The values of the functions in equation 18 for various concentrations of hydrogen fluoride are given in Table V.

TABLE V

HEAT CAPACITY FUNCTIONS FOR AQUEOUS HYDROGEN FLUORIDE AT 25° (CALORIES/MOLE/°C.)

HF, %	$-(\bar{C}p_1 - \bar{C}^0p_1)$	$-(\bar{C}p_2 - \bar{C}^0p_2)$	$-(\bar{C}p - \bar{C}^0p)$
5	0.065	12.6	0.632
10	.111	11.6	1.16
15	.172	11.4	1.71
20	.246	10.9	2.20
25	.352	10.5	2.69
30	.492	10.1	3.17
35	.825	9.26	3.58
40	1.34	8.31	3.95
45	2.25	6.98	4.26
50	3.10	5.96	4.45
55	3.96	5.03	4.52
60	5.10	4.07	4.51
65	6.27	3.32	4.42
70	7.70	2.56	4.22
75	9.18	1.94	3.90
80	11.1	1.30	3.43
85	13.5	0.737	2.83
90	15.0	0.423	2.02
95	17.0	0.176	1.11

Summary

The activities of water and undissociated hydrogen fluoride at 25° have been calculated over the entire range of hydrofluoric acid solutions, and relationships were obtained to express these activities as a function of molality. The partial molal quantities, free energy, enthalpy, entropy and heat capacity, were calculated from available experimental data, and the relative thermodynamic functions per mole of solution were evaluated for the two-component system water and hydrogen fluoride.

WILSON DAM, ALABAMA RECEIVED MARCH 3, 1949

[CONTRIBUTION FROM BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND, MD.]

The Mutual Habit Modification of Sodium Chloride and Dipolar Ions

BY CHARLES P. FENIMORE AND ARTHUR THRAILKILL

A number of more or less detailed mechanisms have been suggested for the habit modification of growing crystals by added substances.[1] The effect must depend on preferential absorption, and Bunn has proposed a condition for strong absorption: that the atomic arrangement in the absorbing face of the host crystal must correspond to that in a face in crystals of the habit modifying substance. That is, the absorbed particles must lie on the crystal surface in nearly the same way as would be stable if these particles were to crystallize alone. A consequence of this view is that habit modification should generally be reciprocal. If substance A modifies the habit of B, one anticipates that the converse will occur unless the atomic arrangement of A which is similar to that of a plane in B exists on a face already prominent in A, in which case it would be impossible to tell whether the prominence of the face has or has not been affected by the presence of B.[2]

The work described in this paper was undertaken to see whether dipolar ions as a class would modify the habit of ionic crystals. In virtue of their dipolar character, the amino acids, for example, interact with dissolved sodium chloride and without regard to detailed mechanism, one might have thought that an interaction between growing sodium chloride crystals and dipoles dissolved in the saturated aqueous solution of sodium chloride would lead to crystal habit modification by almost any amino acid. This expectation was not realized. On the contrary, two of the three new habit modifiers found for sodium chloride appear to provide additional evidence for the absorption criterion stated above.

Results and Discussion

Under conditions of rapid crystallization (a drop of solution on a microscope slide) a solution of 10 g. of glycine in 100 g. of water, saturated with sodium chloride, deposits sodium chloride crystals showing the cube and the dodecahedron in approximately equal development instead of the cube only as is characteristic of sodium chloride grown from pure water. A 15-g. solution of glycine gives dodecahedra only. Since the aliphatic amino acids, almost entirely dipolar in neutral aqueous solution, are at the same time fairly strong acids and fairly strong bases, it is possible to show that the habit modification is due to the free dipoles. For glycine

$$H_3N^+CH_2COO^- + H^+ \rightleftharpoons H_3N^+CH_2COOH \qquad \log K = 2.31$$

$$H_2N^+CH_2(COO^- + OH^- \rightleftharpoons H_2NCH_2COO^- + H_2O \qquad \log K = 4.18$$

the ratio of dipolar to monopolar molecules drops from 5×10^4 to 10^{-1} when the *p*H decreases from 7.0 to 1.3 or increases from 7.0 to 10.8. If the 15 g. glycine solution, saturated with sodium chloride, is adjusted to *p*H 1.3 with hydrochloric acid, only cubes are observed. If it is adjusted to *p*H 10.8 with sodium hydroxide, cubes with an occasional very small octahedral face are obtained. That the effect of *p*H is not directly to cause reversion of growing sodium chloride to cubes, but to des-

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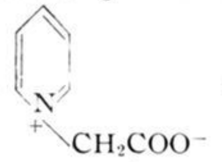
[1] For references, see Wells, "Annual Repts. of Chem. Soc.," **43**, 62 (1946).

