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Chemical Engineering Journal 80 (2000) 43–49

Chemical Engineering Journal

www.elsevier.com/locate/cej

Enhanced flocculation of colloidal dispersions by polymer mixtures

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Abstract

Bridging flocculation and electrolyte coagulation of negatively charged colloidal dispersions in the presence and absence, respectively, of uncharged polymers and polymer mixtures were studied. The relative coagulation and flocculation rates of particles in the presence of electrolyte and small polymer amounts were measured and the stability ratios have been calculated at various ionic strengths. Also, the structure of polymer layers formed in individual adsorption of polymers and in simultaneous competitive adsorption from binary polymer mixtures at particle/solution interfaces was investigated. The electrophoretic mobility and the diffusion coefficient of particles with and without adsorbed polymer were measured by laser Doppler-electrophoresis and photon correlation spectroscopy, respectively, and the electrophoretic and the hydrodynamic thickness of adsorbed polymer layers have been calculated. It was found that the adsorbed polymers may enhance or diminish the rate of successsful encounters between particles, even at low surface coverages, depending on the magnitude of the interparticle electrostatic repulsion. In addition, competitive adsorption of chemically different polymers for particle surfaces may result in considerable alteration in the conformation of macromolecules in the mixed adsorption layer. Close correlation was found between the effectiveness of polymers as flocculants and the thickness of adsorbed polymer layers formed at optimum polymer dosages on the particle surfaces. Binary mixtures of suitable polymers proved to be very efficient flocculants for the dispersions. The enhanced flocculating effect of some mixtures can be ascribed to extended polymer layers formed in competitive adsorption of chemically different macromolecules at particle/solution interfaces. These findings have relevance in many environmental technologies and offer a way of improving the effectiveness of solid–liquid separation processes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Enhanced flocculation; Polymer mixture; Colloidal dispersion; Adsorbed layer thickness; Competitive adsorption

1. Introduction

Removal of solids of nm size range from dispersion is a crucial stage in many environmental technologies. Such colloidal particles are too small to be effectively separated by filtration, flotation or sedimentation, therefore, in many instances the most effective way is to cause the particles to flocculate so those larger units are formed. Extensive studies [1–7] show that kinetic stability of colloidal dispersions can be well controlled by dissolved macromolecules. Polymers can induce particle aggregation even in an intrinsically stable dispersion. The effects observed result from the change of interparticle interactions due to the macromolecules adsorbed at the particle/solution interface, in certain cases, however, the presence of free polymer in the solution may also play a role.

Water-soluble polymers find extensive use as flocculants for many disperse systems, as in water treatment, mineral processing, papermaking and other fields. For most charge stabilised dispersions, non-ionic polymers act by adsorbing at the surface of more than one particle. This phenomenon is usually described as bridging flocculation [1,2]. The chain conformation at the solid/liquid interface and also, the extent of double-layer repulsion operating between particles have a marked effect on how the polymer acts as flocculant. The preferred polymer chains for bridging flocculation should not only well anchored to the particle surfaces but should also give a thick adsorption layer extending into the dispersion medium.

Considerable attention has been paid for years to the question of enhancing the efficiency of flocculation with synthetic polymers. Few attempts have also been made towards investigating the effectiveness of multicomponent macromolecular flocculants. Nevertheless, there is very little information available concerning the interfacial behaviour of mixtures of chemically different macromolecules and also, the structure of mixed polymer layers formed at particle/solution interfaces, but the results may be very important in practice [8–10]. The aim of this work is, therefore two-fold. First, to study the spatial properties of individual and mixed adsorption layers formed from single polymers and binary polymer mixtures, respectively, and second, to show some relation between the layer properties

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PII: S1383-5866(00)00076-9

and the ability of these polymers and mixtures to flocculate colloidal dispersions. To that end, the hydrodynamic and the electrophoretic thickness of the adsorbed layers formed at various polymer concentrations on negatively charged polystyrene (PS) latex and silver iodide (Agl) sol, respectively, and also, the effectiveness of the polymers as flocculants at various interparticle electrostatic repulsions, have been investigated.

