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Irving Langmuir

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The Role of Attractive and Repulsive Forces in the Formation of Tactoids, Thixotropic Gels, Protein Crystals and Coacervates

IRVING LANGMUIR

General Electric Company, Schenectady, New York

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The formation of tactoids from thixotropic sols, of Schiller layers from iron-oxide sols, the separation of tobacco virus solutions and bentonite sols into two liquid layers and the crystallization of proteins are regarded as examples of unipolar coacervation (micelles having like charges) which must involve attractive forces.

Kallmann, Willstätter, Freundlich, De Boer, Hamaker, Houwink and others have assumed that the attraction is due to van der Waals forces. They have also analyzed the stability of colloid systems by diagrams giving the potential energy as a function of the distance between micelles. It is now shown that the Coulomb attraction between the micelles and the oppositely charged ions in the solution gives an excess of attractive force which must be balanced by the dispersive action of thermal agitation and another *repulsive* force. Thus there is no need to assume long range van der Waals forces. The past use of energy diagrams is criticized because it has ignored the effect of the thermal agitation and the attraction of the "gegenions" in solution. Instead of potential energy it is proposed that osmotic pressure p be used, which includes these previously neglected factors. A maximum in p as the colloid concentration increases is the condition for the separation into two phases (coacervation).

The Debye-Hückel theory (1st approximation) for the osmotic pressure of electrolytes takes into account both these factors and permits a rough calculation of the conditions under which coacervation occurs. The 2nd approximation, which considers particle size, does not agree as well with experiment as the first approximation. The reasons for this lack of agreement are discussed.

The micelles in unipolar coacervates are not in contact, but are separated by relatively large distances (10–5000Å). Either a specific repulsive force or a decrease in the Coulomb attraction as the concentration increases (due to decreased charges on micelles) can account for stable coacervates. The assumption of a definite ζ -potential, rather than a definite charge on the micelles, gives automatically just such a decrease in attraction.

The general mathematical theory of coacervation presents great difficulties because the approximations of the Debye-Hückel theory cannot be used. However, the one-dimensional problem of the forces acting between

parallel colloidal platelets can be solved rigorously in terms of elliptic integrals. For highly charged particles in sufficiently dilute solutions of electrolytes, the pressure p in the liquid between the two plates is given by $p = (\pi/2)D(kT/eb)^2 = 8.9 \times 10^{-7}/b^2$ dynes/cm² where b is the distance in cm between the plates and D is the dielectric constant (81 for water at $T = 293^\circ\text{K}$). This pressure which tends to force the plates apart is independent of the charge on the plates and on the electrolyte concentration (univalent ions only). Polyvalent ions decrease the force. This force is of the right magnitude to account for the stability of unipolar coacervates. It also furnishes a quantitative explanation of the Jones-Ray effect, by which low salt concentrations decrease the capillary rise in surface tension experiments with water.

Experimental determinations were made of the relaxation times τ for the decay of birefringence in bentonite and vanadium pentoxide sols, after stirring was stopped. In one sample of bentonite, τ varied with the 22nd power of the concentration, while in V_2O_5 sols the exponent was 1.8. The temperature coefficients of τ were also measured and the activation energies were calculated.

A theory of the relaxation of birefringence was developed, according to which the micelles in dilute thixotropic bentonite sols are arranged normally in a cubic lattice (isotropic). Temporary shear in the liquid orients the micelles and produces birefringence although the lattice remains cubic. The experimental data confirm the theory and indicate that the energy barrier opposing reorientation of micelles in a particular bentonite sol varied with the inverse 20th power of the distance between the micelles. With V_2O_5 this exponent was about 4. Further support for the theory was obtained by experiments which gave "angles of isocline" for bentonite particles in a flowing sol that varied from 65° to 78° .

In bipolar coacervates (which contain micelles of unlike polarities) the electric fields and the charges on the micelles *increase* as the micellar concentration increases. When a certain concentration is reached, the field rises to a value so high as to cause increased hydration which holds the micelles apart and gives stability to the coacervate.

WHEN a solution of pure tobacco mosaic virus containing about 2 percent of the protein is allowed to stand for several days, it separates into two phases.^{1–5} The lower one,

¹ F. C. Bawden, N. W. Pirie, J. D. Bernal and I. Fankuchen, *Nature* **138**, 1051 (1936).

² J. D. Bernal and I. Fankuchen, *Nature* **139**, 923 (1937).

which is the more concentrated, is strongly doubly refracting and consists of a three-dimen-

³ F. C. Bawden and N. W. Pirie, *Proc. Roy. Soc. (London)* **123**, 274 (1937).

⁴ F. C. Bawden and N. W. Pirie, *Nature* **141**, 513 (1938).

⁵ M. A. Lauffer and W. M. Stanley, *J. Biol. Chem.* **123**, 507 (1938).

sional mosaic of small uniaxial liquid crystals arranged in random orientations with respect to each other. The top layer scatters much more light than the lower and is isotropic if undisturbed, but shows double refraction when subjected to shear (streaming double refraction).

During the separation of the liquid into the two phases, spindle-shaped or needle-shaped regions of low or high density, which slowly rise or fall in the solution, appear. The heavier masses which form in the upper part settle to the lower part and there coalesce with one another and with the surrounding liquid which has been enriched in protein by the removal of the lighter masses that have risen into the upper part. In this way the solution gradually separates into two layers which at first have an indistinct transition between them. Gradually, however, the boundary becomes so sharp that it shows distinct total reflection when viewed from a position slightly below the plane of the boundary.

The upper phase in which thermal agitation rapidly brings about a random orientation of the molecules behaves as a slightly viscous, isotropic liquid. If, however, the liquid is made to flow, the shear causes a temporary parallel orientation of molecules, which decays, after the motion stops, with a relaxation time of the order of a second.

The lower phase is a thixotropic gel, which if undisturbed is essentially a solid body made up of uniaxial crystal grains. The more concentrated the original solution, the finer is the observed grain size. The mechanical strength of this gel is very low, for a shearing stress of the order of 10 dynes/cm² causes flow. The gel is liquefied by more vigorous stirring, but on standing sets again to a gel and remains birefringent.

X-ray examination^{1, 2} has shown that in the lower phase the rod-shaped virus molecules are arranged in a hexagonal close-packed lattice of parallel cylinders. The distance between adjacent molecules decreases continuously from about 500Å to about 125Å as the concentration of the protein in the solution increases.

The rod-shaped molecules are presumably held in position in the hexagonal lattice by repulsive forces resulting from negative charges on the protein molecules. According to the Debye-Hückel theory the force acting on a charged

particle at a distance r from another charged particle is equal to the Coulomb force multiplied by an exponential factor, $\exp(-r/\lambda_D)$, where λ_D , which we may call the Debye distance, varies inversely as the square root of the ionic strength of the electrolyte. Thus the conditions under which the two-phase system forms and the spacing of the molecules in the more concentrated phase should be influenced in marked degree by the presence of electrolytes.

The properties of these tobacco virus solutions appear to be similar in many ways to those exhibited by certain thixotropic sols that have been studied by Zocher, Freundlich, Heller and others.⁶⁻⁹

Some thixotropic sols, such as those of V_2O_5 , which contain rod-shaped crystalline particles, spontaneously form "tactoids," which are small, sharply defined, spindle-shaped, doubly refracting masses having higher density than the surrounding sol.

Some sols of iron oxide, having disk-shaped particles, when allowed to stand in a vessel with a flat bottom, may yield a separate denser phase in the form of an iridescent layer on the bottom of the vessel. When examined by white light the reflected light is found to be nearly monochromatic. The plate-like particles are thus arranged in parallel layers (Schiller layers) having a uniform spacing which may be as great as 8000Å (giving a third-order red reflection).⁹

It has been generally assumed that the forces that hold these Schiller layers apart and the particles of tactoids apart, even at these relatively great distances of several thousand Å, are electrostatic forces resulting from the large charges on the colloidal particles.

The properties of the tobacco virus solutions and their behavior during the separation into the two phases show that the phenomena are essentially the same as those involved in the formation of tactoids. In the virus solution, however, the "particle" is a protein molecule of molecular weight of about 50,000,000, while in

⁶ H. Zocher, *Zeits. f. anorg. Chemie* **147**, 91 (1925).

⁷ H. Zocher and W. Heller, *Zeits. f. anorg. Chemie* **186**, 75 (1930).

⁸ K. Coper and H. Freundlich, *Trans. Faraday Soc.* **33**, 348 (1937).

⁹ P. Bergmann, P. Löw-Beer and H. Zocher, *Zeits. f. physik. Chemie* **A181**, 301 (1938).

the V_2O_5 sols the particles are needle-like crystals of much larger size.

BENTONITE SOLS

The monodisperse sols of bentonite that have been prepared by Hauser and Reed,¹⁰ particularly the fractions having the smallest particle size are remarkably thixotropic and, in the presence of minute concentrations of salts, are rheopectic. These sols seem particularly suitable for studies of the nature of the forces that act between colloidal particles. Traces of thixotropic behavior have been observed¹⁰ in presence of salts at concentrations as low as 0.05 percent where the average distance between the particles is of the order of 2000Å.

Mr. V. J. Schaefer and I have recently studied some bentonite sols that were prepared in Dr. Hauser's laboratory by Dr. F. J. Norton. The sample that we used was a monodisperse sol whose equivalent spherical diameter was about 300Å. These sols were made from a white California bentonite whose analysis gave: SiO_2 39.2 percent; Al_2O_3 0.11 percent; Fe_2O_3 0.15 percent; CaO 15.1 percent; MgO 19.2 percent; ignition loss 22.7. Eighteen different dilutions of a single sample of this sol were made up with concentrations ranging from 0.8 to 2.8 percent (as determined by drying at 105°C). Volumes of 4 ml of each of these solutions were sealed into glass tubes about 0.8 cm inside diameter.

These tubes were shaken and then tilted so that the bubbles passed slowly the length of the tube. They were then placed in a rack and were examined between crossed Polaroids while they were standing undisturbed in a vertical position.

The solutions that contained less than 1.4 percent became isotropic within a couple of seconds, while the birefringence of the more concentrated solutions persisted for a time τ which increased rapidly with concentration. The sol containing 1.40 percent gave $\tau = 3$ seconds and this increased to 12 seconds at 1.50 percent, to 40 seconds at 1.57 percent and to 80 hours at 1.8 percent. The sol containing 2 percent after several hundred hours become isotropic in its upper half, while the lower half remained permanently birefringent, showing a fine mosaic structure of

crystal grains having optic axes inclined about 45° to the axis of the tube. With the tube containing the sol of 2.2 percent a sharply defined isotropic portion of about 6 cm depth separated out at the top of the tube. The lower part consisted of the fine grained crystal mosaic. The sols of still higher concentrations appeared to be permanently crystalline throughout. It was only in the concentration range of 2.0 to 2.2 percent that two distinct phases separated after long standing.

The sols that contained from 1.4 to 2.0 percent were thixotropic gels which on standing slowly increased in strength so that (above 1.50 percent) even large bubbles would not move through them when the tubes were inverted. After standing a sufficient length of time, the gels lost their birefringence and became isotropic, but if these gels were shaken very gently or made to oscillate about a horizontal axis they showed temporary birefringence, which disappeared as soon as the agitation stopped. They thus acted essentially like solid elastic bodies which become birefringent when subjected to stress. If the tubes were vigorously shaken, the gel liquefied, and the liquid became anisotropic. It is clear therefore, that, in the case of the bentonite sols, birefringence and the mechanical strength of the gel are not closely associated. With tobacco virus solutions, however, the thixotropy and spontaneous birefringence go together.

It has often been thought^{3, 5, 8} that the property of separation into two phases, one of which is isotropic and the other permanently birefringent, is characteristic only of sols having rod-shaped particles. The optical properties of the bentonite sols, however, prove that the particles are flat plates or disks.

