58. *Salt-inclusion Complexes of Zeolites.*

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Intracrystalline inclusion of salt from aqueous solution and from ionic melts has been investigated for two zeolites with very open anionic frameworks, in one of which, a near-faujasite, the equilibrium uptake of sodium chloride from aqueous solution gives isotherms of the opposite curvature from that of Langmuir's isotherm. The isotherm contour can, however, be interpreted as a Donnan membrane equilibrium, or in terms of the law of mass action.

The silver nitrate inclusion compound formed by a second zeolite, Linde molecular sieve 4A, has been demonstrated to have the composition $Ag_{12}[12AlO_2,12SiO_2]AgAlO_2,9AgNO_3$. X-Ray study has shown that there is an ordered cluster of nine silver nitrate molecules per large cavity in the structure, and that these are probably arranged with a rock-salt configuration, 5 of the $(Ag^+-NO_3^-)$ pairs in a cluster having one orientation and 4 such pairs being oppositely oriented. In the next cage the 5 and 4 pairs have respectively complementary arrangements to those in the first cluster so that a superstructure is observed, and the dimensions of the tetragonal unit cell thereby produced are $A = 2a$, $C = a$, where a is the cubic unit cell dimension of the parent zeolite. The existence of other complexes in which lithium, sodium, and ammonium nitrates replace silver nitrate has also been demonstrated.

ALUMINOSILICATE crystals in which inorganic salts are distributed throughout the anionic framework are not uncommon in Nature. Typical are the scapolites (marialite, wernerite, and meionite) and some felspathoids (sodalite, nosean, ultramarine, helvite, and cancrinite). In addition to the included salts a sufficient number of cations to ensure electrical neutrality is also dispersed through the framework. In the above crystals the salt is present as anion and cation pairs, but the cation may be indistinguishable from any of the additional cations which neutralise the aluminosilicate framework charge. In such structures as that of sodalite there is one anion–cation pair per cavity in the framework,[1] plus the framework cations. The anions are too large to escape from the cavities but

[1] Jaeger, *Trans. Faraday Soc.*, 1929, **25**, 320.

the cations are mobile, and can be exchanged freely.[2,3] Because of the immobilisation of the anions these ions are incorporated during crystal growth and are not liberated without destruction of the aluminosilicate framework.

Recently still more open-framework aluminosilicates have been synthesised[4,5] in which some of the cavities in the crystals are very large, and have wide " windows " linking them into an interconnected channel system. We now have the possibility of multiple occupancy[6,7] of these large cavities by cation–anion pairs (which we can conveniently call salt " molecules "). Moreover, because of the size of the windows the anions as well as the cations can migrate. The possibility therefore arises of studying reversible distributions of salt molecules between aqueous solutions and the interior of these crystals. Such a study is now presented, together with some structural features of salt-inclusion complexes.

The open aluminosilicate frameworks are stabilised by inclusion of fillers, which may be water molecules or salts. Such open frameworks will indeed only form in the presence of fillers, and quantitative measurements of salt inclusion can therefore indicate conditions which must have arisen in Nature for their formation.

EXPERIMENTAL

Materials.—Two zeolites, which have perhaps the most open aluminosilicate frameworks known, were used. These were Linde molecular sieve 13*X*, or Na-*X*, which is a synthetic near-faujasite,[4,5] and Linde molecular sieve 4*A*, or Na-*A*, which is a synthetic zeolite[4,5] without natural counterpart. The structure of both zeolites is known.[7,8,9] Each can be regarded as an arrangement of three kinds of polyhedral unit, one of which, of intermediate size, is common to each and also to sodalite. The polyhedra are built from $(Si,Al)O_4$ tetrahedra. It is, however, the largest of these polyhedral cages in each crystal which are important here; they open into one another by way of " windows," which are rings of twelve $(Si,Al)O_4$ tetrahedra in the faujasite-type crystals and of eight such tetrahedra in molecular sieve 4*A*. Thus two different interconnected channel systems are produced, one characteristic of each crystal. There is considerable information now available regarding the ion exchange[4,10,11] and the gas-sorbing and molecular-sieve properties of each crystal.[4,6]

