

MONODISPERSE COLLOIDAL SYSTEMS, FASCINATING AND USEFUL*

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I. ABSTRACT

Monodisperse colloidal systems may form spontaneously (protein solutions, micellar solutions, micro-emulsions) or be obtained by fractionation (Perrin's suspensions of gamboge) or by cleverly controlled particle growth (Au, S, latex). The controlled particle growth consists of a nucleation or seeding phase and a growth phase in which the size distribution is narrowed. The size and size distribution can be checked by a variety of techniques, such as centrifugation, light scattering, electronmicroscopy. The size distribution of micelles and micro-emulsion droplets is discussed on

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the basis of the thermodynamics of these systems.

Monodisperse systems have many applications, most of them in checking theories of fundamental aspects of colloid science, but also several in industrial applications.

II. PREAMBLE

Before talking about the actual subject of this, the first A.E. ALEXANDER MEMORIAL LECTURE, I want to say a few words about the man to whose memory this series of lectures is dedicated.

Trained as a surface chemist in RIDEAL's Laboratory, ALEXANDER soon included micellar systems, emulsions, proteins and polymers in his interest. When he published in 1949, with P. JOHNSON, the two volumes of "Colloid Science", he established himself as one of the leading authorities in our field.

His activities were by no means limited to surface and colloid science. He was actively interested in University organization and in teaching. He served the world, and Australia in particular, by training a large number of young people and infecting them with his obvious enthusiasm.

Besides he always had an open eye for applications in industry, in agriculture and in cattle farming. It is obvious that it should not be too difficult to select a subject, that he might have enjoyed hearing about, or to which he himself might have contributed.

III. INTRODUCTION

For my subject I have chosen monodisperse colloids, i.e. dispersed systems in which all particles have the same or nearly the same size. It is a curious fact that colloid scientists have been interested in monodisperse (or isodisperse or homodisperse) sols from the early days of this science. ZSIGMONDY's gold sols (ref. 1), LA MER's sulphur sols (ref. 2) and the DOW CHEMICAL COMPANY latices (ref. 3) immediately come to mind as examples of monodisperse systems.

From where does this interest in what appears to be a highly specialized and rare type of system arise? In the first place colloid scientists can often explain the properties of suspensions as due to the sum of contributions of individual particles or pairs of particles. Then, obviously, explanations are more satisfactory and can be tested more critically if all particles have the same size.

A second, more emotional, aspect may help to explain this preference for monodispersity. We are chemists, trained to thinking in terms of molecules, and the particles in suspensions and emulsions are the colloid chemist's "molecules". To a chemist all molecules of the same substance should have rigorously the same size (with apologies to the polymer chemists).

The idea that colloid particles are molecules brings me to the early and very fundamental application of monodisperse systems by JEAN PERRIN (ref. 4). In the early years of this century, PERRIN was studying Brownian motion. One of his aims was to establish the reality of molecules by showing that colloidal particles, which are individually visible, behave quantitatively just as the elusive and invisible molecules. About that time, EINSTEIN (ref. 5) and VON SMOLUCHOWSKI (ref. 6) had given a theoretical treatment of this irregular thermal motion of particles and molecules, and in particular, they had derived equations, in which Avogadro's constant, N_{Av} , is brought in relation to the r.m.s. displacement of particles in Brownian motion. These equations are

$$\langle x^2 \rangle = 2 D t \quad (1)$$

and

$$D = \frac{RT}{N_{Av}} \cdot \frac{1}{6\pi\eta\alpha} \quad (2)$$

where $\langle x^2 \rangle$ is the average square of the displacement in the x -direction in the time t . D is the diffusion coefficient of the particles, R the gas constant, T the temperature, η the viscosity of the medium and α the radius of the spherical particle.

Fig. 1 gives an example of three series of measurements of the displacement of spherical particles ($\alpha = 0.52 \mu\text{m}$) in consecutive intervals of 30 seconds. The particles are suspended in water at 20 °C.

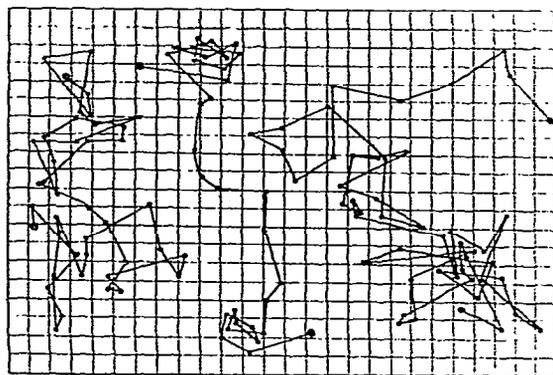


Fig. 1. Brownian displacement of spherical particles (radius $\alpha = 0.52 \mu\text{m}$) at 30 second intervals. The particles are suspended in water at 20 °C. The squares of the lattice have a side of $3.125 \mu\text{m}$. From PERRIN, *Les Atomes* (ref. 4).

Since the vertical component of Brownian motion can overcome the force of gravity to a certain degree, a suspension of small particles does not settle to a dense layer at the bottom of the container, but shows a concentration, that decreases exponentially with the height above the bottom. This situation is very similar, but on a vastly smaller scale, to the distribution in density in the atmosphere. Fig. 2 shows the effect for two suspensions in water at level intervals of $10\ \mu\text{m}$ and $12\ \mu\text{m}$ resp.

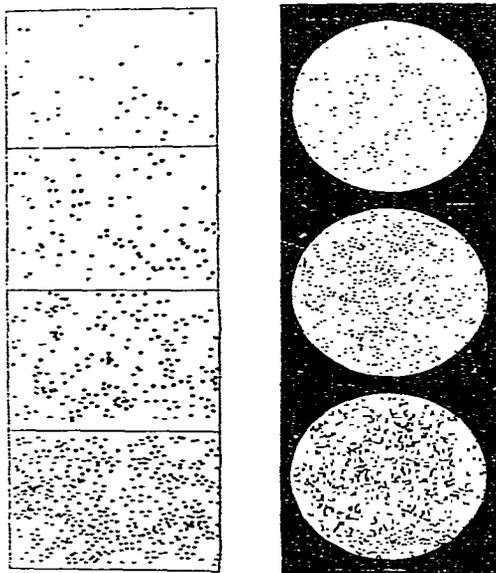


Fig. 2. Two examples of the sedimentation equilibrium of suspensions. Fig. 2a for spheres of gamboge ($\alpha = 0.29\ \mu\text{m}$) at levels, $10\ \mu\text{m}$ apart. Fig. 2b for spheres of mastic ($\alpha = 0.52\ \mu\text{m}$) at levels $12\ \mu\text{m}$ apart. From PERRIN, Ann. Chim. Phys. (ref. 4).

For a valid determination of Avogadro's constant from such measurements, the suspensions should be monodisperse and the size (and density) of the particles accurately known. PERRIN describes how he and his students prepared these suspensions by dissolving gamboge or mastic in methanol and then precipitating the resin again by dilution with large volumes of water. Emulsions of spherical particles, widely varying in size were formed. He then subjected these emulsions to fractional centrifugation, finally obtaining small quantities of monodispersed particles. He states that in one case, starting with a kg of gamboge, he obtained a few hundred milligrams of uniform particles after several months of centrifugations. Fig. 3 shows how a small amount of such a suspension, dried on a microscope slide, contains long rows of uniform particles from which the particle diameter may be derived.