[2] Bunn, *Proc. Roy. Soc.* (*London*), **141A**, 567 (1933).

troy the dipoles and thus permit the growth of cubes, can be demonstrated for acid solutions by working with the well known habit modifier, urea. Under our crystallization conditions, a solution of 15 g. of urea per 100 g. water, saturated with sodium chloride, deposits salt crystals showing equal development of the cube and the octahedron. Since urea is a much weaker base than glycine, the addition of hydrochloric acid to *p*H 1.3 has a negligible effect in this case although the addition of enough acid to neutralize half the urea does cause the sodium chloride crystals to grow as cubes.

For pyridine betaine  a concentration of about 40 g. per 100 g. of water when saturated with sodium chloride gives sodium chloride crystals showing equal development of cube and octahedron. The addition of one equivalent of hydrochloric acid, based on pyridine betaine content, to such a solution inhibits the change, unmodified cubes only being deposited.

β-Alanine (30 g. per 100 g. of water) gives clear cut octahedral truncations on cubes of sodium chloride. The addition of one equivalent of hydrochloric acid causes the formation of cubes only. The addition of one equivalent of sodium hydroxide does not inhibit the octahedral truncations.

α-Alanine, betaine, *α*-amino-*n*-valeric acid and *ε*-amino-*n*-caproic acid are ineffective in modifying the habit of rapidly growing sodium chloride crystals.

Figure 1 shows the appearance of sodium chloride crystals grown under some of the circumstances described above.

