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ORIGINAL CONTRIBUTION

C. L. de Vasconcelos
K. T. de Moura
W. A. Morais
T. N. C. Dantas
M. R. Pereira
J. L. C. Fonseca

Dispersing phase viscometry and zeta potential in alumina dispersions

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C. L. de Vasconcelos · K. T. de Moura
W. A. Morais · T. N. C. Dantas
M. R. Pereira · J. L. C. Fonseca (✉)
Departamento de Química,
Universidade Federal do Rio Grande do Norte, Lagoa Nova, C. P. 1662, 59078–970
Natal, RN, Brazil
E-mail: jlcfonseca@uol.com.br

Abstract The stabilities of alumina dispersions were studied as a function of poly- and low molecular weight electrolyte concentration, using viscometry of the dispersing phase, and zeta potential measurements. The relation of polyelectrolyte adsorption to polymer concentration (at different low molecular weight electrolyte concentrations) was found to depend upon the dimensions of the polymer (which were a priori known to decrease with increasing poly- and low molecular weight electrolyte concentration). The occurrence of flocculation and bridging in the destabilization mechanism of the alumina dispersions was also characterized.

Keywords Polyelectrolyte · Viscometry · Adsorption · Zeta potential · Alumina

Introduction

Due to the presence of anionic or cationic radicals in their chains, polyelectrolytes are charged macromolecules that have unique properties, because the electrostatic interactions between the charges cause repulsion-contraction of the chains [1]. At first, these polymers were mainly used as rheology modifiers [2, 3, 4], but one of the most interesting uses of these materials has been the stabilization of a wide variety of colloidal systems [5, 6, 7, 8]. One can find them used in the stabilization of enzyme colloidal systems which are used in many applications, such as detergents, food processing, household products, textile processing, and biosensors. In these systems, many of the enzymes are unstable and often require either refrigeration to maintain activity, or some sort of stabilization matrix, and so in this case polyelectrolytes have been used as stabilizers [9, 10].

Polyelectrolytes also play an important role in the stabilization of inorganic colloidal particles. TiO_2, for example, is largely used in the paint industry as filler and pigment, the final product shelf-life being extremely dependent on the stabilization of these particles [11, 12, 13]. Polyelectrolyte adsorption is also very important in wet ceramic processing. When these materials are extruded, the use of polyelectrolyte dispersants (as well as binders and plasticizers) is important for the process control and dimensional stability of the bodies in the green state [14]. The resultant dimensions and porosity are also strongly linked to particle agglomeration, and an important factor in agglomeration is the attraction between the particles, which is governed by the amount of adsorbed polyelectrolyte [15].

There are three factors involved in the stabilization of these colloids: (1) the polyelectrolyte conformation in solution, (2) the specificity of interactions between the macromolecules and the surface (whether they are of a purely electrostatic nature, or whether hydrogen bonding predominates), and (3) the specificity of interactions between the particles. The first factor has been studied using methods including viscometry [16, 17, 18, 19, 20, 21, 22, 23], light scattering [1, 24, 25, 26, 27], size exclusion chromatography [28], among others. The second and third factors have been studied mainly through zeta potential measurements [29] and rheological methods [30, 31]. In the case of inorganic oxides dispersed in water, due to the interaction of the solid colloidal particles with the dispersing phase, there will be the development of charged surface sites (depending on the dispersing phase pH) according to these reactions [32]:

$$\text{bulk - MOH} + \text{H}^+ \rightleftharpoons \text{bulk - MOH}_2^+ \rightleftharpoons \text{bulk - M}^+ + \text{H}_2\text{O}$$

$$\text{bulk - MOH} + \text{OH}^- \rightleftharpoons \text{bulk - M(OH)}_2^- \rightleftharpoons \text{bulk - MO}^- + \text{H}_2\text{O}$$

