THE JOURNAL OF PHYSICAL CHEMISTRY Letters

pubs.acs.org/JPCL

Letter

Reorientation Times for Solid-State Electrolyte Solvents and Electrolytes from NMR Spin−Lattice Relaxation Studies

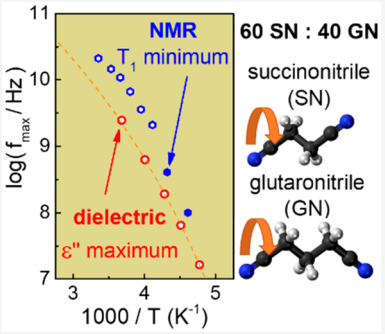
S. K. Davidowski, J. L. Yarger, R. Richert, and C. A. Angell*

Cite This: J. Phys. Chem. Lett. 2020, 11, 3301−3304

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Ionic and molecular plastic crystals have been studied recently as solid electrolytes or solvents, but the specific role of molecular reorientation has not been clarified. We use NMR spin−lattice relaxation times (T_1 minima) to compare the time scale for magnetic fluctuations in a plastic crystal solvent to the molecular reorientation times, as established by dielectric spectroscopy. We focus on a mixture of succinonitrile and glutaronitrile, in which the rotationally disordered phase is stabilized against crystallization. Reorientation times can then be studied over 13 orders of magnitude, down to the glass transition temperature at 144 K. For each nucleus, ^{1}H and ^{13}C, the most probable magnetic fluctuation time is found to be slightly shorter than the reorientation time, but with practically indistinguishable temperature dependence. This facilitates investigation of the relation of solvent reorientation to ion conductivity relaxation times in ionic conducting systems in which the conductivity swamps the dielectric signature of solvent reorientation.



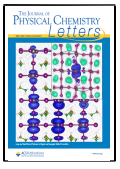
In the quest for high-performance and safe electrochemical power sources, increasing attention is being given to the use of solid-state electrolytes. Glassy[1] and crystalline[2] solid electrolytes have received most of the attention, and promising results have been obtained, but problems of electrode−electrolyte contact reliability have been reported. This has suggested that there may be advantages in using various plastic crystal alternatives, both ionic[3−6] and molecular,[7] that have been described in recent literature.

Of particular interest are those that are plastic crystals by virtue of single anion sublattice degrees of freedom and are single alkali ion conductors, since these do not permit polarization. One of these is the monovalent closo-borate anion, $CB_9H_{10}^-$, the lithium salt of which has a 25 °C conductivity in the 30 mS cm^{-1} range upon supercooling to ambient temperature.[8,9] This is a significantly higher conductivity than that of "standard" $LiPF_6$ in ethylene carbonate/dimethyl carbonate electrolyte. The mechanism of conduction is broadly suggested to involve interstitial Li^+ diffusion and anion rotation. Less highly conducting but potentially more manageable and much less expensive is the more recently described lithium trimethylsilyl sulfate,[6] the conductivity of which is in the vicinity of 10 mS cm^{-1} and the plasticity of which enables impregnation into a nanoporous separator like Celgard to provide mechanical resilience.[6] Again, it has been suggested that the high conductivity may be closely related to the fast reorientation of the molecules, but a quantitative test of the proposal has been lacking. The possible connection of conductivity to anion rotation rates in these various plastic crystals goes back over several decades.[4,10,11] Here we provide essential background studies for the quantitative tests that have been lacking to date.

The present paper is only the first step on the way to establishing the relation between anion reorientation rates and lithium ion conductivity through the direct comparison of reorientation and conductivity relaxation rates in a highly conductive material. Here we will first establish that the characteristic reorientation time, τ_d, of a much-studied rotator phase, succinonitrile ($NC-CH_2-CH_2-CN$, designated SN), in a mixture with its homologue glutaronitrile ($NC-CH_2-CH_2-CH_2-CH_2-CN$, designated GN) to stabilize it against crystallization to any ordered crystal phase, is essentially the same as the characteristic time for magnetic fluctuations, τ_m, (most probable value). The value of τ_m is determined from the identity $\omega\tau_m = 1$ at the temperature of the spin−lattice time (T_1) minimum, where ω is the Larmor frequency for the nucleus under observation. To minimize the ambiguity, we will make the direct comparison using the *most probable* fluctuation frequencies, since these are the quantities yielded directly from the experimental equipment, and the problem of converting most probable to average quantities can be avoided.

