

funnel, thermometer, reflux condenser, and magnetic stirrer. To this was added 0.1 mole of sodium borohydride dissolved in 50 ml. of methanol. The addition was conducted at such a rate as to maintain the temperature between 20–40°. After the evolution of hydrogen had subsided somewhat, the methanol was removed under water-pump vacuum. The residue was suspended in 100 ml. of distilled water and extracted with three 100-ml. portions of ether. The ether was then removed under diminished pressure and the solid material recrystallized to analytical purity from an ethanol-water solution.

Procedure B.—This method was utilized only when the secondary alcohol obtained upon removal of the ether was an oil. The liquid alcohols obtained by Procedure A were dissolved in 100 ml. of anhydrous ether. This ether solution was treated with anhydrous hydrogen chloride and the ether decanted from the sticky mass which adhered to the sides of the flask. A few milliliters of acetone was added and shortly a white solid appeared. This solid material was recrystallized to analytical purity from an ethanol-acetone solution.

Compound number 19 from Table I was prepared

from the corresponding ketonic Mannich base. This Mannich base was prepared from 1-acetonaphthone in a 31% yield according to procedures previously indicated (1). After recrystallization to analytical purity from an ethanol-acetone solution, a m.p. of 219–221° was observed.

Anal.—Calcd. for $C_{21}H_{25}NO \cdot HCl$: C, 73.34; H, 7.62; N, 4.07. Found: C, 73.53; H, 7.59; N, 4.06.

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Kinetics of Rapid Aggregation in Suspensions Comparison of Experiments with the Smoluchowski Theory

By W. I. HIGUCHI, R. OKADA, G. A. STELTER, and A. P. LEMBERGER

Rates of aggregation of initially monodispersed 1.83- μ polystyrene latex particles in various electrolyte solutions at different electrolyte concentrations have been studied. The experiments involved the determination of the distribution of singlets, doublets, and triplets as a function of time with the Coulter Counter. In order to permit a comparison of the data with theory, theoretical calculations of the "bimolecular" rate constants were carried out for both the diffusion-controlled mechanism and the surface-controlled mechanism. These rate constants were employed to construct theoretical curves which were used to evaluate the data. Maximum rates observed approached the Smoluchowski rate to within about a factor of two. With the purified samples the rates were found to be relatively independent of electrolyte concentration and type. Rates observed with the unpurified samples in salt solutions were substantially lower than those for the purified suspension even at high salt concentrations.

MOST STUDIES (1–4) of aggregation in solid-liquid or liquid-liquid dispersed systems have involved methods based on observation of the sedimentation behavior. While in many instances the desired information may be or may best be obtained by these techniques, it is generally difficult to quantitate aggregation, *per se*, from such experiments.

With the introduction of a novel instrument,

the Coulter Counter,¹ it has become possible to conveniently study aggregation without the complicating effects of sedimentation. Recently (5) the reversible aggregation in oil-in-water emulsions was studied with the aid of this instrument. Considerable insight into the problem was gained from this investigation.

In the present communication, results of a study of the kinetics of rapid aggregation of initially monodispersed polystyrene latex suspension particles are reported. The purposes of this work were to evaluate the validity of the existing theories as they apply to rapid aggrega-

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¹ Coulter Industrial Sales Co., Chicago, Ill.

TABLE I.—THE IRREVERSIBLE AGGREGATION INVOLVING UNIFORM-SIZED PRIMARY PARTICLES

$A_1 + A_1 \xrightarrow{k_{11}} A_2$
$A_1 + A_2 \xrightarrow{k_{12}} A_3$	$A_2 + A_2 \xrightarrow{k_{22}} A_4$
$A_1 + A_3 \xrightarrow{k_{13}} A_4$	$A_2 + A_3 \xrightarrow{k_{23}} A_5$	$A_3 + A_3 \xrightarrow{k_{33}} A_6$
$A_1 + A_4 \xrightarrow{k_{14}} A_5$	$A_2 + A_4 \xrightarrow{k_{24}} A_6$	$A_3 + A_4 \xrightarrow{k_{34}} A_7$	$A_4 + A_4 \xrightarrow{k_{44}} A_8$...
Etc.	Etc.	Etc.	Etc.	Etc.

tion of particles in the micron size range and to lay the groundwork for future studies on the role of additives in influencing the aggregation behavior in dispersed systems.

