Colloid Polym Sci 277:881–885 (1999)

SHORT COMMUNICATION

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Influence of the ionic strength in the heterocoagulation process between bare and surfactant-coated latexes

Received: 18 January 1999
Accepted in revised form: 14 April 1999

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Abstract A novel and useful process of heterocoagulation between bare and surfactant-coated latexes is studied. Basically, this process consists of the heterocoagulation of two identical latexes, i.e. of the same size and with charges of the same sign, but distinguished by the degree of coverage by a nonionic surfactant (Triton X-100). The different critical coagulation concentrations (ccc) of this type of sample permitted us to analyze the influence of the ionic strength in the heterocoagulation process between both colloidal samples. Different ratios (2:1, 1:1 and 1:2) of the bare and surfactant-coated latexes were used during the experiments. In all cases, the heterocoagulation rate constants were lower than the homocoagulation rate constant in diffusion conditions; however, for an ionic strength higher than the ccc of both systems, similar values were found for the rate constants.

Key words Colloidal aggregation · Heterocoagulation · Nonionic surfactant · Latex

Introduction

When more than one type of particle coexists within the same isotropic medium, the kind of interaction differs from a system containing one type of particle only. Heterocoagulation experiments permit us to interpret the stability of colloidal dispersions consisting of more than one kind of particle. In some applications, the appearance of particles of different surface charge or size actually occurs and homocoagulation studies are then unsuitable. The generality of the heterocoagulation concept includes a variety of differences, for example, composition and shape [1, 2], size [1, 3, 4], surface potential [5] and charge [6, 7].

A rare but very interesting case in heterocoagulation is the use of particles with an adsorbed layer of additives (polymer, surfactant), which opens the possibility of electrosteric stabilization between two colloidal systems with charges of opposite sign. Vincent et al. [8] analyzed the case of the deposition of small positively charged particles onto large negatively charged particles in the presence of polymers such as poly(vinyl alcohol) or alkyl ethylene oxide. In fact, the adsorption of some commercial nonionic surfactants [9, 10] is also of great interest in oil recovery because in such a way the colloidal stability of a latex suspension could be improved up to an electrolyte concentration of higher than 1 M NaCl + 0.1 M Ca_2Cl.

In a recent paper [7] we reported the influence of the adsorption of the nonionic surfactant Triton X-100 in the homo- and heterocoagulation processes of two polystyrene latexes of equal size but with charges of opposite sign. In fact, it was demonstrated that this case can be useful when we want to provoke an aggregation process (heterocoagulation) in a system previously stabilized with surfactant. Thus, the addition of a system with charge of the opposite sign can provoke the aggregation of the initially stabilized system without the necessity of changing the composition of the medium, i.e. without adding electrolyte. The influence of the ionic strength in the heterocoagulation process of negatively and positively charged systems, and the comparison between simulation and experiment have also been studied [11].

In this work, we report a novel process of heterocoagulation between bare and surfactant-coated latexes. This process consists of the heterocoagulation of two identical latexes, i.e. we use the same latex, but one of the samples has nonionic surfactant adsorbed on the surface. We have selected the sulfonate latex SN4 studied in Ref. [7] because the critical coagulation concentrations (ccc) of bare, partially covered and saturated particles with Triton X-100 are very different. Due to these differences in the ccc, we can study the heterocoagulation process versus the ionic strength of two systems coming from the same original latex and which are only distinguished by the degree of adsorption. This heterocoagulation process, therefore, takes place between particles of equal size and charges of the same sign, but one of the samples has a different solid–liquid interface structure which can provide additional steric stabilization. The main purpose of this work is the determination of the heterocoagulation rate constants in such processes and the comparison with the homocoagulation rate constants of both systems.

Theoretical background

In turbidity studies of coagulation the initial slope of the turbidity versus time curve is measured. The stability factor in homocoagulation (W), defined as the ratio of the fast and slow rate constants of doublet formation, can be evaluated by relating the initial slopes in the fast and slow aggregation processes:

$$W = \frac{\left(\frac{d\tau}{dt}\right)_{o,F}}{\left(\frac{d\tau}{dt}\right)_{o,S}} , \tag{1}$$

where τ is turbidity, t is time and the subscripts F and S refer to fast or slow coagulation, respectively.

