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Study of dispersity of styrene emulsions using the method of small-angle X-ray scattering (SAXS)

Summary — The small-angle X-ray scattering (SAXS) method was used in studies on dispersity of emulsions of potassium oleate micelles and of styrene emulsions obtained in the presence of this emulsifier. A lamellar structure of oleate micelles was observed. The solubilization of styrene in the system of emulsifier micelles was determined by refractometry. 0.6 ml styrene was dissolved in 100 ml of micellar solution of emulsifier. The micellar structure of the system remained almost unchanged. The structure and dispersity of styrene emulsions and the course of phase separation and ordering at the interface in the function of time elapsed from preparation of emulsion by intensive mixing was investigated. Dimensions and surface area of styrene macro- and microdroplets in the system were also determined. In a microemulsion, styrene particles with a diameter of about 10 nm prevailed and the ratio of the surface area of microdroplets to that of emulsifier micelles was about 1:20. The conditions of emulsion preparation had a large influence of the dispersity of emulsions obtained.

INTRODUCTION

It is well known that kinetic mechanism of emulsion polymerization of styrene (process rate, molecular weight characteristics of polymer) as well as distribution of particle size and stability of the reacting systems during synthesis of the final latex depend on the dispersity of styrene emulsion, as this dispersity determines the mechanism of formation of polymer-monomer particles [1—6].

The study of dispersity of monomer emulsion formed in the presence of emulsifiers and suitable surfactants of various nature during their introduction into aqueous monomeric phase of the emulsion and during synthesis of emulsifier at the phase boundary showed [5,6] that it does not correspond with the qualitative pattern of the emulsion system proposed by Harkins [9,15], Yurzhenko [11], and Smith and Ewart [1,2]. It appeared much more complicated. It turned out that styrene emulsion is composed of droplets and microdroplets of monomer and micelles of emulsifier. The ratio of these components and their size depend on the way of emulsion preparation. Highly dispersed emulsions of styrene containing big volume of monomer microdroplets with droplet diameter about 0.2 μm and of macrodroplets with diameter below 10 μm were prepared under conditions of interfacial transfer of emulsifier and surfactants through the phase boundary, according to their solubility in monomer and in aqueous phases during the process of mixing the emulsion at a speed of 500—800 r.p.m. Under these conditions the concentration of the emulsifier in the interfacial adsorption layer becomes higher, thus considerably reducing the interfacial tension and causing an effective breaking of the monomer phase. Such conditions are provided during preparation of emulsion when introducing emulsifier agent into the phase where it is less soluble, synthesising emulsifier at the phase boundary and preparing a concentrated monomer-water-emulsifier system to be diluted thereafter with water and monomer [3—6].

In highly dispersed emulsions the process of formation of polymer-monomer particles may take place from monomer microdroplets and from micelles of the emulsifier containing monomer dissolved in the bulk of micelles. The contribution of each mechanism to the process of polymer-monomer particles formation depends on the volume ratio of micelles of emulsifier to monomer microdroplets in emulsion.

Literature data concerning this problem are practically absent, what is evidently due to the lack of a method enabling the evaluation of the particle diameters in such a wide range of values: from dozens to thousands of nanometers.

EXPERIMENTAL PART AND DISCUSSION OF RESULTS

To determine the dimensions of highly disperse particle fractions (micelles of emulsifier and monomer microdroplets) in styrene emulsions formed by different methods,

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the present work uses the method of small-angle X-ray scattering (SAXS method).

X-ray intestigations of the system were carried out with a small-angle KPM-1 chamber based on CuK$_\alpha$-radiation monochromated with a Ni-filter and with the use of an amplitude discriminator in the recording system. The chamber was provided with a special cell with openings made of a thin polymer film, where the constant temperature (298.2 K) was maintained by a liquid thermostat with an accuracy of 0.1°C. The scattering intensity was measured in the angular range from 0.12° to 5°. The received values of intensity were treated with collimation correction according to the programme elaborated at the Institute of Crystallography of the USSR Academy of Sciences [7].

First of all there has been studied the structure of the micelles of emulsifier — potassium oleate — which was used later for stabilization of styrene emulsions. The emulsifier for this experiments was synthesized from chemically pure oleic acid and potassium hydroxide.

During the work 3% and 6% aqueous solutions of potassium oleate were used which are common in emulsion polymerization of styrene. For the dependence of scattered light intensity I on the angle of scattering φ, see Fig. 1. It is evident that this dependence for 3% (a) and 6% (b) solutions of the emulsifying agent is characterized by the presence of several maximums, what according to publication [8] indicates that the solution contains lamellar structures of potassium oleate micelles at concentrations studied.

