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Removal of chloride ions from an industrial polyethylenimine flocculant shifting it into an adhesive promoter using the anion exchange resin Amberlite IRA-420

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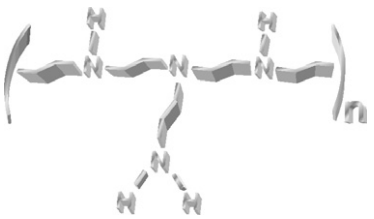
ABSTRACT

Aqueous solutions of polyethylenimines (PEI) are usually used in the manufacture process of paper from pulps to improve the physical strength, and the ink and coatings fixation and to facilitate the printing. When PEI is used as a liquid cationic flocculant in water treatment it is supplied as a cheaper hydrochloride salt. The hydrochloride salt form is easier to handle and may be converted into the free amine form for adhesive purposes by some separation processes. Ion exchange is one of the easiest and cheapest ways to remove chlorides from different aqueous solutions.

The strongly basic ion exchanger Amberlite IRA-420 has demonstrated that it can be used for chloride removal. The equilibrium isotherms of chloride ions i PEI–HCl at 20 and 40 °C, and NaCl and HCl at 30 °C in aqueous solution on Amberlite IRA-420 have been obtained. The presence of $HPEI^+$ as coion exerts an important influence on the ion exchange equilibrium. This behavior can be explained by the competition between the protonated amine groups of PEI and the quaternary groups of the resin for the chloride ions that tends to promote a slightly non-favorable equilibrium. In the same way, the kinetic studies indicated that the chloride ions are slowly removed in presence of polyethylenimine. Finally, the Nernst–Planck homogeneous model allowed obtaining the self-diffusion coefficients for both the chloride and hydroxide ions in the Amberlite IRA-420 and the values are in the same order of magnitude as those reported in the literature.

1. Introduction

Polyethylenimine (PEI) is a highly branched aliphatic polyamine characterized by the following repeating unit:



(1)

The amine groups exist in primary, secondary and tertiary forms with a branching site at every 3–3.5 nitrogen atom in any given chain segment. The N/C relation is usually 1:2 with a broad range of molecular weights between 800 and $2 \cdot 10^6$ g/mol. The PEI is a weakly basic water-soluble polymer, with a wide variety of technical applications based on its physical and chemical properties, surface activity, and its ability to form complexes with anionic species, metal ions and metal complexes [1].

The known commercial use is due to the following abilities: promotes the binding between similar and dissimilar materials; presents a high cationic charge density, over 20 meq/g, and can form chelation complexes with heavy metal compounds [2–4]; presents scavenging capabilities for oxides of carbon, nitrogen, sulfur, and volatile

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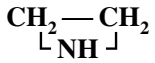
aldehydes; it can also be used in the fields such as biochemistry, in gene transfer processes [5] and as a precipitating agent for protein purification. In the papermaking process, PEI can be used to improve the physical strength, and the ink and coatings fixation and to facilitate the printing [6]. It can also be used in medicine due to the PEI anticancer activity which inhibits the growth of the cancer cells and seems to be suitable as a polymeric matrix for use as a carrier in the drug delivery systems [1]. In fact, the wide versatility of this compound has made the BASF Chemical Company name it as chemical chameleon in its technical bulletin.

PEI is manufactured by an acid-catalyzed ring opening homopolymerization of ethylene imine monomer:



(2)

The ethylene imine polymerization can be carried out in aqueous and anhydrous media. When the goal is to employ it as an adhesive promoter the anhydrous process is recommended. After the polymerization process, the residual catalyst has to be removed from the bulk polymer by a difficult and expensive process. This makes its commercial presentations have a high cost even in the case of its presentation in diluted aqueous solutions (04% w/w). When it is produced in aqueous media, the presence of the acid catalyst favors its further applications as liquid cationic flocculant that reduces the production cost. For this reason it would be very interesting to find an easy and cheap way to remove the catalyst from the PEI obtained in this way.

