

Preparation of composite fine particles by heterocoagulation

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Abstract: To prepare regular composite particles comprised of organic and inorganic compounds, based on heterocoagulation theory, the properties of the mixture of small amphoteric latices ($2a = 250$ nm) and large spherical silica ($2a = 240$ – 1590 nm) were investigated as a function of pH, particle number ratio, particle size ratio and electrolyte concentration in the medium. It is apparent that under suitable conditions, we may prepare a stable mixed suspension comprising uniform composite particles, which are made up of many latices regularly adsorbed on silica surfaces, and each composite particle is undergoing Brownian motion as an isolated unit. This new composite particle is very stable for electrolyte, base and acid medium, and its surface charges (sign and magnitude) can be controlled by changing the pH of the medium.

Key words: Composite particles, heterocoagulation, silica particle, polymer latices, unlike particles.

1. Introduction

Recently, in addition to the ordinary uses, some special needs for fine particles have been gradually increasing in fields such as electronics, biology, pharmacology, the photographic industry, etc. For example, fine particles are used for conductive-paints, plastisol for display devices, carriers in antibody-enzyme diagnostic tests, etc. For these applications, it is necessary that the fine particles have a special quality to meet their own application requirements.

In recent papers, E. Matijevic et al. [1–3] have investigated various behaviours of mixed colloid dispersions obtained by mixing differently preformed particles or by precipitating one kind of solid in the presence of already existing particles. In the former, 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, in this paper, we report on the syntheses and properties of heterocoagulate generated from mixtures of amphoteric polymer latices with a constant particle size ($2a = 250$ nm) 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. We can expect that these new characteristics will serve to extend its usefulness in a wide variety of ways as a functional fine particle.

2. Experimental

Preparation of single dispersion

Four different monodispersed particles of silica ($2a = 240$ nm, 460 nm, 960 nm, 1590 nm) were prepared by essentially the same procedure as in the method of Stöber et al. [4]. The particle size of

the silica samples was subjected chiefly to the conditions (especially temperature) of hydrolysis of $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ by the aqueous NH_3 solutions.

The latex sample consisted of amphoteric polymer particles with a diameter of 250 nm, made by the method described by Hömola et al. [5].

All the single dispersions consisted of high monodisperse spherical particles, with D_w/D_n always < 1.04 , were used after extensive dialysing against distilled water to remove ionic impurities. The characterization data for these samples are shown in Table 1.

Measurements of electrophoretic mobilities

The electrophoretic mobilities of the single particles of latices and spherical silica were determined at various pH values in an aqueous solution of 5×10^{-3} mol dm^{-3} KCl at 25 °C. The measurements were performed in a Rank Brothers micro-electrophoresis apparatus (MK-2) using a rectangular glass cell. The ζ -potential was derived following the method of Wiersema et al. [6].

The sample of composite particles used to determine the electrophoretic mobilities was prepared as follows: a few drops of the heterocoagulates suspension prepared under the various conditions were added to the aqueous solutions of 5×10^{-3} mol dm^{-3} KCl adjusted at a definite pH, and mixed quickly. After the suspensions had been left standing for 2 h, the electrophoretic mobilities of the contents were determined using the same technique with which the single dispersion determinations were performed. Typical results of the electrophoretic mobility for the single silica and the latex suspension are shown in Figure 1.

Preparation of heterocoagulates and characterization

Into glass-stoppered vials (10 ml), 2 ml of salt solutions of various concentrations were carefully added on top of a silica suspension (5 wt%; 2 ml). Thereafter, on top of these, 2 ml portions of latex suspensions of different contents were added, using a pipette. After rotating end-over-end (10 min^{-1}) for 30 min, the system was left to stand to allow the heterocoagulated particles to settle out. The change of extinction of the supernatant was measured using a spectrophotometer (Spectronic 20-A, Shimadzu Co. Ltd., Japan) at a wavelength of 550 nm.