Although most sites are neutral MOH, 20–25% of the sites are usually charged: an ionic atmosphere is formed and, because of these charges, ions of opposite charge tend to cluster. Two regions of charge must be distinguished. First, there is a fairly immobile layer of ions that stick tightly to the surface of the colloidal particle, which may include water molecules. The radius of the sphere that captures the rigid layer, or the radius of shear, is the major factor that determines the mobility of the particle. The inner shell of charge and the outer atmosphere is called the electric double layer; the DLVO (Derjaguin, Landau, Verwey, and Overbeck) theory is widely used to calculate the zeta potential, ζ (the potential at the slipping plane of the double layer) from electrophoretic measurements [33]. As ζ tends to zero, the repulsion between the particles is minimized and they tend to collapse. As $|\zeta|$ tends to higher values, the system tends to be stabilized. There has been plenty of work done on the influence of the adsorption of polyelectrolytes on different oxide surfaces, as well as the correlation of this adsorption to ζ and, therefore, to their stabilities [34, 35].

In the specific case of our group, investigations of the stability of alumina dispersions and the polyelectrolyte effect have been carried out through analyses of the sedimentation kinetics of these dispersions [36], as well as of the rheology of these systems in their concentrated form [31]. In our first work, it was found that sedimentation kinetics of these dispersions at two different polymer concentrations (0.05 and 20.0 g L^{-1}) were similar at an NaCl concentration of 3.00×10^{-2} mol L^{-1}, while they were markedly different at an NaCl concentration of 3.00×10^{-2} mol L^{-1}; the system with lower polyelectrolyte concentration had faster kinetics of sedimentation, which was related to a bigger particle size, due to flocculation. It was shown that this difference could be correlated to the polyelectrolyte effect [37]: as the concentration of polyelectrolyte increases, the higher concentration of counterions shields repulsive interactions between charged groups in the chain, decreasing their average dimensions, so that the higher the amount of low molecular weight electrolyte in solution (NaCl), the less pronounced the polyelectrolyte effect. The second work used these results to show that the pseudoplastic character of these dispersions was increased by the occurrence of flocculation.

The purpose of this work is to show that it is possible to draw a correlation between polyelectrolyte adsorption and polyelectrolyte effect, through viscosity measurements of the dispersing phase. With the help of zeta potential measurements, the relation between the stability of alumina and polyelectrolyte conformation will be investigated, resulting in a better characterization of the previously observed differences in flocculation for this system.

Experimental

Materials

The alumina powder (Alcoa Alumínio S.A., Brazil) used in this work comprised particles with an average diameter of (2.1–3.1) μm, according to the supplier. Also according to the manufacturer, the average surface area, as measured by standard BET N_2 adsorption, was (1.4–1.7) $m^2 g^{-1}$. The chemical analysis data (expressed in terms of weight percentage) were: Al_2O_3 (99.4–99.7)%, SiO_2 (0.030–0.050)%, Fe_2O_3 (0.038–0.050)%, and Na_2O (0.11–0.14)%. The polyelectrolyte used in this work was a sodium salt of poly(styrenesulfonic acid-*co*-maleic acid) ($<M_w> \approx 2 \times 10^4$ g mol^{-1}, Fig. 1, Aldrich, used as received), with a molar ratio 1:1 for styrene to maleic acid. NaCl and $AlCl_3 \cdot 6H_2O$ (P.A., Vetec, Brazil) were used as received.

Adsorption experiments

Alumina dispersions were prepared with 1.50 wt% of solids. The experiments were performed at two salt concentrations: $[NaCl] = 3.00 \times 10^{-3}$ mol L^{-1} (system defined as being of low ionic force) and 3.00×10^{-2} mol L^{-1} (high ionic force system), the polymer concentration depending on the experiment. All of the dispersions were prepared with bidistilled water, immersed in an ultrasonic bath (Transsonic model T460, Germany) for 1 min, and allowed to stand for 4 days at room temperature to reach equilibrium. In all experiments $pH = 8.0 \pm 0.1$ (with or without polyelectrolyte, showing that the macromolecule should be quite neutral). In

