Electrokinetic behavior in synthetic process of composite particles

Kunio Furusawa a,*, O.D. Velev b

a Department of Chemistry, University of Tsukuba, Tennodai-1, Tsukuba, Ibaraki 305, Japan
b Laboratory of Thermodynamics and Physicochemical Hydrodynamics, Faculty of Chemistry, University of Sofia, J. Bourchier Ave. 1, 1126 Sofia, Bulgaria

Abstract

Electrokinetic behavior in synthetic process of composite particles have been analysed under the different combination systems. Firstly, the heterocoagulation process of amphoteric polymer latices on spherical silica was investigated as a function of ζ-potential of component particles, particle size ratio and of electrolyte in the medium. On the basis of these data, subsequent experiments to prepare composite particles with multilayers comprised of usual anionic latices, ultrafine magnetic particles and polystyrene layers have been carried out, especially from the electrokinetic aspects. Finally, a novel technique that allows the assembly of different types of latex particles into ordered multi-component clusters, 'superparticles' has been introduced. The main ideas is to control the size and the composition of the supraparticles during their assembly by gathering and confining their components in a restricted, colloid-size space. Emulsion droplets can be used to provide their restricted space. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Composite particles; Heterocoagulates; Superparticles; Magnetic particles; Electrokinetic behavior

1. Introduction

The exceptional uniform shape and the wide diameter range of latex particles are of interest because their combination with other inorganic colloid particles should extend their application in the field of academic research as well as industrial material development. Especially, in the synthesis of composite particles comprised of organic and inorganic substances, the adoption of monodispersed polymer latices as their one component largely expands the variety of composite particles because many techniques to prepare latex samples with different sizes and structures have already been developed [1].

In the synthesis of inorganic–organic composite particles, the establishment of a method to control the orientation of each element should be regarded as an important factor because the characteristics of the composite particles largely de-
pend on the orientation of the component particles. Simultaneously, since the function of the composite particles is frequently determined by their size and uniformity, the development of a way to fix the particle diameter in a narrow size distribution is also indispensable. In practice, for example, when some magnetic composite particles are applied for the separation of T-cells from B-cells, it can be considered that the further out from the center the magnetic particles are in the composite particles, the more efficiently the separation proceeds. Moreover, when immuno latices, on which surface some antibodies are placed, are applied for diagnosis of pathological symptoms, their shape uniformity and particle size dramatically effect the accuracy [2]. To the end of systematic resolution of these problems, the synthesis method of magnetic composite particles was investigated adopting the concept of heterocoagulation theory; heterocoagulates were prepared from magnetic ultra-fine powder and four types of monodispersed negative latices with different particle diameter.

Finally, a novel technique that allows the assembly of latex particles into ordered multicomponent clusters, ‘superparticles’, has been introduced. The main idea is to control the size and the composition of the superparticles during their assembly by gathering and confining their components in a restricted, colloid-size space. Emulsion droplets and electrostatic interaction can be used to provide their restricted space.

2. Heterocoagulation behavior of polymer latices with spherical silica

In their papers, Matijevic et al. [3] have investigated various behaviours of mixed colloid particles obtained by mixing differently preformed particles. They showed that the nature of a mixing system depends on the conditions of preparation, and concluded that the important parameters to control are the concentration of the particles, the relative numbers of the component particles and their contrast to their relative surface charges. In some cases, pH, temperature and the nature of anions will affect the products in the most sensitive way.

Taking this into consideration, we report here on the syntheses and properties of heterocoagulate generated from mixtures of amphoteric polymer latices with a constant particle size and monodispersed spherical silica with a wide range of particle diameters (240–1590 nm). In these combinations of components, the contrast between surface charge and the particle size ratio of the components can be changed arbitrarily within their wide range of particle size. Furthermore, the heterocoagulates produced are composed of organic and inorganic materials, whose surface charge in both sign and magnitude can be controlled by changing the pH of the medium.