The heterocoagulating state of mixed dispersion was estimated visually by direct observation technique. The optical microscope used was a lateral type metallurgical microscope with a magnifica-

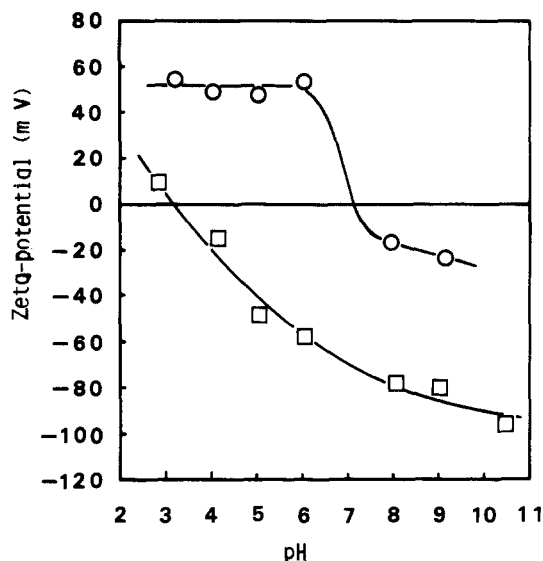


Fig. 1. Zeta-potentials of silica (□) and latex particles (○) as a function of pH at 5×10^{-3} mol dm^{-3} KCl

tion of 2000 \times (Axio Mart, Carl Zeiss Ltd., West Germany). Some amounts of the heterocoagulates were dropped into the observation cell, made of a Pyrex glass tube, 100 mm high and 15 mm in diameter, with a thin glass window at its lower end. The sample was observed through the window by the oil immersion method. Furthermore, the morphology of heterocoagulates was observed by a scanning electron microscope.

Determination of adsorption isotherms

The determination of the adsorption isotherms for the latex particles onto the large silica particles was performed in 25 ml Pyrex glass tubes with screw caps. The concentration of large silica particles was fixed at 5 wt%, whereas the concentration of the small latex particles varied from 0.5 to 2 wt%. Into each tube the silica suspension, electrolyte solution, water and latex suspension were added in this order, and were separately pre-equilibrated at the same pH (e.g. pH 5.2). In each sample, the amount of water was adjusted to give a total volume of 20 ml. All the contents was then mixed by rotating end-over-end at 25 °C for 30 min. After standing for 24 h, the large heterocoagulates were separated by sedimentation and the concentrations of the remaining, unattached latex particles in the supernatant were determined by dry weight analysis. The initial latex concentration was also determined and the amount adsorbed was calculated from the material balance.

Desorption experiments

The reversibility of the adsorption process was checked by a desorption experiment for the mixed systems of latices and silica 300/1 by their number ratio. The surface of the silica was first adsorbed completely by the latices at pH 5.2, according to the usual procedure, and the amount of adsorption was determined by measuring the residual concentration of the latices. Thereafter, the supernatant was replaced with distilled water controlled at a definite pH

Table 1. Particle diameters of spherical silica and latex sample

Sample	Diameter (nm)	D_w/D_n^a	Particle size ratio Silica/latex
Silica-L	1590	1.03	6.36
Silica-M	960	1.01	3.84
Silica-S	460	1.03	1.84
Silica-ss	240	1.04	0.96
Latex	250	1.02	—

^a) Dispersity of the latex particle, where D_w and D_n are the weight- and number-average particle diameters, respectively.

(usually at pH 5.2) and the second mixing was performed in the new medium. After a desorption period of 2 h, the determination of the latex concentration for the supernatant was conducted in the same way as described above, and the adsorbed amount left on the silica was compared with the results of initial equilibration. This process was repeated six times on the same sample.

Thermogravimetry

To clarify the composition of the regular composite, thermogravimetric analysis was conducted using a Thermoanalyzer (Type-560-GH, Seiko Instruments and Electronics Co. Ltd., Japan) equipped with an electron balance. Ca. 60 mg of the sample placed on Pt-pan was analysed thermally in an air flowing atmosphere at the heating rate of 10°C/min.

3. Results and discussion

1. Heterocoagulation behaviour

The properties of heterocoagulates generated from the mixture of amphoteric latices and the largest silica particles (Silica-L) were examined under various conditions. 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 4–6, where the two components were charged with opposite signs (see Fig. 1).

