

THE INFLUENCE OF ULTRASONIC WAVES ON GELS.

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This paper deals with the mechanism of the influence of ultrasonic waves on thixotropic gels and with their peptising effect in general.

1. The Liquefaction of Thixotropic Gels.

Some years ago¹ it was reported that thixotropic hydrogels (*e.g.* those of iron and aluminium oxides, bentonite, barium malonate) and several organo-gels are readily rendered fluid when irradiated with ultrasonic waves of high intensity for several seconds, the time of spontaneous solidification being the same as after vehement shaking. It was proved that this liquefaction is not due to thermal effects (which, after so short an irradiation, are small), as these gels have no tendency to soften or melt when moderately heated; indeed iron and aluminium oxides spontaneously solidify more rapidly at higher temperatures.²

¹ H. Freundlich, *Kapillarchemie* 4, *Auflage*, II. Bd. 1932, p. 616; H. Freundlich, F. Rogowski and K. Söllner, *Z. physik. Chem., A*, 1932, **160**, 469; *Kolloid-Beihfte*, 1933, **37**, 223; N. Marinesco, *C.R.*, 1932, **194**, 1824.

² A. Szegvari and E. Schalek, *Koll. Z.*, 1923, **33**, 326; H. Freundlich, F. Rogowski, and K. Söllner, *Kolloid-Beihfte*.¹

The liquefaction of gels contained in test tubes commences at the interface gel/air, the upper parts becoming liquid at once when irradiated with high energy. With iron oxide gels the process of liquefaction may easily be observed, as the colour of the gel turns to a much darker brown. The liquefied parts move rapidly and drops are thrown out forcibly from the surface. From the very start of the irradiation the whole gels shows brown spots, having a marbled appearance and on longer irradiation the amount of liquid increases, until the whole mass has become liquid.

The importance of the gel/air interfaces in the process of liquefaction may be strikingly demonstrated with transparent aluminium oxide gels,³ on shaking which, air-bubbles may be distributed throughout the whole mass. The creaming-up of these bubbles stops when the sol reverts to a gel, but the latter then contains numerous air-bubbles. When irradiated (preferably with not too high an energy) the bubbles move upwards, coalescing more or less and stopping at once when the irradiation ceases.⁴ Their movement is particularly strong where the oil fountain touches the test tube. In this way air-bubbles may be expelled from the gel, the latter not being rendered wholly fluid; this becomes evident on turning the test tube upside down. Only a thin layer of gel round the bubbles is liquefied, and through this the latter move upwards. Sometimes under these conditions the bubbles tend to form stationary wave patterns.^{5, 6}

When a test tube containing a thixotropic gel is turned upside down and then dipped into the oil fountain the gel does not fall down as a lump, but is rendered liquid at the lower surface; the liquid then runs down the walls of the tube and liquefaction proceeds on the surface until the whole mass is liquid.

In a previous paper a mechanism of emulsification by ultrasonic waves was suggested⁷ and it seemed worth while to investigate, how far the liquefaction of gels may be explained in the same manner.

It was shown that emulsification in oil/water systems is due to cavitation or more correctly to the vehement collapse of cavities. These cavities form when the liquid is unduly stretched during the expansion phases of the sound waves; if an external force (e.g. an external gas pressure) causes these cavities to collapse, violent mechanical processes such as emulsification occur.

This mechanism holds also for the liquefaction of gels; if liquefaction ceases when cavitation can no longer be effective, it must be attributed to cavitation.

Effective cavitation may be prevented,⁷ either by experimenting *in vacuo* so that no external force acts upon the cavities to cause them to collapse, or by applying such a high external pressure that no cavities are formed. Under neither of these conditions do ultrasonics render thixotropic gels fluid.

Experiments *in vacuo*.

Two samples of thixotropic iron oxide sol, having the same time of solidification when liquefied by shaking, were sealed in test tubes, the one (a) under normal pressure and saturated with air, the other (b) *in*

³ H. Freundlich, F. Rogowski and K. Söllner.¹

⁴ See Fig. 3 on page 236 *Kolloid-Beihfte*, 1933, 37.

⁵ E. Newton Harvey, *Biol. Bull.*, 1930, 59, 306; K. Söllner and C. Bondy, *Trans. Faraday Soc.*, 1936, 32, 616.

⁶ Solid particles also move in these gels on irradiation, but very much more slowly. If somewhat small they form stationary wave patterns under suitable conditions; if too big and too heavy, the radiation drives them to and fro, thus liquefying the gel around them slowly till they sink down in course of time.

⁷ C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, 31, 835.

vacuo after careful degassing. When exposed to ultrasonic waves of moderate energy, tube (a) readily liquefied, starting mainly from the top; tube (b) hardly changed, a thin layer only, at the surface being somewhat disturbed after a long time.

With very high energies drops of the gel were torn off and thrown upwards; an occasional small brown (liquefied) spot appeared also in some samples *in vacuo*, as it is difficult to make the gel absolutely gas-free, but even after prolonged irradiation only the top layer of the gel is at all disturbed, its "viscosity" still being obviously very high; the gel as a whole being unaffected. The tearing away of drops from the surface is always observed in the oil fountain over the vibrating quartz plate.⁸ With the air-saturated gel, liquefaction was effected very rapidly.