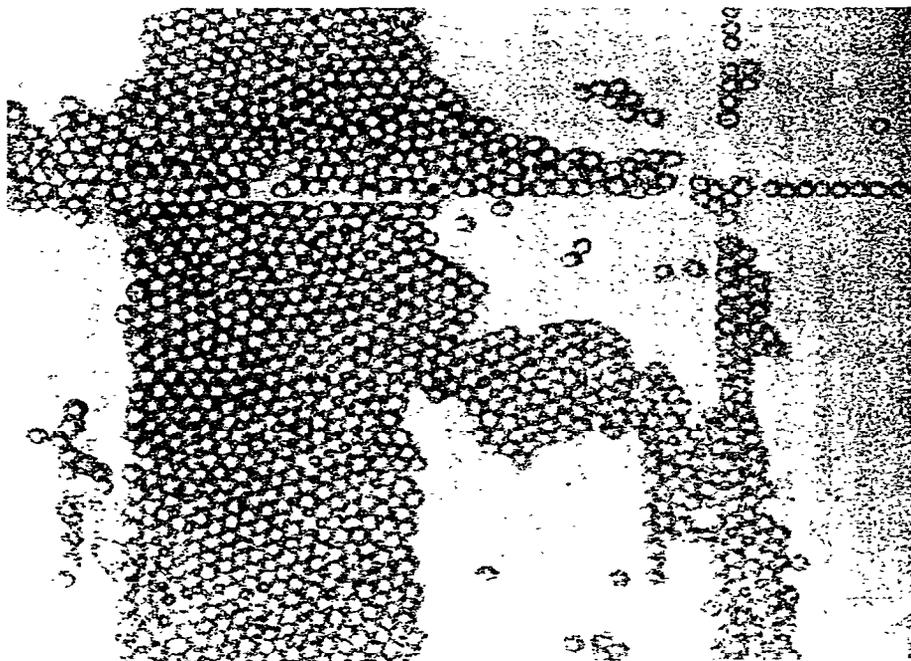


Fig. 3. Microscopic image of one of PERRIN's suspensions dried on a microscope slide. From PERRIN, *Les Atomes* (ref. 4).

From these and similar experiments, values for Avogadro's constant were found around 6.0 to $7.0 \times 10^{23} \text{ mol}^{-1}$, only slightly higher than the best present value. At the time of their determination, these results constituted a veritable breakthrough for which PERRIN justly received the 1926 Nobel prize for physics, with the citation that he had "put a definite end to the struggle regarding the real existence of molecules".

In the same year two more colloid scientists received the Nobel prize, ZSIGMONDY, the postponed 1925 prize for chemistry and SVEDBERG the 1926 prize for chemistry. Both play a role in my story about monodisperse systems. ZSIGMONDY's Nobel citation contained the words: "for proving the heterogeneous nature of colloidal solutions" (referring to his invention of the ultramicroscope) and "for the methods used which have laid the foundation of modern colloid chemistry." Among these methods, the preparation and study of gold sols (ref. 1) stands out. He used with preference the reduction of gold chloride solutions with formaldehyde and stressed the need for extreme cleanliness. In his book, he mentions that all his students had to master the preparation of the formaldehyde gold sol, in order to become aware of the need for precise and clean work in colloid chemistry. His big contribution to the

knowledge of monodisperse systems is the working out of the seed method ("Keimverfahren") (ref. 7), in which all the gold formed in the reduction process precipitates on nuclei added at the start of the process (the extremely fine FARADAY gold sol (ref. 8) with a diameter of the particles of about 3 nm, obtained by reduction with phosphorus dissolved in ether, often serves as the seed solution). Fig. 4 shows that the number of gold particles that is observed at the end of the reduction is strictly proportional to the amount of seed solution, which proves that no new nuclei have been formed.

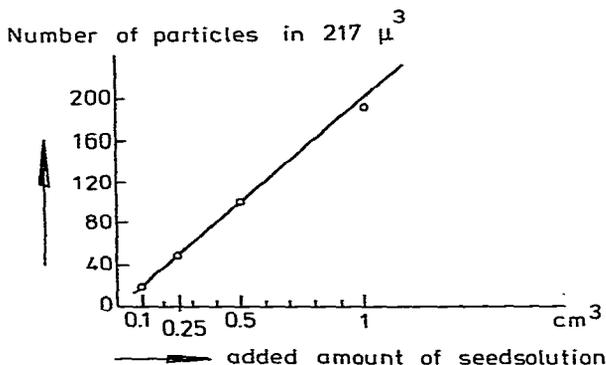


Fig. 4. Showing that in the reduction of a constant amount of gold chloride by formaldehyde the number of particles observed is strictly proportional to the volume of seed solution (Faraday gold sol obtained by reduction with phosphorus). From ZSIGMONDY, (ref. 7).

ZSIGMONDY mentions repeatedly that his gold sols (also the formaldehyde gold sols prepared without seed solution) are rather monodisperse. He concludes from the rate of reduction (ref. 9) that the diameter of the particles grows with a constant rate until close to the end of the process, but he does not give a very stringent proof of the monodispersity.

Later experiments by WESTGREN (ref. 10), however, showed that the ZSIGMONDY type gold sol can be nearly ideally monodisperse. WESTGREN repeated PERRIN's sedimentation experiments with Se sols and Au sols. With two sets of gold particles (radii 21 nm and 26 nm), he found not only a perfectly exponential decay of the concentration with height, but he found also a value of $6.05 \times 10^{23} \text{ mol}^{-1}$ for Avogadro's constant, very close to the present day best value. These results prove that the particles must have been truly monodisperse.

And here we find a link with SVEDBERG. He was awarded the Nobel prize for his work on disperse systems, especially on their Brownian motion, but at the time of the Nobel prize ceremony he was concentrating his attention on his newly developed

ultracentrifuge (ref. 11). One of the earliest experiments with a still rather primitive, mechanically driven ultracentrifuge was the centrifugation of gold sols. His student, RINDE (ref. 12), using both sedimentation velocity and sedimentation equilibrium determined size distributions of various gold sols. Fig. 5 gives the size distribution of a Faraday gold sol slightly grown by reduction of gold with H_2O_2 (average radius 4.7 nm) determined from its sedimentation rate and Fig. 6 that of another sol (a Faraday sol) determined from sedimentation equilibrium.

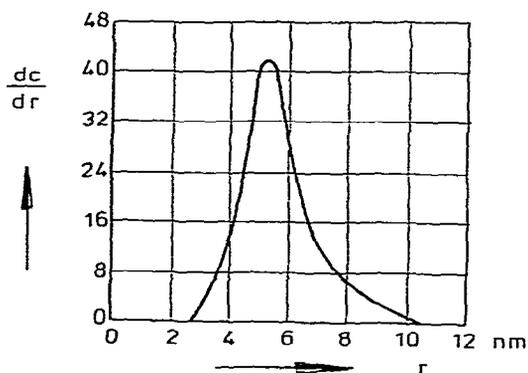


Fig. 5. Particle size distribution of an H_2O_2 gold sol determined from the rate of sedimentation in an ultracentrifuge. From SVEDBERG, book, (ref. 10).

