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The use of dielectric spectroscopy for the characterisation of the precipitation of hydrophobically modified poly(acrylic-acid) with divalent barium ions

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ABSTRACT

The use of dielectric spectroscopy as a monitor for coagulation processes was investigated. Hydrophobically modified poly(acrylic-acid) polymers were used as model macromolecules and coagulated with barium ions. The coagulation process was quantified using a photometric dispersion analyser, thereby serving as a point of reference for the dielectric spectroscopy. It was found that the hydrophobic modification increased the dosage of barium needed to obtain complete coagulation, whereas the dosage required to initiate coagulation was lowered. The coagulation of the polymer samples caused the relaxation time of the measured dielectric dispersion to increase, and this parameter was found to be a good indicator of the formation of polymer aggregates. The magnitude of the dielectric dispersion decreased as a function of barium dosage, but when coagulation was initiated an increase was observed. The observed agreement between the onset of coagulation and the changes in the dielectric dispersion shows the potential use of dielectric spectroscopy for the characterisation of coagulation processes.

1. Introduction

Chemical pre-treatment, such as coagulation or flocculation, is often used prior to solid–liquid separation processes to improve the quality and/or the rate of the process [1–3]. However, very few methods for on-line evaluation of the effect of the chemical dosage are available. For this reason the jar test is often used to assess the effect of the coagulant or flocculant. Although simple to use, this method is time consuming, includes a considerable time delay and may fail to provide accurate data due to the influence of changed temperature, chemical mixing and shear forces. Most of the available on-line methods, e.g. photometric dispersion analyser [4] and streaming current detector [5], are limited to fairly dilute suspensions as compared to most industrial suspensions, where methods applicable for high solid concentrations are needed.

Dielectric spectroscopy (DS) has previously been used for the characterisation of colloidal particles [6–11] and dissolved polymers [12–14] in terms of size and charge, and has the capability of measuring at high solid concentrations [11]. Recently, the use of DS to monitor the flocculation of polystyrene particles [15,16] was investigated. It was found that the characteristics of the measured dielectric dispersion could be related to the flocculation process. The formation of particle aggregates resulted in an increase in the relaxation time of the dielectric dispersion due to the increased length scale of the polarisation, and this parameter was therefore found to be a useful indicator of the onset of flocculation. Furthermore, the neutralisation of particle charges by the adsorption of the charged flocculant was found to result in a decrease in the magnitude of the dielectric dispersion, thus giving information of the particle charge. These studies indicate that DS can potentially be used in the on-line assessment of aggregation processes, but still much work is required to identify the possibilities and restrictions of the method.

Many ‘real life’ suspensions (e.g. raw water, sludges, paper pulp, dairy products, fermentation broths) are constituted partly by colloidal particles, but also by dissolved macromolecules. The previous studies using DS have focussed solely on the flocculation of colloidal particles, and thus an investigation of its use as a monitor for the coagulation of macromolecules is needed.

When applying an alternating electric field to a solution of charged macromolecules, the permittivity of the solution varies with frequency showing two distinct dispersions; one in the kHz range and one in the MHz range. The latter is caused by the polarisation of free counter-ions and takes place at high frequencies due to the small polarisation lengths perpendicular to the macromolecule. The low frequency dispersion is not well understood, but is believed to arise from the migration of condensed counter-ions along the structure of the macromolecule thus polarising the whole structure [17]. As this relaxation process is related to the size of the macromolecular structure it seems likely that changes in structure size caused by coagulation will result in changes of this relaxation process.

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The magnitude ($\Delta\varepsilon$) and relaxation time (τ) of the low frequency dielectric dispersion of the macromolecular solution can be estimated under the assumption of the presence of monovalent counter-ions in a concentration equal to the polymeric charge [17]:

$$\Delta\varepsilon \approx l_B \varepsilon_r f c R^2 \tag{1}$$

$$\tau \approx \frac{\zeta R^2}{6 k_B T} \tag{2}$$

where f is the degree of ion condensation, c the number concentration of charge carrying segments on the macromolecule, R the characteristic length of the macromolecule, ζ the friction coefficient of the condensed counter-ions, k_B the Boltzmann constant, T the absolute temperature, and l_B is the Bjerrum length defined as:

$$l_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B T} \tag{3}$$

where e is the elementary charge, ε_0 the permittivity of vacuum and ε_r is the relative permittivity of the solvent.

Quantitative agreement between these theoretical expressions and measured values of $\Delta\varepsilon$ and τ is generally poor as the predicted values are too high, whereas a qualitative agreement seems to be present, as the predicted dependence of concentration is observed experimentally [17]. From Eqs. (1) and (2) it can be seen that both $\Delta\varepsilon$ and τ are theoretically dependent on the characteristic length of polarisation, and thus both parameters are likely to be sensitive to coagulation of the macromolecules.