2.1. Heterocoagulation behavior

It was confirmed that the most important parameter in controlling the morphology of composite particles is the surface charge of the component particles, especially the contrast between surface charges of the two component particles. A stable system consisting of a regular composite particle could be prepared only in a medium controlled at pH 5–6, where the two components were charged with opposite signs [4]. Typical results of the electrophoretic mobility for the single silica and the latex suspension are shown in Fig. 1.

The next important parameter to control is the particle size ratio of the component particles when they are mixed in the vessel. Figure 2 shows schematic pictures of the morphology of heterocoagulates of different silica particles and amphoteric latices. Figure 3 shows an optical micrograph of the real heterocoagulate generated from different silica samples and amphoteric latex system, where the other conditions (e.g. the particle number ratio, \(N_{\text{silica}}/N_{\text{latex}} = 1/300\); the medium pH 5.6) have kept constant. The microscope used for observation was a lateral-type metallurgical microscope (Axio Mart, Carl Zeiss, Germany). It may be seen that at a particle size ratio \((r = D_{\text{silica}}/D_{\text{latex}}) > 3\), the suspension is composed of uniform heterocoagulate particles and each heterocoagulate is still undergoing Brownian motion as an isolated unit. The insert of Fig. 3(A) shows a scanning electron micrograph of the heterocoag-
ulate. It is apparent that heterocoagulate takes a raspberry shape with one silica particle in the core. In contrast to this, the heterocoagulates generated at a particle size ratio lower than \( r = 3 \) (Fig. 3(C) and (D)), are composed of large irregular aggregates and regular coagulates were hardly formed at any medium pH and particle number ratio investigated [4,5].

It is interesting to analyse the different heterocoagulation behaviours from the concept of the adhesion isotherm for the amphoteric latices on the silica particle. Figure 4 shows some typical isotherms for the latices on Silica-L at various \( \text{K}_2\text{SO}_4 \) concentrations, where all the systems were controlled at pH 5.2. It is evident that the...
Fig. 5. ζ-potentials versus pH curves for heterocoagulate particles prepared at different electrolytes: \( \nabla \), heterocoagulates prepared at \( 2.48 \times 10^{-1} \) M MgCl\(_2\); \( \odot \), heterocoagulates prepared at \( 1 \times 10^{-5} \) M KCl; □, amphoteric latices.

The potential energy of interaction between two dissimilar spherical particles is given as follows

\[
V = \frac{8R^2T^2γ^2εa}{Z^2F^2} \exp(2\kappa h_0) - \frac{A}{6} \left[ \frac{a^2}{2h_0(2h_0 + 2a)} + \frac{a^2}{2(h_0 + a)^2} + \ln \frac{h_0(2h_0 + 2a)}{(h_0 + a)^2} \right]
\]

where

\[
κ = \sqrt{8πn_0Z^2e^2/kT} \quad γ = \frac{\exp(Ze\psi /2kT) - 1}{\exp(Ze\psi /2kT) + 1}
\]

In the above equations, \( R \) is the gas constant, \( 2h_0 \) is the shortest distance of separation between two particles, \( ε \) is the dielectric constant of the medium (78.5 for water at 20°C), \( T \) is the absolute temperature of the suspension, \( Z \) is the valency of the ion, \( n_0 \) is the ionic density, \( e \) is the elementary charge, \( ψ \) is the surface potential of the particle (here, the ζ-potential measured at the appropriate salt concentration), and \( A \) is the Hamaker constant which is reported as \( 0.3 \times 10^{-20} \) J for silica in water and \( 1 \times 10^{-20} \) J for latices in water.

The potential energy of interaction between two dissimilar spherical particles is given as follows

\[
V = \frac{εa_1a_2(ψ_1 + ψ_2)}{4(a_1 + a_2)} \left\{ \frac{2ψ_1ψ_2}{ψ_1^2 + ψ_2^2} \ln \frac{1 + \exp(-2\kappa h_0)}{1 - \exp(-2\kappa h_0)} + \ln[1 - \exp(-4\kappa h_0)] - \frac{A_{12}εa_1a_2}{6h_0(a_1 + a_2)} \right\}
\]

where, \( a_1 \), \( a_2 \) and \( ψ_1 \), \( ψ_2 \) are radii and surface potentials of the respective dissimilar particles and