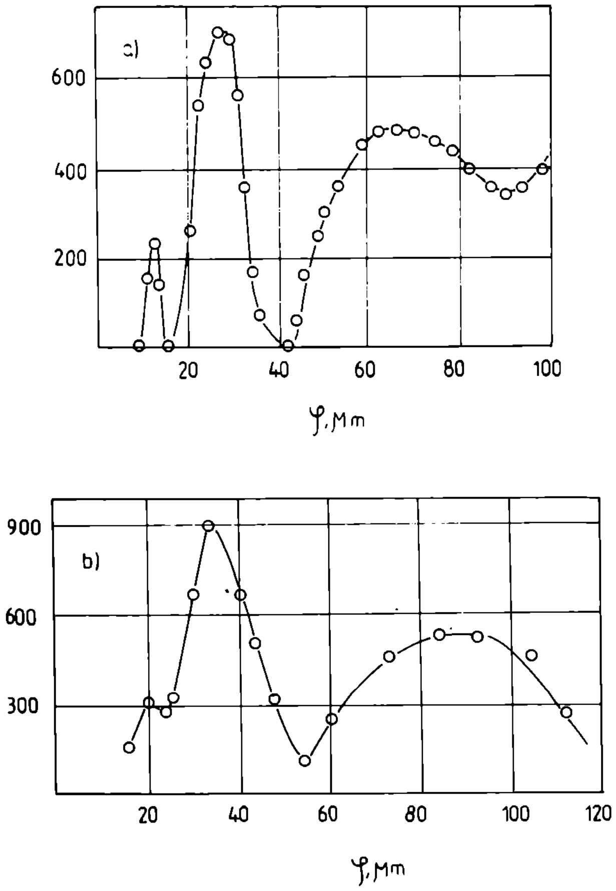

Fig. 1. Dependence of the scattering intensity I on the scattering angle φ for 3% (a) and 6% (b) aqueous solutions of potassium oleate

According to Wulf-Bragg formula $2d \sin \theta = n\lambda$, where n is the reflection order, λ wavelength of X-ray radiation, d interplanar distance in micelles of emulsifier calculated from $d = n\lambda/\varphi$ where φ is the value of the scattering angle at maximum scattering intensity (for CuK$_\alpha$ radiation of 1.54 Å) and $\varphi = 20$. It turned out that the interplanar distances in 3% and 6% solutions of potassium oleate were equal to 48 and 25 nm, respectively, what corresponds to data given in technical literature [9]. The decrease of the value of the interplanar distance between micelles of emulsifier with an increase in its concentration is due to a decrease of water layer thickness, this layer dividing the double adsorption layers of the emulsifier aggregates.

Lamellar structures in micelles of potassium oleate were also found during the study of aqueous solutions of potassium oleate at concentrations from 4 to 30% [10].

It seemed interesting to find out whether the structure of micelles of potassium oleate changed due to styrene solubilization in the micellar volume.

The refractometric method worked out by Yurzhenko was applied to determine styrene solubilization [11]. The refractive indices of aqueous solutions of emulsifier were determined with the help of IRF-22 refractometer. It turned out that 0.6 ml of styrene are soluble in 100 ml of the solution of micelles formed by 6% solution of potassium oleate.

The SAXS structural analysis showed that lamellar structure of micelles was preserved in 6% solution of potassium oleate containing solubilized styrene. The dependence of I vs. φ is similar to that given in Fig. 1. The monomer solubilization in micelles of emulsifier caused a small shift of the maximum values of scattering intensity to the range of big angles, due to a reduction of interplanar distance (d = 19 nm), resulting from swelling of micelles with styrene.

So, when adding styrene to an aqueous solution of emulsifier in quantities smaller or equal to the peak solubilization value, there does not occur any drastic change in the form of micelles.

The dispersity of the fine fraction of styrene emulsions was determined after breaking these emulsions formed at adding emulsifier to monomer as well as during synthesis of potassium oleate at the phase boundary. These emulsions were prepared using a mixing device with a three-level impeller mixer (at 800 r.p.m.).