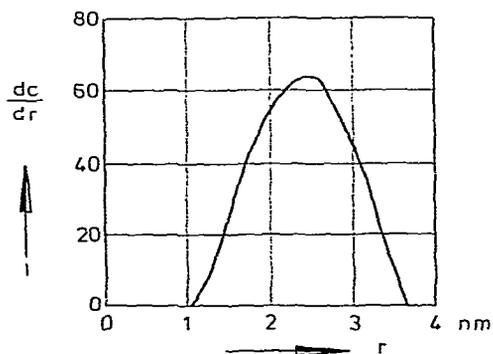


Fig. 6. Particle size distribution of a Faraday gold sol (not the same as that in Fig. 5) determined from the sedimentation equilibrium in an ultracentrifuge. From SVEDBERG, book, (ref. 10).

These sols are not monodisperse at all, but the monodispersity appears in SVEDBERG's work in a completely different field. He investigated not only, even not in the first place, the sedimentation of gold sols and the like, but also the

same for protein solutions. He showed convincingly both in sedimentation velocity and in sedimentation equilibrium experiments, that proteins are truly monodisperse. His preparations might have contained some impurities or a small fraction of aggregates but the bulk of the material behaved as true molecules, all of the same size. Fig. 7 shows the difference in sedimentation rate between a monodisperse protein sedimenting with a sharp boundary and a polydisperse gold sol, where the sedimenting boundary becomes increasingly vague with time.

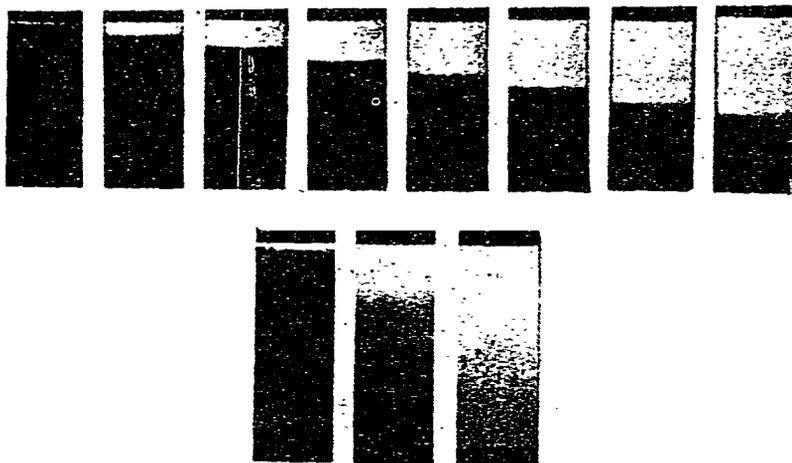


Fig. 7. Progress in time of sedimentation of hemocyanine (from snails blood), sedimenting with a sharp boundary and of a polydisperse gold sol, sedimenting with an increasingly broadening boundary. From SVEDBERG, (ref. 10).

SVEDBERG's early values for the molecular weight of hemoglobin ($M = 68,000$), phycoerythrin ($M = 208,000$), phycocyanine ($M = 106,000$) and egg albumin ($M = 34,500$) may not be the best available now, yet they are still close to the mark and at that time the monodispersity was the main point, proving that proteins were well defined molecules, rather than aggregates of smaller polypeptides.

What a difference between the work of these three great men. PERRIN painstakingly, practically handpicking his resin particles, ZSIGMONDY introducing a chemical method still much in use today for preparing monodisperse systems and SVEDBERG turning to nature and finding his monodisperse solutions nearly ready made.

IV. PREPARATION OF MONODISPERSE SYSTEMS

If we discard fractional centrifugation as not very practical and realize that finding monodisperse suspensions ready made in nature is of very limited applicability, we want to know the essential requirements for preparing monodisperse

systems.

Remarkably enough, all methods used so far can be derived from ZSIGMONDY's seed method. The method has been refined and diversified, but the principle is always the same.

Arrange the formation of the dispersed material in such a way that all nucleation takes place in a very short period and supply additional material so slowly, that it can find its way to the nuclei without the supersaturation reaching a level at which further nucleation could occur.

LA MER (ref. 13) expressed this situation in a simple diagram relating to his preparation of sulphur sols from acidified thiosulphate. See Fig. 8. Sulphur is

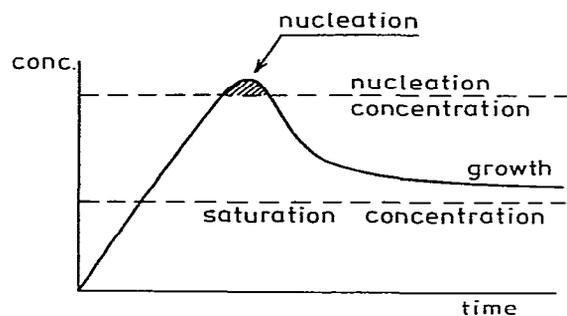


Fig. 8. Illustrating the formation of a monodisperse system by controlled nucleation and growth.

formed by the chemical reaction, its concentration increases, rises above the saturation concentration, until nucleation occurs. This condition results in the formation of many nuclei in a short burst. They grow rapidly, which lowers the concentration to a value below the nucleation concentration, but high enough to allow particle growth to occur at a rate that just consumes all further sulphur that is generated.

The nucleation burst may be replaced by the addition of seed particles.

It is through the work of LA MER and his associates that colloid scientists became aware of the wide potential of the controlled nucleation and growth method for preparing monodisperse systems, not only in water but also in gasses as aerosols. Moreover, LA MER discovered the use of light scattering in the form of higher order Tyndall spectra (H.O.T.S.) for testing the narrowness of the size distribution.

The method has been applied to a great variety of systems, such as aerosols of dioctylphthalate, oleic acid and other oils (ref. 14) (often using NaCl seed particles), and hydrosols of gold (ref. 1), sulphur (ref. 15), silver halides

(refs. 16, 17) chromium hydroxide (ref. 18), aluminium hydroxide (ref. 19), and silica (ref. 20). A very well known application is the formation of monodisperse latex in emulsion polymerization (ref. 21).

These systems and several others have found a variety of applications in the study of light scattering, coagulation, rheology, etc. We will come back to these applications in the last part of this paper.

V. DOES SEEDING OR EARLY NUCLEATION ALWAYS LEAD TO MONODISPERSITY?

If nucleation occurs during the whole precipitation period and therefore nuclei grow during different times, a heterodisperse suspension should be expected. But even if all nuclei grow during the same period, it is not so obvious that they all grow at the same rate so as to produce a monodisperse system.

From nucleation theory (ref. 22), we know that nuclei normally are very small, but even during the brief nucleation burst (see Fig. 8) they may have grown to different (small) sizes and thus one starts with a non-isodisperse system. Consider for instance the size distribution of the Faraday gold sol as shown in Figs. 5 and 6. These "nuclei" vary in size. Why do they still grow at the same rate?