isolomers are all of the very high affinity type with a well defined plateau and the plateau value increases with increasing the K\(_2\)SO\(_4\) concentration within the range from \( 10^{-5} \) to \( 10^{-2} \) mol dm\(^{-3}\). This means that in this concentration range, adhesion proceeds in the way characteristic of monolayer adhesion. This may be due to the strong blocking effect of adhering particles. However, in K\(_2\)SO\(_4\) aqueous solutions more concentrated than \( 2 \times 10^{-2} \) mol dm\(^{-3}\), no reproducible isotherm could be obtained under any conditions tested, and only some irregular aggregates were generated in the course of the experiment [5]. In Fig. 5, the ζ-potentials of the heterocoagulates prepared at the different electrolyte concentrations, are presented as a function of the medium pH, as well as the data on the amphoteric latices. As may be seen, a reversal of charge is observed in all the samples, and the isoelectric point (IEP) in the heterocoagulated systems occurs at about pH 8, which is not so different from the IEP of the single latices. Moreover, the fact that the limiting, net positive ζ-potential attained at pH 6–3, increases with increasing electrolyte concentration, is also in line with the increase in latex adhesion with increasing electrolyte concentration.

2.2. Analyses of heterocoagulation behaviour using heterocoagulation theory

The heterocoagulation between amphoteric latices and silica particles will proceed at the same time as the homocoagulation between latex particles and silica particles themselves. The interaction potential energy between these identical particles (two equal spheres of radius \( a \)) is given by

\[
V = \frac{8R^2T^2γ^2εa}{Z^2F^2} \exp(2\kappa h_0) - \frac{A}{6} \left[ \frac{a^2}{2h_0(2h_0 + 2a)} + \frac{a^2}{2(h_0 + a)^2} + \ln \frac{h_0(2h_0 + 2a)}{(h_0 + a)^2} \right]
\]
for $\psi_1$ and $\psi_2$, the $\zeta$-potentials obtained in the same salt solutions were used. $A_{12/3}$ in Eq. (2) has been calculated from the following equation, using $A_{33} = 4.83 \times 10^{-20}$ J for water in vacuum, $A_{11} = 14.8 \times 10^{-20}$ J for silica in vacuum and $A_{22} = 11.5 \times 10^{-20}$ J for latices in vacuum,

$$A_{12/3} = (A_{11} - A_{33})(A_{22} - A_{33})$$

(3)

In Figs. 6 and 7, the total interaction potential curves between silica–silica, latex–latex and silica–latex particles in $1 \times 10^{-3}$ mol dm$^{-3}$ and $1 \times 10^{-2}$ mol dm$^{-3}$ K$_2$SO$_4$ aqueous solutions are pictured in the same drawing. From Fig. 6, it is clear that in $1 \times 10^{-3}$ mol dm$^{-3}$ K$_2$SO$_4$ solution, strong attraction energy between latex and silica particles appears and heterocoagulation will occur predominantly in comparison with the other two homocoagulations. At this salt concentration, the interaction potential between latex–latex particles shows a high enough barrier to prevent mutual coagulation. However, in $1 \times 10^{-2}$ mol dm$^{-3}$ K$_2$SO$_4$ solution, the height of the potential barrier between latex–latex particles becomes about 10 kT which is the lower limit needed to keep the colloid stable. This analysis indicates that the fractional coverage of latex particles on the large silica surface increases with increasing K$_2$SO$_4$ concentration, but the concentration of $1 \times 10^{-2}$ mol dm$^{-3}$ K$_2$SO$_4$ will be an upper limit to make a stable heterocoagulation, because above $1 \times 10^{-2}$ mol dm$^{-3}$ K$_2$SO$_4$ some aggregates of the latex particles will be generated in the course of the experiments.