It is probable that the repulsive forces between the particles in the bentonite sols, at concentrations above 1.4 percent, cause these particles to assume a lattice-like arrangement (probably a close-packed face-centered cubic type), which gives to the sol its elastic or gel-like properties. This ordered arrangement must start from nuclei and spread to give grain-like lattice regions separated by diffuse boundaries of unordered particles. A very slight shearing motion in the liquid can rotate the grains and allow them to coalesce and so grow in size (rheopexy), but too

¹⁰ E. A. Hauser and C. E. Reed, *J. Phys. Chem.* **40**, 1169 (1936); **41**, 911 (1937).

great a shearing stress disrupts the grains and causes the gel to become liquid (thixotropy).

Although the center of each particle may thus occupy a definite position in a crystal lattice, the disk-shaped particle, at low concentrations, can rotate freely in all directions. With increasing concentrations, however, the potential energy will be a minimum when the disks have definite orientations.

Let us consider, for example, that the particles are negatively charged, electrically conducting disks arranged in a face-centered cubic lattice, with the appropriate number of univalent positive ions distributed in the aqueous phase in accord with the Poisson and Boltzmann equations. Each particle has 12 equidistant neighbors arranged like the midpoints of edges of a cube about its center. Symmetry considerations seem to indicate that the potential energy of a conducting disk will be a minimum when the axis of the disk lies parallel to any one of the three cubic axes of the lattice.

The induced charges on the disk then cause it to act as an octupole and for other orientations there will be even more poles. The energy barrier that must be overcome if the axis of the disk is to pass from one equilibrium position to another must thus increase with some high power ρ (such as 10 or more) of the ratio d/r , where d is the diameter of the disk and r the distance between the centers of neighboring disks. If the disks are not circular, or if they carry permanent dipole moments, ρ will be reduced, and the magnitude of the energy barrier increased.

Let us use this model in analyzing the changes in properties of bentonite sols that occur with increasing concentration, n , of the particles per cm^3 . At very low values of n where the particles are not in lattice positions, there is no energy barrier to oppose free rotation. The Brownian rotation (average angle θ , in time t) should be given approximately by Einstein's equation

$$\theta^2 = kTt/4\pi\eta a^3, \quad (1)$$

where η is the viscosity of the solvate and a the effective radius of the particle (assumed spherical).

The effective diameter of the particles of the bentonite sols we have made, calculated from the sedimentation rate by Hauser's method¹⁰ was

300A. If the particles are thin circular disks of diameter d and thickness b , the effective diameter d_e should be roughly of the order of magnitude of the geometric mean of d and b . If we take $b=20\text{A}$, which is the spacing of layers in wet clay minerals given by x-ray measurements, we get $d=4500\text{A}$, or 0.45μ .

By Eq. (1) for $\eta=0.01$, $a=2.25\times 10^{-5}$, we find $t=0.04\theta^2$ second. Thus if the particles are oriented by artificially produced laminar flow in the liquid, this orientation disappears in a small fraction of a second. The relaxation time of about one second which we observed for bentonite concentrations of 0.8 to 1.2 percent may have been due to the persistence of motion in the liquid after passing the bubble through the tube.

The increased time of 3 seconds at 1.4 percent, however, could not have been due to this cause, for the greater viscosity should have decreased the duration of flow. Thus at concentrations of about 1.4 percent the energy barrier has become great enough to interfere with free rotation. At higher concentrations the axes of the disks normally oscillate about equilibrium positions parallel to the 3 lattice axes, but occasionally pass over a barrier to other equilibrium positions with a relaxation time τ given by

$$\tau = A\eta \exp (Ve/kT), \quad (2)$$

where V is the height of the energy barrier in electron volts, A is a constant and η is the viscosity. Since the rotation of a micelle does not appreciably alter the positions of other micelles, η should be the viscosity of the solvate (water) rather than that of the solution and should thus be independent of the concentration of bentonite.

We may assume that V varies inversely with the ρ th power of the distance r between molecules,

$$V = Br^{-\rho}. \quad (3)$$

By logarithmic differentiation of Eq. (2), remembering that the concentration n varies in proportion to r^{-3} , we obtain

$$d \log \tau / d \log n = (\rho/3)(Ve/kT) = 3870\rho V/T, \quad (4)$$

if V is in volts.

The increase in τ from 3 to 40 seconds for an increase in concentration from 1.40 to 1.57 percent, which we observed for bentonite sols, cor-

responds to a value of $d \log \tau / d \log n = 22.4$ and thus we obtain, at 20°C , $\rho = 1.70/V$.

The value of V can be determined by Eq. (2) from the temperature coefficient of τ . The sealed off tube containing 1.4 percent of bentonite which had been used for the first determinations of τ was immersed in ice water, the tube was tilted so that the bubble traveled half the length of the tube and back and was replaced in the ice bath. The anisotropy between crossed Polaroids disappeared¹¹ after 220 seconds. When this was repeated with the tube immersed in water at 40°C the time for the disappearance of anisotropy was 50 seconds.

This 4.4-fold increase in rate for 40°C , or 1.45-fold for 10°C , corresponds to a total activation energy of 6.3 kcal. per mol or an energy barrier of 0.274 volt. But by Eq. (2) we see that we must subtract the activation energy (4.3 cal. or 0.184 volt) which determines the temperature coefficient of the viscosity of water (decrease from 0.01793 to 0.00657, ratio 2.73 : 1, between 0° and 40°). Thus we find the energy barrier for rotation of the particles in the 1.4 percent bentonite sol is $V = 0.084$ volt. Combining this with our previous result $\rho = 1.70/V$, we find that the exponent ρ in Eq. (3) should be $\rho = 20$. This high value is reasonable for charged nearly circular conducting disks and indicates that the orientation of the particles is not caused by permanent dipole moments on these particles. The energy barrier V varies with the $\rho/3$ or 6.7 power of the concentration. Thus taking $V = 0.084$ volt at 1.4 percent we obtain $V = 0.03, 0.05, 0.13$ and 0.21 volt at concentrations of 1.2, 1.3, 1.5 and 1.6 percent respectively.

The development of permanent anisotropy and the separation into two phases which was found to occur at concentrations of 2.0 to 2.2 percent appears to be due to a mutual orienting effect of neighboring disks, which becomes important at

high concentrations. The axes of all the disks in a crystal grain thus become parallel, and this alters the forces of interaction between the disks so that a new kind of uniaxial crystal grain is formed having a higher density, leaving a less concentrated isotropic intergranular material.

At concentrations above 2.4 percent the stiffness of the sol was apparently too great to permit the separation of the phases, but microscopic examination would probably have shown the isotropic phase between the crystal grains. A slight rocking or tapping motion would probably accelerate the separation into phases (rheopexy), or moderate centrifugation could be used.

According to these views, the birefringence of the bentonite sols is due to orientation of anisotropic bentonite particles rather than to a dissymmetry of the crystal lattice. The isotropic gels obtained by allowing the sols of concentration less than 2 percent to stand quietly for a time τ are birefringent (instantaneously reversible) when subjected to slight shearing stress (below their elastic limit). If, however, the intensity of the stress exceeds a critical value, permanent shear occurs and the anisotropy then decays slowly with the usual relaxation time τ .

These phenomena prove that the axes of the disks in the isotropic gels are not arranged in random directions, but oscillate about definite *equilibrium axes* which are related to the crystal axes. The effect of a small shearing stress is to displace the equilibrium axes with respect to the crystal axes. Because of the large value of the exponent ρ of Eq. (3) only a very slight distortion of the cubic lattice will be needed to give considerable angular displacements.

If the shearing stress is made sufficiently great, slip planes develop in the lattice and permanent displacement results. Because of the crystal lattice the direction of shearing displacement does not generally coincide with direction of the shearing stresses.

If the gel is subjected to continuously increasing displacements or flow, the gel structure is not necessarily completely broken down. With any given rate of shear a balance will be reached between the rate of growth of crystal lattice and the rate of destruction.

¹¹ This determination of the temperature coefficient of τ was made about four months after the solutions were sealed into the glass tubes. There had been a gradual change in the properties of the sols during this time, probably due to traces of substances taken up from the glass. During this time the value of τ for the tube containing 1.4 percent increased from 3 to about 100 seconds and similar increases were found with the other tubes. The property of giving two phases after long standing, which was originally observed with the 2.0 and 2.2 percent sols, was also gradually lost. These properties of bentonite solutions are extremely sensitive to traces of salts and other substances.

During this flow the disk-shaped particles become oriented under the influence of two factors. First, the solvate that surrounds the particles is subjected to laminar flow, probably parallel to the slip planes. This tends to orient the planes of the disks parallel to the slip planes. Second, between slip planes, there are distorted lattice arrangements in which the disks take an orientation different from either the direction of the shearing stress or the direction of the slip.

The following simple experiments show that the planes of the bentonite disks do not coincide with the direction of shear and so prove a crystalline structure even in the flowing liquid.

A 2 percent sol of white bentonite was sucked up into a pipette and allowed to flow steadily into a beaker. The birefringence of the sol flowing down through the vertical tubular part of the pipette (8 mm inside diameter) was observed by placing the tube between a pair of crossed Polaroids. These were held by a frame which permitted them to be rotated about a horizontal axis perpendicular to their plane.

When the two planes of polarization made angles of 45° with the direction of flow, the sol gave good transmission along two side bands separated by a darker central band. With lower concentration, 0.8 to 1.2 percent, the central dark band along the tube axis was more distinct than with the higher concentration.

The presence of a dark central band is characteristic of particles which are disks or flat plates. Rods become oriented in the direction of flow which is also the direction of shear, and so give transmission over the whole width of the tube. Disks or plates in a noncrystalline liquid should become oriented with their planes parallel to the tube axis, but perpendicular to the radius of the cylinder through the particle, for these planes are tangent to the surface of shear.

If the particles are circular disks, they should not change the plane of polarization of light passing through the axis of the tube and thus there should be a black band in the axis when the crossed Polaroids are at 45° . If, however, the particles are plates which are longer than they are broad, so that their long axes are oriented parallel to the tube axis, the intensity of the central band should serve as a measure of the ratio of width to length.

Rough observations with 1 percent bentonite sols show that the central band has an intensity perhaps half that of the side bands. This, with our previous observations of scattering, would indicate that the particles are thin flat plates of irregular shapes having lengths which are not large multiples of the widths.

When a vertically flowing sol is observed between crossed Polaroids having vertical and horizontal planes of polarization, one should expect to get no transmission with either rod-shaped or disk-shaped particles. Actually, however, the 2 percent bentonite sols show distinct transmission (perhaps $\frac{1}{4}$ as intense as with 45° Polaroids) in two side bands with a narrow completely black band between them. If the Polaroids are rotated slightly to the right (clockwise), the central black band moves to the right and becomes broader until at a Polaroid rotation of 12° the whole right side of the tube appears uniformly black, while the left side has increased considerably in brightness. A counter-clockwise rotation blackens the left side.

These phenomena prove that the planes of the disks in the flowing bentonite sol are rearranged so that they lie tangent to the surfaces of cones whose apexes (of half-angle 12°) point in the direction of flow.

The angle of 12° did not seem to vary appreciably with the rate of flow. In fact, with the 2 percent sol, the effect persisted indefinitely after the flow had stopped entirely. However, a noticeable increase in brightness appeared instantly if flow was allowed to start again. The intensity of the light became much less when the concentration of the sol was reduced, but even at 0.8 percent the effect could still be observed and the angle was still about 12° .

