

THE ZONE OF MAXIMUM COLLOIDALITY.¹ ITS RELATION TO VISCOSITY IN HYDROPHILE COLLOIDS, ESPECIALLY KARAYA GUM AND GELATIN.²

(Preliminary Paper.)

BY JEROME ALEXANDER.

Received October 14, 1920.

At the interface between the 2 phases of a colloidal dispersion there exists surface tension due to the unsatisfied attractive forces of the surface layers of molecule. These may attract or adsorb polar molecules or ions and produce at the interface the electrical double layer of Helmholtz. Owing to the repulsion of like charges, the interface tends to bend *away* from the phase having the superior surface charge, and *around* the phase having the inferior surface charge, as is shown by the experiments of Clowes.³ When there is no excess of positive or negative charges on either side of the interface, we have the so-called iso-electric point of Hardy, where the attractive or cohesive forces between the particles of the dispersed phase tend to make them unite and squeeze out from between themselves the balanced double layer. Complete coalescence does not often occur, for the exact iso-electric point is seldom reached and maintained, and even then not in all parts of the system simultaneously. Usually the cohesive forces of the primary particles (which may consist of atomic, molecular, or even larger groups) are not able to force out their surrounding protective surface films; and the particles form secondary groups which may act to a certain extent as units although they are heterogeneous and of colloidal dimensions.

The dispersed phase in colloids is thus usually duplex, possessing an interior structure which especially in hydrophile colloids is capable of changes that are reversible within certain limits.

As molecular groups form and grow (*e. g.*, in cooling gelatin solutions) they represent an increased concentration of the dispersed substance, a dehydration in the case of hydrosols. If the groups become so large that their motion practically ceases, they form flocks. If the concentration is then sufficient they form a gel in which the finer micellular structure originally described by Nägeli coexists with the coarser net, sponge, or foam-like structure described by Bütschli, Quincke, Hardy and others. With unprotected metal hydrosols the powerful molecular attraction dehydrates the micellular groups, the dispersed phase becomes a solid, and a metal sponge results. Dehydration is much slower with alumina and silicic

¹ Read at the November 19, 1920 Meeting of New York Section, American Chemical Society.

² See also "The Colloidal State in Metals and Alloys," read before *Am. Inst. Mining Met. Eng.*, Oct., 1920; "Mining and Metallurgy," No. 166, p. 22.

³ For references and discussion see Bechhold, "Colloids in Biology and Medicine," trans. by J. G. M. Bullowa, p. 38, *et seq.*

acid, which retain more of the micellular structure. With ordinary dry gelatin the micellular complexes retain so much water and are so easily separated again that Lottermoser terms it a solid hydrosol.¹ G. Varga² estimated that particles of stannic acid gel $12.7\mu\mu$ in diameter contain only $\frac{1}{8}$ their volume of massive stannic oxide, the remaining $\frac{7}{8}$ being mainly water. When gelatin jelly is dried the dispersed phase undergoes a gradual change in coherence, which is duplicated to an inferior degree by the differently constituted, more dilute, residual dispersion medium. Mere appearance does not indicate the state that the separate phases assume when in mass; thus emulsions of much oil in little water are quite solid.

The *viscosity* of reversible, emulsoid, or hydrophile colloids, one of their marked characteristics, sometimes increases as the dispersed phase becomes *finer* (as in oil emulsions, homogenized milk) or sometimes as the dispersed phase becomes *coarser* (as with soaps, night-blue, butyric acid). In fact there seems to be with each dispersion a *zone of maximum colloidal-ity*, above which viscosity decreases with coarser subdivision as the Brownian motion becomes sluggish (about $100\mu\mu$), and below which it also decreases as molecular dimensions are approached (about $5\mu\mu$), and the Zsigmondy-Brownian motion becomes violent. This zone has approximate limits and a crest or peak not necessarily the same with various substances—indeed we should expect specific variations.³

The approach toward the zone of maximum colloidal-ity from the side of coarse dispersion is illustrated by clays which hold increasing amounts of water as their particles become smaller. The approach from the side of molecular dispersion is illustrated by the experimental results of Martin H. Fischer⁴ on the sodium salts of the fatty acids. The sodium salts of formic, acetic, propionic, butyric and valeric acids always give molecular dispersions with water. Sodium caproate (with 6 carbon atoms) begins to show signs of "holding" water, while the caprylate (with 8 carbon atoms) gives a jelly when one mol is mixed with 250 cc. of water. With the higher acids in the series the water holding capacity per mol of sodium soap increases rapidly as the molecules become larger: capric (C_{10}), 500 cc.; lauric (C_{12}), 4 liters; myristic (C_{14}), 12 liters; palmitic (C_{16}), 20 liters; margaric (C_{17}), 24 liters; stearic (C_{18}), 27 liters; arachnic (C_{20}), 37 liters.

