

EFFECT OF PARTIAL COAGULATION UPON THE SIZE DISTRIBUTION CURVE IN HETERODISPERSE COLLOIDAL SYSTEMS

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The size distribution of the unaggregated particles remaining after partial coagulation of a colloidal solution of spheres is found to be altered in favor of the large particles as compared to the distribution in uncoagulated control specimens. The results obtained in a di-disperse latex of polystyrene were quantitatively compared with the ones expected on the basis of Müller's theory. The order of magnitude of the effect observed agrees with that expected from the difference in probability of collisions between unequal sized particles as compared to equal sized particles. The same type of shift is found for a heterodisperse polystyrene latex. All results can be explained satisfactorily without the assumption that the collision number (the "stability") varies with particle size within the colloidal range.

Introduction

The coagulation of colloidal solutions differs from an ordinary bimolecular reaction by the fact that the reaction product of a successful collision between two particles represents again a reactant: a "secondary particle" formed may again undergo a successful collision with another single or secondary particle to form a still larger unit. Consequently, an originally monodisperse colloidal system will, during partial coagulation, become polydisperse, and an originally polydisperse system will become still more polydisperse. In the latter instance, the theoretically intriguing and practically significant question arises as to whether or not the unreacted portion of the colloidal solution shows, after partial coagulation, a shift in its distribution curve. No conclusive experimental evidence is available for typical colloidal systems. The present exploratory investigation is concerned with this problem.

Survey of the Problem

Two factors may determine the size distribution of the unreacted portion of an originally polydisperse system: (1) the relative probability of collisions between particles of unequal size and between particles of equal size; (2) the hypothetical variation, with particle size, of the relative collision number (the average number of collisions necessary in order to obtain one successful collision). The first factor has been treated theoretically by Müller.¹ He arrived at the equation

$$W_2 = \frac{(R + r)^2}{4Rr} W_1 = \gamma W_1 \quad (1)$$

where W_1 is the probability of collision of two equal-sized particles, W_2 is the probability of collision of two unequal-sized particles, and R and r are the respective radii in the latter instance. When the radii are not equal, γ is seen to be always greater than unity, meaning that collisions between unequal sized particles are more likely than those between equal sized particles. If factor 2 could be neglected, one would therefore expect a shift of the maximum and of the skewness of the size distribution curve in the unreacted portion of a colloidal solution in favor of large particle sizes.

A variation in the collision number with particle

size would require that the height of the maximum of the potential energy curve between two colloidal particles varies with their size. No simple answer is possible. Verwey and Overbeek² find on the basis of their computations of potential energy curves that "when the particles are small relative to the dimensions of the double layer, stability always increases with increasing particle dimensions." This would work in the same direction as the "Mueller effect" just described. On the other hand, it appears conceivable—as shown by the same authors—that very large particles (diameter $> 1 \mu$) might give rise to a sufficiently deep potential energy minimum (second minimum) so as to produce a "long range" aggregation. This would produce a result opposite to that due to the Mueller effect, *viz.*, preferential coagulation of large particles.

In the earliest work pertinent to factor 1 Wiegner³ and Galecki⁴ showed that during the progressive coagulation of gold sols, the apparent size of the gold particles visible in the ultramicroscope increased while their number remained fairly constant⁵ until it decreased sharply near the end of the coagulation. Wiegner concluded that the large visible particles acted as nuclei for the aggregation of very small particles invisible in the ultramicroscope. This observation is in qualitative agreement with the theory of Mueller developed later. However, the use of the ultramicroscope limits the conclusiveness of the observations very much. For, a constancy in number and an increase in average size of the visible particles would result also if aggregation of ultramicroscopically visible particles were compensated by the growth of originally invisible aggregates to ultramicroscopic dimensions. Later, very extensive investigations by Tuorila,⁶ again conducted with the ultramicroscope, showed that the rate of rapid coagulation in polydisperse systems was faster than in monodisperse systems just as predicted by the Müller theory. During the slow coagulation of gold sols,

(2) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Publishing Co., New York, N. Y., 1948, p. 177.

(3) G. Wiegner, *Kolloid-Z.*, **8**, 227 (1911).

(4) A. Galecki, *Z. anorg. Chem.*, **74**, 174 (1912).

(5) Actually when the electrolyte concentration was low, the number increased slightly at first.

(6) P. Tuorila, *Kolloidchem. Beih.*, **22**, 191 (1926).

(1) H. Müller, *Kolloid-Z.*, **88**, 1 (1926).

on the other hand, Tuorila believed he had found that the particles too small to be visible in the ultra-microscope coagulated more slowly than the larger particles. Particularly noteworthy among the more recent work is that by Figurovskii and Seregin.⁷ These authors actually studied the effect of coagulating agents upon the size distribution curves in suspensions as obtained by sedimentation analysis. Some of the results definitely indicate a shift of the distribution curve toward large particles. Unfortunately the systems studied were coarse suspensions with the particle diameter varying between 4 and 10 μ . In addition, it is not certain that the shape of the non-spherical particles, an important factor in the coagulation rates, was a constant.