2. Experimental

2.1. Materials

2.1.1. Silver iodide sol

The sol was prepared by adding 90-cm^3 aliquot of 10^{-3} M $AgNO_3$ at room temperature to 22 cm^3 of an aqueous solution of 5×10^{-3} M KI by mixing the solutions at a constant rate. Freshly prepared AgI sol with negatively charged particles was used for each measurement. The particle size and the polydispersity of the fresh sol in every preparation were checked by dynamic light scattering measurements. The polydispersity index 60 min after the preparation of the sol used did not exceed 0.1. This showed that the samples were fairly monodisperse with a 34 ± 2-nm volume-average mean particle size. The concentration of the sol in the measurements was 1.26×10^{-2} g dm^{-3}.

2.1.2. Polystyrene latex

Monodisperse PS latex was used in these experiments. The particles are negatively charged with a 3.2 μC cm^{-2} surface charge density. The preparation of the latex dispersions is described elsewhere in detail [4]. The particle size and polydispersity of each dispersion were determined by dynamic light scattering measurements. The mean size of latex particles is 67 ± 1 nm and the polydispersity index is less than 0.05. The concentration of the PS in the measurements was 1.0×10^{-2} g dm^{-3}.

2.1.3. Polymers

Water-soluble uncharged polymers, such as methylcellulose (MC), polyvinyl pyrrolidone (PVP) and their 1:1 (w/w) binary mixtures were used. The polymers were fractionated samples, prepared from commercial products of Tylose MH 50 and MH 200 methylcellulose, as well as GAF K-60 and K-90 polyvinyl pyrrolidone. The degree of polymerization of the MC-1 and MC-2 (the number of glucose rings) is 490 and 760, but that of the PVP-1 and PVP-2 is 1380 and 8120, respectively. (The degree of methylation of the MC samples was 65–67%.)

2.2. Methods

2.2.1. Flocculation measurements

The kinetics of particle aggregation, both in the presence and absence of polymer was investigated by a turbidimetric method as described by Reerink and Overbeek [11]. (When MC-PVP mixture was used as flocculant, the two polymers were added together to the dispersion.) After a 1 h polymer adsorption period, the dispersion was diluted so that the concentration of the AgI sol and the PS latex was 6×10^{11} and 5×10^{11} particles per cm^3, respectively. To initiate flocculation or coagulation (without polymer), electrolyte was mixed within a short time to the dispersion. Immediately thereafter, the turbidity of the dispersion was continuously monitored as a function of time and the initial slope of the curve was assumed to be proportional to the rate of increasing turbidity and hence to the rate of coagulation or flocculation [9].

The stability ratios for collisions in the early stages of flocculation between polymer-covered and bare particle surfaces have been determined from the results of kinetic measurements as suggested by Ash and Clayfield [12]. At surface coverage corresponding to the flocculation maximum, the value of the overall stability ratio (W) is:

$$W=(1/W_{\mathrm{pp}}+1/W_{\mathrm{ss}}-2/W_{\mathrm{sp}})/(1/W_{\mathrm{pp}}\cdot W_{\mathrm{ss}}-1/W_{\mathrm{sp}}^2) \quad (1)$$

Eq. (1) enables the value of the stability ratio (W_{sp}) to be estimated at different ionic strengths for particle collisions, which may result in polymer bridging.

By determining the stability ratios for electrolyte coagulation without polymer (W_{ss}), for flocculation with excess polymer present (W_{pp}) and with optimum polymer dosages (W) that cause maximum flocculation at a given electrolyte concentration, W_{sp} can be calculated. The stability ratios were evaluated from experimental rate constants, and a lower limit of W_{pp} was used in the calculations as described in Ref. [12].

2.2.2. Photon correlation spectroscopy (PCS)

Mean size, size distribution, and polydispersity of the particles with and without adsorbed polymer were measured at 25°C by an advanced technique of photon correlation spectroscopy (PSC) using a Malvern Zetasizer 4 apparatus (Malvern Instruments, UK) with autosizing mode and auto sample time. Analysis of the fluctuations in the intensity of light scattered from particles undergoing random Brownian motion enables the determination of an autocorrelation function $G(\tau)$ that, in effect, is measure of the probability of a particle moving a given distance in a τ time (τ is the correlation delay time).

$$G_i(\tau) \propto \Sigma k_i \exp[-\tau/t_{c,i}(a_i)] \quad (2)$$

The relaxation time (t_c) of fluctuations is related to the diffusion coefficient (D) of particles:

$$t_c = 1/DK^2 \quad (3)$$

from which the particle size can be calculated via the Stokes–Einstein equation (K is the wave vector).

