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14. ABSTRACT We studied the temperature-dependence of mass and charge transport (ionic conductivity, self-diffusion, fluidity, and dielectric relaxation) in polar organic liquids and their electrolytes. Previous studies have described transport in terms of mutually incompatible models that provide inadequate descriptions of experimental data, often using empirical equations whose fitting parameters have no physical significance. Consequently there is no general molecular-level picture that adequately describes temperature-dependent transport in these important systems. We have developed a new approach to this problem, termed the Compensated Arrhenius Formalism (CAF). We					
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Report Title

Final Report: Charge Transport in Nonaqueous Liquid Electrolytes: A Paradigm Shift

ABSTRACT

We studied the temperature-dependence of mass and charge transport (ionic conductivity, self-diffusion, fluidity, and dielectric relaxation) in polar organic liquids and their electrolytes. Previous studies have described transport in terms of mutually incompatible models that provide inadequate descriptions of experimental data, often using empirical equations whose fitting parameters have no physical significance. Consequently there is no general molecular-level picture that adequately describes temperature-dependent transport in these important systems.

We have developed a new approach to this problem, termed the Compensated Arrhenius Formalism (CAF). We write a transport property as an Arrhenius-like expression where the exponential prefactor is a function of the temperature-dependent static dielectric constant. We discovered a scaling procedure in which the transport coefficient is scaled to a reference transport coefficient obtained from experimental data, thereby canceling the exponential prefactor and leaving a compensated transport coefficient. We have demonstrated the validity and self-consistency of the CAF in a variety of organic liquids and their electrolytes over a wide range of salt concentrations (including ionic liquids!). We also developed a molecular-level picture of mass and charge transport in a polar liquid by modifying transition state theory and explicitly accounting for the role of the dipole polarization energy.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
03/29/2013 9.00	Matt Petrowsky, Allison Fleshman, Mohd Ismail, Daniel T. Glatzhofer, Dharshani N. Bopege, Roger Frech. Molecular and System Parameters Governing Mass and Charge Transport in Polar Liquids and Electrolytes, The Journal of Physical Chemistry B, (08 2012): 10098. doi: 10.1021/jp305112f
04/12/2013 11.00	Matt Petrowsky, Allison M. Fleshman, Roger Frech. Application of the Compensated Arrhenius Formalism to Fluidity Data of Polar Organic Liquids, The Journal of Physical Chemistry B, (03 2013): 0. doi: 10.1021/jp312034e
04/12/2013 10.00	Dharshani N. Bopege, Matt Petrowsky, Matthew B. Johnson, Roger Frech. Mass and Ion Transport in Ketones and Ketone Electrolytes: Comparison with Acetate Systems, Journal of Solution Chemistry, (03 2013): 584. doi:
04/22/2015 22.00	Matt Petrowsky, Daniel T. Glatzhofer, Roger Frech. Application of the Compensated Arrhenius Formalism To Explain the Dielectric Constant Dependence of Rates for Menschutkin Reactions, The Journal of Physical Chemistry B, (10 2013): 14432. doi:
04/22/2015 21.00	Roger Frech, Matt Petrowsky. Molecular Model of Self Diffusion in Polar Organic Liquids: Implications for Conductivity and Fluidity in Polar Organic Liquids and Electrolytes, The Journal of Physical Chemistry B, (02 2014): 2422. doi:
04/28/2015 20.00	Matt Petrowsky, Christopher Burba, Roger Frech. Mass and charge transport in 1-alkyl-3-methylimidazolium triflate ionic liquids, THE JOURNAL OF CHEMICAL PHYSICS, (11 2013): 204502. doi:
08/22/2012 5.00	Allison Fleshman, Roger Frech, Matt Petrowsky. Ion Transport with Charge Protected and Non-Charge Protected Cations Using the Compensated Arrhenius Formalism. I. Ionic Conductivity and the Static Dielectric Constant, J Phys Chem B, (05 2012): 5760. doi:
09/11/2013 12.00	Allison M. Fleshman, Matt Petrowsky, Roger Frech. Concentration Dependence of Molal Conductivity and Dielectric Constant of 1-Alcohol Electrolytes Using the Compensated Arrhenius Formalism, The Journal of Physical Chemistry B, (03 2013): 5330. doi:
09/11/2013 13.00	Matt Petrowsky, Mohd Ismail, Daniel T. Glatzhofer, Roger Frech. Mass and Charge Transport in Cyclic Carbonates: Implications for Improved Lithium Ion Battery Electrolytes, J Phys Chem B, (04 2013): 5963. doi:
09/12/2013 14.00	. Extending the compensated Arrhenius Formalism to Concentrated Alcohol Electrolytes: Arrhenius vs. non-Arrhenius Behavior, Electrochimica Acta, (09 2011): 147. doi:

