FLOW METHOD FOR THE X-RAY DIFFRACTION STUDIES OF DISPERSIONS OF NASCENT PRECIPITATES

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A simple flow method has been developed and tested for the X-ray diffraction studies of solids dispersed in liquids, the disperse phase of which either undergoes fast structural changes or is in a labile equilibrium with the mother liquor. The described method is especially useful when dealing with substances that are sensitive to light, X-rays or ionizing radiation.

The usual procedure in the X-ray diffraction studies of suspensions and colloidal dispersions requires to separate at first the solids from the mother liquor and only then the classical Debye-Scherrer method can be applied. In the case of fast reactions between the precipitate and its mother solution the separated and dispersed phases can differ not only by composition but also by structure. The direct X-ray studies of dispersed systems have so far been used only to the identification of aged phases forming hydrosol particles. In a typical arrangement[1] the dispersed system was introduced into an adjusted Debye-Scherrer camera by a thin-wall glass capillary, it flowed coaxially through the cell *via* the capillary and after the interaction with the primary X-ray beam it flowed away through a light-tight tube. Using this method, no difference was observed between the aged solid phase separated from the mother liquor and its dispersed state in the mother liquor. This method can be used for kinetic studies only, if the exposure is negligible when compared with the time necessary for observable structural changes.

The aim of this work was to set up a simple device enabling us to determine the fine structure of the time-variable crystalline phases dispersed in liquids without separating the solids from the dispersing medium.

EXPERIMENTAL

The principle features of the proposed device, which can detect even the fast structural changes in a nascent precipitate, are schematically shown in Fig. 1. The dispersion of the precipitate under study is formed in a mixer by continuous mixing of thermostatted solutions extruded in a chosen ratio from the cylindrical glass containers by pistons pushed under the pressure of an inert gas. The formed precipitate enters immediately into the aging zone designed as a flow reactor with the piston flow[2]. The dispersion moves along this zone by a constant velocity so that the aging period is defined by the tube length. The dispersion passes then through a sieve and it enters into the X-ray camera through a jet, which ejects a cylindrical stream, moving coaxially to the camera and perpendicularly to the direction of the primary X-ray beam. The diffracted radiation is registered by a standard X-ray sensitive film. After the interaction with the primary beam the dispersion leaves the camera through a light-tight tube in the bottom of the camera. The solutions

and the continuously formed dispersion flow through the apparatus by the pressure of nitrogen from a steel flask. The aging period is adjustable from fractions of a second to minutes. In this arrangement we are dealing with an isothermal, non-isobaric system with a steady pressure profile. For longer aging periods it is advisable to use the variant of this method with a flow reactor with ideal mixing[2,3] which serves both as a mixer and an aging zone. The dispersion flowing through the X-ray camera is statistically identical during the exposure so that a possibility to register an accidental structural change is excluded. The construction details of the proposed device are to be found in our previous communication[3]. All the X-ray experiments were done with a flow Debye–Scherrer camera of the diameter of 57·3 and 114·6 mm using the filtered CoK_α radiation (λ 0·179021 nm). The camera is equipped with an adjustable jet made of stainless steel of the inner diameter of 0·6 mm and with a funnel-like collector with the light-tight outlet tube of the diameter of 10 mm. The positions of the diffraction lines were read with the precision of $\pm$ 0·05 mm on a comparator and a correction on the effective diameter of the camera was taken into account. The lattice parameters of the systems under study have been calculated by the Cohen variant of the least-squares method[4] using the Riley–Nelson extrapolation function[5]. The statistical weigths for the individual reflections were taken to be unity.

RESULTS AND DISCUSSION

Aged aqueous dispersions of Fe(III) ferrocyanide, calcium carbonate, barium sulfate, and calcium sulfate, previously prepared by precipitation (outside the apparatus), have been used for testing the outlined device. In these dispersions the presence of Fe(III) ferrocyanide, calcite, barite, and gypsum, respectively, has been unambiguously proved. It was found that with the proposed arrangement it was possible to identify the dispersed system provided that the size of crystallites of the dispersed phase did not decrease under a certain critical limit ($\sim$6 nm). The X-ray diffraction pat-
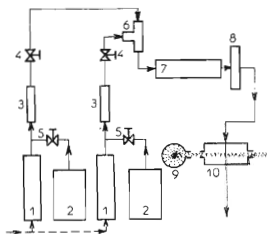

FIG. 1

The Experimental Arrangement for the X-Ray Diffraction Studies of Dispersions

1 Glass pressure cylinders with teflon pistons; 2 reservoirs for stock solutions; 3 flowmeters; 4 needle valves for the fine adjustment of the flow rate; 5 valves; 6 mixer; 7 the aging zone made of a spiral polyethylene tube; 8 desintegration sieve; 9 X-ray source; 10 flow X-ray camera.

terns of these dispersions were compared with the patterns obtained using the classical powder method under comparable conditions. The results obtained with the powder samples were of better quality in all cases due to the facts that (a) in the experiments with dispersions the geometry is worse defined than in the classical powder method, (b) the concentration of the solid phase in the dispersion (per volume unit) is substantially lower than in the powder, and (c) in dispersions the results are unfavourably affected by the interference of X-rays, scattered by the liquid dispersing medium.

