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Extending the compensated Arrhenius formalism to concentrated alcohol electrolytes: Arrhenius *vs.* non-Arrhenius behavior

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ABSTRACT

The compensated Arrhenius formalism is applied to ionic conductivities in alcohol-based electrolytes at concentrations where the salt makes a non-negligible contribution to the static dielectric constant of the solution. The temperature-dependent behavior of the conductivity depends on the amount of added salt. Non-Arrhenius behavior is observed for low to moderate salt concentrations, while Arrhenius behavior occurs at high concentrations. The compensated Arrhenius formalism provides insight into this behavior by analyzing the effect of salt concentration on the temperature dependence of the exponential prefactor. When the compensated Arrhenius prefactors are plotted against the solution static dielectric constants using the E_a obtained from the compensated Arrhenius equation, the prefactors lie on a single master curve. In contrast, a similar plot based on the E_a obtained from a simple Arrhenius plot of the same conductivity data does not yield a master curve.

Application of the compensated Arrhenius formalism requires the construction of a reference curve. It is essential that the range of static dielectric constant values spanned by the reference curve encompasses the range of temperature-dependent static dielectric constant values of the selected alcohol electrolyte. This will allow an accurate interpolation to obtain the appropriate reference conductivity. A detailed description is given for the method used to construct an appropriate reference conductivity curve.

1. Introduction

The temperature dependence of ionic conductivity in rigid solids is usually described by a simple Arrhenius equation: $\sigma = \sigma_0 \exp(-E_a/RT)$. Consequently, in such systems transport is a thermally activated process. For liquid electrolytes as well as polymer electrolytes above the glass transition temperature, the simple Arrhenius expression often inadequately describes the temperature dependence; transport is frequently viewed in terms of hydrodynamic models in which the viscosity plays a central role [1–3]. Consequently, a variety of empirical descriptions have been developed to describe the temperature dependence of transport, particularly ionic conductivity [4–11]. We have previously taken an unconventional view of charge transport in non-aqueous liquid electrolytes by writing an Arrhenius-like expression with an exponential prefactor σ_0 that is a function of the temperature-dependent static dielectric constant [12,13]. The success of this picture argues that even in liquid electrolytes the conductivity is a thermally activated process. Our further work has extended this view to other forms of mass and charge transport such as self-diffusion and dielectric relaxation [14,15]. Self-diffusion coefficients, dielectric relaxation rate constants, and ionic conductivities in a variety of pure liquids and dilute liquid electrolytes can be described using the following equations [15,14,13]:

$$D(T, \varepsilon_s) = D_0(\varepsilon_s(T))\, e^{-E_a/RT} \tag{1}$$

$$k(T, \varepsilon_s) = k_0(\varepsilon_s(T))\, e^{-E_a/RT} \tag{2}$$

$$\sigma(T, \varepsilon_s) = \sigma_0(\varepsilon_s(T))\, e^{-E_a/RT} \tag{3}$$

where $D(T, \varepsilon_s)$ is the diffusion coefficient, $k(T, \varepsilon_s)$ is the dielectric relaxation rate constant (*i.e.*, the inverse of the dielectric relaxation time, τ), $\sigma(T, \varepsilon_s)$ is the ionic conductivity, ε_s is the static dielectric constant,[1] T is temperature, E_a is the activation energy, and $D_0(\varepsilon_s(T))$, $k_0(\varepsilon_s(T))$, and $\sigma_0(\varepsilon_s(T))$ are the exponential prefactors for diffusion, dielectric relaxation, and ionic conductivity, respectively. A scaling procedure (summarized in Section 3) can be used

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[1] The static dielectric constant is the zero-frequency real part of the dielectric constant, referred to as the dielectric constant throughout the rest of this paper.

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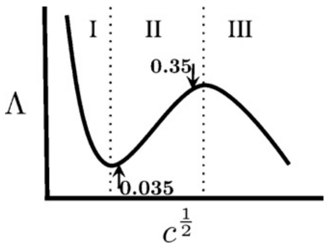

Fig. 1. Schematic of molal conductivity (Λ) *vs.* concentration$^{1/2}$ for organic liquid electrolytes, where $\Lambda = \sigma/c$. The three different regions are marked to represent the distinct qualitative behavior of molal conductivity with increasing salt concentration. The concentrations used in this study (0.035 and 0.35 molal) are indicated on the diagram.

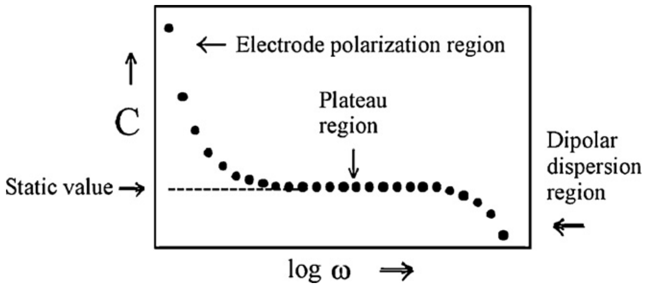

Fig. 2. Schematic illustration of the frequency dependence of the capacitance for an electrolyte.

to eliminate the dielectric constant dependence (contained in the exponential prefactor), yielding Arrhenius behavior from which the E_a is calculated [14,15,13]. The exponential prefactors can then be determined from Eqs. (1) to (3) by dividing either the diffusion coefficient, dielectric relaxation rate constant, or ionic conductivity by the Boltzmann factor $\exp(-E_a/RT)$. Plotting the prefactors *vs.* the dielectric constant results in a master curve. This new perspective of mass and charge transport is termed the compensated Arrhenius formalism.

