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ORIGINAL CONTRIBUTION

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Stability of the polymerizable surfactant stabilized latex particles during semibatch emulsion polymerization

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Abstract The effect of the polymerizable surfactant, sodium dodecyl allyl sulfosuccinate (JS-2), on the stability of polybutyl acrylate latex particles during semibatch emulsion polymerization was investigated in this work. Experimental data show that the ionic strength is the most important parameter in determining the latex stability during the reaction. Both the amount of coagulum produced by intensive coagulation and percentage of the particle volume change (ΔV) caused by limited flocculation increase with increasing electrolyte concentration. The parameter ΔV increases significantly when the concentration of JS-2 in the initial reactor charge ($[\text{JS-2}]_i$) increases. The amount of coagulum increases rapidly when the agitation speed is increased from 400 to 800 rpm. Experiments of coagulation kinetics were carried out to study the stability of latex products toward added salts. The experimental data show that the chemical stability of the latex product increases with increasing pH. Furthermore, the critical coagulation concentration and diffuse potential increase with increasing $[\text{JS-2}]_i$. It is postulated that the increasing electrostatic attraction force between two approaching particles due to the increased $[\text{JS-2}]_i$ can increase the apparent magnitude of Hamaker constant.

Key words Latex stability – polymerizable surfactant – semibatch – emulsion polymerization – coagulation kinetics

Introduction

Semibatch emulsion polymerization [1–4] is widely used in the production of latex products, which can be used directly in such applications as coatings and adhesives. Conventional surfactant species (e.g., sodium dodecyl sulfate) present in the latex product can migrate to the surface layer of the polymeric film and can have a negative effect on applications such as adhesion of the pressure-sensitive adhesives. This problem can be eliminated by means of a polymerizable surfactant, sodium dodecyl allyl sulfosuccinate (JS-2), to replace the conventional surfactant. The chemically incorporated JS-2 molecules in the emulsion polymer are incapable of diffusing toward the surface layer of the polymeric film and deteriorating film properties.

Recently, the authors have demonstrated how to use JS-2 to prepare polybutyl acrylate latices with controlled particle sizes in a semibatch reactor [4]. It has been shown that JS-2 increases the particle surface charge density significantly and, thereby, reduces particle size (as small as 90 nm) of the latex product. Such a small particle size has not been achieved by the surfactant-free technique (normally greater than 300 nm). The concentration of JS-2 in the initial reactor charge is the most important parameter in controlling the particle size of latex products. The data also show that JS-2 plays a similar role in particle nucleation and growth to the conventional surfactant sodium dodecyl sulfate. The soap titration experimental data show that the saturated particle surface area occupied by one molecule of JS-2 is 0.36 nm^2 for the latex prepared by the surfactant-free technique. Furthermore, the saturated particle surface area covered by one molecule of JS-2 increases with particle surface polarity for the JS-2 stabilized latices. The fraction of the chemically incorporated JS-2 buried inside the particles increases with an increase in the final latex particle size.

The objective of this work was to continue with the subject concerning the colloidal stability of JS-2 stabilized latices. For example, coagulation of latex particles induced by mechanical agitation will lead to formation of coagulum during polymerization. This factor can cause problems (e.g., filtration and reactor fouling problems) in the plant and increase the product cost. Note that not all flocculation events will result in the formation of coagulum. In addition to conversion of monomer to polymer inside the particles, these particles can grow through limited flocculation [5] and yet these particles can be still stable enough to remain in water. Limited flocculation can make the task of particle size control more difficult. Chern et al. [2, 3] have shown that the degree of limited flocculation can be evaluated by the percentage of the particle volume change (ΔV) occurring during the monomer addition period. The parameter ΔV can be calculated as follows:

$$\Delta V = [(d_f/d_f')^3 - 1] \times 100\% \qquad (1)$$

where d_f is the measured particle diameter of the final latex. The parameter d_f' is the calculated particle diameter of the final latex if both secondary nucleation and limited flocculation do not occur during monomer addition. For example, if d_{15} (nm) and N_p are the particle diameter and total number of particles, respectively, of the sample taken immediately before the start of monomer emulsion feed, $W_m(g)$ is the total weight of fed monomer and ρ (g/cm^3) is the density of polymer, then d_f' can be calculated according to the following equation:

$$d_f' = [d_{15}^3 + 6 \times 10^{21}\, W_m/(\pi \rho N_p)]^{1/3} . \qquad (2)$$

The objective of this work was to study the effects of various reaction parameters on the coagulation process for semibatch emulsion polymerization of butyl acrylate stabilized by JS-2. Both the parameters ΔV, caused by limited flocculation, and coagulum collection will be used to investigate the effects of various parameters on the latex stability. Another goal of this project was to use experiments of coagulation kinetics [6–8] in combination with DLVO theory [9, 10] to determine the critical coagulation concentration (CCC), diffuse potential (ψ_δ) and Hamaker constant (A) of the latex products.