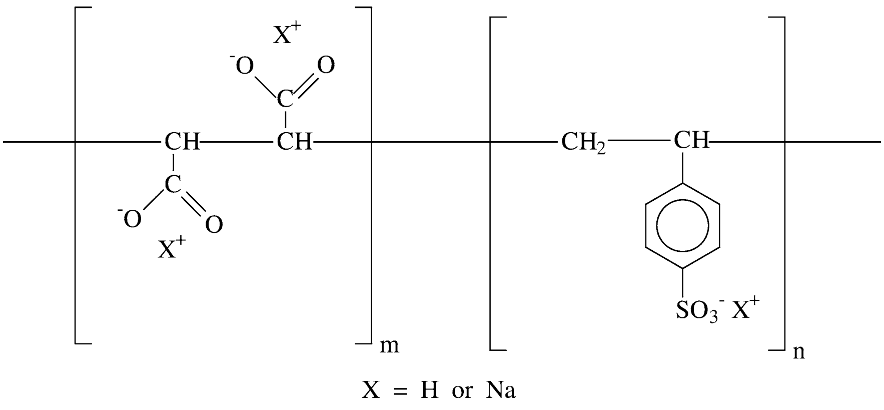

Fig. 1 Chemical structure of the copolymer used in this work

these experiments, no Al^{3+} in the form of $AlCl_3{\cdot}6H_2O$ was added.

Atomic absorption spectroscopy

The content of Al^{3+} ions in the dispersing phase of the samples was determined using an atomic absorption spectrometer Varian Spectraa 110, with the following parameters: wavelength, 309.3 nm; aperture, 0.2 nm; calibration curves with 40, 80, 120, and 160 ppm of Al^{3+}; lamp current, 10 mA; gas, acetylene; support, nitrous oxide; stoichiometry, red cone reductive flame with 1–2 cm height; sensitivity, 0.76 μg L^{-1}.

Viscometry

Viscometry was carried out using a Cannon-Fenske viscometer #100, previously calibrated with different fluids. The flow time in these measurements was never shorter than 100 s. From viscometry, the following quantities were calculated:

$$\Delta\eta(\%) = \frac{\eta_{\mathrm{sup}} - \eta_{\mathrm{sol}}}{\eta_{\mathrm{sol}}} \times 100. \tag{1}$$

$$\frac{\Delta\eta_{\mathrm{sup}}}{\Delta\eta_{\mathrm{sol}}} = \frac{\eta_{\mathrm{sup,l}} - \eta_{\mathrm{sup,h}}}{\eta_{\mathrm{sol,l}} - \eta_{\mathrm{sol,h}}}, \tag{2}$$

Here, η_{sup} is the viscosity of the supernatant (the dispersing phase), η_{sol} is the viscosity of the solution used in the adsorption experiment. The subscripts l and h account for low and high ionic forces, respectively. Equation 1 indicates whether the viscosity of the dispersing phase increases or decreases after adsorption, and Eq. 2 whether the polyelectrolyte effect is enhanced by the process of adsorption.

The supernatant was separated from the solid particles by centrifugation of the dispersions obtained as described in the "Experimental" section for 3 h and 3000 RPM. The concentrations used in these experiments ranged from 0.5–20.0 g L^{-1}.

Electrophoretic measurements

Electrophoretic mobilities of the alumina dispersions were determined for copolymer concentrations ranging from $5.00{\times}10^{-4}$ to 20.0 g L^{-1}. A particle concentration of 0.500 g L^{-1} was achieved by dilution of the alumina dispersions obtained as explained in the "Experimental" section, using copolymer solutions with the same polymer concentration in the dispersing phase, before measurements were carried out. The electrophoretic mobility measurements, μ_E, were carried out using a Zeta-Meter System 3.0+ (Zeta-Meter Inc., USA). The zeta potential, ζ, of a given alumina dispersion was calculated from μ_E by employing the Smoluchowski relationship [38]:

$$\zeta = \frac{\mu_E \eta}{\varepsilon_0 \varepsilon}, \tag{3}$$

where ϵ_0 is the permittivity of vacuum, ϵ is the dielectric constant of water, and η is the viscosity of the dispersing phase.

