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Rheological Effect of Excess Polymer on Latex Suspension

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Effects of free polymers (Hydroxy-Propyl-Cellulose (HPC)) on the flocculation/dispersion feature of latex dispersions stabilized sterically by the same HPC at its lower critical solution temperature(ca. 50 °C) have been investigated from a view point of rheology. The observed curves of relative viscosity of the system under a lower shear rate have a peak about the concentration of free HPC, which depends on the molecular weight of added HPC. These experimental results indicate that, after saturated adsorption, the free HPC molecules induce the dispersion to flocculate in spite of the dense adsorbing layer of HPC on the particles which would tend to give rise to a steric stabilization. This behaviour is interpreted to be a result of depletion effect.

In colloidal systems, added polymers play a great role on the stability of them relating to whether the polymer adsorbs onto colloid particles or not. We usually encounter the alternation of the system stability induced by adsorbing polymer on the colloid particles.1-3) Recent experiments have demonstrated that free (or non-adsorbing) polymers destabilize the dispersions under a suitable situation,4-6) which is called depletion flocculation. This phenomenon was originally interpreted by Asakura et al.,7) as an osmotic effect when free polymers are excluded from the interparticle region.

As regards the rheological properties of the suspension, when the suspension includes hard spheres without any polymers, the rheological behaviour is fairly well described by the equation of Krieger-Dougherty8) to which our results will be compared below. However, once polymers are included, the behaviour shows a complicated dependence on the flocculating or dispersing state of them.9-11) In the present work, the rheological behaviour of sterically stabilized colloidal system especially including excess polymer over the saturated adsorption which was expected to act as free or non-adsorbing polymer was investigated. We have chosen, as the sample, the dispersions of mono-dispersed polystylene latex (2a=380 nm), which has been stabilized sterically by Hydroxy-Propyl-Cellulose (HPC) at its lower critical solution temperature (LCST) about 50 °C, plus free HPC, and examined the rheological effect of excess HPC. As this system can be prepared simply by normal adsorption treatment, it is seemed that the results will be applicable to many real systems which may have industrial importances. The molecular weight of HPC used are 5.6×10^4 for HPC-L, 33×10^4 for HPC-M, and 96×10^4 for HPC-H.

Concerning the adsorption of HPC to the surface of latex particles for steric stabilization, it has been established that the affinity between polystyrene latex and HPC is strong enough to ignore the desorption of adsorbed polymer from the surface.12) The sterically stabilized latex suspension was prepared as follows. Fresh polystylene latex prepared by usual procedure was treated by the HPC-L under the condition of LCST that gives the maximum adsorption. The excess HPC-L remaining in the medium was then removed by repeating the "centrifugation-decantation-redispersion" processes several times. This process also replaces the medium finally with 0.01 M KCl solution to reduce the effect of electrical double layer on their surface. The amount of free polymer dissolved in the medium was adjusted by adding the definite HPC solution to the dispersion.

Rheological measurements were carried out by employing a rheometer with coaxial cylinders. The concentration of solid particles was set at 15 wt.% and temperature at 20 °C throughout the rheological measurement.

If the flow of the sample liquid is influenced only by the hydrodynamic interaction, the rheological data can be analyzed by applying the following Krieger-Dougherty equation,

$$\eta_r=(1-\phi/\phi_m)^{[\eta]\phi_m} \qquad (1)$$

where η_r is the relative viscosity, ϕ is the effective volume fraction including the adsorbing polymer layer, ϕ_m is the maximum volume fraction over which the particles cannot flow, and $[\eta]$ is the intrinsic viscosity. Figure 1 shows the dependency of η_r for the system including HPC-L-covered latex particles without any free polymers on the volume fraction of the particles by assuming for the thickness of adsorbed HPC-L layers to be 20 nm. The triangles, the present experimental data, coincide well with Eq.1, the solid line, and with the values for bare latex, the circle. This result suggests that only the hydrodynamic interaction is existing in these suspensions consisting of HPC covered latex with no free polymer. Further, in the present work, as the concentration of the solid particles is kept constant at 15 wt.%, the relative viscosity η_r may be calculated to be 1.92 from Eq.1.

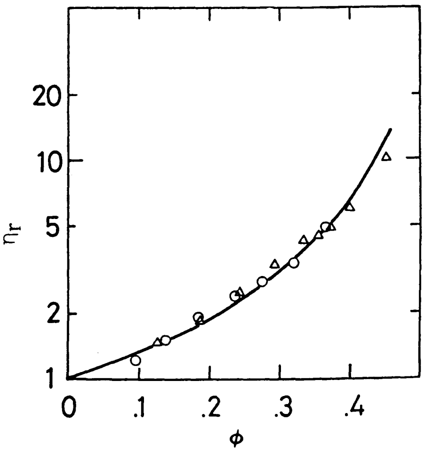

Fig.1. Dependency of relative viscosity of PS latex dispersions on effective volume fraction ϕ ; ○:bare latex, △:HPC-L-covered latex, line:Dougherty-Krieger equation (1)

Figure 2 shows that some typical viscosity vs. shear rate curves for the sterically stabilized dispersion including some amounts of free polymer indicate non-Newtonian behaviour, i.e., the viscosities decrease with increasing shear rate, while the curve for the dispersion without free polymer indicates Newtonian flow. The viscosities of dispersions rise up with the increasing medium viscosities as well as the increasing concentration of colloid particles. In order to show the dependence of viscosity on shear rate, the relative viscosities η_r for two representative shear rates (1 s^{-1}, 100 s^{-1}) were calculated, assuming the particle-free HPC solutions to be the respective continuous phases which give the viscosities of the media. In Fig.3, η_r in the various amounts of free polymers are plotted for the two shear rates against the concentrations of the respective free polymers. It is found from Fig.3 that under the high shear rate (100 s^{-1}), the relative viscosities are dependent on the free HPC concentration only slightly, and their values are described fairly well by Eq.1, which means that under

