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## Research Articles

### Kinetics of Aggregation in Suspensions

#### Effects of Added Electrolytes on the Aggregation Rates of Latex Particles in Aqueous Ionic Surfactant Solutions

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Following procedures developed earlier involving the Coulter counter, the rates of aggregation of polystyrene and polyvinyltoluene particles in aqueous ionic surfactant solutions have been studied. The two surfactants were sodium lauryl sulfate and myristyl- $\gamma$ -picolinium chloride. The rates were determined as a function of both the surfactant concentration and the added electrolyte concentration for different electrolytes. The results of the experiments have been examined by the Derjaguin-Verwey-Overbeek theory. While the data are qualitatively in agreement with the theory, the decrease in rates observed with increasing surfactant concentration at high salt concentrations, particularly for sodium lauryl sulfate, suggests that electrical repulsion is not the only significant factor contributing to the repulsive part of the particle-particle interaction.

**S**URFACE-ACTIVE agents play a major role in determining the gross stability and flow behavior of suspensions through their influence on the aggregation and deaggregation kinetics of suspension particles. In this regard the ionic surfactants have received considerable attention from many researchers (1-5). In nearly all of the significant studies, the investigators have employed the sedimentation rate and the sediment height methods to observe the gross effects of such dispersing agents on suspension behavior and have attempted to deduce the aggregation processes from such studies. While these sedimentation methods in conjunction with adsorption studies have led to considerable understanding of these systems, it is highly desirable to have more direct information on the aggregation process itself.

Recent studies with the Coulter counter (6-8) have indicated that this instrument may be

sued uniquely for direct studies of aggregation behavior in aqueous media. In the present communication, it is demonstrated that the Coulter counter may be employed in quantitating the influences of surfactants and added electrolytes on particle aggregation rates.

#### EXPERIMENTAL

**Materials.**—Uniform size latex particles were employed as the dispersed phase as described previously (7). Polystyrene (PS) latex particles of 2.0- $\mu$  diameter and polyvinyltoluene (PVT) latex particles of 2.05- $\mu$  diameter were selected<sup>1</sup> for these studies. The samples were purified as described previously (7) by repeated centrifugation in alcohol and water. In the present studies, prolonged storage of the purified suspensions in water often led to variable results, with the rates always lower than those obtained with the freshly purified suspensions. Thus, all of the results reported here were obtained from freshly centrifuged samples.

The two surfactants<sup>2</sup> studied were sodium lauryl

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<sup>1</sup> Supplied by Dr. J. W. Vanderhoff and Mr. L. J. Lippie, Dow Chemical Co., Midland, Mich. The present PS sample differed from the 1.83- $\mu$  size sample used in the previous work (7).

<sup>2</sup> The authors are grateful to Dr. K. J. Mysels for supplying us with a highly purified sample of NaLS and to Dr. D. J. Lamb, The Upjohn Co., Kalamazoo, Mich., for a specially purified sample of MPC.

sulfate (NaLS) and myristyl- $\gamma$ -picolinium chloride<sup>8</sup> (MPC). All salts were reagent grade. In all instances recrystallization of the salts from pure water gave essentially the same results; but when a little ethanol was used with water in the recrystallization, significantly lower results usually were obtained. Thus, the reported data were obtained from salts recrystallized from pure water and with unrecrystallized salts.

**Procedure.**—The procedure followed was essentially the same as reported previously (7). The Coulter counter with the 50- $\mu$  aperture was used in following the particle concentration and size distribution changes with time. Special tests were introduced to assure the absence of possible artifact effects. Different pipet bore sizes were employed, and no effects of shear during pipeting were observed. Some aggregation studies also were carried out in a concentric cylinder rotating assembly, and it was found that no deaggregation occurred in the expected shear rate ranges encountered in pipeting and mixing.

In the present work, a slightly different procedure for calculating the rate constants was employed. The initial rate constant,  $k$ , for an initially mono-dispersed suspension may be equated to the rate constant,  $k_{11}$ , for the singlet-singlet reaction (7). Then the relation

$$k = \frac{2(C_1 - C_2)}{C_1 C_2 (t_2 - t_1)} \quad (\text{Eq. 1})$$

may be used. Here  $C_1$  and  $C_2$  are the total suspension particle concentration at times  $t_2$  and  $t_1$ , respectively. Equation 1 is simpler to apply, and only the total concentration of particles is required<sup>4</sup> in the calculation. The present method and the previous more exact method always gave essentially the same resulting  $k$  values when both calculations were carried out.