Experimental

The chemicals used in this work were butyl acrylate (BA) (Formosa Plastics Co.), sodium dodecyl sulfate (SDS) (Henkel Co.), sodium alkyl allyl sulfosuccinate (Eleminol JS-2) (Sanyo Chemical Industries), sodium persulfate (Riedel-de Haen), nitrogen (Ching-Feng-Harng Co.), sodium chloride (Riedel-de Haen) and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance $< 0.057\,\mu\mathrm{S cm}^{-1}$). The monomer BA was distilled under reduced pressure before use. All other chemicals were used as received.

Polymerization was carried out in a 1-liter glass reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a reflux condenser. All process water along with the initial surfactant and monomer were charged to the reactor at room temperature. The initial reactor charge was purged with nitrogen for 10 min to remove the dissolved oxygen while the reactor temperature was brought to 80 °C. The reaction was then initiated by adding the initiator solution to the reactor. After 15 min, the monomer emulsion was fed to the reactor over 240 min by an FMI pump. Polymerization temperature was kept at 80 °C throughout the reaction. After the end of the monomer emulsion feed, the reaction system was maintained at 80 °C for 30 min to reduce the level of the residual monomer. The theoretical solid content at the end of the reaction is 40%.

The latex product was filtered through 40-mesh (0.42 mm) and 200-mesh (0.074 mm) screens in series to collect the filterable solids. Scrap adhering to the agitator, thermometer and reactor wall was also collected. Total solid content was determined by the gravimetric method. The data on the particle size distribution were obtained from dynamic light scattering (DLS, Otsuka Photal LPA-3000/3100). The zeta potential (ζ) of the latex particles was determined by Malvern's Zetamaster. For appropriate measurements, the latex product with a volume of 0.05 ml was diluted with 100 ml water to adjust the number of photons counted per sec (cps) to a proper value of around 5000–15000. The dilution water has the same pH and conductivity as the original latex product. The pH and conductivity of the dilution water were adjusted by using HCl, NaOH, and NaCl. Hence the latex particles should be exposed to a similar aqueous environment as compared to the original latex product after sample preparation. Five measurements were made for each latex sample and the average of these five measurements was reported as the ζ of the latex product.

The absorbance of the dialyzed latex sample (MWCO = 12000–14000, solid content = 0.02%) was measured by a spectrophotometer (Shimadzu UV-160A) at 540 nm for determination of CCC of the latex product. The pH and ionic strength of the latex sample were adjusted by using a NaOH, HCl, and NaCl.

Results and discussion

Latex stability during polymerization

First, a two-level factorial design (three variables, eight experimental points plus one for the midpoint) was used to study the effects of important reaction variables on the latex stability during polymerization. The variables selected for study were: i) X_1 = JS-2 concentration in the initial reactor charge ($[\text{JS-2}]_i = 0.01\%$–0.50% based on water in the initial reactor charge), ii) X_2 = JS-2 concentration in the monomer emulsion feed ($[\text{JS-2}]_m = 0.5\%$–1.0% based on total monomer) and iii) X_3 = concentration of Na^+ ions ($[\text{Na}^+] = 0.15\%$–0.40% based on total water). In the designed experiments, $[\text{Na}^+]$ in the initial reactor charge was maintained constant by means of NaCl. The remaining NaCl, required to adjust the latex product to the designed electrolyte concentration, was placed in the monomer emulsion feed. The initiator concentration was kept constant (0.25% based on water in the initial reactor charge) throughout this work. The agitation speed is 400 rpm unless otherwise stated.