By determining the autocorrelation function for the dispersion in the presence and absence of adsorbed polymer, respectively, the diffusion coefficients and the hydrodynamic radii (a_i) of particles have been evaluated. From the differences in the volume-average mean sizes between polymer-bearing and bare particles, the hydrodynamic thickness (δ^h) of adsorbed polymer layers has been calculated.

2.2.3. Laser Doppler-electrophoresis (LDE)

For electrically charged particles moving in response to an applied electric field with and without adsorbed polymer, respectively, a correlation function of laser Doppler-shift was measured with the Zetasizer 4 apparatus at 25°C and the resulting frequency spectrum was translated to electrophoretic mobility. The zeta potential (ζ) of the particles was calculated from the mobility measurements at various ionic strengths, using the Henry formula.

The adsorbed macromolecules may alter the distribution of ions in the electrical double-layer around particles. As the polymers used are uncharged and in the flocculation region the particle surfaces are only partially covered, the approximation has been made that the polymer molecules do not influence considerably the charge distribution in the diffuse part of the double-layer. The basis for this approximation is that the volume occupied by neutral polymers in the diffuse double-layer is small [13,14]. Under these conditions, the decrease in the zeta potential of polymer-bearing particles may be attributed to the shift of the shear plane outwards with respect to its position in the absence of polymer. The extent of reduction, as compared with the ζ potential of the uncovered particles, may be considered to a first approximation as a relative measure of the thickness of the adsorbed layer.

The electrophoretic thickness (δ^e) of the adsorbed polymer has been evaluated at low ionic strengths, as proposed by Cohen Stuart et al. [14,15] using the formula

$$\tan h(ze\zeta/4kT) = \tan h(ze\psi_d/4kT)\cdot \exp[-\kappa(\delta^e - d)] \quad (4)$$

where e is the unit charge, z is the charge of the counter-ions, ψ_d is the Stern potential, d is the thickness of the Stern layer (about 0.4 nm), κ is the Debye-Hückel parameter, k is the Boltzmann constant and T is the absolute temperature.

3. Results and discussion

3.1. Flocculation kinetics

The kinetic approaches to flocculation by uncharged polymers consider polymer bridging as mainly affecting the probability of adhesion between colliding particles [1,2,12]. At constant ionic strength, low values of W_{sp} stability ratio indicate that the adsorbed polymer is indeed an efficient flocculant. When the adsorption features of polymers at particle/solution interfaces are known, information on the extension of the adsorbed layers can also be obtained from the efficiency of the polymers bringing about on the stability of colloidal dispersions.

Table 1
Stability ratios for electrolyte coagulation (W_{ss}) and bridging flocculation by optimum polymer dosages (W_{sp}) of PS latex[a]

C_{NaCl} (mol dm^{-3})	W_{ss}	W_{sp}		
		MC-2	PVP-1	MC-PVP (1:1 w/w)
0.100	60	1.9	18	4.1
0.150	21	1.4	5.6	2.4
0.200	10	1.3	2.5	1.8
0.250	6	1.2	1.1	1.5

[a] Data are taken from Ref. [16].

As characteristic results, the stability ratios for bridging flocculation of PS latex and silver iodide sol, determined with optimum amount of adsorbed methylcellulose, polyvinyl pyrrolidone samples and of their binary mixture, respectively, and also, for electrolyte coagulation without polymer, are listed together in Tables 1 and 2.

The high values of W_{ss} stability ratio for polystyrene particles at low electrolyte concentrations indicate that in the absence of polymer high electrostatic repulsion operates between particles and there is very little chance for colliding bare particle surfaces to adhere. However, most of the W_{sp} values are well below 10 even at higher values of W_{ss}, i.e. encounters of polymer-covered surfaces with uncovered ones are fairly favourable to allow the particles to stick together. The difference between the two stability ratios decreases as the ionic strength in the medium increases.