Results and discussion

Viscosity measurements

Figure 2 depicts the ratio between the differences in viscosity at low and high ionic forces for different polymer concentrations, $\frac{\Delta\eta_{\mathrm{sup}}}{\Delta\eta_{\mathrm{sol}}}$. One can see that as polymer concentration tends to zero, this ratio also tends to zero. It means that, as polymer concentration decreases, there is the tendency to a null difference (in the case of the supernatant), in terms of polyelectrolyte effect, between low and high ionic force solutions. The main reason is that, as concentration decreases, a higher fraction of the original polyelectrolyte molecules is

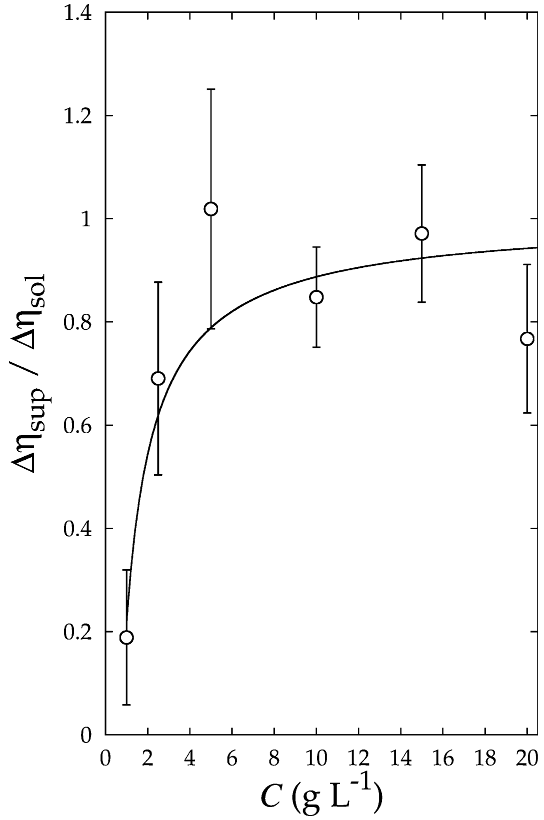

Fig. 2 $\frac{\Delta\eta_{sup}}{\Delta\eta_{sol}}$ as a function of polymer solution concentration

adsorbed on the alumina surface, resulting in a less pronounced difference between higher and lower ionic forces (less polyelectrolyte molecules, lower viscosity difference). As polymer concentration increases, the amount of polyelectrolyte molecules tends to be the same, so that one would expect that $\frac{\Delta\eta_{sup}}{\Delta\eta_{sol}}$ increases as well. A further increase in concentration, however, has two effects: 1) it causes the polymer concentration in the dispersing phase, in both cases, to be the same, and 2) it minimizes the polyelectrolyte effect. As a consequence, $\frac{\Delta\eta_{sup}}{\Delta\eta_{sol}} \rightarrow 1$. Within experimental errors, it seems that this did happen as concentration was increased.

In the last analysis carried out, although there were fewer polyelectrolyte molecules in the dispersing phase after adsorption had occurred, we did not say that there was a decrease in the viscosity of the dispersing phase after adsorption. Although common sense would lead one to this conclusion, Fig. 3, in which the relative variation in dispersing phase viscosity [$\Delta\eta$(%), Eq. 3] is depicted, shows an opposite trend.

