



# Study of solvent relaxation of pristine succinonitrile and succinonitrile–salt mixtures using quasielastic neutron scattering



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## ABSTRACT

Succinonitrile (SN) has been demonstrated as an excellent organic plastic crystalline “solid-like” solvent for dissolution of large variety of salts at ambient temperatures. The SN–salt electrolytes are highly conducting only in the plastic phase of SN. We discuss here the study of solvent dynamics of SN in the plastic crystalline state both in the absence and presence of salts using high resolution quasielastic neutron scattering (QENS, IN16 spectrometer at ILL-Grenoble). Elastic scan versus temperature for SN, 1 M SN–LiClO<sub>4</sub> (SN–lithium perchlorate), 1 M SN–(LiClO<sub>4</sub>)<sub>0.95</sub>(LiTFSI)<sub>0.05</sub> (SN–lithium perchlorate–lithium bis(trifluoromethane-sulfonyl)imide) revealed a sharp order–disorder transition at 233 K. Significant quasielastic broadening was observed above 233 K. The obtained QENS data (T = 245 K) displayed relaxations ≈ 100 ps which is localized and can be accounted on the basis of a one-molecule mathematical model proposed by Bée et al. (assuming all possible molecular conformations in its unit cell). The SN rotational dynamics which determines ionic conductivity is observed to be faster in the SN–salt mixtures than the pristine SN. The high resolution QENS data also revealed the localized diffusion of the whole molecule (which includes the coordinated Li-ion and the counter anion(s)) around its nearest neighbors. Assuming that this molecular diffusion is confined under a potential of spherical symmetry, the estimated value of the radius of the domain for whole molecule diffusion and the corresponding diffusion coefficients are extracted. While the time scale for whole molecular diffusion for pristine SN and 1 M SN–LiClO<sub>4</sub> is found to be very similar, the whole molecular diffusion for SN–(LiClO<sub>4</sub>)<sub>0.95</sub>(LiTFSI)<sub>0.05</sub> is much slower, probably due to increased mass.

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## 1. Introduction

Electrolyte is a key component which mediates an electrochemical reaction occurring at the electrodes of an electrochemical cell via transport of specific ions. Recently, plastic crystalline electrolytes [1] have been demonstrated as potential electrolytes in electrochemical energy devices such as rechargeable batteries [2–4], supercapacitors [5,6] and solar cells [7,8]. The phenomenon of plasticity, which essentially implies existence of orientational disorder in some form in a translationally invariant crystalline lattice above a particular temperature [9], has been observed in a variety of inorganic and organic materials [9–12]. Majority of the organic plastic crystalline compounds exhibit orientational disorder at or near ambient temperatures. Plasticity has been observed to be directly responsible in determining the ionic conductivity, with ionic

