NOTES ON THE DISPERSION OF SOLIDS IN LIQUIDS BY ULTRASONIC WAVES.*

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The peptising action of ultrasonic waves on gel-like substances, precipitates, sediments and gels, has frequently been investigated, and it was found that in all such systems which are characterised by containing pre-formed particles of colloidal or semicolloidal size, these may be easily separated from each other.[1] Little is to be found in the literature,

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[1] R. W. Wood and A. L. Loomis, *Phil. Mag.* (7), 1927, **4**, 417. H. Freundlich, *Kapillarchemie*, 4. Auflage, II. Bd. 1932, p. 616; H. Freundlich, F. Rogowski and K. Söllner, *Z. physik. Chemie, A*, 1932, **160**, 469; *Koll. Bei.*, 1933, **37**, 223; N. Marinesco, *C.R.*, 1932, **194**, 1824; N. Sata, *Koll. Z.*, 1935, **71**, 48; H. Freundlich and K. Söllner, *Trans. Faraday Soc.*, 1936, **32**, 966. *Cf.* also B. Claus, *Z. Physik*, 1932, **77**, 553; *Z. techn. Physik*, 1934, **15**, 74; 1935, **16**, 80, 108, 202. Claus (*l.c.*) in his interesting experiments does not disperse solid matter already present in a coherent state, but during its formation *e.g.*, during electrolysis. Here the metals are not deposited at (suitably chosen) cathodes as coherent mass but redispersed at once as semicolloidal solution into the liquid, when irradiated.

however, as to the action of ultrasonic waves on coherent solid bodies.

W. R. Richards [2] tried to disperse solids (glass, quartz) in liquids. His results, however, were substantially negative, possibly because some at least of his experiments were performed *in vacuo*, where, as we now know, a strong mechanical action is not to be expected.[3]

Rschevkin and Ostrowsky [4] claim to have dispersed in addition to the liquids or semi-solid substances conventionally used, tin, sulphur, bismuth, lead, copper and even silver. The "emulsions" of sulphur, tin, bismuth and lead are said to be true colloidal solutions with a particle size of about 10^{-6} cm. This report, at least so far as metals are concerned, seems rather improbable and contrary to our own experience.

Obviously with the present arrangement—using quartz or glass containers—there is not much hope of dispersing substances such as metals or even glass, since the containers would be liable to break simultaneously. Only brittle and soft substances of moderate hardness and high cleavage seem to offer promise. Thin-walled "Monax" and "Pyrex" test tubes have been used for the following experiments and a rather high energy corresponding to 150 mA anode current was applied.

One can only consider a solid body to be truly dispersed if one starts out with clean surfaces, carefully freed of all adhering dust or foreign substance. This is conveniently done by irradiating the sample under investigation in water for several minutes, the water being changed occasionally. When initially irradiated, nearly all solid substances yield dispersions, if not carefully cleaned beforehand. But the difference between those which really yield dispersions, and those where only adhering material is torn off, becomes apparent after three or four irradiations (lasting two minutes each). Our criterion of a true dispersion was when the seventh to tenth irradiation (of two minutes each) invariably yielded the same positive result.

Silver and tin, glass, quartz and marble are examples of substances totally unaffected by irradiation. Fibres of glass wool are broken, asbestos is split into fibres, and even thin foils of metals (Claus [1]) may be torn apart, but a true dispersion, yielding colloidal or semicolloidal suspensions, is never observed in these and similar cases.

Examples of substances comparatively easily dispersed [5] in water, yielding colloidal or semicolloidal solutions, are (crystals of) mica, gypsum, steatite, haematite, sulphur and (ceylon and flake) graphite. It is advisable to use, instead of pure water, a solution of a suitably chosen electrolyte, *e.g.*, ammonium hydroxide, in order to electrically charge the particles, thus preventing their coagulation.

The suspensions so obtained contain particles of different size, their diameter being of the order of several microns and less. In the case of mica, steatite, haematite and graphite, for example, many of the particles do not show settling after twenty-fours hours (the height of the water column being about 3 cm.), proving that a large proportion are of

[2] W. R. Richards, *J. Am. Chem. Soc.*, 1929, **51**, 1724.
[3] C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, **31**, 835.
[4] S. N. Rschevkin and E. P. Ostrowsky, *Acta physicochemica U.S.S.R.*, 1935, **1**, 740.
[5] As in the preceeding cases (*cf.* C. Bondy and K. Söllner,[3] H. Freundlich and K. Söllner,[1] K. Söllner, *Trans. Faraday Soc.*, 1936, **32**, 1532), the dispersion of solids in liquids is also due to cavitation, as may be shown in the usual way by applying an outside pressure of sufficient height or by experimenting *in vacuo*.

colloidal or semicolloidal dimensions, a fact easily confirmed by the ultramicroscope. The gypsum suspensions are not very stable, their particle size increasing rapidly owing to the high solubility of $CaSO_4 . 2H_2O$ in water.

The concentration of these suspensions is generally rather low, unless the irradiation is continued for a considerable period; *e.g.*, a piece of steatite with an apparent surface of about 5 cm.^{2} yielded 8 mg. dispersed matter in 5 c.c. of water after two minutes of irradiation at 150 mA. Haematite, with a surface of about 8 cm.^{2}, gave 1 mg. under the same conditions, its particles being particularly small and, as was to be expected, distinctly non-spherical.