The stability factor in heterocoagulation (W_{HET}) can be expressed as [3]

$$W_{HET} = \frac{\left(\frac{d\tau}{dt}\right)_{o,HOMO,F}}{\left(\frac{d\tau}{dt}\right)_{o,HET}} , \tag{2}$$

This equation is only valid in the case of heterosystems with similar size [3]. As can be seen, it is necessary to have a previous measurement of the initial slope of a homocoagulation process in diffusion conditions in order to evaluate W_{HET}.

Also, it is possible to evaluate the absolute rate constant of a homocoagulation process if we select a suitable particle number in the cell and the wavelength [3, 12, 13]:

$$\left(\frac{d\tau}{dt}\right)_{o} = \left(\frac{1}{2}C_D - C_S\right)K_D N_o^2 , \tag{3}$$

where C_D and C_S are the scattering cross-sections of the doublet and singlet, respectively, N_o is the initial number of singlets in the cell and K_D is the doublet rate constant.

In the case of heterocoagulation, in order to include the presence of two colloids with different sizes, we can use the equation [3, 6]

$$\begin{aligned}\left(\frac{d\tau}{dt}\right)_{o,HET} &= \left(\frac{1}{2}C_{D1} - C_{S1}\right)K_{D1}N_1^2 \\ &+ \left(\frac{1}{2}C_{D2} - C_{S2}\right)K_{D2}N_2^2 \\ &+ 2K_{D12}N_1N_2\left(\frac{1}{2}C_{D12} - \frac{1}{2}C_{S1} - \frac{1}{2}C_{S2}\right) ,\end{aligned} \tag{4}$$

where subscripts 1 and 2 refer to systems 1 and 2 and K_{D12} is the rate constant for dissimilar dimers. For particles of the same size ($a_1 = a_2$) and nature ($n_1 = n_2$, i.e. the same refractive index), the scattering cross-sections are equal for both singlets and doublets ($C_{S1} = C_{S2}$ and $C_{D1} = C_{D2} = C_{D12}$) and Eq. (4) can be written as [7]

$$\begin{aligned}\left(\frac{d\tau}{dt}\right)_{o,HET} &= (K_{D1}N_1^2 + K_{D2}N_2^2 + 2K_{D12}N_1N_2) \\ &\times \left(\frac{1}{2}C_{D12} - C_S\right).\end{aligned} \tag{5}$$

Experimental

Materials

A polymer colloid having sulfonate groups with a surface charge density of −3.6 μC cm^{-2} and a particle diameter of 370 ± 9 nm was used in the heterocoagulation measurements. The sulfonate latex was synthesized in our laboratory by emulsifier-free emulsion polymerization following the recipe given previously [14]. More details about the latex characteristics (from conductimetric titration and electrokinetic characterization) can be found in previous works [12, 15].

The nonionic surfactant Triton X-100 is a well-known and well-characterized surfactant prepared by the reaction of octylphenol with ethylene oxide. This surfactant has an aromatic ring and a variable chain length. In this work, Triton X-100 (octylphenol-9.5 ethylene oxide chains), gas chromatography grade material from Merck, was used without further purification. More information about the purity of the surfactant sample was obtained previously [16] by mass spectroscopy measurements on a sample with a good polydispersity index (M_w/M_n = 1.031). The advantage of using nonionic surfactants is that they do not alter significantly the surface charge of the colloids from an electrokinetic point of view, with nearly constant electrophoretic mobility for different degrees of coverage by the surfactant [17].

Methods

The rate constants were evaluated from the changes in absorbance with time in a Milton Roy Spectronic 601 instrument. The spectrophotometer was connected to a computer which collected the data and calculated the initial slopes of the turbidity/time curves [15]. The experiments were carried out by adding 1.2 ml of each system to the cell, followed by the injection of 0.6 ml salt solution to give the required ionic strength. As both systems have charges of the same sign no coagulation occurred before the injection of the salt solution. Also, the successive centrifugation–redispersion procedure of the latex–surfactant systems avoided the presence of any surfactant in the aqueous medium that could contaminate the other system (bare particles). The assumption of no desorption of the nonionic surfactant from the totally coated latex when mixed with a bare latex is probably reasonable on the time-scale involved during the heterocoagulation process. The surfactant desorption that takes place after the centrifugation–redispersion procedure was considered [10(a)] for the partially covered latex sample. Anyway, both SN4 latex species were conserved in individual containers.