For the proton resonance, the Larmor frequency is 400 MHz by instrument design, so the T_1 minimum occurs at a

Received: February 14, 2020
Accepted: April 3, 2020
Published: April 3, 2020



temperature where the relaxation frequency ν_m is 4×10^6 s^{-1}. For the carbon nucleus, the Larmor frequency is (coincidentally) exactly 100 MHz, so the T_1 minimum will occur at a lower temperature if both are related to the same molecular reorientation.

In a follow-up paper[12] (as part of a *Journal of the Electrochemical Society* special issue honoring Michel Armand), we apply the findings of the present paper to a case analogous to that of Alarco et al.[7] involving lithium salts dissolved in succinonitrile, but with the difference that our plastic crystal solvent is the mixed nitrile $(SN)_{60}(GN)_{40}$. We note that Geirhos et al.[11] recently showed that the solid solution with $LiPF_6$ as the electrolyte is much more conductive than the same solution in the single plastic crystal SN.

The dielectric relaxation times and corresponding frequencies used in this discussion are taken from the work of Bauer et al.[13] on the SN:GN = 60:40 system. Their raw data showing dielectric peak frequencies extending over 10 decades in frequency in the temperature range 147−271 K are reproduced in Figure 1.

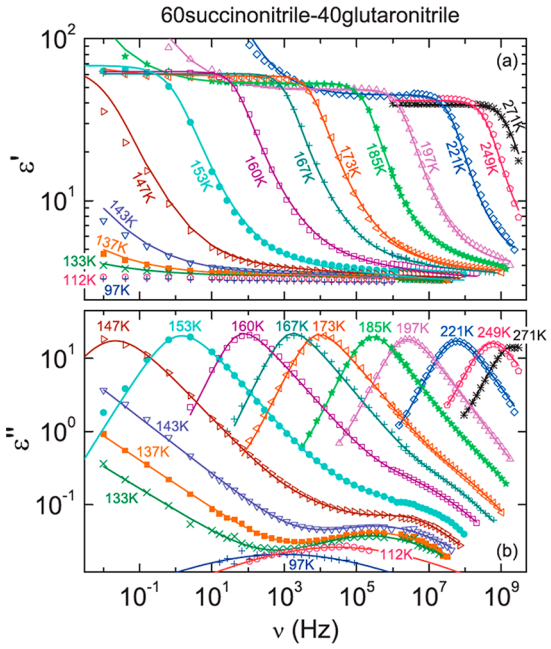


Figure 1. Real and imaginary parts of the dielectric permittivity for the 60:40 mixture of succinonitrile and glutaronitrile. The peak values give the most probable reorientation frequencies for the temperature at which the spectrum was obtained. Reproduced with permission from ref 13. Copyright 2010 American Institute of Physics.

Figure 2 shows the logarithmic spin−lattice relaxation times plotted versus $10^3/T$ (Figure 2a for ^1H and Figure 2b for ^{13}C) and quadratic fits to the lower-range data near the minimum, which we use to identify the temperature of the minimum as precisely as possible. This choice amounts to assuming that there is a single relaxation time (that can be inverted to a single characteristic frequency). It seems appropriate because that is what we have also done to obtain the characteristic frequencies for the dielectric spectra with which we wish to make comparison. So long as the dynamics are not very fragile, it does not make much difference, i.e., the most probable and average relaxation times (or characteristic frequencies) differ very little. We address the fragility of the dynamics in the discussion of Figure 3.