Thus, it is very likely that at high double-layer repulsion, the formation of bridging contacts between particles are mainly responsible for enhancement of the flocculation rates in the presence of optimum polymer dosages. At low ionic strengths, the methylcellulose (MC-2) is the best and the polyvinyl pyrrolidone (PVP-1) is the weakest flocculant for the latex particles.

The results obtained at various electrolyte concentrations for silver iodide sol are shown in Table 2. The values of W_{ss} and W_{sp} stability ratios illustrate that the same holds for the flocculating effect of these polymers on the silver iodide sol, as well.

Nevertheless, it is worth pointing out that at low electrolyte concentrations, the W_{sp} values for the 1:1 (w/w) MC-PVP mixture are significantly lower than that for the

Table 2
Stability ratios for electrolyte coagulation (W_{ss}) and bridging flocculation by optimum polymer dosages (W_{sp}) of silver iodide sol[a]

C_{KNO_3} (mol dm^{-3})	W_{ss}	W_{sp}		
		MC-2	PVP-l	MC-PVP (1:1 w/w)
0.067	>100	4.2	5.2	2.5
0.100	>100	2.1	2.5	1.7
0.133	91	1.6	2.0	1.4
0.167	25	1.3	1.5	1.3

[a] Data are taken from Ref. [16].

MC-2 or for the PVP-1 alone. Namely, the polymer mixture results in greater enhancement of flocculation than either polymer alone. Such synergistic effect has been observed on arsenic trisulphide sol and with other polymer pairs, as well [9]. At higher polymer concentrations belonging to the onset of stabilization enhanced steric stabilization is resulted.

For bridging flocculation to occur, the adsorbed macromolecules must extend far enough from the particle surfaces to span the distance over which electrical repulsion operates. As a consequence, polymers with longer chains protruding into the solution from solid surfaces may develop bridging contacts between particles despite higher double-layer repulsion. Thus, the observed synergism in flocculation can be ascribed to the formation of an extended conformation of the polymers in the mixed adsorption layer as compared to the polymer conformations adopted in the individual adsorption layers. In the mixed layer presumably longer tails are formed, which are especially favourable for establishing bridging contacts between particles even at higher double-layer repulsion.

3.2. Adsorbed layer thicknesses

The thickness of the adsorbed polymer layer is one of the key factors in determining the effectiveness of an uncharged polymer in flocculating and stabilising colloidal dispersions.

The hydrodynamic and electrophoretic thicknesses of adsorbed layers obtained for MC-1, PVP-2 and for their binary mixture after 1 h adsorption on polystyrene latex particles at various initial polymer concentrations (C_i) are shown in Figs. 1 and 2, respectively.

Determination of the hydrodynamic layer thickness (δ^h) at particle/solution interfaces by dynamic light scattering, is based on the fact that the adsorbed polymer layer limits the diffusion of coated particles. The layer thicknesses calculated from the change in the diffusion coefficients of the particles with and without polymer show the expected trend. At low surface coverage the hydrodynamic layer thickness is almost negligible, but when the train density reaches a certain limit tails develop rapidly and a steep increase in δ^h is observed. Definite increase in layer thicknesses at and above the flocculation maximum is resulted. An arrow in the Figures denotes the flocculation maximum (f_m). At high surface coverages, the thickness of each polymer layer approaches to a plateau value.

Similar adsorption features for these polymers can be revealed from the results of laser Doppler-electrophoresis (LDE) measurements, as well. The layer thicknesses obtained at low ionic strength (κa is close to 1) increase with the initial polymer concentration in the bulk and approach to characteristic levels. The formation of a relatively thick layer from the MC-1 and thinner layers from the other polymers on the PS particles are illustrated by the curves in Fig. 2. The order of the electrokinetic layer thicknesses is the same as that of the hydrodynamic ones.

Somewhat different layer characteristics for the polymers adsorbed on silver iodide particles are demonstrated by the results shown in Figs. 3 and 4.

