THEORY OF ELECTROLYTE CRYSTAL GROWTH

THE PARABOLIC RATE LAW

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Abstract - Normally the growth of sparingly soluble electrolyte crystals
in aqueous solution follows a parabolic rate law, rate $\sim (c - c_s)^2$. At non-
equivalent concentrations, and in general, rate $\sim (\Pi^{1/\nu} - K_s^{1/\nu})^2$ where
Π = ionic product, K_s = solubility product, and $\nu = \alpha + \beta$ for the electro-
lyte $A_\alpha B_\beta$. It is shown how this can be explained by the Burton-Cabrera-
Frank theory adapted for electrolytes, assuming that the ions are adsorbed
in electroneutral (equivalent) amounts on the crystal surface. The absolute
rate is controlled by the integrating process and the activation energy
corresponds to the removal of one water molecule from the hydration shell
of the cation in the case of 1,1 and 1,2 electrolytes. For 2,1 and 2,2
electrolytes the ratio between the activation energy and the energy of
removal of a water molecule from the inner hydration shell is between 1.4
and 1.7.

INTRODUCTION

Marc[1] observed that the growth rate of potassium sulphate is proportional to $(c - c_s)^2$, and
Davies and Jones[2,3] found the same dependence for silver chloride. Davies and Jones[2,3] further-
more observed that for independent variations of $[Ag^+]$ and $[Cl^-]$ the rate was a function of
the product $[Ag^+][Cl^-]$. The generalization of these results to an $A_\alpha B_\beta$ electrolyte is

$$\text{rate} \sim (\Pi^{1/\nu} - K_s^{1/\nu})^2 \tag{1}$$

where Π = ionic product = $[A]^\alpha[B]^\beta$, K_s = solubility product (= value of Π at saturation) and
$\nu = \alpha + \beta$. Eq. 1 has later been confirmed for a large number of substances, especially by
Nancollas[4] and coworkers.

The parabolic character (with the power 2.0 on $c - c_s$) has been confirmed for electrolytes
of different valence types, and it makes it likely that the mechanism of growth is a surface
spiral step centered at a screw dislocation. This mechanism has been verified by van Enckevort,
Bennema and van der Linden[5] by observation of low-height growth spirals on crystals grown in
aqueous solution.

The classical paper by Burton, Cabrera and Frank[6] (BCF) deals almost exclusively with cry-
stal growth in gas phase at relatively small supersaturation, and has only a few prudent
suggestion concerning growth from solution, and nothing at all about electrolytes. The ionic
product dependence was discussed by Davies and Jones[3], but their explanation is unacceptable
because it assumes that the individual ions behave differently when the solution is subsatu-
rated and when it is supersaturated.

The following steps may be rate-determining - as well as combinations of them: Transfer of
growth units -

1) From the bulk solution to the solution just outside the crystals

2) From the solution into an adsorption layer

3) From the solution or an adsorption layer to the growth step (surface nucleus or spiral)

4) From the solution, adsorption layer or growth step to the growth site in the step

This leads to the following kinetics:

1) This is called transport controlled growth, and has been treated in Refs. 7-9. The linear growth rate $\dot{r} \equiv dr/dt$ is proportional to $c - c_s$ and to a function of crystal size and shape.

2) This is surface controlled growth with a linear rate law, $\dot{r} \sim c - c_s$.

3) The rate is proportional to $(c - c_s)/y_o \sim (c - c_s)\ln(c/c_s)$, y_o = step distance, or y_o^{-1} = (planar) step density.

4) The rate is proportional to $(c - c_s)/(x_o y_o) \sim (c - c_s)(c/c_s)^{\frac{1}{2}}\ln(c/c_s)$, x_o = kink distance, or x_o^{-1} = (linear) kink density.

(1) and (2) are linear rate laws, linear in $c - c_s$; (3) and (4) are parabolic rate laws meaning that for $c/c_s \approx 1$ the rate is approximately proportional to $(c - c_s)^2$ or $(S - 1)^2$, $S \equiv c/c_s$. For $s > 1.5$ the approximation $(S - 1)^2$ is much better for (4) than for (3).

If two or more of the four mechanism have combined influence on the rate they will be consecutive, and the mechanism that would be slowest at equal driving force will be most rate-determining. It follows that if the kinetics change with the supersaturation, a transition from parabolic at low to linear at high supersaturation will be actual. For small crystals of sparingly soluble electrolytes transition from (3) or (4) to (1) has been observed, and for larger, moderately soluble crystals transition from (3) or (4) to (2) seems to be usual, although distinction between (1) and (2) is not always clear.

In the following we shall need the expression for the kink distance (see figs. 1 and 2)

$$x_o = a\, S^{-\frac{1}{2}}\exp(a^2\sigma/kT) \tag{2}$$

and the step distance of a growth spiral

$$y_o = 4\pi[1 + (3S)^{-\frac{1}{2}}]R_c \tag{3}$$

where the radius of the critical surface nucleus is

$$R_c = \sigma v/(kT\ln S) \tag{4}$$

S = supersaturation ratio $\equiv c/c_s$ or $\equiv (\Pi/K_s)^{1/\nu}$, a = molecular diameter, usually calculated from the molar volume as $a = (V_m/\nu L)^{1/3}$, L = Avogadro constant; σ = interfacial tension crystal solution.

THEORY OF GROWTH RATE

As we have observed a very accurate parabolic law at much higher supersaturation than those where (3) is "parabolic" we shall in the following base the development on the case (4). The rate expression may be divided into two factors, a kinetic term proportional to $c - c_s$, and a term $1/(x_o y_o)$ which may be called "thermodynamic" because x_o and y_o are calculated by assuming equilibrium between the spiral step (at the center) and the kinks (locally) - and the solution. The derivations of the expressions for x_o and y_o are very close to the classical treatments, and may be found in the appendices 1 and 2. The kinetic term has not been treated before for the growth of electrolytic crystals.

As the kinetic factor is proportional to S - 1, we shall try to develop a theory for the rate j of integration of growth units into the kinks with a rate proportional to S - 1, or for an AB-electrolyte:

$$j \sim c_A^{\frac{1}{2}} c_B^{\frac{1}{2}} - K_s^{\frac{1}{2}} \qquad (5)$$

We shall first see how close we can get without paying attention to the electric charges. This may be considered as the theory for growth of a binary non-electrolyte AB which in solution is dissociated into the molecules A and B. The most obvious way of expanding the BCF theory to this case is to express the fluxes of A and B molecules into and out of the kinks by

$$J_A^+ = k_A c_A n_A \quad ; \quad J_A^- = k_A' n_B \quad ; \quad J_B^+ = k_B c_B n_B \quad ; \quad J_B^- = k_B' n_A \qquad (6-9)$$

where n_A is the number of growth sites into which an A molecule would fit, etc.; $n_A + n_B = n$, the total number of growth sites.

If the majority of the molecules entering into the growth sites come from an adsorption layer the same equations will be valid for the concentrations c_{Aad} and c_{Bad} in the adsorption layer (c_{Aad} is defined as the surface concentration Γ_A divided by the adsorption layer thickness, the definition of which is not critical for our conclusions below).