A similar effect was observed with the tube (8 mm inside diameter) of 1.4 percent bentonite sol (which had been used to study the temperature coefficient of τ) when this tube was placed vertically in ice water after having been made isotropic by immersion in water at 40° . After 20 to 60 seconds, examination between crossed Polaroids at 0° and 90° showed two broad side bands; the *left* one became black when the Polaroids were rotated 25° in a clockwise direction. This indicated that the disks lay on a 25° cone with apex up. The effect gradually died

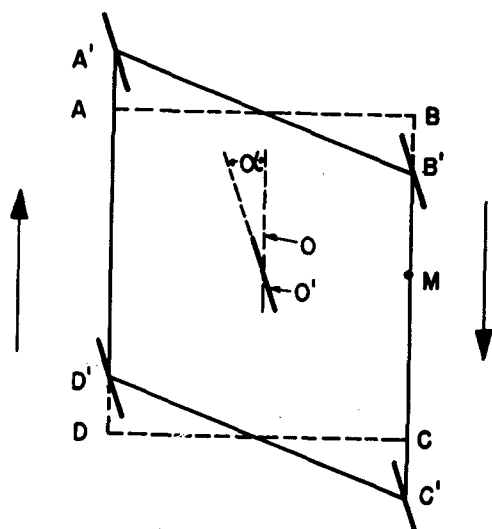


FIG. 1. Orientation of micelles due to shear.

away after a few minutes. After the sol had become isotropic at 0°C, immersion in the 40°C bath caused the side bands to reappear, but now the apex of the cone pointed downward.

These effects are due to vertical convection currents set up within the tube when its temperature is changed. Thus, when the tube is placed in ice water there is a thin layer of descending liquid close to the walls and a central upward return flow.

The direction of inclination of the bentonite disks with respect to the plane of shear is in every case that which we might expect by the following hypothesis. Take two neighboring points in the liquid which initially lie on a normal to the plane of shear. The vector or line connecting these points sweeps through two opposite quadrants of a plane which is perpendicular to the plane of shear and parallel to the direction of shear. We find that the plane of the bentonite particles is perpendicular to the plane containing the vector, and the line of intersection of these two planes, which we may call the line of inclination, lies within the quadrants swept through by the vector and makes an angle α with the line of shear (same angle with plane of shear).

The probable mechanism of the tilting of the disks can be illustrated by Fig. 1. The square $ABCD$ represents the cross section through the center of a cube which has a micelle at the center O and one at the midpoint of each edge. If the liquid is subjected to shear, as shown by the arrows, the square $ABCD$ is changed into the

parallelogram $A'B'C'D'$. Since the micelles at B' and D' are brought closer to the micelle at the center O , the repulsive forces between them are increased. Thus the micelle at O becomes inclined through an angle α , as shown by O' . If the points B' and C' move downward with uniform velocity while A' and D' move upward, α should pass through a maximum and fall to zero when B' reaches M , a point midway between B and C . During the rest of the travel while B moves from M to C , α will be negative. Thus the average value of α should be zero.

However, because of the repulsive forces between the particles, B' will not move with uniform velocity, but will take longer to travel from B to M than from M to C , since it slips through the surrounding liquid in accord with Stokes law. The average angle α will thus be inclined in the direction shown by O' in the figure. A further development of this theory should make it possible to calculate the viscosity of bentonite sols in terms of the distance between the particles and the charges on the particle. We plan to obtain experimental data by which to test these theories.

Let us now consider the optical effects that occur when the tube containing the bentonite sol is dipped into ice water. We should expect that in a layer extending from the wall of the tube to the cylindrical surface where the downward velocity is a maximum, the bentonite particles should be tilted so that their planes intersect the axis below the particle (cone apex downward). Between this surface of maximum downward velocity and the axis of the tube, the planes of the disks should intersect the axis above the level of the particle (cone apex up). In repeating the experiments with the tube plunged into ice water, careful examination between crossed Polaroids showed the presence of very narrow bands near the walls where the particles have the opposite inclination to those nearer the axis.

The lack of parallelism between the axes of rod-shaped micelles and the direction of shear has been studied in detail for V_2O_5 sols by Freundlich, Zocher¹²⁻¹⁴ and others.

¹² H. Freundlich, F. Stapelfeldt and H. Zocher, *Zeits. f. physik. Chemie* **114**, 190 (1924).

¹³ H. Freundlich, H. Neukircher and H. Zocher, *Kolloid Zeits.* **38**, 43, 48 (1926).

¹⁴ H. Zocher, *Kolloid Zeits.* **37**, 336 (1925).

A "cross of isocline"¹⁵ (Wirbelkreuz) was observed when the sol was placed between coaxial cylinders, one of which rotated, and was examined between crossed Nicols in a direction parallel to the axis. This cross was displaced with respect to the planes of polarization by an angle, which Edsall calls the angle of isocline: This is the complement of the angle α which we have used to measure the inclination of the particles to the direction of shear.

The data show that the angle α is close to zero with old V_2O_5 sols. New sols give angles up to 45° , which decrease at high rates of shear but are nearly independent of concentration.

The differences which we observed between the values of α for the bentonite flowing in the pipette (12°) and for the tube in which temperature changes produced convection currents (25°) are undoubtedly due to this dependence of α on the rate of shear.

All the studies of bentonite which have been discussed so far were made with a sample of bentonite sol prepared in July, 1938. Recently Dr. Norton, in Schenectady, has prepared another monodisperse sol from white California bentonite in distilled water. The effective spherical diameter of the particles is approximately the same, 300A, as was found for the sol made previously. However, this new sample shows gel-like properties at considerably lower concentrations. Using sols ranging from 0.80 to 1.20 percent, we have measured the times of disappearance of the birefringence at 0° , 20° , and 40° . A summary of the data obtained is given in Table I.

The three values τ_0 , τ_{20} and τ_{40} for a given concentration were plotted on semilogarithmic paper

TABLE I. Time, τ , for disappearance of birefringence in bentonite sols at 20°C and the temperature coefficient of τ from measurements at 0° and 40°C .

CONCENTRATION PERCENT	τ_{20} SEC.	τ_0/τ_{40}	V VOLTS	V CALC. VOLTS	τ CALC. SEC.
0.80	—	—	—	0.042	1.5
.920	4.2	—	—	.068	4.6
.968	8.	4.25	0.082	.082	8.
1.065	31.	5.1	.116	.114	28.
1.112	59.	5.6	.133	.134	62.
1.137	260.	—	—	.144	96.
1.160	>1000.	—	—	.156	145.

¹⁵ J. T. Edsall, J. Biol. Chem. **89**, 315 (1930).

against $1/T$ and straight lines were drawn which best represented these points. The value of τ at 20°C and the ratio τ_0/τ_{40} obtained from each of these lines are given in the 2nd and 3rd columns of Table I. By Eq. (2) the energy barrier V was calculated as given in the 4th column. Plotting these values of V against the concentration on double logarithmic paper a straight line was obtained whose slope was -3.46 . Three times this, or 10.4, should correspond to the value of ρ in Eq. (3).

When the values of $\log \tau$ from the data in the 2nd column in the table were plotted against $\log n$ a straight line was obtained having a slope 14.3. The mean value of V over the range from 0.97 to 1.11 percent is 0.104 volt. Substituting these values into Eq. (4), we obtain $\rho=10.5$, in agreement with the value of ρ from the temperature coefficient.

Using $\rho=10.5$ in Eq. (3) we calculate V as given in the 5th column of Table I. These values agree well with those calculated from the temperature coefficients. Substituting these values of V into Eq. (2) and choosing a single appropriate value of A , we obtain τ as given in the 6th column. Up to a concentration of 1.11 percent the agreement with the experimental data of the 2nd column is excellent, but at higher concentrations the observed values of τ increase much more rapidly than those calculated. In fact, at 1.16 percent permanent birefringence already sets in.

Dr. Norton finds that with this sol in concentrations from 1.2 to 1.5 percent, a sharply defined polycrystalline phase separates out in about 24 hours of quiet standing or after only 10 minutes of centrifuging. The bounding line is a sharp horizontal plane, and if the tube (6 mm diameter) is tilted, the boundary moves with the tube, but after several minutes in the tilted position the crystalline phase flows sufficiently to bring the boundary nearly back to a nearly horizontal plane. Analysis of the top and bottom phases in one of the tubes gave 1.16 and 1.35 percent, respectively.

A tube 2 cm diameter, 15 cm long was half-filled with a series of bentonite sols of decreasing concentrations. Birefringence could be observed on tilting the tube to a horizontal position even at concentrations as low as 0.05 percent.

Comparing these data with those given by the first bentonite sample, we note that the value of ρ is only a little more than half as great as the value 20 previously found; the concentration at which $V=0.080$ volt is now about 1.0 percent, whereas formerly it was 1.5 percent, and the lowest concentration at which separation into phases occurs is 1.2 instead of 2.0 percent.

The data of Table I indicate that the theory which led to Eqs. (2) and (4) is quite accurately applicable to these bentonite sols, so that the exponent ρ should be an important characteristic of sols of this type. The variations in ρ may be due to changes in the average shape of the micelles, the lower value presumably corresponding to more elongated particles.

We intend to make further studies of these bentonite sols determining the dependence of ρ on the presence of low concentrations of salts and on particle size.

VANADIUM PENTOXIDE SOLS

The bentonite sols whose properties we have investigated constitute perhaps the most striking example of sols containing disk-shaped particles.

For comparison we have studied vanadium pentoxide sols which have rod-shaped particles. We have used a sol, containing 2.0 percent of V_2O_5 in distilled water, which was made up 17 years ago. This was diluted with distilled water to give a series of solutions of different concentrations. When these were allowed to flow through the tube of a pipette (8 mm inside diameter) and examined between crossed Polaroids, birefringence was observed which persisted for several seconds after the flow was stopped, even at a concentration as low as 0.002 percent V_2O_5 .

With increasing concentration, the time τ required for the disappearance of the birefringence after stopping the flow increased with the 1.8th power of the concentration at concentrations in the neighborhood of 0.015 percent, and still more rapidly at concentrations of 0.02 percent. At 0.015 percent τ was 120 seconds. This increase with the 1.8th power of the concentration may be compared to the corresponding exponents 22.4 and 14.3 which we observed with the bentonite sols.

With solutions of concentrations of 0.010, 0.015, and 0.020 percent we measured the temperature coefficient of τ between 0° and 40°C. The temperature coefficient increased with increasing concentration: Thus the ratios τ_0/τ_{40} were 2.9, 3.5 and 4.1, at the concentrations of 0.010, 0.015 and 0.020 respectively. Allowing for the temperature coefficient of η in accordance with Eq. (2), we find that V is negligibly small at 0.01 percent and increases to 0.046 volt at 0.015 percent and to 0.089 volt at 0.020 percent. Applying Eqs. (3) and (4), as for the bentonite, we find the best fit with the data is obtained when we choose $\rho=4$ for V_2O_5 sols as compared to $\rho=20$ and $\rho=10.5$ for the two bentonite sols. The experimental data, however, do not agree with the equations as well as in the case of bentonite, so that $\rho=4$ is a rough approximation.

There are at least two reasons why the equations are not so accurately applicable to the V_2O_5 sols. In the first place the sol had not been made monodisperse by centrifugation, and therefore contained particles having a wide range of sizes. Secondly, the mechanism by which the particles lose their orientation in the V_2O_5 sols is in many ways different from that which we have postulated for bentonite sols, so that the assumptions underlying Eq. (3) are not strictly applicable. Furthermore, the average distance between the particles, which are lined up in parallel directions in the anisotropic sol, does not necessarily vary in proportion to n^{-1} as it does for bentonite, but may vary with n^{-1} if the end-to-end distance between rod-shaped oriented particles is independent of concentration.

We can readily understand why the concentrations at which perceptible persistence of orientation is observable is so much lower with the V_2O_5 sols than it is with the bentonite. For the rod-like particles, with diameters very small compared to their lengths, the length of the rods will be greater than the lateral distances between them even at relatively great dilutions. With the more compact bentonite disks, however, the diameter of the disk becomes comparable with the distance between the particles only at very much higher concentrations.

Let us consider a V_2O_5 sol of parallel rod-shaped particles of such concentration that the average lateral distance between the particles is

a little less than the average length of the particles. If a single particle has its longitudinal axis turned through 90° , the ends of the particle are forced between pairs of adjacent parallel molecules. The potential energy resulting from the repulsion between the displaced molecule and its neighbors will depend upon the lateral distances between molecules. However, this energy will not vary with a high power of this distance. The problem is closely related to that of the potential energy of two charged cylinders of small diameter whose axes are separated by a distance r but are respectively parallel to two axes that are at right angles to one another. (90° skew angle). The value of ρ corresponding to the variation of this potential with r should have a relatively low value.