The rate determining step in the growth of the particles may be:

- a) diffusion towards the particle,
- b) incorporation of new material in the particle by some sort of surface reaction,
- c) in the case of emulsion polymerization, the actual polymerization in the bulk or at the surface of the particle, might be rate determining or instead the migration (by diffusion) of monomers or free radicals to the particle.

A. Diffusion is rate determining

If the diffusion is rate determining and if the particles are so far apart that each can grow at its own rate, we may describe the diffusion towards each particle (assumed to be spherical with radius, a) by FICK'S law, stating that the diffusion flux, J , through any spherical shell (radius, r) is given by:

$$J = 4\pi r^2 D dc/dr, \quad (3)$$

where D is the diffusion coefficient of the diffusing material and c its concentration. We assume that the saturation concentration c_s is maintained at the particle surface and we neglect the influence of the particle size on c_s (KELVIN effect neglected). Then a concentration gradient is set up, which approaches a stationary state in times of the order of a^2/D , as sketched in Fig. 9. In this stationary state, J does not depend on r , and by integration of Equation 3 is found to be:

$$J = 4\pi D a (c_\infty - c_s), \quad (4)$$

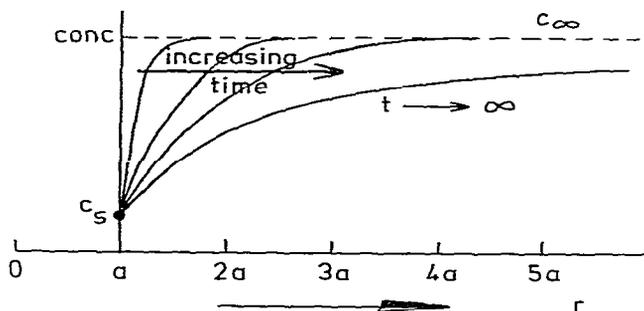


Fig. 9. Sketch of concentration gradient developing around a particle on which all diffusing material precipitates.

where c_∞ is the concentration far away from the particle. The rate of growth of the particle radius is then:

$$\frac{d\alpha}{dt} = \frac{JV}{4\pi\alpha^2} = \frac{D(c_\infty - c_s)V}{\alpha} \quad (5)$$

or

$$\frac{d\alpha^2}{dt} = 2D(c_\infty - c_s)V, \quad (6)$$

where V is the molar volume of the material precipitating on the particle.

This equation shows that *irrespective of the original size, α_0 , of the particle the square of the radius of all particles increases at the same constant rate.*

This whole treatment is oversimplified. It neglects the change in available material with time through chemical production (change in c_∞) or change in temperature (change in c_s) or even by mechanical addition of the precipitating material. It neglects the influence of the growth of the particle on the concentration gradient, and it neglects the mutual influence of all the individual diffusion fields.

It has been shown (ref. 23), however, that so long as the diffusion, and not the incorporation, is rate determining, $d\alpha^2/dt$ will be the same for particles of any size, although not necessarily constant in time. Then, as we shall show now, the particle size distribution narrows with growth.

Calling the absolute width of the distribution $\Delta\alpha$ for radius α and $\Delta\alpha_0$ for the radius α_0 at the start, we have:

$$\alpha\Delta\alpha = \alpha_0\Delta\alpha_0. \quad (7)$$

The absolute width of the distribution becomes narrower in the ratio a_0/a . The relative width decreases even faster, from $\Delta a_0/a_0$ to:

$$\frac{\Delta a}{a} = \frac{a_0 \Delta a_0}{a^2} = \left(\frac{a_0}{a}\right)^2 \frac{\Delta a_0}{a_0} \quad (8)$$

B. Diffusion not rate determining

If the incorporation of the new material, or its formation (e.g. by polymerization) in the particles is rate limiting, we then consider three cases (intermediate cases are possible).

a. The rate of incorporation is the same for all particles, irrespective of their size (this occurs in the SMITH and EWART (ref. 24) mechanism of emulsion polymerization, where on the average one radical grows in each particle half of the time), then $d\alpha^3/dt$ is the same for all particles and the size distribution narrows in a more pronounced way than with diffusion being rate limiting. We obtain:

$$\frac{d\alpha}{dt} = k\alpha^{-2}, \quad (9)$$

where k does not depend on α , but may depend on t . Or:

$$\alpha^2 \Delta \alpha = a_0^2 \Delta a_0 \quad (10)$$

and

$$\frac{\Delta \alpha}{\alpha} = \left(\frac{a_0}{\alpha}\right)^3 \frac{\Delta a_0}{a_0}. \quad (11)$$

b. If the rate of incorporation is proportional to the area of the particles (the incorporation takes place randomly over the surface, as in the presence of many crystallization nuclei), then:

$$\frac{d\alpha^3}{dt} = k\alpha^2 \quad (12)$$

or

$$\frac{d\alpha}{dt} = \text{constant, or } f(t), \quad (13)$$

and although the absolute width of the distribution remains constant, the relative width narrows:

$$\frac{\Delta \alpha}{\alpha} = \left(\frac{a_0}{\alpha}\right) \frac{\Delta a_0}{a_0}. \quad (14)$$

c. Only if the rate of incorporation is proportional to the volume of the particle (e.g. a polymerization with a constant concentration of radicals in the particles) $da^3/dt = k'a^3$ and the absolute width of the size distribution grows proportionally to the particle radius, the relative width thus remaining constant:

$$\frac{da}{dt} = ka \quad (15)$$

or

$$\frac{\Delta a}{a} \approx \frac{\Delta a_0}{a_0} . \quad (16)$$

Comparing Eqs. 9, 5, 13 and 15, we see that, depending on the mechanism, the growth rate of the radius may be proportional to the -2, -1, 0 or +1 power of the radius respectively, and the relative size distribution will become narrower, or at worst remain constant, with growth of the particles. BRADFORD, VANDERHOFF and ALFREY (ref. 25) have already pointed out, that, as long as the growth rate of the radius is proportional to a power, lower than +1, of that radius, the distribution will become narrower with growth, assuming, of course, that all particles grow during the same time.

VI. METHODS FOR THE DETERMINATION OF PARTICLE SIZES AND PARTICLE SIZE DISTRIBUTIONS

For the determination of particle sizes, direct observation in the *microscope*, although obvious, is only feasible in the rare cases where large particles ($> 1 \mu\text{m}$) are involved. When the particles are in contact and form a regular pattern as shown in Fig. 3, even somewhat smaller sizes may be determined.

By introducing dark field illumination and so converting the microscope to an *ultramicroscope* ZSIGMONDY extended the range of observation down to particles of about 10 nm, and by counting the particles in a known volume of the dispersion could obtain their average size. The ultramicroscope gives only rather qualitative information on the size distribution from an estimate of the intensity of the light scattered per particle.

The *electronmicroscope* is ideally suited for determining size distributions in the colloidal size range, although one has to be aware of the possibility of artifacts and of deformations. Particles from an isodisperse latex are often used for calibration.