If the two species independently are in adsorption equilibrium with the solution so that

$$c_{Aad} = K_{Aad} c_A \quad ; \quad c_{Bad} = K_{Bad} c_B \qquad (10-11)$$

then the equations are directly applicable with redefined rate constants containing the adsorption coefficients [e.g. k_A(new) = $K_{Aad} k_A$(old)]. The net currents are

$$J_A \equiv J_A^+ - J_A^- = k_A c_A n_A - k_A' n_B \quad ; \quad J_B \equiv J_B^+ - J_B^- = k_B c_B n_B - k_B' n_A \qquad (12-13)$$

For the formation of a pure AB crystal it is necessary that $J_A = J_B$. Eliminating n_A and n_B one obtains the total current of growth units to the crystal

$$J = J_A + J_B = 2J_A = \frac{2n(k_A k_B c_A c_B - k_A' k_B')}{k_A c_A + k_B c_B + k_A' + k_B'} \qquad (14)$$

This is in general <u>not</u> a function of the product $c_A c_B$ as was found empirically for electrolytes.

At equilibrium $J_A = J_B = 0$ and consequently

$$c_{Ae} n_{Ae}/n_{Be} = k_A'/k_A \equiv K_A \quad ; \quad c_{Be} n_{Be}/n_{Ae} = k_B'/k_B \equiv K_B \qquad (15-16)$$

$$c_{Ae} c_{Be} = k_A' k_B'/k_A k_B = K_A K_B = K_s \qquad (17)$$

Then Eq. 14 may be written, for the current of ions per kink,

$$j = J/n = \frac{2k_A k_B (c_A c_B - K_s)}{k_A c_A + k_B c_B + k_A' + k_B'} \qquad (18)$$

Close to equilibrium the concentrations in the nominator may be approximated by their (constant) equilibrium values and Eq. 18 becomes of the form $j \sim c_A c_B - K_s$. This is of course a function of the product $c_A c_B$, but <u>not the correct</u> empirically found function, Eq. 5. We must conclude that when the solute is treated like a binary non-electrolyte the kinetic factor does not have the form found empirically. Therefore the <u>electric charges must exert an essential effect</u>. What can this be?

Firstly, the electric charges on the ions will make them more disposed for adsorbing at the crystal surface, cations above anions and vice versa. And secondly, as we cannot have any great net electric charge, they must adsorb in equivalent amounts (see Appendix 3), so that for the electrolyte $A_\alpha B_\beta$ we have $c_{Aad}/c_{Bad} = \alpha/\beta$. We take for simplicity a symmetric electrolyte AB

so that $c_{Aad} = c_{Bad}$. Applying Eq. 18 to the concentrations in the adsorption layer we find

$$j = \frac{2k_A k_B (c_{Aad}^2 - c_{Aade}^2)}{(k_A + k_B)c_{Aad} + k_A' + k_B'} = \frac{2k_A k_B}{k_A + k_B} \cdot \frac{(c_{Aad} + c_{Aade})(c_{Aad} - c_{Aade})}{c_{Aad} + (k_A' + k_B')/(k_A + k_B)} \quad (19)$$

This is of the same form as Eq. 5 <u>if</u>:

$$(k_A' + k_B')/(k_A + k_B) = c_{Aade} \quad \text{and} \quad c_{Aad}/c_{Aade} = c_A^{\frac{1}{2}} c_B^{\frac{1}{2}}/K_S^{\frac{1}{2}} \quad (= S) \quad (20\text{-}21)$$

Satisfaction of Eq. 20 is equivalent to having $n_{Ae} = n_{Be}$, as can be seen from Eqs. 15-16. Physically this means that A and B ions are equally strongly bonded at kinks. This is not surprising. Consider for instance a NaCl lattice. An A ion and a B ion, each of them in a kink, will have the same distance to all their corresponding neighbours in the crystal. The signs of all the electric charges are changed, but this does not change the forces, or the bonding energy. The equality of n_{Ae} and n_{Be} also means that the very crystal (in addition to the adsorption layer) is electroneutral.

If Eq. 21 is multiplied by c_{Aade}, squared, and $c_{Aad} = c_{Bad}$ inserted, we get

$$c_{Aad} \cdot c_{Bad} = K_a c_A c_B \quad (22)$$

where

$$K_a \equiv c_{Aade}^2/K_S = (c_{Aade} c_{Bade})/(c_{Ae} c_{Be}) \quad (23)$$

This is nothing but the condition for equilibrium between the adsorption layer and the solution, with K_a = the adsorption equilibrium constant. When Eq. 20-21 are fulfilled, Eq. 19 may be reduced to

$$j = \frac{2k_A k_B (c_{Aad} - c_{Aade})}{k_A + k_B} \equiv k_i V_w (c_{Aad} - c_{Aade})$$

$$= k_i V_w c_{Aade}(S - 1) = k_i V_w (K_a K_S)^{\frac{1}{2}}(S - 1) = k_i V_w K_{ad} c_s (S - 1) \quad (24)$$

where $K_{ad} \equiv K_a^{\frac{1}{2}}$ is the adsorption coefficient, V_w the molar volume of the solvent, and $k_i \equiv 2V_w^{-1} k_A k_B/(k_A + k_B)$ is the integration rate constant on mole fraction basis; $K_{ad} V_w c_s$ is the mole fraction of the solute near the growth site - at solubility equilibrium. For the electrolyte A_α

$$k_i \equiv \nu V_w^{-1} (\alpha/k_A + \beta/k_B)^{-1} \quad (25)$$

Conclusion of the discussion

The empirically found rate law, $\dot{r} \sim (S - 1)^2$, can be explained as follows on the basis of the BCF theory. One of the factors $(S - 1)$ comes from the density of kinks on the crystal face, $(x_o y_o)^{-1}$, where x_o = kink distance, y_o = step distance. For S values well above 1 the classical approximation $(x_o y_o)^{-1} \sim \ln S$ is not accurate enough. Instead one should apply

$$(x_o y_o)^{-1} \sim S^{\frac{1}{2}}(1 + (3S)^{-\frac{1}{2}})^{-1} \ln S \quad (26)$$

which is surprisingly well approximated by $S - 1$. The other factor $(S - 1)$ in $\dot{r} \sim (S - 1)^2$ is of kinetic nature. It is proportional to the net flux per kink of ions from the solution into the crystals. In order to get a factor of the form obtained empirically (with $S = (\Pi/K)^{1/\nu}$) it was found necessary to assume a considerable degree of adsorption of ions on the crystal surface, equivalent amounts being adsorped of the constituent ions, and the adsorption layer has to be in equilibrium with the solution. Furthermore the numbers of A- and B-kinks at equilibrium must be equal which is in accordance with the very high correspondance between the geometry and electric charges around an A and a B ion situated in their respective kinks. These assumptions allow us to derive the right form of the kinetic factor.