At higher concentrations the displaced molecules are brought close to more than four other molecules. At very low concentrations, on the other hand, the lateral distance between molecules should be greater than the length of the rods, and therefore ρ probably increases. Thus for V_2O_5 ρ should not be constant over a wide range, as in the case of bentonite.

When the old V_2O_5 sol that we used flows through the tube of a pipette it acts as a uniaxial crystal. Thus it transmits no light between the crossed Polaroids when these are in the $0-90^\circ$ position. When the Polaroids are turned to the 45° position, the transmitted light reaches a maximum but shows no trace of the central dark band which was observed with the bentonite sols, and which we attributed to the disk-like nature of the bentonite particle.

We must thus conclude that in this V_2O_5 sol, flowing with moderate velocity through a tube, the particles are completely oriented, parallel to the direction of flow so that $\alpha=0^\circ$. This agrees with previous conclusions¹² that α is close to zero for very old V_2O_5 sols in which the particles have great lengths. In such sols, as in tobacco virus solutions,² there is probably no regularity of micelle arrangement in directions parallel to their length, so that the forces illustrated by Fig. 1 which cause the tilting are absent. In new V_2O_5 sols, however, the shorter particles permit a three-dimensional rather than a two-dimensional lattice arrangement and so give $\alpha \neq 0$.

PROTEIN CRYSTALS AND TACTOIDS

Our observations with tobacco virus and bentonite lead us to believe that the separation of thixotropic gels into two phases on standing is a common phenomenon among sols which consist of highly charged particles or molecules. Bernal and Fankuchen² consider that Stanley's so-called needle-shaped crystals of tobacco mosaic virus protein are paracrystals, or sharply defined regions consisting of an anisotropic liquid phase. It seems preferable, however, to recognize the fact that they are tactoids, thus extending the definition of tactoid to include cases where the particles are large molecules.

There seems to be no advantage in regarding a tactoid as a type of liquid crystal; it appears to be essentially a solid crystal, often having such low mechanical strength that it appears to flow like a liquid. The lower phases that separate from a 2 to 3 percent tobacco virus solution or a 1.2 to 2.0 percent bentonite solution are built up of interlocking tactoids which form crystal grains giving a structure much like that observed with single-phase metallic alloys. The structure is permanent if undisturbed and Brownian movement is absent. Yet if the test tube containing the sol is tilted slightly, the phase boundary remains or soon becomes horizontal, showing the exceedingly low mechanical strength of this thixotropic gel.

Tactoids which are formed from more concentrated solutions (or by the addition of salts, as in the case of tobacco virus crystals) may have such high mechanical strength that they would normally be regarded as solids. Tobacco virus "crystals" have two characteristics which seem to distinguish them from most other crystals: (1) The distance between molecules increases continuously as the water content increases. (2) The molecules are not regularly spaced along a direction parallel to the long axes of the molecules.

The first of these characteristics seems to be a general property of protein crystals. Recent x-ray studies¹⁶ of lactoglobulin, tobacco seed globulin, chymotrypsin and haemoglobin have shown that the volume of the unit crystallographic cell shrinks by 27 to 42 percent when

¹⁶ D. Crowfoot, D. Riley, *Nature* **141**, 521 (1938); D. Crowfoot, I. Fankuchen, *ibid.* **141**, 522 (1938); J. D. Bernal, I. Fankuchen, M. Perutz, *ibid.* **141**, 523 (1938).

crystals of these proteins are dried in the air. This shrinkage is accompanied by a disordering of the structure, since the smallest observable x-ray spacings increase progressively from about 2A up to 20A.

The second characteristic of tobacco virus crystals (lack of order along optic axis) is not observed with the other protein crystals and appears to be caused by the unusually great length of the rod-shaped virus molecules.

The fact that a high but indefinite water content forms an essential part of protein crystals justifies us in regarding them all as tactoids. According to this concept, each protein molecule, which is surrounded by an envelope that may contain several thousand water molecules, is held in a position of equilibrium by repulsive forces resulting from charges on the molecule.

COACERVATES

Bungenberg de Jong and his co-workers have published¹⁷ a large number of papers in recent years dealing with the unmixing or coacervation of liquids into two phases. The most striking examples of this kind are furnished by colloidal solutions containing both positive and negative micelles. For example, if a dilute solution of gelatin (positive micelles) is mixed with a dilute solution of gum Arabic (negative micelles), droplets of a liquid phase separate out. We shall call this bipolar coacervation.

Numerous other examples are given where a colloid having charged particles is coacervated by the addition of a salt containing polyvalent ions of opposite sign. For example, if a solution of strontium chloride is mixed with ammonium molybdate, a second liquid phase is formed. This we shall call unipolar coacervation.

When ammonia gas is led into a strong solution of potassium or rubidium carbonate or tripotassium phosphate, a two-phase system is formed, which has been studied in detail by Jänecke.¹⁸ Undoubtedly these are also examples of coacervation (probably bipolar).

Another interesting unipolar coacervate has been called to my attention by Dr. E. P. Part-

ridge. When a strong solution of sodium hexametaphosphate is mixed with a strong solution of calcium chloride, the liquid separates into two isotropic layers, the lower being a very viscous liquid. In this case the negative ions are undoubtedly of very high molecular weight, while the positive ions are sodium ions.

The separations of tobacco virus and of bentonite sols into two phases seem to be typical examples of unipolar coacervation. On this basis we should also look upon tactoids as coacervates. Protein crystals are merely solid coacervates.

Bungenberg de Jong has classified various types of coacervation and has given a "working hypothesis" for the mechanism of their formation. In the case of "complex coacervates," which we call bipolar, the attractive forces between the positive and negative colloidal particles can account for their gathering together in a separate phase. However, since these coacervates usually contain 80 to 90 percent water and are liquid, it is necessary that there should be some repulsive force that prevents the positive and negative particles from coming into contact. The hypothesis is made that the intense electric field draws the dipole water molecules into the spaces between the particles and so holds them apart. The theories of Bungenberg de Jong are not so satisfactory when applied to the unipolar coacervates such as strontium, molybdate, calcium hexametaphosphate, tobacco virus and bentonite.

ATTRACTIVE AND REPULSIVE FORCES IN UNIPOLAR COACERVATES

We have seen from our consideration of the bentonite sols that large negatively charged colloidal particles, because of the repulsive force they exert upon one another, tend to become arranged in a definite crystal lattice. These forces can cause elasticity and anisotropy of thixotropic gels and tactoids and the disappearance of the Brownian movement. However, the spontaneous gathering together of particles into tactoids or into birefringent liquid phases indicates the presence of long range *attractive* forces, which under some conditions can outweigh the effect of repulsive forces.

Kallmann and Willstätter¹⁹ assumed that van

¹⁷ H. G. Bungenberg de Jong, *Kolloid Zeits.* **79**, 223, 334 (1937); **80**, 221, 350 (1937). These articles give references to and a summary of about 30 previous papers.

¹⁸ E. Jänecke, *Zeits. f. Elektrochemie* **33**, 518 (1927).

¹⁹ H. Kallmann and M. Willstätter, *Naturwiss.* **20**, 952 (1932).

der Waals attractive forces between colloidal particles might be of sufficient range and intensity to account for the formation of tactoids.

This idea has been accepted by Freundlich²⁰ and has been developed quantitatively,^{21, 22} and applied to colloid systems²³ by H. C. Hamaker. He calculates that the potential of the van der Waals attraction between two thick flat plates separated by the distance d should vary with d^{-2} . In the case of equal spheres he finds that the potential energy is of the order of kT when the distance between the surfaces of the spheres is 0.1 to 0.5 of their diameter. These calculations, however, are based on the very improbable assumption that these forces involve a kind of "action at a distance" and are not influenced by the medium through which they are transmitted.

Hamaker analyzes the characteristic properties of colloids by means of diagrams in which the potential energy of the forces acting between two colloid particles is given as a function of the distance between them. He then regards this total potential as resulting from the superposition of the potentials of attractive and of repulsive forces. He believes²⁴ that the repulsion is due to the electric charges on the particles in accord with the Debye-Hückel theory, while the attraction is the result of van der Waals forces and is independent of the charge or the ion content of the solution. Adding the two potentials, he shows that a minimum potential may occur when the particles are at distances of the order of 1000 Å.

Houwink^{25, 26} makes a similar analysis of the repulsive electrostatic forces and the attractive van der Waals forces to explain the properties of colloids and in particular the yield value.

In a recent paper Bergmann, Löw-Beer and Zocher²⁷ have calculated the repulsive forces due

to the charges between Schiller layers of tungstic oxide sols and have equated these to the gravitational force. To obtain the repulsion they used a modification of the Gouy-Debye-Hückel theory. They considered only experimental data in which separate phases do not appear. They make the statement that electrostatic forces cannot explain the attractive forces in gels having micelles which all have similar charges.

The authors of these theories of colloidal structure recognize the repulsive forces between micelles of like charges and take it as axiomatic that this charge must be balanced by a long range attractive force which is not of electrostatic origin. They agree that the only conceivable attractive force that will meet their needs is the van der Waals force.

It will be shown in the following pages that there are at least three fundamental fallacies involved in this use of energy diagrams to analyze the stability of colloids.

(A) No direct account is taken of the thermal agitation which by itself would tend to cause the colloid particles and the ions to be dispersed throughout the liquid giving an osmotic pressure $p = \sum nkT$.

(B) The attraction between the charged micelles and the ion atmosphere of opposite sign which extends throughout the intervening liquid is ignored or neglected although it exceeds the repulsive force between the micelles.

(C) The electric charges on the micelles are assumed to be constant, whereas they must be, in general, dependent on the concentration of the micelles.

Let us analyze the general problem of the forces and energies responsible for the stability of colloids. We will first consider a colloidal solution having large positive micelles of charge z_1e , while the equivalent opposite charge is distributed throughout the intermicellar liquid in the form of negative ions of charge $-z_2e$. Let this solution be confined by a piston which is permeable to water but impermeable to both the micelles and to the ions. On the other side of the piston we assume there is pure water.

If the forces due to the interaction of the charges could be neglected, the pressure on the piston (Factor A) would be

$$p = (n_1 + n_2)kT, \quad (5)$$

²⁰ H. Freundlich, *Thixotropy* (Paris, 1935).

²¹ H. C. Hamaker, *Physica* **4**, 1058 (1937).

²² H. C. Hamaker, *Recueil des Travaux Chimiques des Pays-Bas* **57**, 61 (1938).

²³ H. C. Hamaker, *Recueil des Travaux Chimiques des Pays-Bas* **56**, 727 (1937).

²⁴ H. C. Hamaker, *Recueil des Travaux Chimiques des Pays-Bas* **56**, 1 (1937).

²⁵ R. Houwink and W. G. Burgers, *Elasticity, Plasticity and Structure of Matter* (Cambridge University Press, 1937). See especially pp. 338-343.

²⁶ *Second Report on Viscosity and Plasticity* (Committee of the Academy of Sciences at Amsterdam) (Nordermann Publishing Company, N. Y., 1938). See pp. 233-237, of Chapter 4 by R. Houwink.

²⁷ P. Bergmann, P. Löw-Beer and H. Zocher, *Zeits. f. physik. Chemie* **181A**, 301 (1938).

where n_1 and n_2 are the concentrations of the micelles and of the ions, respectively. Since the total charge must be zero, we have

$$n_1 z_1 = n_2 z_2 \quad (6)$$

and thus Eq. (5) becomes

$$p = (1 + z_1/z_2) n_1 kT. \quad (7)$$

This force which is due merely to thermal agitation or Brownian movement is not a repulsive force between particles and so is not explicitly considered in a theory such as Hamaker's which is based on potential energy diagrams.

