



A model for ion-exchange behaviour of polyampholytic resins: Using polystyrene polyampholytic latex



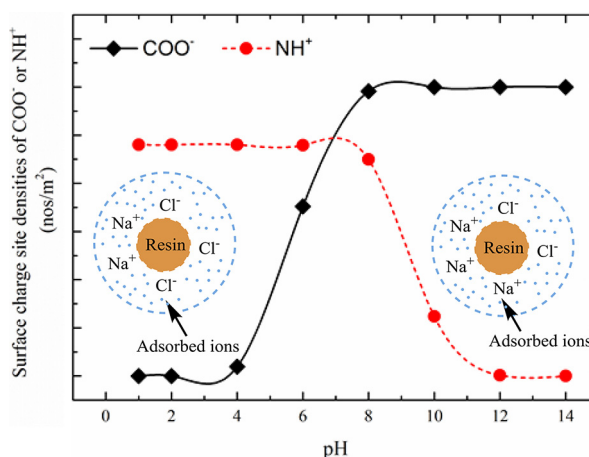
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HIGHLIGHTS

- Polyampholytic latex samples were synthesised containing weak acid and weak base groups.
- These latex particles can be used as a model to explain polyampholytic resin ion-exchange behaviour.
- Surface charge densities at different pH values were determined from zeta potential measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

A polystyrene based polyampholytic (zwitterionic) latex was synthesised with an isoelectric point (IEP) of 6.9 and particle size of about 110 nm. Ion-exchange (IEX) ability of this latex with sodium chloride and ammonium bicarbonate (AB) was studied and it was found that Na^+ , NH_4^+ , Cl^- and HCO_3^- ions exchange with the surface groups following the law of mass action. The latex typically had an adsorption capacity of about 0.11 mmol/m^2 , for both NaCl and NH_4HCO_3 electrolyte solutions. Surface adsorption constants, i.e. K_{NH_2} and K_{COOH} , were assumed to be similar to solution values, that is: $1 \times 10^{-9} \text{ M}$ and $1 \times 10^{-6} \text{ M}$, respectively. Precise ionization ability of the active groups is specific for the type of polymer used to form the latex particles. Calculated surface charge densities, obtained from zeta potential studies, shows that the best pH range for IEX studies with this polyampholytic latex was in the range 6.8–8.0. The average affinity of HCO_3^- ions was found to be higher than Cl^- during the IEX process. This latex was used to demonstrate an ion adsorption model which could be applied to the IEX properties of polyampholytic resins containing the same weak acid (WA) and weak base (WB) groups.

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1. Introduction

Synthetic polyampholytic resins have been used in ion-exchange (IEX) studies, however, a mixed-bed of anion and cation

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exchanging beads is more frequently used, since they are easier to regenerate, and so polyampholytic resins have been largely neglected over the last few decades. Ion adsorption behaviour of such resins composed of weak-acid (WA) and weak-base (WB) have been determined in batch, equilibrium studies [1–6], but there is little evidence on their dynamic properties, that is, in fixed-bed, continuous-flow systems [6–9], probably because of their difficulty in complete regeneration. However, recent studies have shown that ammonium bicarbonate (AB) can be utilized to completely regenerate WA and WB polyampholytic resins [10,11]. Therefore, it is useful to make an ionization model to describe the adsorption/desorption behaviour of such resins, using a similar kind of polystyrene latex colloid synthesised with the same WA/WB groups, in close proximity.

Weak-acid/weak-base polyampholytic resins are not commercially available. Therefore, the surface ion-exchange properties of such resins have not been studied previously and there is no exemplary molecule that can be used to explain the surface adsorption ability of such resins. However, since the resin could be used commercially in future, using our new regeneration method (based on AB), it is useful to study its surface adsorption ability experimentally.

The ionization behaviour of carboxylic and amine groups on amino acids molecules [12,13] in aqueous solution can be used as a basis to explain the ionization behaviour of polyampholytic resins at different pH and temperatures [10], but such simple molecules are unlikely to explain the IEX behaviour of solid resins. Therefore, surface studies of synthesised polyampholytic latices were selected here as a model system for the study of the ionization behaviour of amine and carboxylic groups in these resins.