THE ABSOLUTE RATE

The flux j (Eq. 24) is the rate of integration of ions into the crystal lattice per kink. With the kink distance x_o and the step distance y_o the number of ions to be added at each kink in order to complete one layer of ions is $x_o y_o / a^2$ where a^2 is the area accupied by one ion (assuming for simplicity a NaCl lattice and cubical growth units). See Fig. 2. This takes the time $x_o y_o / a^2 j$ and displaces the surface by the distance, a. Consequently the linear growth rate is

$$\dot{r} = a/(x_o y_o / a^2 j) = ja^3 / x_o y_o \tag{27}$$

Inserting j (Eq. 24), x_o (Eq. A4), and y_o (Eq. A36) into Eq. 27 we obtain

$$\dot{r} = \frac{k_i K_{ad}^O c_s V_w kT(S-1)S^{\frac{1}{2}}\ln S}{4\pi a\sigma \exp(a^2\sigma/kT)[1+(3S)^{-\frac{1}{2}}]} \qquad = k_g\, g(S) \quad ; \tag{28}$$

where K_{ad}^O is the adsorption coefficient for contact adsorption (see Appendix 4) and where

$$k_g = \frac{k_i K_{ad}^O c_s V_w kT}{4\pi a\sigma \exp(a^2\sigma/kT)(1+3^{-\frac{1}{2}})} \quad ; \qquad g(S) = (1+3^{-\frac{1}{2}})(1+(3S)^{-\frac{1}{2}})^{-1}(S-1)S^{\frac{1}{2}}\ln S \tag{29-30}$$

TABLE 1. The function g(S) - and $(S-1)^2$ and $(S-1)\ln S$ for comparison

S	1	1.1	1.5	2	5	10	20
g(S)	0	0.0102	0.266	1.098	18.047	87.409	355.60
$(S-1)^2$	0	0.0100	0.25	1	16	81	361
$(S-1)\ln S$	0	0.0095	0.20	0.69	6.44	20.7	56.9

Reich[11] and Reich and Kahlweit[12] have suggested that k_i could be equal to the rate constant for removal of a water molecule from the (inner) hydration sphere of the cation - the rate constant for the similar process at the anion being much larger and thus not rate-determining. They found agreement with kinetic data on TlBr, but not for other substances. We shall return to this question later in connection with the comparison with empirical rates.

The adsorption coefficients K_{ad}^O for contact adsorption (where the ions are partly dehydrated and thus are supposed to require less activation energy for entering a growth site) are not known, but may be estimated on the basis of ion pair constants, as the forces bonding ion pairs and adsorbed ions are probably rather like (the water molecules screening against the electrostatic forces from the neighbouring lattice ions), whereas the geometry is quite different for adsorbed ions and ion pairs. The ratio between the adsorption coefficient and the ion pair constant depends rather much on the ionic type, as explained in Appendix 4.

Introducing the ion pair constant into Eq. 29 the expression for the over-all rate constant for $\alpha A^{a+} + \beta B^{b-} \rightarrow A_\alpha B_\beta$ (cr.) becomes

$$k_g = k_i K_I c_s kTM(a,b)/[a\sigma \exp(a^2\sigma/kT)] \quad \text{(S.I. unit m/s)} \tag{31}$$

where $1/M(a,b) \equiv 4\pi(1+3^{-\frac{1}{2}})n(a,b) \approx 20n(a,b)$ (see Eq. A88)

$$M(1,1) = 4\times10^{-3}, \ M(1,2) = M(2,1) = 5\times10^{-4} ; \ M(2,2) = 2\times10^{-4}$$

The value of the interfacial tension may sometimes be determined from the induction period of homogeneous nucleation, and related phenomena, as shown by Nielsen[4], Nielsen and Sarig[13] and Nielsen and Söhnel[14]. As shown in the paper with Söhnel[14] there is a good correlation between the solubility and the interfacial tension of ionic crystals (which excludes silver

halides). Later work (not published yet) has shown that there is an even better correlation between c_s and $a^2\sigma$. Therefore, if σ is not known from experiments with the actual electrolyte it may be estimated from the empirical relationship

$$\exp(a^2\sigma/kT) = 16.7(c_s/\text{mol m}^{-3})^{-0.27} \tag{32}$$

or

$$\sigma = a^{-2}[11.6 - 1.12\ln(c_s/\text{mol m}^{-3})]\times10^{-21} \text{ J} \tag{33}$$

(with a in meter the unit for σ becomes J/m^2 or N/m); a is calculated as $(V_m/\nu L)^{1/3}$ where V_m is the molar volume, ν the number of ions in a formula unit ($\nu = \alpha + \beta$) and L is the Avogadro constant.

In Table 2 a few representative examples are given of the empirical rate constants k_g and the corresponding values of k_i that satisfy Eq. 31

TABLE 2. Representative kinetic data, 25 $^\circ$C, aqueous solution

Electro-lyte	c_s $\frac{}{\text{mol/m}^3}$	a $\frac{}{\text{pm}}$	σ $\frac{}{J/m^2}$	K_I $\frac{}{m^3/\text{mol}}$	r $\frac{}{\mu m}$	S	k_g $\frac{}{\text{nm/s}}$	k_i $\frac{}{s^{-1}}$	k_w $\frac{}{s^{-1}}$	$\frac{G_i^\ddagger}{G_w^\ddagger}$
AgCl	0.013	278	0.09	0.00044	0.2-0.7	1.2-2.7	0.85	1.2×10^9	10^9 d	1.06
Ag_2MoO_4	0.095	318	0.14 a	0.1 b	1.2-2.0	1.1-1.8	14	1.0×10^9	10^9 d	1.05
CaF_2	0.25	239	0.28	0.025 b	0.4-5.0	2-4	0.004 c	1.0×10^6	3×10^8	1.68
$BaSO_4$	0.010	350	0.135	0.20	1.7-6.0	5-30	0.0025	4.0×10^6	7.2×10^8	1.65

a estimated, Ref. 14, Fig. 4; b estimated, Fig. 3; c rather uncertain; d estimated.

The last column provides a test of the Reich-Kahlweit hypothesis that the dehydration of the cation is the rate-determining phenomena. We define the (free, or Gibbs) energy of activation $G^\ddagger$ by means of the Eyring equation for a unimolecular reaction rate constant, k_r:

$$k_r \equiv (kT/h)\exp(-G^\ddagger/kT) \quad \text{or} \quad G^\ddagger = kT\ln(kT/hk_r) \tag{34-35}$$

In Table 2, $G_i^\ddagger$ has been calculated by means of Eq. 35 from $k_r = k_i\alpha/\nu$, and $G_w^\ddagger$ from k_w, the rate constant found by Eigen and Maass for the removal of a water molecule from the inner hydration sphere of the cation. For silver ion we have used the value for potassium ion; these two ions are almost of the same size.

The values found for the ratio $G_i^\ddagger/G_w^\ddagger$ (Table 2) show that for electrolytes with a univalent cation the activation energy for the integration jump is the same as for the removal of a water molecule from the hydration shell of the cation, and for divalent cations the ratio is between 1.4 and 1.7, which may be taken as an indication that more than one water molecule must be removed at once in order for the ion to jump from a near-by resting position (presumable contact adsorbed and partly dehydrated) into the growth site. This appears to be reasonable, and confirms the assumptions.

