Delivery of functional polyelectrolytes from complexes induced by salt addition: Impact of the initial binding strength

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ABSTRACT

This paper focuses on polyelectrolyte complexes (PECs) soft nanoparticles and how dissociation occurs upon salt addition. The system is composed of a strong polyanion (polystyrene sulfonate, PSS) and a weak polycation (poly(allylamine) hydrochloride, PAH) in large excess. Soft nanoparticles were obtained by pouring a PSS solution into a PAH one under constant stirring. As the charge density of PAH chain depends on the pH of the polyelectrolyte solution, PEC particles exhibit distinct behaviors under salt addition depending on the pH of the continuous phase. At pH = 5.5, PAH chains are fully charged and the addition of salt produces particle aggregation followed by sedimentation. Conversely, at pH = 10 where PAH is only partially charged, the addition of salt drives a progressive disentanglement of the two polyelectrolytes, as revealed by both viscosimetric and spectroscopic measurements. At sufficiently high ionic strength, the two electrolytes are fully dissociated. Our results emphasize differences in behavior (binding reversibility) between strongly and weakly bound polyelectrolytes of opposite charge upon addition of salt. We discuss the potential use of these systems as stimulus responsive materials for the delivery of scale nucleation inhibitors in application around petroleum recovery.

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1. Introduction

When solutions of two oppositely charged polymer chains are mixed, polyelectrolyte complex (PEC) particles are formed spontaneously. They result from an electrostatic binding between several oppositely charged chains, with counterions release [1–8]. The driving force of complex formation is mainly the gain in entropy due to the liberation of the low-molecular counterions [8]. Two different types of polyelectrolyte complexes are usually obtained by appropriate choice of experimental conditions, *i.e.*, water-soluble PECs forming stable, optically transparent solutions and water-insoluble PECs, which either precipitate in water or exist as homogeneous turbid colloidal systems without phase separation. Water-soluble polyelectrolyte complexes are preferentially formed with polyelectrolytes having a weak charge density and large differences in molecular dimensions when they are mixed in non-stoichiometric ratios [9,10]. Alternatively, polyions having a high charge density and/or similar high molar masses lead to insoluble and highly aggregated complexes [11]. Colloidal dispersions in the sub micrometer range can be obtained by polyelectrolyte complexation, provided polymer concentrations remain low.

Polyelectrolytes complexes (PECs) can be composed of natural and/or synthetic polyions, charged surfactants... They are widely used in various fields such as water treatments, coatings, paper industry and gene therapy. The use of PECs can also be envisaged in the oil industry/petroleum production, and specifically well treatments. Indeed, after drilling and once the exploitation starts, downhole thermodynamic conditions are modified and the solubility of some chemical species ($CaCO_3$, $BaSO_4$,...) can be considerably lowered, resulting in fast scale formation [12]. Mineral precipitation affects oil production by progressively blocking the fluids inside the wellbore. Molecules with specific chemical functions (phosphonates, sulfonates) are used as scale nucleation inhibitors. However, treatments based on these molecules are short term and have to be repeated quite often depending on the composition of the reservoir fluids. Sustainable release systems composed of PECs and at least one polyion presenting anti-scale properties are highly sought after to treat scales and prevent their formation downhole. Polyanions with sulfonate functions (such as poly(styrene sulfonate) hereinafter referred to as PSS) are known to exhibit anti-scale properties. When associated with specific polycations (for example poly(allylamine hydrochloride) or PAH) they form PEC particles [13]. When PAH is in large excess compared to PSS, mixing these two oppositely charged polyelectrolytes in solution leads to formation of positively charged PEC particles in which PSS is entrapped.

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In this paper, our main objective is to gain knowledge about the behavior of PSS/PAH upon addition of salt. It has been found that for complexes between components with strong ionic groups, the addition of NaCl causes mainly secondary aggregation and flocculation [8,9,14]. PECs involving a weak and a strong polyelectrolyte of opposite charge (strong mismatch of the charge densities of the components) swell with increasing NaCl content and dissolve completely above a critical ionic strength [8,9]. Such limiting scenarios have been identified using different polyelectrolyte combinations. Here, we demonstrate that the same phenomenology can be found within a single couple of polyelectrolytes and we try to get deeper understanding into the disentanglement mechanism. PEC particles entrapping PSS chains are formed under well-defined conditions and their potential delivery upon salt addition (NaCl) is examined. Our strategy aims at finding conditions to stimulate the delivery of PSS chains on demand, based on the formulation of stimulus-responsive particles. The pH was used as a lever to control the initial binding strength between the two polyelectrolytes. Because it weakens the electrostatic interaction and enables rearrangement processes, salt plays a crucial role in the behavior of PECs and was used as a stimulus to release polyanion chains. PSS chains are strong polyelectrolytes whose charge remains constant irrespective of the pH value. Instead, the charge of PAH chains is pH-dependent. We estimate the extent of PSS delivery by means of viscosity measurements based on a precise microfluidic tool and via spectroscopic measurements, at two pH values corresponding to very distinct charge densities on PAH chains. Our results emphasize differences in behavior (binding reversibility) between strongly and weakly bound polyelectrolytes of opposite charge.