Polyampholytic latices with small particle sizes which are similar to the polyampholytic IEX resins, consisting of carboxylic and tertiary amine groups have been synthesised recently [14]. Moreover, studies have shown that polyampholytic polystyrene latex can be used for metal ion adsorption and has the ability to adsorb various divalent cations [14] and, in addition, these latices have the ability to IEX with both cations and anions [15]. This behaviour has also been found with protein molecules and for biomolecules, which have both cationic and anionic sites, to bind with multivalent ions [16–18]. A large number of factors influence the ion adsorption properties of these kinds of polyampholytic ion-exchangers, including temperature [6,10,14] duration of equilibration [19], ionic strength of the electrolyte solutions [3,20], pH [14,19,21], the ratio of acid to basic groups and the affinities of counter ions [3,20,22–25].

pH of the IEX system plays a controlling role during the ion adsorption process with WA/WB latex [14], since the ionization of the active sites on the latex surface are pH dependent. Therefore, IEX studies need to be performed considering the pH of the electrolyte solutions. This also helps to understand the IEX behaviour of counter ions with exchanging materials.

Surface ion adsorption models can be used to describe the surface charging behaviour of polyampholytic latex particles, determined from zeta potential measurements taken in an appropriate range of solutions. The measured zeta potentials can be converted to the corresponding surface charge densities depending on the radius of curvature (i.e. radius ' a ') of the latex particles compared with the Debye length (κ^{-1}) of the solution. For large values of the parameter κa (>50) a surface flat-plate model can be used [26], whereas for lower κa values models taking particle curvature into account have to be used [27,28].

These polyampholytic latices are zwitterionic, and mostly exhibit a pH of net zero charge (pzc) or, an isoelectric point (IEP). Surface studies and ionization models can be used to calculate the IEP of such latices and the behaviour of adsorption sites present on the particles [29–31] in different solution conditions. Ions affinity

towards surfaces and ionization constants of charged groups are strongly correlated with the pH [14].

The ion adsorption or ion exchange process can be very complicated and depends on both the adsorbing ion and the chemical and physical properties of the substrate. Studies have shown that hydrolysis of metal ions influences the affinity of adsorption of these ions onto the adsorption surface [32,33] and surface complexation mechanisms can prime the metal-ion adsorption to surfaces by forming chemical bonds with the functional groups present in the adsorbent surface [34,35]. Different adsorbent materials, such as synthetic polymers, metal oxides, active carbon, metal oxides, natural materials and biological substrates have been studied to explain the adsorption behaviour of cations and anions and the affinity of ions towards surfaces [14,35]. Some of the studies have been performed on a qualitative basis and also, ionization behaviour of active groups have been quantitatively studied [33] to explain this adsorption behaviour. Metal-carboxyl ligand stability constants [36–38] for metal-ion adsorption onto biological substrates have also been determined.

In the present study, ionization constants and binding constants were determined to help explain the nature of the adsorption of ions to combined WA/WB resins. Polyampholytic latex colloids with WA and WB surface groups were synthesised and used as a model for these resins. Ion-exchange and adsorption behaviour with sodium chloride and AB solutions were studied. Measurements of zeta potentials of the latex in a wide range of solutions were also obtained and used to provide the surface charging properties of this latex surface to create a charging model to describe the IEX process for surfaces having both WA and WB groups, similar to the polyampholytic resins.

2. Materials and methods

2.1. Materials

Styrene (99%), methacrylic acid (99%), diethylaminoethyl methacrylate (99%) and ammonium persulfate (98%) were used during this synthesis. All the chemicals were purchased from Sigma-Aldrich, Australia, as reagent grade.

Ammonium bicarbonate (99%) was obtained from May & Baker, Dagenham, England and sodium chloride (98%) from Sigma-Aldrich, Australia, and were used as purchased. Sodium ion, chloride ion and ammonium ion standard solutions, in the range 100 ppm and 1000 ppm, were obtained from Hach Pacific Pty Ltd, Australia.

2.2. Synthesis of polyampholytic polystyrene latex colloids

The polyampholytic latex samples were synthesised following the previously published procedure [14,39]. Here, 60 g of styrene monomer, 6 g of methacrylic acid and 12.9 g of diethylaminoethyl methacrylate was mixed in a baffled flask and the reaction mixture was adjusted for pH 1.5 using nitric acid (HNO_3). The total volume of the reaction mixture was maintained to 600 ml. This mixture was sparged with nitrogen gas (AR) over-night to remove any dissolved O_2 from the system, prior to addition of the initiator, 0.3 g of ammonium persulfate. The reaction mixture was then heated at 70 °C in the presence of N_2 gas purging, and the mixture was stirred continuously at 60 rpm for 24 h (see Fig. 1). The resulted suspension was kept for cooling, filtered through glass wool to remove any coagulum present in the reaction mixture. The final product obtained was stored in a glass bottle at room temperature.

The latex samples synthesised was then purified by repeated dispersion in water followed by centrifugation [14,40] at 4000 rpm using initially 4.5 ml of samples with 35.5 ml of Milli-Q water

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