APPENDIX 1. The kink distance

According to Burton and Cabrera[18] the addition of a growth unit at a step may be regarded as the formation of two kinks. Thus, if the Gibbs energy of adding a growth unit is ϕ, the Gibbs energy of formation of a kink is $\phi/2$. (Addition of a growth unit from a saturated solution and from a growth site are energetically equivalent).
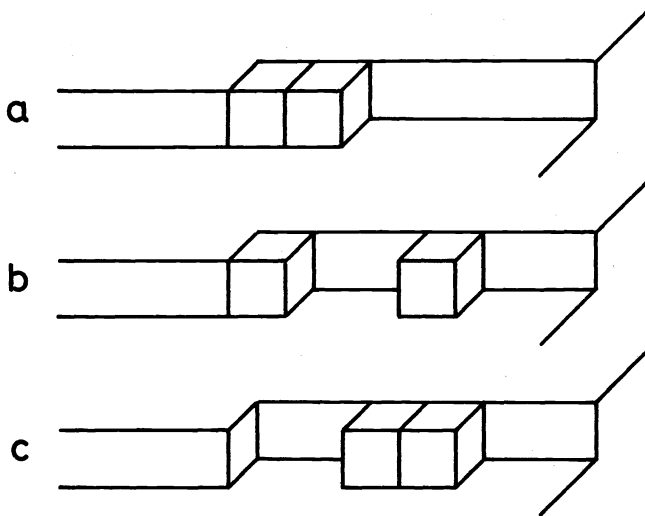

Fig. 1. Formation of a pair of kinks (a → b), $\Delta G = \phi = 2a^2\sigma$.
Displacement of two kinks (b → c), $\Delta G = 0$.

The transfer of a growth unit from one kink to another is energetically neutral, but results in the displacement of the kinks. See Fig. 1. With a sufficiently large kink pool the movements of the individual kinks are in reality independent. Therefore the kinks may be regarded as a one-dimensional gas, with the linear density

$$1/x_o = a^{-1}\exp(-\phi/2kT) \tag{A1}$$

At solubility equilibrium

$$\phi = 2a^2\sigma \tag{A2}$$

and at the supersaturation ratio S

$$\phi = 2a^2\sigma - kT\ln S \tag{A3}$$

Inserting Eq. A3 into A1 we get the expression for the kink distance

$$x_o = a \ S^{-\frac{1}{2}}\exp(a^2\sigma/kT) \tag{A4}$$

APPENDIX 2. The step distance

In the Burton-Cabrera-Frank (BCF) theory[6] for the spiral controlled growth it is assumed that the dependence of the lateral velocity on the curvature of the step is given by

$$u = u_\infty(1 - R_c/R) \tag{A5}$$

where R_c is the radius of a critical nucleus, and R is the curvature radius of the step. This equation is based on an approximation which is only valid for $S \approx 1$, and it is an excellent approximation for the values $1 < S < 1.3$ at which the BCF theory has usually been applied. But in this work we have made growth kinetic experiments at higher supersaturations than previously normal, and therefore have to reconsider the validity of Eq. A5.

The radius of a critical surface nucleus is given by

$$R_c = \sigma v/(kT\ln S) \quad \text{which may also be written} \quad S = \exp(\sigma v/kTR_c) \tag{A6-7}$$

The equilibrium supersaturation S_R at a step with radius of curvature R is given by the analogous equation which may be transformed as follows

$$S_R = \exp(\sigma v/kTR) = [\exp(\sigma v/kTR_c)]^{R_c/R} = S^{R_c/R} \tag{A8}$$

The current of growth units into a kink is assumed to be proportional to S, and the net current to $S - S_R$. If the kink density is proportional to $f(S)$ the lateral velocity of a straight step $(R = \infty, S_R = 1)$ is

$$u_\infty = k_1(S-1)f(S) \tag{A9}$$

and the lateral velocity of a curved step is

$$u = k_1(S - S_R)f(S) = u_\infty(S - S_R)/(S-1) = u_\infty(S - S^{R_c/R})/(S-1) \tag{A10}$$

Letting $S = 1 + x$ we have

$$S^{R_c/R} = (1+x)^{R_c/R} = 1 + \frac{R_c}{R}x + \tfrac{1}{2}\frac{R_c}{R}\left[\frac{R_c}{R} - 1\right]x^2 + \ldots \tag{A11}$$

$$\frac{u}{u_\infty} = \frac{S - S^{R_c/R}}{S-1} \approx \left(1 - \frac{R_c}{R}\right)\left[1 + \frac{R_c}{R}\cdot\frac{S-1}{2}\right] \tag{A12}$$
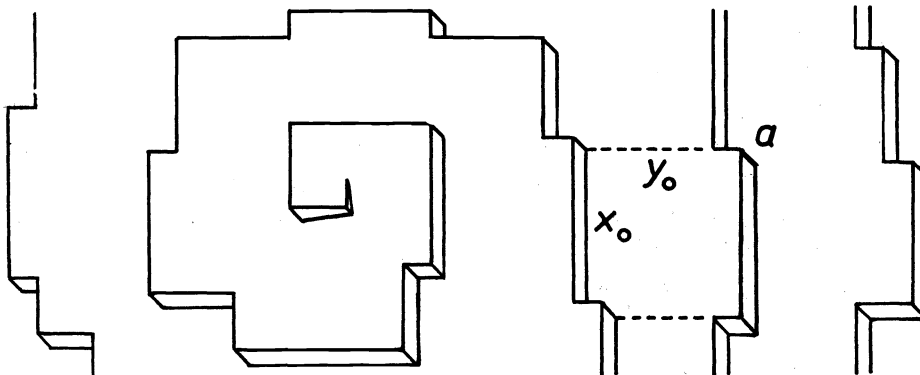

Fig. 2. Schematic drawing of a growth spiral showing the kink distance, x_o, the step distance, y_o, and the step height, a.

For $S \approx 1$ Eq. A12 becomes identical with Eq. A5. For $S > 1$ the two expressions only agree at $R \gg R_c(S-1)/2$. For smaller R-values the velocity calculated by Eq. A12 is greater than accor ding to Eq. A5. The correction of the error will thus lead to a spiral with the same u_∞ but a greater angular velocity, and thus shorter distance (y_o) between the turns, and consequently a faster growth rate than the rate one would calculate by using Eq. A5 at high S values. In the BCF treatment Eq. A5 is used in both the limits $r \simeq 0$ (near the center) and $r \simeq \infty$ (distant from the center). The error is only essential for the first few turns of the spiral. Fortunately it is possible to solve the problem by the BCF method using the exact equation for u/u_∞ at $r \approx 0$ and an approximated equation which converges to the exact form at $r \to \infty$. The exact equation (exact relative to the premises of the model) Eq. A10 may also be written

$$\frac{1}{R} = \frac{1}{R_c} + \frac{1}{R_c\ln S}\ln\left[1 - \frac{S-1}{S}\cdot\frac{u}{u_\infty}\right] \tag{A13}$$

The shape of the spiral is expressed in a rotating polar coordinate system, and when the shape is constant and the coordinate system has the same angular velocity ω as the spiral the

equation for the spiral does not contain the time,

$$\theta = \theta(r) \tag{A14}$$

The angular velocity is

$$\omega = (u/r)[1 + (r\theta')^2]^{\frac{1}{2}} \tag{A15}$$

where $\theta' \equiv d\theta/dr$.

