Self-Diffusion, Phase Behavior, and Li$^+$-Ion Conduction in Succinonitrile-Based Plastic Cocrystals

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ABSTRACT

We study the temperature-dependent molecular dynamics, ion conduction and phase behavior of plastic-crystal electrolytes based on the succinonitrile molecule. We employ calorimetry and dielectric spectroscopy to probe binary mixtures of succinonitrile with glutaronitrile or acetonitrile, and analyze also the effect of dissolving lithium salts in these systems. The glutaronitrile-succinonitrile mixture has the highest conductivity and it is the only plastic-crystal system that displays a perfect correlation between the ion drift and the on-site reorientational dynamics. Doping with lithium ions boosts the conductivity but breaks such perfect correlation. All these features can be rationalized assuming that conduction is due to self-diffusion of a minority of ionized dinitrile molecules. Doping with lithium salts slows down the collective

molecular dynamics, while leaving unaffected the intramolecular relaxation motion. All samples exhibit a very broad melting transition and exist in a mixed liquid plus plastic state near room temperature. Some mixtures undergo phase segregation below 233 K, the transition temperature between the plastic and the fully order solid phase in pure succinonitrile, resulting in the appearance of a space-charge relaxation loss. Phase separation plays therefore an important role in pristine and lithium-doped succinonitrile mixtures.

Introduction.

Plastic crystals are molecular solids that display at the same time translational order, with the molecular average centers of mass defining a crystal lattice, and dynamic orientational disorder, with the constituent molecules undergoing on-site tumbling motions.[1,2] The term "plastic crystal" reflects the plasticity of most of these orientationally disordered phases, which arises from the presence of lattice defects near which the molecules exhibit also translational (diffusion) dynamics. Plastic crystals exhibit a phenomenology similar to that of glass-forming materials, displaying in particular a continuous dramatic slow-down of collective rotational motions (the so-called α relaxation) upon cooling,[3,4] which in some cases even leads to a glass-like transition associated with the rotational freezing.[5,6]

Plastic-crystalline ionic conductors are very interesting as electrolytes for electrochemical devices, because their mechanical flexibility reduces the problem of poor electrical contact with the electrodes caused by volume changes of solid electrolytes, while eliminating the leakage problems associated with liquid ones.[7,8] It has been suggested that charge transport in molecular ionic conductors with orientational disorder may be boosted by the molecular reorientational dynamics, and several efforts have been directed in the past years to investigate a possible connection between molecular reorientational dynamics and ionic charge transport.[7,9–11] However, evidences for such a connection in plastic crystals have been elusive. In the plastic-crystal phase of a phosphonium hexaphosphate, the ion conduction was found to be enhanced by the rotational motion of the phosphonium ions.[12] More recently, the first-ever evidence of a direct correlation of ion drift and molecular reorientational dynamics was reported in a plastic succinonitrile-glutaronitrile cocrystal at high succinonitrile content.[6]

Succinonitrile (N≡C–(CH$_2$)$_2$–C≡N) forms a plastic-crystal phase that behaves as a solid ion or proton conductor in the presence of ionic impurities or when doped with acids or lithium salts, which has led several authors to suggest a possible application as plastic electrolyte.[13–16] Since the plastic phase already melts at 331 K while higher temperatures are generally needed for electrochemical applications, mixed polymer-succinonitrile electrolytes have been implemented to achieve higher mechanical stability. Indeed, when mixed with polymers such as polyacrylonitrile or polyethylene terephthalate, Li-salt doped succinonitrile exhibits mobilities that are up to a factor of 50 higher with respect to pure succinonitrile.[17,18] We study here the conduction properties, phase behavior and molecular dynamics of mixed samples of succinonitrile with two other nitriles (glutaronitrile and acetonitrile), both pure and doped with Li salt.

The plastic-crystalline phase of pure succinonitrile has body-centered cubic (*bcc*) structure of space group *Im3m*.[19,20] In this phase the succinonitrile molecules exist in three isomeric conformations, namely two *gauche* isomers with C_2 molecular symmetry and a less abundant *trans* isomer with C_{2h} symmetry, which are interrelated by 120º-rotation about the central C–C bond.[19,21,22] The *bcc* cell contains two nonequivalent molecules, both with their C–C bond oriented along the diagonals of the cube.[13,21–25] At temperature lower than 233 K, a fully ordered monoclinic phase becomes stable, where all molecules are in a *gauche* conformation.[23,26,27] The disorder in plastic succinonitrile is associated with *trans-gauche* isomeric fluctuations involving a rotation about the central C–C bond of the molecules and to molecular jumps from one diagonal position of the *bcc* cell to another.[21,25] This leads to a significantly lower density of the *bcc* plastic phase compared with the fully ordered monoclinic structure.[20] It has been proposed that the *trans* isomers act as 'impurities' that favor charge transport, creating vacancies that

allow molecular and small-ion diffusion.[23] Similarly, the higher conductivity observed in the succinonitrile-polymer mixtures mentioned above was ascribed to the enhanced molecular dynamics of succinonitrile inside the looser environment of the polymer matrix.[17]