THEORY

We shall concern ourselves with the problem of the rapid irreversible aggregation of an initially monodispersed suspension. It is assumed that stirring is not present and that the effects of sedimentation are negligible. The reactions which must be considered are given in the scheme in Table I. Here the $A_1, A_2, \text{etc.}$, refer to the singlet, doublet, *etc.*, and the k 's are the rate constants for the reactions. The differential equations for this set of bimolecular reactions may be written

$$\frac{d(A_1)}{dt} = - (A_1) [k_{11}(A_1) + k_{12}(A_2) + k_{13}(A_3) + k_{14}(A_4) + \dots]$$

$$\frac{d(A_2)}{dt} = 1/2 k_{11}(A_1)^2 - (A_2) [k_{12}(A_1) + k_{22}(A_2) + k_{23}(A_3) + k_{24}(A_4) + \dots]$$

$$\frac{d(A_3)}{dt} = k_{12}(A_1)(A_2) - (A_3) [k_{13}(A_3) + k_{23}(A_2) + k_{33}(A_3) + k_{34}(A_4) + \dots]$$

$$\frac{d(A_4)}{dt} = k_{13}(A_1)(A_3) + k_{22}(A_2)^2 - (A_4) [k_{14}(A_1) + k_{24}(A_2) + k_{34}(A_3) + k_{44}(A_4) + k_{45}(A_5) + \dots]$$

etc. (Eq. 1)

In these equations $(A_1), (A_2), \text{etc.}$, are the concentrations of $A_1, A_2, \text{etc.}$, in number of particles per ml. and t is time in seconds. These equations cannot be analytically solved for the general case. However, for the special case in which a steady-state² diffusion is assumed and in which all of the rate constants, k 's, are equal, the solutions may be easily obtained (6). Since, as we shall see later, the rate constants may not differ too greatly for the aggregate pairs under consideration in our experiments, the special case of all k 's being equal is a useful approximation.

For cases in which the rate constants are different, the equations may be solved numerically by the usual methods (8). There are two of these cases which are of particular interest to our problem. One of these is the diffusion-controlled (no particle-particle repulsion) case and the other is the surface-

barrier-controlled case. In the diffusion-controlled process, the rate is determined by how rapidly the aggregates can diffuse field-free to each other by Brownian motion. Thus this rate is the theoretical maximum rate.³ The other case of interest is that in which aggregation occurs much more slowly. This may come about if a stabilizing agent acting at the particle surface is able to reduce the effectiveness of particle-particle sticking during collisions between the particles. In this instance the rate will be determined principally by not how quickly the particles can diffuse to each other, but by how rapidly they can overcome the barrier between them after they have nearly gotten together.

The rate constants, k 's, for the surface-controlled process should be proportional to the interfacial contact area between the aggregates. For the diffusion-controlled rate constants this is not the case (6, 7). This difference is the reason for the difference in the aggregate size dependence upon the rate constants between the two processes.

TABLE II.—THEORETICAL RATE CONSTANTS FOR DIFFUSION-CONTROLLED AND SURFACE-CONTROLLED PROCESSES

Rate Constant	D. C.	S. C.
k_{11}	k_{11}	k_{11}
k_{12}	1.03 k_{11}	1.3 k_{11}
k_{13}	1.07 k_{11}	1.5 k_{11}
k_{14}	1.13 k_{11}	1.7 k_{11}
k_{15}	1.16 k_{11}	1.8 k_{11}
k_{22}	1.00 k_{11}	1.5 k_{11}
k_{23}	1.01 k_{11}	1.7 k_{11}
k_{24}	1.03 k_{11}	1.9 k_{11}
k_{33}	1.00 k_{11}	1.8 k_{11}
k_{34}	1.0 k_{11}	2.0 k_{11}
k_{44}	1.0 k_{11}	2.2 k_{11}

The results of the theoretical calculations⁴ of the aggregate size dependence upon the rate constants for these two cases are given in Table II. For these calculations of the rate constants in the diffusion controlled case we started with Smoluchowski's relation (6, 7)

$$k_{ij} = 4\pi(D_i + D_j)(R_i + R_j) \quad (\text{Eq. 2})$$

³ Actually if the theory includes the effects of the attractive long-range London dispersion forces, calculations would predict greater (by the order of about 1 to 10%) maximum rates for particles in the micron size range. See Reference 9 for a discussion of these forces.

