

## A Viscometric Study of the Interaction between Slightly Hydrophobic Starch and Polystyrene Particles

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### ABSTRACT

The interaction between slightly hydrophobic starch and electrostatically stabilized polystyrene particles has been studied. The effective volume fraction of solid phase in the starch-containing suspensions and the corresponding thickness of the adsorbed layers were calculated from measurements of the limiting high-shear viscosity.

### INTRODUCTION

The viscosity of concentrated suspensions of hard-sphere particles has been described in a number of investigations, cf. Krieger and Dougherty<sup>1</sup>, de Kruif et al.<sup>2</sup>, Mewis and D'Haene<sup>3</sup>. If the suspension contains a soluble polymer, the concentration-dependence of the limiting viscosity can be used to evaluate the thickness of the adsorbed polymer layer, as described elsewhere (Liang et al.<sup>4</sup>).

In this investigation, the interaction between slightly hydrophobic starch and electrostatically stabilized polystyrene (PS) particles suspended in water was studied. Both the PS particles and the starch were commercial grades used for the industrial coating of paper.

### EXPERIMENTAL

Two different grades of polystyrene (PS) particles were used: DPP 722E (denoted PS-A) from Dow Sverige AB, Norrköping, Sweden and DPP 711 (denoted PS-B) from Dow Deutschland Inc., Rheinmünster, Germany. The volume fractions of solid phase ( $\phi$ ) in the aqueous suspensions as delivered were 0.468 and 0.470 for PS-A and PS-B respectively. The radii ( $a$ ) of the particles as measured by dynamic light scattering in distilled water and in 10 mM NaCl are given in Table 1. The radius was

slightly smaller when NaCl was added, which indicates the possibility of slightly "hairy" particles. Table 1 also includes the conductivity ( $k$ ) of the aqueous phase as received, the corresponding simple salt concentration ( $c_3$ ) and the electrophoretic mobility ( $U$ ) in 0.1 mM NaCl at pH=5.8 (PS-A) and pH=6.6 (PS-B). These pH-values were the same as the pH-values of the respective suspensions as received.

The starch was a commercial slightly hydrophobic potato starch of paper coating grade (Raisamyl 308H2) from Raisio Chemicals OY, Raisio, Finland. The molecular size of this starch had been reduced compared to that of native starch by hypochlorite oxidation. The viscosities of 5 wt.-% and 8 wt.-% starch solutions at 25 °C, shear rate ( $\dot{\gamma}$ )=230 s<sup>-1</sup> and pH=9 were 5.7 mPas and 11.7 mPas, respectively. The starch molecules possessed some hydrophobic properties since they were grafted with propyl groups. The degree of substitution (with respect to the propyl groups) was 0.06 according to the manufacturer. The received starch was dissolved (hydrated) by means of jet-cooking at 120 °C. The final solution contained ca.17 wt.-% starch.

The starch solution was added to the PS suspensions, and the amount of starch corresponded to 0.93 parts of starch per 100 parts of dry PS (by wt.). The suspensions were diluted with water to an appropriate  $\phi$ -value, the aqueous phases were obtained by filtration and the viscosities were measured with a rotational type viscometer (Bohlin VOR). The suspensions exhibited a shear-thinning region at low  $\dot{\gamma}$  and relatively constant viscosity at higher  $\dot{\gamma}$ . The viscosities of the suspensions were evaluated in the high shear rate limit, at  $\dot{\gamma}$  from 230 s<sup>-1</sup> (low  $\phi$ ) to 1200 s<sup>-1</sup> (high  $\phi$ ).

Table 1. Properties of the PS suspensions: the particle radius (a), the electrophoretic mobility (U), the conductivity (k) of the aqueous phases as received and the conductivity expressed as a corresponding 1:1 electrolyte concentration (c<sub>3</sub>).