The next important control parameter is the particle number ratio (PNR) of the component particles when they are mixed in the vessel. To investigate this parameter, the stability of the mixed systems prepared under the various PNR was examined in a constant ionic medium (pH 5.2, 1×10^{-5} mol dm⁻³ KCl), where the numbers of silica particles were kept constant at 30 mg/ml. Figure 2 shows some typical transmittances of the systems vs. elapsed time curves obtained from the mixtures of different PNR. Figure 3 shows the relation between the transmittance of the system and its PNR at 1 h and 24 h after mixing the two single components. Under the systems with relatively low numbers of latex particles (PNR = 10/1–120/1), the systems coagulated irregularly and settled quickly on account of their large mass, as indicated by the high transmittance values. With increasing particle numbers of latices (PNR = 150/1–500/1), however, the mixed systems became stable and exhibited transmittance comparable with those of the initial single components. The transition in the curves depicting the unstable and stable binary system is rather abrupt. The critical PNR is

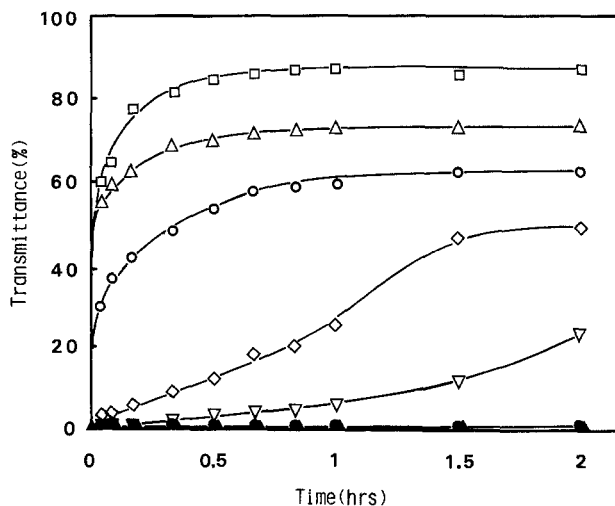


Fig. 2. Relation between transmittance and elapsed time at the various PNR: (□) 20/1, (△) 80/1; (○) 100/1; (◇) 120/1; (▽) 140/1; (●) 0/1; (▲) 160/1–500/1

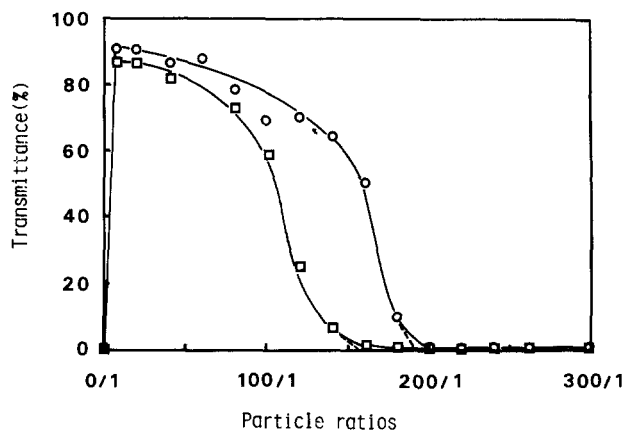


Fig. 3. Transmittance vs. particle number ratio curves at 1 h (□) and 24 h (○) after mixing two component particles

obtained by extrapolating the steep portion of the transmittance vs. PNR curves to the abscissa. The critical value obtained from this analysis enabled calculation of the number of latex particles adsorbed per silica particle. The numbers determined from the two series are 160 and 195, respectively. The average of these two numbers agrees well with the value of 180, calculated by following the method of Matijevic et al. [2].

Figure 4. shows optical micrographs of the heterocoagulates generated under conditions of lower PNR (A) and of higher PNR (B) relative to the critical value. It may be seen that at PNR higher than the critical value, the suspension is comprised of uniform composite particles with white edges, which are composed

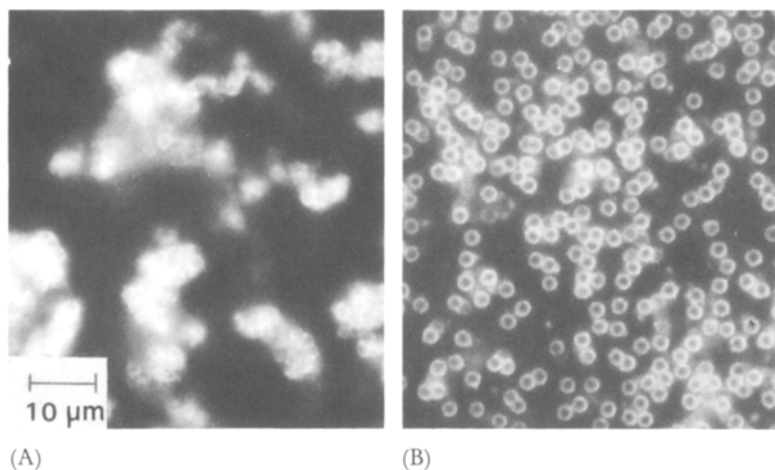


Fig. 4. Optical micrographs showing the heterocoagulates prepared at different PNR: (A) 100/1, (B) 400/1

