Electrochimica Acta 55 (2010) 1289–1297

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Systematics of salt precipitation in complexes of polyethylene oxide and alkali metal iodides

J. Bastek[a], N.A. Stolwijk[a,*], Th. K.-J. Köster[b], L. van Wüllen[b]

[a] *Institut für Materialphysik and Sonderforschungsbereich 458, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany*
[b] *Institut für Physikalische Chemie and Sonderforschungsbereich 458, University of Münster, Corrensstr. 28/30, 48149 Münster, Germany*

ARTICLE INFO

Article history:
Received 7 November 2008
Received in revised form 6 April 2009
Accepted 14 April 2009
Available online 21 April 2009

PACS:
66.10.−x
66.30.Hs

Keywords:
Polymer electrolytes
Salt precipitates
Tracer diffusion
Conductivity
Ion pairs
Nuclear magnetic resonance

ABSTRACT

Conductivity measurements in $PEO_{30}MI$ polymer electrolytes with M = Li, Na, K, Rb, or Cs over the temperature range from about 65 to 200 °C show an increasing tendency for salt precipitation with increasing cation size. The salt precipitation in these complexes upon heating is revealed by the decrease of the dc conductivity starting at a critical temperature T_c. Whereas LiI and NaI complexes do not show precipitation effects, T_c monotonically decreases from about 140 to 65 °C when changing the salt component from KI via RbI to CsI. For the PEO–RbI system, precipitation is further investigated by nuclear magnetic resonance (NMR) and tracer diffusion experiments. NMR analysis unambiguously demonstrates the onset of RbI salt precipitation and the increase of the precipitate fraction with increasing temperature. In diffusion experiments on $PEO_{30}RbI$ with the radiotracers ^{86}Rb and ^{125}I, the precipitation effect is manifested by anomalous features in the penetration profiles, however, without noticeable changes in their depth range. Combining the resulting tracer diffusion coefficients with the dc conductivity data enables us to assess crucial parameters characterizing ionic transport in $PEO_{30}RbI$.

1. Introduction

Salt-in-polymer complexes exhibit a combination of properties that make them potentially attractive for applications as electrolyte material in batteries, solar cells and smart windows [1,2]. For this reason, extensive research efforts have been undertaken over the past three decades to optimize and to understand the characteristics of ionic transport in these polymer-based ion conductors. Complexes of poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO) with alkali metal salts belong to the most frequently investigated prototype systems.

PEO and PPO are characterized by the ability to solvate relatively high salt concentrations in their amorphous state. This is particularly true for salts consisting of large polarizable anions and small cations such as Li and Na, which are of technological relevance [3,4]. The frequent use of such well-behaved systems in basic and applied research on polymer electrolytes may explain why salt precipitation (SP) has been observed rather as a side effect in only a few cases [5–9] and why SP has been made to the object of study even more rarely [10,11]. Furthermore, the tendency for SP appears to be more prominent at elevated temperatures, which are less interesting for most practical applications. However, only few workers in the field seem to have recognized that SP is a basic phenomenon whose understanding may lead to deeper insight into the salt–polymer interaction [10,11].

Most early reports on SP in polymer electrolytes concern PPO that was complexed with sodium salts to a fixed O/Na ratio of (or close to) 8, including $NaClO_4$ [6], NaI [7,10], and NaSCN [7,8,11]. Two studies deal with SP in the PPO–KSCN system [10,11]. Teeters et al. [11] investigated SP as a function of salt concentration in PPO complexed with NaSCN or KSCN and found a monotonic decrease of the SP onset temperature with increasing cation-to-oxygen ratio. They also pointed to the lower precipitation temperatures observed for the salt with the larger cation. Work on SP in PEO-based electrolytes is even more scarce. Only the phase separation of NaI [5] and RbI [9] has been reported.