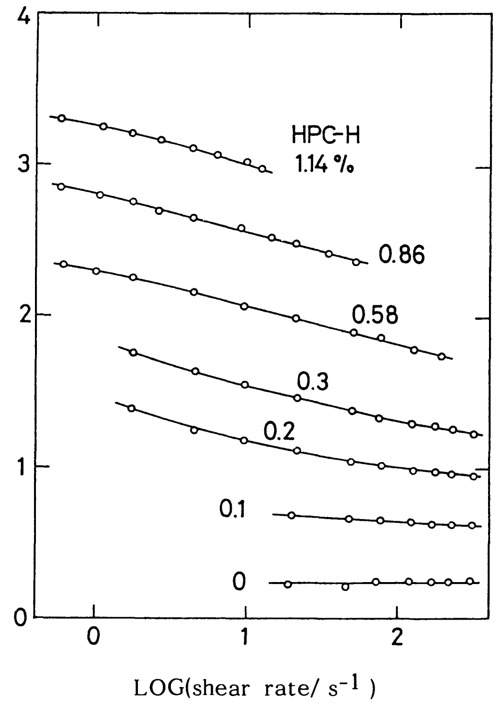

Fig.2. Double logarithmic plot of viscosity of dispersions vs. shear rate; free polymer:HPC-H, concentration of free polymer is shown beside respective curve.

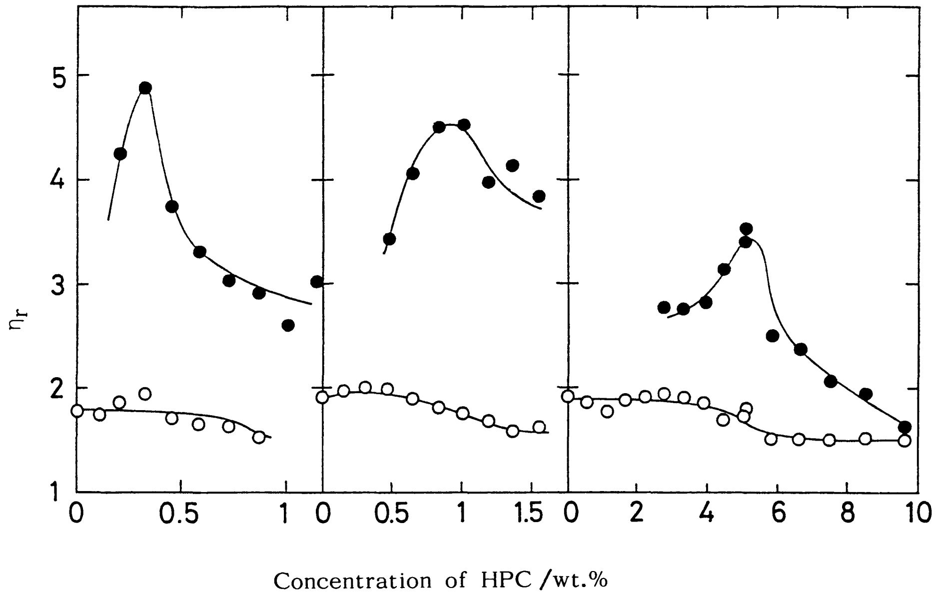

Fig.3. Dependency of relative viscosity, regarding the medium as solution of free HPC, on concentration of respective free HPC; left:HPC-H, center:HPC-M, right:HPC-L; for shear rates of 100s^{-1}:○ , 1 s^{-1}:● ; particle concentration: 15 wt.%

this condition the hydrodynamic interactions are predominant. While under the low shear rate (1 s^{-1}), the relative viscosities rise from those for high shear rate (100 s^{-1}) by the amounts which depend on the concentrations and molecular weight of free polymers. The relative viscosities under the low shear rate become higher with increasing molecular weight of the free polymer and increasing concentration of suspending latex particles. Since relative viscosities are related to the strength of interaction force, these behaviours indicate that there is another interaction between the particles, in addition to the hydrodynamic interaction. And we can interpret it as an interaction coming from the depletion effect arising from the free polymers, i.e., when the free polymers are excluded from the interaction regions, an osmotic effect takes place between the particles, and destabilizes the dispersions since, in such a case, mixing of almost pure solvent from the interparticle regions with the bulk solution decreases the free energy of the system. Also we can see from Fig.3 that the relative viscosity decreases again with increasing concentration of free HPC beyond the peak. This behaviour is characteristic of the case in which the dispersed particles are covered by soft materials like a swelled polymer.6) It can be interpreted as follows; under the high polymer concentration, the polymer molecules will be immersed (or deformed) in each other, and thereby the segments of the polymer can easily intrude into the interparticle regions resulting in a decrease of their osmotic action. Thus, the relative viscosity decreases beyond the peak.

It is a general understanding that the depletion effect exists certainly in the case where the particle surfaces are free of polymers. The present work, however, indicates that, also in the colloidal systems including a adsorptive polymer which makes a dense steric layer on the particles, excess polymer added after saturated adsorption influences the colloid stability by coupled way of the steric effect and the depletion effect.

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