Adsorption and flocculation behaviors of polydiallyldimethylammonium (PDADMA) salts: Influence of counterion

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Abstract

Two modified polymer flocculants of PDADMA salts, PDADMA nitrate (PDADMAN) and PDADMA sulfate (PDADMAS), were prepared from the most widely used commercial product of polydiallyldimethylammonium chloride (PDADMAC). Solution properties such as conductivity and viscosity were investigated, showing that the conductivity follows the order of PDADMAS > PDADMAC > PDADMAN, while the reduced viscosity increases in the order of PDADMAS < PDADMAC < PDADMAN. The results indicate that, compared with PDADMAC, PDADMAN has a more cationic density and a more extended polymer chain, whereas PDADMAS exhibits a smaller coiled polymer size because of the stronger charge affinity of sulfate ion to the polycation of PDADMA. Flocculation experiments were performed on kaolin suspensions. It was found that PDADMAN is the most efficient in turbidity removal, while PDADMAS has wider optimum dosages, larger floc size and more rapid settling rate. Atomic force microscopy (AFM) was employed for imaging the adsorption structures of the three polymers on the negatively charged mica surface. Remarkable differences in molecular conformation were observed. Compared with the pearl necklace-like aggregation of hemispheroids of PDADMAC polymer, PDADMAN takes a sponge-like thin layer structure and PDADMAS exhibits a uniform hemispherical structure.

The above differences in both the solution property and the adsorption and flocculation behaviors are attributable to counterion effects. Different counterions may lead to different adsorption and flocculation mechanisms that PDADMAN adopts a flat and layer–layer adsorption without loops and tails extended from the surface, implying that a charge neutralization mechanism plays more roles, while adsorbed PDADMAS is in the form of coiled spheres with loops and tails so that a bridging mechanism is more involved. Namely, it is the adsorption structure and morphology of the polymer flocculants that is the main factor influencing the flocculation mechanism.

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Keywords: polydiallyldimethylammonium salts; counterion effect; atomic force microscopy (AFM); adsorption structure and morphology; flocculation

1. Introduction

Polydiallyldimethylammonium chloride (PDADMAC), the most important commercial polymer of the allyl monomers, is a cationic functional polymer that has

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outstanding utility in many flocculation applications (Sotiropoulou et al., 2004; Marcelo et al., 2004; Möller and Nordmeier, 2002; Wandrey et al., 1999). Compared with common vinyl monomers, however, allyl monomers polymerize more difficulty and yield relatively lower molecular weight (Matsumoto, 2001; Brain, 1995), which largely affect the adsorption and flocculation behaviors of PDADMA polyelectrolytes. Some advances in PDADMA preparation and modification, such as copolymerization with hydrophobic and hydrophilic monomers (Zhao et al., 2002; Chang et al., 2000), polyelectrolyte complexes (PECs) of oppositely charged macromolecules (Möller and Nordmeier, 2002; Petzold et al., 1996) and cationic particles prepared by polymer being adsorbed or grafted on clays (Zhang et al., 2002; Zhu et al., 2001), have been reported in recent years.

As polyelectrolytes, PDADMA-X salts may couple electrostatic interactions and macromolecular dynamics on solid–liquid interfaces. Structure and amount of polyelectrolyte chains being adsorbed play crucial roles on the performances. Therefore, the adsorption and flocculation behaviors of PDADMA-X are of great scientific and practical interests. A range of experimental techniques, including optical reflection and scattering technique, electrochemical and quartz crystal microbalance (QCM), neutron reflectivity, X-ray reflectivity, hydrodynamic techniques, electron microscopy, etc. (Zhu et al., 2001; Hinderberger et al., 2002), have been used to characterize the structure and adsorption mechanism of polyelectrolytes (e.g. PDADMA-X salts). In flocculation practice, polymers are known binding to particle surfaces in “loops”, “trains” and “tails”, as shown in Fig. 1. Polymer conformation can therefore be tailor-made by selectively pinning down portions of the

polymer, to control the percentage of loops and trains. Many factors can contribute to the adsorbed molecular conformation of a functional polymer, including ionic strength, pH, polymer charge density, molecular weight, particle surface characteristics and so on.

Physicochemical properties of polyelectrolyte solutions depend crucially on strength of inter- and intramolecular coulombic interactions (Benmansour et al., 2003). The effects of pH and ionic strength on the polymer conformation, the absorption morphology and the application efficiency of PDADMAC (Matsumoto, 2001; Brain, 1995) have been well documented. Relatively fewer papers studied the effects of counterions on the properties of cationic polyelectrolytes solution (Hinderberger et al., 2002; Matsumoto, 2001) and mainly pointed at the influence of the counterions on mobility of polyelectrolytes but their flocculation applications. PDADMA salts with counterions other than chloride (e.g. nitrate, sulfate, etc.) cannot be obtained by direct polymerization of monomers mainly due to the degradative monomer chain transfer effect.