In all experiments, the initial total particle concentration,  $C_0$ , was in the range of  $2 \times 10^7$  to  $5 \times 10^7$ /ml.

## RESULTS AND DISCUSSION

The results of the experiments are presented in Figs. 1–8. Here the aggregation rate constants are plotted against the logarithm of the salt concentration (per cent weight) for the various surfactant concentrations.

As mentioned above, only the *initial* rate constants are presented here. In most of the experiments, the rate constants calculated by Eq. 1 or by the method described previously (7) gave essentially the same value, independent of the choice of  $C_1$  and  $C_2$  over the 3- or 4-hr. periods selected from the rate experiments. However, in a few instances at the high surfactant concentrations ( $\geq 0.05\%$ ) with both NaLS and MPC and when the salt levels were high, the rate constants decreased appreciably<sup>5</sup> over the 3- or 4-hr. period. In these cases, the 0 to 1-hr. points were selected for calculating the initial rate constants.

<sup>8</sup> Marketed as Quatresin by The Upjohn Co., Kalamazoo, Mich.

<sup>4</sup> However, the singlet, doublet, and sometimes the triplet concentrations were determined routinely in all of the experiments.

<sup>5</sup> A detailed examination of this time-dependent phenomenon currently is underway.

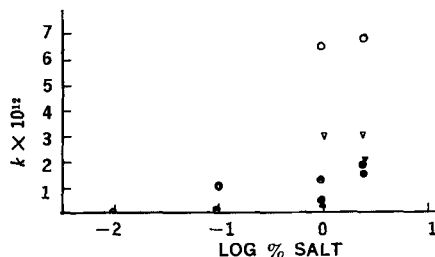


Fig. 1.—Effect of NaCl concentration on the aggregation rate of PVT latex in NaLS solutions at 30°. Key: ○, 0% NaLS; ▽,  $4.7 \times 10^{-4}$ ; ●,  $4.7 \times 10^{-3}$ ; ●,  $4.7 \times 10^{-2}$ ; ▲,  $9.5 \times 10^{-2}$ .

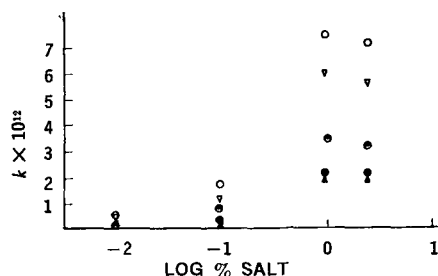


Fig. 2.—Effect of  $\text{MgSO}_4$  concentration on the aggregation rate of PVT latex in NaLS solutions at 30°. Key: ○, 0% NaLS; ▽,  $4.7 \times 10^{-4}$ ; ●,  $4.7 \times 10^{-3}$ ; ●,  $4.7 \times 10^{-2}$ ; ▲,  $9.5 \times 10^{-2}$ .

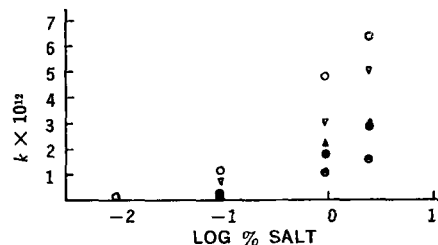


Fig. 3.—Effect of  $\text{Na}_2\text{SO}_4$  concentration on the aggregation rate of PVT latex in NaLS solutions at 30°. Key: ○, 0% NaLS; ▽,  $4.7 \times 10^{-4}$ ; ●,  $4.7 \times 10^{-3}$ ; ●,  $4.7 \times 10^{-2}$ ; ▲,  $9.5 \times 10^{-2}$ .

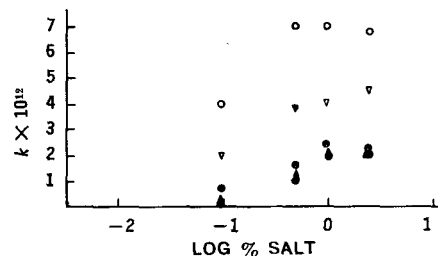


Fig. 4.—Effect of HCl concentration on the aggregation rate of PVT latex in NaLS solutions at 30°. Key: ○, 0% NaLS; ▽,  $4.7 \times 10^{-4}$ ; ●,  $4.7 \times 10^{-3}$ ; ●,  $4.7 \times 10^{-2}$ ; ▲,  $9.5 \times 10^{-2}$ .