In spite of these suggestions and of the widespread belief that the orientational dynamics in plastic succinonitrile is beneficial to its high ionic mobility, however, the correlation between the molecular dynamics and the ionic mobility in succinonitrile systems is controversial.[6,28] To reach a fuller understanding of charge conduction and molecular dynamics in succinonitrile-based plastic materials, we perform dielectric spectroscopy experiments on pure and lithium-salt doped binary plastic cocrystals of succinonitrile with glutaronitrile or acetonitrile, at high succinonitrile concentration. Glutaronitrile ($N\equiv C–(CH_2)_3–C\equiv N$) is chemically very similar to succinonitrile (both are alkane-dinitriles), yielding a relatively good miscibility even in the solid state;[28,29] moreover, the addition of glutaronitrile in sufficient amount effectively enlarges the temperature range in which the plastic phase can be supercooled and thus the available experimental range.[28] On the other hand, acetonitrile ($N\equiv C–CH_3$) is a universal solvent, and mixing it with succinonitrile allows exploring the effect of the reduction in density of the nitrile groups. Dielectric spectroscopy is a particularly suited tool for such study as it allows probing, by means of a single technique, both the dc conductivity and the relaxation motions in polar systems.

With respect to our previous work presented in Ref. 6, we confirm the existence of a perfect correlation between the dc conductivity and the orientational dynamics in pure succinonitrile-glutaronitrile mixtures, by further showing that it holds in a relatively wide stoichiometry range. We also show that this correlation acquires a deeper meaning using the so-called modulus representation, by which it is found that the ratio between the frequencies of the conductivity

relaxation and that of the collective dipolar relaxation is a linear function of temperature with exactly the same slope for all mixtures, a result that bears a direct resemblance with the fundamental Einstein relation, $D/\mu = k_B T/e$. These results indicate that the succinonitrile-glutaronitrile system is a unique example of solid phase possessing liquid-like properties. In contrast, we show that the correlation does not hold for pure succinonitrile or succinonitrile-acetonitrile mixtures (or in Li-salt doped samples), and discuss the possible role of glutaronitrile molecules for the validity of the Einstein relation. We also report on two more relaxation mechanism in the cocrystals, namely a space-charge relaxation and an intramolecular dipolar dynamics, and further show that partial phase transitions and phase segregation take place, a fact that has consequences for the possible utilization of succinonitrile-based mixtures as electrolytes.

Experimental Methods.

  Succinonitrile (SN, 99%), glutaronitrile (GN, 99%), acetonitrile (AN, 99.7%) and three lithium salts (LiBF$_4$ 98%, LiCF$_3$SO$_3$ 99.995%, and LiN(CF$_3$SO$_2$)$_2$ 99.95%) (Sigma Aldrich; the percentage in parenthesis is the molar purity) were weighted and mixed in the correct proportions to obtain the desired stoichiometries. The undoped mixtures were obtained by dissolving the succinonitrile powder in liquid glutaronitrile or acetonitrile. A small amount of a lithium salt, preheated to 400 K to avoid the presence of water, was added in some cases. Sonication at 330 K (above the melting point of the mixtures) was used to favor homogeneous mixing prior to calorimetric and dielectric measurements. Differential-scanning calorimetry measurements were carried out upon heating between 200 K and 350 K at a rate of 5 K min^{-1} (while cooling DSC rates were of 10 K min^{-1}), using a Q100 calorimeter from TA-Instruments.

For dielectric measurements, carried out in the frequency (f) range from 10^{-2} to 10^9 Hz, the sample was placed in liquid form inside a home-made stainless steel capacitor specially designed for liquid samples, and loaded inside a nitrogen-gas flow cryostat (Quatro) to achieve sample temperature control. Isothermal frequency scans were acquired in the range between 350 and 130 K (with a stability of ±0.3 K) upon cooling the sample from the liquid phase to ensure the maximum homogeneity. For measurements between 10^{-2} to $5 \cdot 10^6$ Hz a Novocontrol Alpha analyzer was employed, using a parallel-plate capacitor geometry for the sample; for measurements in the range from 10^6 to 10^9 Hz, a HP4291 impedance analyzer was employed in reflectometry geometry, with the sample capacitor mounted at the end of a coaxial cable.

The isothermal dielectric spectra are complex functions of frequency that can be displayed in several representations, for example as complex permittivity ε (consisting of the dielectric function $\varepsilon'(f)$ and the loss spectrum $\varepsilon''(f)$), as complex conductivity $\sigma = i\, 2\pi f\, \varepsilon_0\, \varepsilon$ (of which the real part $\sigma'(f)$, called ac conductivity, describes charge conduction in the sample), or as modulus $M = 1/\varepsilon$ (of which the imaginary part $M''(f)$ contains information on both dielectric and dc-conductivity loss processes, see main text).[30]

Results and Discussion.