If there are less polyelectrolyte molecules in the dispersing phase, as a result of alumina surface-polyelectrolyte interactions, then either chemical reactions or specific interactions must be occurring with the polyelectrolyte molecules in order to cause this increase in viscosity. The former possibility may be ruled out, so that one could think of this increase as a result of some sort of interaction that would agglomerate polyelectrolyte coils, so that they would, in physical terms, behave as if they were a single bigger coil. Of course, the agent involved in this agglutination must come from the alumina surface. It has been reported in the literature that, when interacting with water, alumina liberates aluminum ions [39]. This liberation, at neutral pH conditions, would involve an equilibrium in which the well-known acid hydrolysis reaction of alumina would be involved as a part of it [40]:

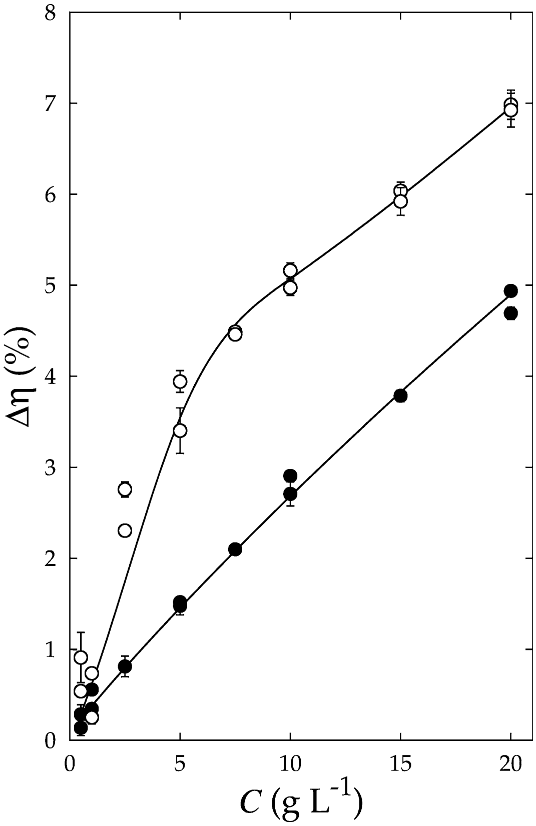

Fig. 3 $\Delta\eta$(%) as a function of concentration. Open circles: low ionic force ([NaCl] = 3.00×10^{-2} mol L^{-1}). Filled circles: high ionic force ([NaCl] = 3.00×10^{-2} mol L^{-1})

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$Al_2O_{3(s)} + 6H_3O^+_{(aq)} + 3H_2O_{(l)} \rightleftharpoons 2[Al(H_2O)_6]^{3+}_{(aq)}$$

In agreement with these authors, it was found by atomic absorption spectroscopy that Al^{3+} was present in the dispersing phase at a concentration of (12 ± 2) mg L^{-1}. These data suggest, then, that the increase in interaction may be due to the formation of macromolecular clusters, resultant from electrostatic interactions between Al^{3+} cations and negatively charged sites in macromolecular coils, as depicted in

Fig. 4. This sort of increase in viscosity due to cluster formation has been reported in the literature: this electrostatic interaction is the main reason for physical crosslinking and gelling in anionic polyelectrolytes by polycharged cations [41, 42, 43].

In order to back up this analysis, viscosity measurements on polymer solutions with low ionic force at three different concentrations of AI^{3+} ions [added in the form of $AlCl_3{\cdot}6H_2O$], and two polyelectrolyte concentrations were carried out. Reduced viscosity, η_{red}, was calculated according to the following expression [44, 45]:

$$\eta_{\mathrm{red}} = \frac{1}{C}\left(\frac{t}{t_0} - 1\right), \tag{4}$$

where C is the polyelectrolyte concentration, t is the flow time for the solution, and t_0 is the flow time for the pure solvent. An increase in η_{red}, the polyelectrolyte concentration being fixed, implies either an increase in macromolecular dimensions [46], or the formation of physically bigger macromolecules by clustering, as pointed out earlier. The results are displayed in Table 1. The first point to be noticed is the occurrence of the polyelectrolyte effect, since for all AI^{3+} concentrations, η_{red} decreases with increasing polyelectrolyte concentration. For the higher polyelectrolyte concentration, η_{red} continually increases with increasing Al^{3+} concentration, as expected. When polyelectrolyte concentration is lower, however, η_{red} initially increases and then it falls (although to a value above the one for the solution without Al^{3+} ions). That could be explained by the fact that, when aluminum ion concentration increases, there is a higher probability of Al^{3+} ions being inside the macromolecular coils: as a result, electrostatic interactions would physically crosslink the coil, resulting in a coil with smaller dimensions. It should also be pointed out that, in the same way that the increase in polyelectrolyte counterion concentration would shield anionic repulsion, it would make Al^{3+} interactions with the anionic sites on the copolymer chains less probable.