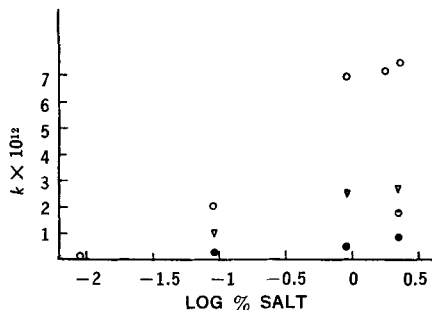


Fig. 5.—Effect of NaCl concentration on the aggregation rate of PS latex in NaLS solutions at 30°. Key: ○, 0% NaLS; ▽,  $4.6 \times 10^{-4}$ ; ⊙,  $4.6 \times 10^{-3}$ ; ●,  $1.8 \times 10^{-2}$ .

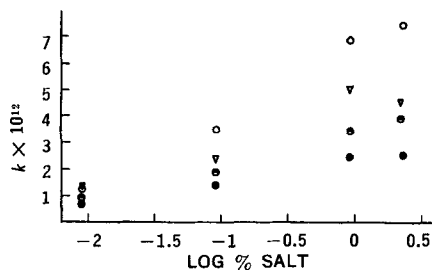


Fig. 6.—Effect of  $MgSO_4$  concentration on the aggregation rate of PS latex in NaLS solutions at 30°. Key: ○, 0% NaLS; ▽,  $4.6 \times 10^{-4}$ ; ⊙,  $4.6 \times 10^{-3}$ ; ●,  $4.6 \times 10^{-2}$ .

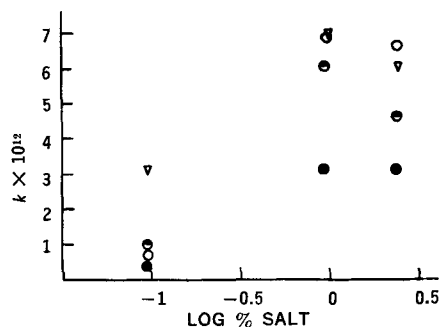


Fig. 7.—Effect of NaCl concentration on the PVT latex aggregation rate in MPC solutions at 30°. Key: ○, 0% MPC; ▽,  $4.7 \times 10^{-4}$ ; ⊙,  $4.7 \times 10^{-3}$ ; ●,  $4.7 \times 10^{-2}$ .

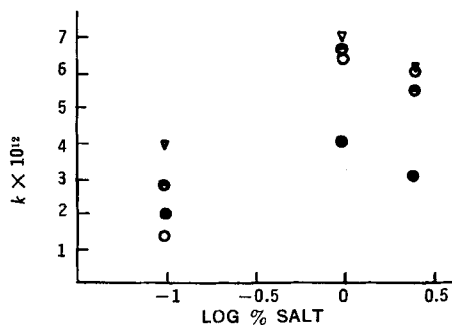


Fig. 8.—Effect of  $MgSO_4$  concentration on the PVT latex aggregation rate in MPC solutions at 30°. Key: ○, 0% MPC; ▽,  $4.7 \times 10^{-4}$ ; ⊙,  $4.7 \times 10^{-3}$ ; ●,  $4.7 \times 10^{-2}$ .

**Effects of NaLS and Electrolyte Concentrations.**—At zero NaLS, the rate constants reached a maximum value of about  $7 \times 10^{-12}$  at high electrolyte concentrations in good agreement with the previous work (7). However, with the present latex samples, a somewhat higher electrolyte concentration than before (see Fig. 5 and Reference 7) was required to attain the same rates. Because repeated centrifugation of the latex particles did not change this situation, the difference in behavior has been attributed to the possible differences in the surface character of the latex particles.<sup>6</sup>

It appears that, for the most part, the simultaneous effects of NaLS and electrolytes are qualitatively the same for all electrolytes. (See Figs. 1–6.) Also, as expected, there is little difference in behavior between the PVT and the PS particles. HCl and  $MgSO_4$  are generally more effective (even on the molal basis) than NaCl and  $Na_2SO_4$  in increasing the aggregation rates in the presence of NaLS. This would be expected if the conventional counter ion factors, *i.e.*, ion size and charge, are important in determining the nature of the interfacial region.

