

## KINETICS OF PRECIPITATION OF SPARINGLY SOLUBLE INORGANIC SALTS

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Received February 2nd, 1971

The kinetics of precipitation of certain sparingly soluble salts of the type 2-2 ( $\text{BaSeO}_4$ ,  $\text{SrWO}_4$ ,  $\text{SrMoO}_4$ ,  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CaMoO}_4$ ,  $\text{PbSeO}_4$  and  $\text{PbC}_2\text{O}_4$ ), 1-1 ( $\text{TiO}_3$ ,  $\text{TlCl}$ ,  $\text{TlBr}$ ,  $\text{TlSCN}$ ) and 1-2 ( $\text{PbI}_2$ ,  $\text{Ag}_2\text{WO}_4$ ,  $\text{Ag}_2\text{CrO}_4$ ,  $\text{Tl}_2\text{CrO}_4$ ) were followed experimentally. From the obtained data the interfacial tension of the solid-liquid interface was calculated for a major part of the salts. The results substantiate the validity of the theory of homogeneous nucleation according to Nielsen.

The theory and method of measurement of sparingly soluble di-divalent electrolytes was elaborated by Nielsen<sup>1-3</sup>. The theoretical relationships were verified on salts of barium, strontium, calcium and lead in the region of homogeneous nucleation, where the dependence of the induction period  $t_1$  and of the logarithm of the number of particles  $N$  on reciprocal square of the logarithm of supersaturation ( $\log^{-2}S$ ) is linear.

The object of the present work is to verify the theoretical relations on other sparingly soluble di-divalent electrolytes, and this also beyond the region of the mentioned linear dependence, and to apply this method to other types of electrolytes.

### EXPERIMENTAL

Supersaturated solutions were prepared by mixing two stable equimolar solutions. For  $t_1 < 1$  s the mixing was accomplished in a mixing apparatus described earlier<sup>2</sup>. The induction period  $t_1$  was determined from a cinematographic record of the change of turbidity in the mixing cell and in the outlet channel. For  $t_1 > 1$  s, the solutions were mixed quickly in a laboratory vessel and the appearance of a turbulence was determined visually against a suitable background. The solutions were prepared by diluting stock solutions made from reagent grade chemicals and their concentration was checked analytically. The stock solutions were filtered through a sintered glass filter with pores smaller than  $1 \mu\text{m}$  and used no sooner than after a week. The alkaline earth metals and thallium were in the stock solutions as chlorides, lead and silver as nitrates. The necessary anions were in solutions as sodium salts. The number of particles was determined in diluted suspensions under a microscope in a counting cell of known volume. The original suspension was diluted and at the same time the coagulates were dispersed by adding either  $0.002\text{M-Na}_4\text{P}_2\text{O}_7$  or 80% aqueous glycerol or 0.02% gelatin. When the coagulation proceeded too rapidly or the coagulates could not be dispersed by shaking with one of the mentioned solutions, the suspension was transferred from the mixing apparatus directly into the peptization agent.

## RESULTS

*Di-Divalent Electrolytes*

Di-divalent electrolytes with cations  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Pb}^{2+}$  are, according to our experience, best suited for the study of precipitation since they form well-defined and hence easily countable particles. If the cation is a heavy metal ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ) the precipitates are gel-like flakes and cannot be dispersed to individual particles. This difference is probably due to the fact that in the first case the salts are not hydrated whereas in the second they have an ill-defined composition of the type  $\text{MX} \cdot x \text{H}_2\text{O}$ .

The dependences of  $\log N$  and  $\log t_1$  on  $\log^{-2} S$  for the studied substances in the region of homogeneous nucleation are linear; the regression lines were determined by the least squares method and their intersections with the axis of ordinates were calculated as 13–22 for  $\log N$  and –5 to –12 for  $\log t_1$  (Table I). The dependence of  $\log t_1$  on  $\log^{-2} S$  is not quite linear in the whole concentration region (in contrast to  $\log N$ ) as is evident from Fig. 1, where the values of  $\log t_1$  for  $\text{SrWO}_4$  in the absence and in the presence of 0.5M and 1M-NaCl are plotted. An arrow indicates the points where the character of nucleation changes as follows from the behaviour of  $\log N$ .