The second factor (B), which takes into account the effect of the electric charges, can be illustrated by considering a sodium chloride crystal. The distance between any ion in this lattice and its oppositely charged neighbor is less than the distance between the ion and its nearest neighbor of like sign. The attractive forces between unlike ions thus exceed the repulsive forces between like ions so that the crystal lattice should tend to shrink.

From simple dimensional considerations it is obvious that the effect of the Coulomb forces alone is to reduce the size of the lattice. Thus a crystal lattice built up of positive and negative point charges ($z_1 e$ and $-z_2 e$, respectively) has an energy per ion (of any given type) equal to

$$E = -\kappa z_1 z_2 e^2 / a, \quad (8)$$

where κ is a constant depending upon the type of lattice, and a is the lattice constant. From this it follows that as a decreases, the energy decreases without limit so that stable equilibrium can occur only if some *repulsive force* other than the Coulomb interaction is called into play.

Exactly the same consideration must apply to a colloidal solution (unipolar) which has micelles of one sign with small ions of the opposite sign distributed within the intermicellar liquid. The interaction of these charges, just as in the sodium chloride crystal, gives an excess of attractive force and in order to have equilibrium it will be necessary not to have an additional *attractive* force, such as the van der Waals force postulated by Hamaker, but some new kind of *repulsive* force.

It is natural, therefore, that as the concentration increases, the effect of the attractive forces

should exceed the dispersing tendency of the Brownian movement and tend to cause the colloid to draw together into a more condensed phase (unipolar coacervate). If no other repulsive force than that which acts between particles in contact were involved we should expect the colloid to form a dense precipitated solid mass from which the water has largely been expelled. Of course, this is just what happens when the concentration of a sodium chloride or other salt solution is increased too much; the salt crystallizes out in an anhydrous form or with a small amount of water of crystallization.

To account for the existence of unipolar coacervates which contain large amounts of water, we must either find some long range repulsive force or we must be able to show that the electrostatic attractive force is such a function of the distance between particles that a state of equilibrium can be reached (Factor C).

Equation (8), from which we concluded that the electrostatic force would tend to cause the separation of a dense phase, was based on the assumption that the charges on the particles remain constant when the distance between the particles is varied. Now in the case of colloidal particles it is probable that the charge on the micelles decreases as the concentration of the colloid increases. From the viewpoint of Eq. (8), therefore, we can see that if $z_1 z_2$ decreases faster than a decreases, the potential energy will rise at increasing concentrations so that there may be a definite concentration which gives a stable second phase.

A complete theory of the interaction of micelles with ionic atmospheres covering the whole range of concentrations would present insuperable mathematical difficulties. However, a very concentrated colloid phase in equilibrium with a dilute phase can be treated by an elementary consideration of two simple limiting cases.

In the theory of the potential distributions in the neighborhood of tungsten filaments in caesium vapor, which I have considered elsewhere,²⁸ there are many features which are fundamentally related to those of colloids. A tungsten filament in equilibrium with a given pressure of caesium has a definite electron emission and positive ion emission at a given tem-

²⁸ I. Langmuir, Phys. Rev. **43**, 224 (1933).

perature. In the interior of the caesium vapor at a large distance from the tungsten surface there are equal concentrations, n_0 , of caesium ions and electrons, so there is no space charge. Taking the potential of this plasma to be zero, the potential of the tungsten filament is a function only of its temperature and of the caesium vapor pressure. It does not depend upon the size or shape of the tungsten surface. One could, for example, have fine tungsten particles distributed in any manner through the space and the potential of every surface would be the same. This corresponds then to the ζ -potential of colloidal particles. Abramson²⁹ has shown that the ζ -potential of quartz particles on which a given protein is adsorbed is independent of the size or shape of these particles.

Now let us consider that we bring some of the tungsten particles (or micelles in a colloid) so close together that their ionic atmospheres overlap. Since the ζ -potentials remain constant, it is necessary that the charges on the particles shall decrease.

Take, for example, a two-phase colloidal system in which a semi-permeable membrane, to which pressure can be applied, separates the two phases. Let the membrane be permeable to electrolytic ions but impermeable to the micelles of the colloid. In the dilute phase at sufficiently large distances from the micelle, the concentrations of positive and negative ions, both assumed univalent, will each be equal to n_0 .

If the micelles are positively charged and have a potential V_1 (the ζ -potential), the concentration of negative univalent ions very close to the surfaces of the micelles is given by the Boltzmann equation

$$n_n = n_0 \exp(V_1 e / kT) = n_0 \exp \eta_1, \quad (9)$$

where for convenience we have put

$$\eta = Ve/kT = 11,600 V/T, \quad (10)$$

if V is expressed in volts. Similarly the concentration of positive univalent ions is

$$n_p = n_0 \exp(-V_1 e / kT) = n_0 \exp(-\eta_1). \quad (11)$$

In the ordinary approximate form of the Debye-Hückel theory η is assumed to be numerically small compared to unity. We wish,

however, to consider colloids which have highly charged micelles, for these are the ones which show the separation into two phases (unipolar coacervation). For such colloids $\eta_1 \gg 1$, since the ζ -potential is far greater than the value 0.025 volt which corresponds to kT at room temperature according to Eq. (10). Close to the surface of a positive micelle, in a region where $\eta > 2$, the concentration of positive ions, by Eqs. (9) and (10), is negligible compared to that of the negative ions, so that there is a sheath of firmly bound negative ions surrounding the positive micelle.

At larger distances, where the potential is less than about 0.04 volt, positive as well as negative ions are present and the conditions postulated in the Debye-Hückel theory are fulfilled. It thus appears that the properties of the dilute phase can be treated by the Debye-Hückel theory if one replaces the micelle with its large positive charge by a point charge having an appropriate fictitious charge. This effective charge is roughly equal to the charge on a micelle reduced by the firmly bound negative ions in the sheath.

Fuoss³⁰ has shown that ion association of this kind plays an important part in the theory of the properties of electrolytes in solvents of low dielectric constant. It also becomes important in solvents of high dielectric constant such as water, if one of the ions has a charge high enough to give a potential above about 0.07 volt.

Let us now examine the conditions that exist within the concentrated phase which is in equilibrium with the dilute phase. Since the potential V_1 of the particles in this phase must be the same as that of similar particles in the dilute phase, we see that the limiting concentration n_1 of negative ions close to the surface of the particles has the same value as for the particles in the dilute phase.

If the particles in the concentrated phase are brought very close together, the charge carried by the solvate between the micelles, since n_n cannot exceed n_1 , must decrease about in proportion to the volume of this solvate included in this denser phase, and there must be a similar decrease in the positive charge on the micelles. When the concentration of the micelles becomes very high, the whole phase tends to acquire a nearly uniform potential throughout, close to V_1 , and the

²⁹ H. A. Abramson, *Electrokinetic Phenomena* (Chemical Catalog Co., New York, 1934). See especially pp. 111-114.

³⁰ R. M. Fuoss, *Trans. Faraday Soc.* **30**, 967 (1934); *Chem. Revs.* **17**, 27 (1935).

charges on the particles and in the solvate become very small. At the phase boundary, however, there is a sharp drop in potential so that, according to the Poisson equation, there must be an electric double layer. In the denser phase the electric forces may become negligible in determining the pressure p which would then be given by

$$p_1 = n_1 kT = n_0 kT \exp(V_1 e / kT). \quad (12)$$

This theory then enables us to calculate a limiting pressure which can exist within the condensed phase as the concentration increases.

If desired, this pressure can be described as a repulsive force existing within the concentrated phase. It has the characteristics of the repulsive force that we have found necessary to counteract the excess of electrostatic attractive forces within the colloid.

At somewhat lower concentrations of the colloid than those we have just considered, the potential V in the intermicellar spaces will range between V_1 at the surface of the micelles to some lower minimum value V_M at points in the liquid which are farthest from the micelles. The pressure within the concentrated phase will then have some value intermediate between p_1 and p_M where p_M can be calculated from Eq. (12) by replacing V_1 by V_M . As the micelle concentration decreases the charge on the micelles increases, and an increasingly large role is played by the electrostatic forces.

THE DEBYE-HÜCKEL THEORY (1ST APPROXIMATION) APPLIED TO THE DILUTE PHASE

The approximate conditions required for the appearance of two phases can be derived from the Debye-Hückel theory of osmotic pressures.³¹ A calculation of this kind has already been made³² for the case of highly ionized caesium vapor at high pressures. The equations that were developed, modified by the introduction of the dielectric constant and the unequal charges on positive and negative ions, are applicable to colloidal solutions.

The osmotic pressure p in an electrolytic solution according to the 1st-order approxima-

tion given by Debye and Hückel is

$$p = kT \sum n_i - e^2 \sum (n_i z_i^2) / 6D\lambda, \quad (13)$$

where λ , which we may call the Debye distance, is

$$\lambda = [DkT / 4\pi e^2 \sum (n_i z_i^2)]^{1/2}. \quad (14)$$

Elimination of λ between these two equations gives

$$p = kT \sum n_i - (\frac{1}{3})(\pi e^6 / D^3 kT)^{1/2} [\sum (n_i z_i^2)]^{3/2}. \quad (15)$$

The first term in the second member of this equation represents the pressure of all the ions, according to the ideal gas law, as if there were no electric forces. The second term gives the (1st-order) effect of the electric charges. It should be noted that the sign of this term is always negative, indicating that the effect of the interaction of the charges is equivalent to a net electric attraction and not a repulsion as was assumed in the theories of colloid structure that have been cited.

We have previously derived Eqs. (5), (6) and (7) for the effect of Factor A (thermal agitation) in the case of large positive ions of charge $z_1 e$ and concentration n_1 with small negative ions of charge $-z_2 e$ and concentration n_2 . We can now apply Eq. (15) to modify these equations to take into account Factor B (electric interaction). Eliminating n_2 from Eq. (15) by means of Eq. (6), we obtain in place of Eq. (7)

$$p = (1 + z_1/z_2)n_1 kT - (\frac{1}{3})(\pi e^6 D^3 kT)^{1/2} z_1^{1/2} (z_1 + z_2)^{1/2} n_1^{3/2}. \quad (16)$$

By choosing appropriate units for p and n_1 this equation can be written in the simple form

$$p = 3n - 2n^{3/2}, \quad (17)$$

for which a plot is given by the curve $OBCG$ in Fig. 2. The maximum, found from Eq. (17) by placing $dp/dn = 0$, is located at $n = 1$, $p = 1$. In a similar way the maximum value of p according to Eq. (16) occurs when

$$n_1 = 4(DkT)^3 / \pi e^6 z_1^3 z_2^2 (z_1 + z_2) \quad (18)$$

and

$$p_M = 4kT(DkT)^3 / 3\pi e^6 z_1^3 z_2^2. \quad (19)$$

The straight line OA in Fig. 2 corresponds to the ideal gas law (Factor A) and the deviations of the curve OBC from this line are due to the electric effects (Factor B).

³¹ P. Debye and E. Hückel, *Physik. Zeits.* **25**, 97 (1924).

³² Reference 28, p. 226.

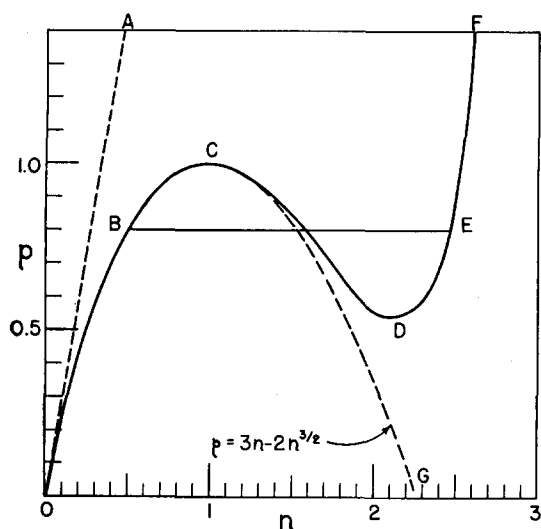


FIG. 2. Pressure-concentration curve illustrating conditions for coacervation.