Factor 2 has, experimentally, found considerable attention particularly during the earlier periods when no theoretical argument of any kind was available as yet as to the possible effect of size on the stability of colloidal solutions. Probably the first investigation of consequence is that by Oden⁸ who succeeded in fractionating sulfur sols by a combination of partial coagulation, centrifugation and peptization. On investigating moderately monodisperse sulfur sols thus obtained, he concluded that colloid stability was larger the smaller the particle size.⁹ Westgren,¹⁰ on the other hand, found no difference in the stability of monodisperse gold sols whose particle sizes differed by a factor of about two. More recent work also is contradictory. Thiessen, Thater and Kandelaky,¹¹ and, more recently, Holliday¹² reported a decrease in the stability of gold sols with increasing particle size. Utzino¹³ and Monterumici,¹⁴ on the other hand, indicated for Se-sols and polymethyl methacrylate latices, respectively, that larger particle systems are more stable.

In the present investigation—which is merely exploratory in nature—an attempt was made to study the size distribution in the residual sols that remain after a sufficiently slow partial coagulation of di-disperse or hetero-disperse colloidal solutions and to compare it with the distribution prior to coagulation. Electron microscopy was used since it does not have the weakness inherent in ultramicroscopy and, to a lesser extent, in sedimentation analysis, that the smallest particles fail to play a role in the analysis. In addition, systems were selected in which all particles were strictly spherical irrespective of size. This identity of shapes is difficult to control particularly in microscopic suspensions of inorganic materials, but it is important since the rate of coagulation is larger the more particles deviate from spherical shape.

III. Experimental Procedure

Polystyrene latices obtained from the Dow Chemical Co.¹⁵ (original solids content: 30–40 weight %) were diluted and

partially coagulated, primarily by addition of electrolyte. The bulk of the aggregated particles was removed by centrifuging and the size distribution curve of the remaining colloidal solution was obtained by electron microscopy. It was compared with the distribution curve of an aliquot portion of diluted latex to which no electrolyte had been added but which otherwise had been treated in the same manner including centrifugation. Two types of latices were investigated: (1) a "didisperse latex," that is, a latex obtained by mixing two monodisperse latices of which one contained particles 557 $m\mu$ in diameter and the other particles 814 $m\mu$ in diameter; (2) a polydisperse latex which had a continuous size distribution curve, the smallest and largest particle diameter being 30 and 1800 $m\mu$, respectively. All particles were rigid enough to exclude coalescence and to avoid the disturbing effect of flattening out in electron microscopy.

A. Treatment of Latex Prior to Coagulation.—Prior to preparing the di-disperse latex, the 557 and 814 $m\mu$ latices were individually diluted with doubly distilled water to a solids content of 0.0430 and 0.0305 g. per 100 g. latex, respectively.¹⁶ The diluted latices were centrifuged for 15 minutes at 320 g . About 90% of the supernatant liquid was removed. Centrifugation and decantation were repeated in a quantitatively identical manner. The finally obtained samples were mixed in a volume proportion of 18.1% small particle latex to 81.9% large particle latex. Thus, the di-disperse latex obtained contained practically equal numbers of large and small particles. Its concentration was 0.0327 g. per 100 g. of colloidal solution and the total number of particles per milliliter was 1.65×10^9 . This di-disperse system represented the stock latex for all the respective experiments. It was kept at about 5° for seven days before the first coagulation experiments were started. This guaranteed reestablishment of equilibrium of the stabilizer adsorption.

The polydisperse latex was treated in the same manner except for reducing the total time of centrifugation to 20 minutes. Its final solids content was 0.034 g. per 100 g. of latex. This was the stock latex used for all respective experiments.

B. Partial Coagulation of the Latex.—Partial coagulation was brought about by addition of suitable amounts of KCl solution to samples of the stock latices. A concentration of 134 mmoles of KCl per liter of latex was necessary to produce in 6 days, a coagulation of about 90% in the di-disperse latex. The polydisperse latex was more sensitive to electrolyte. It required a concentration of 32.4 mmoles of KCl per liter of latex for a 90% coagulation within 2 days. The KCl concentrations used in the actual experiments were generally smaller. They varied, for the di-disperse system, between 101 and 134 mmoles per liter mixture (latex including added electrolyte solution); and for the heterodisperse system between 1.4 and 13.1 mmoles per liter. In all instances, the degree of coagulation was estimated from the turbidity of the residual sol. Following addition of electrolyte, the respective samples of the didisperse system, kept at room temperature, and those of the heterodisperse system, kept at 25.00°, were allowed to coagulate slowly for at least 2 days, and at the most, 3 months. After the desired degree of coagulation had been reached (minimum, 20%; maximum, 95%), the samples were centrifuged at 245 g for 5 or 10 minutes. In the case of the di-disperse system, shaking of the samples for 1 hr., with a frequency of 8.5 sec.⁻¹ preceded centrifugation. The residual colloidal solution was decanted and centrifuged again in the same manner. This twofold centrifugation removed practically all the aggregated particles. In addition, a certain fraction of the unaggregated primary particles also settled out. To neglect this fact would have falsified the size distribution curves in favor of the small particles. In order to exclude this possible major source of error, control samples, taken from the stock latices, brought to an identical polymer concentration, and stored and aged identically, were centrifuged simultaneously with the coagulating samples and were decanted identically.