To test the batch-to-batch variations, the midpoint experiment (recipe: $[\text{JS-2}]_i = 0.255\%$, $[\text{JS-2}]_m = 0.75\%$ and $[\text{Na}^+] = 0.275\%$) was carried out twice. The average d_f, total scrap and ΔV are 159.6 ± 4.6 nm, 2.833 ± 0.066% and 158.0 ± 34.8%, respectively, and the reproducibility of the runs is good except for ΔV. Table 1 summarizes the calculated standardized effects of each variable on the latex stability in the factorial design. The amount of scrap formed during polymerization, for example, will decrease 0.461% with respect to the overall average of scrap when $[\text{JS-2}]_i$ is increased from the lowest level (0.01%) to the highest level (0.5%). Similarly, the parameter ΔV will increase 393.5% with respect to the overall average of ΔV when $[\text{JS-2}]_i$ is increased from the lowest level to the highest level. The parameter $[\text{Na}^+]$ shows a significant effect on the amount of scrap produced. Furthermore, the total scrap can be reduced significantly with increasing $[\text{JS-2}]_m$. This is because the surfactant gradually added to the reactor will increase the surface charge density on the growing particles and thereby greatly improve the latex stability (see the ζ data in Table 1).

Based on the above factorial design, the following empirical, predictive equations for total scrap and ΔV were developed.

$$\begin{aligned}\text{Total Scrap}(\%) = {} & -1.07 + 13.69X_1 - 2.21X_2 + 17.29X_3 \\ & - 17.14X_1X_2 - 90.64X_1X_3 - 56.08X_2X_3 + 1.50X_1^2 \\ & + 6.72X_2^2 + 118.05X_3^2 + 108.52X_1X_2X_3 \end{aligned} \tag{3}$$

$$\begin{aligned}\Delta V(\%) = {} & 95.77 - 1490.74X_1 + 17.41X_2 - 855.63X_3 \\ & + 43.89X_1X_2 + 8309.88X_1X_3 - 167.70X_2X_3 \\ & + 365.44X_1^2 + 23.48X_2^2 + 1648.46X_3^2 \\ & - 1021.88X_1X_2X_3 \, . \end{aligned} \tag{4}$$

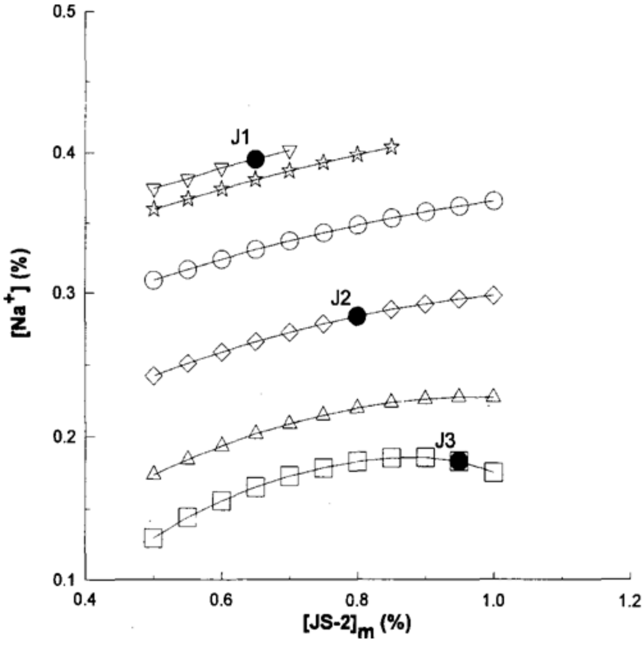
Figure 1 shows a typical contour plot of scrap constructed from Eq. (3), in which $[\text{JS-2}]_i$ is equal to 0.255%. Considering, for example, the curve with the amount of scrap

Table 1 Standardized effects of each variable on total scrap, percentage of particle volume change and zeta potential

	Total scrap (%)	ΔV (%)	$-\zeta$ (mV)
$[\text{JS-2}]_i$ (%)[a]	−0.461	393.5	9.3
$[\text{JS-2}]_m$ (%)[b]	−2.152	−26.7	8.1
$[\text{Na}^+]$ (%)	9.449	462.2	−15.6
Overall Average[c]	4.717	197.4	82.1

[a] JS-2 concentration in the initial reactor charge.
[b] JS-2 concentration in the monomer emulsion feed.
[c] Overall average of the designed experiments.

