THE COPRECIPITATION AND THE RELATIONSHIP BETWEEN THE ADSORPTION, THE OCCLUSION AND THE MIXED CRYSTAL FORMATION

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Since real crystals are in most cases agglomerates, the influence was shown, which the ions adsorbed on the surfaces of primary particles exert. on the composition of the solids. To characterize the processes of adsorption, occlusion, and the mixed crystal formation, the general dispersity function of the intercrystalline boundary phenomena was given. Considering the mixed crystals of the »two-dimensional« type, it was pointed out that their formation proceeds in a way analogous to that of the occlusion; hence the similar effect of occlusion and mixed crystal formation on the change of the diffraction pattern by X-ray analysis may be explained.

Introduction

It is a known fact that real crystals as well as secondary structures of crystalline precipitates in general consist of »blocks« resp. primary particles. Nevertheless, the influence of this complex character of the precipitate, especially of the »internal« adsorption on the substantial and structural composition of the precipitated mass is usally not quite clear. Thus in mixed crystals we may have a group of phenomena which probably could be related to the special adsorption structures on the surfaces of the »blocks« from which the crystal is built up. In the occlusion- and coprecipitation-phenomena the rôle of adsorption is preponderant, and this is the case with the real crystals, where the great number of properties which are sensitive to structure (so called Smekal's »strukturempfindliche Eigenschaften«) indicate certainly the principal lines of approach to the order-disorder phenomena for which the Schottky-Wagner or Hedwall treatment, with vacant and excess lattice points, represent but the first approximation.

From the very beginning of the formation of the new phase, the adsorption is the fundamental controlling factor of the critical conditions of nuclei formation as well as of the agglomeration processes. Moreover, it seems reasonable to suppose that some of the heteropolar mixed crystals are in reality orderly aggregated blocks of only one component, with the second component as an interstitial structure, and that there do not exist systems with a random distribution of the second component. Naturally, the phenomena are very complex, and some schematic construction will be necessary to bridge the gap between the usual adsorption and the formation of the mixed