TOTAL: 10

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

09/12/2013 15.00 Dharshani N. Bopege, Matt Petrowsky, Allison M. Fleshman, Roger Frech, Matthew B. Johnson.
Temperature Dependence of Ion Transport in Dilute Tetrabutylammonium Triflate-Acetate Solutions and
Self-Diffusion in Pure Acetate Liquids,
J. Phys. Chem. B, (12 2011): 71. doi:

TOTAL: 1

Number of Papers published in non peer-reviewed journals:

(c) Presentations

All at the 13th International Symposium on Polymer Electrolytes
Selfoss, Iceland
August 26-31, 2012.

"Modified Transition State Theory to Describe Transport in Polar Liquids"
Roger Frech, Matt Petrowsky
Invited talk by RF 08/31/2012

"Molecular and System Parameters Governing Mass and Charge Transport in Organic Liquids and Oligomers"
Matt Petrowsky, Roger Frech
Contributed talk given by MP 08/31/12

"Describing the Concentration Dependence of the Molal Conductivity for Aprotic Liquid Electrolytes Using the Compensated Arrhenius Formalism."
Allison Fleshman, Roger Frech
Poster presented by AF 08/29/12

" Application of the Compensated Arrhenius Formalism to Fluidity"
Matt Petrowsky, Roger Frech
Poster presented by MP 08/29/12

Number of Presentations: 4.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
04/28/2015 23.00	Dharshani N. Bopege, Matt Petrowsky, Roger Frech, J. E. Moore-Furneaux. Charge Transport, Ionic Association, and Ion-Solvent interaction in Concentrated LiTf-Ketone and LiTf-Acetate Electrolytes, The Journal of Physical Chemistry B ()
08/22/2012 6.00	Dharshani Bopege, Matt Petrowsky, Matthew Johnson, Roger Frech. Mass and Ion Transport in Ketones and Ketone Electrolytes: Comparison with Acetate Systems, J. Soln. Chem. (06 2012)
08/23/2012 7.00	Matt Petrowsky, Allison Fleshman, Mohd Ismail, Daniel T. Glatzhofer, Dharshani N. Bopege, Roger Frech. Molecular and System Parameters Governing Mass and Charge Transport in Polar Liquids and Electrolytes, J. Phys. Chem. B (05 2012)
08/31/2011 1.00	Allison Fleshman , Matt Petrowsky , Jeremy D. Jernigen , R. S. P. Bokalawela , Matthew Johnson, , Roger Frech. . Extending the Compensated Arrhenius Formalism to Concentrated Alcohol Electrolytes: Arrhenius vs. Non-Arrhenius Behavior, Electrochimica Acta (accepted) (08 2011)
08/31/2011 2.00	Dharshani N. Bopege, , Matt Petrowsky , Allison M. Fleshman , Roger Frech , Matthew B. Johnson.. The Temperature Dependence of Ion Transport in Dilute Tetrabutylammonium Triflate-Acetate Solutions and Self-Diffusion in Pure Acetate Liquids, The Journal of Physical Chemistry B (submitted) (08 2011)
09/16/2013 17.00	Matt Petrowsky, Daniel T. Glatzhofer, Roger Frech. Application of the Compensated Arrhenius Formalism to Explain the Dielectric Constant Dependence of Rates for Menschutkin Reactions , Journal of Physical Chemistry B (08 2013)
09/16/2013 18.00	Matt Petrowsky, Christopher M. Burba, Roger Frech. Mass and charge transport in 1-alkyl-3-methylimidazolium triflate ionic liquids, J Chem Phys (09 2013)
09/16/2013 19.00	Roger Frech, Matt Petrowsky. A Molecular Model of Self Diffusion in Polar Organic Liquids: Implications for Conductivity and Fluidity in Polar Organic Liquids and Electrolytes, J. Phys. Chem. B (09 2013)
TOTAL:	8