The COULTER *counter* is good for size and size distribution but not very good for particles below 1 μm .

Sedimentation rate, interpreted with STOKES' law, and sedimentation equilibrium have been used with normal gravity and with the ultracentrifuge (ref. 11). They are suitable for average size and size distribution, especially if the size distribution is wide.

Although *light scattering* by colloids has been known since TYNDALL (ref. 26) and the important theories by RAYLEIGH (ref. 27), LORENZ (ref. 28), MAXWELL-GARNETT (ref. 29), MIE (ref. 30) and DEBYE (ref. 31) were available before 1910, the use of light scattering for the determination of particle sizes and size distribution dates really from 1944 when DEBYE (ref. 32) applied the method to solutions of micelles and polymers. The earlier application by PUTZEYS and BROSTEAUX (ref. 33) was not sufficiently recognized.

For small particles that do not absorb the light, light scattering leads only to an average particle size (molecular weight), but when the particle radius is more than about $\frac{1}{3}$ of the wavelength (λ) of light, interference due to length differences between different pathways of light starts to become important. The scattering develops maxima and minima as a function of the scattering angle and these allow an estimate of the size distribution. Fig. 10 shows such a pronounced profile for sulphur particles in water scattering red light.

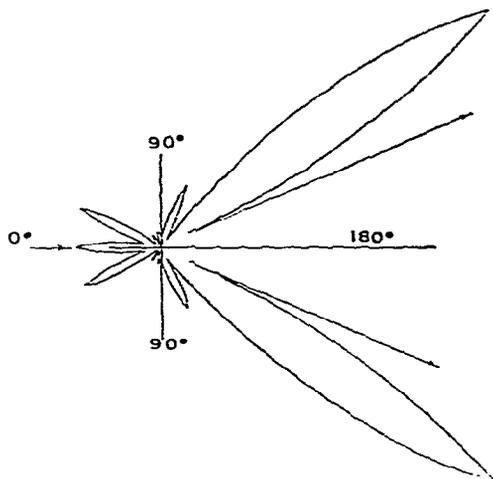


Fig. 10. Intensity of the vertically polarized component of the light scattered by a spherical sulphur particle in water according to the MIE theory. $\alpha = 3\lambda/\pi$. Incident light and direction of observation are horizontal. The distance of the center of the figure to the contour is proportional to the scattered intensity. For a small particle ($(\alpha/\lambda) \rightarrow 0$) the contour is a circle. From I. JOHNSON and V.K. LA MER, J. Am. Chem. Soc., 69, 1184 (1947), fig. 1 p. 1186.

This feature can be used in at least two different ways. Since the angular position of maxima and minima depends on α/λ , rather than on α or λ separately, they shift when the wavelength is changed. Thus, if white light is scattered, not only the intensity but also the color of the scattered light depends on the angle. In practice, one sees a series of red and green bands, which have been called *Hilgher*

Order Tyndall Spectra (H.O.T.S.) by LA MER. The presence of such bands is a sensitive test of near monodispersity and their number and position allow the particle size to be estimated. It is also possible to measure the intensity and polarization of the scattered light at a number of angles, compute these values from the MIE theory for chosen sizes and distribution widths and see which combination of values fits the data best. This approach has been used by KERKER and associates (ref. 34). HELLER (ref. 35) has applied rather similar methods.

With the availability of lasers as light sources, it has become possible to study the change in wavelength of the scattered light as compared to the incoming beam. The Brownian motion of the particles in a suspension causes such a shift in wavelength and by analyzing this shift by photon correlation spectroscopy (ref. 36) the diffusion coefficients, the radius of the particles (see Eqs. 1 and 2), and in principle, also their size distribution can be determined.

VII. THE EXPERIMENTAL SITUATION

Let us now turn to experiments on monodisperse systems and see how well the theories explain them.

ZSIGMONDY (ref. 1) mentions repeatedly that good formaldehyde *gold sols* have rather uniform particles, and that the seed method allows one to prepare sols with uniform particles of a predetermined size. ZSIGMONDY and HÜCKEL (ref. 9), basing their treatment on unpublished work by REITSTÜTTER, postulate that the linear dimensions of the particles grow at a constant rate ($da/dt = \text{const.}$), which would correspond to the reduction occurring as a surface reaction and lead to a narrowing of the size distribution. In several experiments the reduction accelerates faster, especially towards the end of the reduction. The best proof of the near monodispersity of this type of gold sol is found in the sedimentation work of WESTGREN (ref. 10), that we mentioned earlier.

Many years later TURKEVICH and coworkers (ref. 37) studied gold sols prepared in many different ways, measured their size distribution by electronmicroscopy and found an "exponential law of growth":

$$a(t) = a_0 \exp(kt) \quad (17)$$

or

$$da/dt = ka, \quad (18)$$

using light absorption.

They found that reduction (without seeding) by sodium citrate led to rather monodisperse sols ($\alpha = 9-10$ nm, spread about 10%) which could be grown by further reduction by hydroxylamine to $\alpha \approx 50$ nm with the relative width of the distribution

remaining unchanged in agreement with our Eq. 16. There is no good explanation why the reduction accelerates so much as to suggest a reaction in the bulk of the particles.

Aerosols generated by condensation of vapors on nuclei of NaCl, AgCl and the like, prepared by the method of SINCLAIR and LA MER (ref. 14) and refinements of it (ref. 38), vary in radius from about 10 nm to about 1 μm with geometric mean standard deviations of the order of 10-20%, in favorable cases even as low as 3%.

LA MER's *sulphur sols* can have a very narrow size distribution as shown by their light scattering. REISS and LA MER (ref. 23) and ZAISER and LA MER (ref. 39) show that the square of the particle radius grows linearly with time, as expected with diffusion controlled growth (see Eq. 6), and conclude from their theoretical treatment, that the distribution narrows with growth. They derive figures for the concentration of dissolved sulphur above the saturation concentration ($c - c_s = 4.7 \times 10^{-6}$ mol S/l) and for the diffusion coefficient ($D = 2 \times 10^{-6}$ cm² s⁻¹ for S₈) from their growth data.

KERKER *et al.* (ref. 34) in very careful experiments with sulphur sols showed that the relative size distribution (found from an analysis of the MIE light scattering) narrows during the first hours of the preparation, broadens rapidly between 3 and 3.5 hours (some coagulation?) and then stays about constant. In contrast with LA MER's data they conclude that the volume growth is constant in time ($d(\bar{a})^3/dt = \text{const.}$). The difference may be due to slightly different experimental conditions. Fig. 11 shows how the size distribution changes with time.

By studying the competitive growth in an *emulsion polymerization* seeded with a mixture of two monodisperse polystyrene latices of different sizes, BRADFORD, VANDERHOFF and ALFREY (ref. 25) concluded that

$$\frac{d\bar{a}}{d\bar{a}} = k\bar{a}^n, \quad (19)$$

with n having values between 0 and 0.5, and certainly not $n = -2$ as required in SMITH and EWART's theory (ref. 24). BRADFORD *et al.*'s n value points to a mixture of surface reaction ($n = 0$) and reaction in the bulk of the particles ($n = 1$) and is just good enough for some sharpening of the distribution with progress of the reaction. This technique of competitive growth (also used by TURKEVICH (ref. 37) in his work on gold sols) appears to be a powerful technique for studying reaction mechanisms since it is enough to measure the shift of the two peaks in a bimodal distribution, easily done by electron microscopy, rather than having to determine a size distribution in detail.

