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## Transport properties and ion binding in aqueous solutions of alkali metal salts of poly(thiophen-3-ylacetic acid)

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### ABSTRACT

Aqueous solutions of poly(thiophen-3-ylacetic acid) neutralized with LiOH, NaOH, and CsOH were for the first time investigated using conductivity measurements (in concentrations,  $c$ , ranging from  $2 \cdot 10^{-5}$  to  $8 \cdot 10^{-2}$  mol/dm<sup>3</sup> and temperatures from 278.15 to 313.15 K), transport number measurements (at 298.15 K) and osmotic coefficient measurements using vapor pressure osmometry (at 313.15 K) and cryoscopy, in order to identify essential electrochemical characteristics of this conjugated polyelectrolyte. The measurements of the polyion constituent transport number data suggested that a fraction of counterions traveled associated with polyions. The fraction of “free” counterions, determined from the transport measurements by the association theory of Huizenga, Grieger, and Wall was around 0.5, which is in good agreement with the osmotic coefficient data. Neither the fraction of “free” counterions, nor the osmotic coefficient significantly depends on the nature of the counterion species. The results obtained were analyzed in terms of the Poisson–Boltzmann theory, Manning’s condensation approach, and modern scaling theory. Good agreement between the theoretical results and the fraction of “free” counterions, determined from the combination of the transport number and conductivity measurements, was obtained. The osmotic coefficients were well reproduced by the Poisson–Boltzmann cell model theory.

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### 1. Introduction

Polyelectrolytes with conjugated main chains [1,2], also called conjugated polyelectrolytes (CPEs), have attracted much research interest in recent years. The interest is connected with their potential applications in fields such as optoelectronics and sensors [3–16]. These materials are used in electrochromic devices [13], single component light emitting electrochemical cells [14], and in fabrication of light emitting diodes (LEDs). Despite the interest coming from science and industry, studies of the solution properties of CPEs are quite scarce. This is difficult to understand because there are indications that the properties of CPEs in solution are closely correlated with their properties in multilayers [12,17,18]. For example, the performance of a cationic conjugated polymer in light emitting diodes can be controlled by the choice of counterion [12].

The conjugated polyelectrolyte of interest in this study is poly(thiophen-3-ylacetic acid) (PTAA). On neutralization with a base

this polyacid forms salts which are soluble in water. Important previous studies of the salts of this weak polyacid were made by Vallat et al. [19,20] and Kim et al. [21–23]. In a relatively recent study Vallat and coworkers [20] examined the conformational transitions in this polyelectrolyte induced by pH changes using UV/Vis spectroscopy. In previous studies [24,25] we investigated aqueous solutions of regio-irregular poly(thiophen-3-ylacetic acid) with and without methyl-ester groups in the presence of sodium and lithium ions as counterions. We examined how the UV/Vis spectra of solutions change with aging of the PTAA solution, polymer concentration, addition of a low molecular weight salt, temperature and some other parameters. In addition the polyacid behavior during neutralization titration with lithium and sodium hydroxides, carried out under a nitrogen atmosphere, was studied by conductometric and potentiometric titrations.

In the present work we focused on the transport properties and counterion binding in these solutions. We measured the conductivity of aqueous solutions of PTAA neutralized with lithium, sodium, and cesium hydroxide in the concentration range from  $2 \cdot 10^{-5}$  to  $8 \cdot 10^{-2}$  mol/dm<sup>3</sup> and at several temperatures between 278.15 and 313.15 K. We also performed measurements of the polyion constituent transport numbers at 298.15 K. Combination of these measurements allowed us to estimate the fraction of “free” counterions in the solution.

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The transport data were complemented with osmotic coefficient measurements, as another measure of the extent of the counterion-binding in polyelectrolyte solutions. The experimental results were analyzed with regard to various polyelectrolyte theories, such as (i) the Poisson–Boltzmann cell model in cylindrical symmetry, (ii) Manning's condensation approach, and (iii) modern scaling theory.