If, p reaches a maximum at one value of n_1 , it is certain that at still higher values of n_1 it must have a minimum value, since p must rise to very high values when the particles come into contact. Thus, if there is a maximum in p , the curve must have some such shape as $OBCDEF$. The location of the portion DEF will be determined by repulsive forces between particles or by (Factor C) a decrease in z_1 at high values of n_1 . We shall give further consideration to DEF in a later section.

The portion CD of the curve between the maximum and minimum values of p is a region of instability, just as in the van der Waals theory of the continuous transition between the liquid and gaseous states. Therefore, whenever a maximum occurs we have conditions which necessarily cause two phases to appear as indicated by the points B and E with the horizontal line connecting them. The exact location of both B and E must depend upon the shape of the whole intermediate part of the curve $BCDE$. The theory of the CD portion must present almost insuperable mathematical obstacles, but the theories of the two limiting cases corresponding to the portions OBC and DEF are far simpler and can probably be developed without great difficulty. Eq. (16) is a first approximation to such a theory for the portion OBC .

In the case of many colloids, Factor C , which has an effect like that of a repulsive force of the

type illustrated by Eq. (12), may come into play before the concentration has reached the value given by Eq. (18), and this may prevent the occurrence of the maximum in p . The curve then shows a point of inflection while the slope is still positive. This corresponds to a liquid-gas system above its critical temperature. Under these conditions two phases will not occur until such high concentrations are reached that repulsive forces due to contact come into play.

Let us consider an aqueous solution ($D=81$, $T=293^\circ\text{K}$) containing w grams per ml of a substance, of molecular weight M , whose molecules dissociate into one positive ion of charge z_1e and z_1/z_2 negative ions each having a charge $-z_2e$. Then Eq. (18) takes the form

$$w_M = 6.15 \times 10^{-3} M / z_1^3 z_2^2 (z_1 + z_2). \quad (20)$$

Here w_M is the value of w that corresponds to the maximum at C in Fig. 2.

Table II gives data calculated by Eq. (20) for a few typical salt solutions and colloids. In the first three examples w_M has been calculated from the known values of z_1 and z_2 . The fact that these values of w_M are of the same order of magnitude as the solubilities of common inorganic salts illustrates the importance of the factors which we have considered in the derivation of this theory. There are several reasons why exact values for the solubility cannot be given by Eq. (20). The true equilibrium point B in Fig. 2 corresponds to a concentration which is necessarily lower than at the point C in the curve by an amount that depends upon the whole curve $BCDE$. Thus if the condensed phase at E is of

TABLE II. The concentrations, w_M , in g per ml which give a maximum osmotic pressure for solutions of various types. Based on Eq. (20).

EXAMPLE	SOLUTION	M	z_1	z_2	w_M	c ($z_3 = z_4 = 1$)
1	NaCl	58	1	1	0.180	3.1 molar
2	BaCl ₂	208	2	1	0.053	0.8
3	MgSO ₄	120	2	2	0.006	0.19
4	Protein	35,000	4	1	0.67	0.19
	"	"	6	1	0.14	0.085
	"	"	6	2	0.031	—
5	Tobacco virus	5×10^7	53	1	0.04	0.0011
6	Bentonite	10^9	133	1	0.02	2×10^{-4}
7	Spheres 1μ diameter	6×10^{11}	660	1	0.020	—
	"	"	660	2	0.005	—

unusually high stability (for example BaSO_4) the solubility may be far less than given by Eq. (20). On the other hand, hydration of the ions, as illustrated by the water of crystallization in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, may increase the solubility above w_M . Of course, we must consider also that the Debye-Hückel theory on which Eq. (20) is based cannot be expected to apply accurately to solutions as concentrated as those in the first three examples.

A protein of molecular weight of 35,000 has been chosen for Example 4. It was assumed that the protein gives micelles of charge z_1 and univalent ions, $z_2 = 1$, in solution. With $z_1 = 4$ or 6 we obtain values of w_M of 0.65 or 0.14, respectively. Thus the theory indicates that proteins of this molecular weight could be highly soluble in water if they have charges on the micelles which do not exceed about 6. If very low concentrations of divalent ions, $z_2 = 2$, are present the solubility would decrease to about one-quarter. It is known³³ that proteins such as egg albumin have values of z_2 that are positive when the $p\text{H}$ of the solution is below the isoelectric point and negative for values of $p\text{H}$ above the isoelectric point. The rate of change of the charge is about 8 units for each unit of $p\text{H}$. Thus, the value $z_2 = 6$ corresponds to $p\text{H}$ values which differ from the isoelectric point by about 0.8 unit. It is seen that the effect of low salt concentrations as calculated by Eq. (20) is in general accord with the Schulze-Hardy rule.

In Example 5 with tobacco virus having a molecular weight of 50,000,000, we choose for w_M a value twice that at which coacervation was observed. We then calculate $z_1 = 53$. Of course, Eq. (20) cannot hold accurately in this case for it was based on the assumption of spherical molecules, and it is known that tobacco virus molecules are long rods. However, the order of magnitude of the calculated value of z_1 seems reasonable.

The molecular weight of bentonite sols is of the order of 10^9 , and if we again take for w_M twice the concentration (1 percent) needed for coacervation we calculate $z_1 = 133$.

The last example is that of a colloidal solution of spheres 10^{-4} cm in diameter, of density 2, and

therefore molecular weight 6×10^{11} . Here to get coacervation in a 1 percent solution a charge $z_1 = 660$ is required. The presence of divalent ions of the opposite polarity would give coacervation at a concentration only one-quarter as great.

THE EFFECT OF ADDED SALTS

Besides the ions of charge $z_1 e$ and $-z_2 e$, let us assume that we have also a concentration of some salt, giving per unit volume n_3 positive ions with a charge $z_3 e$ and n_4 negative ions with a charge $-z_4 e$. Then in addition to Eq. (6) we have the condition

$$n_3 z_3 = n_4 z_4. \quad (21)$$

Substitution of these values into Eq. (15) gives an expression for p in terms of n_1 and n_3 . If we take the partial derivative of p with respect to n_1 and equate this to zero, we obtain an equation which enables us to calculate roughly the concentration of protein or of salt which will correspond to the maximum C in Fig. 2. This equation is

$$\begin{aligned} n_1 z_1 (z_1 + z_2) + n_3 z_3 (z_3 + z_4) \\ = 4(DkT)^3 / \pi e^6 z_1^2 z_2^2 \\ = 2.79 \times 10^8 D^3 T^3 / z_1^2 z_2^2. \end{aligned} \quad (22)$$

An increase in the amount of added salt thus decreases the colloid concentration at which p becomes a maximum. The concentration c , in mols per liter, needed to reduce n_1 to zero, is given by

$$c = 6.15 / z_1^2 z_2^2 z_3 (z_3 + z_4). \quad (23)$$

The last column of Table II gives values of c calculated from Eq. (23) assuming that the ions of the added salt are univalent ($z_3 = z_4 = 1$). Concentrations only one-quarter as great of a di-di-valent salt would be needed. This would indicate that ordinary proteins are sensitive to salts in 100 to 200 millimolar concentrations, while bentonite sols, in accord with observations, are affected in their coacervation properties by far lower concentrations.

DEBYE-HÜCKEL 2ND APPROXIMATION. EFFECT OF PARTICLE SIZE

The approximate form of the Debye-Hückel theory that we have used has shown that electrostatic forces result in a net attraction that can

³³ L. S. Moyer and J. C. Abels, J. Biol. Chem. **21**, 331 (1937).

account at least qualitatively for unipolar coacervation.

Debye and Hückel, in a kind of second approximation, have considered the effects of the finite sizes of the ions. Their expression for the osmotic pressure³⁴ in the case where the charge and diameter of the micelle (z_1 and a) are large compared to the corresponding values for the ions of opposite sign is

$$p = n_1 k T z_1 / z_2 - e^2 n_1 z_1^2 \sigma / 6 D \lambda, \quad (24)$$

where σ is given by

$$\sigma = 3\beta^{-3} [1 + \beta - (1 + \beta)^{-1} - 2 \ln (1 + \beta)], \quad (25)$$

$$\beta = a / \lambda \quad (26)$$

and a is the effective distance of nearest approach of the negative and positive particles or ions. In the present case a is approximately the radius of the micelle.

Equation (24) can be brought to a simpler form by substituting

$$B = e^2 z_1 z_2 / 2 D k T = 3.50 \times 10^{-8} z_1 z_2 \text{ cm}, \quad (27)$$

if we take $D = 81$, $T = 293^\circ \text{K}$. Here B is the "Bjerrum³⁵ radius," within which the potential energy (to remove an ion to ∞) exceeds $2kT$. We thus obtain

$$p = n_1 k T (z_1 / z_2) (1 - B \sigma / 3 \lambda). \quad (28)$$

By differentiating with respect to λ , taking p , n_1 , and σ as dependent variables, by making use of Eqs. (25), (26), (14), and by putting $dp/d\lambda = 0$, we find, without making further approximations, that p becomes a maximum when the following condition is fulfilled:

$$a/\lambda + \lambda/a + 2 = B/2a. \quad (29)$$

TABLE III. Conditions under which p is a maximum. By Eqs. (32), (29), (25), (28) and (34).

a/λ	$wz_1/\rho z_2$	B/a	σ	$1 - B\sigma/3\lambda$	$\eta_1 z_2$
0.4	0.0027	9.8	0.598	0.220	14.0
0.6	.0071	8.53	.486	.169	10.7
0.8	.0132	8.10	.403	.130	9.0
1.0	.021	8.00	.341	.068	8.0
1.2	.030	8.07	.293	.056	7.4
1.4	.040	8.23	.254	.0242	6.8
1.6	.051	8.45	.223	-.005	6.5

³⁴ P. Debye and E. Hückel, *Physik. Zeits.* **24**, 185 (1923). See especially Eqs. (37) and (33).

³⁵ N. Bjerrum, *Trans. Faraday Soc.* **23**, 433 (1927).

The value of a/λ can be expressed in terms of B/a by combining Eqs. (14) and (27):

$$(a/\lambda)^2 = 8\pi a^3 n_1 (B/a) (z_1/z_2). \quad (30)$$

If ρ is the density of the micelles and w the concentration of the sol in grams per ml, then

$$w = (4\pi/3) a^3 n_1 \rho \quad (31)$$

and therefore in place of Eq. (30) we have

$$(a/\lambda)^2 = 6(wz_1/\rho z_2) B/a. \quad (32)$$

The potential V_1 at the surface of the micelle of radius a according to Debye and Hückel is

$$V_1 = ez_1 / Da(1 + a/\lambda). \quad (33)$$

Combining this with Eqs. (10) and (27)

$$\eta_1 = 2B/az_2(1 + a/\lambda). \quad (34)$$

In order that p shall have a maximum value as n_1 increases Eq. (29) must be satisfied. The minimum value that B/a can have is 8 and this is reached when $a = \lambda$. Column 3 in Table III gives B/a for other values of a/λ . The 5th column shows that the coefficient of $n_1 k T$ in Eq. (28) becomes negative for $a/\lambda > 1.6$, indicating that the Debye-Hückel equation is not applicable to such high concentrations which make λ small compared to the radius of the micelle. The Debye-Hückel theory, although it is frequently used under such conditions, cannot be expected to be valid for large values of $\eta_1 z_2$ for in its derivation ϵ^{n_2} was replaced by $1 + \eta z$.

At low values of a/λ , $\eta_1 z_2$ increases to very high values. The conditions for the validity of the theory are most nearly fulfilled for values of a/λ from 1.0 to 1.4. Here the value of B/a is approximately 8, and thus by Eq. (27) the charge on the micelles needed to give a maximum value of p is roughly $z_1 = 2 \times 10^8 a / z_2$.