The mathematical expression for the curvature of a curve in a polar coordinate system is

$$R^{-1} = (2\theta' + r^2\theta'^3 + r\theta'')/[1 + (r\theta')^2]^{3/2} \tag{A16}$$

where $\theta'' \equiv d^2\theta/dr^2$. Inserting Eq. A15 and A16 into A13 the result is

$$\frac{2\theta' + r^2\theta'^3 + r\theta''}{[1 + (r\theta')^2]^{3/2}} = \frac{1}{R_C} + \frac{1}{R_C\ln S}\left[1 - \frac{S-1}{S}\cdot\frac{r\omega}{u_\infty[1 + (r\theta')^2]^{\frac{1}{2}}}\right] \tag{A17}$$

We follow the BCF method and fit an approximated solution of the form

$$\theta' = a + b/(1 + cr) \tag{A18}$$

to the differential equation so that it satisfies the equation with terms in r for $r \to 0$ and with terms in $1/r$ for $r \to \infty$. For $r \approx 0$, assuming that θ' and θ'' remain finite we cancel terms with r^2 in Eq. A17 and find

$$2\theta' + r\theta'' = \frac{1}{R_C} - \frac{S-1}{S\ln S}\cdot\frac{r\omega}{R_C u_\infty} \tag{A19}$$

From Eq. A18 follows in the limit $r \approx 0$

$$\theta' \approx a + b(1 - cr) = a + b - bcr \quad ; \quad r\theta'' \approx -bcr \tag{A20-21}$$

$$2\theta' + r\theta'' = 2(a + b) - 3bcr \tag{A22}$$

Eqs. A19 and A22 agree if

$$a + b = \frac{1}{2R_C} \qquad \text{and} \qquad bc = \frac{S-1}{3S\ln S}\cdot\frac{\omega}{R_C u_\infty} \tag{A23-24}$$

For $r \to \infty$ terms in r^{-2} are cancelled from Eq. A17 and the resulting equation

$$\frac{1}{r} = \frac{1}{R_C} + \frac{1}{R_C\ln S}\ln\left[1 - \frac{S-1}{S}\cdot\frac{\omega}{u_\infty\theta'}\right] \tag{A25}$$

may be solved for θ',

$$\theta' = (\omega/u_\infty)(S - 1)\left[S - S^{R_C/r}\right]^{-1} \tag{A26}$$

In the limit $r \to \infty$ we have

$$S^{R_C/r} = e^{(R_C/r)\ln S} = 1 + (R_C/r)\ln S \tag{A27}$$

for S however large. This is the more economic approximation that replaces Eq. A5. Now we have

$$\theta' = \frac{\omega}{u_\infty}\cdot\frac{1}{1 - \frac{R_C}{r}\cdot\frac{\ln S}{S-1}} \approx \frac{\omega}{u_\infty}\left[1 + \frac{R_C}{r}\cdot\frac{\ln S}{S-1}\right] \tag{A28}$$

For $r \to \infty$ Eq. A18 may be written

$$\theta' = a + b/cr \tag{A29}$$

which agrees with Eq. A28 when $a = \omega/u_\infty$; $b/c = \omega R_C(\ln S)/u_\infty(S - 1)$ (A30-31)

According to the BCF method we now assume that θ' may be used with constant coefficients for all r values, so that the coefficients a, b and c, and ω as well may be expressed in terms of R_C, u_∞ and S by solving the set of four equations, A23-24 and A30-31:

$$a = \frac{\omega}{u_\infty} = \frac{1}{R_c[2 + 2(3S)^{-\frac{1}{2}}]} \qquad ; \qquad b = \frac{\omega}{u_\infty(3S)^{\frac{1}{2}}} = \frac{1}{R_c[2(3S)^{\frac{1}{2}} + 2]} \qquad \text{(A32-33)}$$

$$c = \frac{S - 1}{R_c(3S)^{\frac{1}{2}}\ln S} \qquad ; \qquad \omega = \frac{u_\infty}{R_c[2 + 2(3S)^{-\frac{1}{2}}]} \qquad \text{(A34-35)}$$

The step distance is the r increase for $\Delta\theta = 2\pi$. For $r \to \infty$ $\theta' \to a$,

$$y_0 = \frac{\Delta r}{\Delta\theta/2\pi} = \frac{2\pi}{\theta'} = \frac{2\pi}{a} = 4\pi[1 + (3S)^{-\frac{1}{2}}]R_c \qquad \text{(A36)}$$

The correction factor to the BCF value of y_0 is

$$f = \frac{y_0(\text{corrected})}{y_0(\text{BCF})} = \frac{1 + (3S)^{-\frac{1}{2}}}{1 + 3^{-\frac{1}{2}}} \qquad \text{(A37)}$$

TABLE 3. Examples of f values (Eq. A37)

$S =$	1	2	3	10	100	∞
$f =$	1	0.8928	0.8453	0.7497	0.6706	0.6340

We observe that the correction is not particularly great. The main result of the investigation in this appendix is to remove the uncertainty. We must, however, remember that even these results are still approximations, and may contain a mathematical error of the order of 10-20 % for $S = 10$.

APPENDIX 3. Adsorption layer electroneutrality

In the discussion of adsorption on an electrolyte crystal we disregarded any influence of a possible electric potential difference between the crystal and the solution. At adsorption equilibrium the following equations are valid for the electrolyte $A_\alpha B_\beta$

$$\tilde{\mu}_{Aad} = \tilde{\mu}_{Asoln} \qquad ; \qquad \tilde{\mu}_{Bad} = \tilde{\mu}_{Bsoln} \qquad \text{(A38-39)}$$

where the electrochemical potentials are given by

$$\tilde{\mu}_i = \mu_i^\ominus + RT\ln a_i + z_i F\phi_j \qquad ; \qquad i = \text{Aad, Asoln, Bad, Bsoln}; \quad j = \text{ad, soln} \qquad \text{(A40-41)}$$

Multiplying Eq. A38 by α and A39 by β and adding, terms with ϕ cancel because $\alpha z_A + \beta z_B = 0$ and the result may be written (with $(A)_{ad} \equiv a_{Aad}$ etc. and dropping indices soln)

$$(A)_{ad}^\alpha (B)_{ad}^\beta = K_a (A)^\alpha (B)^\beta \qquad \text{(A42)}$$

Equation A42 will keep its validity even if ϕ changes although a change in ϕ will imply that at least one of the ratios $(A)/(B)$ and $(A)_{ad}/(B)_{ad}$ changes, too. For $\nu = \alpha + \beta$ $K_a^{1/\nu}$ is identical with the adsorption coefficient K_{ad} introduced in appendix 4.