The values of the lattice parameters obtained for these two types of samples are given in Table I, together with the respective standard deviations. The crystallite sizes were comparable in the both types ($\sim$30 nm). The values of lattice parameters of the dispersed phases are close to the values calculated for the powders of the same compounds. It is thus demonstrated that using the proposed method it is possible to follow reliably the changes of lattice parameters of the magnitude order of about 1 pm. Similarly to the classical method, the accuracy of the determination decreases with the decreasing symmetry and with the decreasing crystallite size of the dispersed system under study, as well as with the increasing number of the disperse components.

The proposed device was also applied to follow up the aging process of nascent precipitates of barium sulfate and calcium carbonate. The dispersion of barium sulfate (38·6 g/l) was prepared by precipitating two volume parts of 0·5M solution of sodium sulfate with one volume part of 0·5M solution of barium chloride in the mixer and the diffraction pattern of the precipitate in the nascent state was recorded after 1, 2, 5, 15, 60, and 300 s of aging at the room temperature. The dispersion flow rate through the apparatus was 25 ml/min. There is no other experimental technique giving information on the structure and physical state of solids with such a short history. The diffraction patterns of the precipitate taken after 1 and 2 s of aging could not be evaluated. The pattern taken after 5 s of aging showed already 9 diffuse but well defined diffraction lines that could be used for a reliable determination of the lattice parameters and also for the determination of the size of crystallites of the nascent phase. Jones method[6] was used for the evaluation of the size of crystallites. An aged dispersion of barium sulfate (6 days of aging plus 1 hour of digestion at 100°C) was used as a standard. The calculated values of lattice parameters and the size of crystallites of the nascent barium sulfate are given in Table II as a function of the aging period.

The data listed in the table indicate that the lattice parameters of the nascent barium sulfate are somewhat lower in the early period than they are in more aged precipitates. The process of aging is accompanied by the increase of the size of crystallites, while in the interval from 5 to 60 s no substantial changes have been observed during the aging. The relative accuracy of the values of crystallite sizes is $\pm15\%$.

The diffraction patterns of the calcium carbonate precipitate, taken after 10 min of aging, revealed the presence of the μ-modification of calcium carbonate, $i.e.$ of

TABLE I
Lattice Parameters of Precipitates Used for Testing of the Proposed Device
The accuracy of the parameters is expressed using a shortened notation, *e.g.* instead of 0.5110 ± 0.0008 only 0.5110 ± 8 is given in the table.

Solid phase	Crystalline structure	Dispersion			Powder		
		a, nm	b, nm	c, nm β, °	a, nm	b, nm	c, nm β, °
Fe(III)ferro-cyanide	cubic	0.5110 ± 8			0.5097 ± 3		
Calcite	hexagonal	0.499 ± 1		1.715 ± 5	0.4972 ± 8		1.690 ± 3
Barite	orthorhombic	0.884 ± 1	0.549 ± 1	0.714 ± 1	0.8863 ± 8	0.5424 ± 7	0.7154 ± 7
Gypsum	monoclinic	0.567 ± 1	1.507 ± 3	0.646 ± 1 118.14 ± 0.10	0.567 ± 1	1.504 ± 2	0.650 ± 1 118.23 ± 0.10

TABLE II
Lattice Parameters and Crystallite Sizes of the Nascent Precipitate of Barium Sulfate
The accuracy of the parameters is expressed by the shortened notation, similarly to Table I.

Aging s	Parameters, nm			Crystallite size nm
	a	b	c	
5	0.882 ± 2	0.541 ± 1	0.709 ± 2	16.0
15	0.879 ± 2	$0.543 \pm 1_5$	0.701 ± 3	17.5
60	0.883 ± 1	0.542 ± 1	0.712 ± 1	15.0
300	$0.887 \pm 1_5$	0.545 ± 1	$0.714 \pm 1_5$	29.0
Standard	0.884 ± 1	0.549 ± 1	0.714 ± 1	

vaterite, on the other hand the patterns of the precipitate taken after 1, 3, and 13 days of aging, showed the diffraction lines characteristic for calcite. The synthetic vaterite was identified also in the dispersion prepared by the precipitation at higher temperatures ($\sim 53°C$), when the diffraction patterns were taken after $5-17$ min of aging.

Under the steady flow conditions the intensity of the dispersed radiation depends only on the concentration of solid particles and not on the flow rate. It is necessary to work with the highest possible concentrations to achieve the desired signal-to-background ratio for the lines.

The described flow arrangement can be used for the determination of the fine structure of dispersed solids that undergo fast transformations or that are in a labile equilibrium with the dispersing medium. The radiation dose, absorbed by the dispersion during the exposure, is entirely negligible as the mean residence time of the

dispersion in the primary X-ray beam is about 10^{-3} s. This is also the reason why this arrangement is exceptionally well suited to the determination of eventual structural changes in compounds sensitive to the ionizing radiation or visible light. However, the described simple device can be used only for dispersions containing minimum ~ 0.05 grammolecules of the solid in one liter of the dispersion. A preconcentrating device, such as a centrifuge or a hydrocyclone, arranged at the X-ray camera inlet, may well extend the application field toward lower concentrations.

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