With these large charges, considerably larger than we calculated in Table II, the concentrations needed for coacervation by column 2 are very much lower than found in Table II and are lower than given by experiment.

POTENTIAL DISTRIBUTION NEAR PLANE SURFACES

In connection with previous studies of metallic surfaces in caesium vapor at high temperature,

the following equation was derived²⁸ for the potential distribution:

$$\theta = -\ln \tanh (\eta/4), \quad (35)$$

where

$$\theta = x/\lambda, \quad (36)$$

x being the distance from the plane surface and λ the Debye distance given by Eq. (14).

Equation (35) is a special solution of the fundamental equation

$$2 \frac{d^2 \eta}{d\theta^2} = e^\eta - e^{-\eta} \quad (37)$$

for the case that the potential gradient vanishes at $x = \infty$.

A plot of Eq. (35) is shown in Fig. 3 by the curve $ABCD$. For low values of η Eq. (35) approaches the limiting form

$$\eta = 4e^{-\theta}, \quad (38)$$

whereas for high values of η the limiting curve is

$$\theta = 2e^{-\eta/2}. \quad (39)$$

These two curves are given in Fig. 3 by FCD and ABE .

The curve FCD , as given by Eq. (38), corresponds to the Debye-Hückel theory. Thus we can replace the actual potential V_1 of a large colloid particle, having approximately a plane surface ($a \gg \lambda$), by the corresponding potential calculated from the curve FCD , and, for values of η less than about 1.5, obtain the same potential distribution as if we used the Debye-Hückel theory.

The portion of the curve AB rises to infinity at $\theta = 0$. Thus apart from a very small displacement $\Delta\theta$ the potential distribution near a charged surface is independent of the charge, provided the potential corresponds to values $\eta > 5$.

From this theory it follows that the potential distribution around large particles, at distances greater than about 0.8λ , can be calculated by the ordinary Debye-Hückel theory if one replaces the true value of η_1 by the fictitious value $\eta_f = 4$. For large spherical particles with $\eta_1 > 5$ ($V_1 > 0.125$ volt) we may put $\theta = (r-a)/\lambda$ and obtain from Eq. (38)

$$V = 4kT/e \exp [-(r-a)/\lambda]. \quad (40)$$

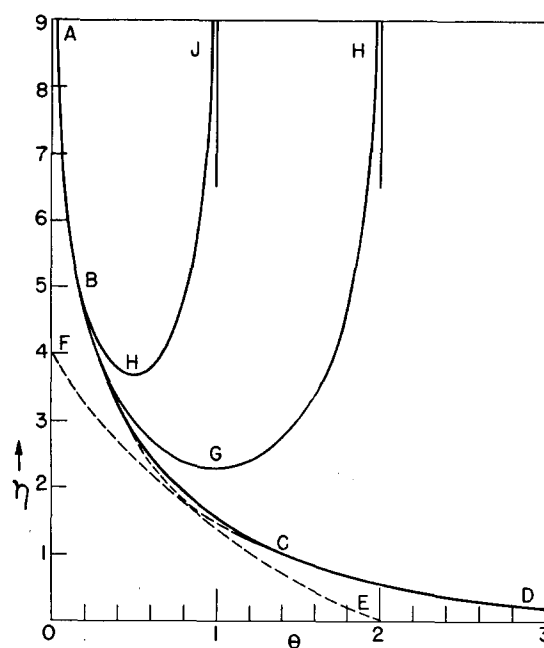


FIG. 3. Potential distributions between parallel plates in an electrolyte.

The potential distribution about a point charge according to the approximate Debye-Hückel theory is

$$V = (ez_1/Dr) \exp (-r/\lambda). \quad (41)$$

Since $r \gg \lambda$ we can replace r in the coefficient of the exponential factor by a and then by eliminating V between (40) and (41) we find

$$z_1 = (4DkTa/e^2) \exp (a/\lambda) = 0.57 \times 10^{-8} a \exp (a/\lambda). \quad (42)$$

Thus, if we take a point charge z_1e as given by Eq. (42) and apply the simple potential distribution law of Eq. (41) we will obtain the same distribution as is given by Eq. (40) for all values of r greater than a . The charge z_1 , however, will have to be greater than that needed if we were dealing with an ion of radius a .

We are now in a position to make a comparison between the two forms of the Debye-Hückel theory which we have used corresponding to Tables II and III or to the first and second approximations which we shall refer to as A and B . Let us assume that z_1 in each case is so chosen that the potential distributions are the same for $r > a$. The essential difference between

the two theories is that they give entirely different distributions for values of $r < a$.

Thus in Case A within the sphere of radius a there will be a distribution of ions of the opposite sign to that of the micelle, so that this is a kind of storage space for ions. As the concentration increases, the number of ions that are drawn into this space increases. The effect of this withdrawal of ions from solution is to decrease the pressure p from the value given by Eq. (7).

In the Case B the effect of taking a finite radius a is to exclude ions from the interior of the sphere so that the storage space is absent. Therefore, as the concentration increases, fewer ions are bound by the charges on the particles than in Case A. We see, therefore, the physical reason for the marked difference between the calculated data of Table III and the theoretical and experimental data of Table II.

The problem before us is to consider the mechanism of unipolar coacervation. This phenomenon will naturally occur best in colloids whose particles are highly charged, so that we may take $\eta_1 > 5$. We see from Fig. 3 that close to the surface of the particle where $\theta < 1$ the potential rises faster than the Debye-Hückel curve FCD . Thus close to the surface of the micelle there will actually be a higher concentration than was given by the theory B. This excess of bound ions close to the surface produces an effect equivalent to that of the storage space in Case A.

For this reason, Theory A, which assumes a point charge, for high values of η_1 will presumably give a better approximation than Theory B. A closer comparison of the data of Tables II and III suggests that Theory A gives too great a storage space, while Theory B gives none. It would seem, therefore, as though a further development, which we may call Theory C, would be desirable in which we take, instead of a point charge, at the center, a sphere of radius a_2 where $a_2 < a$. Then the charge z_1 on this smaller sphere can be chosen to make the storage space between the two spheres approximately equivalent to that which is due to the difference between the two curves $ABCD$ and FCD in Fig. 3.

In Theory C we can still use Table III by replacing a by a_2 . If we take $a_2 = a/8$ we would

make $B/a = 1$ and would bring η to values where the Debye-Hückel theory would be applicable.

In this way, by choosing a suitable value for a_2/a , we can cover transitions between Theories A and B. Of course, closer examination might show that in place of Eq. (25) we would have some other relation to give σ in terms of a/λ . It is also possible that the ratio a_2/a should be a function of the concentration. It hardly seems worth while to develop a theory along such lines until we have far better quantitative experimental data on unipolar coacervation with colloids having particles of known character.

For the present we may conclude that neither of the two forms A or B of the Debye-Hückel theory that has been proposed is applicable quantitatively to the problem of coacervation. The A theory fits available data far better than the B theory, and there are good theoretical reasons why this should be true. Moreover, it is clear that the attractive forces given by the Debye-Hückel theory are of the right order of magnitude to account for unipolar coacervation. The lack of quantitative agreement gives no reason to assume that unipolar coacervation involves other than Coulomb forces.

From the foregoing attempts to apply the Debye-Hückel theory to unipolar coacervation it appears that the separation into two phases occurs under conditions where a/λ and B/a are each approximately equal to unity. Under these conditions the charge z_1 which must be assumed to exist on a fictitious micelle having a radius $a_2 = 0.2a$ is of the order of 1 unit for each A unit in the diameter $2a$.

Some of these conclusions are closely related to those of a recent paper by Fuoss³⁶ where he finds critical transitions in the distribution of ions when $a/\lambda = 0.72$ and where $B/a = 2$. We may conclude that if coacervation occurs it generally occurs under about these conditions. If, however, it fails to occur with rising concentrations, this will probably be in general because of factors such as repulsive forces of the type given by Eq. (12) or forces dependent upon the hydration of the ions.

³⁶ R. M. Fuoss, J. Am. Chem. Soc. **57**, 2604 (1935).

REPULSION BETWEEN PARALLEL PLANES

Equation (35) is the solution of the differential Eq. (37) for the case where $d\eta/d\theta=0$ at $\theta=\infty$. Let us now consider the problem of two positively charged parallel planes at distance b apart. A complete solution of Eq. (37) can be had in terms of elliptic functions. For our present purposes, however, we are interested in the case where $\eta \gg 1$, so that we can neglect $e^{-\eta}$ in Eq. (37). The general solution then becomes

$$\theta = 2 \exp(-\eta_M/2) \tan^{-1} [\exp(\eta - \eta_M) - 1]^{\frac{1}{2}}, \quad (43)$$

where θ is now measured from the median plane at which η has a minimum value η_M .

If we place $\eta = \infty$ we obtain the value of θ at one of the planes.

$$\theta_1 = b/2\lambda = \pi \exp(-\eta_M/2). \quad (44)$$

Now, the planes have forces acting upon them due to the pressure of the ions and to the electric field. The sum of these two forces must, however, be constant across the space between the planes.

The potential distributions between the planes for the two cases where $b=2\lambda$ and $b=\lambda$ are given in Fig. 3 by the curves $ABGH$ and $ABHJ$ respectively. At the median plane where $\theta=0$, $d\eta/d\theta=0$ and there is no electric field. If, then, we get the pressure of the ions at this median plane, we obtain the total forces acting upon the plates. According to Eq. (9), we then have for the concentration n_M at the midpoint

$$n_M = n_0 \exp \eta_M. \quad (45)$$

The pressure $p = n_M kT$ is then given by

$$p = (2\pi\lambda/b)^2 n_0 kT, \quad (46)$$

but according to Eq. (14)

$$\lambda = [DkT/8\pi e^2 n_0]^{\frac{1}{2}} = 3.07 \times 10^{-8} c^{-\frac{1}{2}} \text{ cm}, \quad (47)$$

if $D=81$, $T=293$ and c is the molar concentration. By eliminating λ between these equations we obtain

$$p = (\pi/2) D(kT/eb)^2 = 8.90 \times 10^{-7} / b^2 \text{ dynes/cm}^2. \quad (48)$$

There is thus a repulsive force which is proportional to the surface area and varies inversely as the square of the distance b between the surfaces. This pressure is independent of the charge

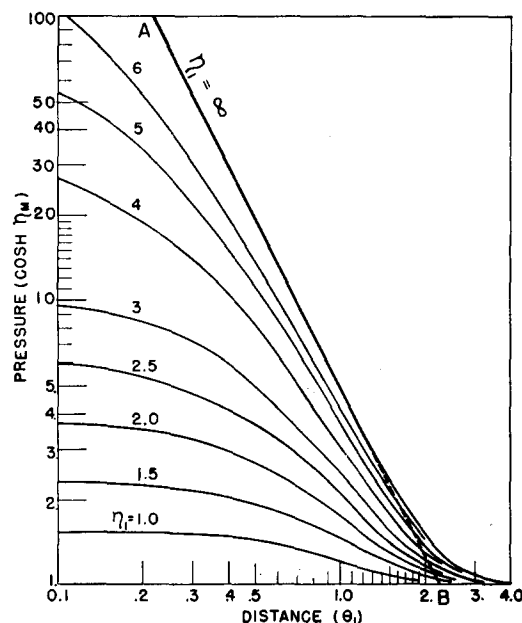


FIG. 4. Double logarithmic plot of the pressure between two plates as a function of the distance between them, for given values of the potentials V_1 on the plates. The actual values of p can be obtained from these data by Eqs. (52), (44), (47) and (10).

on the plates and of the ionic concentration provided the potential V_1 is great enough to make $\eta_1 \gg \eta_M \gg 1$ and the concentration is low enough to make $\lambda > b/3$. These restrictions on the general validity of Eq. (48) result from the neglect of the last term, $e^{-\eta}$, in Eq. (37), and the assumption $\eta_1 = \infty$ in the derivation of Eq. (44).