⁴ Unpublished work. Because of the approximate nature of these calculations, only the outline of the method of computation is presented here.

² See Overbeek, Reference 7, for the validity criterion for this assumption. This steady-state is not to be confused with "Steady-state" concentration of aggregates.

where D_i and D_j are the diffusion coefficients for the i and j aggregates, and R_i and R_j are the respective "collision" radii. The sum, $D_i + D_j$, is the effective diffusion coefficient for the pair, and the sum, $R_i + R_j$, is the interparticle distance (center-to-center) at particle-particle contact. While Eq. 2 is well suited for calculations involving spheres only, it cannot be rigorously applied where nonspheres are involved. In the latter cases approximations become necessary. Thus the singlet-singlet rate constant, k_{11} , was directly obtained by combining Eq. 2 with the Stokes-Einstein relation for a sphere

$$D_1 = \frac{k_o T}{6\pi\eta a} \quad (\text{Eq. 3})$$

where k_o is Boltzmann's constant, T is the absolute temperature, η is the viscosity, and a is the radius of the primary particle. Thus

$$k_{11} = \frac{8k_o T}{3\eta} \quad (\text{Eq. 4})$$

for the diffusion-controlled case. For calculations involving doublets, the translational diffusion coefficient for the doublet was calculated with the assumption that the doublet is a prolate spheroid with an axial ratio of two with the minor axis equal to the diameter of the singlet sphere. Then the equations of Perrin (10) were used to estimate the D value assuming random orientation of the doublet. The effective collision radius, R , for the doublet was obtained using this spheroid model and finding the radius of the equivalent volume³ sphere. For triplets and quadruplets and D and R values were estimated in the same manner but the various arrangements of the primary particles were weighted. For aggregates made up of more than four particles it was assumed that the aggregates were spheres with hydrodynamic radii equal to the radii of spheres of equal mass but with a porosity of 0.5. In all of these calculations the effects of rotational diffusion were neglected.

The rate constant calculations for the surface-controlled case involved primarily the estimation of the available areas of contact between the two aggregates involved. We may write

$$k_{ij} = \frac{\text{(Total Available Contact Area)}}{(D_i + D_j) \alpha} \quad (\text{Eq. 5})$$

where α is a constant for a given system in which the local curvature of the contacting surfaces are the same.⁶ The factor includes the sticking probability determined by the barrier. As before the D 's in Eq. 5 are the diffusion coefficient of the aggregates. These were calculated in the same manner as those for the diffusion-controlled process. The total contacting area for the singlet-singlet is simply $16\pi a^2$. Therefore

$$k_{11} = 32\pi a^2 D_1 \alpha \quad (\text{Eq. 6})$$

With Eq. 3 this becomes

$$k_{11} = \frac{16k_o T a \alpha}{3\eta} \quad (\text{Eq. 7})$$

for the surface-controlled case. The contact areas

³ This equivalent volume sphere calculation compares well with that employing rigorous equations obtained from electrostatic theory (11) with the spheroid model.

⁶ This is generally expected for aggregates composed of uniform size spherical primary particles.

for the multiplets were estimated by calculating the surface generated by the center of one aggregate around the other with aggregate-aggregate contact always present. Equivalent volume sphere approximations based on the spheroidal model were used as in the diffusion-controlled case for the calculations involving doublets and triplets. The larger aggregates were assumed as before to be spheres of equal mass with a porosity of 0.5. Again rotational diffusion of the aggregates was ignored.

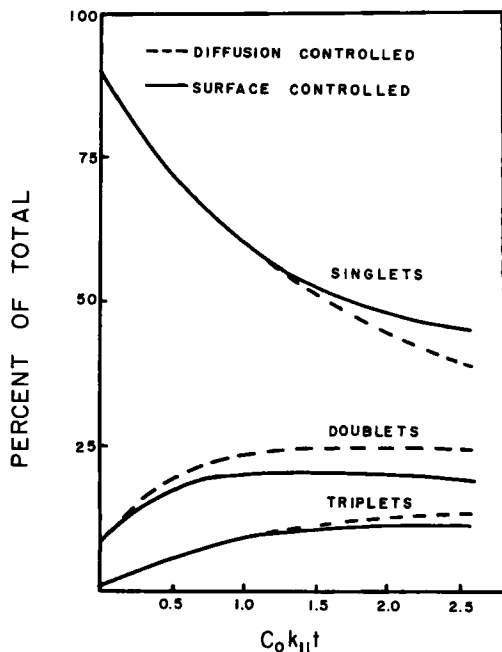


Fig. 1.—Theoretical curves for the per cent of various species as a function of time in a system composed of uniform-size primary particles undergoing irreversible aggregation at zero shear and zero sedimentation.