C. Electron Microscopy and Treatment of Electron Microscopic Data.—Immediately after centrifugation, electron microscope specimens were prepared from the residual

(7) N. A. Figurovskii and A. V. Seregin, *Kolloid. Zhur.*, **17**, 140 (1955).

(8) S. Oden, *Koll. Z.*, **8**, 186 (1911).

(9) S. Oden, *Z. physik. Chem.*, **78**, 682 (1913).

(10) A. Westgren, *Arkiv. Kemi Mineral. Geol.*, **7**, 6 (1917–1918).

(11) P. A. Thiessen, K. L. Thater and B. Kandelaky, *Z. anorg. allgem. Chem.*, **180**, 11 (1929).

(12) A. K. Holliday, *Trans. Faraday Soc.*, **46**, 447 (1950).

(13) S. Utzino, *Kolloid Z.*, **32**, 149 (1923).

(14) R. Monterumici, *Materie plastiche*, **15**, 129 (1949).

(15) Courtesy of Dr. J. W. Vanderhoff, The Dow Chemical Co., Midland, Mich.

(16) The solids content was determined gravimetrically on aliquot portions of the centrifuged samples by drying specimens of known weight in a vacuum.

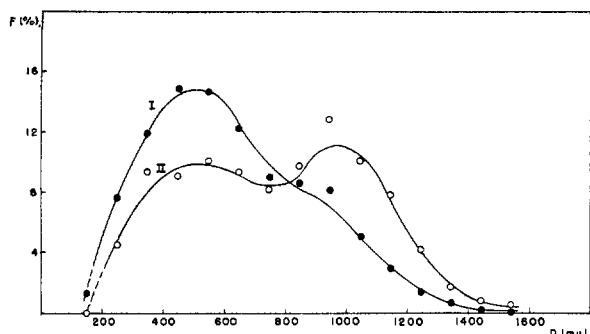


Fig. 1.—Particle size distribution in original polydisperse polystyrene latex (I) and in residual latex (II) remaining after partial coagulation by electrolyte: ●, 2464 particles counted; ○, 758 particles counted; D is diameter.

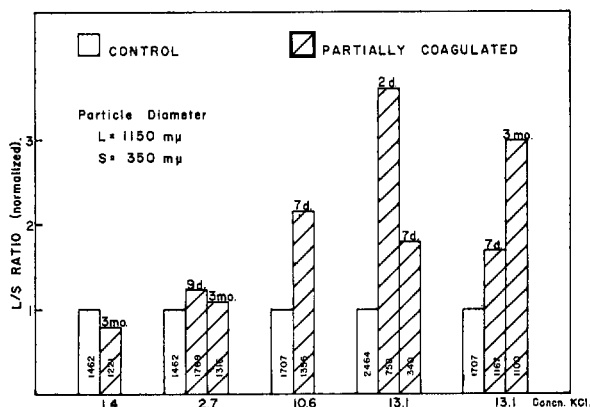


Fig. 2.—Relative frequency of two particle diameters differing by a factor of 3.0, in the original polydisperse polystyrene latex and in the residual latex remaining after partial coagulation. Numbers on top of rectangles, days (d) or months (mo) after addition of electrolyte; numbers within rectangles, numbers of particles considered in analysis of electron micrographs.

colloidal solutions and from the controls using Formvar films as a substrate. The electron micrographs, taken with an RCA electron microscope (model EMU-2B) were projected onto a large screen so as to obtain an over-all magnification of exactly 100,000. In the case of the di-disperse system, analysis was relatively simple because it was sufficient to count the number of large and small particles. A minimum of 670 particles was counted. Extensive tests showed that measurements of the diameter of a minimum of about 1000 particles were desirable in the polydisperse system. Except for two instances of rather highly coagulated samples, this desirable minimum was adhered to.

Results

A. Di-disperse System.—Table I summarizes the results. Column 6 shows that the number ratio of large (L) and small (S) particles was always larger in the residual sol (L/S) than prior to coagulation, (L/S)₀. The smallest excess of (L/S) over (L/S)₀ was 2%, the largest 36%. This indicates that the coagulum contained always an excess of small particles.