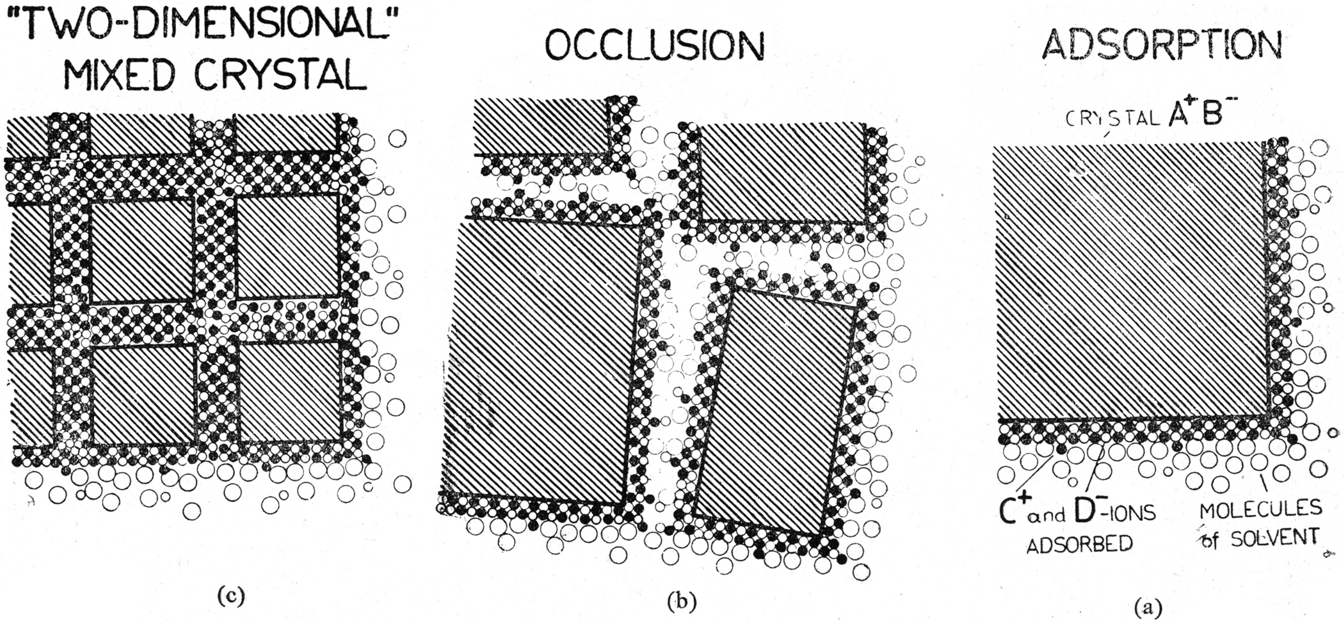

Fig. 1. Schematic presentation of (a) adsorption, (b) occlusion and (c) »two-dimensional« mixed crystal. A^+B^- are the constituent ions of the »blocks« of the carrier crystal; C^+D^- are ions in the adsorbed state.

crystals. Therefore, the adsorption of ions on heteropolar surfaces, the occlusion, the »two-dimensional« mixed crystal, and the ideal type of mixed crystal, may be taken as the elements of our discussion of the coprecipitation.

For the sake of orientation, it would be best to present first the schematic sketch of these stages in one picture. Fig. 1(a) gives us the section of a heteropolar crystal with a row of adsorbed ions and molecules of solvent. The whole surface may be covered with a continuous layer of foreign ions in exceptional cases only; usually the potential determining ions are placed only on certain points, the density of which is a function of many factors (e. g., the solubility of the heteropolar adsorbent). Fig. 1(b) represents the section of the crystalline agglomerate with adsorbed foreign ions and molecules on »internal« surfaces; such an adsorption on the surfaces of the blocks or primary particles may be taken as a special characteristic of occlusion phenomena[1]. Finally, in Fig. 1(c) there is the picture of an ideal »two-dimensional« mixed crystal, where the blocks are of such a dispersity that the molar percentage of the foreign component adsorbed on their surfaces is considerable. For the illustration, it will be of interest to mention here that some kind of »two-dimensional« mixed crystals may be seen in the structures of Riedel and Ruska[2]. Fig. 2 shows the schematic presentation of their electron-microscopic picture with the mixed crystals of sodium chloride and lithium chloride obtained from a $1^0/_0$ solution, in presence of colloidal gold. The magnification is approx. 4× (29,000 : 1).

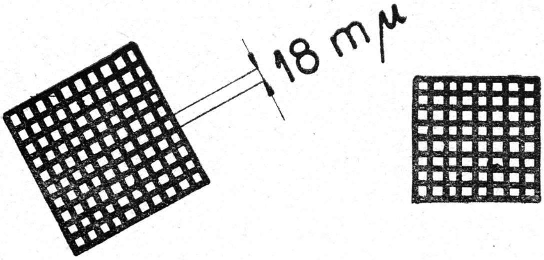

Fig. 2. Schematic presentation of an celectron-microscopis picture of NaCl—LiCl mixed crystals grown from a $1^0/_0$ solution in the presence of colloidal gold; magnification cca 120.000 : 1 (according to Fig. 15 in the paper of Riedel and Ruska, Kolloid-Z. **96** (1941) 86).

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[1] B. Težak, Glas. hem. društva Kr. Jugosl. 3, 25 (1932); 3, 147 (1932); Z. physikal. Chem. **175 A**, 284 (1935); **32 B**, 46, 52 (1936).

[2] G. Riedel und H. Ruska, Kolloid-Z., **96**, 86 (1941).

In discussing these phenomena, we shall rectrict ourselves to some general remarks in pointing out the effects of occlusion and the general relationship between the molar content of the adsorbed component and the dispersity of the primary particles of the carrier component.

The significance of the two stages of the aggregation processes was experimentally outlined by Odén[3]), O. Hahn[4]), Weiser[5]), Traube and Behren[6]), Balarew[7]), Kolthoff[8]), Feitknecht[9]), Težak[10]), and others[11]). For the discussion we shall choose aggregates of barium sulfate as the reference substance; the formation of these aggregates was the subject of our previous investigations[1]), while the interpretation of their structures is somewhat controversial[12]) to our concepts.