In Fig. 1 the results of the numerical integration of Eq. 1 employing the k values in Table II are presented. Where necessary the rate constants given in Table II were supplemented with k 's involving larger (than four) aggregates calculated by the methods outlined above. For the calculations over the range of $C_0 k_{11} t$ given in Fig. 1, only the rate constants involving small aggregates were of major importance. The particular boundary conditions selected for the integrations were at $t = 0$

$$\% \text{ singlets} = \frac{100 (A_1)}{(A_T)} = 90$$

$$\% \text{ doublets} = \frac{100 (A_2)}{(A_T)} = 8 \quad (\text{Eq. 8})$$

$$\% \text{ triplets} = \frac{100 (A_3)}{(A_T)} = 1$$

$$\% \text{ larger aggregates} = \frac{100 \sum_{i=4}^{\infty} (A_i)}{(A_T)} = 1$$

where the total particle number concentration is

$$(A_T) = \sum_{i=1}^{\infty} (A_i) \text{ at any } t$$

and

$$C_0 = (A_T) \text{ at } t = 0$$

This set of conditions was chosen because it approximately conforms to most of the experiments which will be discussed later.

It can be seen from Fig. 1 that according to theory the dependence of the number distribution of aggregate sizes upon $C_0 k_{11} t$ does not differ too greatly for the two processes over the range considered. As expected, the initial portions of the two curves are identical. The singlet curve for the surface-controlled case tends to level off more rapidly than that for the diffusion-controlled case at large times. Also the doublet and triplet curves for the surface-controlled case do not reach as high as those for the diffusion-controlled case.

When data conform to the plots in Fig. 1, it is simply a matter of matching the data curve to the theoretical curves. Then the k_{11} may be determined directly if C_0 is known. The experimental k_{11} values may be compared then with Eq. 4 to see whether the system obeys the Smoluchowski theory or, if not, to see how much stabilization (retardation of aggregation) is present.

Because of the near constancy of the k values for the diffusion-controlled case (see Table II), equating all of the k 's to k_{11} results in a good approximation for this case at small times. As already mentioned, analytical solutions to Eq. 1 exist (6, 7) for this situation. If at time = 0 there are 100% singlets present, then for later times this approximation gives

$$\begin{aligned} \% \text{ singlets} &= \frac{100}{1 + (1/2) C_0 k_{11} t} \\ \% \text{ doublets} &= \frac{50 k_{11} C_0 t}{[1 + (1/2) C_0 k_{11} t]^2} \quad (\text{Eq. 9}) \\ \% \text{ triplets} &= \frac{100 [(1/2) k_{11} C_0 t]^2}{[1 + (1/2) k_{11} C_0 t]^3} \end{aligned}$$

Plots of these equations are essentially identical with those for the diffusion-controlled case given in Fig. 1. The simplicity of Eq. 9 makes them useful when curves of the type given in Fig. 1 are not available.

EXPERIMENTAL

General Considerations.—While it is generally conceded (6, 7) that the Smoluchowski theory explains the data fairly well for the limiting coagulation rates of sols in the 0.01 to 0.1- μ size range, there appears to have been no examination of the applicability of the theory to particles in the micron-size range. Because particle sizes in most pharmaceutical suspensions range mainly in the micron region, mass-wise, a basic understanding of suspension aggregation behavior in this size region is important. To this end, the questions of whether and when the Smoluchowski theory applies are foremost and essential.

The system selected for this study was the suspension of monodispersed polystyrene latex particles⁷ of 1.83- μ diameter. For this system the resolu-

tion of the Coulter Counter is sufficiently great as to permit the classification of the aggregates into singlets, doublets, triplets, and sometimes even quadruplets. This is illustrated for a typical case of a partially aggregated system in Fig. 2. The differences between the plateau values on the curve give the relative amounts of the different species. Thus it was possible to conveniently follow the time change in population of the various aggregates in the suspension.