" AnalaR " salts such as sodium chloride and silver, lithium, ammonium, and sodium nitrates were employed in the study of inclusion, either in aqueous solution or as their melts. Preliminary experiments revealed that Na-*A* did not occlude detectable amounts of sodium chloride from its concentrated solutions, nor did it undergo salt inclusion during ion exchange, so either this process is very slow, or the salt solutions were insufficiently concentrated. Accordingly salt inclusion by Na-*A* was investigated from ionic melts. With the more open lattice of Na-*X*, however, salt inclusion could be examined from aqueous solutions.

Procedure for Aqueous Solutions.—Weighed samples of Na-*X* were treated in sealed tubes with measured amounts of sodium chloride solution of known concentration. The tubes containing the mixtures were rotated for 4 or 5 days at 25° or 100°. Changes in the concentration of salt at equilibrium were small (~1%) so that the following method of measuring the occluded salt was adopted. The liquid was filtered off in a weighed sintered-glass crucible, and the weight of the wet solid determined. The zeolite was then dried by sucking air through the crucible to constant weight. The difference between the weight of the wet and the dry residue gave the amount of adherent water. Hence the amount, W_1, of adherent sodium chloride was found from the sodium chloride concentration in the filtrate. The crystals were then thoroughly extracted with hot water, and the total amount, W_2, of included and adherent salt

[2] Barrer and Raitt, *J.*, 1954, 4641.
[3] Barrer and Falconer, *Proc. Roy. Soc.*, 1956, *A*, **236**, 227.
[4] Breck, Eversole, Milton, Reed, and Thomas, *J. Amer. Chem. Soc.*, 1956, **78**, 5963.
[5] Barrer and Bultitude, in preparation.
[6] Barrer and Sutherland, *Proc. Roy. Soc.*, 1956, *A*, **237**, 439.
[7] Barrer, Report to the 10th Solvay Council, Brussels, May 1956, " Physical Chemistry of some Non-stoicheiometric Phases."
[8] Reed and Breck, *J. Amer. Chem. Soc.*, 1956, **78**, 5972.
[9] Bergerhoff, Koyama, and Nowacki, *Experientia*, 1956, **12**, 418.
[10] Barrer, Buser, and Grutter, *Helv. Chim. Acta*, 1956, **39**, 518.
[11] Barrer and Meier, in preparation.

determined. The amount of included salt was then $W_2 - W_1$, the accuracy being about $\pm 10\%$.

Procedure for Ionic Melts.—Inclusion complexes were prepared from Na-A and ionic melts in the manner illustrated below for the silver nitrate compound. About 2 g. of Ag-A were prepared by ion exchange [11] of Na-A by use of silver nitrate solution. The crystals were thoroughly mixed with about 10 g. of finely powdered silver nitrate, and the mixture placed in a small porcelain crucible. The crucible was then heated slowly (to prevent spitting due to over-rapid release of water during isobaric dehydration of the zeolite) to 250—260°, and kept thereat for at least 8 hr., after which the temperature was gradually lowered to room temperature during at least 6 hr. The product was finely ground and then washed quickly twice with cold water to remove the adherent silver nitrate. The inclusion compounds thus obtained were slightly yellow but were photosensitive and became dark grey if exposed to daylight for some time.

Investigation of Composition of Inclusion Complex (Ag-A,AgNO$_3$).—As it is almost impossible to prepare inclusion compounds by fusion in which the Ag-A lattice is both completely filled with silver nitrate and absolutely free from adherent silver nitrate, since appreciable amounts of the occluded salt (apart from adherent salt) are likely to be removed on continued washing, an e.m.f. method was used to determine the amount of occluded silver nitrate. A weighed quantity of the above unwashed product was finely ground and then added all at once to a vigorously stirred known amount of distilled water. The e.m.f. of the cell