The adsorption isotherm of Triton X-100 on the SN4 latex was obtained by adding known quantities of the surfactant to a volume of colloidal dispersion equivalent to a surface area of 0.25 m^2 as previously described [10(a)]. The surfactant–latex mixture was shaken gently for 4 h at 25 °C. The particles were separated by sedimentation centrifugation and the concentration of the surfactant remaining in the supernatant (c_{equi}) was determined [10(a)]. The adsorbed amount of surfactant (J_{ads}) was calculated from the depletion.

Results and discussion

The adsorption isotherm of Triton X-100 on the sulfonate SN4 latex at pH 5.5 and an ionic strength of 2 mM is shown in Fig. 1. The isotherm could be considered to be of high affinity with practically irreversible adsorption at low surface coverage, as was previously checked with different latexes and the same surfactant [16]. By comparing the plateau value of the adsorption isotherm (55.3 Å^2/molecule) with the area of surfactant occupied in the air–water interface (48-54 Å^2/molecule), we infer that the particles are covered by a dense monolayer of surfactant. In order to make an extensive series of experiments, we selected partially or totally covered (plateau zone) latex–surfactant complexes. For the first case we selected the intermediate value of J_{ads} of 1.75 μmol/m^2.

The ccc for bare particles was 175 mM and increased to 400 mM for partially covered particles [7]. Also, it was impossible to provoke any aggregation process for SN4 particles totally covered (saturated) by Triton X-100 (up to a concentration of 1.5 M NaCl) [7]. As can be seen, by comparing the ccc of bare and partially covered particles, there is a wide interval of electrolyte concentration in which the heterocoagulation process between both samples as a function of the ionic strength can be investigated.

The values of the initial slopes of the absorbance curve $(\mathrm{d}A/\mathrm{d}t)_{\mathrm{o}}$ versus the ionic strength for the heterocoagulation between bare and partially coated particles are shown in Fig. 2. We worked with a different number of particles for both samples, with ratios of 1:1, 2:1 and 1:2 for each system, and in all cases the total initial particle concentration ($N_{\mathrm{o}} = N_1 + N_2$) was 10^{16} particles m^{-3} and the selected wavelength was 700 nm. These experimental conditions avoided multiple scattering [12]. It can be seen that for the three ratios and for an ionic strength value equal to or greater than 400 mM, the initial slopes have a similar value. Also, for the three ratios, there is an evident change in the initial slopes for an ionic strength close to 200 mM. Finally, for an ionic strength below 400 mM a steeper initial slope of the absorbance curve can be seen when the proportion of bare particles is higher.

By using these data and Eq. (2) it is possible to obtain the stability factor, W_{HET}, versus the ionic strength (see Fig. 3), bearing in mind that both systems (bare and covered) are of equal size. The slopes of the fast homocoagulation processes were provided by the experimental data presented previously [7, 15]. Figure 3 shows these data for the three ratios and also the stability factor for the homocoagulation of bare and partially covered SN4 particles. Some conclusions can be extracted from the analysis of this figure.

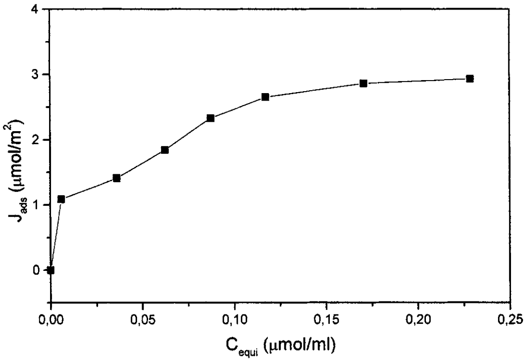

Fig. 1 Adsorption isotherm of Triton X-100 on SN4 latex versus the equilibrium concentration of surfactant (pH = 7, ionic strength = 2 mM)