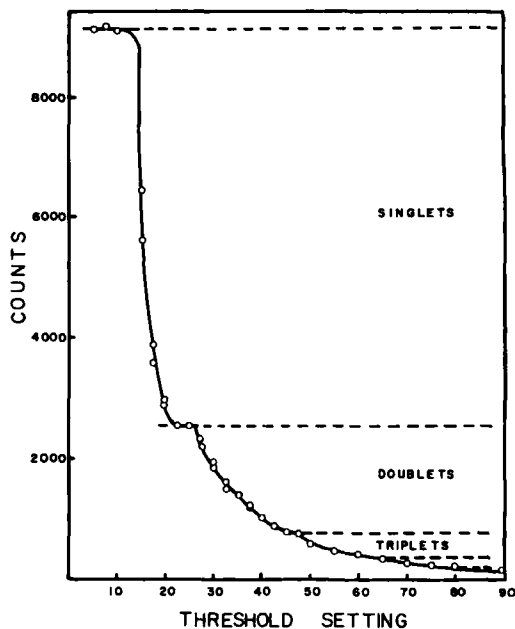


Fig. 2.—Coulter Counter data obtained with a system of partially aggregated suspension composed of 1.83- μ diameter primary particles.

It was decided to carry out the kinetic studies on both a purified suspension as well as on the unpurified sample in the presence of various electrolytes at different electrolyte concentrations. Since it was known (12) that the soluble impurity in the sample as received was a sulfonate type stabilizer, the limiting aggregation rates for the unpurified suspension were expected to also approach the theoretical Smoluchowski rate if the theory was to apply in this instance.

Procedure.—The sample of the latex suspension was diluted to about 1×10^8 particles per ml. A portion of this master suspension was purified by centrifugation in a clinical centrifuge followed by decantation of the liquid and ultrasonic⁸ redispersion in the solvent. This was repeated three times in 70% aqueous ethanol and three times in redistilled water. The other portion of the master suspension was used directly without any purification.

For the runs the suspensions were further diluted and mixed with equal volumes of an aqueous electrolyte solution so that the initial total particle concentration, c_0 , was always in the neighborhood of 1×10^7 to 7×10^7 particles per ml. These suspen-

⁷ Kindly supplied to us by Dr. J. W. Vanderhoff, Dow Chemical Co., Midland, Mich.

⁸ Ultrasonic cleaning unit, model DR-125AH, Acoustica Associates, Mineola, N. Y.

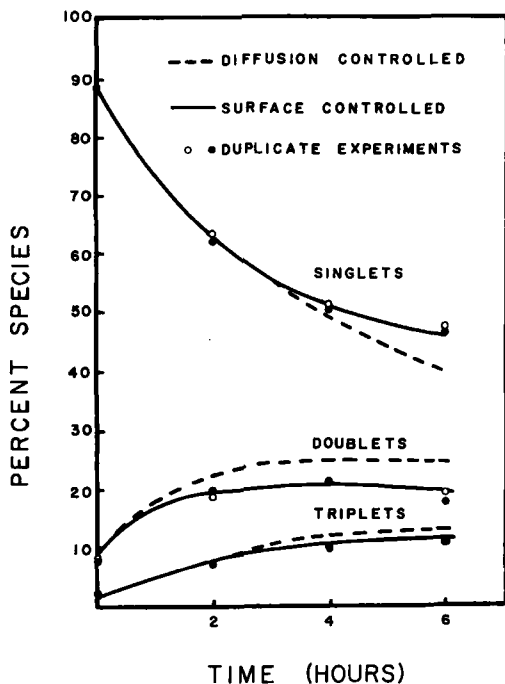


Fig. 3.—Experiment and theory showing aggregation of purified polystyrene suspension particles in 1% MgSO_4 . $C_0 = 1.7 \times 10^7$ particles per ml.

sions were then allowed to stand without agitation⁹ in 25-ml. volumetric flasks maintained at $25.0 \pm 0.5^\circ$. Aliquots were taken periodically, diluted in 0.9% sodium chloride solution, and the distribution of aggregates were determined with the Coulter Counter employing the $50\text{-}\mu$ aperture. The dilutions for counting were sufficiently great so that coincidence effects were negligible. Generally about 1 ml. of the suspension was added to 100 to 250 ml. of saline. The manner of pipeting and mixing the aliquot was found not to influence the results.