Fig. 1 Contour plot of total scrap: $[\text{JS-2}]_i = 0.255\%$; total scrap (%): 0.3 (□), 1 (△), 3 (◇), 6 (○), 9 (☆), 10 (▽)



equal to 3%, $[\text{JS-2}]_m$ required to maintain the same latex stability should increase with $[\text{Na}^+]$. The contour plot also indicates that, at a constant $[\text{JS-2}]_m$, the amount of scrap is greatly reduced when $[\text{Na}^+]$ decreases.

The parameter ΔV is influenced significantly by both $[\text{JS-2}]_i$ and $[\text{Na}^+]$ (see Table 1). The parameter ΔV increases with increasing $[\text{JS-2}]_i$. The positive and large standardized effect associated with $[\text{JS-2}]_i$ strongly suggests that limited flocculation can occur during the monomer emulsion feed period when $[\text{JS-2}]_i$ is high. In spite of the fact that the number of primary particles nucleated increases with $[\text{JS-2}]_i$, the ζ of the small particles ($d_{15} = 44.6 \pm 3.1$ nm, an average of four experiments in the design) formed immediately before the start of monomer emulsion feed is -88.8 ± 1.9 mV for the recipe with the highest $[\text{JS-2}]_i$, which is much higher than that of the large particles for the recipe with the lowest $[\text{JS-2}]_i$ ($d_{15} = 140.8 \pm 9.7$ nm and $\zeta = -55.9 \pm 2.8$ mV). It is then postulated that the probability is greater for the small particles to survive the severe reaction environment because these particles possess a higher value of ζ. This can be achieved by limited flocculation, which results in a decrease in the total particle surface area (i.e., increases the particle surface charge density) and, consequently, further relaxes the shrinkage of electric double layer caused by added sodium ions during the monomer addition period. The flocculation process will diminish when the ζ increases to a critical level. As a result, the lightly flocculated particles still can be stably dispersed in water and a large ΔV is achieved. In addition, ΔV increases rapidly with increasing $[\text{Na}^+]$ because the increased electrolyte concentration can compress the electric double layer of the particles and, hence, reduce the repulsive force among the interactive particles according to DLVO theory [9, 10], as shown by the ζ data in Table 1. This action in turn can increase the degree of limited flocculation during the monomer emulsion feed period. Thus the ionic strength will not only determine the amount of scrap formed inside the reactor, but also cause the particle size of the latex product to deviate from the designed value. Figure 2 shows the contour plot of ΔV according to Eq. (4). The parameter $[\text{JS-2}]_m$ is kept constant at 0.75% in this plot. At constant $[\text{Na}^+]$, ΔV increases with increasing $[\text{JS-2}]_i$, as shown in Fig. 2. The parameter ΔV also increases with increasing $[\text{Na}^+]$ when $[\text{JS-2}]_i$ remains constant.

Three formulae (J1, J2 and J3) were then selected from Fig. 1 to verify Eqs. (3) and (4). The parameter $[\text{JS-2}]_i$ was fixed at 0.255% in this series of experiments. The formulae and results are summarized in Table 2. The experimental data show that the predictive equation for the scrap works pretty well. On the other hand, the deviation between the predicted and experimental data for ΔV is greater in this series, but the trend is still correct. The larger deviation observed for ΔV implies that limited flocculation is very sensitive to changes in the reaction environment. Hence it is very difficult to control the particle size if limited flocculation plays an important role during polymerization.