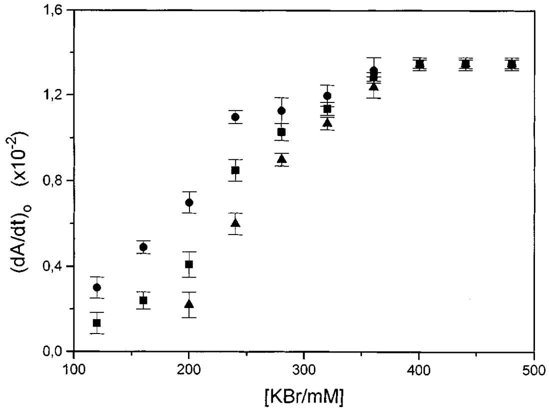

Fig. 2 Initial slopes of the absorbance curve $(\mathrm{d}A/\mathrm{d}t)_{\mathrm{o}}$ versus the ionic strength for the heterocoagulation of bare and partially covered particles in the ratios: 2:1 (●), 1:1 (■) and 1:2 (▲)

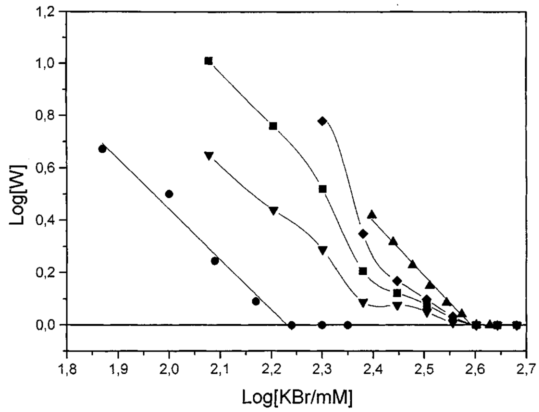

Fig. 3 Logarithm of the stability factor versus the logarithm of the KBr concentration for the homocoagulation of bare SN4 particles (●) and partially covered SN4 particles (▲) and the heterocoagulation of bare and partially covered particles in the ratios 2:1 (▼), 1:1 (■) and 1:2 (◆)

1. There is an increase in the stability of the heterosystem with a higher proportion of partially covered SN4 particles.
2. For the three curves three regions can be differentiated.

A. Log[KBr] < 2.38. The log[W]/log[KBr] curve has a steep slope, which corresponds to the progressive instability of bare SN4 particles (homocoagulation) and the stability of partially covered SN4 particles. Therefore, there is not a constant value of W_{HET} (heterocoagulation curve) in this interval, which seems to indicate a dependence of the heterocoagulation process on the ionic strength. This fact also occurs in region B.

B. 2.38 ≤ log[KBr] < 2.60. The log[W]/log[KBr] curve is less steep, which corresponds to homocoagulation in diffusion conditions of bare SN4 particles and progressive instability of partially covered SN4 particles (homocoagulation).

C. 2.60 ≤ log[KBr]. There is a constant value of log[W] = 0, which seems to suggest simultaneous homocoagulation and heterocoagulation processes similar to the homocoagulation of any of the compound systems in diffusion conditions.

In order to obtain the heterocoagulation rate constants (K_{D12}) between bare and covered particles versus the ionic strength, Eq. (5) can be used. For the evaluation of the scattering sections of singlets and doublets Rayleigh–Gans–Debye theory was used. Previously, we used the homocoagulation rate constants in diffusion conditions for bare and partially covered SN4 particles ($K_{\mathrm{D,F}}$), obtained in a previous work [7], where turbidimetry and nephelometry were used as alternative experimental methods.

The heterocoagulation rate constant K_{D12} versus the ionic strength for the three ratios is shown in Fig. 4. As can be seen, for each value of the ionic strength, the K_{D12} values are the same for the three ratios. Similar results were reported in a previous work [3], but using two latexes of different size permits us to confirm that the heterocoagulation rate constant K_{D12} is not only independent of the total initial number of particles, as for the homocoagulation one, but is also independent of the relative proportion of both latexes.

Finally, the homocoagulation and heterocoagulation rate constants (average values of the three experiments shown in Fig. 4) are compared in Fig. 5. Analysis of this figure permits us to extract some important conclusions.