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Appointed as a David Ross Boyd Professor of Chemistry and Biochemistry

Graduate Students

NAME	PERCENT SUPPORTED	Discipline
Mohd Ismail	0.50	
Matt Petrowsky	0.50	
Allison Fleshman	0.50	
Darshani N. Bopege	0.50	
FTE Equivalent:	2.00	
Total Number:	4	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Matt Petrowsky	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Roger Frech	0.17	
FTE Equivalent:	0.17	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Whitney Booher	0.25	
FTE Equivalent:	0.25	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Matt Petrowsky
Allison Fleshman
Mohd Ismail
Darshani N. Bopege
Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Please see attachment in following section.

Technology Transfer

Statement of the Problem Studied

Decades of studying isothermal and temperature-dependent mass and charge transport in polar organic liquids and electrolytes have resulted in two mutually incompatible models: (1) a hydrodynamic model in which the motion of molecules or ions is opposed by a resistive force determined by the solution viscosity, η , and (2) a thermally activated process characterized by an activation energy E_a . The hydrodynamic model, utilizing the Stokes equation describes isothermal conductivity, self-diffusion coefficient, and the dielectric relaxation time in terms of the viscosity. However, the use of one macroscopic solution property to describe other macroscopic solution properties cannot lead to any particular molecular level insight into the transport processes involved. Further, these equations, although intuitively appealing, often provide inadequate descriptions of experimental data. Descriptions of temperature-dependent transport data of liquids in terms of a thermally activated process are usually unsatisfactory, requiring the use of empirical equations whose fitting parameters have no physical significance. Therefore this approach provides no physical significance into the molecular level nature of the transport process.

These two general pictures of transport, the thermally activated model and the hydrodynamic model, are incompatible and do not lead to any degree of self-consistency in describing the various kinds of mass and charge transport phenomena in polar liquids and polar liquid electrolytes. A direct consequence of this inconsistency is the lack of a general molecular-level model that adequately describes both isothermal and temperature-dependent transport phenomena in these important systems. As an alternative, we have developed a new approach to this problem that we term the Compensated Arrhenius Formalism, which is briefly summarized below.

Brief Summary of the Compensated Arrhenius Formalism (CAF)

Our research under ARO support has resulted in a new approach to study the temperature dependence of mass and charge transport in polar liquid electrolytes, focusing on ionic conductivity, self-diffusion, viscosity, and dielectric relaxation. We treat all four transport coefficients in exactly the same manner, resulting in the same mathematical description of their temperature dependence. Our approach, termed the Compensated Arrhenius Formalism (CAF), contains no adjustable parameters and is based on two fundamental postulates (using the conductivity as an illustration):

1. The conductivity obeys an Arrhenius equation with an exponential prefactor that depends on both temperature and the static dielectric constant ϵ_s , i.e.

$$\sigma(T, \epsilon_s) = \sigma_0(T, \epsilon_s) \exp(-E_a/RT). \quad (1)$$

2. All of the temperature dependence of the prefactor is due to the intrinsic temperature dependence of the static dielectric constant, i.e.

$$\sigma(T, \epsilon_s) = \sigma_0(\epsilon_s(T)) \exp(-E_a/RT). \quad (2)$$

The first postulate reflects the experimental observation that the ionic conductivity in polar electrolyte solutions is a function of the static dielectric constant as well as the temperature. The second simply reflects the fact that the static dielectric itself is a function of the temperature. In other words, if $\ln(\sigma)$ is plotted against $1/T$, the experimentally observed non-Arrhenius behavior (curvature) is due to the temperature dependence of the dielectric constant contained in the exponential prefactor.