Figure 1 shows the dielectric function $\varepsilon'(f)$, dielectric loss $\varepsilon''(f)$, ac conductivity $\sigma'(f)$ and imaginary modulus spectra $M''(f)$ of the plastic phase of a $SN_{0.87}GN_{0.13}$ sample between 140 and 250 K. Similar results (not shown) were obtained also at slightly lower or higher GN stoichiometry, and also in the plastic-crystal phase of pure SN and of SN-AN mixtures, albeit in a smaller temperature range than that of Fig. 1 since SN and SN-AN mixtures underwent a transition to a fully ordered crystal phase between 233 and 220 K upon cooling. At temperatures

above 300 K (not shown) the spectra exhibited a clear change of lineshape signaling the transformation from the plastic crystal to the liquid. This confirms that the data shown in Fig. 1 are relative to the plastic phase and not to a possible supercooled liquid phase. [28] Analogous liquid-to-plastic transitions were observed in pure SN and in SN-AN mixtures, as discussed also in the following.

The dielectric function (Fig. 1a) exhibits at low frequency a plateau corresponding to the static relative permittivity ε_s of the sample. This is followed at higher frequency by a drop in the value of ε', which takes place at the characteristic frequency (f_α) of the so-called primary or α-relaxation, visible as a peak the loss spectra (Fig. 1b). The α relaxation is the spectral signature of the collective reorientational motions of the molecular dipoles under the applied ac field. The α-relaxation frequency f_α coincides with the step-like decrease in ε'(f) due to the Kramers-Kronig causality relations.[30] As visible in both panels (a) and (b), f_α shifts to smaller values as the temperature is decreased, as a lower thermal energy entails slower molecular dynamics. It may be observed from panel (b) that the α process reaches a frequency of 10^{-2} Hz at around 143 K. This temperature is consistent with the glassy transition temperature measured by calorimetry (between 143 and 150 K depending on the stoichiometry).[28] For clarity, in the loss spectra (Figure 1b) only the α relaxation peak is shown; the dc-conductivity background inversely proportional to the frequency, normally visible as a straight line in the low-frequency portion of the logarithmic loss spectrum,[31] is instead omitted for better clarity.

Dielectric spectroscopy is only sensitive to the change in the dipole moment of the sample, hence to changes of the molecular orientation (rotations or rototranslations). Although (as mentioned in the introduction paragraphs) in plastic crystalline phases there is in general a contribution to the molecular dynamics from rototranslational processes due to a minority of molecules diffusing

through lattice defects, [7,12,32,33] the α relaxation feature stems mainly from pure-rotation motion of the majority molecules at a fixed position in the *bcc* lattice.
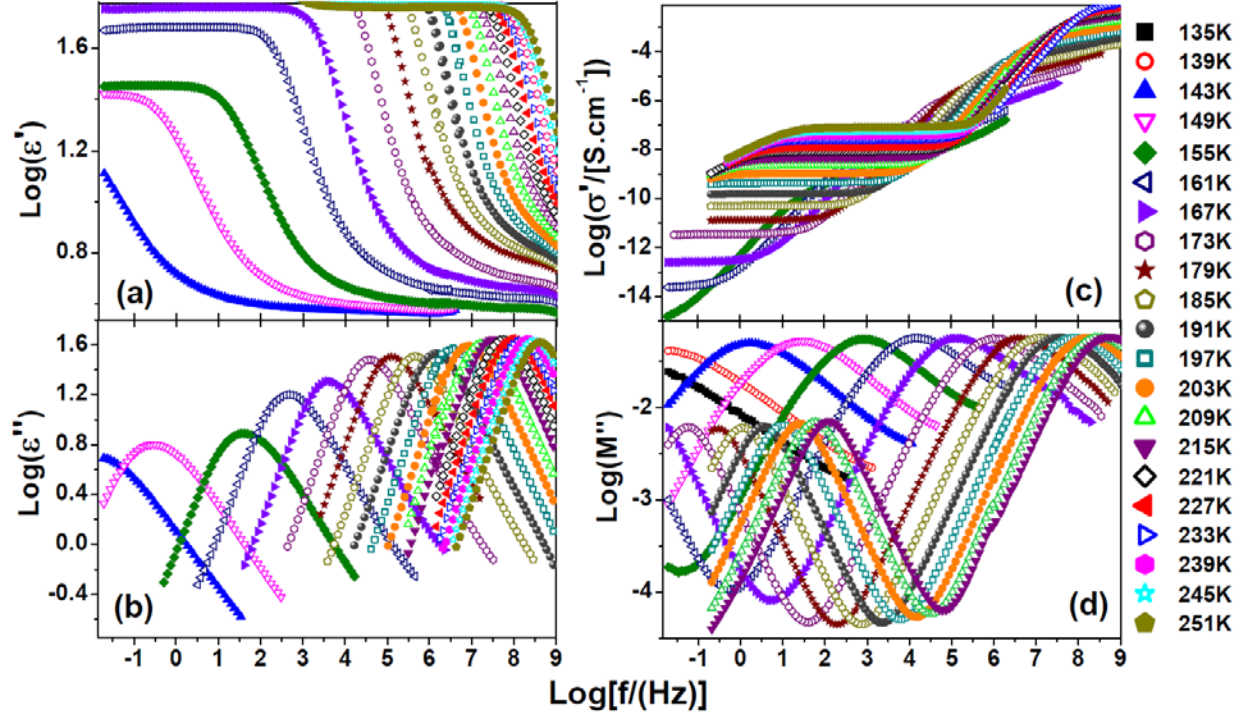