The present work deals with PEO complexed with different alkali metal iodides. SP in these systems is investigated at different levels of sophistication and with different methods of analysis including differential scanning calorimetry (DSC), ionic conductivity measurements, magic angle spinning nuclear magnetic resonance (MAS NMR), and radiotracer self-diffusion experiments. First, chemical trends in the SP behaviour are detected with the aid of DSC and conductivity analysis by varying the alkali-metal cation species (Li,

---

* Corresponding author. Tel.: +49 251 83 39013; fax: +49 251 83 38346.
E-mail address: stolwij@uni-muenster.de (N.A. Stolwijk).

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.04.040

Na, K, Rb, or Cs) of the salt iodide component. Then, the dependence of SP on the salt concentration is explored for the PEO–RbI system by means of DSC, conductivity and NMR MAS measurements. Finally, the precipitation of RbI from the $PEO_{30}RbI$ complex is subjected to close examination by using the radiotracers ^{86}Rb and ^{125}I in extensive diffusion experiments covering a wide temperature interval. Here it is shown that the radiotracer technique is able to provide diffusivity data for the minor fraction of cations and anions that remain in solution after SP.

2. Experimental procedures

Only brief descriptions of sample preparation and the employed experimental methods are given here. For more details the reader is referred to our earlier publications [12–14].

Appropriate amounts of PEO with a molecular weight of 8×10^6 (Aldrich) and alkali-metal salt (various suppliers) were dried under dynamic vacuum at elevated temperature and subsequently dissolved in water-free acetonitrile. The purity of the salts was certified to be 99.9% or more, except for NaI (99.0%), while the PEO purity may be specified as 98.4%.[1] After evaporation of the solvent under dynamic vacuum (10^{-5} h Pa), the mass density of the salt-in-polymer complexes as determined by the Archimedes method was found to vary between $1.25 \pm 0.02\,g/cm^3$($PEO_{120}RbI$) and $1.36 \pm 0.02\,g/cm^3$ ($PEO_{20}RbI$). To avoid contact with ambient moisture and air all critical preparation steps and experimental procedures were carried out in a nitrogen-flushed glovebox or in gas-tight containers.

DSC analysis of the complexes was performed over the temperature range from 20 to 200 °C with a PerkinElmer DSC-7 instrument. To this aim, a small amount of solvent-free substance was sealed in aluminium capsules in the glovebox environment. In all cases, thermograms were repeatedly recorded at varying heating rates using several samples of the same complex.

Ionic conductivity was investigated by means of impedance spectroscopy using a HP Agilent 4192A LF impedance analyser covering the ac frequency range from 5 Hz to 13 MHz. The electrolyte was enclosed in a cylindrical cavity between two coplanar $1.00\,cm^2$ stainless steel electrodes. Mechanical pressure could be adjusted by a spring system. Temperature was controlled by a silicon-oil heating circulator connected to a double-walled glass assembly encapsulating the measuring cell and recorded by a Pt-100 sensor located close to the sample. The cell was operated under a continuous flow of pure nitrogen gas. The reproducibility of the data was verified by repeated heating and cooling cycles on multiple samples originating from the same or different production batches.

^{87}Rb and ^{127}I MAS NMR spectra were recorded on a Bruker DSX 400 spectrometer with resonance frequencies of 131.0 and 80.1 MHz for ^{87}Rb and ^{127}I, respectively, employing a 4 mm Bruker MAS probe and spinning frequencies of 9000 Hz [14,15]. The spectra were referenced to an 1 M aqueous RbI solution for both nuclei.

For self-diffusion experiments on $PEO_{30}RbI$, the radiotracers ^{86}Rb (half-life 18.6 d) and ^{125}I (60 d) were purchased in the form of aqueous solutions of $^{86}RbCl$ and $Na^{125}I$, respectively. Small amounts of one of these solutions were added to a thin $PEO_{30}RbI$ film, which – after subsequent drying – acted as diffusion source on the upper face of a cylindrical $PEO_{30}RbI$ sample [12]. It should be emphasized that the composition of the source film remained virtually unchanged by the addition of the radiotracer, which is a major characteristic of the method [16]. Using suitable encapsulants, the samples were subjected to isothermal diffusion treatments in an oil-bath thermostat operated between 75 and 200 °C. After quenching in water at room temperature, diffusion profiles were determined by microtome sectioning and liquid scintillation counting of the sections' β-activity.