Definite rise in both the hydrodynamic (Fig. 3) and the electrophoretic (Fig. 4) thicknesses of polymer layers at the flocculation maximum and just above can be observed on the AgI sol, as well. In the flocculation region, the thickness of the polymer layers formed in individual adsorption from the MC-1 and the PVP-2 is nearly the same, despite the considerable difference in their molecular weights. At higher polymer concentrations, the formation of a thin layer by the preferentially adsorbed PVP, and a relatively thick adsorbed layer with MC is illustrated by these curves.

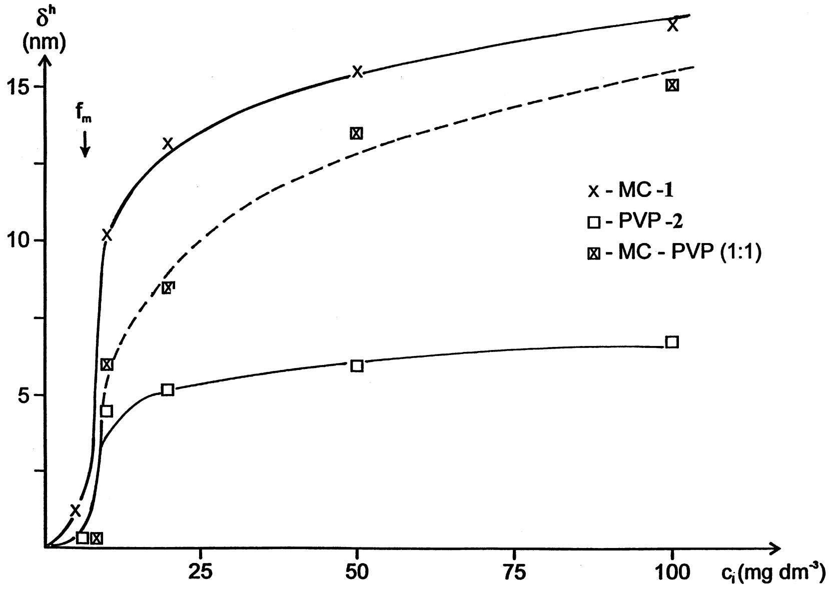

Fig. 1. Dependence of the hydrodynamic thicknesses (δ^h) of adsorbed polymer layers on the polymer concentration (C_i) on polystyrene latex particles.

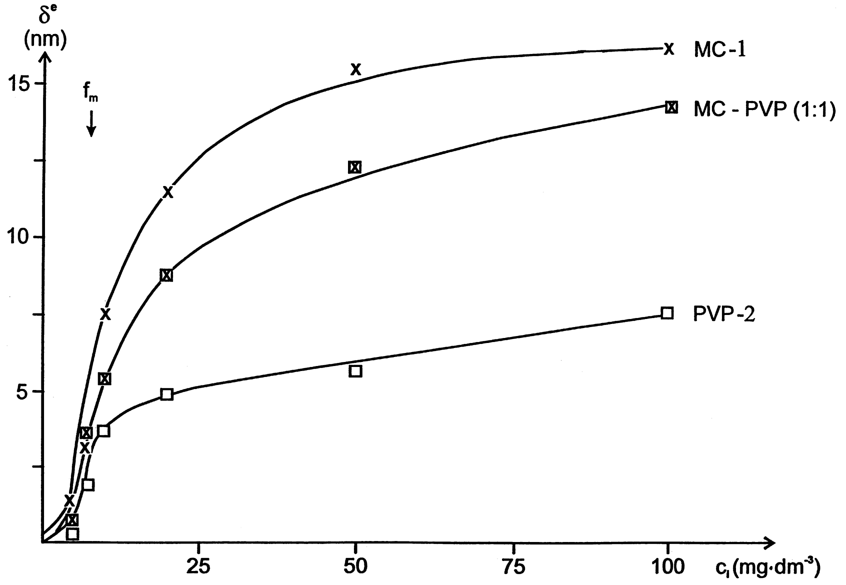

Fig. 2. Dependence of the electrophoretic thicknesses (δ^e) of adsorbed polymer layers on the polymer concentration (C_i) on polystyrene latex particles (κ (m^{-1}): 33×10^6, κa: 1.2).