of many adsorbed latex particles, and each composite particle is still undergoing Brownian motion as an isolated unit. Figure 5 shows a scanning electron micrograph of one composite particle prepared at PNR = 300/1, which defines in detail the structure of the composite particle. It is apparent that the composite takes a raspberry shape with one silica in the core. In contrast to this, the heterocoagulates generated under the conditions of PNR lower than the critical value, are composed of large, irregular aggregates, which explains well why these systems settle quickly.

Finally, the effect of the particle size ratio on the composite formation was investigated. When Silica-M ($2a = 960$ nm) was used as one component, the heterocoagulation behaviour was almost identical to that of Silica-L except that the Silica-M had a different criti-

cal value of PNR (80). On the other hand, where Silica-S ($2a = 460$ nm) and Silica-SS ($2a = 240$ nm) were used as the silica components, the regular composite hardly occurred, at all pH and PNR investigated.

2. Adsorption isotherm

Figure 6 shows some typical isotherms for the amphoteric latices on the largest silica sample (Silica-L) at the various K_2SO_4 concentrations, where all the systems were controlled at pH 5.2 using KOH and HCl aqueous solutions. It is evident that the isotherms for the positive latices on a negative silica surface are all of the very high affinity types within the K_2SO_4 concentration range of 10^{-5} mol dm^{-3} to 10^{-2} mol dm^{-3} , with a well-defined plateau. This means that in these

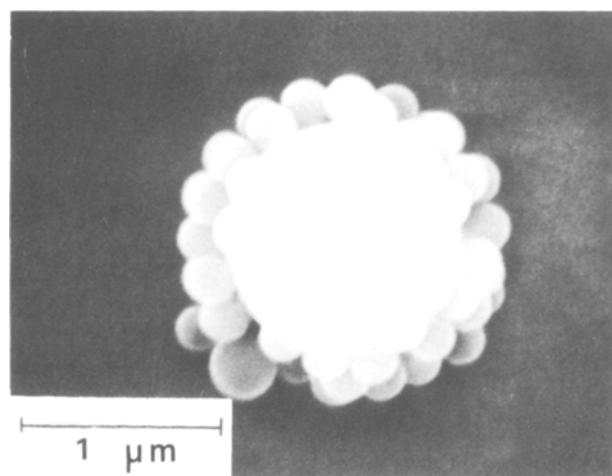


Fig. 5. Scanning electron micrograph of one composite particle prepared at PNR = 300/1

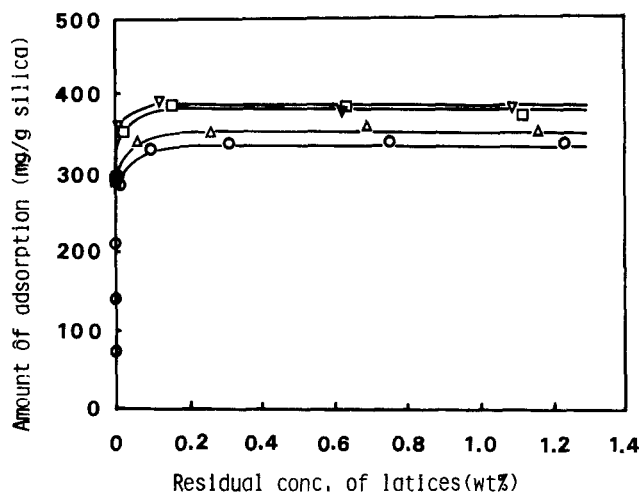


Fig. 6. Adsorption isotherms of amphoteric latices onto silica at various K_2SO_4 concentrations: (∇) 1.46×10^{-2} mol dm^{-3} ; (\square) 1.46×10^{-3} mol dm^{-3} ; (\triangle) 1.46×10^{-4} mol dm^{-3} ; (\circ) 0 mol dm^{-3}

concentrations, adsorption proceeds as the characteristic of the monolayer, physical adsorption [2]. This may be due to the strong blocking effect of adsorbing particles, i. e. the plateau being caused by the strong electrostatic repulsion between the adsorbing latices and the suspending latex particles [7]. However, in K_2SO_4 aqueous solutions higher than $2 \times 10^{-2} \text{ mol dm}^{-3}$, no reproducible isotherm could be obtained under all conditions tested; only some irregular aggregates were generated in the course of the adsorption experiment.