## 2. Experimental

### 2.1. Polymer synthesis and sample preparation

The synthesis, purification and preparation of the sample followed procedures used in our previous work [24]. Because the PTAA sample for the experiments described in this paper was synthesized *de novo* its characteristics slightly differ from the previous one [24,25]. The main features of the sample preparation are summarized below while the details can be found in Supplementary data to this paper.

The PTAA precursor, PTAME (poly(methyl thiophen-3-ylacetate)), was synthesized by oxidative polymerization of methyl thiophen-3-ylacetate. The resulting polymer was fractionated on the basis of the molar mass-dependent solubility of PTAME. High molecular-mass fraction of PTAME was converted to PTAA by alkaline hydrolysis (NaOH) and used in further experimental work.

Synthesis was followed by purification of PTAA. The solid sample was first dissolved in 0.1 M alkali hydroxide (LiOH, NaOH, or CsOH), filtered through a cellulose nitrate filter (pore size 1.2  $\mu\text{m}$ , Sartorius AG, Goettingen, Germany), precipitated by HCl, and isolated by centrifugation. The procedure was repeated twice in order to remove impurities, mostly iron. The precipitation/dissolution procedure was used also in the conversion of sodium salt of PTAA, obtained by alkaline hydrolysis of PTAME, into lithium and cesium PTAA salts. As it was later found by atomic spectroscopy, this conversion was not quantitative (complete) and about 2% of sodium counterions still remained in prepared stock solutions of  $\text{Li}^+$  and  $\text{Cs}^+$  salts of PTAA (Table 1). The sample was finally dissolved in the desired alkali hydroxide and filtered through a cellulose nitrate filter (pore size 0.45  $\mu\text{m}$ , Sartorius AG, Goettingen, Germany), and the pH decreased to a value of 5.1. The solution was used to fill dialysis tubes (Spectra/Por 3, relative-molecular-mass-cut-off 3.5 kDa) and dialyzed against triply distilled water for about one month. The final step in the preparation of the stock solution was the adjustment of the level of neutralization to about 97%. The concentration of the non-neutralized PTAA was determined by titration. The stock solution (its composition is given in Table 1) was stored under a nitrogen atmosphere.

### 2.2. Determination of PTAA molar mass

#### 2.2.1. MALDI-TOF MS analysis

MALDI-TOF MS measurements were performed with a Bruker UltrafleXtreme MALDI-TOF-TOF mass spectrometer (Bruker Daltonik, Bremen, Germany) equipped with a 337 nm nitrogen laser, capable of executing reflector mode-analysis. Trifluoroacetic acid (TFA) (99%)

and 2,5-dihydrobenzoic acid (DHB) (>99.0%), used in the matrix preparation, were obtained from Sigma-Aldrich, USA. Mass spectrum was acquired in reflector positive ion mode by summing spectra from 500 selected laser shots. The calibration was made externally with a Peptide calibration standard II and Protein Calibration Standard I (Bruker Daltonik). Aqueous solution of sodium poly(thiophene-3-ylacetate) (13.5 mg/mL) was mixed with the solution of DHB (20 mg/mL), dissolved in a 30/70 (v/v) mixture of acetonitrile/aqueous 0.1% TFA, in a volume ratio 1/10. 0.5  $\mu\text{L}$  of this mixture was deposited on MALDI target and allowed to dry on air.

We were only able to obtain mass spectrum with unresolved "isotopic envelope" (see Supplementary data). The apex of the peak, belonging to protonated PTAA, was at 4250 Da.