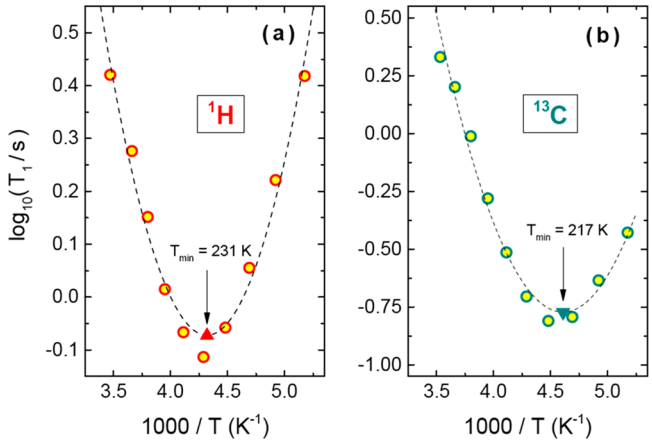


Figure 2. Spin−lattice relaxation times of ^1H and ^{13}C nuclei in the $(SN)_{60}(GN)_{40}$ plastic crystal of Figure 1. From the relation $\omega\tau_m = 1$ (where ω is the Larmor frequency and τ_m is the most probable magnetic fluctuation (relaxation) time of the sample at the temperature of the minimum), we obtain the most probable fluctuation frequency for direct comparison with those of Figure 1 using the relation $f_m = 1/(2\pi\tau_m)$.

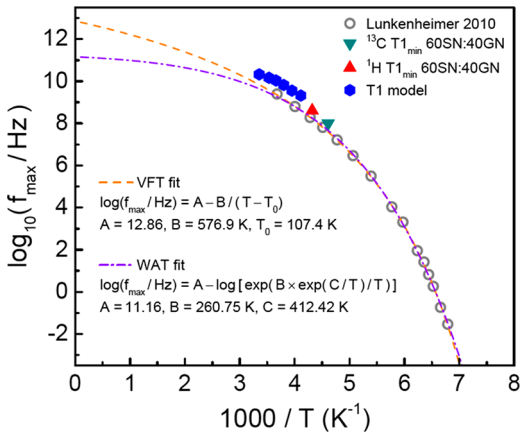


Figure 3. Matchup of most probable frequencies of molecular reorientation from dielectric relaxation spectroscopy (Figure 1 peak values) and magnetic fluctuations from NMR spectroscopy. The hexagons (larger than the experimental uncertainties) are for reorientation times from a standard NMR model valid in the high-temperature domain (see the text). Evidently the latter occur on slightly shorter time scales than the reorientation times from dielectric relaxation, but they should be valid as an indication of molecular reorientation times when the latter cannot be measured directly by dielectric relaxation spectroscopy.

Using the T_1 minimum, we obtain an unambiguous (model-free) value for the most probable relaxation time for magnetic fluctuations in the liquid at the temperature at the T_1 minimum from the above-mentioned relation $\omega\tau_m = 1$. It is the inverse of τ_m in units of Hz (i.e., $f_m = 1/(2\pi\tau_m)$) that we want to compare with the dielectric peak frequencies observed in Figure 1. This comparison is made in Figure 3. While the identity with a characteristic time for magnetic fluctuations is unambiguous, the physical nature of the fluctuations can be complex. At temperatures above the minimum, however, the fluctuations can be reliably identified with the rotational

https://dx.doi.org/10.1021/acs.jpclett.0c00502
J. Phys. Chem. Lett. 2020, 11, 3301−3304

motions of the molecules, as detailed below, where we introduce additional data obtained in this simpler higher-temperature domain.

Figure 3 shows how the most probable magnetic fluctuation characteristic frequencies f_m for ^{13}C and ^{1}H obtained from the relations $\omega\tau_m = 1$ and $f_m = 1/(2\pi\tau_m)$ at the temperatures of the T_1 minima match up against the most probable dielectric relaxation frequencies at the same temperatures. The close relation between the two characteristic frequencies seen in Figure 3 suggests that NMR spectroscopy may be used to give a close estimate of the reorientation time of molecular solvents or anions in systems in which the dielectric relaxation cannot be observed directly because of "swamping" by the flux of ions that decays the applied field before the molecules can rotate.[14] The engulfing of the solvent reorientation peak by the moving conductivity relaxation peak occurs at a rather low ionic content, about 2.5 mol % salt, in the case cited,[14] and it is therefore clear that reorientation time information for any single component or concentrated solution fast ionic conducting system must be quite inaccessible using any standard dielectric susceptibility approach.

