Concentrated graphite suspensions in aqueous polymer solutions

Abstract  The present paper reports the interactions of several polyacrylamides having high molecular weight and variable content of ionizable groups with concentrated colloidal suspensions of graphite spherical particles. The method of electric conductivity dispersion with frequency has shown that within the range of small KCl concentrations, the adsorbed polymer layer expands, and it then contracts, with the increase of ionic strength. The KCl concentration, at which the contraction of polymer begins, decreases with molecular weight at the same hydrolysis degree and with the increase of hydrolysis degree for the same molecular weight. The expansion of the adsorbed layer increases with number of hydrolyzable groups on the chain and with the amount of adsorbed polymer.

Key words  Graphite suspensions – polyacrylamide adsorption – dispersion of electric conductivity with frequency

Introduction

The interactions between polymers in solutions and colloidal suspensions, made up of solid particles, have not been sufficiently investigated yet, due to both the system complexity and to the great number of interfering parameters. Finally, the polymer–solid particle interactions may lead to the stabilization of the initial particles, to the formation of some redispersible aggregates or to the total destabilization of the colloidal system.

The present paper reports interactions of several polyacrylamides having high molecular weight and variable content of ionizable groups with dilute and concentrated colloidal suspensions of graphite containing spherical particles [1]. Using the dispersion of the electric conductivity, the influence of electrolytes was followed on the concentrated suspensions with particles having, on their surface, layers of adsorbed polymer, of thickness comparable with the size of the particles. The behaviour of the suspensions in electric field, within the range of low frequencies, gives interesting information on the solid–solution interface [2, 3]. The study of the polyacrylamides adsorption, largely used polymers, onto solid surfaces of different nature is a topic still under investigation [4–7].

Materials and methods

The polymers used were poly(acrylamides) (PAM), having high molecular weights and varied degrees of hydrolysis obtained from Sanpoly–Sankyo Chem. Ind. Ltd. Tokyo (Table 1).

Viscosity-average molecular weights \( M_v \) were determined with an Ubbelohde viscometer in aqueous sodium nitrate 1 mol/l at 300 K and calculated by means of relation:

\[
[\eta] = 3.73 \times 10^{-4} \, M_v^{0.66},
\]

were \([\eta]\) is the intrinsic viscosity. Degrees of hydrolysis (DH) were determined by conductometric and pH-metric
methods [8]. In water and electrolyte solutions, the hydrolyzed polyacrylamides behave like weak polyelectrolytes.

Graphite suspensions with spherical-shaped particles (Fig. 1a) were obtained by a previously described method [1]. Figure 1a shows the geometrical shape by “visualizing” the biggest graphite particles.

Before the contact with the PAM solutions, the graphite particles were centrifuged and washed with bidistilled water for removing the grinding additives.

Adsorption of the polymer onto the solid-liquid region was measured using the solution depletion method: 1.73 g graphite was dispersed in 100 cm$^3$ of polymer aqueous solution of different concentration with or without required salinity (KC1). The suspensions were gently shaken from time to time during 48 h. The amount of polymer in solution was determined interferometrically with an ITR-2 device (Russia), at 25 °C, from a calibration curve, after ultracentrifugation of suspensions.

Sedimentation analysis in gravitational field was made with a Sartorius automatic balance, when the maximum PAM adsorption was reached, in the presence and absence of KC1. Comparatively, graphite dispersions with lamellar-shaped particles, obtained through a different method, were studied under same conditions [9]. Microscopy under reflected light of the resin-included particles revealed anisotropic, lamellar shapes having micrometric sizes (agglomerated lamellae) (Fig. 1b). Analysis by x-ray diffractograms confirmed the hexagonal structure of the graphite. Both the concentrated graphite suspensions with spherical particles and those having lamellar particles contained an appreciable amount of particles of submicronic colloidal sizes which did not sediment in the gravitational field.

Turbidimetric method (Specol spectrophotometer) was applied to the dilute spherical graphite suspensions. The dilution was made in aqueous solutions at constant PAM concentration (0.004%).

The average diameter of graphite particle $D$, was calculated from the equation:

$$\lim_{c \to 0} \frac{\zeta}{c} = KD^3$$

where $\zeta$ is turbidity, $c$ is graphite suspension concentration (g cm$^{-3}$). $K$ was calculated according to the equation:

$$K = \frac{16}{9} \frac{\pi^4 d}{\lambda^4 d_p} \left( \frac{n_p}{n} - 1 \right)^2,$$

where $\lambda$ is the wavelength of the incident light (450 nm), $d$ and $d_p$ are the densities of the suspension medium and

**Table 1** Average diameter of graphite particles calculated from turbidimetric data

<table>
<thead>
<tr>
<th>No</th>
<th>Additive</th>
<th>$M_\ast \times 10^{-6}$</th>
<th>$DH$</th>
<th>$K \times 10^{-17}$</th>
<th>$D$</th>
<th>Maximum amount of PAM adsorbed $\times 10^4$ g/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PAM 500-20</td>
<td>5.0</td>
<td>20</td>
<td>137.9</td>
<td>55.4</td>
<td>5.78</td>
</tr>
<tr>
<td>2</td>
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<td>0</td>
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<td>59.7</td>
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<tr>
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<td>6.1</td>
<td>20</td>
<td>194.4</td>
<td>70.0</td>
<td>5.20</td>
</tr>
<tr>
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<td>40</td>
<td>142.9</td>
<td>64.3</td>
<td>8.72</td>
</tr>
<tr>
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</tr>
<tr>
<td>6</td>
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<td>-</td>
<td>-</td>
<td>129.5</td>
<td>50.6</td>
<td>-</td>
</tr>
</tbody>
</table>

PAM 0.004%.