#### 2.2.2. Size exclusion chromatography

SEC measurements of PTAA were carried out in 0.1 M  $\text{NaNO}_3$  with 0.02% azide at pH = 10 using an Agilent 1260 HPLC Infinity instrument, an Aquagel OH 20 analytical column (7.5 mm  $\times$  300 mm) with a pre-column (Agilent Technologies) and a refractive index (RI) detector. The nominal eluent flow rate was 1 mL/min, the injection volume was typically 100  $\mu\text{L}$  and the mass of the samples injected onto the column was typically 150  $\mu\text{g}$ . For the data acquisition and evaluation a WinGPC v.7 (Polymer Standards Service GmbH) was utilized. According to column calibration with polyethylene glycol (PEG) standards of narrow-molar-mass distribution, the molar mass characteristics of PTAA were estimated to be (average values of two runs):  $M_n = 7.2$  kg/mol,  $M_w = 13.4$  kg/mol, and  $M_w/M_n = 1.86$ .

### 2.3. Measurements

#### 2.3.1. Concentration determination

Potentiometric titrations of the polyacid were performed at 298.15 K using a 736 GP Titrimo automatic titrator and a Metrohm combined glass electrode (6.0233.100). The pH-meter was calibrated using buffer solutions with pH values equal to 6.86 and 9.18. The solution was kept under a nitrogen atmosphere during titration. The titrant ( $\text{CO}_2$ -free solutions of 0.0988 M LiOH, 0.1022 M NaOH, and 0.0847 M CsOH) was added in 0.01 mL volume steps. The time interval between two consecutive additions was 6 min.

The concentration of low molecular weight salt solutions (LiCl, NaCl, and CsCl) was determined at 298.15 K using the 736 GP Titrimo automatic titrator. A Metrohm chloride-sensitive electrode (6.0502.120) was used as the indicator electrode and a saturated mercury(I) sulfate electrode as the reference electrode. The titrant was standard 0.1 M  $\text{AgNO}_3$  solution.

The concentrations of  $\text{Li}^+$  and  $\text{Na}^+$  ions in the stock solutions were determined by atomic absorption spectroscopy (AAAnalyst 600, Perkin Elmer), while the concentration of  $\text{Cs}^+$  ions was determined by atomic emission spectroscopy (AAAnalyst 600, Perkin Elmer). In all cases the response of the instrument was calibrated by an external standard.

#### 2.3.2. Electrical conductivity

The electrical conductivity was obtained by measuring the resistance of the solution in an arrangement of eight capillary cells with different cell constants (medium concentrations), or in a three-electrode cell designed for measuring the conductivities of very dilute solutions [26,27]. A high-precision thermostat (Lauda UB 40J, WK 1400), with a reproducibility better than  $\pm 0.003$  K, was used to maintain a constant temperature chosen from the interval between 278.15 and 313.15 K. Cell constants were determined by calibration with standard potassium chloride solution. The values of the electrical resistance of solutions measured at  $\nu = 4$  kHz by an Agilent 4284A precision LCR meter were used in further calculations. The specific conductivity of the pure water ( $\kappa_w = 5 \cdot 10^{-7}$  S/cm) used for the preparation and dilution of

**Table 1**

Composition of stock solutions from which measured solutions were prepared. The abbreviations PTALi (PTANa, PTACs) stand for the lithium (sodium, cesium) salt of the poly(thiophen-3-ylacetic acid). Here  $c$  and  $\alpha_N$  denote the concentration of polyelectrolyte in moles of ionized monomer units per  $\text{dm}^3$  and the degree of neutralization, respectively. The ratio  $c(\text{Na}^+)/c$  represents extent of  $\text{Na}^+$  ions in the samples in comparison with the total counterion concentrations. See Section 2.1 Polymer synthesis and sample preparation for further details.

Salt	$c/\text{mol dm}^{-3}$	$\alpha_N$	$c(\text{Na}^+)/c$
PTALi	$7.406 \cdot 10^{-2}$	95.8	2%
PTANa	$8.114 \cdot 10^{-2}$	97.7	100%
PTACs	$6.253 \cdot 10^{-2}$	98.1	2%

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