The appearance of a zone of maximum colloidal-ity is not limited to the so-called emulsoid colloids. Thus with steel the Fe_3C -Fe dispersion reaches its maximum hardness in martensite, and becomes softer if the

¹ The work of C. R. Smith (THIS JOURNAL, 41, 135-150(1919)) indicates a difference between gelatin dried at above 35° , and that dried at below 15° .

² *Kolloidchem. Beihfte*, 11, 1-36 (1919).

³ It is interesting to note that the sun repels particles of colloidal dimensions, although smaller ones as well as larger ones are attracted. See J. Alexander, "Colloid Chemistry," D. Van Nostrand Co., 1919, p. 37.

⁴ Fischer, *Chem. Eng.*, 27, 155-62 (1919).

dispersion becomes greater (austenite) or less¹ (troostite, sorbite, pearlite). A similar zone of maximum hardness exists in the dispersion of copper aluminide (CuAl_2).²

There are here reported a few preliminary experiments made to throw some light on the relation of the degree of dispersion to viscosity by observing the behavior of masses of various sized particles of Karaya gum dispersed in distilled water. Karaya or Kadaya gum, swells greatly in cold water without undergoing any great degree of solution. A lot of the gum was ground and graded by sifting through bolting silks. The samples used had been stored for over 5 years in paper parcels. Equivalent weights of the several meshes were shaken up and dispersed in 50 cc. of water. The results show that the viscosity increases with increasing fineness of subdivision from 5 to 10-mesh (about 4 mm.) to 200-mesh (about 0.10 mm.). With the coarser meshes, above about 80-mesh, the full viscosity was reached so gradually with the swelling of the particles, that its increase could be readily followed. *Increase in viscosity accompanies the hydration and swelling of the particles.* In fact, with hydrophile or emulsoid colloids, as the dispersed phase becomes *less* viscous by swelling, the colloid as a whole becomes *more* viscous.³

A 2% solution of 200-mesh gum flows as a coherent viscous liquid around the walls of a 20-cm. test-tube; but at about 100-mesh the gum solution begins to separate in chunks, and does not adhere to the walls of the tube. Ultramicroscopic examination of the swollen gum reveals the reticulated structure common to the massed ultramicros of gels, such as agar or coagulated casein. When a particle of gum swells, water is adsorbed at its interior interfaces and also at its exterior or rind surface. The finer ground the gum the greater the rind surface area for the same weight of gum. Assuming for the sake of illustration that the primary particles of the gum are homogeneous spheres $10\mu\mu$ in diameter, and that the gum fragments are spheres consisting of these, the following theoretical table was prepared.

TABLE SHOWING THE RELATION INTERIOR AND EXTERIOR SURFACE AREAS OF LARGE SPHERICAL PARTICLES BUILT UP OF HOMOGENEOUS SPHERES $10\mu\mu$ IN DIAMETER.

Dia. of particles. μ .	No. of particles per cu. mm.	Total surface area in sq. μ .	Rind surface in sq. μ . $V.\pi.d^2$.	Interior or micellar surface in sq. $\mu\mu$.	Relative rind or exterior surface.
0.01 (= $10\mu\mu$)	10^{15}	$\pi 10^{11}$	$\pi 10^{11}$	$\pi (10^{11} - 10^{11}) = 0\%$	10,000
100 (= about 200 mesh)	10^3	$\pi 10^{11}$	$\pi 10^7$	$\pi (10^{11} - 10^7) = 99.99\%$	10
1000 (= about 20-30 mesh)	1	$\pi 10^{11}$	$\pi 10^8$	$\pi (10^{11} - 10^8) = 99.999\%$	1

¹ See Alexander, *loc. cit.*, *supra*.

² See Mercia, Waltenberg and Scott, "The Heat Treatment of Duralumin," p. 942, Bur. Standards, *Bull.* 150 (1919).

³ Viscosity also may increase as ultramicros condense or aggregate, as in cooling gelatin.

A 4% solution of 200-mesh (100μ) gum is a thick, viscous fluid adherent to the tube, whereas a 4% solution of 20 to 30 mesh (1000μ) gum is full of air bubbles, looks jelly-like, slides readily in the tube, and allows free water to be extracted from it by the suction of a medicine dropper. Four % solutions of 10 to 20 and 5 to 10 mesh gum show visible free water which can be drained off. The remarkable difference between 20 to 30 mesh and 200-mesh gum in adhesiveness, water-holding capacity and state, follows a mere (approximate) 10-fold decrease in average diameter, which increases the rind surface about 10 times, although it decreases the interior and micellular surface by only about 0.009%. As colloidal dimensions are approached the rind surface becomes the predominating factor. The experiments show that above the colloidal range increasing rind surface goes hand in hand with increasing viscosity. Why is this?

