CRYSTAL HABIT VARIATION IN SODIUM FLUORIDE*

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CONTENTS

ABSTRACT

The effect of 143 inorganic and organic cosolutes, other than dyes, on the crystal habit of NaF was investigated experimentally. The cosolutes which effect variation from the ordinary cubical habit of NaF fall into two groups:

(1) Cosolutes which contribute OH ion to the solution cause a change in habit to octahedral. With increasing cosolute (OH^-) concentration, the NaF progressively crystallizes as cubes, skeletal cubes, skeletal octahedra and, above a liminal value, as octahedra. At still higher concentrations, a habit reversal, from octahedral back to cubic, may be observed.

The habit change is due to the substitutional adsorption of OH^- for F^- in the surface of the growing NaF crystals. The mechanism correlates with that found by Buckley for crystals of MRO_x and foreign ions of the type RO_x. The process by which the adsorption effects the change in habit finds explanation in terms of the growth mechanism demonstrated by Kossel and by Stranski for ionic crystals of the NaCl-type.

(2) Cosolutes which react to form double-salts with NaF. The habit variation is related to structural coincidences between crystals of NaF and of the double-salt, and marks an

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approach to a double-salt phase boundary in the solute-cosolute system. The adsorption is not by substitution, but involves the formation of a two-dimensional, essentially crystalline, double-salt phase in ordered apposition to the surface ions of the NaF crystals. The arrangement and spacing of the units composing the adsorbed layer of double-salt is so effected, by choice of adsorbing plane in the NaF, to be that proper to crystals of the double-salt itself. The habit variation in the NaF is a concomitant of this choice of adsorbing plane. The general situation correlates with the theory of double-salt formation advanced by Seifert and with the point of view of habit variation taken by Bunn.

The essential continuity of the crystal-adsorption mechanisms of Buckley and of Bunn is pointed out.

INTRODUCTION

It is a familiar fact that the habit of a crystal may be made to vary by the addition of a cosolute to the crystallizing solution. In recent years investigations directed at the cause of this effect have been largely concerned with the interpretation of crystal-adsorption in terms of crystal chemistry. In this direction, the researches of Buckley (1) have led to the recognition of similarities in size and shape between single ions of the cosolute and of the growing crystal as factors in the adsorption. On the other hand, Bunn (2) and later Royer (3) and Frondel (4) have emphasized the importance of coincidences in structure between the growing crystal and crystals of the cosolute in influencing the adsorption.

An essential difference is found between these views. According to Bunn, the adsorbed material is an essentially crystalline, continuous, two-dimensional phase which plates the surface of the adsorbing crystal much in the manner of an oriented overgrowth. The kind and degree of structural coincidence between the growing crystal and the adsorbed crystal-phase, and the habit of the latter, determines both the occurrence of adsorption and the direction of habit change. Buckley, on the contrary, views the adsorbed units as being scattered over the adsorbing surface, independent of each other and without the mutual interaction necessary to define crystallinity between themselves. The occurrence of adsorption and the choice of adsorbing plane in this view involves only geometrical considerations between the types of single ions involved.

OBJECTIVES OF THE INVESTIGATION

The present study was undertaken in hope of evaluating in the alkali halides the adsorption controls advanced by Buckley and by Bunn. The influence of inorganic and organic cosolutes, other than dyes, on the crystal habit of NaF and some related halides is described in this paper. Approximately 600 separate crystallizations were made, with 143 different cosolutes. The influence of 112 dyes on the habit and optics of NaF, LiF, NaCl, KCl, KBr and KI have been described in a previous paper (8).

Most of the recent work in the field has been concerned with substances, mostly salts of oxy-acids, that are relatively complex in structure and motif-configuration. The alkali halides of the NaCl-type seem specially suited for investigation, by reason of their simplicity of structure and motif, the detail in which their crystal chemistry is known, and the wealth of older experimental observations on their habit. Most important, the mechanism of growth from pure solution of the ionic NaCl-type crystals has been semi-quantitatively analyzed, by Kossel (5) and by Stranski (6), and is in agreement with observation (7).

EXPERIMENTAL TECHNIQUE

The crystallizations were made from 200 cc. volume by partial evaporation at 80°C. in an electric oven. This temperature was selected to permit parallel experiments on other alkali halides, some of which crystallize as hydrates at lower temperatures. The time of crystallization was usually 40 to 60 hours. Glass wool was added to the solutions, in the absence of free HF or strong alkali, to permit free development of the crystals. Beakers coated with alkali- or acid-resistant resin were used when necessary.

TYPES OF HABIT VARIATION IN NaF

CRYSTAL HABIT OF NaF FROM PURE WATER SOLUTION

NaF crystallizes as cubes from pure water solution at temperatures from 22° to *ca.* 100°C. and under conditions of either fast or slow growth. The other halides of the NaCl-type (Table 1) also crystallize from pure water as cubes. The habit from water is unknown for LiBr, LiI and β-CsCl and uncertain for CsF.

TABLE 1. ALKALI HALIDES OF THE NaCl-TYPE

a_0		a_0		a_0		a_0		a_0	
LiF	4.020	NaF	4.619	KF	5.333	RbF	5.63	CsF	6.008
LiCl	5.14	NaCl	5.628	KCl	6.278	RbCl	5.54	β-CsCl	7.10
LiBr	5.490	NaBr	5.962	KBr	6.578	RbBr	6.854		
LiI	6.000	NaI	6.462	KI	7.052	RbI	7.325		

The reason for the assumption of a cubical habit by these substances has been demonstrated by Kossel and by Stranski. Analysis of the energy changes accompanying the removal from solution, dehydration and ordered packing of alkali halide ions into a NaCl-type structure shows that the most stable configuration of surface ions is that of {100} planes. The ability to resolve accretion, or growth rate, of the {100} planes is hence a minimum, and the crystals develop as cubes.