More importantly, the results of both the PCS and the LDE measurements alike demonstrate the existence, in a wide concentration range, of a thicker adsorbed layer for the MC-PVP 1:1 (w/w) mixture, which exhibited an enhanced flocculating effect on the sol, than for the single polymers. These findings are in line with that of the flocculation kinetic measurements and provide an independent experimental evidence that in simultaneous competitive adsorption for the solid, an expanded mixed adsorption layer may form, at least at some surface coverages [16].

Considering the interfacial behaviour of the polymers, the MC and/or the PVP molecules when competing for silver iodide surfaces, presumably adopt a non-equilibrium conformation with longer tails at particle/solution interfaces over longer time. In accordance with theoretical considerations, these results strongly support the notion that the layer thickness of neutral polymers depends in a characteristic way on the adsorbed amount and also, on the chain conformations at the interfaces.

Investigations of the spatial properties of individual and mixed adsorbed layers together by the different experimental techniques such as PCS and LDE provide further information on how the adsorbed macromolecules affect other interfacial processes relevant at charged particle surfaces.

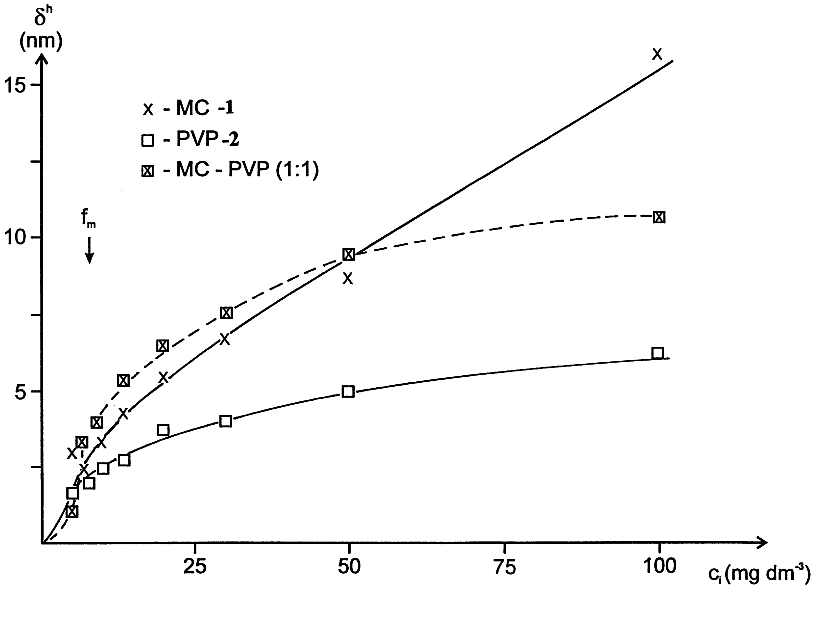

Fig. 3. Dependence of the hydrodynamic thicknesses (δ^h) of adsorbed polymer layers on the polymer concentration (C_i) on silver iodide sol particles.