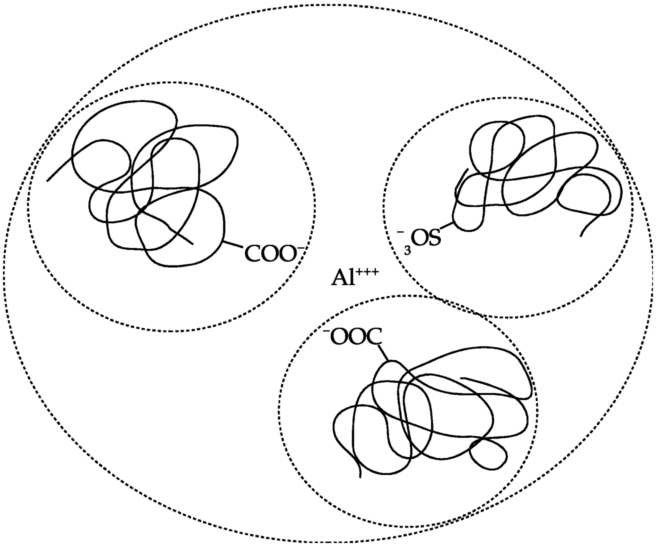

Fig. 4 Scheme representing a bigger macromolecular coil formed by the interaction of three smaller coils with Al^{3+}

Zeta potential and electrophoretic mobility measurements

Figure 5 shows the variation of electrophoretic mobility (μ_{E}) with time for an alumina dispersion with a polymer concentration of 20.0 g L^{-1}, at high ionic force ([NaCl] = 3.00×10^{-2} mol L^{-1}). From this figure one can

Table 1 Reduced viscosity as a function of polymer concentration (C) and concentration of Al^{3+}

C (g L^{-1})	η_{red}(mL g^{-1}) [Al^{3+}] = 0	[Al^{3+}] = 13 mg L^{-1}	[Al^{3+}] = 26 mg L^{-1}
2.9200 ± 0.0002	2.28 ± 0.06	2.72 ± 0.01	2.52 ± 0.02
29.200 ± 0.002	1.21 ± 0.01	1.267 ± 0.008	1.71 ± 0.01

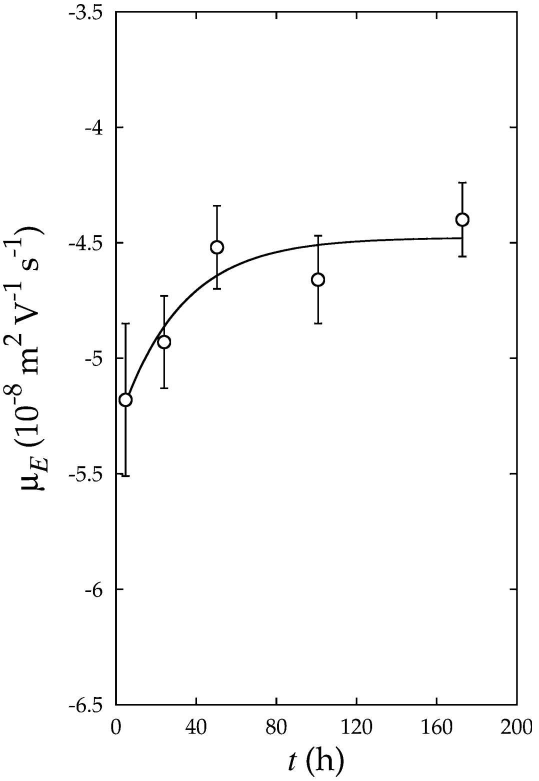

Fig. 5 Electrophoretic mobility as a function of time for an alumina dispersion with a polymer concentration of 20.0 g L^{-1}, at high ionic force (3.00×10^{-2} mol L^{-1})