Figure 1. Logarithmic spectra of the dielectric function (a), dielectric loss (b), ac conductivity (c) and modulus spectrum (d) of the plastic-crystal phase of $SN_{0.87}GN_{0.13}$, at the indicated temperatures.

The ac conductivity spectra (Fig. 1*c*) exhibit a horizontal plateau at intermediate or low frequencies, corresponding to the dc conductivity regime. Especially at high temperature, the conductivity is observed to decrease at the lowest frequencies (spectral bending) due to the accumulation of ions at the electrode-sample interface (electrode polarization effect). At high frequency, the σ' spectra display a bump-like feature in correspondence with the α relaxation (as expected because σ' = $2\pi f \, \varepsilon_0\varepsilon$"). The modulus spectra M"(*f*) (Fig. 1*d*) are characterized by two peaks of quite different shape and intensity, a more intense peak at high frequency,

corresponding to the dielectric α relaxation loss, and a weaker one at low frequency, referred to as dc-conductivity peak. It may be observed that the dc-conductivity peak in the modulus representation is centered at a frequency f_σ which lies approximately in the middle of the plateau corresponding to the dc conductivity in the σ' spectra.

From dielectric data such as those presented in Fig. 1 one may obtain, for each measurement temperature, the value of the static permittivity, the dc conductivity σ_{dc}, the characteristic frequency f_α of the collective α process, and the characteristic frequency f_σ of the dc-conductivity loss (lower-frequency modulus peak). The value of σ_{dc} was taken to be value of the ac conductivity spectra σ'(f) (panel b) in the middle of the plateau. In order to obtain f_α and f_σ, the α feature in the dielectric loss spectra (b) and the dc-conductivity peak in the modulus spectra (d) were fitted assuming a Havriliak-Negami profile, whose analytical expression for the permittivity is:[30]

$$(Eq.\ 1)\ \varepsilon_{HN}(f) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left(1+(i2\pi f/f_{HN})^\beta\right)^\gamma}.$$

Here, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric strength (equal to the step variation of the real part of the permittivity ε', and proportional to the density of molecules taking part in the relaxation process), and ε_∞ and ε_s are the high-frequency and static low-frequency limits of ε'(f). The parameters β and γ, which lie in the range from 0 to 1, are related with the shape and asymmetry of the relaxation loss lineshape; finally, f_{HN} is a fitting parameter from which the characteristic frequency f_{max} at which the dielectric loss is maximum is obtained as:

$$(Eq.\ 2)\ f_{max} = f_{HN}\left(\sin\frac{\beta\pi}{2+2\gamma}\right)^{1/\beta}\left(\sin\frac{\beta\gamma\pi}{2+2\gamma}\right)^{-1/\beta}.$$

Similar equations can be given for the Modulus spectrum and for the frequency of spectral maximum f_σ.[30] The Havriliak-Negami function is a phenomenological generalization of the Debye model, given by:

(Eq. 3) $\varepsilon_{Debye}(f) = \varepsilon_\infty + \dfrac{\Delta\varepsilon}{1+i2\pi f/f_D}$,

where f_D is the Debye frequency (the frequency of maximum loss in this model).

Fig. 2 shows the Arrhenius plots of f_α (a) and σ_{dc} (b) of the $SN_{0.87}GN_{0.13}$ cocrystal as obtained from the dielectric spectra of Fig. 1. In the same figure we also report the analogous values obtained for the plastic phases of pure SN and of a mixture with acetonitrile. It may be observed from Fig. 2a that the α relaxation frequency in $SN_{0.87}GN_{0.13}$ at a given (high) temperature is virtually identical to that of pure SN. In fact, for all studied SN-GN mixtures, the α peak is observed at roughly the same frequency position independent of the stoichiometry (not shown).[6,28,29] These observations are consistent with the fact that the glass transition temperature of SN-GN mixtures is almost constant regardless of the stoichiometry,[29] indicating that the molecular dynamics in the presence of GN is identical (or at most only slightly slower than) that in pure SN.

