

Nucleation in Barium Sulfate Precipitation*

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In precipitation experiments with barium sulfate the number of crystals per unit volume was reduced to one-tenth or less by first cleaning the glass mixing vessel with condensing steam. During the precipitation higher order Tyndall spectra were observed.

It is concluded that under normal conditions the greater part of the nuclei does not originate from a homogeneous process but from the walls of the glass.

In theories of the precipitation of sparingly soluble salts such as barium sulfate different authors assume that the nuclei (i) exist before the mixing of the stable solutions, or (ii) are formed spontaneously at the moment of mixing, or (iii) originate from a homogeneous chemical process during a certain period of time in the beginning of the experiment.

As shown in a previous paper¹, the kinetics of the precipitation process measured for instance as the electric conductance in dependence of time can be made to agree with all three assumptions. It is therefore of interest to obtain a different kind of quantitative information such as the number of crystals formed per unit volume or, what is equivalent, their final size. Fischer and Rhinehammer² showed that the particle size and O'Rourke and Johnson³ that the number of crystals depend on the age of the solutions used. It seems impossible to account for this phenomenon by means of any sort of theory with a nucleation process starting at the moment of mixing, that is (ii) or (iii) above.

In the experiments reported below it was found that the number of crystals formed also depends on the method of cleaning the glass vessel. The introduction of a new cleaning technique (proposed by J. A. Christiansen) reduced this number to one tenth or even less.

* This is a part of the paper that was read before the 9. Nordiske Kemikermøde in Århus, August 1956.

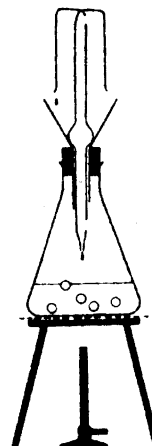


Fig. 1. The steam condenses at the inside of the beaker and through the funnel the water returns to the flask.

EXPERIMENTAL

50 ml 0.002 M BaCl₂ and 50 ml 0.002 M K₂SO₄ were taken up in pipettes, which were then emptied in less than 3 s in such a way that the two liquids met before reaching the bottom of the 250 ml Pyrex beaker. The solution was allowed to rest for 5 min, the precipitate became visible in 10 to 15 s and settled in a few minutes. 5 min after the moment of mixing the mixture was stirred with a glass rod and a drop of the slurry transferred to a blood cell counting chamber. It was found important to place the cover glass in less than 2 s since the precipitate sediments very quickly. At least either some 100 crystals — or all crystals inside the 9 mm² (0.9 mm²) counting field were counted.

The results were controlled through sedimentation experiments. The level of the uppermost crystals was easily measured during the first two or three minutes. From a plot the sedimentation velocity was found. If v = velocity in cm/s, r = radius of a sphere with the same volume as the crystal, g = acceleration of gravity, d = density of crystal, d_0 = density of medium, f = a form factor determined from the experiments ($f = 1$ for spheres of radius r), η = viscosity, n = number of crystals per liter, $c = 0.001$ = molarity of BaSO₄ just after mixing, M = molecular weight, m = weight of a crystal, — then

$$\begin{aligned} v &= (4/3)\pi r^2 g (d - d_0) f / 6\pi \eta r \\ n &= cM/m; \quad m = (4/3)\pi r^3 d \\ \therefore \log f &= \log v + (2/3)\log n - 3.60 \end{aligned}$$

The f -values found lie between 0.38 and 0.65 which is very reasonable.

The 250 ml Pyrex beaker used as a mixing chamber was cleaned before every experiment except the first one in a series by first rubbing it with a brush and rinsing in hot water. Then it was placed, bottom up, over boiling water, see Fig. 1, so that the steam condensed on the inside of the glass. After 10 min it was placed on a few layers of filter paper and allowed to cool.

RESULTS

In the beginning of a series of experiments usually about 2 000 or more crystals were found per mm³. After one or two cleanings of the beaker the number decreased to about a hundred of crystals per mm³, or 10⁸ per liter, and the counts might seem to obey a Poisson distribution. But occasionally, without change in technique, the counts were as low as 25 mm⁻³ several times. See Figs. 2 and 3.