see that, in terms of adsorption kinetics, the system could be considered to be in equilibrium after a time of 80 h. This is the reason for allowing the system to undergo adsorption for 4 days (96 h) before carrying out any sort of analysis.

Another important observation is that μ_E becomes less negative with time. That would correlate either with the picture of a negatively charged particle adsorbing a positively charged polyelectrolyte segment or with an increase in positively charged sites on the surface with time (independently of the polyelectrolyte adsorption). Regarding the dispersing phase, the copolymer used in this work does have an anionic nature, a fact that disqualifies the first hypothesis, so we should look more closely at the latter. All of the measurements with the alumina dispersions were carried out at pH = 8.0 ± 0.1, and, from the literature, the isoelectric point of alumina is at a pH≈8.5–9.0 [47, 48]: as a consequence, at pH = 8.0 alumina particles are positively charged [49]. However, one must bear in mind that any impurities present on the surface (Na_2O and SiO_2, for instance) may shift ζ to less positive values [50] by their dissociation into negative ions (which would remain on the surface) and positive ions (which would be present in the dispersing phase). Electrophoretic mobility measurements of alumina dispersed in NaCl 3.00×10^{-3} mol L^{-1} (without polyelectrolyte) proved this hypothesis to be correct: the electrophoretic mobility changed from $(4.4 \pm 0.2)\times10^{-8}$ $m^2V^{-1}s^{-1}$ (1 h after preparation) to $(5.0 \pm 0.2)\times10^{-8}$ $m^2V^{-1}s^{-1}$ (4 days after preparation). In the case of the alumina in NaCl 3.00×10^{-2} mol L^{-1} dispersions, the change was from $(3.4 \pm 0.1)\times 10^{-8}$ $m^2V^{-1}s^{-1}$ to $(3.6 \pm 0.1)\times10^{-8}$ $m^2V^{-1}s^{-1}$. However, there is still the problem that the increase in μ_E is less pronounced in the case of pure alumina. This may be due to the following reasons: 1) there strong polyelectrolyte adsorption over short times, followed by desorption over longer times; 2) the adsorption of polyelectrolyte via hydrogen bonding on the surface may cause slower kinetics of surface charging, and; (3) as polyelectrolyte concentration gets higher on the surface, condensation of Na^+ ions on COO^- or SO_3^- groups would occur with the same result, in terms of μ_E.

The data depicted in Figure 6, in which zeta potential data are plotted versus polymer concentration, can be used for a further analysis of the adsorption process. First of all, confirming the discussion carried out in the last paragraph, when using pure alumina suspensions, the values of zeta potential were positive: (57 ± 1) mV for low ionic force, and (41 ± 1) mV for high ionic force. Analyzing the same figure, one can see that for high and low ionic forces, as polymer concentration increases, zeta potential decreases, with the difference that there is a minimum in the case of low ionic force. The influence here for this minimum may come from the polyelectrolyte effect: as the concentration of anionic polyelectrolyte increases, there are more counterions within the macromolecular coil to shield the repulsion between the negatively charged SO_3^- and COO^- groups. As a consequence, this coil will have smaller dimensions, increasing the process of adsorption on the alumina surface: zeta potential will dramatically decrease until it reaches a minimum. A further increase in counterion concentration, on the other hand, will have the effect of promoting the condensation of the counterions to the negative charges of the polyelectrolyte (so that it becomes less negatively charged): hydrogen bonding will play an important role in adsorption (as in the case of high ionic force). As a result, zeta potential values in high and low ionic force systems will tend to be the same as concentration increases.