This paper prepared PDADMA sulfate and PDADMA nitrate from PDADMA chloride, via anionic replacement reactions with silver salts. Then, the absorption and flocculation mechanism of the polyelectrolyte as well as the counterion effects were investigated. Furthermore, atomic force microscopy (AFM) was applied for detailed research on the adsorbed molecular structure of the PDADMA polyelectrolytes at a nanoscale level. As one part of our researches on high efficient polymer flocculants (Zhao et al., 2002; Chang et al., 2000), this study is valuable for PDADMAC modification to obtain new functional polymers and for understanding flocculation mechanisms of PDADMA polymers.

2. Materials and methods

2.1. Reagents

A 40 wt.% of PDADMAC aqueous solution (Florage, SNF, France) was purified using Pellicon™ ultrafiltration system equipped a Millipore™ tangential flow filter membrane with molecular weight cut-off (MWCO) of 100kDa and freeze dried. Its molecular weight was determined to be 0.48×10^5 using viscometrical method (1.0M NaCl , 25°C $[\eta]$ ($\text{ml} \times \text{g}^{-1}$) = $6.1 \times 10^{-3} \text{M}^{0.82}$ according to the Mark-Houwink-Sacurada equation).

Silver salts of nitrate and sulfate were of analytical reagent grade (Beijing Chemical Reagent Agent, China). Double distilled water was used in the whole test.

Fig. 1. Schematic of the molecular conformation of polyelectrolyte polymers on the surfaces of different charges densities (a) at low charge densities and (b) at high charge densities.

2.2. Preparation of PDADMAN and PDADMAS

10ml PDADMAC aqueous solution (0.3mol/l in terms of monomer) was mixed with the stoichiometric amounts of silver salt of nitrate or sulfate under stirring. After 0.5h of reaction, the suspension solution was centrifuged and the supernatant was freeze-dried. The contents of NO_3^- and SO_4^{2-} and the residual Cl^- as well in the prepared polydiallyldimethylammonium salts were measured by Ion Chromatography 4500i (Dionex CO, USA), and the conversion rates were found to be 99.5% and 99.7%, respectively.

2.3. Characterization of the modified polymer flocculants of PDADMAN and PDADMAS

2.3.1. Reduced viscosity (η_{sp}/C) measurement

Viscometric measurements were carried out by an Ubbelohde viscometer (4ml, 0.6mm) at $25 \pm 0.1^\circ\text{C}$. All polymer solutions were made up in double-distilled water. The solutions were filtered by sand filter and kept overnight. Prior to the measurements, the solutions were kept about 15min at ambient for temperature equilibrium. The concentration (C_p) of PDADMA-X ranged from 2.5×10^{-3} to 5.0×10^{-2} mol/l in this test. In this concentration region, the kinetic energy and shear rate were regarded as negligible, and the density of solution was considered approximately the same as that of pure water. According to Nishida et al. (Minakata et al., 2002), reduced viscosity (η_{sp}/C) can be calculated in the following equation: $\eta_{sp}/C = \eta_{intra}/C + \eta_{inter}/C$, where η_{intra}/C is intramolecular hydrodynamic contribution and η_{inter}/C represents intermolecular electrostatic contribution.

2.3.2. Conductivity measurement

Solution conductivity was measured on a Conductometer (HACH-11A, Japan), reproducible to within $\pm 0.05\%$ for all polymer solutions. All measurements were carried out under a slowly stirred condition in a thermostatic bath at $20 \pm 1^\circ\text{C}$. Polymer solutions were prepared by using a weighted fraction of 50ml polymer and expressed in molar concentration (mol/l). The concentration (C_p) range of PDADMA-X was from 1.0×10^{-5} to 16×10^{-5} mol/l in this test. A relative linear relation between the conductivity and C_p can be obtained in this region according to Nishida et al. (2002).