$$\text{Ag} \quad | \quad \underset{\text{(I)}}{\text{AgNO}_3} \quad || \quad \underset{\text{(II)}}{\text{AgNO}_3} \quad | \quad \text{Ag}$$
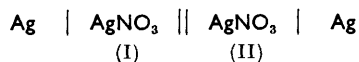
was then determined as a function of time. In the above cell compartment (I) contains the variable silver nitrate content derived from the crystals and compartment (II) is a standard reference concentration. A result is shown in Fig. 1. The silver nitrate concentration rose very steeply in the first few minutes until all the adherent silver nitrate was dissolved. The further increase in the silver concentration clearly obeys the $\sqrt{t}$ diffusion law ($t = $ time) and was regarded as due to extraction of included silver nitrate. This diffusion of intracrystalline silver nitrate from the well-ground powder is assumed to begin at zero time, and the amount of adherent silver nitrate, W_3, could thus be found by graphical extrapolation of the linear part of the graph of Fig. 1. The amount of intracrystalline silver nitrate, W_i, was then $W_i = W_4 - W_2$, where W_4 is the total quantity of silver nitrate present in the sample, which was determined by standard analytical methods.

The following results were thus obtained for the silver nitrate content of the pure inclusion compound of Ag-A: (i) 35·5%, (ii) 34·3%, (iii) 35·1% of AgNO$_3$. The mean value of 35·0% of AgNO$_3$ corresponds to 9·15 molecules of silver nitrate per unit cell of the zeolite, since the samples were anhydrous. This leads to the ideal formula

$$\text{Ag}_{12}[12\text{AlO}_2,12\text{SiO}_2]\text{AlO}_2,9\text{AgNO}_3$$
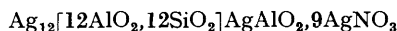
for the filled zeolite, the term in the square brackets denoting the composition and amount of the anionic framework per unit cell of the original zeolite.

Practically all the included silver nitrate could be extracted within 4 days with hot water in a Soxhlet apparatus, but only 65% of the total silver nitrate content was removed by percolating the sample with water for 10 days at room temperature.

Occlusion Isotherms of Sodium Chloride in Na-X.—By the above method we obtained the results in the Table for the amounts of sodium chloride, C_i (mmoles/g. of anhydrous Na-X) in equilibrium with solutions of normality C. When C_i is plotted against C the

Equilibrium occlusion of sodium chloride by Na-X.

Temp.	C of NaCl aq. (N)	C^2	C_i (millimoles of NaCl/g. of anhydrous Na-X)	Temp.	C of NaCl aq. (N)	C^2	C_i (millimoles of NaCl/g. of anhydrous Na-X)
25°	1·90	3·61	0·17	100°	1·00	1·00	0·07
	2·57	6·60	0·31		1·99	3·96	0·24
	3·36	12·32	0·45		3·06	9·38	0·63
	3·40	12·60	0·42		3·98	15·80	0·74
	4·09	16·75	0·74		4·62	21·4	1·21
	4·90	24·0	0·90				

isotherms have an upward inflexion, and so show a curvature in the opposite sense to that shown by Langmuir's isotherm. The amount of occlusion is thus negligible in dilute solutions, but becomes rapidly more important in very concentrated solutions. It can be seen qualitatively that the chloride ion, even with an accompanying sodium cation, will not be likely freely to enter the negatively charged aluminosilicate framework of the zeolite, unless its concentration in aqueous solution becomes large.

The phenomenon appears to be amenable to treatment from the viewpoint of a Donnan membrane equilibrium. At equilibrium we have the following system:

Solution	*Crystal*
Na^+ C; Cl^- C	Na^+ C_m; R^- C_r; Cl^- C_i

R^- refers to the anionic framework and C_r denotes the concentration of negative charge on the anionic framework which, provided the zeolite does not swell or shrink as a result of occlusion of sodium chloride, is constant. This condition is very nearly fulfilled. Also for electrical neutrality

$$C_m = C_i + C_r \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

At equilibrium, any transference of water as a result of salt occlusion being neglected, the Donnan equation takes the form

$$a_i a_m = a_\pm^2 \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

We then have from eqns. (1) and (2)

$$C_i(C_i + C_r) = \frac{C_\pm^2 f_\pm^2}{f_i f_m} = \frac{C^2 f_\pm^2}{_i f_\pm^2} \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