When these experiments are performed in long tubes⁹ the results are still more pronounced. Only a slight surface movement is observed *in vacuo*, but with the air-saturated gel liquefaction always occurs (where in the emulsification experiments emulsification was seen), preferably at the top and secondly where the oil fountain touches the glass, the intermediate part being liquefied only after prolonged irradiation with high energy.

A more or less regular structure—dark brown/yellowish brown—is often observed, reminding one of the stationary wave patterns previously described.⁹ Effective cavities may to some extent be formed here also in the middle part of the tube; occasionally some of the darker spots grow rapidly, and then a gas bubble (due to degassing) will always be seen moving about in a liquefied zone, just as in the case of aluminium oxide gel, where, in the absence of formation of stationary waves in short columns, gas bubbles are driven to the surface, owing partially to radiation pressure, partially to their buoyancy.

Experiments under gas pressure were also carried out in long tubes, the external pressure of compressed gas being applied from a cylinder of compressed air. On irradiating now, even with high energy, nothing happens, except a slight movement of the meniscus; this does not cause true liquefaction, except perhaps in a thin upper layer. After prolonged irradiation this upper layer becomes slowly saturated with gas and liquefaction takes place in a narrow zone, the bulk of the gel being absolutely unaffected. When the pressure is turned off, liquefaction begins at once, cavitation now being possible.

These experiments show that the liquefaction of thixotropic gels occurs under exactly the same conditions as where emulsification is observed, *i.e.*, when cavitation (as defined in an earlier paper) is possible. Without cavitation the sound waves cannot even destroy the very weak structure of thixotropic gels.

These experiments show also that the particles of the gels investigated are too small to scatter any appreciable energy, since otherwise stationary wave patterns⁹ ought to appear; the gel behaves as a homogeneous medium.¹⁰ Foreign particles, *e.g.*, of quartz of several μ diameter, which are big enough to scatter sufficient energy to be affected individually, form stationary wave patterns in these gels just as in liquids.¹¹

⁸ W. R. Wood and A. L. Loomis, *Phil. Mag.*, (7) 1927, 4, 417.

⁹ K. Söllner and C. Bondy, ⁵.

¹⁰ Some phenomena observed in gel-like systems with particles large enough to be moved individually by the sound waves will be described shortly.

¹¹ The velocity of sound in these gels is nearly the same as in the medium of dispersion.

2. The Peptising Action of Ultrasonics.

In the peptisation of gels by ultrasonics¹² exactly the same result is obtained: neither *in vacuo* nor under a sufficiently high external pressure (so long as the system is not saturated with gas) is peptisation observed.

A sheet of commercial gelatine was rolled together and pushed to the bottom of a test tube, so that it could not be moved by the radiation pressure, when irradiated; then water was added. Three samples were thus prepared: the first (*a*) was left in that condition, the second (*b*) was carefully degassed and sealed off, and the third (*c*) was partially degassed to remove at least all gas bubbles adhering to the gelatine and then connected (with a high column of water on the top) to a cylinder of compressed gas, under a pressure of several atmospheres.

The three tubes were irradiated with medium energy; the gelatine foil in tube (*a*) started to collapse after 10 to 20 seconds, formed a voluminous clod, and was peptised entirely after about 40 to 60 seconds, the whole process being more rapid with higher energies. In the other two tubes, even after several minutes of irradiation and on applying high energy, the gelatine foils were quite stiff and unaffected, the water remaining quite clear.

Obviously the rate of swelling of suitable substances is much increased when peptisation occurs on irradiation.

Substantially the same result was obtained with many other substances, *e.g.* glue, rubber in different organic liquids, aluminium oxide in dilute HCl, so long as the adherent and enclosed gas is removed, when experimenting *in vacuo* or under pressure, a condition not always too readily fulfilled in the case of gels.

When combining the above facts with the results of many earlier investigations,¹³ one may conclude that all the destructive and disruptive effects in non-metallic systems (also in biological systems) reported by many authors must be attributed to cavitation, as defined in an earlier paper.⁷

Mention may also be made of two further points of importance in the peptisation of gels: the vigorous movement to be seen in two-phase systems when irradiated, and the heat developed.

The movement of suspended particles and the stirring effects due to large interfaces in heterogeneous systems were described in an earlier paper⁹ and the results obtained there may be applied accordingly to the peptisation.

When a liquid is irradiated, heat is always developed, particularly in the presence of large interfaces.¹² This is due partly to the absorption of sound energy (most pronouncedly with very viscous liquids, *e.g.* glycerol), but much sound energy is scattered and thus transformed into heat by interfaces. It seems, however, that cavitation also may play an important rôle.¹⁴ This question still needs more thorough investigation, specially as to how the occurrence of cavitation depends upon the presence of interfaces.

¹² W. R. Wood and A. L. Loomis; ⁸ H. Freundlich, F. Rogowski and K. Söllner, *Kolloid-Beihfte*.¹

¹³ *E.g.* E. Newton Harvey; ⁵ C. Bondy and K. Söllner.⁷

¹⁴ This seems to be correlated with the well-known fact that the propagation of sound is much feebler in liquids containing gas, than in gas-free ones.

Summary:

The liquefaction of thixotropic gels and the peptisation of gels in general by ultrasonic waves are due to the same effect as emulsification in non-metallic systems, *i.e.* they are due to cavitation. If the latter is prevented, either by external pressure or by experimenting *in vacuo*, no liquefaction and no peptisation is observed, when irradiating with ultrasonics.

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