Monodisperse sols of *silver halides* have been prepared in various ways. All methods have in common that the nucleation or seeding stage is separated in time from the growth phase. The particles formed are rounded cubes, octahedra or other

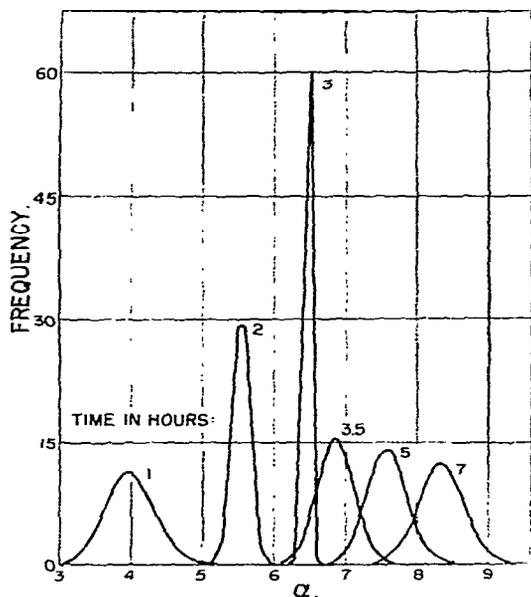


Fig. 11. Size distribution in LA MER type sulphur sols at different times after mixing of the ingredients ($\text{Na}_2\text{S}_2\text{O}_3$ and HCl). $\alpha = 2\pi a/\lambda$, where λ is the wave length of light (436 nm), is plotted on the abscissa. Each unit corresponds to 69.4 nm in the radius. From KERKER et al. (ref. 34) fig. 5, p. 2111.

crystal shapes, *rarely spheres*. OTTEWILL and WOODBRIDGE (ref. 16) prepared silver halides by careful dilution of complex solutions or in the case of AgBr , which is 40 times more soluble at 100°C than at 20°C , by cooling a hot solution. KLEIN and MOISAR (ref. 17) obtained monodisperse crystals by preparing nuclei of silver halide in gelatin solution and allowing these nuclei to grow by careful addition of further halide and silver nitrate. Fig. 12 gives electron microscope pictures obtained by OTTEWILL and WOODBRIDGE.

Fairly recently, MATIJEVIĆ and coworkers have added a group of metal oxides and hydrous oxides to the systems that can be prepared in relatively monodisperse form. The first of the group was chromium hydroxide (ref. 18), followed by various others and including the hydrous oxides of Cu , Fe and Al , TiO_2 and basic ferric sulphates (refs. 19, 40). The technique used consists in allowing solutions of the metal salts, usually in the presence of complex forming sulphate or phosphate ions, to hydrolyze slowly at elevated temperatures. It seems that the slow hydrolysis provides the material of the particles which reaches a concentration at which a burst of nucleation occurs, after which the growth with narrow size distribution continues. The conditions of hydrolysis vary between the different metals.

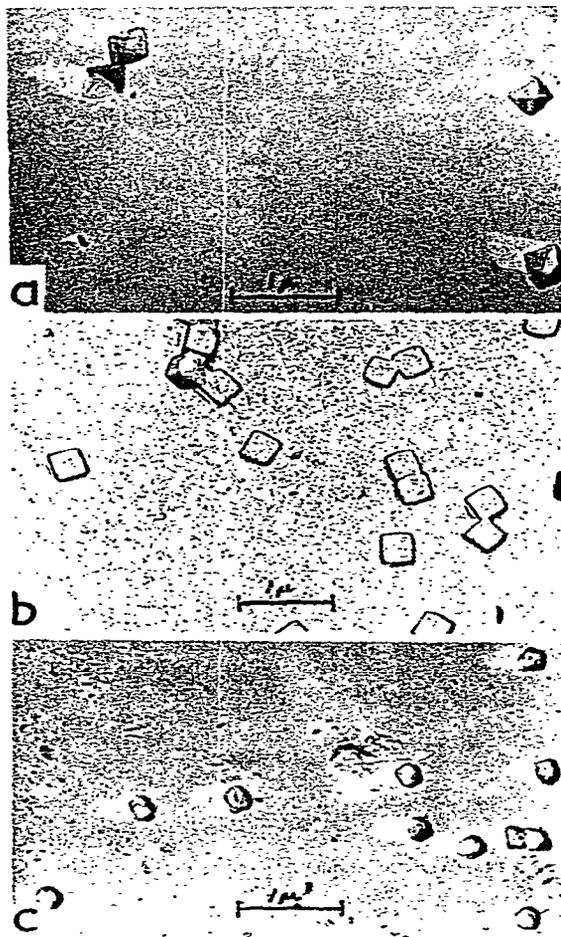


Fig. 12. Electron micrographs of carbon replicas shadowed with Cr at a 60° angle. a) AgBr prepared from excess NH_4Br . b) AgBr prepared by cooling a 2×10^{-5} M solution from 100°C to room temperature. c) AgBr prepared from excess AgNO_3 . From OTTEWILL and WOODBRIDGE (ref. 16), fig. 4, p. 588.

The particles are sometimes spherical, but many deviating forms have been found. Fig. 13 gives a few examples. Particles may be clearly crystalline or amorphous.

As a last example we mention silica particles. In view of the many applications of colloidal silica (known as Ludox and under other tradenames) it is not unexpected that sols with a narrow size distribution have been prepared. In the BECHTOLD and SNYDER (ref. 20) process, a seed solution is formed by heating 3.5% silicic acid containing some NaOH to 100°C . The seed particles are 2-3 nm in radius. These

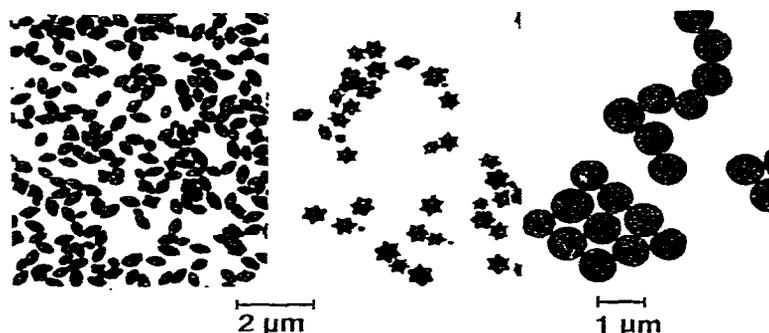


Fig. 13. From left to right: electron micrographs of particles of $\alpha\text{-Fe}_2\text{O}_3$ obtained from nitrate solution; $\alpha\text{-Fe}_2\text{O}_3$ from perchlorate solution; aluminum hydrous oxide from $\text{Al}_2(\text{SO}_4)_3$ solution. From MATIJEVIĆ et al. (ref. 18), Fig. 1, p. 375 and (ref. 19) Fig. 1a, p. 3694.

particles are allowed to grow by addition of a similar solution containing smaller particles. The added silica passes from the small particles to the large ones leading to final radii of 5-65 nm. More porous particles, but having quite a narrow size distribution are prepared according to STÖBER, FINK and BOHN (ref. 41) by hydrolysis of ethylorthosilicate in alcoholic solution in the presence of ammonia. The slow reaction in which particles of up to 1 μm diameter may be formed, presumably passes a stage of nucleation followed by growth. Fig. 14 gives three examples of such particles with surfaces afterwards esterified with stearylalcohol, prepared by VAN HELDEN, JANSEN and VRIJ (ref. 42).