To answer all the open questions in this field, it would be necessary to perform experiments where all modern physical and chemical tools including low angle scattering of electrons, electron-microscopic, ultramicroscopic, and microscopic observations, as well as the application of tracer indicators and other techniques, should be applied.

The mechanism of occlusion

Oden[3]) showed that nearly all precipitates of barium sulfate are represented by the secondary structures. From author's experiments[13]), which are in their main lines an

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[3]) S. Odén, Arkiv. Kemi, Min., Geol. **7**, 26 (1920); **9**, 23 (1926); Svensk. Kem. Tidskr., **44**, 2, 35, 66 (1932).

[4]) O. Hahn, Ber., **59**, 2014 (1926); Z. angew. Chem., **43**, 871 (1930); O. Hahn u. L. Imre, Z. physikal. Chem., **144**, 161 (1929).

[5]) H. B. Weiser and J. L. Sherrick, J. Physical Chem., **21**, 314 (1919.); H. B. Weiser and W. O. Milligan, Advances in Colloid Science, p. 227, New York, 1942.

[6]) J. Traube u. W. Behren, Z. physikal. Chem., **138 A**, 85 (1928); **146 A**, 1 (1930).

[7]) D. Balarew, Der disperse Bau der festen Systeme, Dresden u. Leipzig, 1939.

[8]) I. M. Kolthoff, J. Physical. Chem., **36**, 860 (1932); I. M. Kolthoff and C. W. Carr, J. Physical Chem., **47**, 148 (1943).

[9]) W. Feitknecht, Kolloid-Z., **92**, 257; **93**, 66 (1940).

[10]) B. Težak, Kolloid-Z., **68**, 60 (1934); Z. physikal. Chem., **175**, **A**, 219 (1935); **190 A**, 257 (1942); **191**, 270, (1942); **192**, 101 (1943); Arhiv za kem., **19**, 9, 19 (1947).

[11]) G. M. Schwab, Handbuch der Katalyse, IV. Bd., Springer, Wien, 1943; R. Fricke, p. 1—150; K. E. Zimens, p. 151—268; M. Straumanis, p. 269—294; VI. Bd., G. F. Hüttig, 322—508.

[12]) G. Walton and G. H. Walden, J. Amer. Chem. Soc., **68**, 1742 (1946).

[13]) B. Težak, Z. physikal. Chem., **175** A, 284 (1935); **32 B**, 46, 52 (1936).

extension of Odén's investigations, it may be taken as an established fact that the occlusion is directly connected with aggregation processes. It was, namely, found that the character of the occluded ions is shown by their peptizing effects. The composition of such adsorption films on the primary particles must be chiefly dependent upon the conditions of precipitation, and it represents an approach to the equilibria between the various influences acting at the moment of aggregation of the primary particles into secondary structures. As the general character of the surfaces of primary and secondary particles is the same, we have no reason to assume that the adsorption on the primary particles is different in principle from the known adsorption on the surfaces of the secondary structures. The similarity[14]) of the adsorbed ions to the constituent ions of the adsorbent must be in this case of the same importance as in the adsorption processes in general.

If the precipitation is performed in a medium where there is a distinctive excess of one of the »lattice« ions, then there is a great probability that the occlusion of the »lattice« ion is accompanied by one foreign ion of the opposite charge. Actually, such an occlusion is a very frequent phenomenon.

It is not difficult to explain the preferential adsorption of the »lattice« ion; this is a natural consequence of the crystal growth. The formation of such an adsorption film must be a normal intermediate stage in the process of building the ions in the space lattice of the crystal. Of course, the probability of adsorption of the »lattice« ion, which is usually the potential determining ion of the primary particles, must be greater, if the counter ions show a greater similarity to the other constituent ion of the adsorbent. In general, the occlusion of one of the »lattice« ions should depend: first, on its excess in the precipitation medium, and second, on the character of the counter ion present.