The red-dashed curve through the dielectric relaxation points in Figure 3 is a best fit to the well-known Vogel−Tammann−Fulcher (VFT) equation, while the purple dash-dotted line is the best fit to the empirical Waterton viscosity equation of 1932.[15] An equation of the same (transcendental) form was derived by Angell and Bressel from a "bond lattice" model in 1972[16] and again by Mauro et al. from an entropy model in 2009,[17] who demonstrated that their version (the MYEGA equation) fitted a wide variety of accurate high-temperature glass former data a little better than the VFT equation. This form does not predict a vanishing of the most probable relaxation frequency (divergence of the most probable relaxation time) at any finite temperature, as does the VFT equation. A detailed comparison of the relative fitting abilities of the VFT and Waterton forms for molecular liquids has been given by Lunkenheimer et al.[18] The Waterton form seems to have distinct advantages for very fragile liquids, while for nonfragile liquids there is little to favor one over the other.[18]

The VFT parameter B (in the classical expression shown in Figure 3) is often replaced by the combination $B = DT_0$ because then D expresses the deviation from Arrhenius behavior in a way that permits comparisons among liquids of all types. A large value of D indicates a small deviation from Arrhenius behavior, while a small value of D indicates a large deviation or so-called "fragile" behavior. For the data in Figure 3 this relation yields $D \sim 13$, which is typical of intermediate fragility, like that of glycerol, in the spectrum of liquid values but *high* fragility relative to those of most reorientationally disordered solids. In the VFT extrapolation, one should note the proximity of the limiting high-temperature value to that of the typical far-infrared absorption frequency for molecular solvents, 10^{13} Hz (the cage "rattling" frequency and, perhaps more relevantly, the anomalous low-frequency edge of this far IR absorption band, represented by the so-called boson peak). The VFT parameters for the most probable relaxation times plotted in Figure 3 are almost indistinguishable from those reported earlier for the *average* relaxation times in the same system.[13] This is characteristic of intermediate and strong systems, in which the shape of the relaxation spectrum is only weakly sensitive to temperature.

In addition to the reorientation times obtained from the ^{1}H and ^{13}C T_1 minima, dynamic information can be obtained from the ^{13}C T_1 measurements themselves. At temperatures above the T_1 minimum, the assumption that the H−C dipole interaction is the dominant interaction driving the T_1 relaxation can be safely made. This assumption allows for the use of a simple relation between the rotational correlation time and T_1.[19,20] The rotational correlation times thus obtained, which are indicated by blue hexagons in Figure 3, lie slightly above the dielectric relaxation data points and cover the temperature range from that of the minimum to some 50 K above it. They are seen to have the same slope and curvature as the dielectric frequencies in that temperature range, again emphasizing a close relation between their physical origins.

The close relation between the two characteristic frequencies, NMR and dielectric, seen in Figure 3 suggests that NMR spectroscopy may be used to give a good estimate of the reorientation times of molecular solvents or anions in systems in which the dielectric relaxation cannot be observed directly because of "swamping" by the flux of ions that decays the applied field before the molecules can rotate.[14]

Additional T_1 minimum data could be obtained from measurements made at higher field frequencies using variable-field instruments available in some laboratories, but the self-consistency of the data shown in Figure 3 would seem sufficient to establish the close relation between magnetic fluctuation frequencies and reorientational frequencies, which was the object of this study. The application of this knowledge to investigation of the relation between ionic conductivities (which are determined by the *average* conductivity relaxation times) and the most probable reorientation relaxation times for magnetic fluctuations is the subject of the companion paper.[12]

Finally, we should note that the NMR techniques we have adopted for this presentation are not alone in their ability to detect reorientational motion independent of translational motion. A further, though demanding, approach is to use the difference between polarized and depolarized Raman scattering spectra of a symmetric mode as it has been applied to the high-temperature rotator phase of Li_2SO_4 by Borjesson and Torell.[21] This technique interrogates rotational relaxation times on the shorter time scale of picoseconds and thus offers an important possible extension of the present study.

