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STERIC INTERFERENCE TO DIFFUSION IN LINDE A ZEOLITE

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Introduction:

The activation energy of diffusion of molecules or ions in a zeolite may well contain both repulsive and attractive energy contributions. The relative importance of these types of interactions is often very uncertain. For example, Freeman and Stamires¹ found that the activation energy of electrical con-

(1) D. C. Freeman, D. N. Stamires, J. Chem. Phys., 35, 799 (1961).

duction of a Linde A zeolite containing mostly potassium as mobile ions is high compared to that of the sodium exchanged form of the same zeolite. They decided that this must be due to the steric repulsion the K^+ ion encounters, since the reverse trend is found in the more open Linde zeolites of type Y. The activation energy of conduction is very probably the same as that for ionic diffusion. Interestingly, the activation energy of ethane diffusion in a similar K^+ exchanged zeolite of Linde A type was found to be lower²

(2) W. W. Brandt, W. Rudloff, J. Phys. Chem. Solids, in press.

(*) Abstracted, in part, from the work done by W. Rudloff in partial fulfillment of the research requirement for the Ph.D. degree in the Department of Chemistry at Illinois Institute of Technology.

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than the quantity measured by Freeman and Stamires,¹ even though ethane molecules are distinctly larger than unsolvated K^+ ions.³ One may suspect, there-

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- (3) R. M. Barrer, *Quat. Revs.*, 3, 293 (1949); L. Pauling, "The Nature of the Chemical Bond", Cornell University Press (1948), p. 346.
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fore, that steric effects are relatively unimportant to the activation energies discussed here.

The present study is intended to test these ideas. To this end, the diffusion rates of ethane were measured in Li^+ , Na^+ and K^+ exchanged forms of a Linde A type zeolite with various amounts of water adsorbed prior to the diffusion measurements. If steric effects are of prime importance, the diffusion coefficients are expected to decrease with increasing H_2O concentration, and vice versa.

Experimental:

The samples used in the present study are the same ones examined previously.² Flame photometric measurements showed that the Ca^{++} and Na^+ present in the original zeolite used in this work are not exchanged completely by the percolation method described by Freeman and Stamires.¹ The approximate mole ratios of [~~alkali introduced/residual calcium (plus sodium)~~] are 1.3, 2.4, and 2.0, for the Li^+ , Na^+ , and K^+ forms, respectively. The degassed zeolite contained less than 0.05% H_2O prior to the experiments.

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- (4) R. M. Barrer, B. E. F. Fender, *J. Phys. Chem. Solids*, 21, 1 (1961).
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The experimental method and the data treatment were described previously.^{5,6}

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- (5) W. W. Brandt, W. Rudloff, *J. Phys. Chem. Solids*, 25, 167 (1964).

- (6) W. W. Brandt, W. Rudloff, *Z. phys. Chemie (N.F.)*, 42, 201 (1964).
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Results and Discussion:

The ethane diffusion coefficients obtained at several temperatures for the various cation exchanged forms of the Linde A zeolite are listed in Table (1).

The diffusion coefficients in the Li^+ exchanged form increase markedly with increasing H_2O content. This is consistent with the results reported earlier² and is plausible if one assumes that Li^+ and H_2O preferentially move as a loose pair which can leave its lattice sorption site more readily than a Li^+ ion alone could.^{2*} According to Freeman and Stamires,¹ the sites available to unsolvated Li^+ ions seem to be particularly efficient in holding on to this cation. Alternatively, one might assume that the Li^+ essentially stays at its preferred site, and that the strongest sorption sites for H_2O and ethane are located close to it. The ethane molecule looses out in this competition and can, therefore, diffuse freely if H_2O molecules are present.

The ethane diffusion coefficients in the K^+ exchanged form are much lower than those obtained for the Li^+ form. This may indicate that the K^+ must frequently move away from its "normal" site, in order to permit the ethane molecule to pass the narrow portions ("windows") of the zeolite lattice.² ~~On the other~~ ——— hand, the diffusion rates again increase with increasingly H_2O content, indicating that steric hindrance, if it exists, does not constitute the major contribution to the activation energy barrier. This conclusion was already reached earlier.² Presumably, the attractive forces between K^+ and the lattice, or between K^+ and the diffusing ethane are most important to the diffusion process. Since K^+ ions apparently have to move, to enable an ethane diffusion jump, we now prefer the first version of the interpretation offered in the case of the Li^+ form (*).

The ethane diffusion coefficients measured on the Na^+ exchanged form are perhaps the most interesting. They are higher than those for the Li^+ form, when little H_2O is present, but they decrease markedly with increasing H_2O content. By contrast, Na^+ ions are found to become more mobile with increasing H_2O content.⁷ Presumably, the H_2O present enable the Na^+ ions to move more

(7) D. N. Stamires, J. Chem. Phys., 36, 3134 (1962).

freely than before, in analogy to the situation encountered in the Li^+ and K^+ forms of this zeolite, were it not for the overriding steric effect of the additional H_2O molecules present, or for the bulkiness of the now solvated Na^+ ions.'

In summary, the additional H_2O molecules present seem to affect the ethane diffusion coefficients through their strong attraction to the mobile cations present. Presumably, the motion of the cations is facilitated, and, therefore, retards the ethane molecules, only little. The H_2O present also sometimes "blocks" diffusion paths; this effect is pronounced in the Na^+ form.

The presence of at least two different effects is evident in the conductivity data of Stamires⁸ even though the nature of these effects is not clear from

(8) Figures (3) and (9) of Reference 6.

this author's data only. Also Barrer and Peterson recently discussed zeolitic diffusion in terms of steric effects, but concluded that other effects are at times important.⁹

(9) R. M. Barrer, D. L. Peterson, J. Phys. Chem., 68, 3427 (1964).

T (°C)	H_2O sorbed (molecule/cage)	$D \times 10^{11}$ (cm ² /sec)
Lithium exchanged zeolite:		
25	0.0	0.20
"	0.9	0.66
"	1.9	0.84
"	3.2	1.1
"	5.1	1.5
"	6.3	2.0
22.4	0.0	0.24
"	0.0	0.22
78	0.0	2.4
"	0.038	2.8
"	0.28	3.2
"	1.3	3.9
"	2.4	4.7
"	3.4	5.2
75	6.3	10
Sodium exchanged zeolite:		
25	0.0	0.47
"	1.1	0.39
24.5	6.1	0.050
25	1.4	0.34
"	4.3	0.14
82	0.0	3.4
"	1.5	2.7
"	5.1	0.79
"	6.1	0.29
22.9	0.0	0.44
"	0.0	0.42
Potassium exchanged zeolite:		
25	0.0	0.00047
"	2.6	0.055
"	2.9	0.060
"	0.0	0.00053
22.5	0.0	0.00053
"	0.0	0.00054
72	0.0	0.0044
"	0.0	0.0044
75	2.7	0.030

Table (1): Diffusion Coefficients, D , of ethane in several ion exchanged zeolites of type Linde A, with various amounts of H_2O (molecules per zeolitic cavity or cage) sorbed prior to the diffusion experiment.