Although the swollen gum particles are not spheres, we may consider them such for the purpose of comparative calculation; and it is probable that as the particles become very small, surface tension makes them spherical. If the spheres are close packed in cubic arrangement, the free adsorption volume around one sphere (A_c), equals the volume of the circumscribed cube minus the volume of the sphere. $A_c = d^3 - \pi/6 \cdot d^3 = 0.4762 d^3$. If the spheres are close packed in tetrahedral arrangement, the free volume around one sphere = $0.4146d^3$, or only about 13% less than with the cubic. In reality the particles are seldom, if ever, close packed, for there is usually an adsorption layer preventing their immediate contact.

The total adsorption volume in a given quantity of solution is the adsorption volume around one sphere multiplied by the number of spheres; and as this latter quantity varies as $1/d^3$, the total adsorption volume (with rigid close packed sphere) is constant. But with a coarse subdivision the adsorption volume consists of relatively few large spaces; whereas with a fine subdivision it consists of many small spaces, and its greater rind surface is separated on the average by a much smaller distance. The individual adsorption volume with 20 to 30-mesh spheres is about 1,000 times greater than with 200-mesh spheres, and 10^{14} times greater than with $10\mu\mu$ mesh spheres.

The water in each space strives to form a sphere and draw with it its adherent particles of gum; and in the case of the small spheres because of the relatively enormous development of surface, the sum total of these surface tension effects is tremendous. The finest commercial lead shot ("dust") clumps together when wet, and in the flotation of ores similar forces control the formation of air bubbles with their armadillo-like casing of ore. With the large gum particles the relatively free surface water visibly acts as a "lubricant," allowing the swollen particles to slide past each other and the glass; but the finer gum particles, being closer and

separated by more rigidly held and probably more rigid¹ water, adhere more firmly and show greater viscosity.

The molecular groups at the interior of the largest gum fragments are under greater compression, gravitational and molecular, and *à priori* we should expect that they would adsorb least; this experiment shows to be the case. The lessened interior adsorption of the large pieces of gum permits the accumulation of free water at and between their exterior or rind surfaces.

To illustrate this further, 2 g. of 5 to 10-mesh gum was dried without discoloration (at about 200°) until the weight was reduced to 1.55 g. When shaken with 50 cc. of distilled water this gum swelled slowly, for a long time appearing as discrete lumps with much free water, and even after 8 weeks showed a viscosity much inferior to that of the unheated gum. This indicates that the protective aqueous films surrounding the micells or the primary particles of the micells had been partially driven away, and that some of the molecules or molecular groups had approached so closely that their attraction for water or its ions was unable to separate them as far as if the gum were unheated. This is similar to the behavior of gelatin, which, when dried at 130°, shows diminished swelling capacity and becomes insoluble. It confirms the view advanced by the writer² that collagen is a highly dehydrated gelatin converted into an insoluble or irreversible gel by the close approach of its constituent particles, rather than an anhydride of gelatin, as Schützenberger claimed. Further confirmation is offered by Bridgman,³ who found that egg white is coagulated at room temperature by high hydrostatic pressure; 5000 atmospheres for 30 minutes produced perceptible stiffening; 6000 atmospheres, an appearance like curdled milk; 7000 atmospheres, apparently complete coagulation.

Before "boiling" ossein to produce gelatin, it is generally swollen or "plumped" in dil. alkali (usually lime-water) so that on heating, hydration may occur with minimum hydrolysis. The addition of a little sodium hydroxide to the 4% solution of the dehydrated gum caused it to swell more than the control, to take up all the free water, and to adhere to the tube. On dilution and standing, a flocculent precipitate settled out, bulky in appearance, but of small dry weight. The adsorption of the alkali at the interior of the micells causes the gum to swell in a manner quite analogous to what occurs initially in the peptization of stannic acid gel as described by Zsigmondy⁴ and confirmed by Varga,⁵ the first

¹ P. W. Bridgman has shown that under high pressures water forms 4 different kinds of ice, each denser than water.

² Allen's "Commercial Organic Analysis," 4th ed., 8, p. 586.

³ *J. Biol. Chem.*, 19, 511 (1914).

⁴ "The Chemistry of Colloids" (trans. by E. B. Spear). J. Wiley & Son. 1917.