1. When the doublet rate constant of bare SN4 particles is lower than the diffusion value and the partially covered SN4 particles are stable, K_{D12} is zero.
2. The ionic strength influences K_{D12} when the bare SN4 particles aggregate at a rapid rate, while the doublet rate constant of partially covered SN4 particles is lower than the diffusion value; however, K_{D12} is always lower than $K_{\mathrm{D,F}}$.
3. When both systems aggregate in diffusion conditions, $K_{\mathrm{D12}} = K_{\mathrm{D,F}} = 2.75 \times 10^{-18}$ m^3/s. In a previous work [7] the same value for the homocoagulation rate constant of the SN4 latex was obtained, independent of the surfactant coverage. This result was justified within the ambit of "extended DLVO theory" under consideration of osmotic and elastic potentials [10(b), 18, 19]. Thus, the energy barrier can be eliminated at any degree of Triton adsorption with increasing ionic strength [11, 18]. In the case of heterocoagulation, we have shown that above the ccc of the more stable component, the heterocoagulation process ocurs as a simple homocoagulation process.

Finally, this heterocoagulation case can be applied as a test of the proposed heterocoagulation potentials.

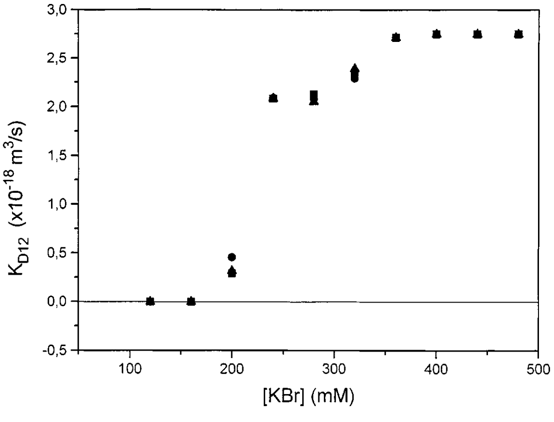

Fig. 4 Heterocoagulation rate constants (K_{D12}) of bare and partially covered SN4 particles in the ratios: 2:1 (●), 1:1 (■) and 1:2 (▲)

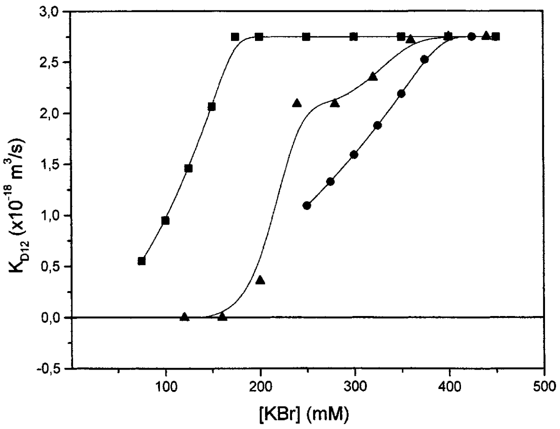

Fig. 5 Homocoagulation rate constants of bare SN4 particles (■) and partially covered SN4 particles (●) and heterocoagulation rate constants of bare and partially covered SN4 particles (▲)

Thus, recently (besides classical approaches [6, 20, 21]), the theoretical aspect of the heterocoagulation has been studied using a Brownian dynamics simulation [11, 22], but was limited to the classical heterocoagulation process between particles of opposite charge. In this work, we have presented a completely different case of heterocoagulation, that opens up the possibility of testing different proposed heterocoagulation potentials. By mixing bare and surfactant-coated latexes an intermediate rate constant value can be obtained (lower than that found for homocoagulation of bare latex) which tends to diffusion-controlled aggregation at high ionic strengths.

Conclusions

A new and very interesting case of heterocoagulation between bare and surfactant-coated latexes has been studied. The difference between both colloidal species consists of a different degree of adsorption by a nonionic surfactant Triton X-100. Under certain conditions, the influence of the ionic strength on the value of the heterocoagulation doublet rate constant (K_{D12}) is found; this value is always lower than the doublet rate constant in diffusion conditions ($K_{D,F}$) for homocoagulation. On the other hand, for an ionic strength higher than the ccc of both systems, the same values for $K_{D,F}$ and K_{D12} have been found. In all cases, K_{D12} is independent of the relative ratio (2:1, 1:1, 1:2) of bare and covered samples.

Acknowledgements The financial support provided by the Comisión Interministerial de Ciencia y Tecnología (CICYT), under project MAT96-1035-C03-03, is greatly appreciated.

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