In Figure 7, the adsorption isotherms for the latices on four kinds of silica samples with different particle size, obtained under the same ionic conditions (pH 5.2, $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ KCl}$), are compared. The amount adsorbed, A , is expressed in the form of the fractional coverage, θ , as given by $\theta = \frac{A}{A_s}$, where A_s is the maximum number of latex particles calculated by following Matijevic et al. [2]. A remarkable feature is the dependence of the θ value on the particle size of a silica sample, i. e. the θ value decreases with decreasing particle size, and round-like isotherms appeared in the systems of Silica-S + latices and Silica-SS + latices. This behaviour may be explained as being due to the coagulation state of the component particles, i. e., in the state of irregular flocculation, one latex particle may be adsorbed simultaneously with two or three adjacent silica particles, by interparticle bridging, and the

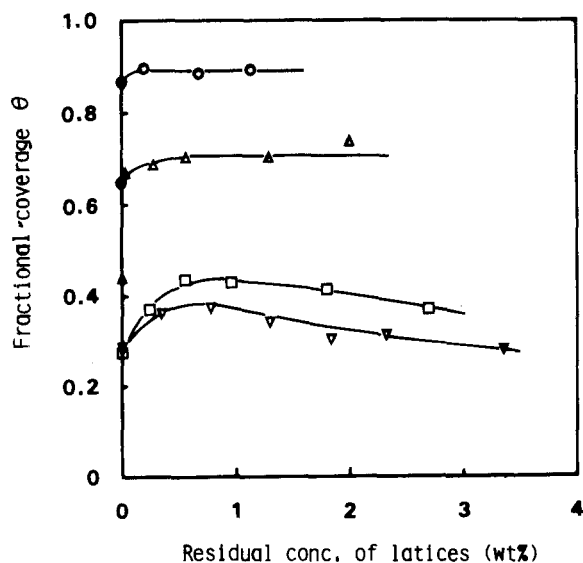


Fig. 7. Adsorption isotherms of amphoteric latices onto silica particles with different size; (O) $2a = 1590 \text{ nm}$; (Δ) $2a = 960 \text{ nm}$; (\square) $2a = 460 \text{ nm}$; (∇) $2a = 240 \text{ nm}$

limited adsorbable area on the silica surface is thus saturated more easily than in regular heterocoagulation. Therefore, a small θ value and a marked round-like isotherm are observed in the system of Silica-SS + latices, especially at the high concentration region of the latex particles.

3. Desorption behaviour

To check the structural stability of the composite material, the desorption behaviour of the latex particles from the silica surface was investigated. In Figure 8, the adsorbed amounts of latex particles left on the silica after washing with pure water maintained at a different pH are compared with the initial values of adsorption as a function of the number of washing times, where the initial equilibration was performed in the medium held at pH 5.2. As may be seen, repeated washing has no significant effect on adsorbed amounts left on the silica, except for pH 11.8, i. e. it is clear from Figure 8 that under the usual washing condition, the adsorption of the present system behaves as an irreversible process. Further, the irreversibility of the present adsorption was confirmed by thermogravimetric analysis. Figure 9 presents a typical thermogram for the final composite particles after washing six times with water at pH 5.2, where the thermograms under the single component systems of latex and silica are also indicated. It may be seen from Figure 9 that the thermogram for the composite particles exhibits a marked mass loss at ca. 300°C . This can be attributed to the decomposition of any organic (latex) component included, and it can be seen from the same figure that the

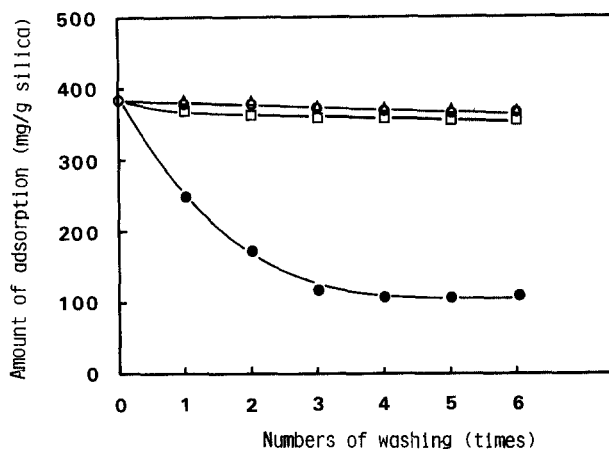


Fig. 8. Effect of pH of washing medium on the desorption efficiency: (O) pH = 5.2; (Δ) pH = 9.1; (\square) pH = 10.4; (\bullet) pH = 11.8