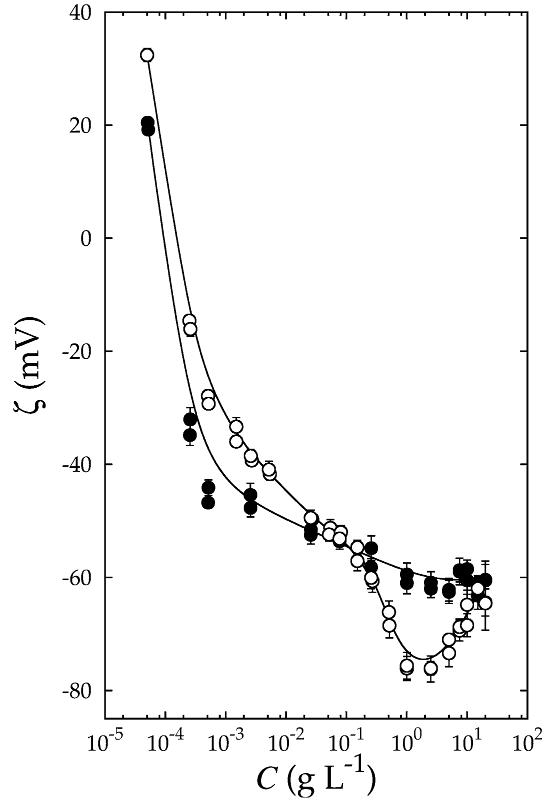

Fig. 6 ζ potential as a function of polymer concentration for dispersions with low ionic force ([NaCl] = 3.00×10^{-3} mol L^{-1}, open circles) and high ionic force ([NaCl] = 3.00×10^{-2} mol L^{-1}, filled circles)

It would also be interesting to get new insights from further correlations of data from zeta potential experiments to data from viscosity measurements. In terms of viscometry, it was seen that, at a polymer concentration of ~5 g L^{-1}, $\frac{\Delta\eta_{sup}}{\Delta\eta_{sol}}$ begins to tend to a constant value (Fig. 2). On the other hand, in terms of $\Delta\eta(\%)$, at the same concentration, the slope of the $\Delta\eta(\%)$ versus C curve for the solutions with lower ionic force begins to change (Fig. 3), reaching a value closer to the slope for the higher ionic force suspensions. Glancing at Fig. 6, one can see that, at this concentration, there is a strong decrease in the zeta potential for the low ionic force suspensions, which must be due to a higher adsorption of polyelectrolyte at this point, due to coil contraction at this concentration. Then zeta potential starts increasing, tending to the values found for higher ionic force suspensions; the net result (in terms of dispersing phase) being that the amount of solubilized polyelectrolyte follows the same behavior as the way it increases with original solution concentration (in other words, the slope of $\Delta\eta(\%)$ versus C).

Finally, regarding the settling and rheological experiments mentioned in the "Introduction", one can see that, in terms of ζ potential, at both polymer concentrations used in the experiments we have discussed (0.0500 and 20.0 g L^{-1}), there is not a significant difference between these quantities at high and low ionic forces. Therefore, this suggests that mosaic flocculation can be ruled out as the mechanism involved in particle destabilization, so that bridging flocculation must be the predominant flocculation mechanism.

Conclusions

Polyelectrolyte adsorption widely governs the stabilization of alumina suspensions. In turn, polyelectrolyte adsorption is strongly dependent on macromolecular dimensions, which, in non-isoionic dilution, decrease as polyelectrolyte concentration increases, which therefore increases polyelectrolyte adsorption. The increase in polyelectrolyte adsorption could be characterized by the occurrence of a minimum in the zeta potential versus polymer concentration curve, as well as by viscometry of the dispersing phase. Regarding viscosity measurements, polyelectrolyte adsorption resulted in an increase in the viscosity of this phase, a fact that was correlated to the clustering of polyelectrolyte macromolecules around polycharged cations Al^{3+}, which were found to be present in this phase.

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