the lower frequency side in the overlapping peaks, peak I, decreases with increasing  $x$ , while the peak at the higher frequency side, peak II, increases. Activation

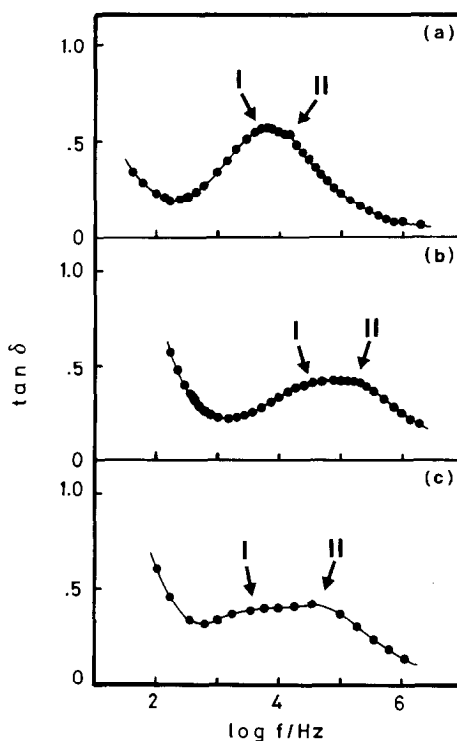


FIG. 1. Spectra of loss tangent for  $\text{Ca}_x\text{Na}_{11.8-2x}\text{-A}$  zeolite. (a)  $x = 1.9$ ,  $623.3 \text{ K}$ ; (b)  $x = 3.1$ ,  $718.5 \text{ K}$ ; (c)  $x = 3.9$ ,  $638.2 \text{ K}$ . Marks I and II denote peaks I and II, respectively.

energies of cation jumps concerned with the peaks I and II,  $E_{\text{Itan}}$  and  $E_{\text{IItan}}$ , are respectively determined from slopes of plots of  $\ln f_{\text{tan}}$  vs  $1/T$ , and are shown in Fig. 4, where  $f_{\text{tan}}$  is the frequency at the peak of  $\tan \delta$ .

Cole-Cole plots of  $\epsilon''_{\text{obsd}}$  vs  $\epsilon'_{\text{obsd}}$  superficially show two kinds of losses, an arch-shaped loss in the smaller  $\epsilon'$  region and a large loss in the larger  $\epsilon'$  region, as illustrated in Fig. 2, where the subscript "obsd" denotes observed values. Usually a large loss in the larger  $\epsilon'$  (lower frequency) region is attributed to a conductivity loss (10-12). If the loss is caused by conduction, it is described with the equation for conductivity loss,  $\epsilon''_c = \sigma/2\pi f\epsilon_0$ , where  $\sigma$  and  $\epsilon_0$  are the apparent dc conductivity and the permittiv-

