



Ionic transport processes in polymer mixture solutions based on quaternized polysulfones



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ARTICLE INFO

Article history:

Received 22 August 2016

Received in revised form 25 November 2016

Accepted 28 November 2016

Available online 29 November 2016

This paper is dedicated to the memory of Dr. Ecaterina Avram (1950–2016).

Keywords:

Cationic polysulfones
Polymer mixtures
Specific conductivity
Transport processes
Specific interactions
Mathematical approach

ABSTRACT

High-performance ionic polysulfones for advanced applications, derived from chloromethylated polysulfones and tertiary amines, *i.e.*, *N,N*-dimethylbutylamine, were synthesized by a two-step polycondensation reaction and analyzed by the conductometric method. Ionic transport processes developed in ternary systems consisting of an ionic polymer (quaternized polysulfone), a neutral polymer (cellulose acetate phthalate or polyvinyl alcohol), and a dipolar aprotic solvent (*N*-methyl-2-pyrrolidone) offer information concerning the combined action of the electrostatic repulsive interactions, of associations which can take place inside the same polymer chain (intra-molecular interactions) or between different chains (inter-molecular interactions). Conductometric experimental data for polyelectrolyte/neutral polymer/solvent ternary systems are macroscopic results that can be interpreted on the basis of these interactions, and are reported as a function of the factors controlling the transport properties, such as the polymer solution concentration, polymer mixture composition, charge density, and polarity of the solvent. Additionally, the validity of Manning's theory was applied to the studied ternary systems and important discrepancies between the theory and experiment were observed.

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1. Introduction

Polyelectrolyte systems have gained great interest in various scientific fields, due to their particular behaviour in solution. The solution properties of ionic polymers considerably differ from those of the neutral polymer solutions. The origin of this specificity lies in the combination of properties derived from long chain molecules with those derived from charge interactions. The high charge density of the polyion produces a strong ionic field which attracts counterions. This strong ionic interaction is the source of the characteristic properties of polyelectrolytes [1,2].

Theoretical evaluation of polyelectrolyte solutions represents a challenge for scientists, due to their complicated behaviour, as a result of the combined action of electrostatic and hydrodynamic interactions. Literature [3–6] shows that the polyion-counterion interactions and also the properties of ionic polymers in solution depend on various parameters related to the characteristics of the polymer chain (chemical structure of the monomer units, chain length, charge density, type of ionic groups, and sequence distribution of the charge groups), counterion nature (size, valency, and polarizability), and medium properties (ionic strength, pH, and sol-

vent polarity). However, the most significant parameter affecting the solution properties of a polyelectrolyte remains linear charge density, whose importance has been promoted by Manning in his counterion condensation theory [7].

Investigation of transport properties, such as viscosity and conductivity, is very useful in the study of polyion-counterion interactions, as depending on some experimental variables affecting polyion charge density. Specific conductance and equivalent conductivity are parameters capable to describe the electrolytic transport properties of polyelectrolyte solutions, as these properties take into account the movement of any charged entity present in the system under the influence of an externally applied electric field [8]. Therefore, information on the competition between the hydrophobic and electrostatic interactions generated by the number of hydrophobic and charged groups from the polymer, as well as by the size of hydrophobic units, can be obtained from conductometric measurements. Consequently, conductometry appears as a rapid, inexpensive, sensitive method, applicable over a wide range of concentrations, for investigating the polyion-counterion interactions.

Additionally, the study of polyelectrolyte behaviour in polymer mixture solutions, besides its theoretical interest, is necessary for gaining insight into several biological processes, as well as for technological and environmental applications [9,10]. In this context,

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processable solutions of cationic polysulfone containing quaternary ammonium side groups (PSF-DMBA) have received widespread attention for their promising role as anionic exchange membranes, antimicrobial coatings, and dialysis membranes, due to their special properties [10,11–18]. Binary mixtures of PSF-DMBA with other synthetic polymers, namely cellulose acetate phthalate (CAP) and polyvinyl alcohol (PVA), selected for their excellent and versatile characteristics [19–22], can generate new types of materials with specific properties designed for specific applications in biomedical field [23–25]. Therefore, the characterization of polymer mixture solutions based on quaternized polysulfones and also establishing of their impact on the different properties is required.

In this context, the aim of the present study is to obtain, starting from the transport properties of ternary systems – PSF-DMBA/CAP/N-methyl-2-pyrrolidone (NMP) or PSF-DMBA/PVA/NMP – the necessary information concerning the behaviour of these polyelectrolytes in dilute solutions and, implicitly, on the balance between the specific interactions from the systems. In this way, more useful information will be provided, for a suitable selection of the polyelectrolyte characteristics required in future for certain applications.

2. Experimental

2.1. Materials

Commercial polysulfone in powder form (PSF, UDEL-3500 – Union Carbide Company, Texas) was purified by repeated precipitation from chloroform and dried for 24 h at 40 °C, before being used in the synthesis of chloromethylated polysulfone (CMPSF, purified by repeated precipitation from chloroform and dried in vacuum for 24 h at 40 °C) [26]. Analytical chloroform with high mass fraction purity of 0.998 (Fluka, Germany) was washed with distilled water in a separatory funnel and dried on anhydrous Na₂SO₄, and then distilled. Subsequently, the cationic polysulfones containing quaternary ammonium side groups (PSF-DMBA) were synthesized by reacting CMPSF with a tertiary amine, N,N-dimethylbutylamine (DMBA). The quaternization reaction was performed in N,N-dimethylformamide (DMF, vacuum distilled over P₂O₅), as solvent, at a CMPSF/tertiary amine molar ratio of 1:1.2, for 24 h at 80 °C. The quaternary polymers were isolated from the reaction medium by precipitation in diethylether, washed 3 times with diethylether, and dried for 48 h under vacuum, at room temperature.