In this study the use of DS to monitor coagulation of a model macromolecule has been investigated. Hydrophobically modified poly(acrylic-acid) polymers are coagulated using barium ions and the process is characterised using a photometric dispersion analyser. The results are compared to the observed changes in the dielectric spectrum during the coagulation process, and the potential of DS to describe the formation of polymer aggregates is evaluated.

2. Materials and methods

2.1. Hydrophobically modified poly(acrylic-acid)

Hydrophobically modified poly(acrylic-acid) was synthesised in 1-methyl-2-pyrrolidone (Aldrich, >99%) using the procedure described in Wang et al. [18]. Dodecylamine (Acros, 98%) was attached to a fraction of the carboxylic groups on a 100 kDa poly(acrylic-acid) (Aldrich) using dicyclohexyl carbodiimide (Acros, 99%) as initiator.

After the synthesis the system was cooled to room temperature and crystals of dicyclohexylurea formed from the initiator were removed by filtration. The crystallisation was aided by the addition of 10 vol%. demineralised water before filtration. The polymers were then precipitated by addition of a 5 M NaCl/1 M NaOH solution to the filtered synthesis product. After repeated centrifugation and washing with the NaCl/NaOH solution, the pH of the polymer solution was adjusted to 3 using HCl and the solution was dialysed against demineralised water (conductivity of 3 μS/cm) using a Spectra/Por dialysis tubing with a 6–8 kDa cutoff. The concentration of the polymer solution was then increased by freeze drying. To remove any large impurities and polymer aggregates the solution was filtered through a 0.45 μm filter prior to use. The structure of the product was confirmed using ^{1}H NMR. Determination of the content of weak acid groups on the polymers (σ_{pol}) was made using potentiometric titration with NaOH on a TIM900 Titration Manager (Radiometer Copenhagen).

Four polymer samples were synthesised differing by the degree of hydrophobic modification. The samples are denoted HMPAA-X, where X is the modification percentage. A non-modified poly(acrylic-acid) polymer (PAA) was also used as a reference. In Table 1 the measured charge content can be seen.

Using ChemSketch software the distance between two charged groups (b) on a poly(acrylic-acid) polymer was estimated to 0.4 nm. As the hydrophobic side-chains are expected to be randomly distributed along the polymer [18], the concept of an average distance between charges is reasonable. A similar distance was calculated using the degree of modification for the hydrophobically modified polymers. These distances were used to estimate the fraction of ion condensation (f) seen in Table 1 using the Manning model [19].

$$f = 1 - \frac{b}{l_B |z_p z_c|} \tag{4}$$

where b is the distance between charges on the macromolecule, z_p and z_c are the valences of the charges on the macromolecule and of the counter-ions.

2.2. Coagulation experiment

The polymer solution was diluted to a concentration of 20 μM (equal to 2 g/L for the PAA) using demineralised water. A $Na_2B_4O_7$ buffer (Merck, purity >99.5%) was added from a stock solution of 0.1 M to a final concentration of 1 mM. The pH was adjusted to 9.3 using 2 M KOH (Fluka, pro analysi). A beaker containing 0.25 L of the buffered and pH-adjusted polymer solution was placed in a water bath (30 ± 0.1 °C) and stirred using a single bladed propeller and a Heidolph stirrer (100 rpm). The polymer solution was pumped through a PDA and an impedance measurement cell using a peristaltic pump and a flow of 9 mL/s. A silicone tube with an inner diameter of 5 mm was used. The experimental setup can be seen in Fig. 1.

A 0.25 M $BaCl_2$ solution (Riedel-De Haën, >99%) was gradually added to the polymer solution using a computer controlled membrane pump (Iwaki model EH). The PDA signal was measured with a 10 min equilibration delay after each addition of $BaCl_2$ and after every third addition the impedance spectrum was measured as well. This was continued until sufficient $BaCl_2$ had been added to cause precipitation of the polymer. As the amount of barium needed to cause precipitation is related to the polymeric charge, the barium dosages are given as a charge equivalent ratio (CR) defined as:

$$CR = \frac{2 V_{BaCl_2} c_{BaCl_2}}{m_{pol}\sigma_{pol}} \tag{5}$$

where V_{BaCl_2} and c_{BaCl_2} are the volume and concentration of the added $BaCl_2$ solution and m_{pol} is the mass of the polymer.

2.3. Electrophoretic mobility

The electrophoretic mobility of the five polymer samples were measured as a function of barium dosage. The polymer solutions used in the coagulation experiments were diluted ten times using a 1 mM $Na_2B_4O_7$ buffer at pH 9.3. Barium chloride was then added

Table 1
Data on the hydrophobically modified poly(acrylic-acid) polymers.

Polymer sample	Degree of modification (%)	Titrated charge (meq/g)	Distance between charges (b) (nm)	Degree of condensation (f)
PAA	0	13.8	0.40	0.45
HMPAA-1	1	13.5	0.40	0.44
HMPAA-3	3	12.7	0.41	0.43
HMPAA-6	6	11.0	0.42	0.41
HMPAA-8	8	10.0	0.43	0.40