At lower and higher concentrations than indicated in Table I the points deviate from the straight line. At lower concentrations (heterogeneous nucleation) it is possible to draw approximately a straight line with a slope  $\alpha$  through the given points, where  $|\alpha_{\text{het}}| \approx 1 < |\alpha_{\text{hom}}|$ . At higher concentrations the controlling factor is the rate of mixing of the solutions; therefore, with our experimental technique which did not permit to increase this rate the points deviate towards lower values of  $N$  or  $t_1$ . In calculating the supersaturation, we used the thermodynamic activities of the electrolytes, therefore the concentrations were multiplied by activity coefficients calculated from the Debye–Hückel equation

$$\log f_i = -0.509z^2 \sqrt{I/(1 + \sqrt{I})}, \quad (1)$$

where  $I$  denotes ionic strength and  $z$  ionic charge number. From the experimental dependences, the surface tension  $\sigma$  and the number of ions  $n^*$  in the critical nucleus were calculated with the use of the equations

TABLE I

Experimental Results and Calculated Interface Tension  $\sigma$  for Sparingly Soluble 2–2 Electrolytes

Salt	$-\log t_{1\infty}$	$\log N_{\infty}$	$-\log D_{\text{exp}}$	$-\log D_{\text{mob}}$	$\frac{D_{\text{exp}}}{D_{\text{mob}}}$	$n^*$	$\sigma$ erg/cm <sup>2</sup>
$\text{BaSeO}_4$	9.7	17.5	3.93–4.19	5.04	6.9–13.0	19–24	88
$\text{SrWO}_4$	5.6	17.4	4.93–5.32	5.07	0.6–1.3	35–53	62
$\text{SrMoO}_4$	10.5	16.9	4.18–5.54	5.05	0.4–7.4	16–27	99
$\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	11.6	15.2	4.00–4.65	5.06	2–18	16–22	76
$\text{CaMoO}_4$	11.9	22.0	5.02–5.59	5.05	0.3–1.1	18–25	117
$\text{PbSeO}_4$	4.8	13.4	4.58–5.10	5.04	0.9–2.9	25–46	71
$\text{PbC}_2\text{O}_4$	—	14.2	3.12	5.02	80	—	147

$$\begin{aligned}
 (\sigma/kT \ln 10)^3 &= 5(\log t_1 + 10) (\log S)^2 / 2\beta v^2 = 5(22 - \log N) (\log S)^2 / 3\beta v^2 = \\
 &= 5\alpha_t / 2\beta v^2 = -5\alpha_N / 3\beta v^2, \quad (2)
 \end{aligned}$$

$$n^* = 5(\log t_1 + 10) (\log S)^{-1}, \quad (3)$$

where  $\beta$  denotes geometrical factor (we used the value of  $\beta = 32$  for a cube),  $v$  volume of one molecule,  $\sigma$  tension of the crystal-solution interface,  $\alpha_t$  and  $\alpha_N$  slopes of the dependences of  $\log t_1$  and  $\log N$  on  $\log^{-2} S$ . Furthermore, the diffusion coefficient was calculated from the experimental data ( $D_{\text{exp}}$ ) as well as from the Nernst equation ( $D_{\text{mob}}$ ):

$$-\log D_{\text{exp}} = \log t_1 + \frac{2}{3} \log N + \frac{1}{3} \log c_0 + 0.24, \quad (4)$$

$$D_{\text{mob}} = (2kT/qF) l_K l_A / (l_K + l_A), \quad (5)$$

where  $c_0$  denotes concentration of the dissolved species,  $l_K$  and  $l_A$  mobilities of cations and anions (velocities in unit electric field), and  $q$  absolute value of ionic charge (for the case of symmetrical electrolytes).