3. Synthetic process of magnetic composite particles

3.1. Preparation of magnetic heterocoagulates

A synthetic process to prepare composite particles comprised of usual polymer latices, ultra fine magnetic particles and a polystyrene layer was examined under the various solution conditions. As an inorganic material, the magnetic ultrafine powder, NiOZnOF$_2$O$_3$, offered by Sumit-
omo Chemical Co, Japan, was used without further purification. On the other hand, four different polystyrene latices were employed as organic species. The latex-L ($2r = 900$ nm) is a standard sample offered by Japan Synthetic Rubber Co. The other three latex samples, the latex-M ($2r = 600$ nm), the latex-S ($2r = 530$ nm), and the latex-SS ($2r = 180$ nm) were synthesized by the surfactant-free emulsion polymerization in our laboratory [6].

The procedure to prepare the heterocoagulates from the latex-M and the magnetic particles is as follows. To begin with, 200 ml of pure water was added to a beaker containing 0.25 g of the magnetic powder and sonicated for 20 min with a 600 W homogenizer (T-180; Ultrasonic) at the best tuning. Meanwhile, the original latex-M dispersion was diluted with purified water to control the particle number ratio to magnetic particles at 1/4500. These two suspensions were blended and ultrasonic emission was used for another 3 min to promote complete mixing. Next, the pH of the blend suspension was adjusted with nitric acid to pH 2.5 to insure that each particle acquired the opposite charge to one another [7]. After the suspension was kept for 24 h at room temperature, the heterocoagulates, comprised of the latex-M (core) and the magnetic particles (shell), accumulated at the bottom of the vessel. The supernatant was replaced by purified water to remove the residual magnetic particles which did not adhere to the latex surface. The product was repeatedly washed in purified water and kept in a stock bottle. Approximately 0.5 g of the heterocoagulates can be obtained by this procedure.

Fig. 8. Electron micrographs showing the heterocoagulates prepared from different latex samples: (A) Latex-L, (B) Latex-M, (C) Latex-S, (D) Latex-SS.
The model proposed by Hansen et al. [3] calculates the fractional coverage of the heterocoagulates (θ) to be ~1. This high coverage is attributed to the formation of partly multi-particle layers of the magnetic particles on the latex surfaces. Furthermore, it should be noted that the heterocoagulates took over the uniformity as the original latex particles under the suitable mixing conditions. The composite particles were formed by the heterocoagulation of the magnetic particles onto the large latex particles with a constant layer, and they exactly maintain the uniformity of the latex particles after the heterocoagulation with the magnetic particles.

In Fig. 9, the ζ-potential profile of the latex-M particles and the magnetic particles are presented as a function of medium pH, along with that of the heterocoagulates prepared by mixing their original suspensions at pH 2.5. The heterocoagulates display zero ζ-potential at pH 2.5 due to the charge neutralization between the two component particles. This suggests that the rapid sedimentation of the products after the heterocoagulation is attributed to the homoaggregation of the products rather than to the increase of their diameter or density. However, the dynamic light-scattering measurement and the transmission electron microscopy confirm that the aggregated products are re-dispersed into single particles by moderate ultrasonication without any desorption of the magnetic particles from the surfaces of the composite particles. Furthermore, Fig. 9 indicates that the ζ-potential of the heterocoagulates approaches that of the original magnetic particles in the alkaline medium. This behavior suggests that the magnetic particles, which cover the surface of the core latex in the acid and neutral pH systems, desorb from their surface in the alkaline system where the pH is above 9. This implied that the interaction between the surfaces of the two component particles changes from lateral electrostatic attraction into electrostatic repulsion according to the increase of medium pH. From these results, it can be seen that the pH of the system largely dominates the following three aspects of heterocoagulates; the generation and sedimentation in the acidic system, the dispersion in the neutral pH region due to their high surface charge, and the decomposition in the alkaline system.