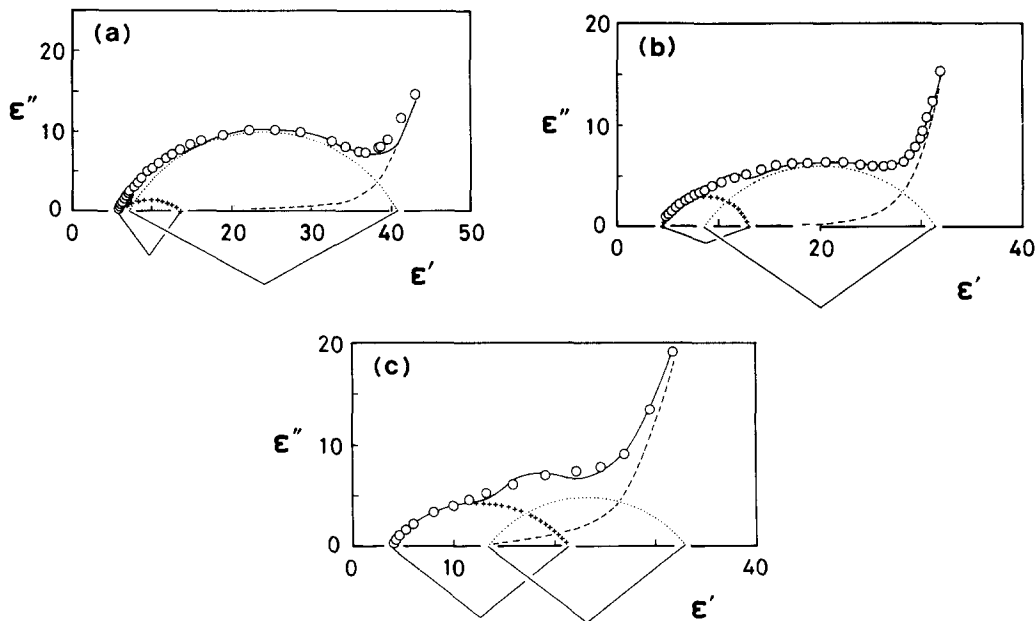


FIG. 2. Cole-Cole plots for  $\text{Ca}_x\text{Na}_{11.8-2x}$ -A zeolite. (○) observed value; (···) arc I; (---) arc II; (---) conductivity loss; (—) superposition of arc I, II, and conductivity loss. Conductivity loss is calculated from the equation  $\epsilon''_c = \sigma/2\pi f\epsilon_0$ , where  $\sigma$  is an apparent dc conductivity and  $\epsilon_0$ , the permittivity of vacuum. (a)  $x = 1.9$ , 623.3 K; (b)  $x = 3.1$ , 718.5 K; (c)  $x = 3.9$ , 638.2 K.

ity of vacuum, respectively. The large losses observed are well described by the equation, as shown in Fig. 2, and thus are assigned to the conductivity losses.<sup>2</sup> The observed loss was corrected for the conductivity loss by the equation of  $\epsilon''_{\text{obsd}} - \epsilon''_c (= \epsilon''_r)$ . Plots of  $\epsilon''_r$  against  $\epsilon'_{\text{obsd}}$  show a curve consisting of two swellings and the curve is thereby separated into two circular arcs (Fig. 2). Since a single relaxation process causes a single Cole-Cole circular arc (14), the curve of  $\epsilon''_r$  vs  $\epsilon'_{\text{obsd}}$  indicates the existence of two relaxation processes. The larger arc in the larger  $\epsilon'$  region, arc I, decreases with increasing  $x$ , while the arc in

the smaller  $\epsilon'$  region, arc II, increases. A maximum value of the arc  $\epsilon''_{\text{Im}}$  (or  $\epsilon''_{\text{IIIm}}$ ), is determined from Fig. 2 and plotted against  $x$  as shown in Fig. 3, where the plot is expressed as the relative value to the largest

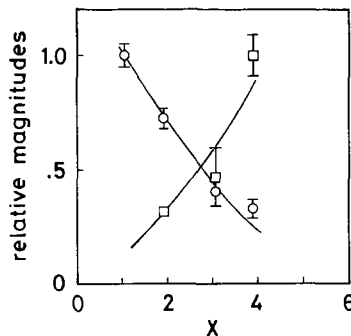


FIG. 3. Dependence of maximum value of relaxation loss upon calcium content. (○) arc I; (□) arc II. A datum at  $x = 1.05$  is quoted from Ref. (7).

<sup>2</sup> We think that the losses are due to a quasi dc conduction which takes place in a powder sample (13). Whether the conduction is a quasi dc conduction or a true one, the following discussion is not influenced since charge carriers move beyond the unit cell dimension in either conduction.

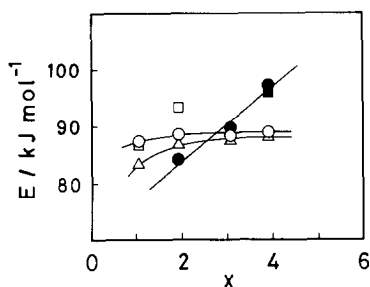


FIG. 4. Activation energies. (○)  $E_I$ ; (●)  $E_{II}$ ; (□)  $E_{Itan}$ ; (■)  $E_{IItan}$ ; (△)  $E_c$ . Subscripts I, II, Itan, IItan, and c denote values concerned with arcs I, II, peaks I, II, and conductivity loss, respectively. Data at  $x = 1.05$  are quoted from Ref. (7).

$\epsilon''_{Im}$  ( $\epsilon''_{IIIm}$ ).<sup>3</sup> The activation energy,  $E_I$  ( $E_{II}$ ), and frequency factor,  $\omega_0$ , for the first (second) relaxation process are determined from plots of  $\ln f_I$  ( $f_{II}$ ) vs  $1/T$  and are illustrated in Figs. 4 and 5, where  $f_I$  is the frequency at  $\epsilon''_{Im}$  and  $\omega_0$  is defined as  $\ln f_I = \ln \omega_0/2\pi - E_I/RT$ .

### Analyses

In a jump mechanism, vacant sites are necessarily required to accept jumping cat-

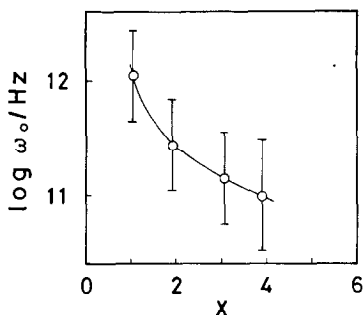


FIG. 5. Dependence of frequency factor for arc I upon calcium content. A datum at  $x = 1.05$  is quoted from Ref. (7).