The duration of mixing was calculated from the kinetic data of neutralization of oleic acid with the alkali during formation of emulsifier on the phase boundary — it was equal to 40 minutes [5]. The prepared emulsion was separated into layers in a centrifuge to eliminate the fraction of microdroplets. Then, SAXS measurements of aqueous phases were carried out at phase boundary during formation of emulsifier. This boundary is a layer of microemulsion taking an intermediate place between the aqueous and the hydrocarbon phases. The I—φ dependence (Fig. 2, curve 1) for aqueous phase of the emulsion obtained by introducing emulsifier into water revealed that the structure of the system changed. In the earlier studied systems the I—φ dependence had a number of clearly expressed maximums, but now we had one maximum only. Such dependence could be explained basing on the data of work [12] by the presence of a short-range order in the location of spherical micellar particles. These micelles form limited areas with the face-centered cubic lattice. Due to a defined size of such areas and some polydispersity of the system, the scattering curve shows, however, one maximum only, since the remaining peaks are smeared. The diameter of micelles with monomer solubilized in them was calculated according to Guiniér [13]; it was equal to 10.4 nm.

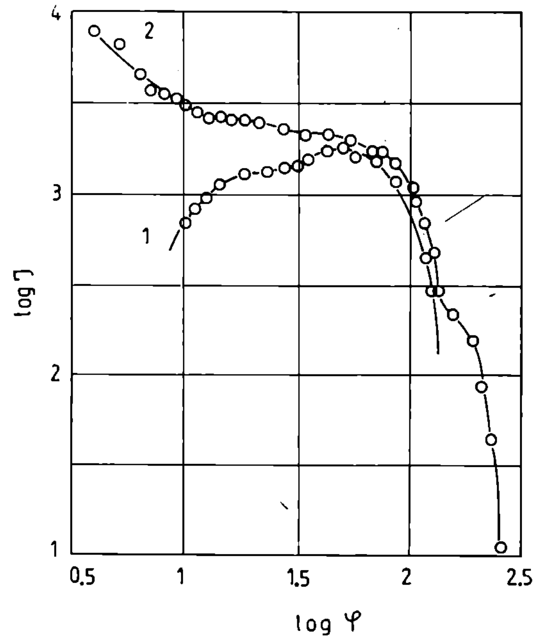

Fig. 2. Dependence of the scattering intensity I on scattering angle φ for aqueous phases of emulsions prepared by: 1 — introducing the emulsifier into aqueous phase; 2 — forming emulsifier at the phase boundary

The study of the aqueous phase of emulsions showed that the I—φ curve was composed of two parts (Fig. 2, curve 2). The first part of the curve reflects X-ray scattering from big particles and the range of big angles corresponds to X-ray scattering of small particles. The size of particles was calculated according to Guiniér: larger particles (microdroplets of monomer) had diameter of 55 nm and smaller ones (micelles of potassium oleate) 4.8 nm. Since the X-ray scattering of the aqueous phase of emulsion was studied immediately after its preparation, therefore the repartition of monomer between droplets and micelles of emulsifier probably could not take place; that is why the micelles remained "empty". To find out the possibility of styrene repartition between monomer droplets and micelles of potassium oleate, the samples were kept for three days after being prepared. The character of the I—φ dependence practically did not change, but the calculations revealed that the size of monomer microdroplets diminished to 50 nm. These data showed that when storing the aqueous phase of the emulsion containing both monomer microdroplets and micelles of emulsifier, the monomer solubilization took place in micelles of potassium oleate. Monomer penetrated into these micelles from monomer microdroplets by diffusing through the aqueous phase.

It is to be noted the identity of the I—φ dependence received at studying styrene microemulsion and aqueous phase of the emulsion, and during synthesis of emulsifier at the phase boundary.

So, the dispersity of styrene emulsions obtained by monomer emulsification with an aqueous solution of potassium oleate and under conditions of synthesizing this emulsifying agent at phase boundary, differed considerably.