In eqn. (2) a_i and a_m denote the activities of intracrystalline Cl^- and Na^+ and $a_\pm$ is the mean activity of sodium chloride in solution; in eqn. (3), $C_\pm$ is the mean concentration of salt in solution, $f_\pm$ and $_i f_\pm$ are the mean activity coefficients of sodium chloride in solution and in the zeolite respectively. $_i f_\pm^2 = f_i \cdot f_m$ where f_i and f_m are the activity coefficients of Cl^- and Na^+ within the crystal. If we denote $f_\pm^2 / _i f_\pm^2$ by R then

$$C_i^2 + C_r C_i - R C^2 = 0 \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

The constant concentration C_r is about 12 equiv. per 1000 cm.³ of crystals while the Table shows that C_i in terms of moles per 1000 cm.³ of crystals is substantially smaller. Thus eqn. (4) approaches

$$C_i = R C^2 / C_r \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

and provided R does not depend very much upon C or C_i, C_i is proportional to C^2. Thus the observed upward inflexion of the isotherm is explained. Fig. 2 shows C_i plotted against C^2, and demonstrates that eqn. (5), or its more exact counterpart eqn. (4), is satisfactory in form. A little more salt is occluded at 100° (●) than at 25° (○).

If, per mole of sodium chloride included, n moles of water are displaced from crystal to aqueous solution, the inclusion process can be represented as

$$m H_2O_{aq} + m_i H_2O_i + Na^+_{aq} + Cl^-_{aq} \longrightarrow Na^+_i + Cl^-_i + (m + n)H_2O_{aq} + (m_i - n)H_2O_i$$

and the equilibrium constant becomes *

$$(a_i a_m / a_\pm^2)\{(a_{H_2O})_{aq}^n / [(a_{H_2O})_i^n]\} = K \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

This reduces to the form of eqn. (4) with $R = K(a_{H_2O})_i^n f_\pm^2 / [(a_{H_2O})_{aq}^n \cdot _i f_\pm^2]$ and, again provided R does not depend strongly on C and C_i, leads to the same conclusions.

The foregoing treatment is based on the important assumption that anion-sieve effects do not arise. These effects could inhibit anion uptake entirely in crystals in which cations

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* This equilibrium condition can be further simplified by assuming that for the distribution of water between crystals and solution an additional condition is $(a_{H_2O})_i = (a_{H_2O})_{aq}$. This assumption does not change our conclusions.

FIG. 1.

FIG. 2.

FIG. 3.

A

B

C

D

FIG. 4.

$2\nu_{rad}\left(Cu-K_{\alpha}\right)$

0·1   0·2   0·3   0·4

Powder pattern of primitive cubic lattice

P

(hkl) 100 110 111 200 210 211 220 {300 221} 310

Powder patterns showing superstructure

P I

P II

P III

P IV

1   2   3   4   5   6   8 9 10

$\left(h^2+k^2+l^2\right)$

Type

FIG. 5.

A

2a

A

● Ag^+
○ NO_3^-

FIG. 6.

α-cage

9·6 Å

FIG. 7.

$AgNO_3$ cluster

9·8 Å

interchange freely, since anions are normally larger than cations. The constancy of the exchanger volume for these crystals contrasts with the processes of swelling and shrinking with gel exchangers. These processes make interpretation of the experimental results for gels more difficult. Thus Bauman and Eichhorn,[12] who studied the uptake of anions by the cation-exchanger Dowex 50, could not interpret their results quantitatively on the basis of a simple Donnan treatment.