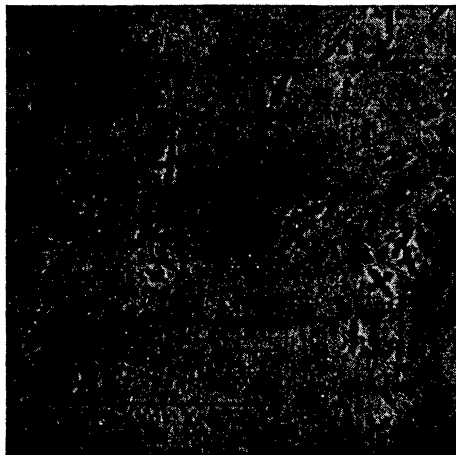


Fig. 2. The barium sulfate precipitate from an experiment where the glass had only been ordinarily cleaned. 2 050 crystals were found per mm^2 . In order to get more than one crystal on the photo (at a reasonable magnification) the precipitate was concentrated by sedimentation.

These results may be compared with those of O'Rourke and Johnson³ who in the same sort of experiments (except for the cleaning technique) found 1.1×10^9 particles per liter. That is about ten to fifty times as many as found in the present work.

Very often it was observed that *after* the sample had been withdrawn for counting, the solution became milky, and during the second sedimentation two distinct bands separated. Under the microscope another sample now displayed that new, much smaller crystals had appeared. These must be attributed to the stirring: either are new nuclei brought into the system with the stirring rod, or, what is more likely, the crystals already formed are crushed yielding nuclei. The easy breaking of the crystals upon handling was also observed by Fischer and Rhinehammer².

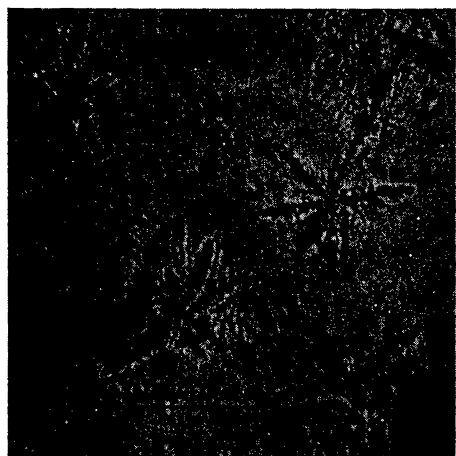


Fig. 3. The precipitate from an experiment where the glass had been cleaned as shown in Fig. 1; everything else was performed as in the experiment of Fig. 2. Only 30 crystals appeared per mm^2 . The magnification is the same in Figs. 2 and 3.

When the precipitation was observed in parallel light higher order Tyndall spectra ³⁻⁵ were observed. In these experiments the glass was not treated with steam.

When looking in a direction 135° to that of the original light beam, a red and a green light were observed during 5 to 15 s after the moment of mixing. When the concentrations were 0.0025 M before mixing both first and second order red and green were observed, together with violet in between.

After about 25 s all colours had disappeared, and only white light was observed.

These colours were obtained with Merck's K₂SO₄ but not with Analar's Na₂SO₄. The cause of this difference was not sought.

The appearance of the colours imply that the crystals are equally large since otherwise the lights would mix to yield white in all directions.

CONCLUSION

It seems impossible to explain that improving of the cleaning technique of the glass can reduce the number of crystals without assuming that those extra crystals formed when the glass is not cleaned so well originate from the walls of the glass. Since this number amounts to between 90 and 98 % of all the crystals formed under ordinary conditions we may conclude that by far the greater part of these, and perhaps all of them, do not originate from spontaneous nucleation but from impurities on the glass.

The appearance of higher order Tyndall spectra indicates that the precipitate at this time is very monodisperse and from this fact, too, we may conclude that the nuclei are not formed in a homogeneous process, since they must have all started growing at very nearly the same time.

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REFERENCES

1. Nielsen, A. E. *J. Colloid Sci.* **10** (1955) 576.
2. Fischer, R. B. and Rhinehammer, T. B. *Anal. Chem.* **25** (1953) 1544.
3. O'Rourke, J. D. and Johnson, R. A. *Anal. Chem.* **27** (1955) 1699.
4. Sinclair, D. and LaMer, V. K. *Chem. Rev.* **44** (1949) 245.
5. LaMer, V. K. and Dinegar, R. H. *J. Am. Chem. Soc.* **72** (1950) 4847.

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