Aqueous silica sols contain a certain amount of NaOH and the particle size is smaller the more alkali is present. According to YATES (ref. 43), the lowering of the interfacial free energy by adsorption of NaOH might make these systems thermodynamically stable, and then the monodispersity would be an equilibrium property, rather than due to the kinetics of the formation process.

An interesting question presents itself now. Would it be possible to prepare monodisperse systems from any desired substance? A definitive answer cannot yet be given, but for substances of sufficiently low solubility the chances seem to be good. Providing the burst of nuclei or using a seed solution, possibly heterogeneous (e.g. gold nuclei for silver particles), should be feasible. The essential difficulty may then be to provide further material slowly by chemical reaction, change of temperature, even slow addition, especially if nuclei are already formed at small supersaturation.

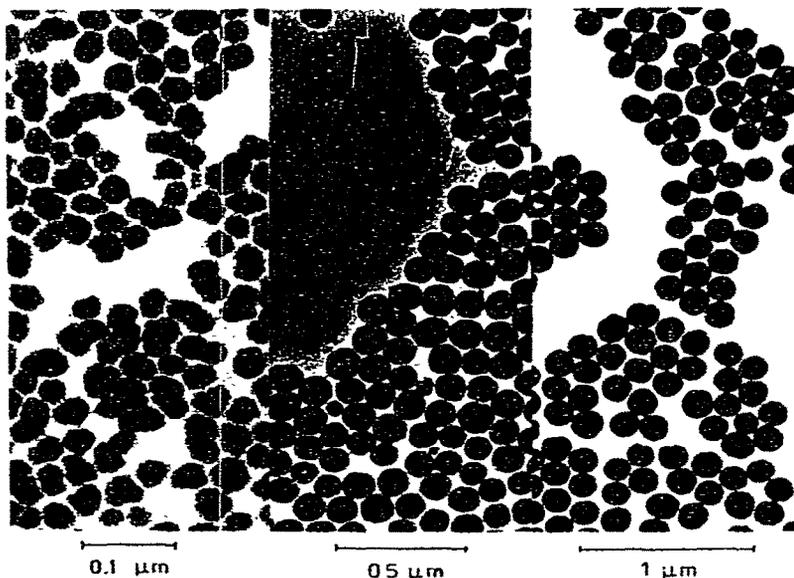


Fig. 14. Electronmicrographs of three different silica samples prepared by hydrolysis of ethylsilicate and coated with stearyl groups. From VAN HELDEN (ref. 42) Fig. 4, p. 15. Also: A.K. VAN HELDEN, J.W. JANSEN and A. VRIJ (ref.42) Fig. 4, p.360.

VIII. THERMODYNAMICALLY STABLE DISPersed SYSTEMS

Whether alkaline silica sols are thermodynamically stable or not is still an open question. But there are several categories of dispersed systems that are without a doubt thermodynamically stable. In the first place, we have the solutions of proteins and other macromolecules, only differing from ordinary solutions in the size of the solute molecules. More interesting for us are the systems in which the dispersed phase consists of aggregates containing amphipathic molecules, that is solutions of micelles, and vesicles and the micro-emulsions. Two tendencies oppose one another. The oleophilic, hydrophobic parts of the molecules tend to separate from water and form a separate oily phase. This effect makes a negative contribution to the free energy per aggregate, rather strictly proportional to the number of amphipathic molecules in the aggregate. The hydrophilic groups tend to keep their contact with water, they repel one another, make a positive contribution to the free energy per aggregate, and then packing considerations (ref. 44) lead to the formation of finite often rather small aggregates instead of to a macroscopic phase separation. Whether these aggregates are monodisperse or not depends mostly on the relation between the positive contribution to the free energy and the number of molecules in the aggregate. If this contribution increases faster than linearly with the number of molecules, a fairly pronounced minimum of

free energy (per molecule) will exist for a certain size of the aggregates and a narrow size distribution around a fairly small average size will result.

If, however, the hydrophilic positive contribution to the free energy is also nearly proportional to the number of molecules, as is the case for long cylindrical micelles, the only factor which prevents the aggregates from becoming infinitely large is the Gibbs entropy of mixing, which will always work in favor of a large number of aggregates. But in such cases micelles (and similar aggregates) tend to be large and heterodisperse (ref. 45).

In low electrolyte concentrations, ionic micelles tend to be small and to have a narrow size distribution, essentially caused by the long range of the electrostatic forces. STIGTER (ref. 46) has already pointed this out. Fig. 15 shows two calculated size distributions in micelles of sodium dodecylsulphate. Similar considerations apply to microemulsion droplets (ref. 61).

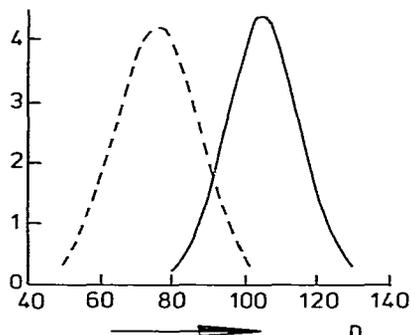


Fig. 15. Size distributions of micelles of sodium dodecylsulphate. n = number of molecules per micelle. Vertical coordinate proportional to mass of dodecylsulphate in micelles of size n . ----- in water; ——— in 0.05 M NaCl.

TAUSK (ref. 47) showed, that non-ionic micelles of short chain lecithins have a narrow size distribution if the chain length of the fatty acids is 6, a wider distribution for 7 carbon atoms and very large micelles with a very wide distribution for 8 carbon atoms in the fatty acids.

The average size of these micelles was determined from light scattering or ultracentrifugation, the size distribution was found indirectly from the influence of the concentration of micelles and added electrolyte on the average size.

IX. APPLICATIONS

In the applications of monodisperse systems, two aspects can be distinguished. In the first group of applications, monodispersity is essential for testing theories or for using these systems as models. In the second group, monodisperse systems are

used in production processes.