Of particular significance is that, even at relatively high electrolyte concentrations ( $\sim 2.0\%$ ), only a small amount of NaLS appreciably retarded the aggregation rate. This is somewhat surprising if the mechanism of surfactant action involved only electrical charging of the surface, in which case at such high electrolyte levels the repulsive electrical component of the particle-particle interaction should have been completely overwhelmed (9, 10) by the relatively long-range attractive London dispersion forces. Thus, it appears that either the expected London forces were not operating at distances the order of tens of angstroms with the expected strength, or that some type of nonelectrical factor was involved. There is much evidence (11), both theoretically and experimentally, that the long range attractive forces should be present in our systems. Therefore, it is more likely that some kind of nonelectrical phenomenon was responsible for the reduced rates at the high salt levels. A nonelectrical repulsion of the magnitude necessary to explain the present results may arise from the presence of an extremely weakly adsorbed thick hydrophilic layer at the interface. Admittedly, it is difficult to envisage or justify the existence of such an adsorbed interfacial structure on a purely hydrophobic surface, particularly at the lower NaLS concentrations. It may be that the latex particles themselves are lyophilic and highly swollen to some depth near the surface and therefore subject to further swelling in the presence of NaLS. Clearly, more work and with other dispersed phase materials is needed.

A rather interesting behavior with NaLS at high concentrations ( $\lesssim 0.05\%$ ) in the presence of NaCl and  $Na_2SO_4$  was noted. (See Figs. 1 and 3.) The initial rates in these cases suddenly increased at the highest salt concentrations. In some instances, the rates exceeded the rates for the lower surfactant concentrations at constant salt levels. This behavior appears to correlate with the observation of several investigators (1–3)<sup>7</sup> that at sufficiently high ionic surfactant concentrations the suspending power

<sup>6</sup> Possibly due to permanent residual surface charges. (See under *Effects of MPC and Electrolyte Concentrations.*)

<sup>7</sup> Lemberger (3) has discussed some of the possible causes of this type of behavior.

TABLE I.—THEORETICAL ELECTRICAL REPULSIVE ENERGY,  $V_R$ , AND ATTRACTIVE ENERGY,  $V_A$ , FOR TWO SPHERES

$H, \text{ \AA.}$	$V_R(\text{ergs})$				$V_A(\text{ergs})$		$V_A/kT$
	$\psi = 50 \text{ mv.}$		$\psi = 25 \text{ mv.}$		$A = 5.10 \cdot 10^{-13}$	$A = 2.10 \cdot 10^{-12}$	
	$K = 2 \times 10^6$	$K = 10^7$	$K = 2 \times 10^6$	$K = 10^7$			
50	$3.9 \times 10^{-11}$	$8 \times 10^{-13}$	$1.0 \times 10^{-11}$	$2.0 \times 10^{-13}$	$5.5 \times 10^{-12}$	$2.2 \times 10^{-12}$	50-130
100	$1.5 \times 10^{-11}$	$5.4 \times 10^{-16}$	$4 \times 10^{-12}$	$1.1 \times 10^{-15}$	$2.0 \times 10^{-12}$	$8 \times 10^{-13}$	20-50
200	$2.1 \times 10^{-12}$	$1.2 \times 10^{-19}$	$5 \times 10^{-13}$	$3.0 \times 10^{-20}$	$6.5 \times 10^{-13}$	$2.4 \times 10^{-13}$	6-15
400	...	...	...	...	$1.8 \times 10^{-13}$	$7 \times 10^{-14}$	2-4

decreases with increasing surfactant concentration and increasing salt. The NaLS and salt concentrations where the phenomenon is expected to occur are consistent with the present results.

