On the extraction of ion association data and transference numbers from ionic diffusivity and conductivity data in polymer electrolytes

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ABSTRACT

The degree of ion association in polymer electrolytes is often characterized by the Nernst–Einstein deviation parameter Δ, which quantifies the relative difference between the true ionic conductivity directly measured by electrical methods and the hypothetical maximum conductivity calculated from the individual ionic self-diffusion coefficients. Despite its unambiguous definition, the parameter Δ is a global quantity with limited explanatory power. Similar is true for the cation transport number t^*_{cat}, which relies on the same ionic diffusion coefficients usually measured by nuclear magnetic resonance or radiotracer methods. Particularly in cases when neutral ion pairs dominate over higher-order aggregates, more specific information can be extracted from the same body of experimental data that is used for the calculation of Δ and t^*_{cat}. This information concerns the pair contributions to the diffusion coefficient of cations and anions. Also the true cation transference number based on charged species only can be deduced. We present the basic theoretical framework and some pertinent examples dealing with ion pairing in polymer electrolytes.

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1. Introduction

Over the last decades solid polymer electrolytes (SPEs) and room temperature ionic liquids (ILs) have been extensively investigated for applications in batteries, electrochemical solar cells, smart windows, etc. [1,2]. In this context, optimal ion transport properties require not only high ionic mobilities but also high concentrations of charged or 'free' ions. Therefore, ion association has been a crucial issue in most studies of mass and charge transport in SPEs and ILs.

The most elementary form of ion association is pair formation. In particular, neutral ion pairs contribute to the diffusivity of the cation and the anion but they do not contribute to the electrical conductivity σ. Also the occurrence of higher-order clusters, such as triplets, diminishes the number of charged species, and moreover, tends to reduce the average mobility of the charge carriers.

To quantify the impact of ion association, or more specifically ion pairing, one usually calculates the Nernst–Einstein deviation parameter Δ [3]. This so-called delta parameter is defined by the relation

$$\sigma = \sigma_{diff}(1 - \Delta), \qquad (1)$$

where σ_{diff} is the hypothetical overall conductivity derived from the joint individual contributions of all ionic diffusion coefficients (D^*_{cat} and D^*_{an}) obtained either by pulsed field gradient nuclear magnetic resonance (PFG-NMR) or radiotracer diffusion (RTD) [3]. For monovalent electrolytes σ_{diff} is written as

$$\sigma_{diff} = \frac{e^2 C_s}{k_B T}(D^*_{cat} + D^*_{an}), \qquad (2)$$

where k_B denotes the Boltzmann constant, T is temperature, e is elementary charge, and C_s is the known total salt concentration (number density of molecules). It should be emphasized that these diffusion coefficients, marked by an asterisk, are concentration-weighted averages over all cation-containing and anion-containing mobile species, respectively. For full dissociation of the salt, all ions contribute to charge transport, so that $\Delta = 0$ holds under the provision that ionic motion occurs in an uncorrelated manner. Conversely, in the case of strong cation–anion pairing the concentration of charge carriers becomes very low, which is reflected by Δ approaching the value of 1.

In spite of its usefulness as a global indicator of the degree of ion association, the true meaning of the empirically defined parameter Δ remains obscure. Nevertheless, in many studies on electrolytes, the value of Δ serves as a major characteristic. However, in cases where neutral ion pairs dominate over higher-order aggregates, the meaning of Δ can be specified. For instance, this situation occurs for polymer electrolyte with a sufficiently low salt concentration.

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Another global characteristic of electrolytes is the cation transport number given by

$$t_{\text{cat}}^* = \frac{D_{\text{cat}}^*}{D_{\text{cat}}^* + D_{\text{an}}^*}, \tag{3}$$

which relates the cation diffusivity to the sum of the ion diffusion coefficients. D_{cat}^* and D_{an}^* will generally contain contributions of ion pairs and larger aggregates. Therefore, t_{cat}^* must be distinguished from the cation transference number t_+, which only refers to charged species. It is generally believed, however, that transference numbers cannot be directly determined from conductivity and diffusion data.

In this work, we will derive an expression for the Nernst–Einstein deviation parameter Δ under conditions where ion association is governed by the formation of neutral pairs. In addition, the pair contributions to the diffusion coefficient of cations and anions are deduced from Δ and t_{cat}^*. Within the same simple theoretical framework, the effective diffusivities of the free ionic species and ion pairs are calculated either directly from the measured conductivity and diffusion coefficients or indirectly using Δ and t_{cat}^*. It will be also shown, how t_+ can be obtained from the same experimental data. Results will be given for polymer electrolytes based on poly(ethylene oxide) (PEO) with salts of different type and concentration including the alkali metal iodide NaI and the ionic liquids 1-ethyl-3-methyl-imidazolium iodide (EMImI) or 1-ethyl-3-methyl-imizadolium bis(trifluoromethylsulfonyl)imide (EMImTFSI).

2. Charge diffusivity and Haven ratio

The definition of σ_{diff} in Eq. (2) involves the conversion of diffusivity into a quantity with the dimensions of a conductivity. This is based on the Nernst–Einstein equation, which in its reversed form, transforms the measured conductivity to the charge diffusivity D_σ, i.e.,

$$D_\sigma = \frac{k_B T}{C_s e^2} \sigma. \tag{4}$$

It should be emphasized that the denominator contains the known total salt concentration C_s instead of the *a priori* unknown concentration of free (dissociated) ions. With this definition, D_σ is closely related to the molar conductivity given by $\Lambda = \sigma/c_s$, where c_s is the same salt concentration in molar units.