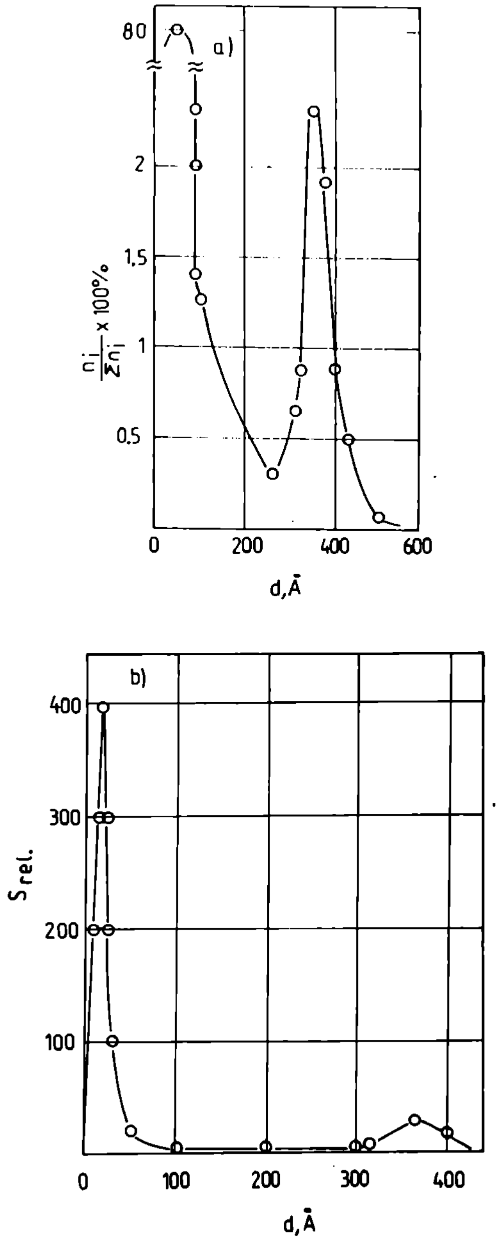

Fig.3. Distribution of the particles of microemulsion: (a) according to size, (b) according to distribution of particle surface area

In the first case, when styrene emulsion was prepared by emulsifying monomer with an aqueous solution of potassium oleate, it is composed of micelles of emulsifier containing styrene dissolved in their bulk (the diameter of micelles according to SAXS results was 10.4 nm), and monomer macrodroplets with average diameter (according to laser spectroscopy data [5,6]) about 400 nm.

In the second case, when preparing styrene emulsion under conditions of emulsifier synthesis at the phase boundary, the monomer emulsion was composed of the micelles of potassium oleate containing dissolved macro- and microdroplets of styrene. The numerical distribution according to size of droplets of monomer microemulsion and micelles of emulsifier was shown in Fig. 3a.

Fig. 3b gives the data on the ratio of surface area of monomer microdroplets to that of micelles of emulsifier. It is evident that in styrene microemulsion predominated particles of 10 nm diameter and the ratio of surface area of monomer microdroplets to that of micelles of emulsifier was equal to 1:20. It should be reminded that the ratio of the surface area of monomer microdroplets and to that of micelles of emulsifier in monomer emulsions formed during styrene emulsification with an aqueous solution of potassium oleate was equal 1:1000.

Thus, these results are a proof that the initial emulsions of hydrophobic monomers, such as styrene, have a more complicated dispersity than it was shown in the qualitative presentation by Harkins and Yurzhenko. They are particularly sensitive to the methods of their preparation (conditions of mixing, way of introducing emulsifier into emulsion). Under certain conditions it is possible to obtain highly dispersed styrene emulsions, where micelles of emulsifier together with monomer microdroplets of about 50 nm diameter will participate in the formation of polymer-monomer particles.

REFERENCES

1. Piirma I.: "Emulsion Polymerization", N. Y., 1982, p. 454.
2. Smith W. V., Ewart R. M.: *J. Chem. Phys.* 1948, **16**, 592.
3. Gritskova V. A., Sedakova L. I., Muradyan D. S., Pravednikov A. N.: *Dokl. Akad. Nauk SSSR* 1978, **238**, 607.
4. Simakova G. A., Kaminskii V. A., Gritskova I. A., Pravednikov A. N.: *Dokl. Akad. Nauk SSSR* 1984, **276**, 151.
5. Pravednikov A. N., Simakova G. A., Gritskova I. A., Prokopov N. I.: *Coll. J.* 1985, **47**, 189.
6. Ibidem, p. 192.
7. Chedrin B. D., Feygin L. A.: *Kristallografiya* 1966, **11**, 159.
8. Kitaygorodskii A. I.: "X-ray structural analysis of crystalline and amorphous bodies" (in Russian), State Publishing House, Moscow 1952, p. 154.
9. Harkins W. D., Matoon R. W., Corrin M. L.: *J. Coll. Sci.* 1946, **1**, 105.
10. Reiss-Husson, Luzatti V.: *J. Phys. Chem.* 1964, **68**, 350.
11. Yurzhenko A. I.: *Zh. Obshch. Khim.* 1946, **16**, 1171.
12. Kovalchuk M., Shen S.-H., Huang J.-S., Kim M. V.: *Phys. Rev. Lett.* 1984, **53**, 941.
13. Guiniér A.: "Roentgenography of crystals" (in Russian), State Publishing House, Moscow 1961, p. 539.
14. Plavnik G. M.: *Dokl. Akad. Nauk SSSR* 1981, **260**, 672.
15. Harkins W. D.: *J. Amer. Chem. Soc.* 1947, **69**, 1428.