If we put

$$K = \exp(-\eta_M) \quad (49)$$

and replace η by a new variable ϕ defined by

$$\sin \phi = \exp [-(\eta - \eta_M)/2], \quad (50)$$

integration of Eq. (37), without simplifying assumptions, gives

$$\theta = 2K^{\frac{1}{2}} [F(\pi/2, K) - F(\phi, K)], \quad (51)$$

where $F(\phi, K)$ is the elliptic integral of the first kind for which tables are available.

The exact expression for the pressure is

$$p = 2n_0 kT \cosh \eta_M = (\pi/2) D(kT/eb)^2 R, \quad (52)$$

where

$$R = 2(\theta/\pi)^2 \cosh \eta_M. \quad (53)$$

When $R=1$, Eq. (52) reduces to Eq. (48).

The variation of pressure with the distance between the plates is illustrated in Fig. 4 which has been constructed by means of Eq. (51). The ordinates, on a logarithmic scale, measure $\cosh \eta_M$, which, according to Eq. (52), varies in proportion to the pressure acting between the plates. The abscissas, also on a logarithmic scale, give θ_1 , which, by Eq. (44), measures the distance b between the plates. The straight line AB corresponds to the inverse square law of Eq. (48).

The deviations from this limiting expression are of two kinds. When $\theta > 1.5$, or $b > 3\lambda$, the pressure may rise above the values given by Eq. (48); *viz.*, R may exceed unity. These deviations, however, are only 17 percent at $b = 4\lambda$. At still greater values of b the pressure rapidly approaches the limit $2n_0kT$.

The second factor, the approach of η_M to its limiting value η_1 , causes the curves in Fig. 4 to break away from the straight line AB at low values of θ_1 and to become approximately horizontal. When $\eta_M > 2$ (or $\cosh \eta_M > 3.8$) a good approximation may be had by using Eq. (43) without assuming that $\eta_1 \gg 1$. Substitution of K and ϕ , as defined by Eqs. (49) and (50), into Eq. (43) gives

$$\theta = 2K^{\frac{1}{2}}(\pi/2 - \phi). \quad (54)$$

The shape of the curves for small values of θ_1 , where η_M approaches its limit η_1 , may be had by assuming that $\eta_1 - \eta_M \ll 1$ in Eq. (50). Eq. (54) then becomes

$$\theta_1^2 = 4(\eta_1 - \eta_M) \exp(-\eta_M). \quad (55)$$

The limit of p at low θ_1 , shown by Eq. (55) and by the curves of Fig. 4, corresponds to the pressure p_1 given by Eq. (12).

The whole of the pressure calculated from Eq. (52) cannot be regarded as a true repulsive force between the plates. Consider, for example, two colloid particles in the form of plates of widths large compared to λ . If these, with their faces parallel, are brought within a distance 3λ there is a pressure between them given by Eq. (52), but on the outer surfaces of each particle there is a pressure $2n_0kT$ acting in the opposite direction. The net repulsive force between the particles thus corresponds to a pressure p_r given by

$$p_r = 2n_0kT(\cosh \eta_M - 1). \quad (56)$$

It has been shown in a recent note³⁷ that these equations can also be used to calculate the pressure exerted by a solid surface upon the air-water interface of a film of water on this surface. This accounts apparently quantitatively for the Jones-Ray effect according to which very low concentrations of salts lower the capillary rise in surface tension measurements.

REPULSIVE FORCES BETWEEN MICELLES IN COLLOIDS

These equations for the forces between parallel planes are directly applicable to theories of the structure of laminar coacervates such as those formed in iron oxide and tungstic oxide sols that show Schiller layers.

The force given Eq. (48) is of the right magnitude to account for the formation of these coacervates. Thus if $b = 5000\text{\AA}$, we calculate $p = 350$ dynes/cm² which is a reasonable osmotic pressure for colloids of this kind. For example, if we assume $z_2 = 1$, $z_1 = 1000$ and $p = 350$, Eq. (7) gives $n_1 = 10^{13}$ per cm³ (roughly 10^{-8} molar). A sol containing 5 percent by weight of plate-shaped particles 2000\AA square, of a thickness 250\AA and density 5 (molecular weight 3×10^8) gives this value of n_1 .

The theory of repulsive forces which has been developed in the foregoing pages has been limited to the one-dimensional case to avoid the serious mathematical difficulties involved in the analogous 2- and 3-dimensional problems. The results obtained indicate that forces of the same general nature are effective in all types of unipolar coacervation, whether they involve 1-, 2- or 3-dimensional structures. There are, however, some differences that should be pointed out.

Three types of coacervates may be recognized which differ in the lattice arrangement of their particles:

One-dimensional coacervation. Iron oxide and tungstic oxide coacervates (Schiller layers) have plate-shaped particles arranged in parallel planes (1-dimensional lattice) with no regularity of distribution within the plane.

Two-dimensional coacervation. The tobacco virus coacervates and V_2O_5 tactoids are examples in which the rod-shaped micelles are arranged in

³⁷ I. Langmuir, *Science* **88**, Nov. 5 (1938).

a 2-dimensional lattice without regularity in an axial direction.

Three-dimensional coacervation. The white bentonite sols, although they contain plate-like micelles, form coacervates whose particles are arranged in a 3-dimensional lattice. There are probably numerous other cases where particles are in 3-dimensional amorphous arrangements (isotropic liquids).

In each case the dilute phase in equilibrium with the coacervate has a 3-dimensional amorphous arrangement of its micelles. This fact seems to be essential for the coexistence of the two phases. To make this clear let us consider the possibility of coacervation in a 1-dimensional system such as that represented in Fig. 4. A plot of p against $1/\theta$ should give a kind of "equation of state" that can be compared to Fig. 2. According to the theory we have given we see, however, that for the 1-dimensional system (Fig. 4), there can be no maximum value of p at large values of θ_1 (low concentrations) and therefore a separation into two phases cannot occur.

The actual existence of 1-dimensional coacervates therefore depends upon the 3-dimensional character of the dilute phase. This means that certain dilute 3-dimensional sols must have higher osmotic pressures p than more concentrated 1-dimensional coacervates.

This difference between the 1- and 3-dimensional phases appears to depend upon the fact that ion association in a 3-dimensional electrolyte becomes negligible at infinite dilution but this does not occur in a 1-dimensional system. Thus in the phase having the 3-dimensional structure the pressure by Eq. (7) is large because z_1 is large, but in the phase having the 1-dimensional structure the effective charge z_1 may be smaller because many of the ions are bound more firmly by the particles (greater ion association).

A complete theory of even 1-dimensional coacervation must therefore involve a calculation of the pressure in a phase having a 3-dimensional arrangement of micelles.

THE POTENTIAL V_1 AND THE ζ -POTENTIAL

It is known²⁹ that the ζ -potential, which is calculated from the electric mobilities of particles, is generally much less than the thermo-

dynamic or electrochemical potential. What value should be used for V_1 in the equations that have been derived?

It is of interest that practically all the values of ζ given in Abramson's book²⁹ lie below a rather definite limit of 100 mv. This corresponds to $\eta=4$, which is the value at the point F in Fig. 3 where a very rapid rise in η begins.

By differentiation of Eq. (39) we find that the potential gradient at the surface of a large particle is given by

$$\begin{aligned} dV/dx &= -(kT/e\lambda) \exp(\eta_1/2) \\ &= -(0.025/\lambda) \exp(\eta_1/2) \text{ volts/cm.} \end{aligned} \quad (57)$$

With a $10^{-5} M$ salt solution, $\lambda=10^{-5}$ cm and the potential gradient corresponding to $\eta_1=4$ is then 19,000 volts/cm.

In a discussion of the dielectric constants of dilute salt solutions Debye³⁸ has calculated that strong electric fields near the ions cause a dielectric saturation. The effect is the same as if the water in regions of field strength exceeding 150,000 volts/cm contributed nothing to the dielectric constant. Actually, of course, the loss of dielectric power is gradual and Debye gives a curve showing the calculated values of D as a function of the distance from the center of the ion.

It is perhaps possible that fields of the order of 20,000 volts/cm which exist when $\eta_1>4$ cause an interference in the motions of ions which accounts for the limitation in the observed values of ζ . Probably far higher potential gradients, of the order of 150,000 volts/cm (corresponding to $\eta_1=8$), are needed to give a layer of water of hydration (impenetrable to ions).

It seems therefore that when ζ is small, V_1 and ζ are equal, but when ζ approaches its limit of about 100 mv, V_1 can rise considerably above 100 mv. Contact potential measurements of monolayers of proteins and fatty acid derivatives on water give potentials as high as 400 mv. It seems that similar or even higher potentials must be active in many colloids.

BIPOLAR COACERVATION

The cases of coacervation most intensively studied by Bungenberg de Jong have been those in which there are colloidal particles of both

³⁸ P. Debye, *Polar Molecules* (Chemical Catalog Co., New York, 1929), p. 118.

signs. With these bipolar coacervates, if V_1 is to remain unchanged for particles of both kinds, the electric fields and the charges on the micelles increase when the concentration increases, whereas with unipolar coacervates the fields decrease. The fact that the particles in the bipolar coacervates remain separated by considerable distances and do not come into contact proves the presence of some other kind of repulsive force than that given by Eq. (48). Hydration seems to be the most reasonable explanation.

The very intense fields that develop when the particles come close together are apparently able to draw water in between the particles and so hold them apart.

It seems, therefore, that Bungenberg de Jong's working hypothesis for this type of coacervation should be accepted. It should be noted that in bipolar coacervates the particles are far closer together than they are in such unipolar coacervates as bentonite, tobacco virus and iron oxide sols.

Quadrupole Contributions to London's Dispersion Forces

HENRY MARGENAU

Sloane Physics Laboratory, Yale University, New Haven, Connecticut

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The contribution of terms in R^{-8} and R^{-10} to the dispersion forces is expressed by a simple, approximate formula (Eq. (7)) involving only measurable quantities (polarizability, absorption frequency, oscillator strength). The formula is applicable when the dispersion curve of the substance can be represented with the use of a single resonant frequency. Numerical values of the terms in question are calculated for a number of molecules (Table II). Except in the case of the alkalis, where the convergence of the sequence in inverse powers of R fails at distances around 6A, the R^{-10} term is generally negligible, while the R^{-8} term contributes appreciably in the region of the van der Waals minimum.

FOR large distances of separation (R), the interaction energy of two neutral molecules is given with good approximation by C_1/R^6 , where C_1 is a coefficient which may be calculated with considerable precision for simpler molecules and atoms. For the case where the dispersion curve of the substance in question is given with sufficient accuracy by an expression involving but a single resonant frequency, ν , London¹ has derived the particularly simple and beautiful formula:

$$C_1 = -\frac{3}{4} h \nu \alpha^2, \quad (1)$$

which, in applications, has proved fairly successful.

On the other hand, it is known that C_1/R^6 is only the first term of an expansion to which multipoles contribute higher powers in $1/R$. In detailed investigations, and especially when

attention is given to values of the intermolecular distance in the neighborhood of the van der Waals minimum, these higher power terms are important. I wish to point out in this note that, under the conditions for which (1) is valid, equally simple formulas are available for the coefficients of the higher terms.

Expression (1) is derived most directly with the use of a model which possesses only a single frequency, the simple harmonic oscillator.¹ The state function for two three-dimensional isotropic oscillators, infinitely far apart, and vibrating in quantum states n_1, n_2, n_3 , and n_4, n_5, n_6 , respectively, is given by

$$\psi(n_1 \cdots n_6) = \prod_1^6 H_{n_i}(\beta^{1/2} x_i) \exp [-(\beta/2) x_i^2], \quad (2)$$

where the x_i stand for the 6 coordinates of the two oscillators, each referred to the center of mass of its molecule. The parameter β measures

¹ F. London, *Zeits. f. physik. Chemie* **B11**, 222 (1930); *Trans. Faraday Soc.* **33**, 8 (1937).