It should be emphasized that the choice of surface configuration of ions, or habit, necessarily is an expression of the same factors that fix the choice of internal configuration of ions, or structure-type. These factors include the size, charge, hydration and polarizability of the ions concerned and, in addition, what may be termed environmental factors, namely, temperature, pressure, and the presence of foreign ions. Thus hydrostatic pressure may effect variation in structure-type, as with RbCl (9), and may also effect variation in crystal habit (10). The influence of temperature and of foreign ions on both choice of structure-type and of habit is a commonplace of genetic crystallography. Habit is the surface response of a crystal structure, or phase, to environmental conditions varying within the limits of stability of the phase itself.

CRYSTAL HABIT OF NaF FROM SOLUTIONS CONTAINING COSOLUTES

Variation from the ordinary cubic habit of NaF is found to accompany the presence of particular kinds of cosolutes in the crystallizing solution. The habit-varying cosolutes can be separated into two broad groups:

(1) Cosolutes which contribute OH ion to the solution, when present above a liminal concentration, change the habit of NaF to octahedral. The experimental observations which characterize this type of habit variation, and the mechanism by which the adsorption effects the change in habit, are described in Part I of this paper.

(2) Cosolutes which react to form double-salts with NaF. The experimental observations which characterize this type of habit variation, and the mechanism by which the adsorption effects the change in habit, are described in Part II.

PART I. EFFECT OF HYDROXYL ION ON THE HABIT OF NaF

SUMMARY OF EXPERIMENTAL OBSERVATIONS

The experimental observations which relate to the effect of hydroxyl ion on the habit of NaF may be summarized as follows:

1. The habit of NaF is changed to octahedral by all cosolutes which afford OH ion. The OH^- may be contributed directly, as by NaOH and other bases, or by hydrolysis, as with Na_2CO_3 and other salts of strong bases and weak acids. The data from which this conclusion is drawn are listed in Tables 2 and 3.

2. The habit-varying property of the OH-affording cosolutes is lost if the solution is made acid. Neutral cosolutes (NaCl, glycerin, etc.), cosolutes acid by hydrolysis $((NH_4)_2(SO_4))$ and acids do not cause habit variation. Some specific exceptions to the latter statement are described in Part II.

3. A certain cosolute (or OH^-) concentration, which differs for different cosolutes, is necessary before octahedra are formed. In general, as the OH^- concentration is increased from zero, the outward form of the NaF progressively changes from perfect cubes through

skeletonized cubes, skeletonized octahedra and, finally, above the liminal OH⁻ concentra-
tion, to perfect octahedra. With Na_2CO_3 a progressive habit reversal, from octahedral
through cubo-octahedral back to cubic, may occur if the concentration is increased still
further. This sequence does not refer to changes in a given crystallization, but to successive
experiments carried out at stepped cosolute concentrations. The experimental data for a
particular cosolute, Na_2CO_3 are cited in Table 3, and the corresponding growth forms are
represented in Figs. 1 to 9.

The concentration of a few OH-affording cosolutes, including very weakly alkaline sub-
stances and cosolutes which react to prohibit the crystallization of NaF, cannot be built
sufficiently high to cause the formation of anything other than skeletal growths.

4. The habit-varying effect of OH ion is peculiar to the alkali fluorides: NaF, LiF and
KF. RbF and CsF were not investigated. Neither octahedra nor skeletal growths are pro-
duced by OH⁻ with the alkali chlorides, bromides or iodides. The experimental data for
these substances is given in Table 4.

TABLE 2. INEFFECTIVE COSOLUTES, AND EFFECTIVE COSOLUTES OF THE HYDROXYL-TYPE

Cosolute concentration given in mols per mol NaF, unless otherwise stated.

INEFFECTIVE COSOLUTES

Halides. NaCl 1.0, 0.02. NaI 0.35, 0.02. NaBr 0.4, 0.02. NH_4F 1.0, 0.02. NH_4Cl 4.7, 1.0,
0.02. NH_4Br 1.0, 0.02. NH_4I 1.0., 0.02. LiF sat'd soln. KF 3.0, 0.02. KCl 1.0, 0.02. KBr 0.2,
0.10, 0.02. KI 0.2, 0.02. $SnCl_2$ (acid) 0.05. Also saturated with the following substances
(the solubilities are very small): CdF_2, CoF_2, CuF_2, CaF_2, FeF_3, PbF_2, SbF_3, ZnF_2, ThF_4,
CeF_4 and LaF_4.

Salts of inorganic acids. $NaClO_3$ 0.4, 0.2, 0.05. $Na_2Cr_2O_7$ 0.15, 0.05. Na_2CrO_4 0.15, 0.06,
0.02. $NaIO_3$ 0.125. Na_2MoO_4 0.17, 0.08, 0.01. $NaNO_3$ 0.8, 0.06. $NaNO_2$ 0.6. $Na_2S_2O_3$ 0.1.
$Na_2S_2O_6$ 0.2, 0.04. NH_4NO_3 0.5. $(NH_4)_2CrO_4$ 0.27. $(NH_2OH)_2 \cdot H_2SO_4$ 0.52. $KClO_3$ 0.25.
$KClO_4$ sat'd soln. K_2CrO_4 0.2, 0.06. KIO_3 0.19, 0.09. $K_2Cr_2O_7$ 0.15, 0.05. $KMnO_4$ 1.25, 0.1.
KNO_3 0.6, 0.05. $TlSO_4$ 0.1.

