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Study of the compositional heterogeneity in poly(*N*-isopropylacrylamide–acrylic acid) microgels by potentiometric titration experiments

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Abstract

The compositional distribution of acrylic acid (AA) residues in poly(*N*-isopropylacrylamide–acrylic acid) [poly(NIPAM–AA)] microgels has been investigated using alkaline titration experiments. It is found that the apparent acid dissociation constant (pK_a^{app}) of the AA residues increases with the degree of dissociation. This is due to the electrostatic effect that arises as AA residues dissociate, and the pK_a^{app} change depends on the local concentration of AA residues in the gel network. Nevertheless, it is found that the pK_a^{app} change is independent of the overall AA content. This indicates that the AA residues in poly(NIPAM–AA) microgels are clustered and not uniformly distributed in the gel network. A two-phase model based on the Donnan concept is developed to predict pK_a^{app} values, and a good fit to the experimentally estimated pK_a^{app} values is obtained if a block copolymer is assumed.

Keywords: Microgels; Copolymer composition; Potentiometric titration; Block copolymers; Polymeric colloids

1. Introduction

Filtration, sedimentation and centrifugation are unit operations used for solid–liquid separation. They are used in many industries for example for solid–liquid separation of fermentation broth, minerals, paper pulp, and sludge. In order to optimise these processes, it is important to have knowledge of the operation time, the need of energy and the finale dry matter content of the solid material. Therefore research has been done to develop mathematical models based on well-characterised model materials to predict these parameters. Up to today these model materials has mainly been hard, and low charged particles such as anatase, kaolin, and clay. The mathematical models obtained from these studies are suitable for solid–liquid separation of minerals. However this is often not the case for solid–liquid separation of cell broth, pulp and sludge. Contrary to minerals, cell broth, pulp and sludge contains soft, and highly charged particles. The explanation might therefore be that the models have been developed for hard, and low charged particles and not soft, and highly charge particles. Thus candidates for well characterised, highly charged, and compressible model materials are of interest for the further study of solid–liquid separation.

One such candidate is cross-linked poly(*N*-isopropylacrylamide) [poly(NIPAM)] microgels with reported particle sizes ranging from 0.1 to 1 μm at 25 °C [1]. Poly(NIPAM) microgels shrink reversibly in aqueous solutions when the temperature is increased above the volume phase transition temperature (VPTT) around 32 °C [2], and, unlike macrogels, they swell and shrink rapidly [3,4]. Furthermore poly(NIPAM) microgels exhibit reversible, temperature-dependent adsorption/desorption of proteins [5], and uptake/release of ions and heavy metals [6,7]. These properties make poly(NIPAM) microgels a potential material for controlled drug delivery [8] and removal of heavy metals from aqueous environments [1]. Moreover, the narrow size distribution of poly(NIPAM)

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microgels [9] makes the microgels an appropriate model material.

Preparation and characterisation was first reported by Pelton and Chibante [10], who prepared poly(NIPAM) microgels by a surfactant-free emulsion polymerisation reaction in the presence of *N*-isopropylacrylamide (NIPAM) and *N*,*N*′-methylenebisacrylamide (BA) monomers, and an initiator (persulphate). Both monomers are uncharged in water solutions, and the only charged groups in poly(NIPAM) microgels are introduced from the initiator [11].

Microgels with higher charge densities are sometimes needed to increase the adsorption of heavy metals [7], increase VPTT [4] or extend the application of microgels as a model material. Fortunately, it is possible to introduce other water-soluble vinyl monomers into the poly(NIPAM) microgel polymer backbone and thereby increase the charge density [2]. Snowden et al. [12] have prepared poly(*N*-isopropylacrylamide–acrylic acid) [poly(NIPAM–AA)] microgels by adding acrylic acid (AA) monomers at the synthesis step. Poly(NIPAM–AA) microgels exhibit temperature- and pH-dependent swelling [7,12]. Furthermore, VPTT is higher than for poly(NIPAM) microgels, for example, it has been reported that VPTT increases to ca. 55 °C at pH 6.5 for poly(NIPAM–AA) microgels containing 5% AA residues [12].