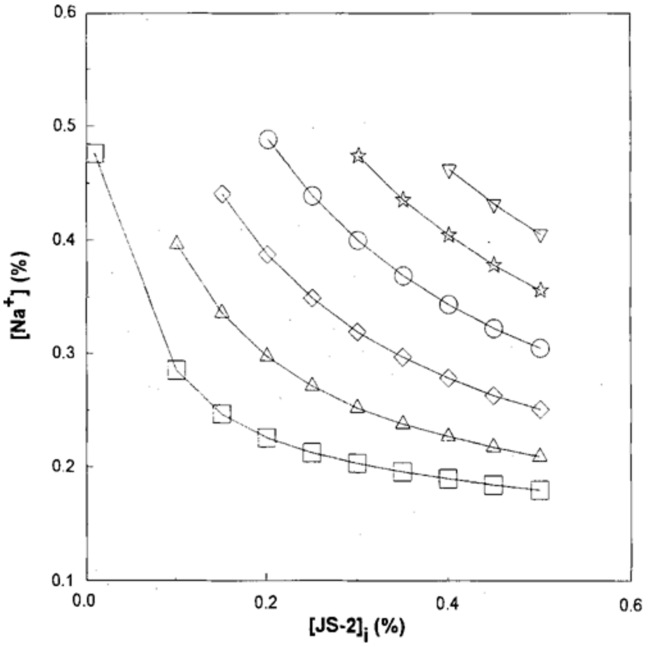


Fig. 2 Contour plot of percentage of particle volume change: $[\text{JS-2}]_m = 0.75\%$; ΔV (%): 50 (□), 150 (△), 300 (◇), 500 (○), 700 (☆), 900 (▽)

Table 2 Experiments designed to verify predictive equations for toal scrap and percentage of particle volume change ($[\text{JS-2}]_i = 0.255\%$)

	J1	J2	J3
$[\text{Na}^+]$ (%)	0.396	0.285	0.185
$[\text{JS-2}]_m$ (%)	0.650	0.801	0.950
Predicted scrap (%)	10.000	3.000	0.300
Experimental scrap (%)	9.134	2.561	0.408
Predicted ΔV (%)	416.5	173.6	1.8
Experimental ΔV (%)	663.9	246.8	-16.9

Corresponding to experiments J1, J2 and J3, a series of experiments stabilized by conventional SDS was carried out to study the effect of type of surfactants on the latex stability during polymerization (see Table 3). Note that J*i* and S*i* ($i = 1, 2, 3$) have exactly the same surfactant concentration in the initial reactor charge ($[\text{S}]_i$) and in the monomer emulsion feed ($[\text{S}]_m$). For experiments J3 and S3 containing the highest $[\text{S}]_m$ and the lowest $[\text{Na}^+]$, both experiments are relatively stable and show similar polymerization behavior. On the other hand, for experiments J1 and S1 containing the lowest $[\text{S}]_m$ and the highest $[\text{Na}^+]$, the latex stabilized by JS-2 (J1) shows higher

Table 3 Experiments designed to study effect of type of surfactants on latex stability during polymerization ($[S]_i = 0.006$ M)[a]

Latex	$[S]_m$ (M)[b]	$[Na^+]$ (%)	d_{15} (nm)	d_f (nm)	Total Scrap (%)	ΔV (%)
J1	0.058	0.396	55.6	284.5	9.134	663.9
J2	0.072	0.285	44.4	174.6	2.561	246.8
J3	0.085	0.185	45.1	110.3	0.408	− 16.9
S1	0.058	0.396	41.2	224.6	1.944	824.7
S2	0.072	0.285	43.4	155.6	1.076	162.9
S3	0.085	0.185	43.6	97.8	0.509	− 36.1

[a] Surfactant concentration in the initial reactor charge.
[b] Surfactant concentration in the monomer emulsion feed.

Table 4 Effect of agitation speed on latex stability during polymerzation ($[JS\text{-}2]_i = 0.255\%$, $[JS\text{-}2]_m = 0.801\%$ and $[Na^+] = 0.285\%$)

	Agitation Speed (rpm)		
	400	600	800
Total scrap (%)	2.561	13.139	39.851
ΔV (%)	246.8	77.8	–

values of d_f and total scrap in comparison with that stabilized by SDS (S1). Furthermore, the total scrap data indicate that latices stabilized by SDS are generally more stable than those stabilized by JS-2. This trend can be attributed to the fact that a fraction of chemically incorporated JS-2 can be buried inside the particles and, therefore, fewer JS-2 molecules adsorbed on the particle surface are available for stabilization [4].

Table 4 shows the effect of mechanical agitation (400–800 rpm) on the latex stability during the reaction. In this series of experiments, $[JS\text{-}2]_i$, $[JS\text{-}2]_m$ and $[Na^+]$ are set at 0.255%, 0.801% and 0.285%, respectively. The amount of scrap formed increases rapidly with increasing agitation speed. This is because the shear force generated by intensive agitation can cause significant turbulence in a stirred-tank reactor. This action can increase both the force and frequency of collisions among the particles and, hence, enhance the formation of coagulum.