Scanning electron micrographs (see Fig. 8) show four kinds of heterocoagulates provided from the suspensions of latices with different sizes and magnetic particles. All of these heterocoagulates were prepared by mixing the same NiO-ZnO-Fe₂O₃ dispersion and the respective latex dispersions at pH 2.5 where the ζ-potential of the magnetic particles has the opposite sign to that of the latex particles as shown in Fig. 9. The detail process to prepare the heterocoagulates is given in the literature [7]. The heterocoagulates generated from the latex-L, the latex-M, and the latex-S are composed of the uniform composite particles depositing the small magnetic particles onto the large latex surfaces and all the heterocoagulates are separated as an isolated unit. In contrast with these systems, the heterocoagulates prepared from the latex-SS are made of large irregular aggregates and the regular heterocoagulates were difficult to recognize under any mixing conditions investigated. From thermogravimetric analysis for the uniform composite particles (Fig. 9(B)) indicated that the composition of the heterocoagulates is calculated to be 60.7% latex-M and 39.3% NiO-ZnO-Fe₂O₃ particles by wt%. The application of the model proposed by Hansen et al. [3] calculates the fractional coverage of the heterocoagulates (θ) to be ~1. This high coverage is attributed to the formation of partly multi-particle layers of the magnetic particles on the latex surfaces. Furthermore, it should be noted that the heterocoagulates took over the uniformity as the original latex particles under the suitable mixing conditions. The composite particles were formed by the heterocoagulation of the magnetic particles onto the large latex particles with a constant layer, and they exactly maintain the uniformity of the latex particles after the heterocoagulation with the magnetic particles.

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3.2. Encapsulation of magnetic heterocoagulates

Concerning the heterocoagulates, both desorption of the magnetic particles and dissolution of ion species decrease their value as bioreactors because they inactivate biological functions. Hence, the optimal condition of encapsulation polymerization, in which the heterocoagulate surface is covered with a thin polystyrene layer, was examined. After 24 h on dialysis, a fixed amount of the heterocoagulates prepared from the latex-M was used to examine the eight polymerization conditions set up with regard to the amount of styrene monomer, the kind of initiator, and the presence of a surfactant. An initiator which provides a positive terminal group, azo-bis(isobutylamide hydrochloric acid) was employed, while potassium persulfate was selected as a negative-terminal initiator. Moreover, sodium oleate aqueous solution was adopted to promote hydrophobicity of the magnetic particles on the heterocoagulate surfaces. Approximately 0.2 g of the seed heterocoagulates was dispersed into 180 ml of water using the homogenizer, before it was moved into a special 200 ml vial with a screw cap. After that, distilled water containing a definite amount of K2S2O8 and C17H33COONa was carefully added to the vial. The pH of the sodium oleate aqueous solution was primarily adjusted to pH 6.0 with nitric acid, because the magnetic particles on the heterocoagulates desorb from the latex surface in the alkaline medium (Fig. 9). This vial was set on the rotating disk of polymerization equipment and polymerized for 36 h at 60°C. The conditions and their results are shown in Table 1. As seen in the line of product on Table 1, it is considered that the best condition in the list is the system no. 3 where ideal encapsulation was virtually accomplished. Under the conditions of systems no. 1, no. 2, no. 5 and no. 6 bridging flocculation among the seed particles or the generation of independent latex particles occurred in the course of the polymerization. Similarly, in systems no. 4, no. 7, and no. 8, the flocculation and new particle generation were observed although a part of the seed particles were encapsulated. As a result, it can be considered that sodium oleate is indispensable for the encapsulation of the heterocoagulates, and that potassium persulfate is a suitable initiator for this system.

![Fig. 10. Microphotograph showing the multilayer composite particles after the encapsulation polymerization.](image-url)
Figure 10 is a transmission electron micrograph of the encapsulated composite particles whose surface was covered with a thin polymer layer, and it shows smoother surface than that of the seed particles (Fig. 8).

Figure 11 shows the preparation process of the multilayer magnetic composite particles.

The heterocoagulates were produced from the magnetic ultra-fine powder and the polymer latices with various sizes and functional groups. In this case, the particle size ratio and the $\zeta$-potential of the two components should be noted in order to prepare the heterocoagulates whose fractional coverage is $\sim 100\%$. The prepared heterocoagulates take over the uniformity of the latex particles adopted as the core.

Using the heterocoagulates as the seeds, the optimum condition of encapsulation polymerization with styrene monomer was examined. In this case, it is indispensable to promote the hydrophobicity of the heterocoagulate surface with oleate ions.

