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Permalink

<https://escholarship.org/uc/item/18w7j27m>

Journal

Journal of The Electrochemical Society, 166(2)

ISSN

0013-4651

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Publication Date

2019

DOI

10.1149/2.0591902jes

Peer reviewed

Theoretical Interpretation of Ion Velocities in Concentrated Electrolytes Measured by Electrophoretic NMR

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Abstract

Electrophoretic NMR (eNMR) is emerging as a powerful technique for characterizing ion transport in electrolyte systems. We show that the standard approach for analyzing eNMR data is valid only for dilute electrolytes and provide a theoretical framework for interpreting eNMR results for all binary electrolyte systems with univalent salts. We derive relationships between the velocities of the ion species and the solvent in terms of the electrochemical Stefan-Maxwell diffusion coefficients and provide modified expressions for correctly calculating the transference number and conductivity from eNMR data in concentrated electrolytes. Our approach suggests that it is necessary to measure not just the displacement of ion species during the application of current in an eNMR experiment but also the displacement of the uncharged solvent in order to correctly calculate ion mobilities and the transference number.

Introduction

Transport in concentrated electrolyte solutions containing a binary salt is governed by three transport properties, the ionic conductivity, σ , the concentration-based salt diffusion coefficient, D_m , and the cation transference number, $t_{+,\text{ii}}$, and the salt activity coefficient, γ_{\pm} .¹ From measurements of these four properties one can calculate the Stefan-Maxwell diffusion coefficients, $D_{+,0}$, $D_{-,0}$, and $D_{+,-\text{ii}}$:

$$D_m = D \frac{c_T}{c_0} \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right) \quad (1)$$

$$D = \frac{2D_{+,0}D_{-,0}}{D_{+,0} + D_{-,0}} \quad (2)$$

$$t_{+i} = \frac{D_{+,0}}{D_{+,0} + D_{-,0}} \quad (3)$$

$$\frac{1}{\sigma} = \frac{RT}{c_T F^2} i$$

taken from Equation 12.12 and Table 12.1 of Ref. 1, where c_T is the total concentration of the electrolyte, c_0 is the solvent concentration, $\frac{d \ln \gamma_{\pm}}{d \ln m}$ is the change in the activity coefficient as a function of molal salt concentration m , R is the gas constant, T is the temperature, and F is Faraday's constant. The Stefan-Maxwell diffusion coefficients quantify frictional interactions between the species in the electrolyte: the cation, $+i$, the anion, $-i$, and the solvent, 0. Complete characterization of a few electrolyte systems using these electrochemical techniques has been presented.²⁻⁵ Knowledge of all three Stefan-Maxwell transport coefficients is essential for modeling electrochemical cells.

An emerging technique for characterizing ion transport in electrolytes is electrophoretic NMR, where ion velocities are measured under applied electric fields. A powerful aspect of this method is that both the magnitude and the direction of ion velocities can be measured directly while interpretations of ion velocities from conventional electrochemical measurements are indirect. In an electrophoretic NMR experiment, a dc electric field, E , is applied across the electrolyte at time $t=0$, and the displacement of a chemical species of interest under the influence of the field is measured over a short period of time, $t \approx 1 \text{ ms}$. The displacement is measured in a manner that is similar to the measurement of self-diffusion coefficients using pulsed-field gradient NMR. The standard approach for interpreting electrophoretic NMR assumes that the velocity of the species of interest, v_i , is a linear function of E and is related to the ionic mobility u_i . For univalent systems,

$$v_i = u_i E \quad (5)$$

Measurement of v_i as a function of E allows the determination of the electrophoretic mobility u_i . Theoretical background and practical implementations of the technique can be found in a number of seminal works.⁶⁻¹¹ Ion mobilities in several electrolyte solute ions have been determined from linear fits of v_i vs. E data.¹²⁻²¹

The relationships between the electrophoretic mobilities, u_{+} and u_{-} , and the three electrochemically determined transport coefficients remains to be established. The purpose of this paper is to create a theoretical framework for relating electrophoretic NMR results to classical electrochemical characterization using concentrated solution theory. We derive relationships between the Stefan-Maxwell coefficients and the velocities of the charge carriers measured by electrophoretic NMR. We provide expressions for the transference number and conductivity in terms of the species velocities and mobilities. Our definitions for the mobilities account for the fact that diffusional fluxes are related to velocity differences rather than absolute velocities. It is therefore important to measure the electric field-induced solvent velocity (electro-osmotic drag) during an electrophoretic NMR experiment.