The values of  $D_{\text{exp}}$  for the studied range of concentrations vary as consequence of errors in the determination of  $t_1$  and  $N$ . Therefore, in Table I are given the limits of  $D_{\text{exp}}$ . The dependence of the number of particles on supersaturation was determined for the studied substances in the concentration range which is limited from above

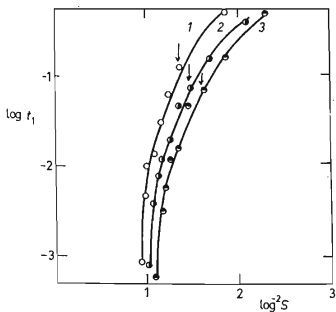


FIG. 1

Dependence of  $\log t_1$  on  $\log^{-2} S$ 

1  $\text{SrWO}_4$ , 2  $\text{SrWO}_4$  in 0.5M-NaCl, 3  $\text{SrWO}_4$  in 1M-NaCl.

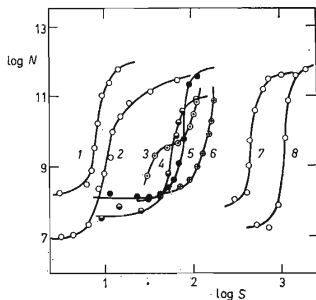


FIG. 2

Dependence of  $\log N$  on  $\log S$  for 2-2 Electrolytes

1  $\text{SrWO}_4$ , 2  $\text{PbSeO}_4$ , 3  $\text{SrC}_2\text{O}_4$ , 4  $\text{BaSeO}_4$ ,  
5  $\text{SrMoO}_4$ , 6  $\text{CaMoO}_4$ , 7  $\text{BaWO}_4$ , 8  $\text{CaWO}_4$ .

by the solubility of the less soluble component and from below by the concentration at which the induction period is of the order of 1 hour. The measured dependences of  $\log N$  on  $\log S$  are shown in Fig. 2.

### Uni-Univalent Electrolytes

It was possible to study by our method the kinetics of precipitation of  $\text{TlCl}$ ,  $\text{TlBr}$ ,  $\text{TlSCN}$  and  $\text{TlIO}_3$ . Since the dependences of  $\log t_1$  and  $\log^{-2} S$  are not so clearly defined as in the case of di-divalent electrolytes the values of  $\sigma$  were calculated as

$$\sigma = 5.77(\log S)_{\log N=10}^{2/3} V_m^{-2/3} \cdot 10^3, \quad (6)$$

where  $V_m$  denotes molar volume of the salt divided by the number of ions in the molecule.

The measured dependences of  $\log N$  on  $\log S$  are plotted in Fig. 3 and the calculated values of  $\sigma$  are 87, 92, 92 and 65  $\text{erg/cm}^2$  for  $\text{TlIO}_3$ ,  $\text{TlCl}$ ,  $\text{TlBr}$  and  $\text{TlSCN}$ , respectively.

### Other Electrolyte Types

Attempts to study the kinetics of precipitation of other types of electrolytes were unsuccessful except for uni-divalent electrolytes such as  $\text{Ag}_2\text{WO}_4$ ,  $\text{Tl}_2\text{CrO}_4$ ,  $\text{Ag}_2\text{CrO}_4$  and  $\text{PbI}_2$ . For these the dependence of  $\log N$  on  $\log S$  is little characteristic. The number of particles in the range of highest concentrations decreases initially steeply but then very slowly down to  $S \approx 5$  where a further drop by 2–3 orders of magnitude occurs as shown in Fig. 4. The induction period  $t_1$  corresponding to the first drop is about 0.01 s, that corresponding to the second about  $10^3$  s. Hence, the decrease in the number of particles in the range of highest concentrations can be attributed to homogeneous nucleation and this enables to calculate the surface tension  $\sigma(\text{Ag}_2\text{CrO}_4) = 107 \text{ erg/cm}^2$  and  $\sigma(\text{Tl}_2\text{CrO}_4) = 111 \text{ erg/cm}^2$ .