The individual (L/S)₀ and (L/S)₁-values, given in columns four and five, are only of secondary interest, but they give an approximate idea on the precision of the results in column 6. (L/S)₀ should be expected to be ≤ 1.0 , values < 1.0 being likely on account of the partial settling of unaggregated particles during centrifugation. The average (L/S)₀-value is 0.97. The only significant deviation

TABLE I
EFFECT OF PARTIAL COAGULATION, BY ELECTROLYTE, ON THE SIZE DISTRIBUTION OF PRIMARY PARTICLES IN DI-DISPERSE POLYSTYRENE LATEX

(Diameter of particles: $L = 814 \mu\text{m}$; $S = 557 \mu\text{m}$) 25°

Expt.	Mmoles KCl per l. latex	t^a	(L/S) ₀	(L/S) ₁	(L/S) ₁ / (L/S) ₀
1	101	30	0.93 (1552) ^b	1.11 (1355) ^b	1.19
2	101	88	1.08 (1448)	1.26 (927)	1.16
3	122	53	1.04 (670)	1.06 (2095)	1.02
4	134	14	0.86 (1353)	1.17 (1268)	1.36
4a	101	14	0.86 (1353)	0.97 (808)	1.13

^a Days elapsed since addition of electrolyte. ^b Number of particles considered in the analysis.

tion in the direction of (L/S)₀-values > 1.0 is represented by the value of 1.08. The value of 8–10% may therefore be considered as a measure of the over-all uncertainty inherent in the results. The major cause of this uncertainty is the occasional formation of hexagonal patterns, in electron microscopy, of one size group only. A series of special experiments showed that this phenomenon introduced an average uncertainty of 7.5% into the statistical analysis of electronmicroscopic data. (This complication did not arise with the polydisperse systems discussed below.)

B. Polydisperse System.—Five experimental series were carried out on the effect of partial coagulation on size distribution in the polydisperse latex. In four of the series, the size distribution curve in the residual sols changed decidedly in favor of the large particles. (In the single series which showed the opposite trend, the change was within the range of experimental error.) The most pronounced change found in the distribution curve is illustrated by Figure 1 (KCl, 13.1 mmoles per liter of mixture; status two days after addition of electrolyte). In order to express the results of all series graphically in a simple fashion, an L/S ratio was calculated, representing the number ratio of 1150 μm diameter particles to 350 μm diameter particles. The results are thus summarized in Fig. 2, where (L/S)₀, after centrifuging, is normalized throughout.

Shaking the electrolyte containing samples prior to centrifuging did not have any clear cut effect.¹⁷ In the two instances investigated, the effect, if any, seemed to be opposite to that produced by electrolyte coagulation alone.

Discussion

The results obtained on the di-disperse and polydisperse system show that during slow coagulation, by electrolyte addition, the small particles participate preferentially in the process of aggregation. This effect, though modest, is definite. A quantitative comparison between theory and experimental results is possible only for the di-disperse system since eq. 1 applies to such a system. The

(17) It should be noted, however, that shaking in the absence of electrolyte produced no coagulation in these systems.

probability of a large and small particle colliding should be here 4% larger than that for a collision between equal-sized particles. The actually observed values of $(L/S)/(L/S)_0$ (Table I) are of the proper order of magnitude. Since, therefore, the "Müller effect" can account for the effects observed it is unnecessary to assume that the collision-number (stability) of colloidal particles varies, in a given system, with particle size within the limits used in the di-disperse system. Müller's theory being limited to di-disperse systems, no definite quantitative comparison between theory and experiment is possible for the polydisperse system. In a di-disperse system containing particles with a diameter of 30 and 1800 $m\mu$, respectively, in equal numbers, the probability of a small particle colliding with a large particle would be 1750% larger than the probability of collision between equal-sized particles. These are the extreme

sizes in the polydisperse system investigated. In a di-disperse system containing particles with a diameter of 350 and 1150 $m\mu$, the result would be 40%. These are the sizes taken as a reference in Fig. 2. In view of the actual presence in the polydisperse system of sizes considerably smaller and somewhat larger, the effect observed for the 2 reference sizes should be within the two limiting values. The maximal effect actually observed (Fig. 2) is 260%. This at least suggests that the Müller effect alone might be sufficient here also to account for the observations.¹⁸

(18) It should be noted that the actual shift in the size distribution curve in the residual sols of the polydisperse system in favor of the large particles is bound to be slightly larger than that observed. The reason is that a certain portion of small particle aggregates which are formed, although statistically less often, must have remained in the residual sol after centrifugation. This must have altered, to some modest extent, the electron microscopic evidence in favor of the small particles.