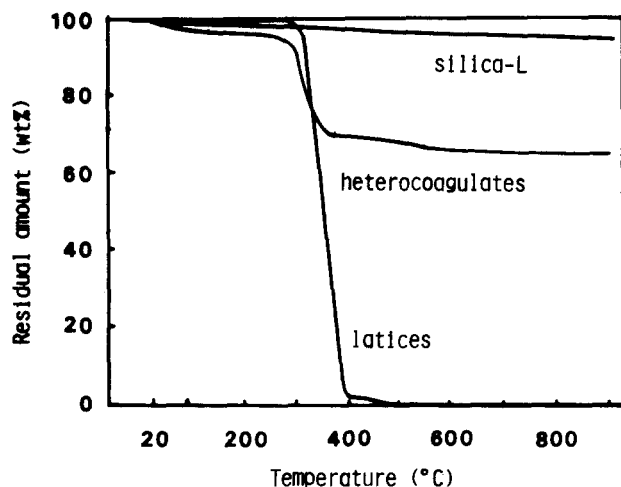


Fig. 9. Thermograms of heterocoagulates, latices and silica sample (Silica-L)

single latices are completely decomposed near 300°C, while single silica mass remains almost the same up to 600°C. Therefore, the individual compositions of the silica and latices, included in the final composite, can be evaluated by analysing the weight fraction of mass loss for the total weight from the thermograms. Table 2 shows the values of residual latices on silica after washing six times with a different washing medium. It is apparent that almost all of the initial adsorbed latices remain on silica, even after washing six times under the ordinary washing conditions.

On the contrary, some different behaviour was noted when desorption was initiated in a strong basic medium (pH 11.8). In the case, over 97% of adsorbing latex particles were removed from the silica surface by the washing of composite particles. This finding, qualitatively, agrees with the result obtained from the analytical experiment, as shown in Figure 8.

Such a different behaviour in the desorption of latices from a silica surface by changing the washing

Table 2. Residual amounts of latices onto silica after washing six times under different washing mediums

pH of washing medium	^{a)} Residual amount of latices (mg/g silica)
5.1	380.0
9.1	371.6
10.4	375.3
11.8	9.9

^{a)} from thermogravimetry

medium, can be explained by the different interaction forces between latices and silica particles, i.e. from electrophoretic measurements (see Fig. 1), it is expected that the interaction force between these two kinds of particles changes from lateral electrostatic attraction to lateral repulsion, as the pH of the medium is changed.

4. Effect of electrolyte concentration

As may be seen from Figure 6, the amount of adsorption is affected by the ionic condition in the medium. Figure 10 shows the relation between the electrolyte concentration and the maximum adsorption under the two systems (Silica-L + latices and Silica-M + latices), where all experiments were carried out at 25°C in solutions maintained at pH 5.2; the amount adsorbed is expressed in terms of the fractional coverage, θ . It is evident that θ for both systems increases either with a different dependence by increasing the K_2SO_4 concentration and eventually approaches $\theta = 1$ at $1.46 \times 10^{-2} \text{ mol dm}^{-3} K_2SO_4$ for a large size. The different dependence of θ with K_2SO_4 concentration may be explained by the effect of the curved surface of adsorbent silica, i.e. with decreasing particle size ratio of the two component particles, the small particles seem to be adsorbed on a curved surface. This effect will weaken the double layer interaction between the adjacent adsorbing particles.