PS-type	a (nm) (in distilled H <sub>2</sub> O)	a (nm) (in 10 mM NaCl)	U 10 <sup>8</sup> (m <sup>2</sup> s <sup>-1</sup> V <sup>-1</sup> )	k (μS cm <sup>-1</sup> )	c <sub>3</sub> <sup>b</sup> (mM)
PS-A	270±7	266±1	-2.8±0.2	11.2	0.09
PS-B	150±6	142±1	-2.7±0.3	10.0	0.08

b) Calculated from the conductivity, assuming that NaCl is the only salt present.

## RESULTS AND DISCUSSION

The limiting viscosity of the suspension ( $\eta$ ) was scaled with the viscosity of the aqueous phase ( $\eta_0$ ), in order to obtain the relative viscosity:

$$\eta_r = \eta / \eta_0 \quad (1)$$

The maximum packing fractions ( $\phi_m$ ) in the starch-free suspensions were obtained from the graph of  $\phi$  vs.  $\sqrt{1/\eta_r}$  by extrapolation to  $\sqrt{1/\eta_r} = 0$ . The data points arranged themselves along a straight line, in accordance with an equation for the concentration dependence of  $\eta_r$  given by Quemada<sup>5</sup>. Values of  $\phi_m = 0.678$  and  $\phi_m = 0.653$  were obtained for PS-A and PS-B, respectively.

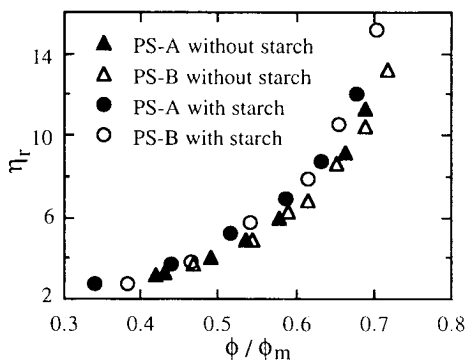
Alternatively, the concentration dependence of  $\eta_r$  can be expressed by the Krieger-Dougherty equation<sup>1</sup>:

$$\eta_r = (1 - \phi/\phi_m)^{-[\eta]\phi_m} \quad (2)$$

where  $[\eta]$  is the intrinsic viscosity. The zeta-potentials ( $\zeta$ ) of PS-A and PS-B were -46.6 mV and -49.5 mV, respectively, as calculated from the U -  $\zeta$  relation given by Wiersema et al.<sup>6</sup>. At these  $\zeta$ -values, the primary electroviscous effect was calculated following a method outlined by Watterson and White<sup>7</sup>, resulting in  $[\eta] = 2.54$  and  $[\eta] = 2.58$  for PS-A and PS-B respectively. Values of  $\eta_r$  calculated from Eq. 2 showed poor agreement with experimental data, if the used  $\phi_m$ -values were obtained by

extrapolation to  $\sqrt{1/\eta_r} = 0$ . This probably reflects the influence of the secondary electroviscous effect on  $\eta_r$ . The  $\phi^2$ -coefficient in the power series expression for  $\eta_r$  for PS-B suspensions was larger than that for PS-A suspensions, as calculated from a scale analysis given by Russel<sup>8</sup> valid for dilute and moderately dilute suspensions.

The value of  $\phi_m$  depends on  $\zeta$  and  $\kappa a$ , where  $\kappa$  is the inverse of the electrostatic double layer. For the two types of PS particles,  $\kappa$  was estimated to be ca.  $3.0 \cdot 10^{-2} \text{ nm}^{-1}$ . In Fig. 1 the values of  $\eta_r$  for the starch-free suspensions are plotted against  $\phi/\phi_m$ . As expected, the experimental data for the different suspensions fall on the same line. The viscosity data for the two starch-containing suspensions also arranged themselves along a common, but different, line (Fig. 1). Thus, the difference between the starch-free and starch-containing suspensions shown in Fig. 1 may reflect the adsorption of starch.