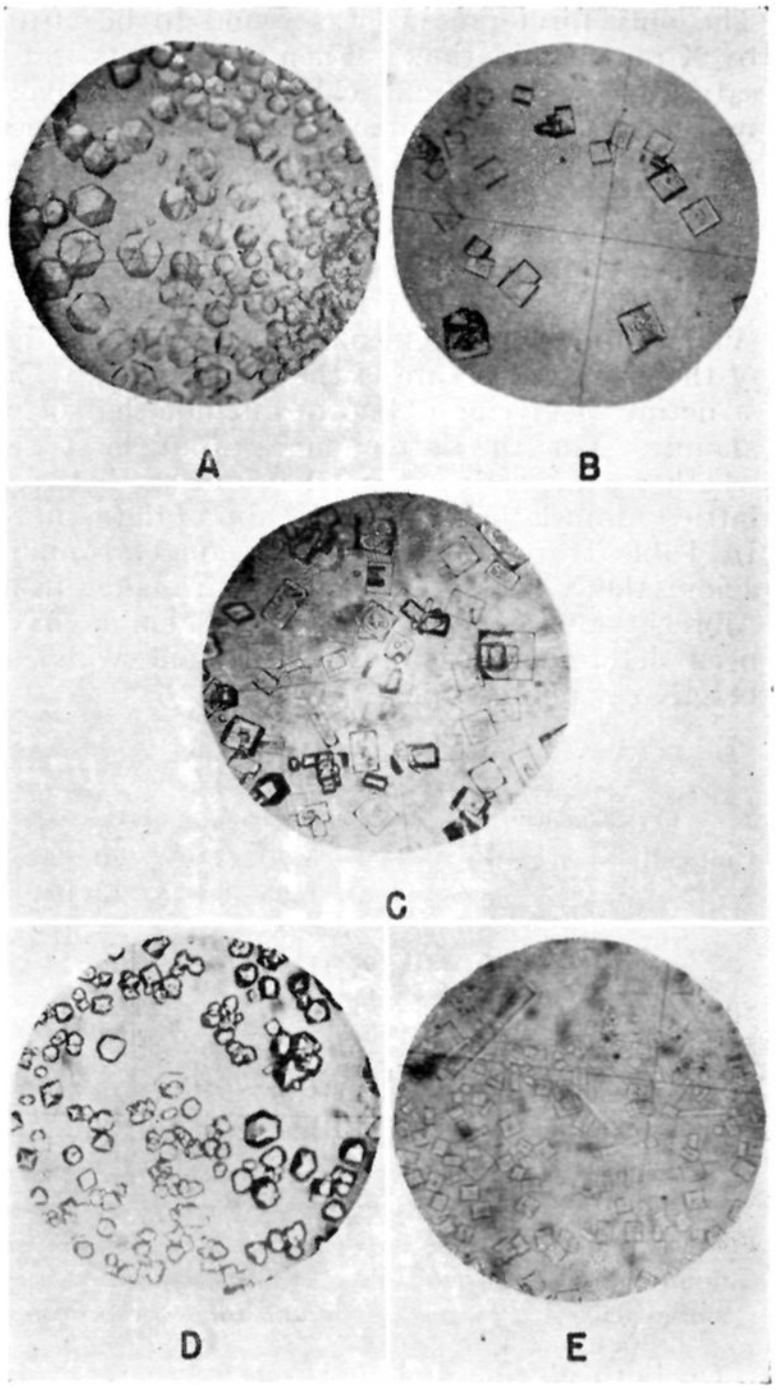


Fig. 1.—Photo-micrographs of sodium chloride crystals grown from: A, 15 g. glycine per 100 g. water saturated with sodium chloride; B, solution used in A adjusted to *p*H 1.3 with hydrochloric acid; C, solution used in A adjusted to *p*H 10.8 with sodium hydroxide; D, 40 g. pyridine betaine per 100 g. of water saturated with sodium chloride; E, solution used in D with one equivalent of hydrochloric acid added.

The aforementioned modifiers are much less effective on potassium chloride than on sodium chloride. Glycine has scarcely any effect, pyridine betaine and *β*-alanine cause slight development of octahedral truncations on the cube. On sodium bromide no effect was noted. For this substance the crystallization conditions were necessarily different to avoid the formation of sodium bromide dihydrate, and the sodium bromide crystals were grown more slowly at 58°.

It is clear from these experiments that dipolar ions are not in general habit-modifiers for sodium chloride, although some of them are. Because of the evident specificity, we have investigated the possibility that the substances which are effective in modifying growing sodium chloride crystals might themselves be modified when grown from saturated aqueous solutions of sodium chloride.

Glycine crystals (monoclinic 2/m) possess the forms {010}, {011}, {120}, {110} when grown slowly from water.[3,4] We have reindexed the forms given in Groth because the *a* axis used there must be halved in view of the X-ray results. When grown slowly from an aqueous solution saturated with sodium chloride, the crystals show a major change. The [010] zone, totally absent before, is developed. By optical goniometry, we have observed the forms {100}, {$\bar{1}$01}, {301} and {201}. The largest new faces are those of {100}.

Pyridine betaine grows as very thin platelets both from water and from water saturated with sodium chloride. Because of the inconvenience of working with them and the difficulty of observing truncations and habit variations, these crystals were not examined further.

β-Alanine grows from pure water as thick unterminated slabs with somewhat curved faces.

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(3) Groth, "Chemische Krystallographie," part 3, p. 96, Leipzig, 1920.

(4) Albrecht and Corey, THIS JOURNAL, **61**, 1087 (1939).

The only form present was found to be $\{010\}$ by X-ray examination. When grown from water saturated with sodium chloride, comparatively well formed orthorhombic crystals were obtained presenting $\{010\}$, $\{210\}$ and $\{101\}$ on goniometric examination.

Evidently there is reciprocal habit-modification between sodium chloride and two of the amino acids. To say whether the faces involved have similar atomic arrangements requires a knowledge of the crystal structure of the amino acids. The structure of glycine is known but not that of β-alanine. For the latter one can at least see whether a metric correspondence exists between lattice translations in the appropriate nets. In Table I are listed some data on two amino acids: the X-ray data for glycine are taken from Albrecht and Corey,[4] those for β-alanine have been determined from oscillation and Weissenberg X-ray photographs.