Inserting Eq. A40 into Eqs. A38-39 and solving both of the resulting two equations for $\Delta\phi \equiv \phi_{ads} - \phi_{solv}$ we get expressions of the type

$$\Delta\phi = E_A^\ominus + \frac{RT}{z_A F} \ln \frac{(A)}{(A)_{ad}} = E_B^\ominus + \frac{RT}{|z_B|F} \ln \frac{(B)_{ad}}{(B)} \qquad \text{(A43)}$$

We now approximate activity with concentration. Multiplying the two expressions for $\Delta\phi$ with z_A and $|z_B|$ and adding we get

$$(z_A + |z_B|)\Delta\phi = E_O + \frac{RT}{F} \ln \frac{[A][B]_{ad}}{[B][A]_{ad}} \tag{A44}$$

There is no reason to believe that an increase of $[A]/[B]$ will decrease $[A]_{ad}/[B]_{ad}$. Therefore, a tenfold increase of $[A]/[B]$ will not change the logarithm by more than $\ln 10$, and consequently $\Delta\phi$ will not change by more that $(RT\ln 10/F)/(z_A + |z_B|) < 0.03$ V. Somewhere in the experimental range - but not exactly at equivalence - the crystals have no electric charge. In all the experimental range we may therefore assume that the net electric charge q on the crystal is not larger that corresponding to an electric potential of the order of 0.03 V. For a sphere with radius r in a medium with the dielectric constant ε, $q = 4\pi\varepsilon r\Delta\phi$ (A45) With $r = 0.1$ μm, $\Delta\phi = 0.03$ V, $\varepsilon = \varepsilon_{H_2O} = 7\times10^{-10}$ C/Vm Eq. A45 gives $q = 4\pi(7\times10^{-10})(10^{-7})(0.03)$C $= 2.6\times10^{-17}$ C. This charge is partly due to the difference between the charges on adsorbed cations and adsorbed anions and partly to nonstoichiometric composition of the crystal lattice. The crystals may be assumed to have close to perfect lattices and relatively few kinks in surface steps compared with the number of adsorbed ions, and so q is given primarily by the adsorbed ions which, according to the Paneth-Hahn-Fajans rule (see ending of appendix 4) in our case are mainly the constituent ions, and we have

$$q = q_+ - |q_-| = FV_{ad}(z_A[A]_{ad} - |z_B|[B]_{ad}) \tag{A46}$$

where V_{ad} = the volume of the adsorption layer. With $V_{ad} = 4\pi(0.1$ μm$)^2(1$ nm$) = 1.3\times10^{-22}$ m^3, $[A] \approx 0.1$ mol/m^3, $K_{ad} = 600$ we calculate $q_+ = FV_{ad}z_AK_{ad}[A] = 10^5\times1.3\times10^{-22}\times2\times600\times0.1 = 1.5\times10^{-15}$ C. So we have

$$\frac{z_A[A]_{ad} - |z_B|[B]_{ad}}{z_A[A]_{ad}} = \frac{q}{q_+} = \frac{2.6\times10^{-17}}{1.5\times10^{-15}} \ll 1 \tag{A47}$$

For most of the experimental conditions the ratio is even smaller. Therefore we may conclude that the ions are adsorbed in equivalent amounts, and that the adsorption layer is electroneutral.

APPENDIX 4. Adsorption coefficients

1. Ion pair constants

The ion pair equilibrium constant is defined by

$$K_I = \left(\frac{[AB]}{[A][B]}\right)_{eq} \tag{A48}$$

In Fig. 3 we have plotted in a logarithmic diagram the equilibrium constants K_I for the ion pairs AB as a function of the solubility of the electrolytes $A_\alpha B_\beta$. Empirical values (from the literature[16,19]) are plotted with solid (black) symbols, and values calculated from the ionic radii and charges by the Bjerrum theory[19-20] are shown with open (white) symbols. The following patterns are obvious:

1) Most of the empirical points lie within three horizontal bands about one decade wide, one band containing the points for ion pairs of ionic type 1,1, one for ionic types 1,2 and 2,1, and one the points for 2,2 ion pairs. The three bands center around the values, $K_I = 3\times10^{-4}$, 0.03 and 1 m^3/mol, respectively.

A clear exception to this three band pattern is the silver halides, and also the thallous halides show a tendency to mingle with ion pairs of higher ionic type. This is obviously a consequence of the covalent bonding, and reminds of the similar effect displayed in the interfacial tension (Ref. 14).

2) Simultaneously most of the points lie within a band about one decade wide, with the slope −1. This pattern is even followed by the silver and thallous halides as well. In order to see what kind of information this is we notice that the degree of dissociation of an ion pair α satisfies

$$K_I = (1 - \alpha)/\alpha^2 C \qquad (A49)$$

(which may be shown by inserting $[AB] = (1 - \alpha)C$, $[A][B] = (\alpha C)^2$ into A48). - Taking logarithms we get

$$\log K_I = -\log C + \log [(1 - \alpha)/\alpha^2] \qquad (A50)$$

Eq. A50 shows that a straight line with slope = -1 in the logarithmic, diagram Fig. 3 corresponds to points at which the ion pairs are equally much dissociated. The lines corresponding to $\alpha = 0.5$ and 0.95 are shown in the diagram. The very clear correlation between ion pair formation, solubility and interfacial tension may be taken as evidence that these phenomena are very closely related and are caused by nearly the same forces.
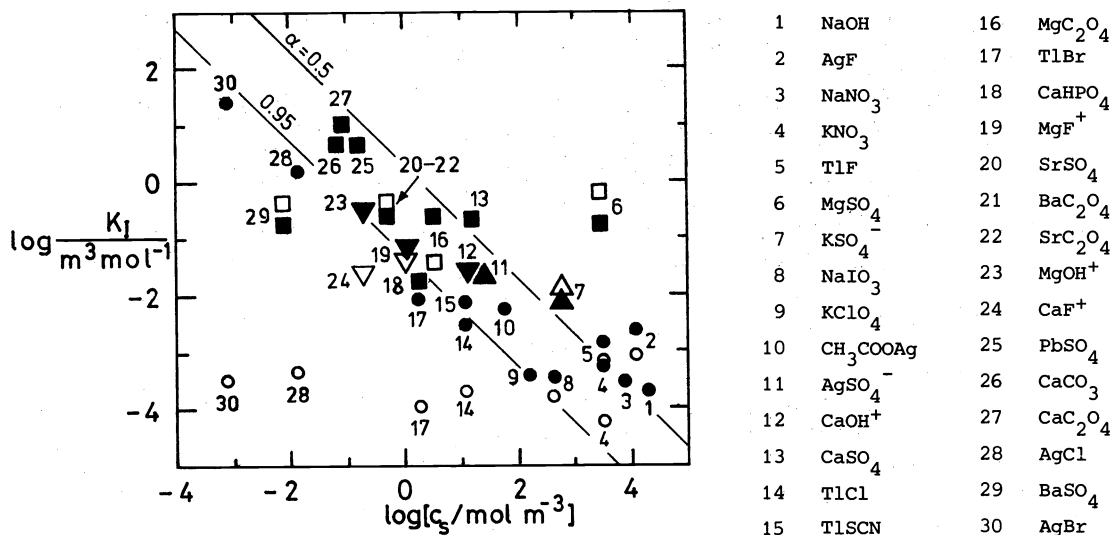
1	NaOH	16	MgC_2O_4
2	AgF	17	TlBr
3	$NaNO_3$	18	$CaHPO_4$
4	KNO_3	19	MgF^+
5	TlF	20	$SrSO_4$
6	$MgSO_4$	21	BaC_2O_4
7	KSO_4^-	22	SrC_2O_4
8	$NaIO_3$	23	$MgOH^+$
9	$KClO_4$	24	CaF^+
10	CH_3COOAg	25	$PbSO_4$
11	$AgSO_4^-$	26	$CaCO_3$
12	$CaOH^+$	27	CaC_2O_4
13	$CaSO_4$	28	AgCl
14	TlCl	29	$BaSO_4$
15	TlSCN	30	AgBr