<sup>3</sup> The dependence of relative magnitudes upon  $x$  do not change much, even if  $\epsilon''_{Im}$  and  $\epsilon''_{IIIm}$  were respectively corrected for the Cole-Cole central angles.

TABLE I  
ALLOWED CATION-JUMP IN  $\text{Ca}_x\text{Na}_{12-2x}\text{-A}$  ZEOLITE  
WITH  $1 \leq x \leq 4$

Kind of jump <sup>a</sup>	Abbreviated name	Jumping cation
8-ring → 4-ring	8-4 jump	$\text{Na}^+$
6-ring → 4-ring	6-4 jump	$\text{Na}^+$ , $\text{Ca}^{2+}$
6-ring → 8-ring	6-8 jump	$\text{Na}^+$ , $\text{Ca}^{2+}$
8-ring → Another 8-ring	8-8 jump	$\text{Na}^+$
8-ring → Same 8-ring	intra-8-ring jump	$\text{Na}^+$
SI ↔ SI'	SI-SI' jump	$\text{Na}^+$ , $\text{Ca}^{2+}$

<sup>a</sup> 8-ring, site in the 8-ring plane; 6-ring, site near the 6-ring; 4-ring, site near the 4-ring; SI, site near the 6-ring in the large cage; SI', site near the 6-ring in the sodalite cage.

ions. Thus, in the jump mechanism, the frequency of occurrence of the cation jump per unit volume, to a first approximation, is proportional to concentrations of the jumping cation and the vacant site (12). Since a magnitude of dielectric loss is proportional to the frequency of occurrence of the cation jump, we have for a  $j$ th kind of jump

$$\epsilon''_j = K_j \times [\text{jumping cation}]_j \times [\text{vacant site}]_j,$$

where  $K_j$  and brackets denote a proportional constant and a concentration, respectively. The concentrations of the jumping cation and the vacant site are obtained from a cation distribution of  $\text{Ca}_x\text{Na}_{12-2x}\text{-A}$ , which has been already determined (1, 2, 15). If  $K_j$  is constant, the relative magnitude of the loss caused by the  $j$ th jump can be calculated as a function of  $x$ , by the above equation. Allowed jumps in  $\text{Ca}_x\text{Na}_{12-2x}\text{-A}$  with  $1 \leq x \leq 4$  are confined to several kinds (6, 7), as listed in Table I. If the allowed jumps cause relaxation losses, variations of the magnitudes of losses with  $x$  are calculated as shown in Fig. 6.

### Discussion

As can be seen from Figs. 3 and 6, the dependence of the magnitude of the arc I

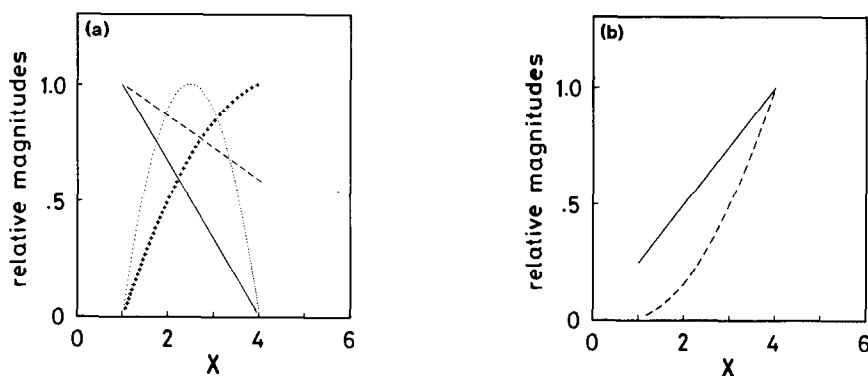


FIG. 6. Variations of relaxation losses with calcium content. (a) Losses caused by jumps of  $\text{Na}^+$ ; (—) 8-4 or intra-8-ring jump; (---) 6-4 or SI-SI' jump; (···) 8-8 jump; (- - -) 6-8 jump. (b) Losses caused by jumps of  $\text{Ca}^{2+}$ ; (—) 6-4 or SI-SI' jump; (---) 6-8 jump.