RESULTS AND DISCUSSION

Time Dependence.—The results of two of the kinetic runs are presented in Figs. 3 and 4. The data are plotted as per cent species *vs.* time to permit comparison with theory. For the particular experiment the theoretical curves were obtained by selecting a suitable single value for k_{11} and replottting the curves in Fig. 1 with the experimental C_0 so that the singlet theoretical curve would give the best fit to the singlet data.

For these and for the other electrolyte systems the fit of the data was more often somewhat better for the surface-controlled theoretical case, but in some instances the fit was equally good for both theoretical cases. As we shall see later, the Smoluchowski rate constant for the singlet-singlet reaction as predicted by Eq. 4 was never reached in any of the experiments, although closely approached particularly by the runs with the purified suspension and by the runs in 1.0% hydrochloric acid with the unpurified suspen-

sion (Fig. 4). Thus it is reasonable that most of the data did fit the surface-controlled theory or fit somewhere in between the two. However, because in many cases the experimental uncertainty was not much less than the differences between the two theoretical predictions, no conclusions can be made regarding the correct mechanism on this basis alone. Up to this point, however, it can be said that the time-dependent behavior of the aggregate distribution was found to be in good agreement with theory.

Dependence of k_{11} on Electrolyte Concentration.—By means of the method described above for matching theoretical curve to data, values for k_{11} were determined for all of the runs. The results are presented in Figs. 5 and 6 for the purified and the unpurified suspensions, respectively.

It is first worthwhile to note from these results that the k_{11} value as predicted by the diffusion controlled theory of Smoluchowski (see Eq. 4), *viz.* $k_{11} = 1.2 \times 10^{-11}$, has been closely approached in most of these experiments. In particular, with the purified suspension, all salt systems gave maximum k_{11} values within about a factor of two of the theoretical value. Because it is believed that these latex particles are typically hydrophobic, similar maximum k_{11} values can be expected with most unprotected suspensions and emulsions. Thus a useful upper limit for rate of aggregation has been experimentally established.

The salt runs with the unpurified suspension consistently gave lower k_{11} values and showed greater concentration dependence in the range of study than the runs with the purified sample. While it was expected that the concentration dependence would

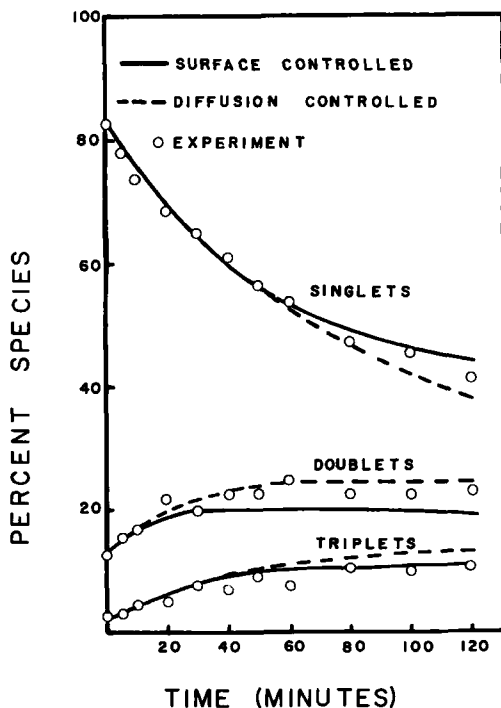


Fig. 4.—Experiment and theory showing aggregation of unpurified polystyrene latex suspension particles in 1% HCl . $C_0 = 5.2 \times 10^7$ particles per ml.

⁹ Both from Stokes' law consideration and actual experimental observations, sedimentation effects were judged to be negligible during the experiments.

be generally greater for the unpurified suspension because of the stabilizing action of the sulfonate additive at low salt concentration, it was somewhat surprising to find that maximum k_{11} values nearer to the theoretical k_{11} were not obtained in this series of runs. A sulfonate would normally be expected to operate as a charge-conferring agent. At such high salt concentrations (1 to 5%) the electrical double layer would be very thin and therefore should be completely canceled out at all interparticle distances by the attractive long-range London dispersion forces (7) between the primary particles. Thus it was expected that repulsive interactions would be entirely absent. The real situation is perhaps more complex than this simple picture. It may possibly involve aggregation of the sulfonate in a gel-like structure at the particle surface.