We then developed a scaling procedure in which an experimentally measured conductivity ($\sigma(T, \epsilon_s)$) is divided by a reference conductivity, $\sigma_r(T_r, \epsilon_s)$ at reference temperature T_r . The experimentally determined reference conductivity is chosen so that the value of $\epsilon_s(T_r)$ is the same as $\sigma(T, \epsilon_s)$.

$$\frac{\sigma(T, \epsilon_s)}{\sigma_r(T_r, \epsilon_s)} = \frac{\sigma_o(\epsilon_s(T)) \exp(-E_a / RT)}{\sigma_o(\epsilon_s(T_r)) \exp(-E_a / RT_r)} \quad (3)$$

Since the exponential prefactor depends on the value of ϵ_s , the two exponential factors in eq 3 cancel, resulting in the Compensated Arrhenius Equation, CAE.

$$\ln \left(\frac{\sigma(T, \epsilon_s)}{\sigma_r(T_r, \epsilon_s)} \right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r} \quad (4)$$

In a CAF analysis of temperature-dependent transport data, there are three stringent requirements that must be met:

1. A plot of the left hand side of eq 4 against reciprocal temperature must be linear over the entire temperature range studied.
2. The values of E_a determined independently from the slope and the intercept must agree. (These are found to agree within about 1 % for all systems studied to date).
3. A plot of the prefactors as a function of the solvent dielectric constant must result in a single master curve for each family of solvents,

A typical plot of the master curve is shown in Figure 1 for purposes of illustration.

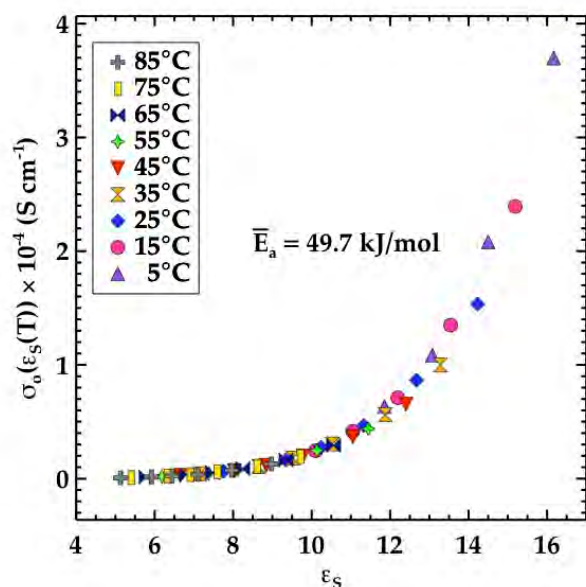


Figure 1. Exponential prefactor plotted against ϵ_s for 0.035 m TbaTf in a series of 1-alcohols.

Our initial extensions of the CAF to a variety of solvent-based electrolytes and pure organic liquids included ketones, acetates, nitriles, thiols, methyl-capped oligomers of poly(ethylene oxide), cyclic carbonates, and linear alcohols. We considered several families of alcohol electrolytes with significant differences in their extensively hydrogen-bonding networks. Our early work was with dilute electrolytes (0.0055 M), therefore we explored concentrated solutions up to the solubility limit of some of our electrolyte solutions. The extreme case of a concentrated “solution” was our study of an ionic liquid: 1-alkyl-3-methylimidazolium trifluoromethanesulfonate (triflate). Most of our work focused on two salts: lithium triflate and tetrabutylammomium triflate. Although these two salts have a common anion, the nature of these cations defines two extremes of behavior. The very strong cation-anion interactions in lithium triflate solutions result in very highly associated systems with contact ion pairs, triples and other more highly associated species. In contrast, the bulky butyl groups of tetrabutylammomium cation prevent the formation of any detectable level of ionically associated species.

In all electrolyte solutions studied during the course of this research project, the CAF yielded linear plots with self-consistent values of the activation energy and the formation of simple master curves when the exponential prefactors was plotted against the static dielectric constant. This result was astonishing to us, considering the very non-ideal nature of some of the electrolyte solutions examined.

During this project we attempted to develop a molecular-level picture of mass and charge transport in a polar liquid by looking at transition state theory with a focus on diffusion. We considered a region in the liquid containing N dipolar molecules in a transient state of local equilibrium. The region contains a sufficient number of molecules so the potential energy environment of a target molecule in the interior of the region roughly approximates its potential