Coagulation kinetics

The fomulae and d_f data of latices JS-2-i ($i = 1, 2, 3$) selected for this study are listed in Table 5. For comparison, the corresponding latices SDS-i ($i = 1, 2, 3$) with the same molar concentration of surfactant in the initial reactor charge are also included in this work. In this manner, JS-2-i and the corresponding SDS-i show comparable values of d_f (e.g., the d_f data of JS-2-1 and SDS-1 are 68.7 and 67.7 nm, respectively, as shown in Table 5). Typical absorbance vs. time profiles with various levels of [NaCl] for latex JS-2-1 at pH 5–6 are illustrated in Fig. 3. The parameter [NaCl] represents the concentration of NaCl solution used in the coagulation experiment.

According to Fuchs [11], the stability ratio (W) is defined as the ratio K_r/K_s, where K_r is the rapid flocculation rate constant and K_s is the slow flocculation rate constant. The parameter W (e.g., at [NaCl] = 0.7 M) can be estimated as the ratio of the asymptotic slope of the absorbance vs. time curve at zero time (e.g., the initial slope as [NaCl] → 1.3 M in Fig. 3) to the slope of the absorbance vs. time curve at zero time (e.g., the initial slope at [NaCl] = 0.7 M in Fig. 3) because K_r or K_s is proportional to the initial slope of the absorbance vs. time curve. Typical log W-vs.-log[NaCl] profiles for latices JS-2-1 and SDS-1 at pH 5–6 are shown in Fig. 4. The discontinuous point in the log W-vs.-log [NaCl] profile is then identified as the critical coagulation concentration (CCC) of the latex sample. In addition, the diffuse potential (ψ_δ)

Table 5 Formulae and final particle size data used for experiments of coagulation kinetics ($[I]_i = 0.25\%$ and $[S]_m = 2.5\%$)[a]

Latex	JS-2-1	JS-2-2	JS-2-3	SDS-1	SDS-2	SDS-3
$[S]_i$ (%)	1.495	0.149	0.0148	1.00	0.10	0.01
$[S]_i$ (M)	3.49×10^{-2}	3.47×10^{-3}	3.47×10^{-4}	3.49×10^{-2}	3.47×10^{-3}	3.47×10^{-4}
d_f (nm)	68.7	144.9	237.7	67.7	136.9	235.6

[a] $[I]_i$ = initiator concentration in the initial reactor charge.
$[S]_m$ = suractant concentration in the monomer emulsion feed.

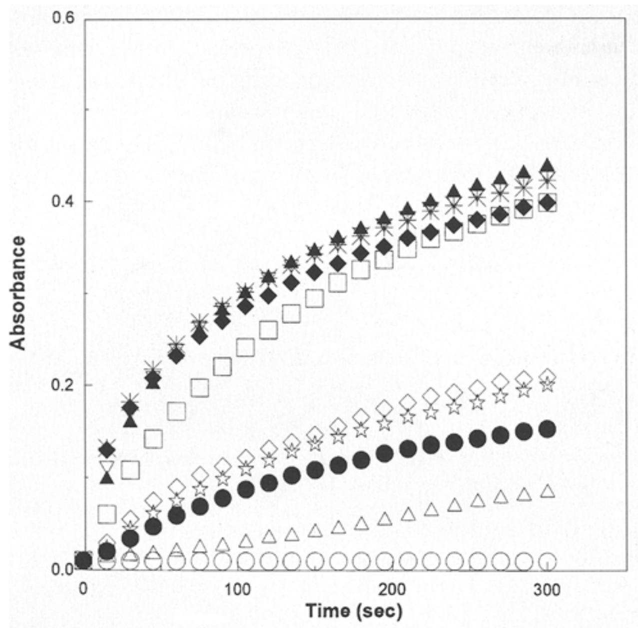


Fig. 3 Typical absorbance vs. time profiles for latex JS-2-1 at pH 5–6: [NaCl] (M): 0.1 (○), 0.3 (△), 0.4 (●), 0.5 (☆), 0.6 (◇), 0.7 (□), 0.9 (▲), 1.1 (▽), 1.3 (∗), 1.5 (◆)