The effect of hydrochloric acid on the aggregation rate of the unpurified suspension was most interesting (see Fig. 6). The protective action of the stabilizer appeared to have been nearly completely destroyed in 1.0% hydrochloric acid. At this hydrochloric acid concentration the k_{11} was found to be approximately the same as those limiting values found with the purified suspension. The decrease in rate at higher hydrochloric acid concentrations has not been explained.

The dependences of k_{11} upon both the electrolyte type and the electrolyte concentration were relatively small with the purified suspension. This was not surprising since the few charge-producing ions present in these systems were not expected to

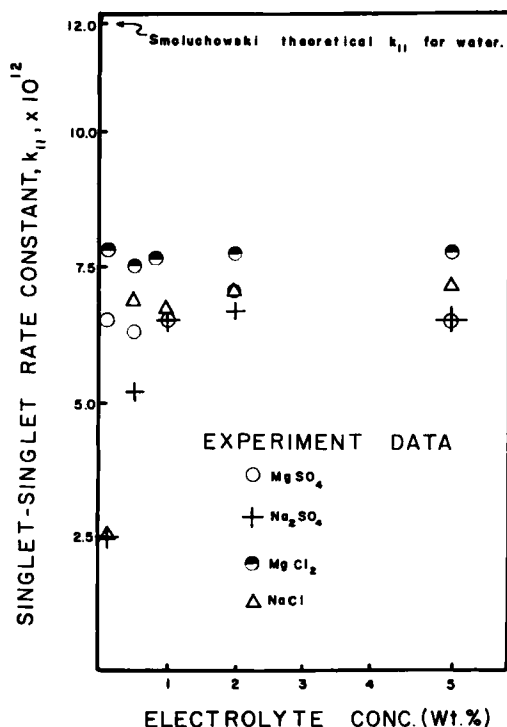


Fig. 5.—Experimental k_{11} values obtained with purified polystyrene suspension as function of electrolyte type and concentration. Note theoretical $k_{11} = 1.2 \times 10^{-11}$.

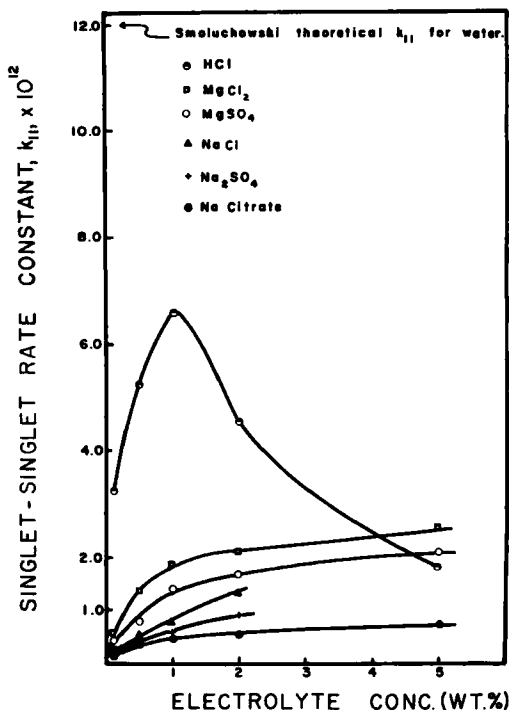


Fig. 6.—Experimental k_{11} values obtained with unpurified polystyrene latex suspension as function of electrolyte type and concentration. Theoretical $k_{11} = 1.2 \times 10^{-11}$.

be very effective. To within about $\pm 10\%$, the maximum k_{11} values observed in this series were found to be the same in all electrolyte systems studied.

While it may be purely academic, it is interesting to note that these experiments suggest that the correct diffusion-controlled rate is somewhat less than that predicted by the Smoluchowski theory. The correction factor appears to have a value somewhere between 0.5 and 0.8. It is reasonable that this might arise from the neglect of particle-particle hydrodynamic interactions which become important when the particles are near (order of a particle diameter) each other.

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