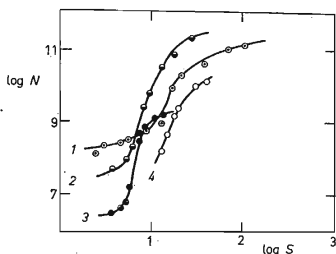


FIG. 3  
Dependence of  $\log N$  on  $\log S$  for 1–1  
Electrolytes

1  $\text{TlBr}$ , 2  $\text{TlSCN}$ , 3  $\text{TlCl}$ , 4  $\text{TlIO}_3$ .

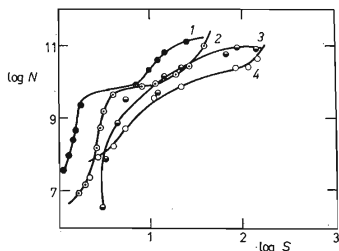


FIG. 4  
Dependence of  $\log N$  on  $\log S$  for 1–2  
Electrolytes

1  $\text{Ag}_2\text{WO}_4$ , 2  $\text{PbI}_2$ , 3  $\text{Ag}_2\text{CrO}_4$ , 4  
 $\text{Tl}_2\text{CrO}_4$ .

## DISCUSSION

The results for di-divalent electrolytes are in accord with the published conclusions<sup>3</sup>. The dependences of  $\log t_1$  and  $\log N$  on  $\log^{-2} S$  intersect the axis of ordinates at  $\log t_{1\infty} = -10$  and  $\log N_{\infty} = 22$  in rough agreement with the theory. That a better agreement cannot be expected is obvious from Fig. 1 where a curve is approximated by the straight line while last points are neglected. This neglect is substantiated by the fact that a) the given supersaturation the rate of mixing plays a role in addition to the rate of nucleation and b) the smallest  $t_1$  values are on the lower limit of sensitivity of our method and are therefore subject to a large error.

Whether the crystal growth is governed by diffusion (the basic assumption in deriving the theoretical relationships) can be decided on the basis of the criterion  $D_{\text{exp}}/D_{\text{mob}}$ . This is not much different from unity with the studied substances, an evidence that the growth is governed by diffusion except for  $\text{PbC}_2\text{O}_4$  where that ratio is equal to 80. This can be attributed to a deviation of the shape of the  $\text{PbC}_2\text{O}_4$  particles (dendrites) from spherical assumed in the theory.

The number of particles for di-divalent electrolytes in the region of heterogeneous nucleation and in the region where the rate of convection is important remains approximately constant. A drastic change in the number of particles (by six orders of magnitude) occurs only in a relatively narrow range of supersaturation. Together with the rapid growth of the number of particles the induction period of the reaction shortens by about three orders of magnitude. The course of the studied dependences for uni-univalent electrolytes is analogous although less distinct.

With uni-divalent electrolytes, changes of  $N$  and  $t_1$  with concentration were also observed. In the region of highest concentrations, they proceed in the same range of supersaturation for  $\text{Ag}_2\text{CrO}_4$  and for  $\text{Tl}_2\text{CrO}_4$  whence we conclude that the homogeneous nucleation is concerned. Therefore, the surface tension of these substances can be calculated from experimental data according to the equation given above.

The reason for the second drop in the number of particles at low concentrations, which is common to all studied electrolytes, is not clear but apparently bears no relation to a change in the character of nucleation.

*The author is indebted to Prof. A. E. Nielsen, Medicinsk-Kemisk Institut, University of Copenhagen, for efficient help.*

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Translated by K. Micka.