energy environment in the bulk. In the initial state, the target molecule is confined by its local potential energy environment and its molecular motion consists of intramolecular, librational, and translatory vibrations. We adopt Kauzmann's picture of a transition state¹ where thermal fluctuations create a less rigid and more open environment. In a key step, we assumed that this environment is not homogeneous at a molecular scale. In particular, the fluctuations may open a transient channel in which a translatory vibration of a target molecule in the direction of the channel can momentarily become a pure translational motion. In this direction the fluctuation-driven reduced local density of molecules serves as a concentration gradient. After a small translational movement of the target molecule, the neighboring molecules then relax back to a locally stable configuration, which can be regarded as the final state. In other words, thermal fluctuations lead to transport of the target molecule through a series of thermally activated, discrete jumps. In our modification of transition state theory, we explicitly account for the difference between the vibrational partition function of the target molecule in the initial state and the translational partition function in the transition state. This results in a significantly different temperature dependence in the final results than is given in the usual transition state theory as developed by Eyring.² The motion of the target molecule is coupled to the motion of its surrounding molecules, and the activation energy is the collective energy required to open a channel through which transport can occur.

Brief Summary of our Work

1. In our first paper in this area,³ we introduced our two fundamental postulates, carefully described the construction of the reference curve and gave a brief summary of the scaling procedure. This first paper focused on conductivity studies of 0.0055 M solutions of tetrabutylammonium trifluoromethanesulfonate (TbaTf) dissolved in a ketones and linear alcohols, although electrolyte solutions of lithium trifluoromethanesulfonate (LiTf) and LiI were also briefly examined. This work was the first tentative step in our understanding of a variety of transport phenomena using the CAF.
2. We then successfully extended the CAF to dielectric relaxation in polar liquids such as linear alcohols, n-alkyl bromides, n-nitriles, n-acetates.⁴ We incorporated our two postulates into an expression for the temperature dependence of the dielectric rate constant k , writing $k(T, \epsilon_s) = k_0(\epsilon_s(T) \exp(-E_a/RT))$. This equation is completely analogous to eq 2 for the conductivity. The extension to dielectric relaxation appeared to be satisfactory as judged from the linearity of the temperature-dependent scaled dielectric relaxation rate constants and the formation of a single master curve for each solvent family. However this study had the rather severe limitation of using only dielectric relaxation data taken from the literature. Since we did not have access to appropriate instrumentation to measure dielectric relaxation data ourselves, this was our only study of dielectric relaxation, undertaken to extend the generality of the CAF.
3. We were concerned that the CAF had only been applied to electrolyte solutions consisting primarily of LiTf, LiTba and LiI at a single concentration (0.0055 M). Therefore we measured the temperature-dependent conductivities of LiTf, NaTf, KTf, LiI TbaBr, and TbaTf over a concentration range from 0.0055 M down to about 4.30×10^{-5} M.⁵ The activation energies were similar in each of these sets of measurements.

We then wrote a proposal to ARO requesting grant support based on the results of this early and admittedly incomplete work. Our proposal had five objectives (to quote directly from the proposal):

- 1. Extend studies of the temperature dependence of ionic transport in organic liquid to concentrated salt solutions (concentrations > ca 0.01 M).*
- 2. Demonstrate the applicability of the CAE analysis to the temperature dependence of diffusion coefficients in organic liquids and organic liquid electrolytes.*
- 3. Determine the applicability of the CAE analysis to organic liquid electrolytes containing lithium salts, modifying the CAE analysis as required to accommodate the extensive ionic association which occurs.*
- 4. Expand the application of the CAE analysis to oligomers and oligomer-based electrolytes as an initial step toward a study of high molecular weight polymer.*
- 5. Broaden the application of the CAE analysis to ionic liquid based electrolytes, specifically (a) pure ILs, (b) selected IL-solvent mixtures that are miscible in all proportions, and (c) IL-lithium salt systems.*

I wish to note at this point that all five objectives have been accomplished (and much more!)

4. While the proposal was being considered, we successfully extended the CAF analysis to temperature-dependent self-diffusion data for 1-propanol, 1-butanol, 1-hexanol and 1-octanol. The temperature-dependent self-diffusion coefficient D was written $D(T, \epsilon_s) = D_0(\epsilon_s(T) \exp(-E_a/RT))$, analogous to eq 2 for conductivity. We measured the necessary self-diffusion data ourselves using pulsed-field-gradient PFG-NMR techniques. We obtained activation energies with values strikingly similar to those found for the same alcohol electrolytes via ionic conductivity and dielectric relaxation.⁶ The discovery that the CAF analysis could be successfully applied to describe the temperature dependence of self-diffusion data was a major step forward in our research program, because it offered the potential for providing extensive data that complemented our conductivity studies.