EXPERIMENTAL SECTION

Succinonitrile (99%) and glutaronitrile (99%) were obtained from Sigma-Aldrich and used without further purification. Neither is hygroscopic. Sample handling was performed in an argon-filled drybox. The sample was prepared by adding 20 mmol (1.88 g) of glutaronitrile and 30 mmol (2.40 g) of succinonitrile to a 20 mL scintillation vial and stirring the mixture on a hot plate at approximately 60 °C until the materials formed a homogeneous solution. Approximately 700 μL of the solution was pipetted into a 5 mm NMR tube and cooled to room temperature.

All of the NMR measurements where obtained using a Varian 400 MHz VNMRS system equipped with a 5 mm HX broad-band probe. The resonant frequencies for the nuclei of interest were 399.65 and 100.5 MHz for ^{1}H and ^{13}C, respectively. The sample was cooled to below −80 °C using liquid nitrogen boil-off gas, and then the temperature was controlled using the probe heater; the system was allowed to equilibrate for at least 20 min at each temperature before measurements were begun. T_1 relaxation measurements were

https://dx.doi.org/10.1021/acs.jpclett.0c00502
J. Phys. Chem. Lett. 2020, 11, 3301−3304

obtained using the standard inversion recovery pulse sequence (π–τ–$^{\pi}/_{2}$–detect). ^{1}H T_1 NMR measurements were carried out using a recycle delay of 13 s, a 90° pulse width of 10.6 μs, four scans, and interpulse delays (τ) ranging from 0.0125 to 12.8 s. ^{13}C T_1 NMR measurements were carried out using a recycle delay of 13 s, a 90° pulse width of 14.9 μs, eight scans, and interpulse delays (τ) ranging from 0.0125 to 12.8 s. The ^{1}H and ^{13}C chemical shifts were referenced externally using 1% tetramethylsilane dissolved in $CDCl_3$ prior to the measurements.

AUTHOR INFORMATION

Corresponding Author

C. A. Angell − *School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-1604, United States;* orcid.org/0000-0002-8485-1480; Email: austenangell@gmail.com

Authors

S. K. Davidowski − *School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-1604, United States;* orcid.org/0000-0003-2556-4630

J. L. Yarger − *School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-1604, United States;* orcid.org/0000-0002-7385-5400

R. Richert − *School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-1604, United States;* orcid.org/0000-0001-8503-3175

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.0c00502

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Department of Defense (DOD) Army Research Office (ARO) under Grant W911-NF19-10152. J.L.Y. acknowledges support from the National Science Foundation (NSF-DMR-BMAT-1809645) and the DOD Air Force Office of Scientific Research (AFOSR) under Award FA9550-17-1-0282. The authors appreciate helpful discussions with Peter Lunkenheimer.

REFERENCES

(1) Seino, Y.; Ota, T.; Takada, K.; Hayashi, A.; Tatsumisago, M. A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries. *Energy Environ. Sci.* **2014**, *7*, 627.

(2) Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; et al. A lithium superionic conductor. *Nat. Mater.* **2011**, *10*, 682.

(3) Macfarlane, D. R.; Huang, J.; Forsyth, M. Lithium-doped plastic crystal electrolytes exhibiting fast ion conduction for secondary batteries. *Nature* **1999**, *402*, 792.

(4) MacFarlane, D. R.; Forsyth, M. Plastic crystal electrolyte materials: New perspectives on solid state ionics. *Adv. Mater.* **2001**, *13*, 957.

(5) Abu-Lebdeh, Y.; Alarco, P. J.; Armand, M. Single-phased organic plastic crystal electrolytes. *J. New Mater. Electrochem. Syst.* **2004**, *7*, 29.