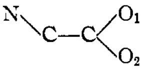
TABLE I

Crystal system	Glycine monoclinic	β-Alanine orthorhomic
Unit cell	a 5.10	a 9.82
	b 11.96	b 13.45
	c 5.45	c 6.04
	β 111° 38′	
Space group	$P2_1/n$	Pbca
Molecules per unit cell	4	8
Forms developed by sodium chloride in observed order of decreasing importance	$\{100\} = \{200\}$	$\{210\}$
	$\{\bar{1}01\}$	$\{101\} = \{202\}$
	$\{301\}$	$\{110\} = \{220\}$
	$\{\bar{2}01\} = \{\bar{4}02\}$	
Form developed on sodium chloride by the amino acid	dodecahedron	octahedron

On both glycine and β-alanine more than one new form is developed and we must decide which of them to compare with the appropriate form of sodium chloride as to mesh dimensions and structural arrangement. The choice is based on the extended law of Bravais which permits one to list the forms in their expected order of importance.[5] The law states that the expected order of importance of forms is the order of interplanar spacing, provided that forms are represented by their multiple indices (obeying the space group criteria). In the case of glycine, $\{100\}$ must be replaced by $\{200\}$ and $\{\bar{2}01\}$ by $\{\bar{4}02\}$. This substitution is indicated in Table I and the analogous transformation is made for β-alanine. The propriety of using the modified law of Bravais is suggested because the law is fairly well obeyed by the amino acids when grown from pure water: expected order for glycine is $\{020\}$, $\{011\}$, $\{110\}$, $\{120\}$; order found is $\{020\}$, $\{011\}$, $\{120\}$ all well developed, $\{110\}$ small: while the single form found on β alanine when grown from pure water, $\{020\}$, is the form expected to be most important.

Deviations from the expected order of importance are generally due to the intervention of strong structural features, and it appears reasonable to assume that deviations from the expected order in the new forms developed by sodium chloride are due to peculiarly strong interaction between sodium chloride and these planes. Any anomalously important form among those developed by sodium chloride will be picked therefore for comparison with sodium chloride. In glycine the order of importance of the new forms should be $\{\bar{1}01\}$, $\{200\}$, $\{301\}$, $\{\bar{4}02\}$ according to the generalized law of Bravais. The fact that $\{200\}$ is out of its proper order in being the most important new form observed suggests that this is the form which interacts most strongly with sodium chloride. In β-alanine $\{202\}$ is most unexpectedly prominent since it occurs far down the list in the expected order of importance. We compare, therefore, $\{200\}$ of glycine with the dodecahedron of sodium chloride, and $\{202\}$ of β-alanine with the octahedron of sodium chloride.

The dodecahedral faces of sodium chloride are composed of parallel rows of ions of like charge. The distance within a row between ions of the same type is 3.97 Å.; and $3 \times 3.97 = 11.91$ which differs by 0.4% from the b period in glycine. In the same faces of sodium chloride, the distance between ions of opposite charge is 2.81 Å.; and $2 \times 2.81 = 5.63$ which differs by 3.3% from the c period in glycine. Thus there is a good correspondence between the mesh of (200) in glycine and a multiple mesh on the dodecahedral faces of sodium chloride. Furthermore, (200) in glycine presents molecules



whose atomic coördinates in units of the primitive translations are

	x	y	z
O_1	0.805	0.410	0.740
N	.800	.410	.245

so that the vector, $N \rightarrow O_1$ (2.75 Å. in magnitude), is within 2.2% of the $Na \rightarrow Cl$ vector in length and almost exactly parallel to it when the b and c periods in glycine are directed as indicated and (200) in glycine is placed on the dodecahedral face of sodium chloride. It may be noted however that only one-fourth of the glycine molecules can occupy equivalent positions on sodium chloride because the b period in glycine, extending over four molecules of glycine, extends over only three ions of the same type in sodium chloride.

Between (202) of β-alanine and the octahedral faces of sodium chloride the metrical correspondence is fairly good. The octahedral faces of sodium chloride are composed of sheets of ions of like charge at the corners of equilateral triangles 3.97 Å. on a side and of 3.44 A. altitude. The mesh of (202) in β-alanine is rectangular;

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(5) Donnay and Harker, *American Mineral.*, **22**, 446 (1937).

13.45 (4 × 3.44 = 13.76) by 11.53 (3 × 3.97 = 11.91). The two pairs of comparable lengths differ by 2.3 and 3.3%, respectively. Our ignorance of the structure of this acid limits the comparison to mesh dimensions only.

Acknowledgment.—We have had the good fortune to be able to discuss this material with Prof. J. D. H. Donnay.