2.3.3. Atomic force microscopy (AFM) observation on polymer conformation and on adsorbed layer structures

Atomic force microscopy (AFM) imaging was performed to characterize molecular conformations

and adsorbed layer structures of the three PDADMA-X salts. The AFM used was a NanoScope IIIa Multimode Scanning Probe Microscopy Instrument (Digital Instruments, Santa Barbara, CA) equipped with an E-scanner operating in air at room temperature with 50–60% humidity. Tapping mode was employed and images were taken with a 256×256 data points (pixel resolution), acquired by using the retrace signal. The silicon cantilevers with $125\mu\text{m}$ in length and 300kHz in frequency (Nanoprobe, Model RTESP14) were employed. The scanning speed and the loop gain factors were varied during the imaging process. Line scan rates were typically set at 1.0Hz for tapping mode with other scan parameters such as scan size, set point, integral gain and proportional gain varied and optimized. In order to avoid tip-related artifact, imaging was performed with a minimal force and image features were reproduced before being accepted as representative. The drop deposition method was adopted for sample preparation, and a 0.02ml of polymer solution was deposited onto the freshly cleaved mica surface and dried 15min at 20°C in a thermostated container. For each experimental condition, two mica sheets were prepared and at least three images were obtained for each mica sheet sample. Images were taken with online filtering and subsequently by flattening to remove the background slope. Using NanoScope Image analysis software, section analysis of images was conducted to measure the size of particles and their aggregates.

2.3.4. Flocculation experiments

A stock suspension of purified kaolin (Beijing Chemical Reagent Agent, China; the composition of kaolin is SiO_2 50.1%, Fe_2O_3 0.28%, Al_2O_3 35.8%, K_2O 0.05%, Na_2O 0.06%, CaO 0.07%, MgO 0.06%, TiO_2 0.15%) was prepared to a concentration of 100 g/l. Size distribution of the kaolin suspension was determined on a Laser Particle Analyser (Mastersizer 2000, Malvern CO, UK). $D(0.9)$ of the particles was $2\mu\text{m}$, with a mean size of about $0.92\mu\text{m}$. Working suspensions were prepared by diluting the stock suspension in a test solution containing $5 \times 10^{-4}\text{M}$ of both NaNO_3 and NaHCO_3 to provide fixed concentrations of electrolyte and alkalinity.

For flocculation experiments, a clay concentration with 1000mg/l was used. The flocculation experiments were carried out in a 1l cylindrical vessel, stirred by the flat-blade paddle. The flocculation experiments were conducted by 1min of rapid mixing at 300rpm followed by 10min of slow stirring at 40rpm. Flocs were allowed to settle in 30min. Residual turbidity (RT) and the zeta potential of fine particles remaining in the supernatant

were measured on a HACH 2100N Turbidimeter (Hach, Loveland, Co.) and a Zetasizer 2000 (Malvern CO, UK), respectively. Throughout the mixing and flocculation periods, the suspension was continuously sampled by peristaltic pump and monitored by a photometric dispersion analyzer (PDA2000; Rank Brothers Ltd.) to obtain a flocculation index (FI). From 60s before the addition of flocculant, monitoring was initiated to establish a baseline reading and then continued for a further 15 min to follow the progress of flocculation. The flocculation index (FI) has been clearly defined in the literature (Wang et al., 2002).

3. Results and discussion

3.1. Solution properties of PDADMAC, PDADMAN and PDADMAS

Concerning interactions between the polyion and counterions, much work has been done both experimentally and theoretically (Nishida et al., 2002; Benmansour et al., 2003). The nature of counterions is known to be one of the key factors influencing the polymer solution properties. The conductivities ($K-K_S$) of PDADMA-X polymer with different counterions (Cl^- , NO_3^- and SO_4^{2-}) in aqueous solution were shown in Fig. 2. It was clear that the conductivity ($K-K_S$) of all the three PDADMA-X polymer solutions increases linearly with the concentration (C_p), indicating that they all showed typical features of strong polyelectrolytes. Compared with the $K-K_S$ value of PDADMAC, PDADMAS shows a higher value, while PDADMAN gives a lower one at a given concentration, following the order of PDADMAS > PDADMAC > PDADMAN. The difference can be attributable to the change of overall conformation of polyions according to the ion conden-

Fig. 2. Comparison of the conductivity of PDADMAC, PDADMAN and PDADMAS aqueous solutions at different concentrations.

Fig. 3. Reduced viscosity (dl/g) versus concentration curves for PDADMAC, PDADMAN and PDADMAS in the salt-free solution.

sation theory. For monovalent counterions such as Cl^- and NO_3^- , conductivity decreases with increasing counterion size because big ions are weakly or not associated to the backbone (Benmansour et al., 2003). However, for bivalent anions, e.g. SO_4^{2-} , the charge affinity to PDADMA polycation is considerably larger than that of monovalent ones (Nishida et al., 2002), causing PDADMAS a higher conductivity.