5. At this point our proposal to ARO was funded. With grant support, we began a systematic study of the role of the static dielectric constant in transport properties. We started with a study of conductivity and self-diffusion in 0.0055 M solutions of TbaTf in n-butyl acetate, n-pentyl acetate, n-hexyl acetate, n-octyl acetate and n-decyl acetate.⁷ This was the first step in a comparative study of low permittivity liquids and electrolytes. Acetates and their electrolyte solutions have low permittivities compared with alcohols and ketones. Both temperature-dependent diffusion coefficients and ionic conductivities were accurately described by the CAF. Activation energies were found to be higher for conductivity data of 0.0055 M TbaTf-acetates compared to diffusion data of pure acetate liquids. We returned to this interesting observation in a subsequent study described later.

6. We also began more formal attempts to understand the underpinnings of the CAF by closely examining the role of static dielectric constant in 0.30 molal TbaTf- and LiTf-1-alcohol solutions.⁸ This work also moved us towards more concentrated electrolyte solutions than previously studied. Beginning with this study, we switched from a molar concentration basis to a molal concentration basis. This was done because reproducibility of our data and results by

other workers was deemed of paramount importance, and salt concentrations on a molal basis are independent of the temperature at which they are prepared and subsequently used. Because this was essentially a comparative study of the Tba cation and the Li cation, it was useful to introduce the concept of a charge-protected (e.g. Tba) and non-charge-protected (e.g. Li) cation. The Tba cation is charge-protected because the bulky butyl groups surrounding the charged central nitrogen atom prevent the formation of ionically associated species to any measureable degree.

7. A second part of this study was a comparison between ionic conductivity and self-diffusion in linear alcohol solutions and acetate solutions; the salts were LiTf and TbaTf, thereby extending the comparison between charge-protected and non-charge-protected cations.⁹ The usual relationship between conductivity and diffusion is the Nernst-Einstein equation,

$$\sigma = \frac{nq^2}{k_B T} (D_+ + D_-) \quad (3)$$

General trends based on temperature and alkyl chain length are observed when conductivity is plotted against the cation or anion diffusion coefficient, but there is no clear pattern to the data. However, when the CAF is applied to both conductivity and diffusion data, a plot of conductivity exponential prefactors against those for diffusion results in four distinct curves: one each for the TbaTf-1-alcohol, LiTf-1-alcohol, TbaTf-n-acetate, and LiTf-n-acetate data, with the TbaTf-alcohol and TbaTf-acetate data “in line” with each other.

8. A critical component of the CAF is writing a temperature-dependent transport coefficient as an Arrhenius-like expression that explicitly includes a static dielectric constant (ϵ_s) dependence in the exponential prefactor. A very important step in the development of a molecular level picture of transport was the use of Onsager’s model of the dielectric constant to describe how the dielectric constant affects mass and charge transport in organic liquids and organic liquid electrolytes.¹⁰ Specifically, the molecular and system parameters governing transport are the molecular dipole moment μ and the solvent dipole density N . The temperature dependence of ϵ_s and therefore the temperature dependence of the exponential prefactor is due to the quantity N/T , where T is the temperature. We demonstrated this important fact by scaling out the N/T dependence instead of the ϵ_s dependence in the CAF procedure. We previously showed that a plot of the prefactors versus ϵ_s results in a master curve, and in the paper cited above, we showed that a master curve also results by plotting the prefactors against N/T . Therefore, the CAF can be applied by using temperature-dependent density data instead of temperature-dependent dielectric constant data. This application was demonstrated for diffusion data of n-nitriles, n-thiols, n-acetates and 2-ketones, as well as conductivity data for dilute TbaTf-nitrile electrolytes. In systems in which it is very difficult to accurately measure ϵ_s , one can use the quantity N/T in applications of the CAF with no loss of accuracy.