The author has found an interesting result in the influence of the counter ion on the occlusion of the »lattice« ion in the case of precipitation of barium sulfate with solutions of barium chloride and nitrate.[15]) When the precipitation under special conditions is performed with a barium chloride solution as the precipitating reagent, a great number of the negative primary particles is found, while if the barium nitrate reagent is used under the same conditions, the peptized primary particles show a positive charge. In the first case more »sulfate-bodies«, and

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[14]) B. Težak, Kolloid-Z., **59**, 158 (1932); Arhiv za kem., **11**, 58 (1937).

[15]) B. Težak, Z. physikal. Chem., **32 B**, 52 (1936).

in the second more »barium-bodies« have been formed. This difference may lie in the higher grade of similarity of the nitrate ion to the sulfate ion, and in the greater solubility of barium chloride against the nitrate.

For the other anions and cations there is a relative parallelism between the orders of adsorbility and the orders of occlusion also.[13]).

But as the occlusion is a typical adsorption phenomenon on the surfaces of the primary particles, it must depend also on the general conditions of precipitation, and thus the radius of the primary particles as well as their aggregation velocity must be taken into account. With the coarser particles the possibility of their irreversible aggregation is small, and the total amount of the ions adsorbed on the surfaces is quite negligible. On the other hand, if the primary particles are very small, their aggregation proceeds in most cases with such a velocity that the particles are at the moment of formation of the secondary structures enclosed in a relatively thick layer of the ions and molecules of the precipitated mass. Hence, the typical phenomena of occlusion could be found if one works under such conditions that the aggregation proceeds at a moderate rate, and the primary particles are of a size of 60 to 30 mμ approximately.

During the formation of the precipitates from concentrations higher than 0.3 M of the precipitating substance the ions are so near to one another that the precipitation may be regarded as a condensation of the precipitating ions which are already under the direct influence of their mutual attraction forces.

The general dispersity function of the intercrystalline boundary structures

About twenty years ago Grimm and Wagner[16]) formulated the laws of formation of the »neuartige Mischkrystalle«, and on the system barium sulfate — potasium permanganate they showed the consequences of their theoretical considerations. In this connection it was pointed out by van Arkel and de Boer[17]) that for salts which are composed from ions of various charges, e. g., A^{++} B^{--}, and C^{+} D^{-}, it is difficult to assume that the ions of one salt can be in an ideal distribution of threefold periodicity with the ions of the other.

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[16]) H. G. Grimm, Z. Elektrochem., **30**, 467 (1924); H. G. Grimm u. G. Wagner, Z. physikal. Chem., **132**, 131 (1928); Z. anorg. Chem., **220**, 31 (1934); H. G. Grimm, Cl. Peters u. H. Wolf, Z. anorg. Chem. **236**, 57 (1938).

[17]) A. E. van Arkel u. J. H. de Boer, Chemische Bindung als elektrostatische Erscheinung, Leipzig 1931, p. 259.

Balarew[7]) also assumes that the high percentage of the potassium permanganate in the precipitates of barium sulfate must be the result of the »inner« adsorption where the majority of the potassium permanganate is dissolved in a solution which is retained in the amicronic system of the porous barium sulfate.

For explanation of such phenomena we shall follow our lines of approach. In an ideal case, we shall suppose that on the surfaces of the primary particles complete monomolecular films of the adsorbed ions are formed. Thus, with a decrease of the primary particles the percentage of the adsorbed substances will increase according to a special function. Taking the system $A^+B^- — C^+D^-$, where the constituent ions of the component A^+B^- represent the solid phase precipitated first, and the ions of the component C^+D^- the substance adsorbed on the primary particles of A^+B^-, the actual relation between these salts will be given by the dispersity of the component named first. The supposed difference in the behavior of the A^+B^- and the C^+D^- may lie in various factors, e. g., in the difference in solubility, in melting point, in various crystallisation velocities, or in any other cause.