As is seen from Fig. 11, the size of multilayer composite particles can be controlled by the diameter of the core latices which are applied primarily. This method realizes the localization of the magnetic particles on the outside of the composite particles covered with a thin polystyrene layer, therefore, they can give full function to the surrounding system.

4. Fabrication of latex superparticles by using emulsion droplets as templates

A novel technique that allows the assembly of different types of colloid particles into ordered multicomponent cluster (superparticles) has been investigated. The main idea is to control the size and the composition of the superparticle during their assembly by gathering and confining their components in a restricted, colloid-size space. Emulsion droplets can be used to provide this restricted space [8].
4.1. Assembly scheme of the negatively charged latices

The superpartides were assembled from the negatively charged 'surfactant free sulfate polystyrene latex'. The stability of the original latex suspension is based only on the electrostatic repulsion between the microspheres [9]. After experimenting with different substances and conditions, we formulated the assembly flowchart, presented in Fig. 12. The latex particles in their original state do not adsorb on the oil droplets. Therefore, the first step (step 1) required is to modify their surface properties so that the microspheres become adsorbable on the oil/water interface. This process is denoted as 'sensitization'. Out of the substances tried as sensitizers, the amino acid lysine worked best. Lysine was used in the form of its monohydrochloride salt at a concentration of 0.017 M. The pH of the thus prepared solution is neutral. The used latex treated with lysine under these conditions did not coagulate. It was however able to slowly adsorb on the octanol/water interface and to form 2D ordered structures. This process was greatly enhanced and quickened by the homogenizer. As the next step (step 2), octanol is emulsified into the sensitized latex suspension. The latex particles are tightly adsorbed onto the droplet interfaces to form structures. At this stage, the interfacial mobility of the particles is of crucial importance. To prevent breakdown, the next immediate step undertaken was the stabilization of the latex/droplet assemblies. This was achieved by quick mixing of the emulsion with casein solution (step 3). By adding casein solution, all coalescence and flocculation processes of the system blocked. The concentration of casein in the system was adjusted at 0.5–1 mg ml\(^{-1}\). It is known that casein blocker is able to gently bind the latex particles around droplets. This possibly results from bridging of the adjacent particles by protein molecules adsorbed on their surfaces. To preserve the superparticle structure during the dissolution of the carrier droplets, the addition of a stronger binding agent (coagulant) is necessary. We used a mixture of HCl and CaCl\(_2\) (step 4), both of whose components are known to be strong coagulants of the used latex beads [10]. The final concentration of the substances in the system after step 4 of the process amounted to 10\(^{-2}\) M HCl and 5 \times 10^{-3} M CaCl\(_2\). The microstructured shells were prepared for the droplet

![Fig. 12. Concrete flowchart [8] for the multistage, interaction-tailored assembly of ordered hollow supraparticles from the sulfate latex. The boxes on the right briefly describe the physical processes that take place at each step.](image-url)
Fig. 13. Optical ‘cross-sectioning’ of two of the obtained supraparticles [8]. By moving the focal plane of the objective up and down, one is able to observe the outer shell structure or the inside of the assemblies. The crack in the big particle allows us to demonstrate that the oil droplet inside it has been dissolved. Bar = 10 μm.

extraction that was carried out by adding 50 vol.% ethanol (step 5). We found empirically that the best yield is obtained when the ethanol is introduced as quickly as possible—this was achieved by injection. After the carrier octanol droplets are dissolved, the supraparticle assemblies remain suspended in water/ethanol environment.

The supraparticles obtained in this way posses a structure of empty ordered shells from the coagulated latices. Microscopical pictures of suspended assemblies are presented in Fig. 13. It is seen that the particles within the shell preserve the 2D ordered pattern that was formed during the adsorption on the droplet surface. As the focal depth of the objective is only a few microns, the bigger superparticles could be optically ‘cross-sectioned’ by focusing on their top, bottom or equatorial planes. The ‘cross-sectioning’ technique allows us to prove that most of the obtained spherical shells are ordered all around and that no oil droplet is present inside.