Salts of organic acids. Na acetate 0.2, 0.05, 0.01. Na oleate 0.01% soln. Na oxalate 0.24.
Na salicylate 0.25. NaCNS 0.5. NH_4 acetate 0.52, 0.05. NH_4 citrate 0.1, 0.015. NH_4 oxalate
0.18, 0.06. NH_4H oxalate 0.04. NH_4 tartrate 0.22. K acetate 0.4, 0.2, 0.05. K oxalate 0.22,
0.05. $K_4Fe(CN)_6$ 0.1. $K_3Fe(CN)_6$ 0.1. KH phthalate 0.2, 0.05. KH oxalate 0.3, 0.04. KH
tartrate 0.21.

Organic substances. Acetamide 1.0. Asparagine 0.04. Carbamide (urea) 6.0, 3.3, 1.0; also
ineffective at 6.0 at 23°C. Dextrose 0.3. Diethylene glycol 2.0. Formamide 1.5, 0.75.
Gelatin 1% soln. Glycerine 2.7. Glycocoll 1.0. Gum arabic 4% soln. Pectin 0.5% sol.
Resorcinol 0.05. Starch 0.5% soln. Succinamide 0.5. Sucrose 0.3. Terpin hydrate 0.05.
Thiocarbamide 1.0. Quinine sulphate sat'd soln.

Acids (concentrations in normalities). Acetic 0.3. Benzoic 0.25. Carbolic 0.43 (at 23°).
Citric 0.3, 0.07. Formic 3.0 (at 23°). HCl 0.3, 0.05. HNO_3 0.3, 0.05. H_2SO_4 0.3, 0.08, 0.01.
H_3PO_4 0.42, 0.15, 0.05. Lactic 2.0 (at 23°). Oxalic 0.1, 0.01. Picric 0.005. Propionic 2.0
(at 23°). Salicylic 0.08. Tannic 0.5% soln. Tartaric 0.1, 0.01.

EFFECTIVE COSOLUTES. SEE ALSO TABLE 6.

o = octahedra a = cubes

NaOH: o at 0.3, 0.1, 0.05, 0.025; a at 0.0025, 0.001. KOH: o at 0.7, 0.25, 0.09; a at 0.045, 0.017, 0.009. Na_2CO_3 (see Table 3). K_2CO_3: o at 0.46, 0.072; a at 0.0009. $NaHCO_3$: o at 0.5, 0.06; a at 0.001. $KHCO_3$ o at 0.4; a with small o faces at 0.05; a at 0.001. $Na_2B_4O_7$: o with small a faces at sat'n.; a at 0.125, 0.06, 0.02. NaCN: o at 1.0, 0.05. KCN: o at 1.0. Na_2SO_3: o at 0.32. Na_2WO_4: o at 0.15, a with small o faces at 0.06. K_2WO_4: a with small o faces at 0.1, a at 0.055. Sodium citrate: o with small a faces at 0.15, 0.075, 0.0037, 0.0015; a at 0.0001. Sodium tartrate: o with small a faces at 0.5; a at 0.2. Potassium tartrate: cubo-octahedra at 0.5; a with small o faces at 0.2, a at 0.07. NaK tartrate: a with small o faces at 0.15; a at 0.05.

TABLE 3. VARIATION IN OUTWARD FORM OF NaF WITH OH⁻
(Na_2CO_3) CONTENT OF THE SOLUTION

| Initial concentration of Na_2CO_3 in g./100 cc. NaF solution.[a]	Outward Form of NaF crystals
0	Cubes. Fig. 1
<0.001	Imperfect, composite, cubes; parallel aggregates of cubes.
>0.005 <0.03	Skeletal cubes. Figs. 2 and 3.
>0.05 <0.1	Skeletal octahedra, grading to composite octahedra. Figs. 4 and 5.
>0.2 <1	Octahedra. Fig. 6.
>2 <8	Octahedra modified by (100); (100) increasing in size with concentration. Figs. 7 and 8.
>10 to 30	Cubes. Fig. 9.

[a] Summarized from 76 separate crystallizations at stepped concentration intervals. Check runs over portions of the sequence agreed internally, but did not correlate exactly with other sequences.
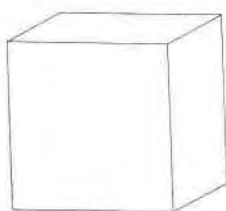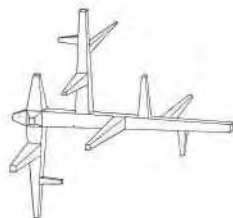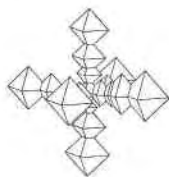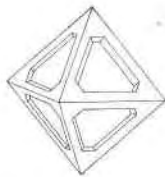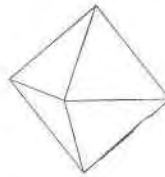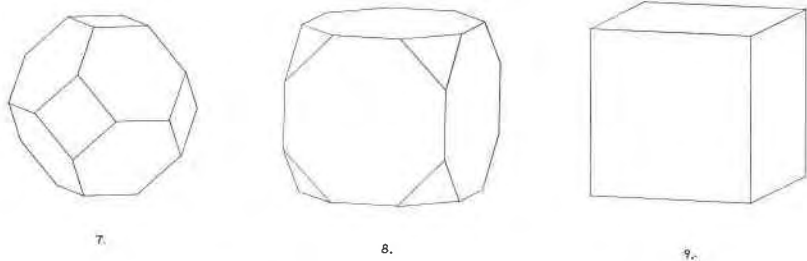

FIGS. 1-6. Sequential habit variation in NaF.