Cellulose acetate phthalate (CAP, high mass fraction purity ≥0.995) was purchased from Sigma-Aldrich, USA, and used as such. This polymer has a number-average molar mass, $\bar{M}_n = 2534 \text{ g}\cdot\text{mol}^{-1}$, and a degree of substitution for acetyl and phthaloyl groups of 1.07 and 0.77, respectively.

Polyvinyl alcohol (PVA Celvol, high purity powder, not more than 0.2% residue after ignition) was purchased from Celanese Corporation (Texas), and also used as such. According to product specifications, Celvol PVA has a hydrolysis degree around 98.8% and an average weight molar mass, $\bar{M}_n = 23,000 \text{ g}\cdot\text{mol}^{-1}$. The general information of the materials used in this work is summarized in Table 1.

Binary mixtures containing PSF-DMBA and CAP, as well as PSF-DMBA and PVA were prepared by weighing the appropriate amount of the components on an electronic balance (Shimadzu ATX224) with a precision of $\pm 10^{-4} \text{ g}$. The concentration of the polymer solutions, noted c_1 – c_6 , varies between (0.07 and 0.99) $\text{g}\cdot\text{dL}^{-1}$ (8×10^{-6} – 1.97×10^{-3}) $\text{mol}\cdot\text{L}^{-1}$. Subsequently, homogeneous solutions of PSF-DMBA/CAP (covering the whole studied composition range with the corresponding uncertainty of mole fraction less

than $\pm 1 \times 10^{-5}$) were prepared by dissolution in NMP (stated mass fraction purity of 0.995, Sigma-Aldrich) and kept for 24 h at room temperature. At the same time, PSF-DMBA/PVA solutions (with the same concentrations and mole ratios) were obtained by dissolution in NMP heated at 85 °C followed by dissolution in a water bath with a constant temperature of 80 °C under continuous stirring for 2 h. Finally, all solutions were let to equilibrate for 24 h prior to use in experimental measurements.

2.2. Methodology

Fourier transform-infrared (FT-IR) spectra were performed on a Thermo-Nicolet-6700 spectrometer (Thermo Electron Corporation), being recorded over the (4000–500) cm^{-1} range. Powder samples were compressed into KBr pellets.

The ¹H NMR spectra were obtained with a Bruker Avance DRX 400 NMR (Rheinstetten, Germany) at 25 °C, using dimethyl sulfoxide (DMSO-*d*₆) as a solvent.

The electrical conductivity measurements were carried out with an InoLab 740 conductometer (WTW GmbH, Weilheim, Germany) equipped with active multifunction boxes and a TetraCon 325 conductivity cell (cell constant 0.475 cm^{-1}). The conductometer ensured direct-current electrical conductivity measurements, and the cell electrodes were made of platinum and coated with platinum black to minimize the electrode polarization. The experimental cell was calibrated with 0.01 $\text{mol}\cdot\text{L}^{-1}$ KCl standard solution and the resulting cell constant is 0.478 cm^{-1} . It was checked from time to time to control any possible evolution. All measurements were carried out at (25.00 ± 0.03) °C, under a nitrogen atmosphere and experimental values represent the mean of three measurements which were made to check the reliability of the results. The uncertainty for electrical conductivity was less than 1%.

3. Results and discussion

3.1. Synthesis and characterization of polysulfones with pendant quaternary ammonium groups

Polymer-analogous reactions are generally developed for obtaining macromolecular compounds with desirable functional groups in the side chain, which can be used as reagents or catalysts in various macromolecular organic or inorganic syntheses. The method, consisting of introducing functional groups into the polymer main chain, has the advantage of not being conditioned by the synthesis of a particular monomer [27].

Polysulfones, produced through polycondensation, are known as high-performance materials with superior thermal, chemical, and mechanical properties, which represents an advantage for many applications, such as filtration membranes [28–32], coatings [33,34], composites [35–37], microelectronic devices [38], thin film technology [39], biomaterials [25,37,40], and fuel cells [41–44]. Introduction of functional groups into polysulfones solves some limitations, and also extends the range of potential applications of these high-performance materials through the specific properties gained, and thus provides wider scope. Therefore, chemical modification by introduction of a chloromethyl group modifies the hydrophobic–hydrophilic balance of the macromolecular chain, causing an increase in membrane permeability. Recently, it has been reported that quaternary ammonium-functionalized polysulfones have been used as membranes with novel properties. Thus, the quaternization reaction of CMPSF with tertiary amine, N,N-dimethylbutylamine (DMBA), is a bimolecular nucleophilic substitution (Scheme 1). Consequently, on the one hand, the strategy of synthesis involves control of chain flexibility and mobility of segments by incorporation of reactive functional groups and, on

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