4.2. ζ-potential of the latex particles at the different stages of the process

The assembly scheme presented in Fig. 12 involves and makes use of many types of colloid interactions. To clarify this point, we carried out electrophoretic measurements on the ζ-potential of latex beads immersed in environments similar to the ones in the assembly process. The obtained data are presented in Table 2. The table also includes data for the measured ζ-potential of the octanol emulsion droplets.
The sensitization and adsorption of the latex particles onto the droplet surfaces (steps 1 and 2) seems to be closely related to the electrostatic charge of the particles. This charge might prevent adsorption in two ways: (i) by electrostatic repulsion between the particles and the droplets, as both of these are negatively charged; and (ii) because of hydration forces [11]. The high negative potential of the sulfate latex at the beginning of the process makes the adsorption process impossible. After sensitization with lysine, a decrease of the potential magnitude of about 20 mV is recorded (Table 2). We expect that the positively charged lysine molecules decrease the surface potential of the microspheres by binding to the negative sulfate groups. The properties of polylysine as a high molecular weight polyelectrolyte that binds to the latex surface decreases its potential, and causes flocculation are well known [12]. The activity of monomolecular lysine at the used concentration appears to be lower, so it modifies the surface charge but without inducing flocculation. On the basis of the well-known formulae and using the typical parameters from the literature [13], we have estimated the homocoagulation threshold of the used latex to be \( \approx -20 \) mV. The \( \zeta \)-potential of the latex-sensitized latex is above that point, and it cannot coagulate or spontaneously adsorb onto the droplet surfaces. The sensitized microspheres however are able to adsorb on the oil surfaces when propelled and pressed against the oil droplets by the homogenizer action. After adsorption, we observe that the beads remain mobile on the droplet surface and structure is induced by the restricted 2D space and the repulsion between the adsorbed microspheres. The lysine may also play a role by decreasing the hydration repulsion between the latex and oil and by involving depletion interactions in the system, but at present we do not have direct evidence how these interactions are involved in the process.

A further decrease of the potential is recorded after casein is introduced to the system and adsorbed on the latex surfaces (Table 2). On the basis of literature data [14], this decrease of the \( \zeta \)-potential can be attributed to the movement of the shear plane further into the solution rather than an actual decrease of the surface charge of the particles. The major role of casein however is not to modify the electrostatic interaction but to evoke steric repulsion by covering the latex and droplet surfaces with a voluminous protein adsorption layer [13]. This prevents any further processes of interdroplet coalescence or latex flocculation.

The \( \zeta \)-potential of the latex falls down to negligible values after HCl and CaCl\(_2\) are introduced. This leads to very strong sticking of the microspheres in contact and blocking of any electrostatic repulsion that could lead to disassembly after the template droplets are removed. As suggested in the literature [15], the Ca\(^{2+}\) ions may also be involved in electrostatic bridging of the closely situated particle surfaces. The low pH and the calcium ions may lead to changes within the casein adsorption layer, though they obviously do not affect too much its steric protection barrier around the assembled supraparticles. Thus, the main role of the coagulation step in the overall assembly scheme is to increase the structural stability within the latex shells.

### Table 2

Zeta-potentials of systems involved in supraparticle preparation

<table>
<thead>
<tr>
<th>System</th>
<th>( \zeta )-potential (mV)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate latex</td>
<td>(-9.12 \pm 4.89)</td>
<td>6.0</td>
</tr>
<tr>
<td>Sulfate latex + lysine</td>
<td>(-69.79 \pm 6.47)</td>
<td>5.5</td>
</tr>
<tr>
<td>Sulfate latex + lysine + casein</td>
<td>(-48.78 \pm 3.50)</td>
<td>5.6</td>
</tr>
<tr>
<td>Sulfate latex + lysine + casein + HCl + CaCl(_2)</td>
<td>(0 \sim -20)</td>
<td>2.1</td>
</tr>
<tr>
<td>Octanol emulsion droplets</td>
<td>(-22.65 \pm 11.09)</td>
<td>6.1</td>
</tr>
<tr>
<td>Octanol emulsion droplets + lysine</td>
<td>(-15.83 \pm 7.91)</td>
<td>5.8</td>
</tr>
</tbody>
</table>

### References