A. Testing theories; use as models

- a. The very important aspects of investigating Brownian motion and determining Avogadro's constant have been discussed already.
- b. At least two aspects of colloid stability have been approached with monodisperse latices. An experimental proof of a refinement of SMOLUCHOWSKI's (ref. 48) theory of rapid coagulation, which takes the extra friction into account when two particles are close together, has been given by LICHTENBELT *et al.* (ref. 49). The influence of particle size on the rate of slow coagulation was investigated by OTTEWILL and SHAW (ref. 50) and found not to agree with the theoretical expectations. WIESE and HEALY (ref. 51) have made an interesting, but not completely convincing, attempt to reconcile theory and experiment. Further work with other monodisperse systems might shed more light on this problem.
- c. Reaction mechanisms of the emulsion polymerization (refs. 3, 25) and of the formation of sulphur from $S_2O_3^{2-} + H^+$ (ref. 39) have been tackled with monodisperse latices or sulphur sols, respectively.
- d. Monodisperse dispersions have been used to check the theory of light scattering. Later, the confidence in the theory became so strong that light scattering was used to obtain information on dispersions (refs. 34, 35).
- e. Diffusion coefficients in supersaturated (but very dilute) solutions have been determined by LA MER and coworkers (refs. 13, 23).
- f. LA MER and GRUEN (ref. 14) confirmed the KELVIN equation from the swelling of aerosol particles with toluene or chloroform. UGELSTAD (ref. 52) prevented the degradation of emulsions by diffusion driven by the Kelvin effect by adding oil soluble solutes of low water solubility to the emulsified oil, and on the same basis could prepare monodisperse latices of very large (10-15 μm) droplet size.
- g. Concentrated monodisperse latices, silica sols and micro-emulsions have been used as models for hard sphere (and soft sphere) liquids (ref. 53) and phase transitions of these liquids to crystalline "solids" have been observed (refs. 54, 55). Fig. 16 shows the diffraction colors (in black and white) that are observed when a beam of white light passes through the crystal-like sediment of a polymethylmethacrylate latex (crosslinked with divinyl benzene) of 209 nm radius (swollen) in benzene.
- h. Dilute and concentrated monodisperse suspensions (and emulsions) are good for rheological studies.
- i. The influence of particle size on the retention of aerosols in filters and in the lung (ref. 56) and on the deposition on leaves has been measured.

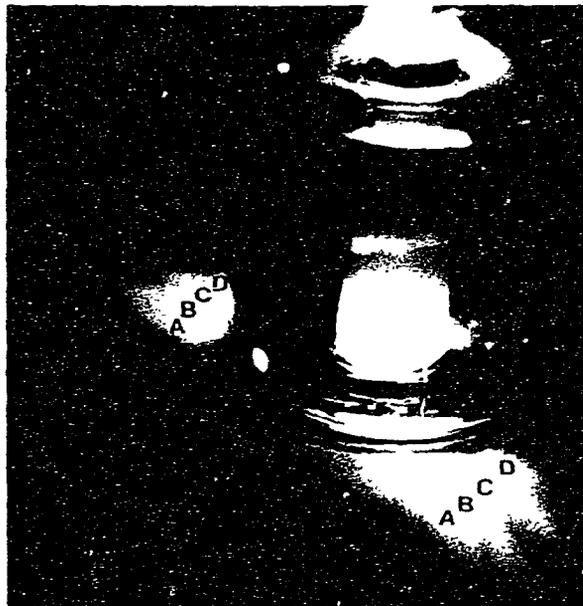


Fig. 16. Diffraction of white light in a crystal like sediment of polymethylmethacrylate latex in benzene. The test tube with latex is placed in a wider toluene bath to avoid reflections at the glass wall. The primary beam passes from right to left. At its exit a white spot can be seen on the outer glass wall. The colors are A = blue, B = green, C = yellow, D = red. From E.A. NIEUWENHUIS, Thesis, Utrecht, 1980, Fig. 14, p. 34. Also: E.A. Nieuwenhuis and A. VRIJ, *J. Coll. Interf. Sci.*, 72(1979)321.

B. Technical applications

- a. Polystyrene and other hard latices serve as calibration standards for electron-microscopy (refs. 3, 21).
- b. The iridescent colors of precious opals appear to be caused by a regular packing of silica spheres about 100-300 nm in diameter (ref. 57). GASKIN and DARRAGH (ref. 58) patented a process for making synthetic opal like material based on such a silica "lattice" in which the space between the spheres was filled with a material having about the same refractive index as the silica particles. Similar optical effects are given by latex "crystals" as shown in Fig. 16.
- c. It has been suggested (ref. 59) to use the surface structure of dried and partly coalesced layers of latex particles as diffraction gratings. See Fig. 17.
- d. Packed monodisperse spheres e.g. of SiO_2 can form a base for catalysts with a well defined, rather open, pore structure. The same structure is useful in chromatographic columns.
- e. Optical effects of thin layers of deposited silica and other particles are used in antireflection coatings.

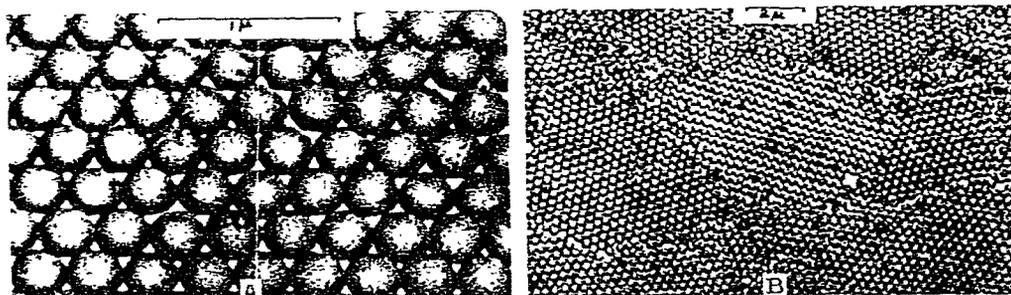


Fig. 17. Crystalline latex formed by allowing latex to dry out to a film about 1 mm thick. The electronmicrographs are made from silicon monoxide replica's of the surfaces of the films. From BRADFORD and VANDERHOFF, J. Polymer Sci., Part C. 3, 41 (1963), fig. 12, p. 53. Published earlier by E.B.BRADFORD, J.Appl.Phys., 23(1952)609.

f. Composite materials e.g. silica in rubber can be based on monodisperse particles.

g. In photography, monodisperse AgBr may have an advantage. Colloidal silica plays an essential role in Polaroid photographic material (ref. 60), in the layer in which the silver image is developed.

h. Colloidal silica has many other applications, such as forming thin insulating layers, hydrophilizing surfaces, changing viscosity, friction and adhesion. For more details, we refer to ILER's book (ref. 20).

i. Monodisperse dispersed dyestuffs would have optical advantages if the size of the particles is matched to the optical absorption coefficient.

j. Pharmaceutical and agricultural preparations will probably act more reproducibly if they are monodisperse.

In many of these practical applications strict monodispersity is not so important as the fact that particles are in a suitable size range and that both extremely small and very large particles are avoided.

X. CONCLUSION

Isodisperse systems are pretty to look at; it is fascinating how they are made, by nature or by man. They have found and still find numerous applications in fundamental science. There are interesting although - as yet - relatively few technical applications. It seems that apart from the cases of silica and latexes, there may well be still undiscovered (or undisclosed) fields of applications such as exploiting the optical effects and also in magnetic tapes or fluorescent screens.

This field may be an area of "solutions in search of problems to be solved".

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