FIGS. 7–9. Sequential habit variation in NaF.

TABLE 4. EFFECT OF OH ON THE HABIT OF SOME NaCl-TYPE ALKALI HALIDES

Cosolute concentrations cited are in mols per mol AB or in mols per liter; other data from literature. Crystallized at 80° for new data, and at ca. 24° for literature. The pure solution habit of these halides is cubic.

	NaOH	KOH	Na₂CO₃	K₂CO₃	NaCN	KCN
LiF	111 (Table 5)					
NaF	111 (See Tables 2 and 3)	111	111	111	111	111
NaCl	100[a] 0.1, 0.25 M/M	100	100 0.2 M/M	100		
NaBr	100 0.1, 1.0 M/M				100 3 M/L	
NaI	100 0.1 M/M					
KF		111[b] 0.1, 10 M/L				
KCl	100 0.2 M/M	100 0.1, ~sat'd	100 0.1, sat'd	100[d]		100 4 M/L
KBr	100 0.05 M/M	100[c]	100	100		100 4 M/L at 40°
KI	100 0.05 M/M	100				100 5 M/L at 40°

[a] 10% NaOH is said to give tiny modifying {111} faces, and 20% NaOH slightly larger {111} faces. "Strong" NaOH is said to give cubes in fast growth and cubo-octahedra in slow growth. NH₄OH gives cubes.

[b] At 40°C. A birefringent hydrate (?) was obtained at lower temperatures. KF crystallizes with difficulty.

[c] KOH is variously said to give cubes or cubo-octahedra.

[d] K₂CO₃ is variously said to give cubes or octahedra.

Mechanism of the Habit Variation

Substitutional Adsorption of Hydroxyl Ion. In the foregoing discussion the habit-varying property possessed by a number of cosolutes for the alkali fluorides was identified as OH ion. As is seen from the accompanying list, the ionic radius of OH^- is nearly identical with that of F^- and is considerably smaller than that of Cl^-, Br^-, or I^-.

	OH^-	F^-	Cl^-	Br^-	I^-
Ionic radius (for C.N.6):	1.35	1.33	1.81	1.96	2.19

This suggests that during the growth of the fluoride crystal an OH ion can slip into a position intended for an F ion. Isomorphous substitution between these ions is, in fact, found in many minerals.

NaF crystals grown from solutions containing OH^- and F^- in the ratio of 1:2 were found analytically[1] to contain only 0.003 per cent OH, corresponding to 1 substituted OH ion for about 13,500 F ions. This amount of OH^- seems entirely too small to be alone responsible for the habit variation, although no evidence can be brought to justify this view. Admitting the essential role of OH^-, the habit variation may also be ascribed to OH ions which substitute for surface F ions of the growing NaF crystals and, after a brief life span (adsorption) on the surface, are displaced by F ions through competition from the solution.

The consequences in point of habit variation of a substitution of OH^- for F^-, either transient or permanent, may now be considered. As shown by Kossel and by Stranski, the growth of {100} planes in an ionic NaCl-type crystal takes place essentially *per saltum*, by the deposition of successive ion layers. Accreting ions or ion-pairs are not attached with equal ease to the various positions of surface coordination in the {100} planes, but deposit most readily at corner positions, less readily at edges, and least readily in face interior positions. An ion-layer once initiated tends to complete itself, by spreading laterally row by row over the surface, before the deposition of a new layer, since less energy is required to continue the growth of an already initiated layer than to start a new layer. This mechanism emphasizes the effect of substitution, in that a few foreign ions, strategically placed at the corners or at the ends of incomplete rows, may block the spreading of an entire layer. The idea is implicit that the foreign ion is unable to fill the role in the growth process proper to the ion species for which it substitutes.

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[1] The OH content was estimated by comparing the *pH* of a solution of NaF crystals previously re-crystallized from pure water with that of crystals grown slowly (60 hours) from a solution containing added NaOH. The crystals were repeatedly washed in saturated NaF solution made acid with HF, and in water. The x-ray powder patterns of the two preparations were identical in spacing and intensities.

Substitutional blocking of the nature described, involving an equal ease of substitution of the foreign ion at all surface positions, would only result in a general slowing of growth of the crystal without habit variation. It is well known, however, that there are relative differences in the ease of attachment of foreign ions and of crystal ions to the various surface positions. The edges and corners of crystals are found to play a special role in this regard, and serve as active spots in crystal adsorption.[2] The development of skeletal growths and of octahedra in NaF is believed primarily due to the preferential deadening of the cube-corner centers of nucleation by the substitution of OH ions therein. This places greater emphasis in the growth process on nucleation from face-interior positions, which, while inherently less favorable during pure growth, are now relatively more free from foreign ions. The lateral spreading of ion-layers thus initiated, however, generates new corner positions, which may then be selectively occupied and deadened by additional foreign ions.

Octahedra as a Consequence of Ion Substitution. The essential circumstance for the development of octahedra is the incomplete overlap at the cube-corners of successive ion-layers. The geometry of the situation is such that the successive coplanar set-backs thus generated define an octahedron. In terms of Haüy's derivation of secondary forms, the regular periodicity in the deposition of successive non-overlapping layers of "molecules integrantes" defines a (coplanar) surface with rational indices.