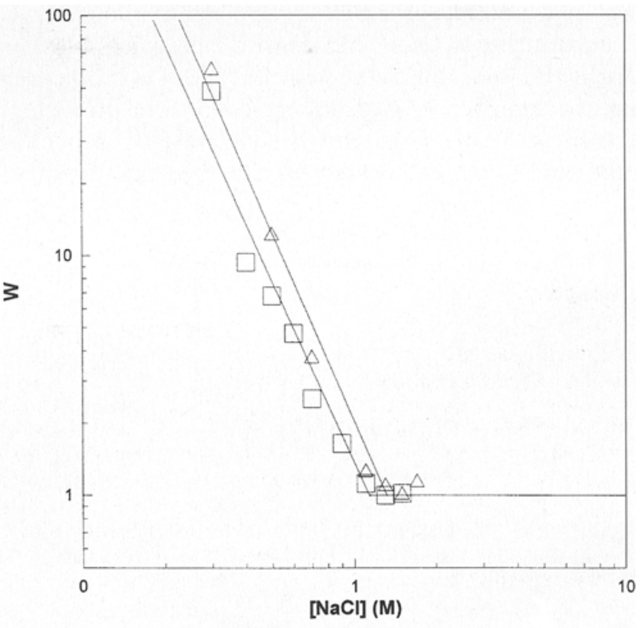


Fig. 4 Typical stability ratio vs. sodium chloride concentration profiles at pH 5–6: JS-2-1 (□), SDS-1 (△)

and Hamaker constant (A) of the latex product can be calculated according to the following equations [12]:

$$-d\log W/d\log[\mathrm{NaCl}] = 2.15\times10^{7}\,r\gamma^{2}/z^{2} \qquad (5)$$

$$A = [1.73\times10^{-36}\,(d\log W/d\log[\mathrm{NaCl}])/r^{2}z^{2}\mathrm{CCC}]^{1/2} \qquad (6)$$

where r is the particle radius, $\gamma = \tanh(ze\psi_\delta/2kT)$, z is the valence of ions, e is an electron charge, k is Boltzmann constant and T is the absolute temperature.

The parameters CCC, A and ψ_δ thus obtained from experiments of coagulation kinetics are summarized in Table 6. The parameter ψ_δ of the latex particles should depend on those parameters such as the particle surface charge density, particle size and ionic strength, etc. For a certain latex sample, ψ_δ increases with increasing pH. At relatively low pH, in addition to Na^+ ions, H^+ ions also can contribute to the ionic strength of the solution. When pH is decreased form 6 to 3, the increased ionic strength can compress the electric double layer of the particles and, hence, lead to a decrease in ψ_δ. However, it is quite difficult to explain the maximum ψ_δ data observed at pH 11. This is probably caused by ionization of the carboxyl groups derived from the hydrolysis of the sulfate end-groups and subsequent oxidation of the generated hydroxyl groups [13]. The parameters CCC and A also show similar trends with respect to pH. Thus the stability of the latex sample toward added salts should increase with increasing pH.

As shown in Table 6, at constant pH, ψ_δ increases with increasing $[S]_i$, which is attributed to the increased particle surface charge density with $[S]_i$. Consequently, the latex product containing a higher level of surfactant in the initial reactor charge should be more stable toward added

Table 6 Critical coagulation concentration, Hamaker constant and diffuse potential of latex products obtained from experiments of coagulation kinetics

	CCC (M)			A (10^{-21} J)			$-\psi_\delta$ (mV)		
Latex	pH 3	pH 5–6	pH 11	pH 3	pH 5–6	pH 11	pH 3	pH 5–6	pH 11
JS-2-1	1.17	1.14	2.07	1.95	2.85	3.03	15.92	19.16	23.06
JS-2-2	0.87	1.02	1.72	1.14	1.49	1.74	11.25	13.39	16.54
JS-2-3	0.78	1.04	–	0.49	0.95	–	7.13	10.70	–
SDS-1	0.92	1.32	1.66	1.89	2.80	3.01	14.70	19.72	21.74
SDS-2	0.83	1.19	1.57	0.94	1.08	1.53	10.09	11.89	15.17
SDS-3	0.72	0.98	1.51	0.90	1.07	1.35	9.52	11.22	14.08

salts and, indeed, it generally shows a higher value of CCC. The parameter A also increases with increasing $[S]_i$. This result is consistent with the work of Patey [14]. Considering two approaching particles possessing a relatively high particle surface charge density, electrostatic attraction force can be induced between the adsorbed anionic surfactant molecules on one particle surface and the counterions around another particle. This factor can greatly enhance the affinity between two approaching particles and, therefore, increase the apparent magnitude of A. Finally, no significant difference between the JS-2 and SDS stabilized latex products is observed in terms of chemical stability.

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