In order to further determine effects of counterion on the overall conformation of polycation in aqueous solution, the reduced viscosity (η_{sp}/C , dl/g) versus concentration C_p curves for PDADMAC, PDADMAN and PDADMAS were shown in Fig. 3. It is clear that all the polymer solutions follow a typical polyelectrolyte behavior, as demonstrated by the shape of the curves that are in general agreement with the viscosity of most other polyelectrolytes in the tested concentration range. The reduced viscosity exhibits an initial slight increase with decreasing C_p , followed by a rapid increase at higher dilution. Based on most textbooks and literatures (Minakata et al., 2002), this behavior can be very well explained in terms of the expansion effect of a polyion chain when the intramolecular electrostatic repulsive force is released from the screening effect with decreasing concentration. In particular, for the given concentration, it can be seen that the reduced viscosity increases in the order of PDADMAN > PDADMAC > PDADMAS. Thus, the molecular size of PDADMA-X in the aqueous solution follows the same order of PDADMAN > PDADMAC > PDADMAS to decrease. This change tendency can also be facilitated by the interaction differences between the polycation chains and the counterions, since the intramolecular electrostatic attractive force decreases in the order of SO_4^{2-} > Cl^- > NO_3^- as indicated by the above conductivity

Fig. 4. AFM images of PDAMAC, PDAMAN and PDAMAS adsorbed on the surfaces of oppositely charged mica from aqueous solution ($C_s = 1.0 \times 10^{-3}$ mol/l, NaCl) at two different concentration levels (C_p) of 5 mmol/l (left: a, c and e) and 0.05 mmol/l (right: b, d and f), respectively. (a, b) PDAMAC, (c, d) PDAMAN, (e, f) PDAMAS.

measurement results (Fig. 2). It is therefore indicative that, compared with PDADMAC, PDADMAN has a more cationic charge density and a more extended polymer chain, whereas PDADMAS behaves more like a smaller coiled macromolecule in aqueous solution under the same conditions.

3.2. Adsorption of PDADMA-X on the surfaces of oppositely charged mica

As a powerful tool for imaging surface structure at nanometer scale, atomic force microscopy (AFM) has been widely used in characterization of adsorbed layer structures of polymers. In order to gain more detailed information on the structure and morphology of the polymer flocculants with different counterions (Cl^- , NO_3^- and SO_4^{2-}), molecular conformation and adsorbed layer structures of the three PDADMA-X salts on mica were investigated by AFM at two different concentration levels, 5 mmol/l and 0.05 mmol/l, respectively. As shown in Fig. 4, sponge-like membrane structures with the height of 2 to 4.5 nm were observed when $C_p = 5$ mmol/l, showing little difference in adsorbed layer morphology for all the three polymers (Fig. 4a, c and e). When $C_p = 0.05$ mmol/l, however, the adsorption morphologies of PDADMA-X are completely different. While a uniform hemispherical structure with 8–10 nm in height and 40–55 nm in width was found for PDADMAS polymer, a pearl necklace-like aggregation structure of uniform hemispheroids with the height of 15 to 20 nm and the width of 25 to 45 nm was observed for PDADMAC polymer, and a sponge-like layer structure with the height of 1 to 5 nm was given for PDADMAN polymer under the same experimental conditions (Fig. 4b, d and f). The polymer sizes of PDADMA salts given by the AFM are very consistent with the data obtained by light scattering or by molecular dynamics calculation in literatures (Rivas et al., 2004; Marcelo et al., 2004); furthermore, the obtained structural features are of high uniformity. Such results infer that AFM is a valuable tool for studying on polymer adsorption at single molecular level.

The differences in adsorption morphology of the three polymers in dilute solution ($C_p = 0.05$ mmol/l) can be attributable to the effect of the different counterions. It has been known that the physico-chemical properties of polyelectrolyte solutions depend crucially on the strength of coulombic interactions between the counterions and the charged groups of the polyion (Greenwood and Kendall, 2000). Polyelectrolytes usually develop a more extended structure in dilute solution at low ionic strengths, due to the mutual repulsions among the