The above situation can hold only above a limiting incidence of OH⁻, to be identified with the experimentally observed liminal OH⁻ concentration, at which the corner positions are occupied and deadened as soon as they are generated. At lesser rates of substitution of OH⁻ (low cosolute concentrations) one or more exactly superposed ion-layers may be deposited, as in growth from pure solution, before the growth is interrupted by the substitution of an OH ion into a corner position. This mechanism presumably applies to the formation of the skeletal crystals observed below the liminal concentration of OH⁻. No simple geometrical explanation of the process is apparent.[3]

[2] The substitutional adsorption of ThB for Pb in the edges and corners of growing $PbCrO_4$ crystals, demonstrated by Schwab, G. M. and Pietsch, E. (*Zeits. phys. Chem.*, **2B**, 262, 1929) is an instance in point. The frequent localization of a super-crystallizing mineral to the edges and corners of the incrusted crystals is a further illustration (Frondel, C.: *Am. Mus. Nat. Hist. Novit.*, **759**, 1–15, 1934).

[3] The development of skeletons is peculiar to OH⁻ in low concentrations. Ordinary cubes are obtained from pure solution in either slow or fast growth, from solutions containing gum arabic, gelatine, starch and other thickening agents, and from solutions containing acids and other non-alkaline ineffective cosolutes.

Habit Reversal at High Cosolute Concentrations. Na_2CO_3 has a peculiar effect, not hitherto noted in habit variation studies, on the habit of NaF. If the concentration of Na_2CO_3 is increased considerably above that necessary to produce octahedra, modifying cube faces appear on the octahedra and gradually increase in size with concentration (in separate crystallizations) until finally only simple cubes are formed. The experimental data are tabulated in Table 3, and the habits shown in Figs. 7, 8 and 9. Habit reversal was not observed with Na_2SO_4, Na_3PO_4 or H_3BO_3. Other cosolutes were not systematically investigated in this regard.

LiF was also found to exhibit habit reversal, in the presence of NaOH. The data are listed in Table 5. The liminal concentration of OH^- necessary to produce octahedra in LiF is much greater than with NaF.

TABLE 5. VARIATION IN OUTWARD FORM OF LiF WITH OH^-
(NaOH) CONTENT OF THE SOLUTION

Final conc. of NaOH in g./100 cc. LiF solution[a]	Outward Form of LiF crystals
<1	Mixtures of cubes and skeletal cubes.
>5 <15	Mixture of warty cubic crystals and aggregates with ordinary cubes and skeletal cubes. Some crystals with octahedral faces at higher concentrations.
>20 <80	Mostly cubo-octahedra mixed with octahedra; some cubes and warty growths.
>100	Cubes.

[a] Summarized from 18 separate crystallizations.

The variation from octahedral back to cubical appears to be the final consequence of the substitutional-adsorption mechanism previously outlined. Cube faces make their first appearance on the octahedra when the concentration of OH^- becomes sufficiently high to interfere with nucleation from the face-interior positions. The preferential substitution of OH^- at the corners, which is responsible in the first place for the formation of octahedra, is then relatively less important, and OH^- and F^- compete on a more equal basis for all positions of surface nucleation. This is equivalent to the situation in pure growth, and a cubical habit develops.

Part II. Effect of Double-Salts on the Habit of NaF
### Summary of Experimental Observations

A group of cosolutes can be recognized which effect habit variation in NaF by a mechanism different from that of the OH-affording cosolutes described in Part I. These cosolutes comprise the normal and, to a less extent, the acid, alkali sulphates, phosphates, arsenates and vanadates, and probably also H_3BO_3 and Na_2BrO_3. The experimental data relating to these substances are summarized in Table 6. The distinctiveness of the group is indicated by the following considerations.

1. Hydroxyl ion is not the habit-varying agent, since the cosolutes remain effective if the crystallizing solution is made faintly acid.

2. Substitution of the cosolute anions in place of single ions in the NaF structure, analogous to the substitution of OH^- for F^-, appears impossible because of marked differences in the size, shape and charge of the ion-species involved. Dimensional coincidences are also lacking for the attachment of the (tetrahedral) cosolute anions to the crystal by the substitution of a face or edge of the tetrahedron for groups of adjoining F ions in the NaF. While a triangular configuration of F ions is found in {111} planes of the halide, the interionic distances are considerably greater than the triangle sides of the cosolute tetrahedra. The values for the halides increase in the series $Li^+ \rightarrow Rb^+$ and $F^- \rightarrow I^-$ from 3.26 Å in NaF to 5.18 in RbI. These values compare with a triangle side, or 0–0 distance, of *ca.* 2.8 in the RO_4 ions.

3. The habit variation is independent of the cosolute ions as individuals, but instead appears to be connected with the presence of a definite combination of foreign ions in the solution. Thus Na_2SO_4 is effective, but other sulphates, as $(NH_4)_2SO_4$, H_2SO_4, $TlSO_4$, hydroxylamine sulphate and quinine sulphate, are ineffective. Similarly, phosphates other than the specific ones mentioned are ineffective. If the effect was dependent on the SO_4, PO_4, BO_3, etc., ions as such, then all cosolutes affording these ions should be comparable in efficiency, just as OH is effective largely without regard to the particular cosolute affording it. A complicating factor enters in that the degree of ionization of the cosolutes in the NaF solution, and the effect that this has on the adsorption, is unknown.