2. Materials and methods

The samples of PSS and PAH were polydisperse commercial products. The polyanion used was PSS with $M_w = 70,000$ g mol^{-1} (M_w being the weight averaged molecular weight), with a sulfonation degree equal to $x = 0.51$, and the polycation was PAH with $M_w = 70,000$ g mol^{-1}. The molecular structure of both components is schematized in Fig. 1. Being a strong polyion, PSS is fully dissociated whatever the pH from 1 to 14 [2]. Conversely, PAH is a weak polyelectrolyte whose charge density is pH-dependent: it is fully charged for pH < 5.5, and for higher pH values the protonation degree decreases and becomes almost zero at pH = 11 [2]. Both polyelectrolytes were purchased from Sigma–Aldrich and the average molecular weights were given by the supplier. Sodium chloride, sodium hydroxide and hydrochloric acid were from VWR. MilliQ water was used for the preparation of all the solutions.

Polyelectrolyte solutions were obtained by adding the polymer in powder form in the aqueous phase at the desired pH under magnetic stirring until complete dissolution. Various PEC suspensions were then prepared at different weight concentration ratios $R_c = C_{PSS}/C_{PAH}$, namely 0.12, 0.17, 0.20, 0.25 and 0.30. The pH of the polyelectrolyte solutions to be mixed was adjusted at either 5.5 or 10 using 0.1 mol L^{-1} HCl or NaOH solutions and the ionic strength was fixed by dissolving NaCl. The weight polycation concentration, C_{PAH}, was kept constant at 1% in all samples. For each R_c ratio, PEC suspensions were obtained by drop wise addition of 25 mL of PSS solution into 25 mL of PAH solution (at 2 wt.%) under intense magnetic stirring (1800 rpm) with à cylindrical bar (length = 3 cm, diameter = 0.5 cm, vial diameter = 5 cm). The PSS solutions were introduced into the PAH ones at a rate of 1 mL min^{-1}. Magnetic stirring was maintained at least 15 h. All solutions and suspensions were prepared at room temperature (22 ± 1 °C).

2.1. Particle size

Particles size and polydispersity were measured at 25 °C by photon correlation spectroscopy (PCS) at a detection angle of 173°, using a Zetasizer Nano ZS (Malvern Instrument) equipped with a He–Ne laser. The particle size range accessible to the apparatus is 1 nm–5 μm. The detection angle of 173° is large enough to ensure that the signal is perturbed neither by multiple scattering nor by the presence of dust particles. The reduced path length of the laser beam in the measuring cell allows measurements on turbid samples, at their neat concentration (no dilution). The hydrodynamic diameters were calculated from diffusion coefficients using Stokes–Einstein equation. Each value reported on the graphs was an average over 12 repetitions. All analyses were performed with the software supplied by the manufacturer.

2.2. Electrophoretic mobility

Electrophoretic mobility measurements were carried out at 25 °C using a Zetasizer Nano ZS (same as for size measurements), after allowing the mixture to equilibrate for 10 min. This technique is based on the comparative phase analysis of the light scattered from the colloidal dispersion and a well-known frequency reference beam. The phase difference is related to the particle velocity and, therefore, to the electrophoretic mobility. Each value results from 15 measurements.

2.3. Turbidity

The two primary solutions containing PSS and PAH were optically transparent. However, after mixing them, the obtained suspensions became turbid because of the relatively large size of PECs (diameter comparable to visible light wavelength) and polymer compaction within the cores. We characterized the evolution of turbidity by measuring the transmittance, i.e. the percentage of transmitted light through the samples. Measurements were carried out using a Turbiscan MA2000® (Formulaction, France) at a wavelength of 880 nm.

2.4. Viscosity

The relative viscosity of polymer solutions and PEC suspensions was measured at 25 °C using a high-precision Rheosense® viscometer (Rheosense Inc., San Ramon CA, USA). The apparatus obtains a viscosity reading by measuring the pressure drop as a liquid flows through a microfluidic channel. Pressure is measured at positions of increasing distance from the inlet. The slope of the straight line in the plot of the pressure vs. sensor position is proportional to the viscosity [15]. This viscometer allows measuring absolute viscosities of the order of 10^{-3} Pa s with 5% precision. The error bars reported on the graphs are mean standard deviations from 3 repetitions.
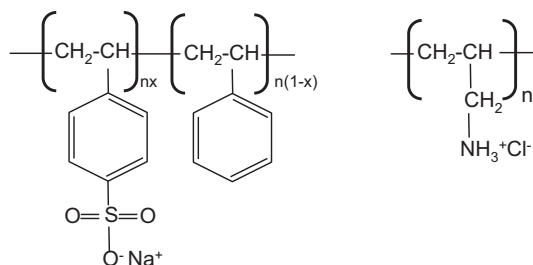

Fig. 1. PSS (left) and PAH (right) molecules.