Such typical functions showing the relations between the molar composition and the dispersity are shown on Fig. 3, where the molar percentage of the component C^+D^- in a mixture with A^+B^- is plotted against the logarithm of the diameters of the particles A^+B^-. The upper curve represents the limit of the theoretically posible cases, the radius of the adsorbed ion being approx. equal to the average size of the constituent ions of the adsorbent, and on each of the surface ions A^+B^- one couple C^+D^- is adsorbed. The lower curve gives the possible occlusion effects in the case when the similarity between A^+ and C^+ or B^- and D^- is diminished.

When we consider this variation of the composition of the system $A^+B^- — C^+D^-$, it is clear that the changes will depend chiefly on the conditions which control the formation of the adsorption films of the component C^+D^- on the surfaces of the particles $A^+ B^-$.

As it has been shown it appears from the examples of barium sulfate which we discussed previously, that there are two important factors influencing the possibilities of fixation of the foreign ions on the surfaces of the primary particles: (1) the similarity of the adsorbed ions to the constituent ions of the adsorbent, and (2) the rate of aggregation of the primary particles into secondary structures. Thus, the possibilities of adsorption will increase with increasing similarity between the cations A^+ and C^+ as well as anions B^- and D^-. From the stereochemical point

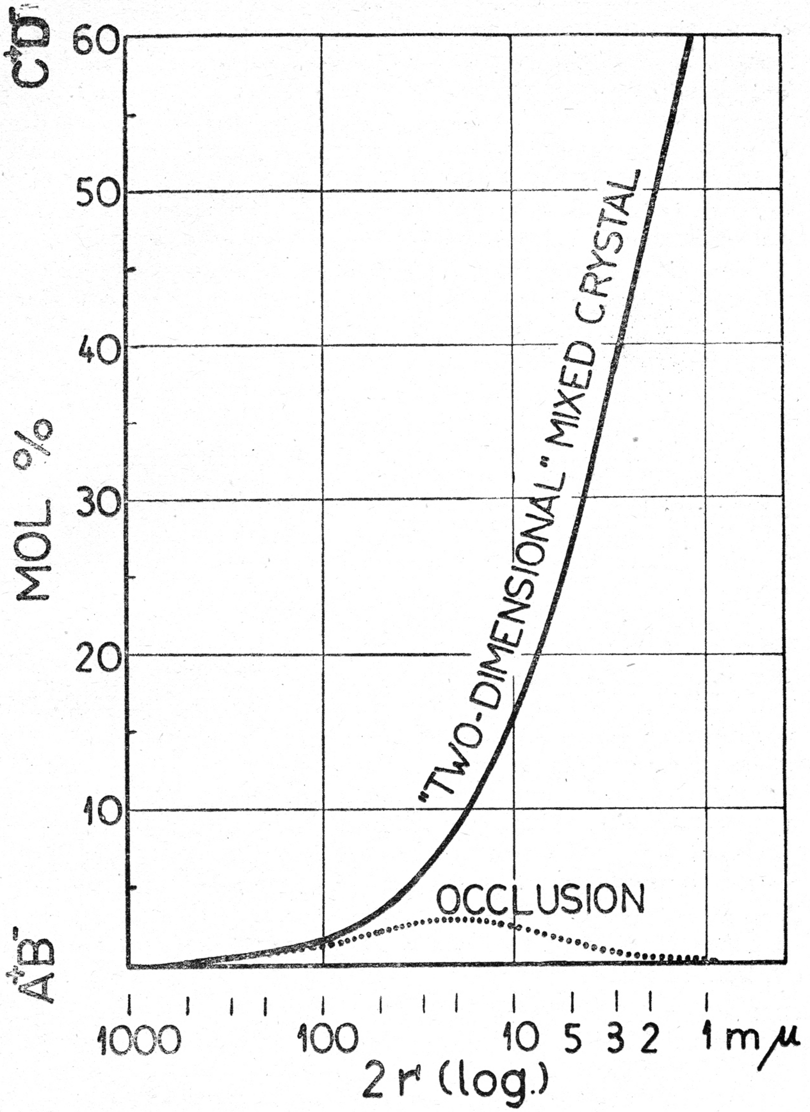

Fig. 3. Relation between the molar content of the adsorbed ionic component C^+D^- and the dispersity of the »blocks« of the carrier component A^+B^-. The »Two-dimensional« mixed crystal curve gives the cases of great similarity between ions A^+B^- and C^+D^-, while the occlusion curve represents the usual cases of contamination where the foreign ion of small similarity to the contituent ion of the carrier crystal is accompanying (as a counter ion) the adsorption of the »lattice« ion which is in excess.