4. In a series of acid salts of the effective cosolutes, the effectiveness decreases with increasing acidity. The following sequences were observed:

$$Na_3PO_4 > Na_2HPO_4 > NaH_2PO_4$$
$$Na_2SO_4 > NaHSO_4$$
$$Na_3AsO_4 > Na_2HAsO_4$$
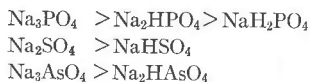
This behavior also suggests the adsorption of a specific compound, i.e., the normal salt, or a compound containing the normal salt such as the double-salt, $Na_2SO_4 \cdot NaF$. The decreasing effectiveness with increasing acidity would then reflect the smaller concentration of normal salt available in the solution. However, ionization effects, as noted in 3 above, may also be involved.

5. The present cosolutes are distinguished as a group by the fact that they form double-salts with NaF. These double-salts are closely related in the geometry and dimensions of their lattices to NaF. The double-salts themselves can be crystallized out from the NaF solutions at high cosolute concentrations. Compound formation of this type is lacking with the OH-affording cosolutes, and with the ineffective cosolutes in general.

TABLE 6. COSOLUTES EFFECTIVE WITH NaF, CONTINUED.
DOUBLE-SALT-FORMING TYPE

*Cosolute concentrations given in mols per mol NaF. Liminal
concentration for {111} is between limits given.*

	R_2PO_4	R_2HPO_4	RH_2PO_4	R_2SO_4	$RHSO_4$
Na	111 > .003 100 < .0004	111[a] > .11 100 < .02	100[b] > .3 100 < .15	111[d] > .12 100 > .001	100 < .2
K	111 > .02 100 < .0006	111 > .06	111 at .7[e] 100 < .037	111 > .03	111 > .75 100 < .3
NH$_4$		100[b] at .3 100 < .15	100[b] at .17 to .35	100[c] < .3	100 < .17

NaNH$_4$HPO$_4$:cubo-octahedra at .2   Na$_3$AsO$_4$:111 > .4, 100 < .18
Na$_2$HAsO$_4$:100 < .2   Na$_3$VO$_4$:111 at .27
NaBrO$_3$:111 > .3, 100 < .15   KBrO$_3$:111 > .25, 100 < .03
H$_3$BO$_3$:110 from .65 to 3.0, 100 from .4 to .03

[a] With small 100 modifying faces.   [d] Cubes with small 111 at .015.
[b] With small 111 modifying faces.   [e] Some with very small 111 faces at .3.
[c] Cubo-octahedra at 0.3.

It appears from the foregoing considerations that the adsorption, if the habit variation is so ascribed, cannot be referred to an ion-substitution mechanism such as found with OH ion and NaF and, earlier, by Buckley with RO$_4$ ions and oxysalts. An interpretation of the habit variation consistent with the observed and inferred relations is found, however, from the general point of view of Bunn, and is described on the following pages.

MECHANISM OF THE HABIT VARIATION

Structural Control of Double-Salt Formation. The correlation between compound formation and habit variation noted in 5, above, recalls the findings of Retgers (11) and of Orloff (12), to whom most of the earlier work on habit variation in the alkali halides is due. These experimenters concluded that the habit-varying effect which a cosolute had for an alkaline halide did not rest in the cosolute itself, but in its ability to form double-salts with the halide. The actual mechanism by which the habit variation was effected was not explained.

The underlying reason for the correlation has become apparent through the work of Seifert (13) on the theory of double-salt formation. Habit variation is a concomitant of structural relations between solute

and cosolute which determine, in the first place, the formation of a double-salt between these substances. Seifert has shown that a large class of double-salts have what may be termed sandwich structures, in which the several components of the double-salt may be recognized as discrete layers periodically alternating in the structure. The Mg_2SiO_4 and $Mg(OH, F)_2$ layers in the minerals of the humite group and the Al_2SiO_5 and $Fe(OH)_2$ layers of staurolite illustrate the principles of the arrangement. According to Seifert, double-salts are formed from solutions that contain two compounds (solute and cosolute as here spoken of) which are structurally related and which are present in proportions at or near the required stoichiometric proportions for the double-salt. Under these circumstances the two compounds may intercrystallize along the planes of structural resemblance, affording the regularly stacked layers which compose the structure of the double-salt.

In illustration, the formation of the double-salt $KPbCl_2 \cdot H_2O$ from KCl and $PbCl_2$, as shown by Mehmel and Nespital (14) and, later, by Seifert, is conditioned by the identity of arrangement and spacing of Cl^- in the $\{323\}$ and $\{121\}$ planes of the double-salt with the $\{111\}$ Cl^- planes of KCl. If, in the crystallization of the double-salt, the Pb^{++} concentration is decreased relative to K^+ and Cl^-, a point is reached at which KCl appears and crystallizes in oriented fashion upon the earlier formed double-salt crystals. The law of orientation is $(111)_{KCl}//\{323\}_{D-s}$ and $(11\bar{1})_{KCl}//\{\bar{1}21\}_{D-s}$, in which $\{323\} \wedge \{\bar{1}21\} \sim (111) \wedge (11\bar{1})$. The KCl crystals formed in this stage are *octahedra*. As the Pb^{++} concentration is further decreased the KCl forms *cubes*. The KCl crystals contain a small amount of Pb^{++}.