Theory

Following the concentrated solution theory (Equation 12.1 of Ref. 1), multicomponent diffusion is described by

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T D_{ij}} (v_j - v_i) \quad (6)$$

where c_i , c_j , and c_T are the concentrations of species i and j , and the total species concentration, $\nabla \mu_i$ is the gradient of the electrochemical potential of species i , R is the gas constant, T is the temperature, D_{ij} is the Stefan-Maxwell diffusion coefficient describing interactions between species i and j , v_i and v_j are the velocities of species i and j .

The gradient of the electrochemical potential of each species can be expressed in terms of the gradient in potential across the electrolyte and the gradient in concentration. The salt concentration and potential within a binary electrolyte in an electrophoretic NMR experiment is shown in Fig. 1. We assume that applying dc current for a short amount of time, $t \approx 1 \text{ ms}$, results in concentration gradients that are localized near the electrode-electrolyte interfaces. The electrophoretic NMR experiment is designed to measure velocities in the bulk of the electrolyte where the salt concentration is uniform. This assumption will be valid as long as the time-scale for data acquisition in the electrophoretic NMR experiment is much smaller L^2/D , where L is the separation between the electrodes and D is the diffusion

coefficient of the salt. The electrophoretic NMR experiment is designed to minimize convection due to resistive heating. Our analysis assumes that convection is negligible.

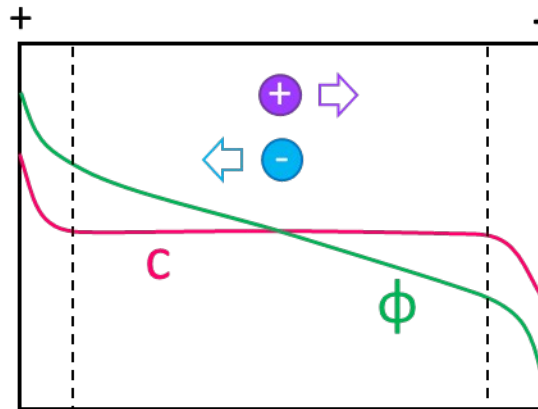


Figure 1. Schematic of the salt concentration and the electric potential in an electrolyte as a function of position between the electrodes in an electrophoretic NMR experiment. Species velocities are defined relative to reference frame fixed to the electrochemical cell. Velocities are defined to be positive if a species moves towards the right. The analysis in the paper applies to the bulk of the electrolyte between the dashed lines where the salt concentration is uniform.

We use the quasi-electrostatic potential (Equations 3.18-3.20 of Ref. 1) derived from the Gibbs-Duhem relationship to relate the electrochemical potential of each species to the electric potential in the region of uniform concentration,

$$\nabla \mu_{+i} = F \nabla \phi \quad (7)$$

$$\nabla \mu_{-i} = -F \nabla \phi \quad (8)$$

$$\nabla \mu_0 = 0 \quad (9)$$

where μ_{+i} , μ_{-i} , and μ_0 are the electrochemical potentials of the cation, anion, and solvent, F is Faraday's constant, and $\nabla \phi$ is gradient of electric potential. We note that $E = -\nabla \phi$, and our simplifying assumption where we neglect the potential drop near the electrodes implies that $\nabla \phi$ is equal to the potential applied across our symmetric cell divided by L . Eq. 7-9 are valid for both liquid and polymer electrolytes containing a salt comprised of two univalent ions. It is straightforward to extend this approach to other electrolyte systems containing three species, e.g. a mixture of two ionic liquids with a common ion or electrolytes comprised of multivalent salts. Substituting eq. 7-9 into eq. 6 we get three expressions relating the velocities of the ions and solvent to the applied potential,