X-Ray Investigation of the Inclusion Compound Ag-*A*–AgNO$_3$.—Fig. 3 shows *X*-ray powder photographs of the following substances: (A) Ordinary Ag-*A*; (B) AgNO$_3$ inclusion compound washed twice with cold water; (C) completely extracted inclusion compound; (D) silver nitrate (for comparison). The most striking features in these *X*-ray powder photographs are the additional lines in the powder pattern of the inclusion compound B, which disappear completely on extracting the occluded silver nitrate from the zeolite (C) thus giving the initial pattern, *A*, again. It can easily be seen that these new lines do not correspond to the silver nitrate pattern (D). It must therefore be concluded that they represent superstructure lines, since they cannot be indexed on the basis of the cubic unit cell of Ag-*A* which has a cell constant $a = 12·3$ Å. The observed superstructure means that the included phase is ordered with respect to the host lattice and that the particular arrangement of the intracrystalline silver nitrate gives rise to a multiple unit cell. In addition there must be exactly 9 AgNO$_3$ units per unit cell, and hence per large or α-cage in the ordered arrangement, to agree with the composition given earlier (p. 301). Theoretical superstructure patterns were then considered in order to interpret the observed superstructure lines. The simplest of these patterns, which are shown in Fig. 4, are

P I: $A = 2a$ $B = a$ $C = a$ P III: $A = 2a$ $B = 2a$ $C = 2a$
P II: $A = 2a$ $B = 2a$ $C = a$ P IV: $A = a$ $B = a$ $C = 3a$

Comparison of the observed pattern with these theoretical patterns revealed that the observed lines were all compatible with pattern P II. The lines in the *X*-ray photographs of the filled Ag-zeolite could thus be indexed on the basis of a new tetragonal unit cell with the constants $A = 2a$ and $C = a$, where *a* is the unit cell constant of Ag-*A*.

Only one arrangement of the 9 silver nitrate units per unit cell could be found which satisfies both the type of superstructure and the available space in the large or α-cages of the structure. This probable arrangement of the Ag$^+$ and NO$_3^-$ ions is shown in Fig. 5,[13] where the direction of view is along the *C*-axis. The nitrate ions are drawn as spheres and are grouped together with the silver cations in small aggregates or clusters forming a cubic arrangement of the rock-salt type, the unit cell dimensions in two dimensions being thus doubled. It is also interesting that the arrangement leads to an antiparallel polarisation of neighbouring clusters. Figs. 6 and 7 illustrate the available space in the large cage and the size of the suggested silver nitrate clusters respectively. *X*-Ray investigation of this inclusion compound has not been carried further, since the actual positions of the nitrate ions can hardly be located by *X*-rays in the presence of the strongly scattering silver cations. Fig. 3 shows in addition that a slight expansion of the zeolitic framework is brought about by the occlusion of silver nitrate. Measurements revealed a relative expansion of 0·9%.

Quenching of the reactant mixture in the fusion experiment led to products whose rather diffuse *X*-ray patterns (with hardly any superstructure lines) indicated marked disorder. This shows that the gradual cooling of the reactant mixture is essential in the preparation of the filled species. Other inclusion compounds were prepared in the manner as described (p. 301) with molten lithium, sodium, or ammonium nitrates and the respective cationic form of the *A*-zeolite. The melts were held about 20° above the m. p. of the salt used. Extensive salt inclusion was observed in all these cases but quantitative compositions were not obtained because the e.m.f. method could not be applied.

[12] Bauman and Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2830.
[13] Cf. Barrer and Meier, *Helv. Phys. Acta*, 1956, **29**, 229.

The powder patterns of all these preparations revealed lattice expansions of about 1% as in the case of the silver nitrate inclusion compound. However, superstructure lines were observed only in the case of the Li-A–$LiNO_3$ complex, and this superstructure was of the same type as in the silver nitrate inclusion compound. This means that the arrangement of the included species must be essentially the same in both these cases in spite of the apparent differences in the ionic radii of Ag^+ and Li^+. Moreover, the absence of superstructure lines in the X-ray patterns of the sodium nitrate and ammonium nitrate compounds does not necessarily indicate structural differences between these compounds and the silver nitrate adduct. The superstructure may not be observable in these cases since the scattering factors of the Na^+, NH_4^+, and NO_3^- ions do not differ appreciably.

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