⁵ *Loc. cit.*

small additions of potassium hydroxide are adsorbed mainly at the internal surfaces of the micells forming water and potassium stannate whose dissociation yields tin trioxide, which is adsorbed by the dioxide, and potassium ion, which produces peptization by electrical repulsion.¹

With complex colloids like albumen, gelatin, starch, gum, etc., the action of electrolytes is complicated by iso-colloidism or by the mutual adsorption of distinct chemical substances which may act as protectors to one another. With gelatin the effects produced by traces of acids or alkalis or by any percentage of magnesium chloride, are practically entirely reversed upon dialyzing out the reagent; but the effects produced by larger percentages of acids and alkalies or by prolonged boiling, are not reversible, indicating in such cases that the primary colloidal complexes themselves have undergone change. Their constituent chemical or adsorption compounds disintegrate into simpler "gelatoses" and "gelatones," which because of their superior solubility and diffusibility tend to accumulate in the dispersion phase, increasing its quantity, to some extent perhaps diminishing the micellular hydration, and thus reducing both jelly strength and viscosity. The flocculent precipitate which usually forms in highly degraded glue or gelatin does not represent a decrease in the dispersion of the gelatin as suggested by R. H. Bogue,² but rather *an increased dispersion* involving or followed by the formation of a small quantity of an insoluble chemical or adsorption compound. Wide differences exist in the colloidal properties of the constituents of complex hydrophilic colloids, *e. g.*, the various albumoses resulting from the disintegration of egg white³ and even the fractions separated from egg white itself by fractional precipitation with ammonium sulfate.⁴

By using dispersions of carefully graded powdered gelatin in cold water, the zone of maximum colloidality can also be approached from the side of relatively coarse dispersion. These experiments will be made as soon as the properly graded gelatin can be prepared. Thus with gelatine it may be possible to fix approximately inferior and superior limits to the zone of maximum colloidality. Both the jelly strength and viscosity of the *cold* aqueous dispersions of commercial ground glues and gelatins increase with *decrease* in particle size.

The optimum conditions for maximum viscosity are not identical with those for maximum jelly strength; thus sodium nitrate decreases the viscosity and jelly strength of gelatin, whereas magnesium chloride decreases jelly strength but raises viscosity. The formation of a gel involves the

¹ See also Tolman and Stearns, *ibid.*, 40, 264 (1918); Tolman and Bracewell, *ibid.*, 41, 1503 (1919).

² *Chem. Met. Eng.*, 23, 61 (1920).

³ E. Zunz, *Bull. Soc. Roy. Scien. nat.*, 64, 187-203 (1906); *Arch. Inter. Physiol.*, 5, 111, 245-56 (1907).

⁴ Schultz and Zsigmondy, *Hofmeister's Beitr. chem. Physiol.*, 3, 138-60 (1902).

aggregation of small motile groups into larger non-motile masses, whose "jelly strength" is gaged by the pressure necessary to produce a certain distortion or a rupture. Viscosity¹ is measured by the force required to keep the particles of the dispersed phase flowing past each other at a certain rate, and involves such factors as rate of shear, Brownian-Zsigmondy motion (which depends on particle size), and degree of hydration of swelling of the particles. Colloidal dispersions or coarse suspensions which do not yield swollen particles do not show appreciable viscosity unless concentrated.

With added electrolytes we must reckon with ionization, differential diffusion, the selective adsorption and concentration of ions, and chemical combination which may be followed by dissociation. Ions are adsorbed not only at the interface between the dispersed phase and dispersion medium where they may change the potential difference, but also within the micells where they may cause swelling, peptization or disintegration of the colloidal groups; and the nature of the dispersion will depend upon the balance between these adsorptions and their consequences. By dispersing finely powdered and graded gum, gelatin and other colloids, or mixtures of them, in a variety of solvents (water plus electrolytes and non-electrolytes, *e. g.*, alcohol) it may be possible to follow this balance quantitatively. It will be especially interesting to see the behavior of particles the size of ordinary plant or animal cells. Besides opening up a method for determining the approximate range of the zone of maximum colloidal, experiments with finely pulverized colloids will throw light on the structure of gels, on the relation of the degree of dispersion to the adhesive properties of colloids, and on the mechanism of adhesion itself.

NEW YORK, N. Y.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO].

THE ISOTOPISM OF MESOTHORIUM AND RADIUM AND THE SEPARATION OF THESE ELEMENTS FROM BARIUM.

By RALPH K. STRONG.

Received October 15, 1920.

Shortly after the discovery of mesothorium, it was stated by Marckwald² that this element is completely similar to radium in its chemical properties, no reaction having been found that gave a separation of the two. Marckwald also found that mesothorium accompanies radium in the process of fractional crystallization of barium chloride containing these 2 radioactive elements. Soddy³ also confirmed this conclusion in subsequent experiments in which it was found that if any separation did

¹ For literature and discussion see Wo. Ostwald, "Handbook of Colloid Chemistry," trans. by M. H. Fisher. P. Blakiston's Son Co., 1915, p. 145, *et seq.*

² Marckwald, *Ber.*, 43, 3420 (1910).

³ Soddy, *Trans. Chem. Soc.*, 99, 72 (1911).