$$\frac{F \nabla \phi}{RT} = \frac{c_0}{c_T D_{0+i} \ddot{i} \ddot{i}}$$

$$\frac{-F \nabla \phi}{RT} = \frac{c_0}{c_T D_{0-i} \ddot{i} \ddot{i}}$$

$$0 = \frac{c_{+i}}{c_T D_{0+i} \ddot{i} \ddot{i}} \ddot{i}$$

where c_0 , c_{+i} , and c_{-i} are the concentrations of the solvent, cation, and anion, respectively, v_0 , v_{+i} , and v_{-i} are the velocities of the solvent, cation, and anion, respectively, and D_{0+i} , D_{0-i} , $D_{\pm i}$ are the Stefan-Maxwell diffusion coefficients describing interactions between pairs of species in the electrolyte indicated by the subscripts. These diffusion coefficients can be measured by electrochemical methods.²² Only two of the eq. 10-12 are independent. This implies that electrochemically determined D_{0+i} , D_{0-i} , and $D_{\pm i}$ cannot be used to predict v_0 , v_{+i} , and v_{-i} . Conversely, electrochemical NMR cannot be used to determine the three electrochemical transport properties: D_{0+i} , D_{0-i} , and $D_{\pm i}$. We choose to solve for the velocities of the ions v_{+i} and v_{-i} ,

$$v_{-i} = c_T D_{0-i} \frac{D_{\pm i} \nabla \phi}{\ddot{i} \ddot{i}}$$

$$v_{+i} = -c_T D_{0+i} \frac{D_{\pm i} \nabla \phi}{\ddot{i} \ddot{i}}$$

The velocities of the ions depend on the velocity of the solvent. Equations 13 and 14 are really expressions for velocity differences based on eq. 6. This is a nontrivial result that has implications for many electrolyte systems where the application of an electric field results in a non-negligible solvent velocity. The velocity of the cation, v_{+i} , is defined to be positive when the potential gradient is negative, and the cation is migrating towards the negative electrode, as illustrated in Fig. 1. The velocities of the anion and solvent are also positive if they migrate towards the negative electrode. In simple electrolytes, the anion migrates toward the positive electrode and the velocity is negative. Note that all three velocities, v_{+i} , v_{-i} and v_0 , depend on $\nabla \phi$. We expect the dependence of the solvent velocity on salt concentration to be non-monotonic. At low salt concentrations, v_0 will increase with increasing salt concentration as an increasing number of ions interact and migrate with the solvent. However, increasing salt concentration also increases viscosity which will decrease v_0 . The dependence of v_{+i} and v_{-i} on salt concentration is likely to be much more complex due to effects such as ion-ion interactions and clustering.

Eq. 13 and 14 have additional usefulness in the absence of a solvent velocity, such as in solid electrolyte systems. When $v_0=0$, eq. 13 and 14 can be used to calculate the direction in which each of the ions moves under an applied electric field solely from the Stefan-Maxwell diffusion coefficients derived from electrochemical measurements of the three transport properties and the thermodynamic factor.

The equation for the migration velocity of a charged species due to an applied potential is

$$v_{i,migration} = -z_i u_i F \nabla \phi \quad (15)$$

where u_i is the mobility of a species i and z_i is the charge of species i . In cases where v_0 is nonzero, the relationship between ion velocity and migration velocity, suggested by eq. 13-14 is

$$v_i = v_{i,migration} + v_0 \quad (16)$$

and

$$v_i = -z_i u_i F \nabla \phi + v_0 \quad (17)$$

Combining eq. 13,14 and 17, we obtain expressions for the mobilities of the charge carriers,

$$u_{-i} = c_T D_{0-i} \frac{D_{+i}}{D_{+i} + D_{-i}} \frac{i}{RT}$$

$$u_{+i} = c_T D_{0+i} \frac{D_{-i}}{D_{-i} + D_{+i}} \frac{i}{RT}$$

It is interesting to note that the mobility of both of the ions depends on all three Stefan-Maxwell diffusion coefficients. Specifically, the mobility of the cation, u_{+i} , depends on D_{0-i} , the Stefan-Maxwell diffusion coefficient describing interactions between the anion and the solvent, and the mobility of the anion, u_{-i} , depends on D_{0+i} .