Fig. 3. Ion pair constants as a function of solubility - logarithmic diagram. Ionic types: ● 1,1; ▲ 1,2; ▼ 2,1; ■ 2,2. ●▲■ empirical values[16]; ○△□ calculated (Bjerrum theory[19,20])

This is the basis for the following attempt to estimate the extent of ionic adsorption by means of these forces. We find the analogy to ion pairing greater than to interfacial tension or solubility, and shall explicitly express the adsorption coefficients in terms of ion pair constants.

According to Eigen and Tamm[21] a 2,2 valent ion pair in aqueous solution may have n = 0, 1 or 2 molecules of hydration water between the two ions, see Fig. 4
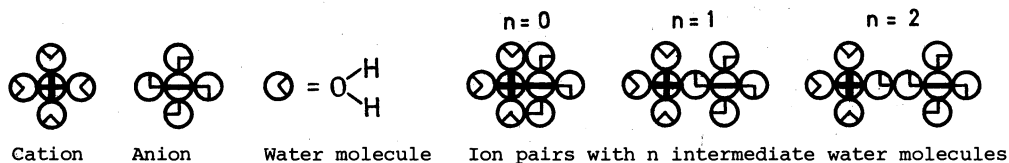
Fig. 4. Schematic drawing of the structure of hydrated ions and ion pairs.

The ratio between the numbers of the three kinds of ion pairs is approximately 1:10:10. For the estimates to be made in the following we shall assume all ions and water molecules to be spheres with the same radius (r_w) and volume (v_w). When the position in space of the center of one of the ions of an ion pair is given, the center of the other ion may be anywhere on a spherical surface with radius $(2n + 2)r_w$. A sphere with radius r_w running through all these positions describes the volume

$$v_n = [(2n + 3)^3 - (2n + 1)^3]v_w \qquad (A51)$$

or $v_o = 26 v_w$, $v_1 = 98 v_w$, $v_2 = 218 v_w$. If the coordination number of nearest neighbours of an ion is 6, the number of statistically different positions in the first shell is 6. The number of different possible position in the other shells may be set equal to the volume ratios v_1/v_w and v_2/v_w, so that we have the statistical weights

$$p_n = 6 \text{ , 98 and 218 (n = 0, 1 and 2)}$$

The probability of finding a B ion on a position in the bulk solution is equal to the mole fraction of B ions

$$x_B = [B]v_w \tag{A52}$$

The probability of finding a B ion in a position where the energy is lower by e is (according to the Boltzmann distribution law)

$$x_B(e) = x_B \exp(e/kT) \tag{A53}$$

When e_o is the dissociation energy (in aqueous medium) of an AB contact ion pair (n = 0) the probability that an A ion has a B ion in one of its six nearest neighbour position is

$$f_{A,0} = 6 x_B \exp(e_0/kT) \tag{A54}$$

and the probability that an A ion is a member of an ion pair with n intermediate water molecules is

$$f_{A,n} = p_n x_B \exp(e_n/kT) \tag{A55}$$

For the chemical equilibrium

$$A + B \rightleftharpoons AB(\text{ion pair}) \qquad [AB] = K_I[A][B] \tag{A56-57}$$
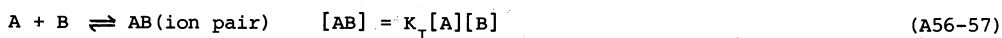
If we distinguish between ion pairs according to n = 0, 1 or 2

$$[AB]_{(n)} = K_{I(n)}[A][B] \tag{A58}$$

$$K_{I(0)} + K_{I(1)} + K_{I(2)} = K_I \tag{A59}$$

$$K_{I(0)} : K_{I(1)} : K_{I(2)} = [AB]_{(0)} : [AB]_{(1)} : [AB]_{(2)}$$
$$= f_{A,0} : f_{A,1} : f_{A,2} = p_0 \exp(e_0/kT) : \text{etc.} \tag{A60}$$

The fraction of A molecules that form any kind of ion pair with a B ion is

$$f_A = f_{A,0} + f_{A,1} + f_{A,2} \quad ; \quad f_A/(1 - f_A) = [AB]/[A] = K_I[B] \tag{A61-62}$$

For small concentrations $f_A \ll 1$ and

$$f_A \approx K_I[B] \quad ; \quad K_{I,n} = f_{A,n}/[B] = v_w p_n \exp(e_n/kT) \tag{A63-64}$$

When the ratios are assumed to be

$$[AB]_{(0)} : [AB]_{(1)} : [AB]_{(2)} = 1 : 10 : 10 \tag{A65}$$

it follows that

$$f_{A,0} = \frac{1}{21} f_A = \frac{1}{21} K_I[B] \quad ; \quad f_{A,1} = f_{A,2} = \frac{10}{21} K_I[B] \tag{A66-67}$$

$$p_0 \exp(e_0/kT) = f_{A,0}/x_B = \frac{1}{21} K_I/V_w \quad ; \quad p_1 \exp(e_1/kT) = p_2 \exp(e_2/kT) = \frac{10}{21} K_I/V_w \tag{A68-69}$$

$$\exp(e_0/kT) = \frac{1}{6 \times 21} K_I/V_w = \frac{1}{126} K^* \quad , \quad K^* \equiv K_I/V_w \tag{A70}$$

$$\exp(e_1/kT) = \frac{10}{98 \times 21} k^* \approx \frac{1}{206} K^* \quad ; \quad \exp(e_2/kT) = \frac{10}{218 \times 21} K^* \approx \frac{1}{458} K^* \tag{A71-72}$$

$$e_0 - e_1 = kT \ln \frac{206}{120} = 0.5 \text{ kT} \quad ; \quad e_1 - e_2 = kT \ln \frac{458}{206} = 0.8 \text{ kT}$$

Taking $K_i = 1$ m^3/mol as a representative value for a 2,2 electrolyte and $V_w = 1.8\times10^{-5}$ m^3/mol for water, $K^* = 5.6\times10^4$ and

$$e_0 = kT \ln(K^*/126) = 6.1 \text{ kT} \quad ; \quad e_1 = 5.6 \text{ kT} \quad ; \quad e_2 = 4.8 \text{ kT}$$

It is remarkable that the dissociation energies are nearly the same for the three kinds of ion pairs in spite of the very different ion-ion distances. In vacuum the potential energy of two ions would vary as r^{-1}, which is in the ratio $1 : \frac{1}{2} : \frac{1}{3}$ or $6.1 : 3.05 : 2.03$. The values of e_1 and e_2 are very close to the bond strengths of hydrogen bonds (3-5 kT) and it is very reasonable that the bonding of these ion pairs is hydrogen bonding, which conveys the forces between the two doubly charged ions through two intermediate water molecules.