Both pure SN and $SN_{0.92}AN_{0.08}$ display a phase transition to a fully-ordered crystal phase below 233 K. This is visible by the sudden decrease of the dc conductivity around this temperature (Fig. 2b), and by the fact that only the SN-GN mixture displays a relaxation frequency down to low T (Fig. 2a). In the case of pure SN, the conductivity drops by roughly three orders of magnitude in the fully-ordered phase compared to its value in the plastic phase. Such conductivity drop is expected because the ionic mobility is lower in the perfectly ordered crystal phase due both to its higher density[20] with respect to the plastic phase and to the absence

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of the beneficial effect of molecular rotations.[6] For $SN_{0.92}AN_{0.08}$ the drop in σ_{dc} is only of one decade, possibly due to an only partial phase transformation or to a larger concentration of defects due to the size mismatch between SN and AN moieties. It may be observed from Figure 1 that a partial transition to a fully ordered phase takes place (albeit at lower temperature) also in $SN_{0.87}GN_{0.13}$, where it is visible as a decrease of the static permittivity ε_s (Fig. 1a) and of the dielectric strength of the α relaxation (Fig. 1b) below 170 K.[34]
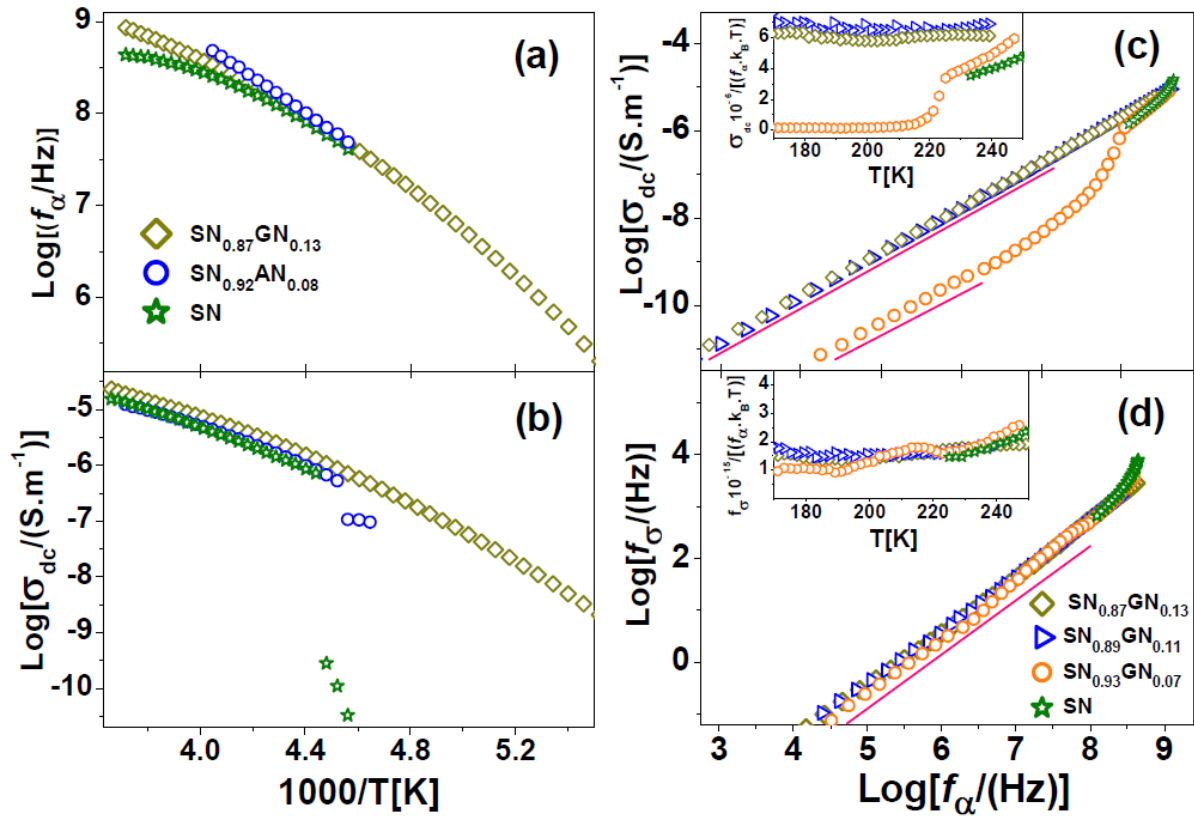

Figure 2. Semilogarithmic plot of f_α (a) and of σ_{dc} (b) *vs* $1000/T$, for pure SN and for the $SN_{0.87}GN_{0.13}$ and $SN_{0.92}AN_{0.08}$ plastic cocrystals. (c,d) Walden plots of Log (σ_{dc}) (c) and of Log(f_σ) (d) vs Log(f_α) of $SN_{1-x}GN_x$ samples at different GN content ($x = 0, 0.07, 0.11, 0.13$). The continuous lines are guides to the eyes with slope equal to 1. Insets: plot of $\sigma_{dc} / (f_\alpha k_B T)$ (c) and of $f_\sigma / (f_\alpha k_B T)$ (d) *vs* temperature for the same samples (the vertical scales are in SI units).