charged segments of the polyelectrolyte chain, and adsorb at particle surfaces in a way mainly determined by the electrostatic interactions. As shown in Fig. 5, the electrostatic combination of the chloride counterions onto the polycation chain of PDADMA lessens the charge density of the polycation chain and leads to a lower intramolecular repulsive interaction so that PDADMAC polymer coils up and adsorbs itself on the oppositely charged mica surface with loops and tails. Moreover, the intermolecular interaction is not strong enough to completely inhibit the congregation among polymer chains of PDADMA; therefore, a pearl necklace-like aggregation structure with a heterogeneous surface coverage was obtained for the PDADMAC polymer (Fig. 5a). For the PDADMAS polymer, however, the bivalent sulfate counterions have a very strong electrostatic interaction on both the intramolecular attraction and the intermolecular repulsive forces, so that the extended polymer chains coil up into small compact spheres and adsorb uniformly on the mica surface with loops and tails (Fig. 5b). For the PDADMAN polymer, the larger size of the monovalent nitrate counterions leads to a higher cationic density in the polymer chain, a stronger intramolecular repulsive force and a more extended molecular chain, so that PDADMAN adopts a flat and layer-layer adsorption without loops and tails extended from the surface, and therefore develops a sponge-like structure (Fig. 5c).

3.3. Flocculation test of kaolin suspension solution with PDADMA-X

Flocculation experiments on kaolin suspensions at constant pH of 7.5 were performed using PDADMA-X as flocculants in order to investigate the effects of different counterions (Cl^- , NO_3^- and SO_4^{2-}) on flocculation behaviors such as zeta potential, residual turbidities, flocculation index, etc. As shown in Fig. 6, for all the three polymers, zeta potential of the supernatant

Fig. 5. Schematic of the absorption morphology of a single functional polymer with counterions of different nature: (a) PDADMAC, (b) PDADMAS, (c) PDADMAN.

Fig. 6. The effects of different counterions (Cl⁻, NO₃⁻ and SO₄²⁻) on the flocculation of 1000 mg/l kaolin suspensions at pH=7.5 using PDADMA-X as flocculants: (a) zeta potential, (b) residual turbidities, (c) flocculation index.

rapidly increases with increasing PDADMA-X dosage until it begins to level off at the dosage of above 3.1×10^{-6} mol/l. The effects of the three polymers on the zeta potential of particles in the supernatant are in the

order of PDADMAN > PDADMAC > PDAMDAS (Fig. 6a). The residual turbidities measured after coagulation and sedimentation with the aforementioned system are shown in Fig. 6b. Corresponding to the rapid increasing region of the zeta potential, significant turbidity removal can be found for all the three polymers. As the dosage of PDADMA-X is above 3.1×10^{-6} mol/l, obvious restabilization (increased turbidity) occurs. Compared with PDADMAC, PDADMAS shows the wider optimum dosage region, whereas PDADMAN has the optimum residual turbidities. The FI of kaolin suspension at the optimum dosage were shown in Fig. 6c. It is interesting that, in contrast with the more extended polymer chain of PDADMAN, both the floc size and the settling rate of PDADMAN are smaller than those of PDADMAS or PDADMAC. These results seem to be paradoxical with the higher reduced viscosity in aqueous solution of PDADMAN. Nevertheless, they indicate a different flocculation mechanism with that of PDADMAS or PDADMAC. From the AFM images of polymer conformation and adsorbed layer structures, it can be concluded that PDADMAN adopts a flat and layer-layer adsorption without loops and tails extended from the surface so that the kaolin suspension was mainly flocculated via the charge neutralization mechanism, whereas PDADMAS adsorbs with loops and tails at the particle surface so that a bridging mechanism can be involved.

4. Conclusions

Two polymer flocculants of PDADMA salts with nitrate and sulfate counterions (PDADMAN and PDADMAS) were prepared from the commercial PDADMAC polymer product through the anionic replacement reaction via the formation of the insoluble silver salts. Measurement of the solution properties indicates that, compared with PDADMAC, PDADMAN has a more cationic density and a more extended polymer chain, whereas PDADMAS exhibits a smaller coiled polymer size. Flocculation experiments on kaolin suspension show that PDADMAN has stronger flocculation efficiency, while PDADMAS has the wider optimum dosage, larger floc size and more rapid settling rate. AFM study on the adsorption morphology of the polymers on mica shows a great difference in their molecular conformation. Compared with the pearl necklace-like aggregation of hemispheroids of PDADMAC polymer, PDADMAN takes the sponge-like thin layer structures, whereas PDADMAS shows a uniform hemispherical structure. These different behaviors suggest a different flocculation mechanism, in which

PDADMAN adopts a flat and layer–layer adsorption without loops and tails extended from the surface, implying where a charge neutralization mechanism is preponderant, while PDADMAS adsorbs in the form of coiled spheres with loops and tails so that a bridging mechanism is involved.

The adsorption morphology of polymer flocculant on particles is the main factor influencing flocculation mechanism of the PDADMA-X polymers. AFM image of single polyelectrolyte polymer is a very valuable tool for analyzing absorption and flocculation mechanism of polyelectrolytes.

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