of view it seems correct to assume that for the fixation of the ions on the polar surfaces the influence of the ratio of the ionic radii must be decisive, but the electrostatic forces (valency factor) will control the possibilities that such an ion can be actually built into the crystal lattice. If there is a great similarity between ionic radii, valency and deformability, the formation of the ideal mixed crystals of the threefold periodicity should be expected. In other cases, where the valency is different or the similarity is not so marked, the formation of the special form of »two-dimensional« mixed crystals may result.

As mentioned before, apart from these factors of the ideal boundary equilibria, the processes of aggregation must also be considered. At greater concentrations of the precipitating reagents — owing to the quick aggregation of the primary particles — the aggregating particles are enclosed in a sphere of more or less hydratized complexes of the precipitated ions; hence, on the intercrystalline boundaries of the secondary structures, which are agglomerates of very small particles, only foreign ions of a high degree of similarity can be adsorbed. Therefore, with regard to the normal phenomena of occlusion of foreign counter ions, we may expect the relation: occlusion — dispersity to go through a maximum. Of course, the magnitude and position of this maximum of contamination will vary with the character of the precipitated substance, as well as with the general conditions of the precipitation. With greater similarity of the contaminating ions the possibility for their adsorption will steadily increase with decreasing primary particles. In the case where the agglomerates show the characteristics of a crystal form, our systems may be considered as a first approximation to the mixed crystals. However, these mixed crystals will be of a special »two-dimensional« type. For the ideal mixed crystals of threefold periodicity the conditions of the complete isomorphism must be fulfilled.

For the systems barium sulfate — barium nitrate, Walden and Cohen[18]), and for barium sulfate — ammonium, potassium, sodium and lithium sulfate, Walton and Walden[12]), found by means of X-ray investigations that the lattice spacing of the systems show small but definite changes proportional to the content of barium nitrate resp: alkali sulfate. Similar effects were found by Averel and Walden[19]), and Wa-

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[18]) G. H. Walden and M. U. Cohen, J. Amer. Chem. Soc., **57**, 2591 (1935).

[19]) P. R. Averell and G. H. Walden, J. Amer. Chem. Soc., **59**, 906 (1937).

gner[20]), if the contaminations of barium sulfate by potassium permanganate or hydronium and permanganate ions were increasing. The same effects are caused in cases of variable hydration of precipitated barium sulfate[21]). For us, it seems plausible, that in the examples mentioned, there are the phenomena of »two-dimensional« mixed crystals, very similar or of the same nature as the occlusion, rather than the systems of a random substitution of the lattice ions with the contaminating ions.

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IZVOD

Koprecipitacija i odnos između adsorpcije, okluzije i stvaranja mješovitih kristala

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Budući da su realni kristali u većini slučajeva aglomerati, istražen je utjecaj, koji vrše joni adsorbirani na površini primarnih čestica na njihov kemijski sastav. Da bi se mogli procesi adsorpcije, okluzije i stvaranja mješovitih kristala bolje da prikažu, dana je opća funkcija disperziteta za pojave, koje se javljaju na granicama primarnih čestica unutar kristala. Prigodom razmatranja mješovitih kristala »dvodimenzionalnog tipa« pokazano je, da njihovo stvaranje teče analogno pojavama okluzije. U tom leži i razlog zašto i okluzija i stvaranje mješovitih kristala utječu na jednaki način na promjenu difrakcione slike kod rentgenografske analize.

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[20]) G. Wagner, Z. physikal. Chem., **2B** **27** (1928).

[21]) G. Walton and G. H. Walden, Jr., J. Amer. Chem. Soc., **68**, 1750 (1946).