It is worth noticing that the value of the dc conductivity in the plastic-crystal phase of pure SN and of the binary mixtures is remarkably high, considering that all nitrile molecules are neutral closed-shell molecules, so that no *intrinsic* electronic or ionic conduction is expected. In all samples, both the maximum loss frequency and the dc conductivity follow a super-Arrhenius temperature dependence, giving rise to a curved lineshape. A non-simply-activated behavior of the relaxation frequency is rather common feature in glass forming materials and plastic phases,[35,36] and it is consistent with recent studies on the SN-GN binary system,[6,28] where it was shown that the temperature dependence of f_α (a) and σ_{dc} can be described by the Vogel-Fulcher-Tammann equation.[30] The negative curvature in the Arrhenius plot of σ_{dc} (Fig. 2*b*) is characteristic of ionic conduction in disordered systems,[28] while electronic conduction leads to a positive curvature.[37] The relatively high conductivity of succinonitrile plastic phases is therefore indicative of a very high mobility of ionic impurities. With respect to pure SN and to the cocrystal of SN with AN, the SN-GN system displays yet higher conductivity (as visible in Fig. 2*b*), by a factor between 2 and 3 depending on the concentration.

Figure 2*c* shows the plot of Log(σ_{dc}) *vs* Log(f_α) (Walden plot) for a series of $SN_{1-x}GN_x$ samples ($x = 0.07, 0.11, 0.13$) and for pure SN. At least at low temperatures, the plot of all SN-GN plastic cocrystals exhibit a slope close to one, *i.e.*, they follow the so-called Walden rule characteristic of ideal electrolyte solutions. This is quite unexpected for translationally ordered solids.[6] The Walden rule states that in dilute electrolyte solutions the product of the limiting molar conductivity and the solvent's viscosity η (which is proportional to the frequency f_α of collective diffusion processes in the solvent) is constant;[38] it is a consequence of the Stokes-Einstein relation, according to which the motion of bulky ions in a viscous liquid is limited by the viscosity of the medium, so that $\frac{D}{k_B T \eta} \simeq const$, where D is the diffusivity (proportional to the

conductivity σ_{dc}) and k_B is Boltzmann's constant. This relation is valid for solutions of large, weakly coordinating ions in solvents with nonspecific ion-solvent interactions.[39]

The plot of σ_{dc} / (f_α $k_B T$) vs temperature is shown in the inset to Fig. 1*c*. It may be observed that all studied $SN_{1-x}GN_x$ samples fulfill the Stokes-Einstein relation (at least at low temperature). This observation confirms the existence of a perfect correlation between molecular reorientations and ionic conductivity in the SN-GN mixtures.[6] In the case of the $SN_{0.93}GN_{0.07}$ sample, σ_{dc} exhibits a kink just below the transition temperature to the fully ordered phase (monoclinic) of pure SN (233 K). The presence of a kink and the simultaneous observation of relaxation dynamics below this temperature are clear indications that the $SN_{0.93}GN_{0.07}$ sample undergoes an only partial transition to the fully ordered phase, *i.e.*, a de-mixing into quasi-pure SN ordered crystals and plastic domains richer in GN, the latter displaying relaxation dynamics also below 233 K. For this sample, the Stokes-Einstein and Walden relations appear to be valid only at low temperature, where the GN concentration in the plastic domains is higher. Instead, above 233 K neither pure SN nor $SN_{0.93}GN_{0.07}$ follow a Walden behavior.

Some authors have pointed out that the modulus representation M"(*f*) is better suited than the ac conductivity to extract information on the microscopic properties of ion transport.[40,41] Figure 2*d* and its inset show the Walden plot and the Stokes-Einstein plot obtained for the same samples but using the frequency f_σ of the modulus maximum instead of σ_{dc} (see Experimental Methods). The anomaly near 233 K is much less pronounced in the logarithmic plot of f_σ *vs* f_α, leading to an overlap of all Walden plots. This indicates the microscopic ion diffusion processes are not significantly affected by the partial solid-solid phase transformation. In fact, the ratio f_σ / (f_α $k_B T$) is independent of temperature in all cases, and it has moreover approximately the same value

($\sim 10^{15}$ J^{-1}) for all GN stoichiometries. This confirms once more that the microscopic diffusion of ionic species is perfectly correlated with the on-site molecular rotations in these plastic crystals.

The applicability to a plastic crystal of a Stokes-Einstein rule involving molecular rotations is surprising, given that translational and rotational degrees of freedom are in general independent from each other; to the best of our knowledge, the SN-GN plastic cocrystals are the only examples of such connection, while other plastic crystals show in general a decoupling of charge carrier diffusion and orientational dynamics. We argue that there are only two possible conduction mechanisms that may rationalize the results presented in Fig. 2. The first one is the incoherent inter-molecular hopping of protons or other moieties able to form ionic complexes with the nitrile species (Grotthuss exchange). According to the Grotthuss' mechanism consecutive hops in the same direction can only occur if the molecules reorient during or in-between hops,[42] so that charge hopping is effectively limited by the on-site molecular rotational dynamics.