Habit Variation in NaF by Adsorption of Double-Salts. The variation in habit of NaF in the presence of the double-salt-forming alkali sulphates, phosphates, etc., is believed to be a consequence of the attachment (adsorption) of double-salt molecules, or of normal salt molecules, to the surface of the growing NaF crystals. This takes place under the impetus of the same forces which act in compound formation. The process can be viewed as a surface chemical reaction resulting in the formation of an "anchored" double-salt phase, in which the NaF part, or layer, of the double-salt is constituted by the surface ion-layers of the NaF crystal. The tendency for the formation of such a layer, and hence the strength of the adsorption, must increase as the solution (solute-cosolute system) approaches the phase boundary of the double-salt (e.g., KCl and $PbCl_2$). The outer portion of the double-salt layer is necessarily relatively mobile, but must tend for an ordered arrangement among its separate units in response to the same urge for a stable configuration that is expressed, at the proper cosolute concentration, by the formation

of actual crystals of the double-salt. The most stable arrangement and spacing would be that obtaining in crystals of the double-salt itself, or more specifically, since only two-dimensional or surface arrangements are involved, that obtaining in the growth surfaces of crystals of the double-salt. Accordingly, adsorption is facilitated upon any plane of the NaF which stands in structural relation to the double-salt, and that plane may thereby have its growth rate reduced sufficiently to cause it to appear on the NaF crystal.

Habit variation is not a necessary concomitant of the adsorption, but depends on the nature of the structural coincidences between the adsorbed substance and the crystallizing substance (NaF), and the crystal habits of the adsorbed and crystallizing substances. In general, habit variation may be expected (1) with an overall similarity of structure if the habits of the two substances are different, and (2) with a partial similarity in structure if the similarity is not in the normal habit of the crystallizing substance or in a vicinal plane of the crystallizing or adsorbed substances.[4]

The effect of the double-salt-forming cosolutes on the habit of NaF may now be considered from this point of view.

Na_3PO_4, Na_3AsO_4, Na_3VO_4

The crystallographic properties of the double-salts formed by these compounds with NaF are listed below.

$2Na_3PO_4 \cdot NaF \cdot 19H_2O$. Isometric (15). Habit octahedral.
    Isomorphous with the arsenate and vanadate analogues.
    X-ray data (16): Face-centered cubic; space group *Fd3c*; $a_0 = 27.86$; $N = 40$.
$2Na_3AsO_4 \cdot NaF \cdot 19H_2O$. Isometric. Habit octahedral.
    Cell dimensions not known.
$2Na_3VO_4 \cdot NaF \cdot 19H_2O$. Isometric. Habit octahedral.
    Cell dimensions not known.

The phosphate compound has a complete dimensional and geometrical analogue in NaF, with $a_{0NaF} = 4.619$ and $a_{0D-S} = 27.86$ where $27.86 = 6.0 \times 4.619$. Both lattices are face-centered cubic. Adsorption layers with a double-salt periodicity could hence form on any growth surface or plane of NaF regardless of indices. Crystals of the double-salt, however, are octahedral, and adsorption should therefore be favored on {111} planes. This would induce an octahedral habit in the NaF, as is observed. The cell dimensions of the octahedral arsenate and vanadate double-salts are doubtlessly close to that of the phosphate compound, with which they are isomorphous.

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[4] For further discussion of some of these factors see Bunn, C. W.: *Proc. Royal Soc. London*, **141A**, 567 (1933).

Na₂SO₄

When Na_2SO_4 is present in relatively high concentrations in NaF solution the double-salt $Na_2SO_4 \cdot NaF$ (*schairerite*) crystallizes out. With decreasing Na_2SO_4 concentration the NaF forms octahedra, skeletal cubes (due to hydrolysis of the Na_2SO_4) and, finally, at very low concentrations, simple cubes. The crystallographic properties of $Na_2SO_4 \cdot$ NaF are described below.

$Na_2SO_4 \cdot NaF$. Natural crystals (*schairerite* (17)) are rhombohedral with large $\{10\bar{1}1\}$ and small $\{0001\}$, $\{10\bar{1}1\}$ and $\{10\bar{1}3\}$. Artificial crystals are flattened on $\{0001\}$ with $\{02\bar{2}3\}$, $\{10\bar{1}1\}$ and $\{10\bar{1}3\}$; these crystals show evidence of cyclic twinning of individuals of lower symmetry and have been said (18) to become homogeneous (rhombohedral) only above 105°. X-ray Weissenberg study by the writer on a natural crystal of the composition $Na_2SO_4 \cdot Na(F_{.81}Cl_{.19})$ gave a hexagonal cell inconsistent with the morphology, with $a_0 = 12.12$, $c_0 = 19.19$, $z = 21$, $G = 2.67$ (calc.), 2.61 (obsvd.). A rhombohedral interpretation with c_0 tripled (space group $R\bar{3}m$) is consistent with the morphological orientation and ratio but is unproved.

A dimensional coincidence exists between the hexagonal nets $\{111\}$ of NaF and $\{0001\}$ of the double-salt, with the long diagonal of the former net $= 2.1$ times $d_{[11\bar{2}0]}$ in the latter. The actual dimensional relations are somewhat uncertain since the data for the double-salt refer to material containing Cl in substitution for F, with correspondingly larger cell dimensions, and possibly to an inverted hexagonal modification. As a consequence of this relation, the adsorption of double-salt from the solution would be facilitated upon $\{111\}$ planes of the NaF, since the adsorbed material thereby approaches the stable $\{0001\}$ configuration of its own crystals.

H₃BO₃

H_3BO_4 is of special interest in that it produces dodecahedra, sometimes modified by very small $\{100\}$ and $\{111\}$ faces, in NaF. H_3BO_3 and NaF react in water solution, but the nature of the reaction is little known (19). $NaBO_2$ and $NaBF_4$ are the principal products, and the reaction is approximately represented by the equation:

$$4NaF + 6H_3BO_3 = NaBO_2 + NaBF_4 + NaB_4O_7 + 9H_2O$$
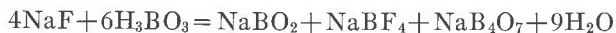
Complex double-salts between $NaBO_2$ and NaF have been reported but are considered mixtures (19). However, $NaBO_2$ forms a double-salt with NaCl as the mineral *teepleite*, $NaBO_2 \cdot NaCl \cdot 2H_2O$ (20). Efforts to prepare the fluoride analogue of teepleite were unsuccessful.