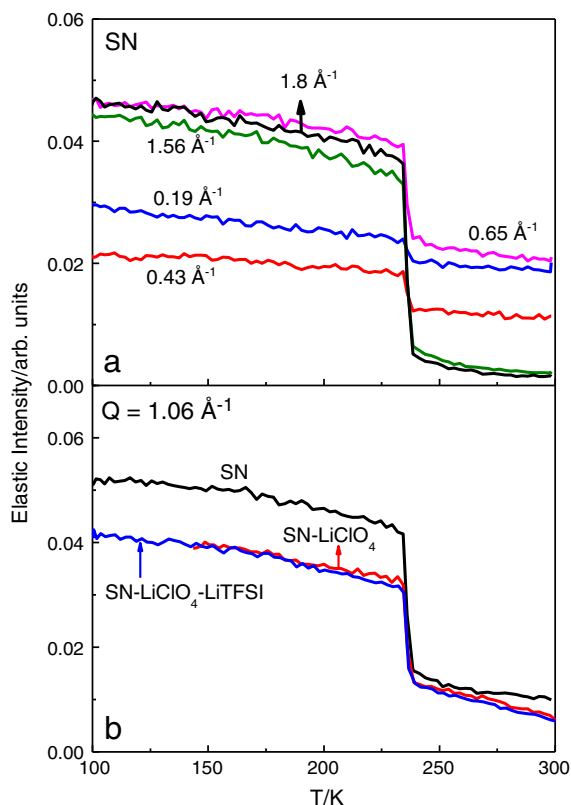
conductivities in the plastic phase being much higher than in the normal crystalline phase of the material. Due to the achievement of the high conducting phase at ambient temperatures, organic plastic crystalline materials (including ionic liquids) have gained a lot of importance in a variety of electrochemical applications. Succinonitrile (SN, N≡C–CH<sub>2</sub>–CH<sub>2</sub>–C≡N) [13–17] has been recently demonstrated as a versatile solid organic plastic crystalline solvent for a variety of salts. SN is a non-ionic, polar (dielectric constant, ε = 55) wax-like solid displaying plasticity over a wide temperature range (T ~ –35 °C to 58 °C). In the plastic phase SN exists in (two) *gauche* and (one) *trans* conformations and the orientational disorder originates from the conversion from *gauche* to *trans* and vice versa which occurs via the rotation of CN moieties about the central C–C bond. On the addition of salts, the dynamics along with the crystal structure of the solvent get significantly affected. Pristine SN crystallizes in the monoclinic crystalline structure below  $T_{np}$  (normal to plastic crystalline transition temperature) and body centered cubic structure above  $T_{np}$ . In the presence of salt, especially at high salt (≈ 1 M) concentration, SN has been shown to crystallize in other forms such as in the orthorhombic crystal system [18]. The SN–salt system displays excellent ionic conductivity in the plastic phase. The dynamical transformation in isomer conformations, which exist

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**Fig. 1.** Elastic scan of (a) pristine SN at different  $Q$  values and (b) SN-salt mixtures at  $Q = 1.06 \text{ \AA}^{-1}$  at different temperatures.

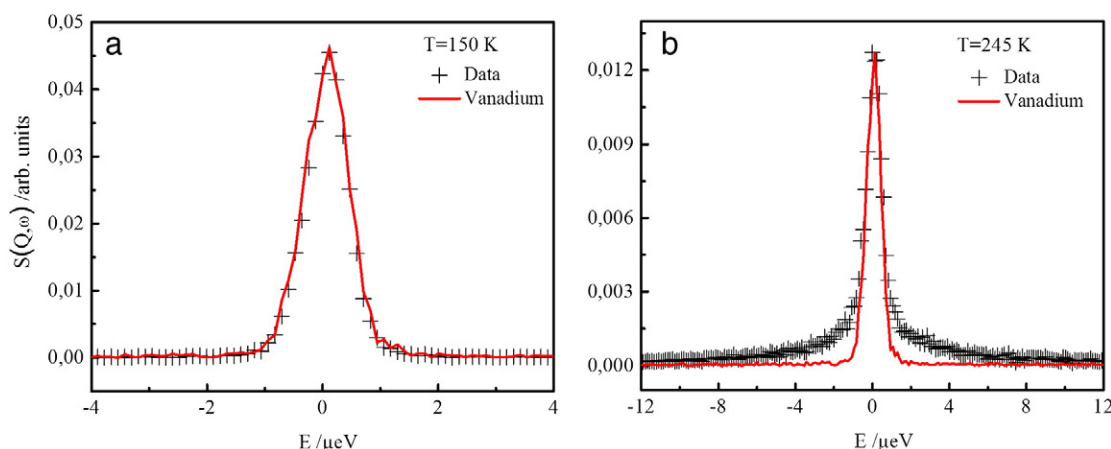
only in the plastic phase, has been proposed to be responsible for the fast ion transport. In the normal crystalline phase (i.e. below  $T_{np}$ ) the ionic conductivities are however, very low. This has been attributed to the complete lack of solvent dynamics due to the freezing of the SN molecule in a single *gauche* conformation.