Eq. (1) compares mass and charge transport in units of conductivity. Alternatively, such a comparison can be made on the diffusivity scale by means of the Haven ratio, H_R given by [4,5]

$$H_R = \frac{D_{\text{cat}}^* + D_{\text{an}}^*}{D_\sigma}. \tag{5}$$

Combining this expression with Eqs. (2) and (4) it readily follows that the identity relationship

$$\frac{\sigma}{\sigma_{\text{diff}}} = \frac{1}{H_R} \tag{6}$$

must hold. The ratio $\sigma/\sigma_{\text{diff}} = \Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ has been termed the 'ionicity' [6] or the 'dissociation degree' [7] of the electrolyte under investigation. Here, the indices of the molar conductivity Λ refer to 'impedance measurements' and 'PFG-NMR analysis', respectively. Using Eqs. (1), (5) and (6) we obtain for the delta parameter the expression

$$\Delta = 1 - \frac{1}{H_R} = 1 - \frac{D_\sigma}{D_{\text{cat}}^* + D_{\text{an}}^*}, \tag{7}$$

which only contains diffusion coefficients as parameters.

Also the Haven ratio can be used as a measure of ion association. For $H_R = 1$ we have $\Delta = 0$, which implies full dissociation of the

salt. Higher values of H_R (>1) reflect an increased degree of association. Approaching the limit of complete association, H_R diverges to infinitely high values.

3. Predominance of ion pairing

3.1. Basic equations

In SPE-complexes of moderate or low salt concentration, the formation of cation–anion pairs according to the reversible reaction

$$\text{cat}^+ + \text{an}^- \rightleftharpoons \text{pair} \tag{8}$$

appears to be the predominant ion-aggregation process [8–10]. Thus, neglecting higher-order clusters, the ion-specific diffusion coefficients measured by PFG-NMR or RTD (D_{cat}^* and D_{an}^*) may be written as

$$D_{\text{cat}}^* = D_{\text{cat}^+}^{\text{eff}} + D_{\text{pair}}^{\text{eff}} \equiv (1 - r_{\text{pair}})D_{\text{cat}^+} + r_{\text{pair}}D_{\text{pair}} \tag{9}$$

$$D_{\text{an}}^* = D_{\text{an}^-}^{\text{eff}} + D_{\text{pair}}^{\text{eff}} \equiv (1 - r_{\text{pair}})D_{\text{an}^-} + r_{\text{pair}}D_{\text{pair}}, \tag{10}$$

where $r_{\text{pair}} = C_{\text{pair}}/C_s$ denotes the relative concentration of neutral pairs (or pair fraction). Consistently, D_{cat}^* and D_{an}^* represent the total diffusion coefficient of cations and anions, respectively, averaged over all relevant mobile species. On the contrary, the plain D symbols (D_{cat^+}, D_{an^-}, and D_{pair}) designate the true (or inherent [11]) diffusivities of the individual species (cat$^+$, an$^-$, and pair), which are related to the respective mobilities. Furthermore, D's labelled with the superindex 'eff' ($D_{\text{cat}^+}^{\text{eff}}$, $D_{\text{an}^-}^{\text{eff}}$, and $D_{\text{pair}}^{\text{eff}}$) are so-called effective diffusion coefficients which also involve the relative concentration of the respective species (r_{pair} or $1 - r_{\text{pair}}$). Thus, in this notation D_σ is given by the sum of the contributions of charged species, i.e.,

$$D_\sigma = D_{\text{cat}^+}^{\text{eff}} + D_{\text{an}^-}^{\text{eff}} \equiv (1 - r_{\text{pair}})D_{\text{cat}^+} + (1 - r_{\text{pair}})D_{\text{an}^-}. \tag{11}$$

Eqs. (9)–(11) apply to spatially homogeneous SPEs with uniform charge distributions in thermal equilibrium. The various self-diffusivities entering the model characterize the purely statistical (entropy-driven) diffusion and thus do not contain contributions due to thermodynamical (enthalpic) or electrical driving forces. Although the measurement of D_σ involves electrical fields, the small amplitudes and the high ac frequencies employed warrant negligible deviations from the ideal reference state.

It should be mentioned that the evaluations in this paper will be restricted to the level of 'effective diffusivities'. To decompose $D_{\text{pair}}^{\text{eff}}$ in r_{pair} and D_{pair} or $D_{\text{cat}^+}^{\text{eff}}$ in $1 - r_{\text{pair}}$ and D_{cat^+} further assumptions about the temperature dependence of the pair fraction and the true diffusivities are necessary [12,13]. Thus, ignoring the right-hand sides of Eqs. (9)–(11), we have 3 equations with 3 *a priori* unknowns, viz., $D_{\text{cat}^+}^{\text{eff}}$, $D_{\text{an}^-}^{\text{eff}}$, and $D_{\text{pair}}^{\text{eff}}$. Solving this equation system yields the effective diffusivities as a function of the measured data, i.e.,

$$D_{\text{cat}^+}^{\text{eff}} = \frac{1}{2}(D_{\text{cat}}^* - D_{\text{an}}^* + D_\sigma) \tag{12}$$

$$D_{\text{an}^-}^{\text{eff}} = \frac{1}{2}(D_{\text{an}}^* - D_{\text{cat}}^* + D_\sigma) \tag{13}$$

$$D_{\text{pair}}^{\text{eff}} = \frac{1}{2}(D_{\text{an}}^* + D_{\text{cat}}^* - D_\sigma). \tag{14}$$

Altogether, the effective diffusivity of each ionic species can be obtained from the experimental data in a straightforward manner.

Conceiving a potentially strong role for ion pairs, it is useful to specify the relative pair contributions to cation and anion transport