**Effects of MPC and Electrolyte Concentrations.**—In contrast to the NaLS results, Figs. 7 and 8 show that electrolytes have a greater effect on the aggregation rates at the higher MPC concentrations. These results are more in accord with the idea that electrical repulsion is the primary factor retarding the rates and that at the high salt concentrations ( $\geq 1.0\%$ ), there should be little resistance to aggregation. Only at the highest surfactant levels was there a significant retardation of the rate. The MPC concentration where this retardation became noticeable is near or above the expected critical micelle concentration (CMC) for MPC<sup>8</sup> at these salt levels. Thus, the idea that surfactant aggregation at the interface leads to a thick hydrophilic interfacial region is more reasonable in this case than for NaLS.

Also, in contrast to the NaLS results, a small amount of MPC added *increased* the rate at the lower salt concentrations. This supports the already mentioned inference that the PVT particles possessed a residual negative charge.

**Semiquantitative Examination of the Results with the Derjaguin-Verwey-Overbeek Theory.**—It is instructive to examine the present results by means of the existing theory for the stability of lyophobic colloids (13, 14). In their paper on the sedimentation rates of sulfonated polystyrene particles, Schenkel and Kitchener give the equations for estimating  $V_R$  and  $V_A$ , the electrostatic repulsion energy and the London attractive energy for two particles, respectively. These energies have been calculated by the appropriate equations<sup>9</sup> and are given in Table I.  $V_R$  has been calculated for two  $\psi$  values and two  $K$  (Debye-Hückel  $\kappa$ ) values at the three  $H$  values, where  $H$  is the closest distance between the surfaces of the two spheres. In calculating  $V_A$ , two values for the Hamaker constant,  $A$ , have been employed.  $A = 5 \times 10^{-13}$  is the one suggested by Schenkel and Kitchener, and  $A = 2 \times 10^{-13}$  represents a probable lower limit value.

Let us first note from the last column in Table I that if the distance of separation of the two particles is greater than 200  $\text{\AA.}$ , there is only a few  $kT$  of attractive energy permissible. Therefore, even if there was no electrical repulsion, it would be doubtful that irreversible binding of two particles would take place at such distances.<sup>10</sup> Hence only distances

<sup>8</sup> Estimate based on data (12) on other surfactants of comparable chain length.

<sup>9</sup> Equation 1 of Reference 10 was used to calculate  $V_R$ . Equations VII, X, and XI in the Appendix of Reference 10 were used for calculating  $V_A$ .

<sup>10</sup> It can be estimated that the *net* attractive energy must be around 10-15  $kT$  to insure irreversibility in these experiments. This assumes that the width of the energy well is the order of 100  $\text{\AA.}$

$H \gtrsim 200 \text{ \AA.}$  are of interest to the present situation. At  $H = 100 \text{ \AA.}$ , even the conservative estimate shows that the London energy would be sufficient for rapid aggregation, *provided* that  $V_R$  is small enough. At  $H = 100 \text{ \AA.}$   $V_R$  is negligible compared to  $V_A$  for  $K = 10^7$  (corresponds to about 0.6% NaCl). Therefore, rapid aggregation should occur in this case. However, at  $H = 100 \text{ \AA.}$  and for  $K = 2 \times 10^6$  (corresponds to about 0.02% NaCl),  $V_R$  is always significantly greater than  $V_A$ . Thus, the aggregation rate would be negligible in this instance.

Recent studies by Sawyer and Rehfeld (15) on the mobilities of polystyrene latex particles in NaLS solutions suggest that the zeta potentials in 0.05 and 0.10  $M \text{ Na}^+$  are of the order of 50 mv. Therefore, the above calculations are for reasonable  $\psi$  values. It should be emphasized that the magnitude of the potential  $\psi$  used in these calculations is far less important than the effect of  $K$  on the rates.

The conclusions derived from Table I are consistent with both the NaLS and the MPC results in a qualitative fashion. However, from a quantitative point of view the reduced rates, particularly for NaLS at high salt concentrations, are difficult to explain on the basis of theory.

There is an interesting point that one can observe from the results of Table I. If it would be possible to provide a charged lyophilic layer of about 50  $\text{\AA.}$  thickness on the surface of each particle, then the effective  $H$  value for attraction would be about 100  $\text{\AA.}$  greater; but the effective  $H$  value for  $V_R$  may remain essentially unchanged. Table I shows that this situation would just provide cancellation of  $V_A$  by  $V_R$ , and aggregation would be retarded or inhibited. It would be reasonable then to expect that weakly adsorbed surface micelles may provide this type of situation.

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