The commercial use of PEI started out as a cationic flocculating agent in paper manufacture [1]. Besides, it has been usually used in wastewater treatments as clarification or oil emulsification agent at concentrations lower than 0.05% in water depending on the application. It acts with negatively charged colloids neutralizing the charges and thus, the electrostatic repulsion between particles is reduced and the polymer bridging in which independent movement of particles is restricted by the adsorption of polymer molecules simultaneously on the neighboring particles [7]. The PEI solution used as a flocculant exhibits acidic characteristics indicating that the amine groups of the polymer are highly protonated [1]. Thus, these positive charges should be neutralized in solution by the negative ones that usually are chloride ions.

This material when used as anhydrous or unprotonated polymer is a very effective adhesive agent for printing inks, using solutions in inks between 0.5 and 1% by weight. In aqueous solution, the product is weakly basic and can be only employed with pigments and ligands which are alkali resistant. Besides, at these conditions it is widely used in paper production, being easily adsorbed by the paper due to its cationic character. The basic nature of amines makes the polymer easily ionizable. Its high cationic charge reduces the high amount of anions that usually load the paper and interferes with the drainage/retention of inks and other process chemical additives.

As indicated above, the cheapest presentation of polyethylenimine is usually supplied as a hydrochloride salt and it can be converted into the free amine form by neutralization with a base. Nevertheless, for specific applications when the objective is the expensive unprotonated polyethylenimine, the metal or chloride ions must be completely removed for the final product usage.

Several methods for chloride removal from polyethylenimine solutions could be applied. These methods available for the removal of chlorides are ion exchange, adsorption, liquid extraction, membrane technologies, etc. The ion exchange process seems to be most suitable for small-scale applications because of its simplicity, effectiveness, selectivity, recovery and relatively low cost [8–9]. The ion exchange process involves passage of the water solution of protonated polyethylenimine through a resin bed containing strong-base anion exchange resins on which chloride ions are exchanged for hydroxyl ions and the water formation takes place by neutralization of the protons with the hydroxyl ions eluted until the resin exchange capacity is exhausted. The spent resin is usually regenerated using a concentrated solution of sodium chloride or hydroxide [10,11].

In this case, the problem is the possible competition that would be established between the amine groups of polyethylenimine and the fixed quaternary ammonium group of the resin for the chloride ions. This competition leads to two difficulties. One is it can limit the useful capacity of the resin depending on the alkalinity of the groups of both the polymers (soluble and resin). The second difficulty could be related with the relative dissociation of the chloride ions and its diffusion rate. If the dissociation of chloride anions is low and they remain relatively fixed to the polyethylenimine amine groups, the rate of exchange would be restricted by the diffusion of the large polymer in the solution or even inside the resin, resulting in a diminution of the observed exchange rate. It has been observed in the previous works of this group dealing with the exchange of large ions or conventional cations associated to polymer or in nonaqueous media [12].

The aim of this work is to study ion exchange equilibrium and kinetics between chloride-polyethylenimine solution and OH^- form of the strong anionic resin Amberlite IRA-420 at different temperatures and thus to evaluate the possibility to apply the ion exchange technology to convert the polyethylenimine flocculant solution (Cl^- form) into an adhesive product for printing applications.

2. Experimental procedure

2.1. Chemicals

An aqueous solution of cationic polyethylenimine (50% w/w) was supplied by LAMIRSA S.A., and hydrogen chloride (37% w/w) and 96% pure sodium hydroxide (PRS grade) were supplied by Panreac. Demineralised water was conventionally treated in our laboratory (final conductivity less than 1 μs/cm). A commercial ion exchanger gel-type strongly basic Amberlite IRA-420 supply by Rohm and Haas was used. It is an amine quaternary cross-linked styrene/divinylbenzene copolymer. Table 1 shows a summary of the resin properties.