Another, more likely explanation was already suggested in Ref. 6: if charge transport is due to the self-diffusion of a fraction of ionized nitriles through structural defects, then a correlation between σ_{dc} and f_α may result from the similarity of rotational and diffusional timescales reported for the SN-GN binary system.[29] For example, charged molecular impurities might be present in the as-received materials; also, pairs of oppositely charged molecular ions may form by loss of a molecular hydrogen via protonation of a nitrile group (although the equilibrium constant for such process is relatively low[14]) or by reaction with impurity water molecules. On the other hand, the simple scenario of small-ion (H$^+$) drift through the intermolecular voids would not lead to the validity of the Stokes-Einstein relation, as it will be shown in the case of Li$^+$ ions in the final part of this work.

The dc conductivity is the product of the charge density and the ion mobility μ. Assuming singly ionized molecules and similar mobilities of both positive and negative molecular ions (or else a single dominant type of carrier), the dc conductivity can be written as $\sigma_{dc} = ne\mu$ where e is the elementary charge and n is the number density of charged species. The molecular mobility can be estimated from the coefficient of self-diffusion D by means of the Einstein relation $D = \mu k_B T/e$. For pure SN, taking the value of $\sigma_{dc} \simeq 4 \cdot 10^{-5}$ S/m observed in Fig. 1b at room temperature (298 K) and the diffusivity of $D = 1.3 \cdot 10^{-10}$ m^2/s obtained by NMR pulsed field gradient diffusion experiments in Ref. 15, the molecular ion density is found as $n \sim 5 \cdot 10^{22}$ m^{-3}. Since the total number density of molecules in pure SN is[20] $7.867 \cdot 10^{27}$ m^{-3}, this entails that of the order of one molecule every 10^5 in pure SN is ionized and mobile. If the observation of very similar relaxation frequency may be taken as indication that the diffusivity is the same in all samples, then the higher value of σ_{dc} in SN-GN plastic crystals entails that the fraction of ionic and mobile molecules is higher in the SN-GN mixture by a factor equal to the ratio of the respective dc conductivities, i.e. at least by a factor of 2. Another possibility is that the self-diffusion rate is higher in the SN-GN mixture due to a less compact *bcc* arrangement induced by the steric mismatch between SN and GN molecules. It should be recalled from the introduction that an earlier study suggested that the *trans* succinonitrile isomers in pure SN act as "impurities" facilitating self-diffusion and ion conduction; the same might be true for GN moieties present in mixtures with low GN concentration.

Fig. 3a shows the DSC curves of SN$_{0.93}$GN$_{0.07}$ and SN$_{0.85}$GN$_{0.15}$ acquired upon heating from low temperature after cooling the homogeneous liquid mixtures. Both thermograms display, besides an extended endothermic feature above room temperature, also a weaker endothermic feature well below it. This entails that the transition from the plastic phase to the liquid does not

occur at once; rather, melting of the plastic crystal starts below 0 ^{0}C and is only complete slightly above room temperature. These lineshapes are typical of binary mixtures, where solid-to-liquid transitions normally occur in two steps: nucleation of the liquid phase takes place across the lower-temperature endotherm, followed by a temperature interval in which the sample coexists in a liquid and solid phase (each in a different amount and with distinct stoichiometry); melting is only completed in correspondence with the second peak at higher temperature. The same behavior was observed in succinonitrile doped with LiBF$_4$.[14]