In order to derive expressions for the transference number and conductivity in terms of the species velocities we can rearrange eq. 13-14 to get

$$D_{0+i} = c_0 D_{\pm i} \frac{RT}{i} \frac{v_{+i} - v_0}{v_{+i} - v_{-i}}$$

$$D_{0-i} = -c_0 D_{\pm i} \frac{RT}{i} \frac{v_{-i} - v_0}{v_{+i} - v_{-i}}$$

The concentrated solution transference number is defined by eq. 3. Substituting eq. 20-21 into eq. 3 we get

$$t_{+i} = \frac{v_{+i} - v_0}{v_{+i} - v_{-i}}$$

The transference number can be obtained by electrophoretic NMR only if all three velocities, v_{+i} , v_{-i} and v_0 , are measured. The cation transference number is defined as the fraction of current carried by the cation in an electrolyte of uniform concentration.^{1,23} Equation 22 is consistent with this definition. Using the relationship between mobility and velocity as defined by eq. 17, the transference number expressed in terms of mobility simplifies to the commonly used expression

$$t_{+i} = \frac{u_{+i}}{u_{+i} + u_{-i}(23)}$$

The mobilities in eq. 23 must be calculated from eNMR data using eq. 17.

The conductivity of concentrated solutions is given by eq. 4. Substituting eq. 20-21 into eq. 4 we get

$$\sigma = Fc_{+i}v_{+i} + Fc_{-i}v_{-i}$$

where $c = c_{+i} + c_{-i}$. Unlike the transference number, conductivity can be calculated using only the two velocities of the charge carriers. Substituting eq. 17 into eq. 24 leads to the commonly used expression for conductivity in terms of the mobilities of the charge carriers

$$\sigma = F^2 c (u_{+i} + u_{-i})$$

Eq. 25 is often used to describe ion transport in electrolytes.

In the dilute limit $c \rightarrow 0$, $c_T/c_0 \rightarrow 1$, and eq. 13 and 14 reduce to

$$v_{+i} = \frac{D_{+i}}{RT} F \nabla \phi + v_0(26)$$

$$v_{-i} = \frac{D_{-i}}{RT} F \nabla \phi + v_0(27)$$

where the Stefan-Maxwell diffusion coefficients D_{0+i} and D_{0-i} simplify to D_{+i} and D_{-i} , which are the diffusion coefficients of free ions in a solvent in the limit of infinite dilution. In this limit, the solvent velocity is negligible, $v_0 \rightarrow 0$, $u_i = D_i/RT$ and eq. 26 and 27 reduce to the commonly used form of eq. 5. In other words, interpretations of electrophoretic NMR data using eq. 5¹²⁻²¹ are valid in the dilute limit or if $v_0 = 0$.

Conclusions

Concentrated solution theory is used to derive relationships between the electrochemical transport coefficients t_{+i} and σ and the velocities of the charge carriers and the solvent measured during electrophoretic NMR experiments. Our work shows that in the presence of a solvent velocity,

motion of the solvent has a significant contribution to calculations of the ion mobilities and the electrochemical transference number. The expression for conductivity, however, remains the same in both dilute and concentrated solutions. Additionally, one can use the equations derived here to show in which direction the charged species are moving under applied electric fields. The equations are applicable to all three component electrolyte solutions comprised of a solvent and a binary salt of univalent ions. In future work, we will apply the framework developed here to interpret electrophoretic NMR measurements of polymer electrolytes.

Acknowledgement

This work was intellectually led by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Contract No. DEAC02-06CH11357.

List of Symbols

c_i concentration of species i , mol/cm³

c_{+i}, c_{-ii} cation and anion salt concentration, mol/cm³

c_0 solvent concentration, mol/cm³ (moles of monomers per unit volume for polymeric solvents)

c_T total solution concentration, mol/cm³

D_{ij} Stefan-Maxwell diffusion coefficient for interaction of species i and j , cm²/s

$D_{0+i}, D_{0-ii}, D_{\pm ii}$ Stefan-Maxwell diffusion coefficients describing the interactions between cation-solvent, anion-solvent, and cation-anion, cm²/s

E electric field, V/cm

F Faraday's constant, 96485 C/mol

R Universal gas constant, 8.3143 J/(mol K)

t_{0+i}, t_{0-ii} cation and anion transference number

T absolute temperature, K

u_{+i}, u_{-ii} mobilities of the cation and anion, mol cm²/(Js)

v_i velocity of species i , cm/s

v_{+i}, v_{-i}, v_s velocity of the cation, anion, and solvent, cm/s

z_{+i}, z_{-i} charges on the cation and anion, +1 and -1 for a univalent electrolyte

ϕ applied potential, V

σ ionic conductivity of electrolyte, S/cm

μ_i electrochemical potential of species i , J/mol

$\mu_{+i}, \mu_{-i}, \mu_0$ electrochemical potentials of the cation, anion, and solvent, J/mol

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