1. Limiting high shear viscosities vs.  $\phi/\phi_m$  at 25 °C and pH=5.9±0.1 (PS-A) and pH=6.7±0.1 (PS-B).

The higher value of  $\eta_r$  for the starch-treated PS suspensions can be explained as a steric interaction in terms of an effective radius ( $a_{\text{eff}}$ ), where  $a_{\text{eff}} = a + \Delta$ , with  $\Delta$  being the adsorbed layer thickness. An effective volume fraction ( $\phi_{\text{eff}}$ ) is given by

$$\phi_{\text{eff}} = \phi(1 + \Delta/a)^3. \quad (3)$$

A value of  $\Delta = 3.6$  nm for starch adsorbed on PS-A was obtained by fitting (method of least squares) the curve for the starch-treated PS-A to that for the starch-free PS-A suspension. Similarly, a value of  $\Delta = 2.4$  nm was obtained for starch adsorbed on PS-B.

The values of  $\Delta$  might to some extent be affected by the relatively large thickness of the electrostatic double layer. However, the viscometric measurement gave adsorbed layer thicknesses in good agreement with results for other types of paper coating grades of starch reported elsewhere<sup>9</sup>.

The smaller  $\Delta$  for adsorption on PS-B could be an effect of the larger specific surface of that pigment. The viscosity of the aqueous phase when the starch was added to PS-B was very close to that of pure water, indicating that complete coverage was not achieved with PS-B. Alternatively, the differences in  $\Delta$  can be explained in terms of the average interparticle separation ( $\bar{h}$ ), given by<sup>10</sup>:

$$\bar{h} = 2a \left[ (1/3\pi\phi + 5/6)^{0.5} - 1 \right] \quad (4)$$

In the most concentrated starch-containing suspensions ( $\phi = 0.46$ ), the values of  $\bar{h}$  were estimated to be 17.0 nm and 9.5 nm for PS-A and PS-B, respectively. The lower  $\Delta$ -value for PS-B may then be a consequence of the compressibility of the adsorbed layer.

## CONCLUSIONS

Viscosity measurements gave a good insight into the interaction between commercial grades of PS-particles and slightly hydrophobic starch. Values of the adsorbed starch layer thickness at high concentrations of PS were calculated.

## REFERENCES

1. I.M. Krieger and T.J. Dougherty, "A Mechanism for Non-Newtonian Flow in Suspensions of Rigid Spheres", *Trans. Soc. Rheol.*, vol. 3, pp. 137-152, 1959.
2. C.G. de Kruif, E.M.F. van Iersel, A. Vrij and W.B. Russel, "Hard Sphere Colloidal Dispersions: Viscosity as a Function of Shear Rate and Volume Fraction", *J. Chem. Phys.*, vol. 83, pp. 4717-4725, 1985.
3. J. Mewis and P. D'Haene, "Prediction of Rheological Properties in Polymer Colloids", *Makromol. Chem., Makromol. Symp.*, vol. 68, pp. 213-225, 1993.
4. W. Liang, Th.F. Tadros and P.F. Luckham, "Rheological Studies on Concentrated Polystyrene Latex Sterically Stabilized by Poly(ethylene oxide) Chains", *J. Colloid Interface Sci.*, vol. 153, pp. 131-139, 1992.
5. D. Quemada, "Unstable Flows of Concentrated Suspensions", *Lect. Notes Phys.*, vol. 164, pp. 210-247, 1982.
6. P.H. Wiersema, A.L. Loeb and J.Th.G. Overbeek, "Calculation of the Electrophoretic Mobility of a Spherical Colloid Particle", *J. Colloid Interface Sci.*, vol. 22, pp. 78-99, 1966.
7. I.G. Watterson and L.R. White, "Primary Electroviscous Effect in Suspensions of Charged Spherical Particles", *J. Chem. Soc., Faraday Trans. 2*, vol. 77, pp. 1115-1128, 1981.
8. W.B. Russel, "The Rheology of Suspensions of Charged Rigid Spheres", *J. Fluid Mech.*, vol. 85, pp. 209-232, 1978.
9. R.B. Bjorklund, H. Arwin and L. Järnström, "Adsorption of Anionic and Cationic Polymers on Porous and Non-Porous Calcium Carbonate Surfaces", *Appl. Surf. Sci.*, in press.
10. L.V. Woodcock, "Developments in the Non-Newtonian Rheology of Glass Forming Systems", *Lect. Notes Phys.*, vol. 277, pp. 113-124, 1987.