Summary

Glycine, pyridine betaine and β-alanine in aqueous sodium chloride solutions modify the crystal habit of growing sodium chloride; the first causes the formation of dodecahedra, the other two give octahedra. Glycine and β-alanine are themselves modified by sodium chloride. The largest or most unexpected (on the basis of the modified law of Bravais) new form developed on the amino acid is compared with the form developed on sodium chloride by the amino acid. A fairly good correspondence of mesh dimensions is found in both cases and a structural correspondence is found in the case of glycine.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1273]

The Coulometric Titration of Tripositive Antimony by Means of Electrolytically Generated Bromine and an Amperometric End-point

BY RAYMOND A. BROWN AND ERNEST H. SWIFT

Introduction

In the course of the work on the formal potential of the antimonous–antimonic half-cell in hydrochloric acid solutions described in the following article, the necessity arose of determining quantities of antimony ranging from 10 to 1,000 micrograms. The method and apparatus described by Myers and Swift[1] for the determination of arsenic which involved a coulometric titration with electrolytically generated bromine and an amperometric end-point seemed to offer distinct advantages. Therefore, an investigation of the application of this method to the titration of antimonous solutions in hydrochloric acid was undertaken. Since iodine was present in the solutions on which the potential measurements were being made, the study was extended to determine the effect of its presence.

Experimental Part

Chemicals.—A standard solution of tripositive antimony was prepared by dissolving an appropriate weight of the oxide in hydrochloric acid. Antimony trioxide was prepared according to the procedure described by Schumann.[2] The solution was standardized by titration with permanganate according to the procedure of Hillebrand and Lundell.[3]

Iodide solutions were prepared gravimetrically from dried reagent grade potassium iodide which had been tested for carbonate and iodate.

Reagent grade potassium bromide, free of extraneous oxidizing or reducing material, was used.

For reasons discussed below, most of the coulometric titrations were made in solution 2 v. f. (volume formal) in hydrochloric acid and 0.2 v. f. in potassium bromide. The reagent grade of concd. hydrochloric acid was found to give a titer corresponding to approximately 4×10^{-7} equivalent of reducing material per 10 ml. This was eliminated by adding a calculated amount of diluted 30% hydrogen peroxide and boiling the solution. At times the distilled water used contained as much as 2×10^{-7} equivalent of an oxidizing agent, believed to be chlorine. This was eliminated by bubbling air through the water while it was being boiled.

Apparatus.—The apparatus and procedure used were essentially the same as those described by Myers and Swift.[1] Preliminary experiments showed that antimony was reduced and deposited on the generator cathode. Therefore, this electrode was enclosed in a glass tube open at the top and provided at the bottom with a sintered glass plug. To prevent diffusion of solution from the titration cell into the cathode compartment, the solution therein was kept at a higher level and greater ionic strength.

Procedure.—The desired quantities of antimony, taken as Sb_2O_3 dissolved in 2 v. f. hydrochloric acid, were pipetted into the titration vessel and the appropriate volumes of hydrochloric acid, sodium bromide and water were then added to give the concentrations indicated. The titration procedure was carried out as described by Myers and Swift.[1] The end-point correction was determined by interpolation using a curve obtained by generating bromine in solutions of the same acid and bromide concentration as those of the titration and recording the indicator current readings at short time intervals. In the titrations with iodide present, the end-point was calculated in the same manner. The assumption was made that iodine was unipositive at the end-point. The titration in the presence of iodide is discussed below.

Discussion of the Method.—The data obtained from confirmatory titrations made under various conditions are collected in Table I. Experiments made to determine the effect of the hydrochloric acid concentration showed that in 1.5 formal hydrochloric acid there is some indication of a tendency towards negative errors, and that hydrolysis of the antimony became pronounced at lower concentrations of acid. When 4.0 formal hydrochloric acid was used, the indicator current gradually increased as the titration proceeded with the result that in the neighborhood of the equivalence-point the change in current was not rapid enough to give a clearly defined end-point. Measurements presented in the following paper indicate that the equilibrium antimonous–antimonic formal potential in 3.5 formal

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[1] R. J. Myers and E. H. Swift, THIS JOURNAL, **70**, 1047 (1948).

[2] R. Schumann, *ibid.*, **46**, 52 (1924).

[3] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1929.