Although the compensated Arrhenius formalism describes several different forms of mass and charge transport, the emphasis in this paper is on the ionic conductivity of moderately concentrated alcohol-based liquid electrolytes. The schematic in Fig. 1 shows molal conductivity *vs.* concentration$^{1/2}$ for organic liquid electrolytes with low dielectric constants ($\varepsilon_s < 10$). The three regions marked I, II, and III represent the different qualitative behaviors of the molal conductivity with respect to concentration. Previous work has explored the concentration dependence of ionic conductivity for dilute alcohol-based electrolytes (concentrations within Region I) using the compensated Arrhenius formalism [12,13]. In Region I the solution dielectric constant is close in value to that of the pure solvent [16–19], and therefore it is a reasonable approximation to treat the dielectric constant dependence in the exponential prefactor as having only a solvent contribution. However, in more concentrated electrolytes the solution dielectric constant can differ considerably from that of the pure solvent. Here we apply the compensated Arrhenius formalism to ionic conductivity data at two different concentrations: one at each boundary of Region II. At these concentrations, the salt makes a substantial contribution to the solution dielectric constant. The salt, tetrabutylammonium trifluoromethanesulfonate (TbaTf) is chosen because ionic association is minimal due to the charge-protected cation [20,21,18,22], thus simplifying the analysis since only “free” ions are present in solution. The two chosen salt concentrations, 0.035 and 0.35 molal, show markedly different conductivity behavior. The lower concentration shows non-Arrhenius behavior as previously seen in Region I [13], while the higher concentration shows Arrhenius-like behavior. The results of the compensated Arrhenius analysis will help explain the differences in behavior. Furthermore, a comparison will be made between Arrhenius and compensated Arrhenius behavior in order to demonstrate that the scaling procedure must still be performed even when the conductivity exhibits Arrhenius behavior.

2. Experimental

All solvents and salts (99% pure) were obtained from Sigma–Aldrich and used as received. All chemicals were stored, all samples were prepared, and all measurements were taken in a glovebox ($\leq$1 ppm H_2O) under a nitrogen atmosphere. All liquid electrolytes were made at ambient glove box temperature (approximately 27 °C) by dissolving salt into solvent until the appropriate molal concentration (moles salt/kg solvent) is obtained, and then stirred for 24 h. The capacitance (C), conductance (G), and phase angle (θ) were measured using a HP 4192 A impedance analyzer with a logarithmic sweep over a frequency range 1 kHz–13 MHz. The instrument was set to parallel circuit and averaging (slow) mode. A short compensation was performed at 10 MHz. The sample holder was an Agilent 16452A liquid test fixture. The electrodes are circular disks made from nickel-plated cobalt (Fe 54%, Co 17%, Ni 29%) and have a diameter of 38 mm. The largest spacer (2 mm thickness) was used in order to reduce the effects of electrode polarization [23]. A Huber ministat 125 bath was used to regulate the temperature to ±0.1 °C from 5 to 85 °C, in 10 °C increments. The conductivity σ is calculated from the measured conductance G through the equation $\sigma = L \times G \times A^{-1}$, where L is the electrode gap and A is the electrode area. The static dielectric constant ε_s is calculated from the measured capacitance C through the equation $\varepsilon_s = \alpha \times C \times C_0^{-1}$, where α is a variable to account for stray capacitance, and C_0 is the atmospheric capacitance [24].

Measuring the static dielectric constant of an ionically conducting solution is not trivial, and therefore further details for the determination of ε_s will now be given. It is straightforward to calculate ε_s in a pure solvent by using the above equation to divide the limiting low frequency value of the capacitance by the atmospheric capacitance. However, in an electrolyte the capacitance in the limit of low frequency is artificially high due to electrode polarization effects [25–29], as depicted in Fig. 2. The electrode polarization dies off as the frequency increases and a plateau region is observed. The capacitance then decreases from the plateau value at high frequencies due to dipolar dispersion [30,31]. The HP 4192A cannot reach frequencies high enough to observe the dipolar dispersion. We consider the static capacitance as the value in the plateau region. This plateau region is determined by taking the square of the difference between consecutive capacitance values with frequency and isolating the minimum of the curve. The same procedure is used for determining the conductance, which also varies with frequency but has a broad plateau that is simple to determine. There is an additional complication in solutions with high conductivities. The impedance analyzer models the electrolyte as a capacitor and resistor in parallel. For highly conducting solutions, the electrolyte behaves mostly as a resistor (*i.e.*, very small phase angle) and the accuracy of the capacitance measurements deteriorates [32,33,29]. To help quantify the error in the dielectric constant measurements, we determined ε_s for $LiClO_4$–ethyl acetate solutions at several different salt concentrations and then compared these values to literature values [16]. For a 0.80 M solution at 25 °C there is roughly a 0.6% difference between our ε_s and the literature value, ours being higher. Therefore, we consider the quality of the capacitance data to be satisfactory if the conductivity is less than that of the 0.80 M solution (2.35×10^{-3} S cm^{-1}) in addition to the phase angle being greater than that of the 0.80 M solution (1.1°). These conductivity and phase angle limitations for accurate measurement