The amount dispersed depends appreciably upon the irradiated specimen; well developed crystals are less liable to destruction.

The solid substance to be dispersed need not necessarily be of macroscopic size; suspended particles have been subjected to a further breakdown and successfully dispersed.

Suspensions of mica or mosaic gold are carefully freed, by sedimentation, from all particles below 10 or 20 μ diameter. After irradiation of the suspension many particles below this limit may be seen, their number becoming greater with increasing time or energy of the irradiation. A great number of them fall within the colloidal realm. It is interesting to note that whereas the edges of the original particles, *e.g.*, mica, prior to irradiation are rather straight, they lose their original contour after having been exposed to ultrasonics, as a result of small pieces having been broken off irregularly.

The particles of truly colloidal solutions may be also broken down by irradiation.

A V_2O_5 sol (1·2 per cent.) about ten years old was used. When investigated in a suitably low concentration with a slit ultramicroscope, the particles were found to be truly colloidal in two dimensions, their length being between 10-15 μ prior to irradiation. Their Brownian movement was weak. This sol was irradiated in the concentrated state for about four minutes at 150 mA anode current. After this treatment, only particles not longer than 3 μ, in violent Brownian movement, were visible. The effect is still more pronounced, and obtained in a shorter time, if the sol is diluted several times prior to irradiation. The decrease in particle size on irradiation is in no way connected with the rather moderate heat effects, since even prolonged heating at much higher temperatures does not affect the sol. Substantially the same results are obtained with colloidal graphite suspensions. The number of particles visible with bright field illumination decreases on irridation, the number of particles visible in the dark field increasing greatly. The increase in particle number continues after practically all particles visible in the bright field have vanished, thus indicating that particles truly colloidal in all three dimensions are further broken down.

The tendency of the V_2O_5 sols to show streaks, on flowing, is reduced markedly as their particle length decreases.

This simple behaviour is not shared by gypsum suspensions. Here the tendency to form streaks is increased (but only for a short time after irradiation) when a medium or strong sound field is applied for several seconds. As may be seen in the microscope, the particles of gypsum suspensions form irregular aggregates when left at rest and these aggregates are split by even a short irradiation into single crystals, which in this free state may be well orientated on flowing. In a short time, however,

aggregates build up again and the tendency to form streaks diminishes. This behaviour of gypsum suspensions of course is not changed when they are irradiated for a considerable time at high energies.

Semi-quantitative experiments have shown that the dispersing action of ultrasonics in suspensions and sols may be particularly effective in many cases, especially with graphite sols. Here each particle, being more or less hydrophobic, acts as a weak spot, thus promoting cavitation. This explains why the hissing noise during irradiation is very strong in the case of this substance. Generally, the large interfacial area of suspensions exposed to the action of ultrasonics may be responsible for their effectiveness in promoting dispersion; likewise the fact that there is always matter to be dispersed present in the most active region, *i.e.*, near the interface liquid-gas, is undoubtedly of great importance.[6]

Concerning the dispersion of metals (see above) it suffices to say that carefully cleaned silver or tin, even at the first irradiation, shows not the slightest formation of a suspension, colloidal or otherwise. With the other metals, the tendency to do so may be greatly reduced by removing beforehand the oxidised surface films which are otherwise dispersed at the first irradiation. This formation of oxide or hydroxide sols may be almost entirely inhibited merely by using water saturated with nitrogen or hydrogen in an atmosphere of these gases instead of normal distilled water in the presence of air. The extremely dilute and faintly opalescent solutions so obtained [7] bear, moreover, not the slightest resemblance to metal sols; they are obviously very diluted sols of the oxides or hydroxides. Metals of the nature of lead in a state of dispersion, as claimed by Rschevkin and Ostrowsky,[4] would be readily oxidised in normal distilled water. As far as the metals are concerned these authors appear to have been misled by the peptisation of oxides present either at the beginning of the experiment, or formed during irradiation.

The result obtained is not at all astonishing. The hammering action of the collapsing cavities [3] is capable of dispersing solid bodies of moderate cohesion. If one could increase the applied energy, as will probably be done in the future, the range of substances liable to destruction and dispersion may be extended; but there is not much hope of directly dispersing, by ultrasonics, ductile substances, such as metals.[1]

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Summary.

1. Solid bodies of low cohesion, *e.g.*, mica, steatite, gypsum, graphite, sulphur, haematite are dispersed in liquids by the action of ultrasonic waves.

2. The dispersions so obtained contain many particles of semi-colloidal and colloidal size.

[6] K. Söllner, *Trans. Faraday Soc.*, 1936, **32**, 1532, and Patent Application in the name of Karl Söllner and Messrs. E. G. Acheson, Ltd.

[7] Occasionally only some minute residue just visible with the unaided eye is left upon evaporation on a watch-glass.

3. The particles of suspensions and sols are also subject to further disintegration when irradiated with ultrasonics of high energy. This process is sometimes particularly effective and rapid.

4. Solid metals, owing to their high cohesion and high ductility, have not, thus far, been dispersed by ultrasonics.

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