Teepleite has a simple tetragonal lattice with $a_0 = 7.27$ and $c_0 = 4.84$. A resemblance is found in $\{110\}$ of NaF to $\{110\}$ of teepleite, the dimensions of these rectangular nets being 4.84×10.28 for teepleite and

4.619×3.266 for NaF where $3 \times 3.266 = 9.798$. A closer correspondence would obtain in the fluoride analogue of teepleite due to the smaller radius of F^-. It appears possible from this that the variation to dodecahdral caused by H_3BO_3 on NaF is due to the appositional adsorption of an unstable structurally-related double-salt on $\{110\}$ of NaF. Some support for this belief is found in that H_3BO_3 does not effect the habit of KCl or NaCl and does not react with those substances.

NaBrO₃

NaBrO₃ produces octahedra with weak anomalous birefringence in NaF. NaIO₃ and NaClO₃ are ineffective. Double-salts between NaBrO₃ and NaF are unknown, although NaBrO₃ forms a double-salt with NaBr, and NaIO₃ forms double-salts with NaI and NaCl (21). Structural coincidences appear to be lacking between NaBrO₃ and NaF, and the habit variation cannot be ascribed with reason to the double-salt type.

Structure-Apposition Adsorption in Halides other than NaF. Many instances of habit variation in alkali halides other than NaF are found to be in line with the theory of compound formation and adsorption under structural control described above.

NaCl forms a double-salt with NH₃ and crystallizes from liquid NH₃ as octahedra; KCl does not form a double-salt with NH₃ and crystallizes from liquid NH₃ as cubes (22).

Na₂SO₄ and Na₃PO₄ do not modify the habit of NaCl or KCl and do not form double-salts with those substances.

Urea changes the habit of NaCl to octahedral, as a consequence of the formation of the double-salt $CO(NH_2)_2 \cdot NaCl \cdot H_2O$ (23), and orients upon NaCl (2). On the other hand, urea does not affect the habit of NaF, KBr, KI and LiF, and does not possess structural coincidences or form double-salts with them.

KCl and KBr form double-salts with a number of di- and trivalent metallic halides and are often modified in habit by such substances. Retgers remarks in this connection that NaCl, on the other hand, has a much less marked tendency to form double-salts with the metallic halides and is rarely modified in habit by them.

Instances are also known of double-salt formation by the cosolute which are not accompanied by habit variation. Thus, $C_{12}H_{22}O_{11}$ and $C_6H_{12}O_6$ form double-salts with NaCl but do not cause habit variation in that substance. Retgers notes other exceptions. As already remarked, the occurrence of habit variation depends on the nature of the structural coincidences and on the habits of the substances concerned, which may be such as to cause selective adsorption by the normal (pure-solution) habit. Moreover, the structure of the compound formed may not be of

the sandwich-like double-salt type on which the preceding discussion is based.

DISCUSSION

The mechanism of habit variation in NaF based on the appositional adsorption of structurally related cosolutes illustrates the point of view of crystal-adsorption taken by Bunn. A minor point of difference is found in that Bunn relates the occurrence of adsorption to the impetus of mixed crystal formation, while the present instances take place under the impetus of compound formation. A few of the examples cited by Bunn, notably $NH_4Cl + CuCl_2$ and $NaCl + urea$, are to be referred to compound formation. Doubtlessly relations between a growing crystal and a cosolute other than mixed crystal or compound formation also give rise to structure-apposition adsorption. Compound formation is relevant to habit variation in NaF only in that it presages a particularly strong adsorption relation.

The mechanism of habit variation in NaF based on the substitutional adsorption of OH ion is essentially similar to the mechanism found by Buckley. This mechanism should also apply to other alkali halides for the adsorption of monovalent foreign ions which approximate in size to the cation or anion of the halide. The direction of habit variation in such instances should always be to octahedral. Appositional adsorption, on the other hand, may give rise to a variety of habits, according to the nature of the structural coincidences and the habits of the substances involved.

Influence of the Counter-Ion in Substitutional Adsorption. The nature of the foreign counter-ion in substitutional adsorption must also be of effect, although it does not play the essential role that it does in structure-apposition adsorption. It is well known that the adsorption of salts by colloidally dispersed crystals is, as a rule, influenced by the nature of the counter-ion. The amount of the adsorption is frequently roughly paralleled by the solubility in the dispersion medium of the counter-ion—inner-ion compound. The influence of the counter-ion may be expected to be less marked with growing crystals than in colloidal systems, because of the dilution in the double-layer by the relatively large concentration of unlike crystal-ions of the same sign as the counter-ion of the cosolute.

Some observations by Buckley (24) on the substitutional adsorption of $SO_4^=$, $CrO_4^=$ and $SeO_4^=$ (as K salts) by growing $KMnO_4$ crystals are in line with a solubility effect. The strength of the adsorption, as evidenced by the efficiency in producing habit variation, is

$$SeO_4^= < CrO_4^= < SO_4^=$$

which is the order of increasing insolubility of the K salts.

Increasing influence of the counter-ion must, in general, mark a transition from substitutional to structure-apposition adsorption. The crystallization of a substance in the presence of a cosolute which can enter into extensive solid solution in that substance, the counter-ions being identical, would represent an intermediate case.

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