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# Abstract

Poly(thiophene-3-ylacetic acid) (PTAA) was synthesised and characterised. Sample of PTAA was dissolved in different alkaline hydroxides solutions. Degree of neutralisation was set to a level at which the polymer can be assumed to be practically fully neutralised. Electrical conductivity concentration and temperature dependence of PTAA alkaline salts aqueous solution were measured. Concentration and temperature dependence of equivalent molar conductivities of PTAA alkaline salts were calculated from these data and compared to values calculated from the Manning theory. A combination of electrical conductivities and transport numbers of polyion constituent was used to calculate the fraction of free counterions in the studied solutions. In order to extend the observed concentration range to higher concentrations, self-diffusion coefficients were measured using NMR-spectroscopy, from which the fractions of free counterions were calculated. NMR-spectroscopy was applied in the same way to calculate the fractions of free counterions in aqueous solutions of PTAA tetraalkylammonium salts. Measured fractions of free counterions were compared to values calculated using both Manning's theory or solutions of Poisson-Boltzmann equation in cells of different symmetries. Additionally, measured values of fraction of free alkaline counterions were compared to data obtained from conductivities and Scaling theory.

Isothermal titration calorimetry was used to determine enthalpies of dilution of PTAA alkaline and tetraalkylammonium salts aqueous solutions and enthalpies of mixing of PTAA alkaline salts aqueous solutions with solutions of alkaline and tetraalkylammonium chlorides. Measured values of dilution enthalpies show strong dependence on the PTAA salt studied. Enthalpies of mixing depend on both, the counterion already present in solution and the added salt. In order to attain insight into the processes in solution upon adding simple salts the self-diffusion coefficients of counterions and polyion were measured using NMR-spectroscopy for process of mixing of lithium salt of PTAA aqueous solution with solutions of alkaline and tetraalkylammonium chlorides. Some additional information on binding mechanism was extracted from the measurement of NOESY spectra and simulations of molecular dynamics.

It was shown that the fraction of alkaline counterions which bind to PTAA does not

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depend on the type of the alkaline ion within experimental error. The fraction of free counterions becomes smaller when length of tetraalkylammonium alkyl chains is increased. Enthalpies of mixing depend on the enthalpies of hydration of the added counterion. Enthalpy of mixing is decreased when added alkaline counterion enthalpy of hydration is increased. Contrary, in case of mixing with tetraalkylammonium salts the enthalpies of mixing increase when added counterion enthalpy of hydration is increased. Changed trend could be consequence of hydrophobic groups introduced in solution. Next to that interactions of tetraalkylammonium counterions with PTAA may be different from interactions of alkaline counterions with PTAA. Results of molecular dynamics simulations suggest that changed trend is consequence of hydrophobic interactions between alkyl chains of tetraalkylammonium counterion and PTAA aromatic rings.

**Keywords:** poly(thiophene-3-ylacetic acid), conjugated polyelectrolyte, ion specific effect, electrical conductivity in aqueous solutions, transference number, ion binding, calorimetry, enthalpies of dilution, enthalpies of mixing, NMR-spectroscopy, self-diffusion coefficients