Apart from the influence of solvent dynamics on ionic conductivity, Das et al. have convincingly demonstrated the influence of ion association on ion transport using dielectric relaxation spectroscopy [19] and Brillouin scattering [20]. Ion association is highly detrimental and is the dominant factor at high salt concentrations. We probe here the competing influences of the solvent dynamics and ion association in ion transport using incoherent quasielastic neutron scattering (QENS) [21–25]. Among the various experimental tools which can probe the

intrinsic dynamics of organic systems, incoherent QENS is an extremely useful tool as molecular dynamics of the organic system can be studied on a very wide time window [23–32]. Added advantage of incoherent QENS technique is that because of high incoherent scattering of neutron by hydrogen atoms, one can directly probe the dynamics of the organic molecules through their hydrogen atoms. Neutron scattering techniques have been already employed to study the dynamics in organic plastic crystalline materials including succinonitrile. The earlier neutron measurements of pristine succinonitrile molecule revealed the existence of two types of molecular motions attributed to isomerization between two *gauche* and *trans* conformation and rotational motions of *trans* form along its long axis which lies approximately along one of the fourfold symmetry axes of the lattice, in the plastic phase [24,29]. Later, the effect of the addition of salt in succinonitrile was studied by Eijck et al. [32] using QENS where they showed that salt has a noticeable effect on the dynamics of SN and it disturbs the localized character of the solid matrix. In this study, we discuss the solvent dynamics of pristine SN and its mixtures with salt 1 M SN-(LiClO<sub>4</sub>)<sub>1-x</sub>(LiTFSI)<sub>x</sub> (LiClO<sub>4</sub>: lithium perchlorate; LiTFSI: lithium bis(trifluoromethanesulfonyl)imide) below and above  $T_{np}$  using QENS.

## 2. Experimental materials and methods

Succinonitrile (SN, Aldrich) was sublimated twice to remove impurities. Lithium perchlorate (LiClO<sub>4</sub>, lithium battery grade, Chemetall GmbH) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma Aldrich, 99.9%) were preheated at 120 °C under vacuum to rule out effects arising out of physisorbed water. The plastic crystalline electrolyte was prepared by adding a requisite amount of Li salt in molten SN and stirred at 60 °C under dry N<sub>2</sub> atmosphere until a homogeneous mixture was obtained. Homogeneous transparent samples were obtained for all concentration ratios of LiClO<sub>4</sub> and LiClO<sub>4</sub> + LiTFSI. The motivation for the introduction of an additional salt (with a different anion) is to explore possibilities for further enhancement in ionic conductivity of SN-LiX electrolytes. In our case, enhancement in ionic conductivity by one order in magnitude is observed by replacing a small proportion of LiClO<sub>4</sub> by a salt containing a larger and isovalent anion viz. N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup> (abbreviated TFSI<sup>-</sup>, Fig. S1). The increase in ionic conductivity in the 1 M SN-(LiClO<sub>4</sub>)<sub>0.95</sub>(LiTFSI)<sub>0.05</sub> sample may be attributed to the difference in the size of ions and extent of charge delocalization. Additionally, introduction of another salt may enhance disorder in the sample as observed from the X-ray diffraction of various electrolyte samples (Fig. S2). The XRD-patterns show that the electrolytes become more amorphous on the addition of LiTFSI. The solidified melt was stored in glass vials under vacuum at 25 °C until further use. Two electrolyte samples (SN-(LiClO<sub>4</sub>)<sub>1-x</sub>(LiTFSI)<sub>x</sub>, with  $x = 0-0.5$ )



**Fig. 2.** Typical QENS spectra for pristine SN at  $Q = 1.0 \text{ \AA}^{-1}$  at (a) 150 K and (b) 245 K. The resolution has been measured on a vanadium sample.

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