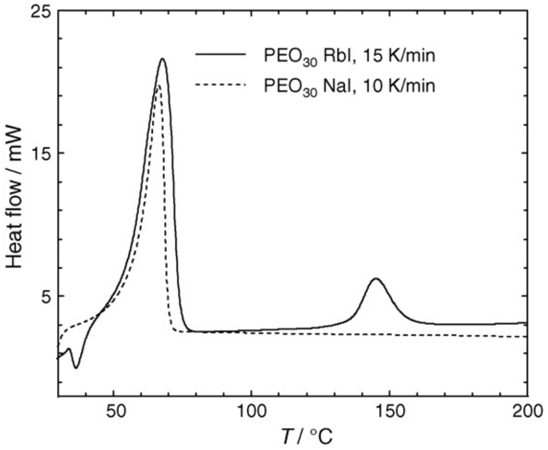

Fig. 1. DSC thermographs of $PEO_{30}RbI$ and $PEO_{30}NaI$ at heat rates of 15 and 10 K/min, respectively. Both complexes show the endothermic melting peak of PEO near 70 °C. Additionally, $PEO_{30}RbI$ reveals a second peak near 150 °C, which is attributed to salt precipitation.

3. Results and discussions

3.1. Salt precipitation in $PEO_{30}MI$ electrolytes

3.1.1. DSC data

Fig. 1 shows a typical thermogram of $PEO_{30}RbI$ upon heating (second or higher numbered cycle) in comparison to that of $PEO_{30}NaI$. Both measurements reveal endothermic peaks near 70 °C, which are characteristic of PEO melting. It is remarkable, however, that only $PEO_{30}RbI$ exhibits a second endothermic peak in the investigated temperature range from about 70 to 200 °C. This reversible feature near 130 °C is indicative of RbI precipitation, as will be verified by the results of other methods of analysis to be presented below. Similar evidence for salt precipitation but at a somewhat higher temperature (145 °C at 15 K/min) was observed for $PEO_{30}KI$, whereas $PEO_{30}LiI$ like $PEO_{30}NaI$ was characterized by the absence of any heating effects apart from PEO melting. In the case of $PEO_{30}CsI$, the appearance of a single but comparatively broad peak near 70 °C seemed to indicate that the SP temperature was close to the melting point of PEO. This assumption was confirmed by conductivity measurements (see below).

To determine the SP temperatures more accurately, DSC measurements were performed at different heating rates. Fig. 2 shows for $PEO_{30}RbI$ and $PEO_{30}KI$ the monotonic decrease of the temperature at the SP peak maximum, T_{max}, and the SP onset temperature, T_c, with decreasing heating rate. For comparison, similar data for PEO melting are also displayed in Fig. 2. It is obvious that for this melting transition the $PEO_{30}RbI$ data virtually coincide with the $PEO_{30}KI$ data.

3.1.2. Conductivity data

Fig. 3 displays the temperature dependence of the dc conductivity σ for the five $PEO_{30}MI$ complexes under investigation. For the systems with the smallest cations, $PEO_{30}LiI$ and $PEO_{30}NaI$, the common behaviour for PEO-based electrolytes is observed. This includes a steep increase of σ within the semi-crystalline phase of the complexes, i.e., from room temperature up to the PEO melting temperature at about 65 °C. Entering the amorphous phase upon further heating leads to a moderate monotonic increase of σ up to

---

[1] According to the pertaining lot specification, the base PEO material contained 1.4 wt% SiO_2 and 0.2 wt% CaO. These contaminations, which are inherent to the manufacturing process, are present in the form of small particles; see also [24].