9. The next major step in extending the CAF to other transport phenomena came with our work with fluidity, which is simply the inverse of viscosity. Viscosity has been studied for over a century, but there are still no realistic theoretical models available. Consequently, viscosity has been described by an astonishing number of empirical equations with adjustable fitting parameters, none of which leads to any molecular-level understanding. We treated the fluidity f ($=1/\eta$) as we had the conductivity, dielectric relaxation, and self-diffusion, writing $f(T, \epsilon_s) =$

$f_0(\epsilon_s(T)) \exp(E_a/RT)$. We collected fluidity data from 5-85°C for pure n-acetates, 2-ketones, n-nitriles, and n-alcohols and analyzed these data with the CAF. The success of this effort is dramatically summarized in the graphic that accompanied the publication of this study in the Journal of Physical Chemistry.¹¹

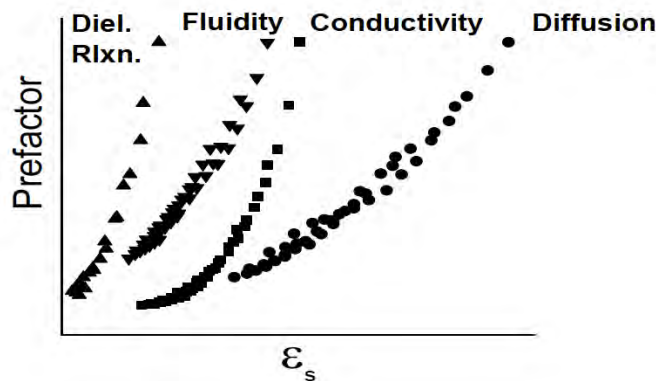


Figure 2. Schematic comparison of the exponential prefactors obtained from self-diffusion, conductivity, fluidity and dielectric relaxation measurements using the CAF.

We found that the fluidity average activation energies of the aprotic liquids were comparable in value, whereas the average activation energy for the n-alcohols was higher.

10. The important role of the static dielectric constant on solution transport properties was the focus of a comparative study of ketone electrolytes and acetate electrolytes with TbaTf as a common salt; this was complemented by a study of pure ketones and acetates using self-diffusion techniques.¹² TbaTf was chosen as the common salt to eliminate any complications caused by ionic association. The average activation energies are summarized in Table 1.

Table 1. Comparison of activation energies for 0.0055 M solutions of TbaTf in acetate and ketone solvents.

	$E_a(\text{conductivity}) \text{ kJ mol}^{-1}$	$E_a(\text{self-diffusion}) \text{ kJ mol}^{-1}$
acetates	36 ± 1	26 ± 1
ketones	25 ± 1	24 ± 1

11. One of the more puzzling observations in the field of electrolytes is the concentration dependence of the molal conductivity, Λ , defined as the ionic conductivity, σ , divided by the total salt concentration. As the salt concentration increases, Λ initially decreases to a minimum and then increase to a maximum, followed by another decrease. This behavior was explained by many authors as originating in strong ionic association effects. However, we reported the same behavior in TbaTf electrolytes in which ionic association could not occur because of the charge-protected nature of the Tba cation. We undertook a concentration-dependent study of the molal conductivity in a series of 1-alcohols and analyzed the resulting data in terms of the CAF.¹³ We showed that the increasing molal conductivity after the initial decrease results from the combined

effect of (1) a decrease in the energy of activation (calculated from the CAF), and (2) an inherent concentration dependence in the exponential prefactor that is partly due to the dielectric constant.

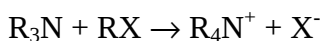
12. At this point we had enough confidence in the CAF to apply it to an electrolyte system relevant to rechargeable lithium battery technology. We examined mass and charge transport in a comparative study of LiTf and TbaTf solutions in cyclic carbonates.¹⁴ The ionic conductivity of lithium ion battery electrolytes is often optimized by mixing a cyclic carbonate, e.g. propylene carbonate, with a lower viscosity liquid. Conventional wisdom, based on a hydrodynamic picture of ion transport, states that the conductivity in propylene carbonate is relatively low because the viscosity of propylene carbonate is relatively high. In this picture, the addition of a low viscosity liquid raises the conductivity simply through the effect of lowering the viscosity of the solution. However, we frame this argument differently by stating that the strong intermolecular interactions that exist in propylene carbonate due to its high dipole moment cause the activation energy to be high and consequently the conductivity to be low. These intermolecular interactions also cause the viscosity to be high. The addition of a low dipole moment component to propylene carbonate disrupts these strong dipole-dipole interactions, thereby lowering the activation energy and increasing the conductivity.