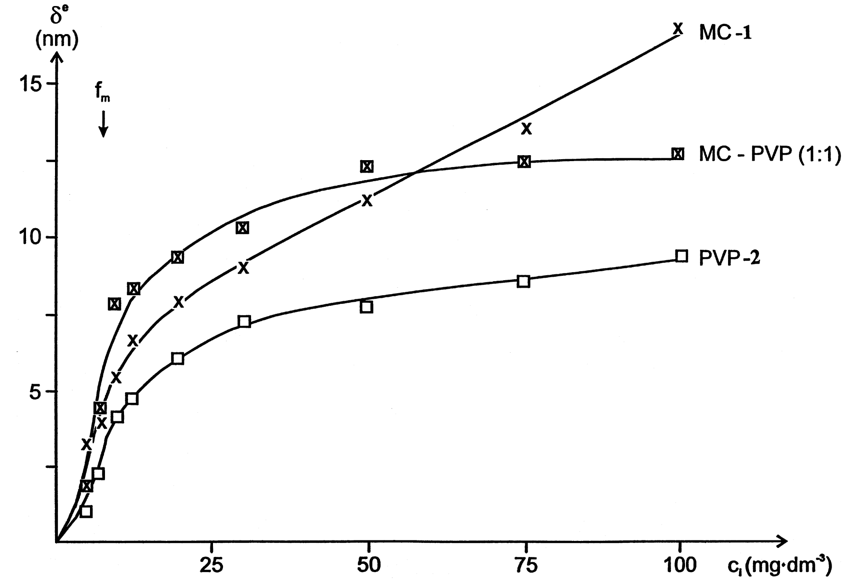

Fig. 4. Dependence of the electrophoretic thicknesses (δ^e) of adsorbed polymer layers on the polymer concentration (C_i) on silver iodide sol particles (κ (m^{-1}): 83×10^6, κa: 1.7).

It is well known that an adsorbed polymer layer suppresses the motion of the solvent along the particle surface. Long, dangling tails are very important in this respect, because they screen the inner layers from the liquid flow. For long chains, therefore, the hydrodynamic layer thickness is almost completely determined by the size and number of tails. The ionic strength, at least at low κ values, does not have notable influence on the hydrodynamic layer thickness formed from uncharged macromolecules.

Neutral polymers do not add any charge to the electrical double-layer, but the adsorbed polymer layer may alter the total amount and the distribution of ions in the neighbourhood of particle surfaces. At higher adsorbed amounts, these effects strongly depend on the electrolyte concentration in the bulk solution and are reflected in the values of δ^e, as well.

Cohen Stuart et al. [14] showed that if the influence of the adsorbed polymer on the static double-layer properties is negligible, the electrokinetic layer thickness is always below δ^h for a wide concentration range. At very high ionic strength δ^e tends to 0, and for $\kappa \rightarrow 0$, δ^e approaches δ^h asymptotically. In Tables 3 and 4, the differences between δ^e and δ^h obtained at some initial polymer concentrations (C_i) for the single polymers and their mixture on PS latex and AgI particles, respectively, are shown together.

These data clearly demonstrate that at higher polymer concentrations, there are definite (but not very great) differences between the electrokinetic and hydrodynamic layer thicknesses on both particle surfaces. Moreover, all the layer thicknesses calculated from electrophoretic mobility data exceed the hydrodynamic layer thicknesses for each polymer. For the binary mixture, $\delta^e - \delta^h$ at each polymer concentration is nearly the same as that obtained for the PVP itself. From this polymer, relatively thin and dense adsorption layers form on both surfaces. Considering the reasonable approach by Cohen Stuart et al., these results suggest that the adsorbed macromolecules, mainly in the region of steric

Table 3
Differences between the electrokinetic (δ^e) and hydrodynamic (δ^h) thickness of adsorbed polymer layers on PS-67 particle surfaces

C_i (mg dm^{-3})	$\delta^e - \delta^h$		
	MC-1	PVP-2	MC-PVP (1:1 w/w)
5	–	–	–
10[a]	<1	<1	<1
20	1	2	2
50	2	2	2
100	1	2	2

[a] Flocculation maximum; κ (m^{-1}): 33×10^6, κa: 1.2.

Table 4
Differences between the electrokinetic (δ^e) and hydrodynamic (δ^h) thickness of adsorbed polymer layers on AgI-34 particle surfaces

C_i (mg dm^{-3})	$\delta^e - \delta^h$		
	MC-1	PVP-2	MC-PVP (1:1 w/w)
5	–	–	–
7[a]	<1	<1	<1
10	2	1	2
13	2	2	2
20	2	3	2
30	2	3	2
50	2	3	3
100	1	3	3

[a] Flocculation maximum; κ (m^{-1}): 83×10^6, κa: 1.7.

stabilization, cause some changes in the static double-layer parameters, as well. They also show that the more compact is the conformation adopted by the adsorbed macromolecules at the particle/solution interfaces the greater is the alteration caused by the polymer layer in the charge distribution and/or capacity of the inner part of the electrical double-layer.

The results of these investigations can be utilised in controlling the stability/flocculation behaviour of aqueous colloidal dispersions. They offer a way of selecting optimal conditions for flocculation of small particles by uncharged macromolecules, involving water and wastewater treatments, as well.

Acknowledgements

This work was supported by the Hungarian Science Foundation under grant OTKA T 022923.

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