upon  $x$  is close to those for the 8-4 and intra-8-ring jumps of  $\text{Na}^+$ . Thus the cation jump as a candidate for the arc I is either the 8-4 or intra-8-ring jump. It has been found from studies on ZK4 zeolites (6, 7, 9) that the intra-8-ring jump is not observed in the temperature and frequency ranges studied herein. If the 8-4 jump occurs, two kinds of losses will be observed, from relaxation and from conduction. The relaxation loss is brought about by the jump of 8-ring  $\leftrightarrow$  4-ring and the conductivity loss by the jump of 8-ring  $\rightarrow$  4-ring  $\rightarrow$  another 8-ring, etc. For the relaxation and conductivity losses caused by the same jump mechanism, the expression  $E_r - E_c = RT$  is valid, where  $E_r$  and  $E_c$  denote the activation energies for the relaxation and conductivity processes, respectively (9). In the present systems, both relaxation and conductivity losses are observed and the activation energies satisfy the above equation within experimental error. Hence, arc I is attributable to the 8-4 jump of  $\text{Na}^+$ .

The activation energy of the 8-4 jump of  $\text{Na}^+$  for  $1 < x < 4$  is considerably larger than those (45-48 kJ mole $^{-1}$ ) of  $\text{Na}^+$  movements for  $x = 0$  (7, 16). The difference stems from a difference between jump mechanisms. In  $\text{Na}_{12}$ -A,  $\text{Na}^+$  on the 4-ring site is the most mobile and the movements of the

cation preferentially occur, hiding other movements.

In studies of gas adsorptions on zeolite A, Takaishi and co-workers (3, 4) observed that gas molecules larger than a size of the window (= 8-ring) aperture can pass through the aperture and the passage becomes easier with increasing content of divalent cation. In order to explain the results, they proposed an adsorption mechanism, named indirect control mechanism. The mechanism was supposed to consist of two effects brought about by the divalent cations introduced. In the first, the divalent cation displaces the equilibrium position of the 8-ring cation outside of the 8-ring plane. Thus the blocking action of the 8-ring cation becomes incomplete and gas molecules can penetrate into the zeolite. This effect was already confirmed by X-ray structural analyses (17). In the second, the form of the potential surface experienced by the 8-ring cation is converted to more gentle one and the cation is easily displaced to open a way for a visiting molecule. If the second effect operates, the frequency of vibration of the cation is expected to be reduced with increasing content of  $\text{Ca}^{2+}$ . Figure 5 indicates that the expectation is valid; that is, the second effect operates.

The variation of the magnitude of arc II

with  $x$  is close to the variations for three kinds of jumps of  $\text{Ca}^{2+}$ , the 6–8, 6–4, and SI–SI' jumps. In the three jumps, the SI–SI' jump may be the most appropriate to arc II, for the following reason: In the former two,  $\text{Ca}^{2+}$  must escape from the 6-ring's attraction region. The bond energy between  $\text{Ca}^{2+}$  and the 6-ring site is much larger than that between  $\text{Na}^+$  and the 8-ring site (18), and thus the activation energies of the 6–8 and 6–4 jumps of  $\text{Ca}^{2+}$  are expected to be larger than that of the 8–4 jump of  $\text{Na}^+$ . The activation energy determined for arc II is comparable to that of the 8–4 jump. Thus the 6–8 and 6–4 jumps may not be appropriate to arc II. This idea is partially supported by results of Schoonheydt and De Wilde (12). They studied cation movements in Ca-exchanged faujasite and assigned a relaxation loss with the activation energy of 84–106 kJ mole<sup>-1</sup> to the jump between neighboring sites of  $\text{Ca}^{2+}$  on sites I and/or I'.

It is necessarily expected, from the above idea, that a jump of  $\text{Na}^+$  on the 6-ring site is also observed in these zeolites. In all A and ZK4 zeolites studied ( $\text{Na}_{11}$ -ZK4,  $\text{K}_3\text{Na}_8$ -ZK4 (6),  $\text{Rb}_3\text{Na}_8$ -ZK4 (9),  $\text{Ca}_1\text{Na}_{10}$ -A (7)), a small scarcely discernible loss was observed in the lowest  $\epsilon'$  region of Cole–Cole plots, though it is not discerned in the present zeolites owing to arc II. Its origin may be the jump of  $\text{Na}^+$  on the 6-ring site, since all the zeolites contain  $\text{Na}^+$ 's on the 6-ring sites in common.

There is a difference at  $x = 3.9$  between the observed (in Fig. 3) and the estimated values (in Fig. 6a). The observation indicates existence of  $\text{Na}^+$  on the 8-ring site

at  $x = 3.9$ . On the other hand, the cation distribution diagram (1) tells us that there is little  $\text{Na}^+$  on the 8-ring site at  $x = 3.9$ . The disagreement may arise from an incompleteness of the diagram.

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