13. An attempt to apply the CAF to an ionic liquid represents an extreme test of the CAF. Previous to this study, the most concentrated liquid electrolyte we had studied was a 0.8 m solution. Therefore we undertook a study of 1-alkyl-3-methylimidazolium triflate ionic liquids, is explained using the compensated Arrhenius formalism (CAF), where the conductivity or fluidity assumes an Arrhenius-like form that also contains a dipole density dependence in the exponential prefactor. The resulting CAF activation energies for conductivity and fluidity are much higher than those obtained from polar organic liquids and electrolytes. The CAF very accurately describes the temperature dependence of both conductivity and fluidity using only system properties (i.e. density, activation energy).¹⁵ These results imply that the transport mechanism in molten salts is very similar to that in polar organic liquids and electrolytes. It is usually not possible to measure the dielectric constant of ionic liquids using standard capacitance and voltammetric techniques, and dielectric relaxation spectroscopy as an alternative relies heavily on the choice of fitting procedure and data extrapolation methods. Here our work in # 8 described earlier proved invaluable; we used the values of N/T in place of the static permittivity. The dipole density N was determined from temperature-dependent mass density measurements over the temperature range of interest. This procedure gave excellent, self-consistent results for the ionic liquids.

14. Many of our previous publications had been criticized for not providing a molecular model or basis for the CAF. Therefore we modified transition state theory as originally developed by Henry Eyring,² using self-diffusion as the transport property of interest.¹⁶ We explicitly recognized the contribution of the polarization energy originating in the dipolar medium, noting that this contribution occurs in a very natural way in the formulation of transition state theory. Expressing the polarization energy in terms of molecular properties, e.g. the molecular dipole moment, and system properties, e.g. the dipole density, allowed us to identify these quantities as the static dielectric constant. Therefore, accounting for the role of the polarization energy in transition state theory of transport properties in polar liquids leads to a dielectric constant dependence in the exponential prefactor of the self-diffusion (or any of the other three transport properties studied in the course of this research project. The molecular picture accompanying

our modification of standard transition state theory emphasized the coupling of the diffusing molecule's motion with the dynamical motion of the surrounding matrix.

15. It has been known for many years that the reaction rate of the Menshutkin reaction is dependent on the dielectric constant of the solvent. In a Menshutkin reaction, a tertiary amine reacts with an alkyl halide to form a tetraalkylammonium halide salt according to



The general trend observed is that the reaction rate increases with increasing permittivity, however the tremendous scatter in the data does not allow the identification of any functional relationship. We applied the CAF to the reaction rate of a typical Menshutkin reaction and demonstrated that previously observed scatter in the reaction rate data was due to the neglect of the polarization energy in the exponential prefactor, which is very nicely scaled out in the CAF.¹⁷ This work opens up a new area: reaction kinetics (e.g. charge-transfer reactions) in polar organic liquid solvents.

16. A study begun somewhat earlier was concerned with the problem of highly associated electrolytes (lithium triflate) dissolved in both high permittivity solvents such as ketones and low permittivity solvents such as acetates. Using quantitative vibrational spectroscopic techniques, we demonstrated that the nature of the ionic association was quite different in these two solvents, particularly the temperature dependence of the ionic association. We then examined why the CAF was so successful in describing the conductivity behavior in spite of the differences in ionic association and their temperature dependence.¹⁸

17. We undertook a careful analysis of the thermodynamics underlying the CAF, with the goal of understanding more deeply the physical significance of the activation energy obtained using the CAF. The key was a comparison of several polar liquids with their non-polar analogs. For example, decane is the non-polar analog of the polar compound 2-decanone. Each compound can be viewed as having an alkyl chain $\text{CH}_3(\text{CH}_2)_7-$, with decane terminated by a $-\text{CH}_2\text{CH}_3$ unit and 2-decanone terminated by a $-\text{COCH}_3$ unit. We compared several nitriles and ketones with their non-polar analogs using both self-diffusion coefficients and fluidity coefficients.¹⁹ One essential finding was that the activation energy of the polar liquid differed from that of the non-polar liquid by an amount equal to the polarization energy calculated from an expression given by Onsager.²⁰

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