Poly(NIPAM–AA) gels or microgels are used to study different models that describe the swelling behaviour [13] and the mobility [14] of polyelectrolyte gels. Both swelling behaviour and mobility depend on the compositional distribution of charged groups in the gels [13–15]. Nevertheless, knowledge about the compositional heterogeneity of AA residues in the poly(NIPAM–AA) microgels is scant. Kokufuta et al. [13] state that poly(NIPAM–AA) gels are random copolymers, that is, that the AA residues are uniformly distributed in the gel network. However, Morris et al. [7] have observed a gradual increase in the observed swelling behaviour for poly(NIPAM–AA) microgels, which has been attributed to an inhomogeneous distribution of charged groups. Xue et al. [16] have found that the relative incorporation of NIPAM monomers in the growing chain is much faster than that of AA monomers, which results in a block copolymer. In contrast, Shibayama et al. [17] have reported that the polymerisation of AA monomers is faster than that of NIPAM monomers. The synthesis method may influence the compositional distribution [18]. Bulk polymerisation is used to prepare poly(NIPAM–AA) gels and emulsion polymerisation to prepare poly(NIPAM–AA) microgels. Thus, the compositional distribution of AA residues in poly(NIPAM–AA) microgels might differ from that of poly(NIPAM–AA) gels. More studies of the compositional distributions of AA residues in poly(NIPAM–AA) microgels are therefore needed in order to use the microgels as a model material.

In this report, an indirect method is developed to evaluate the compositional distribution of AA residues in the poly(NIPAM–AA) microgel network.

2. Experimental

2.1. Materials

200 kDa poly(acrylamide-*co*-acrylic acid) polymer with 10 wt.% acrylic acid, *N*-isopropylacrylamide (NIPAM), *N*,*N*′-methylenebisacrylamide (BA), acrylic acid (AA) and $K_2S_2O_8$ from Sigma–Aldrich were used as received. All solutions were made with water obtained from Milli-Q water.

2.2. Preparation of microgels

Poly(NIPAM) and poly(NIPAM–AA) microgels were prepared by a surfactant-free emulsion polymerisation reaction (Table 1). The monomers were dissolved in 500 mL Milli-Q water in a 1 L round-bottomed flask equipped with a condenser, a nitrogen inlet and a stirrer. Oxygen-free nitrogen was bubbled into the solution, and the system was kept at 70 ± 2 °C and 350 rpm. A 5 mL degassed aqueous solution of 0.3 g $K_2S_2O_8$ was added to initiate the polymerisation, and the reaction was continued for 22 h. Afterwards the microgel dispersions were centrifuged for 45 min at 15,000 × *g* and the precipitate dispersed in Milli-Q water and dialysed in 6–8 kDa dialysis tubes (Spectra/por Membrane MWCO 6-8000) for 2 weeks. All microgel dispersions were stored in the dark.

2.3. Characterisation of microgels

The dry weight of each microgel dispersion was measured after drying 5 mL purified microgel dispersion at 110 °C overnight and was used to determine the dry-matter content (dw).

The hydrodynamic diameter of the microgels was measured at different pH by dynamic light-scattering measurement. Samples with 0.2 g dw microgels/L were prepared by diluting the microgel stock dispersions in Milli-Q water or 0.1 M $NaClO_4$. The pH was adjusted prior to measure-

Table 1
Composition (g) of monomer solutions

	AA	BA
B0.6-A0	–	0.3
B0.6-A2.5	0.11	0.3
B0.6-A5	0.21	0.3
B0.6-A10	0.42	0.3
B0.6-A15	0.63	0.3
B0.6-A20	0.84	0.3
B1.2-A0	–	0.6
B1.2-A2.5	0.11	0.6
B1.2-A5	0.21	0.6
B1.2-A15	0.63	0.6
B1.2-A20	0.84	0.6

All solutions contain 6.3 g NIPAM monomers and 500 mL Milli-Q water. The solutions are denoted B*x*–A*y*, where *x* is the concentration of BA monomers (g/L) and *y* is 100× the mole ratio of AA to NIPAM monomers.