Figure 11 shows the desorbing behaviour for the composite particles prepared in the concentrated salt solutions, where the desorption efficiency is compared

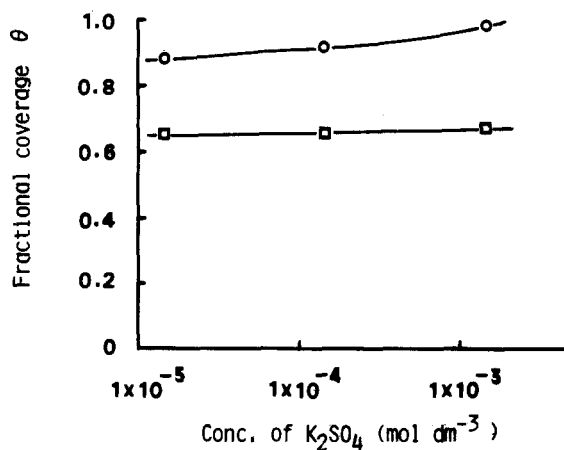


Fig. 10. Relation between amount of adsorption (θ) of latices onto silica with different particle size, and concentration of K_2SO_4 : (O) $2a = 1590 \text{ nm}$; (\square) $2a = 960 \text{ nm}$

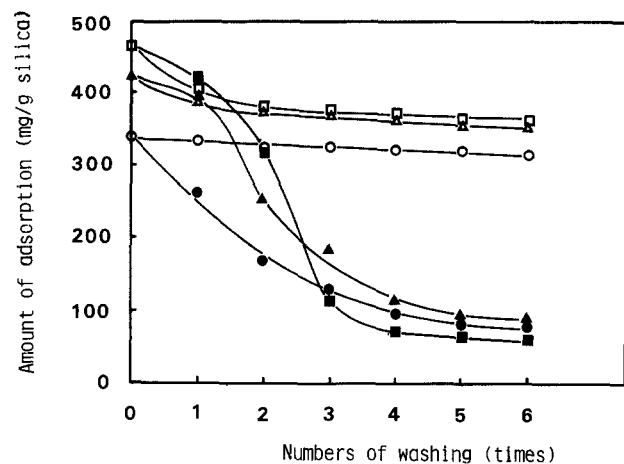


Fig. 11. Desorption behaviour of amphoteric latices from the composite particles prepared in the concentrated salt solutions, where two different washing mediums (open symbols: pH 5.2; solid symbols: pH 11.8) were used: (□) $2.48 \times 10^{-1} \text{ mol dm}^{-3} \text{ MgCl}_2$; (Δ) $7.27 \times 10^{-2} \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$; (○) $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ KCl}$

for two different washing mediums (pH 5.2 and pH 11.8). The behaviour observed is almost similar to the results seen in Figure 8, but it is important to notice that the residual amount on the silica, after washing six times with pure water at pH 5.2, increases with increasing electrolyte concentration.

In Figure 12, the electrophoretic mobilities of the composite particles prepared at the different electrolyte concentration after washing six times, are presented as a function of the medium pH, as well as data on the amphoteric latices. As may be seen, a reversal of charge is observed in all the samples, and the isoelectric point (IEP) under the composite system occurs at ca. pH 8, which is not so different from the IEP of the single latices. Moreover, the fact that the limiting, net positive mobility, attained at pH 6–3, increases with the increasing electrolyte concentration, is also in line with the increase in latex adsorption with increasing electrolyte concentration.

Furthermore, it is very important to know that the content of inorganic material and organic material in composite particles can be controlled easily by changing the electrolyte concentration in the medium.

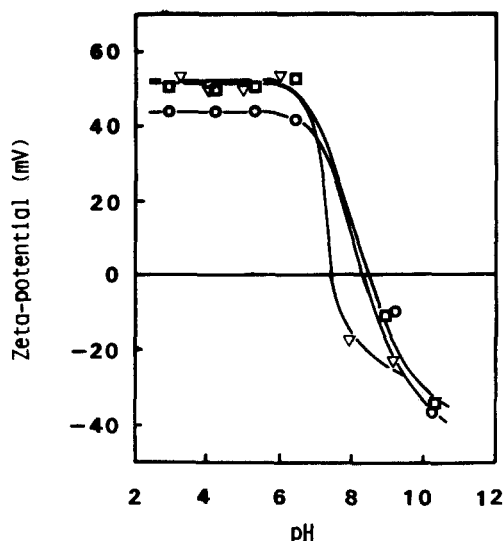


Fig. 12. Zeta-potentials vs. pH curves for composite particles prepared at the different electrolyte concentrations: (□) composite particles prepared at $2.48 \times 10^{-1} \text{ mol dm}^{-3} \text{ MgCl}_2$; (○) composite particles prepared at $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ KCl}$; (▽) amphoteric latices

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