(6) Klein, I. S.; Davidowski, S. K.; Yarger, J. L.; Angell, C. A. A new version of the lithium ion conducting plastic crystal solid electrolyte. *Adv. Energy Mater.* **2018**, *8*, 1801324.

(7) Alarco, P. J.; Abu-Lebdeh, Y.; Abouimrane, A.; Armand, M. The plastic-crystalline phase of succinonitrile as a universal matrix for solid-state ionic conductors. *Nat. Mater.* **2004**, *3*, 476.

(8) Tang, W. S.; Matsuo, M.; Wu, H.; Stavila, V.; Zhou, W.; Talin, A. A.; Soloninin, A. V.; Skoryunov, R. V.; Babanova, O. A.; Skripov, A. V.; et al. Liquid-like ionic conduction in solid lithium and sodium monocarba-closo-decaborates near or at room temperature. *Adv. Energy Mater.* **2016**, *6*, 1502237.

(9) Udovic, T. J.; Matsuo, M.; Unemoto, A.; Verdal, N.; Stavila, V.; Skripov, A. V.; Rush, J. J.; Takamura, H.; Orimo, S. Sodium superionic conduction in $Na_2B_{12}H_{12}$. *Chem. Commun.* **2014**, *50*, 3750.

(10) Cooper, E. I.; Angell, C. A. Ambient temperature plastic crystal fast ion conductors. *Solid State Ionics* **1986**, *18*–*19*, 570.

(11) Geirhos, K.; Lunkenheimer, P.; Michl, M.; Reuter, D.; Loidl, A. Conductivity enhancement inplastic crystalline solid-state electrolytes. *J. Chem. Phys.* **2015**, *143*, 081101.

(12) Davidowski, S.; Young-Gonzales, A. R.; Richert, R.; Yarger, J.; Angell, C. A. Relation of ionic conductivity to solvent reorientation times in dinitrile plastic crystal solvents. *J. Electrochem. Soc.* **2020**, *167*, 070553 (Armand honor issue).

(13) Bauer, Th.; Köhler, M.; Lunkenheimer, P.; Loidl, A.; Angell, C. A. Relaxation dynamics and ionic conductivity in a fragile plastic crystal. *J. Chem. Phys.* **2010**, *133*, 144509.

(14) Floriano, M. A.; Angell, C. A. On the relation between Debye and nonexponential relaxation in supercooled monohydric alcohols and water: A solution study. *J. Chem. Phys.* **1989**, *91*, 2537.

(15) Waterton, S. C. The viscosity-temperature relationship and some inferences on the nature of molten and of plastic glass. *J. Soc. Glass Technol.* **1932**, *16*, 244.

(16) Angell, C. A.; Bressel, R. D. Fluidity and conductance in aqueous electrolyte solutions. Approach from the glassy state and high-concentration limit. I. Calcium nitrate solutions. *J. Phys. Chem.* **1972**, *76*, 3244.

(17) Mauro, J. C.; Yue, Y.; Ellison, A. J.; Gupta, P. K.; Allan, D. C. Viscosity of glass-forming liquids. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 19780.

(18) Lunkenheimer, P.; Kastner, S.; Köhler, M.; Loidl, A. Temperature development of glassy α-relaxation dynamics determined by broadband dielectric spectroscopy. *Phys. Rev. E* **2010**, *81*, 051504.

(19) Bloembergen, N.; Purcell, E. M.; Pound, R. V. Relaxation effects in nuclear magnetic resonance absorption. *Phys. Rev.* **1948**, *73*, 679.

(20) Callaghan, P. *Principles of Nuclear Magnetic Resonance Microscopy*; Oxford University Press, 1991.

(21) Borjesson, L.; Torell, L. M. Reorientational motion in superionic sulfates: A Raman linewidth study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1985**, *32*, 2471.

https://dx.doi.org/10.1021/acs.jpclett.0c00502
J. Phys. Chem. Lett. 2020, 11, 3301−3304