A similar effect is not observed with 1,1 ion pairs, where only contact ion pairs are of importance. K_I being typically 3×10^{-4} m^3/mol

$$\exp(e_0/kT) = K_I/6V_w = 2.8 \quad ; \quad e_0 = kT \ln 2.8 = 1.0 \text{ kT}$$

If ion pairs with n = 0 and 1 are taken into account, then even $e_0 = e_1 = 0$ would lead to a too large value for K_I

$$K_I = K_{I,0} + K_{I,1} = V_w(p_0 + p_1) \exp(0) = (1.8\times10^{-5} \text{ m}^3\text{/mol})(104)(1) = 1.9\times10^{-3} \text{ m}^3\text{/mol}$$

and larger e_n values would give yet larger K_I values.

We cannot in a similar straightforward way decide about the relative importance of the ion pair types for a uni- and a bivalent ion, but the simplest way to generalize the above results will be to assume that each bivalent ion can convey its electrostatic attraction through one water molecule, and univalent ions cannot. So, for 1,2 ion pairs the types n = 0 and 1 should be considered. For 1,1 pairs we have $e_0 - e_1 = e_0 = 1.0$ kT and for 2.2 pairs $e_0 - e_1 = 0.5$. In lack of better arguments we assume that for a 1,2 ion pair $e_0 - e_1 =$ the mean value, 0.75 kT so that $f_{A,0}/f_{A,1} = (p_0/p_1) \cdot \exp(0.75) = (6/98)\times2.12 = 0.130$; $f_{A,0} = 0.115$; $f_{A,1} = 0.885$; $K_{I,0} = V_w \cdot 6 \exp(e_0/kT)$; $K_{I,1} = V_w \cdot 98 \exp(e_1/kT)$; $K_I = V_w\exp(e_0/kT)[6 + 98 \exp(-0.75)] = 52\cdot V_w\exp(e_0/kT)$; $\exp(e_0/kT) = K_I/52\cdot V_w = K^*/52$; $\exp(e_1/kT) = \exp(e_0/kT) \exp(-0.75) = K_I/110 V_w = K^*/110$. With the typical value $K_I = 0.003$ m^3/mol

$$e_0 = kT \ln[0.03/(52.3\times1.8\times10^{-5})] \quad ; \quad e_1 = 2.7 \text{ kT}$$

2. Adsorption coefficients

The main assumption that allows us to make an estimate of the adsorption of ions on electrolyte crystals is that the energy of an adsorbed ion is similar to the energy of an ion paired ion with the same number of intermediate water molecules. This is due to two effects of the water molecules, they convey forces through hydrogen bonding and they screen against the repulsive forces from neighbouring ions to the bonding ion in the crystal surface. More specifically the energy in each of the three layers closest to the crystal is equated to minus the dissociation energies e_0, e_1 and e_2, but the steric factors are all set equal to unity for n = 1 and 2, and equal to α/ν and β/ν, respectively, in the contact layer. So we have

$$[A]_{ad(0)} = [A](\alpha/\nu)\exp(e_0/kT) \tag{A73}$$

$$[A]_{ad(1)} = [A]\exp(e_1/kT) \quad ; \quad [A]_{ad(2)} = [A]\exp(e_2/kT) \tag{A74-75}$$

and similarly for $[B]_{ad}$. Inserting Eq. A73-75 we find for a 2,2 electrolyte

$$K_{ad(0)} \equiv [A]_{ad(0)}/[A] = \frac{\alpha K^*}{126\nu} = \frac{K^*}{252} \quad ; \quad K_{ad(1)} = \frac{K^*}{206} \quad ; \quad K_{ad(2)} = \frac{K^*}{458} \tag{A76-78}$$

$$K_{ad} = \left(\frac{1}{252} + \frac{1}{206} + \frac{1}{458}\right) K^* = \frac{K^*}{91} \approx \frac{K^*}{100} \tag{A79}$$

For a 1,2 electrolyte (and, mutatis mutandis, a 2,1 electrolyte)

$$[A]_{ad,0} = [A](\alpha/\nu)\exp(e_0/kT) = [A](2/3)K^*/52 \quad ; \quad [B]_{ad,0} = [B](1/3)K^*/52 \tag{A80-81}$$

$$K_{ad,0} = \left([A]^2_{ad,0}[B]_{ad,0}[A]^{-2}[B]^{-1}\right)^{1/3} = (2^{2/3}/3)K*/52 = 0.53 \; K*/52 \approx K*/100 \quad \text{(A82-83)}$$

$$[A]_{ad,1} = [A]\exp(e_1/kT) \qquad\qquad \text{(A84)}$$

$$K_{ad,1} = \exp(e_1/kT) = K*/110 \quad ; \quad K_{ad} = K*(1/100 + 1/110) \approx K*/50 \qquad \text{(A85-86)}$$

Finally, for a 1,1 electrolyte only contact adsorption counts, so that

$$K_{ad,0} = K_{ad} = (\alpha/\nu)\exp(e_0/kT) = K*/12 \qquad\qquad \text{(A87)}$$

We are most interested in the contact adsorption coefficients which may all be expressed by

$$K^o_{ad} = K_I/V_w n(a,b) \quad ; \quad n(1,1) = 12; \; n(1,2) = n(2,1) = 100; \; n(2,2) = 250 \qquad \text{(A88)}$$

TABLE 4.   Adsorption coefficients and ion pair constants (A^{a+} and B^{b-})

a,b	1,1	1,2 & 2,1	2,2
$K_I/m^3 \; mol^{-1}$	$10^{-4} - 10^{-3}$	$10^{-2} - 10^{-1}$	$0.2 - 6$
$K* = K_I/V_w$	$5 - 50$	$500 - 5000$	$10^4 - 3\times10^5$
K_{ad}	$K*/12 = 0.5 - 5$	$K*/50 = 10 - 100$	$K*/100 = 100 - 3000$
K^o_{ad}	$K*/12 = 0.5 - 5$	$K*/100 = 5 - 50$	$K*/250 = 50 - 1000$

Adsorption specifities

From the arguments above it follows generally speaking that adsorption is strong if the ions being adsorbed and some of the ions of the crystal are able to form strongly bonded ion pairs. And ion pair constants obviously increase with decreasing solubility when different electrolytes are compared. A corollary of this is that when the adsorption of different ions on the same electrolyte crystal are compared those ions that are able to form the least soluble salt with the constituent ions of opposite electric sign will be most adsorbed. This is the Paneth-Hahn-Fajans rule[22].

As the electrolyte crystals we are growing in our experiments always represent the least soluble of the salts that can be formed by the ions present it follows that the majority of the ions in the adsorption layer are the constituent ions.

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