It may be observed from Fig. 3a that, with respect to pure SN, the final melting temperature is shifted to lower temperature the higher the GN doping level, as expected and in agreement with previous studies,[28,29] and that the width of the higher-temperature DSC feature increases with increasing GN content. Given that in the temperature interval between the two DSC peaks of Fig. 3a the sample is in a mixed phase, this entails that the succinonitrile mixtures are partially liquid at room temperature, a fact that prevents their application as solid-state electrolytes. The heterogeneity of the sample is also reflected in the anomalous behavior of the conductivity across the melting of the plastic-crystalline phase visible in Fig. 3b. This σ_{dc} anomaly was not reported in Ref. 6 as the authors focused there on the dynamics at lower temperature, where no liquid phase is present. It may be observed that even for pure succinonitrile the dc conductivity displays non-monotonous changes across the liquid-plastic transition upon cooling.
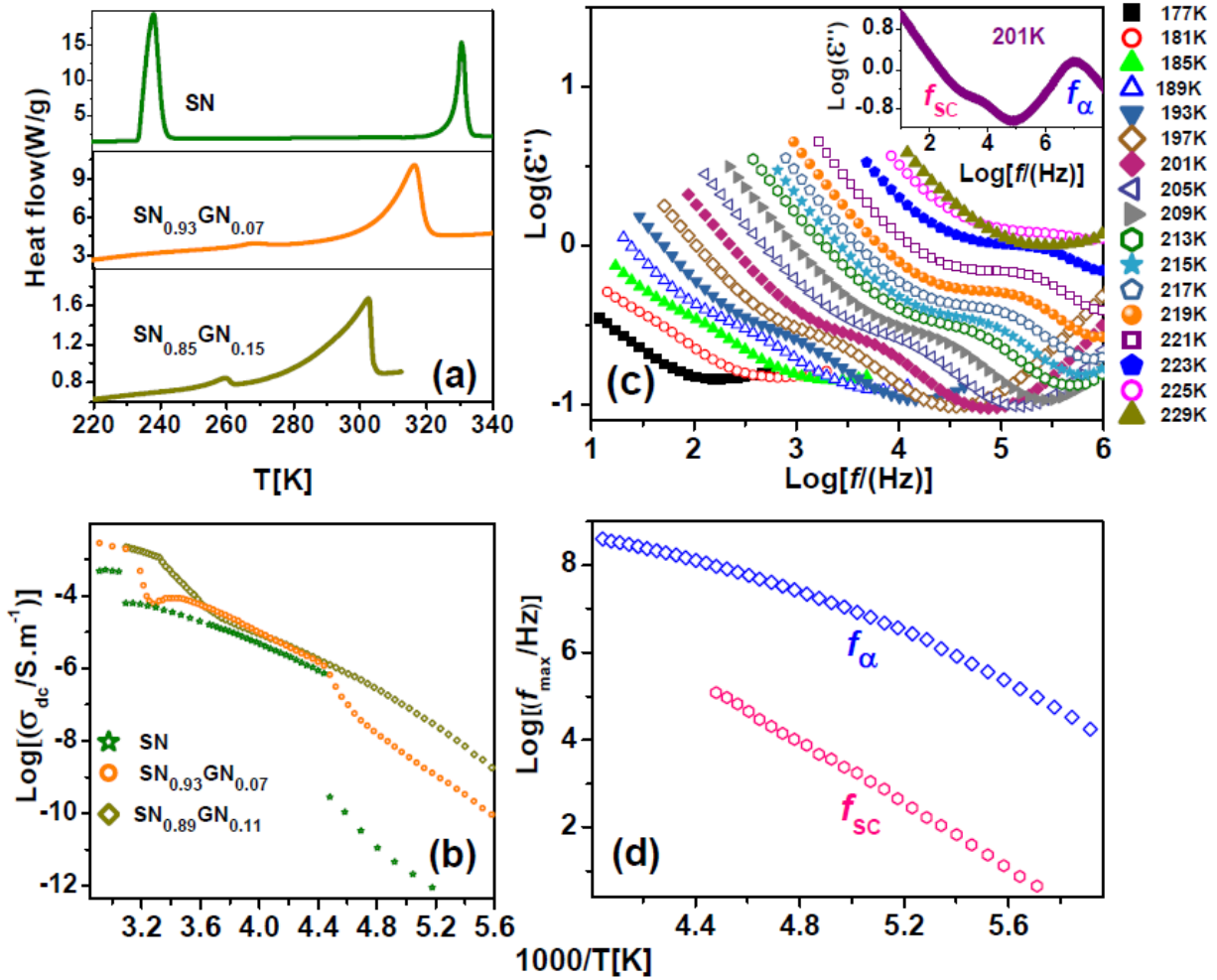
Figure 3. (a) DSC spectra of pure SN, $SN_{0.93}GN_{0.07}$ and $SN_{0.85}GN_{0.15}$, acquired upon heating. (b) Arrhenius plot of the dc conductivity of different SN-GN mixtures. (c) Low-frequency portion of the loss spectra of a $SN_{0.93}GN_{0.07}$ sample between 177 and 229 K every 4 K. The inset shows a full spectrum where both the space-charge and primary relaxations are visible. (d) Arrhenius plot of the space-charge (SC) relaxation of the same sample. The α relaxation frequency is also shown for comparison.

At lower temperature the temperature-dependence of the dc conductivity is strongly affected by the (partial) transition to the fully ordered phase, which as discussed is marked by a sharp drop in

pure SN and by a kink in $SN_{0.93}GN_{0.07}$. Concerning such solid-solid transition, it is interesting to note that the spectra of the roughly equimolar SN-GN mixture of Ref. 28 are characterized, apart from the α relaxation, also by a weaker loss feature at frequencies intermediate between the primary relaxation and the low-frequency conductivity background. The authors of Ref. 28 have suggested that this loss feature may be related to the ionic conduction. One possible explanation for the existence of this feature could be a conductivity-related space-charge dielectric loss associated with the sample's heterogeneity.[37] To test this idea, we compare our results on the SN-GN mixtures at lower GN stoichiometry with the results of Ref. 28 at higher GN content.

The inset to Fig. 3c depicts the loss spectrum of the $SN_{0.93}GN_{0.07}$ sample at 201 K. A loss feature is observed at a lower frequency (f_{SC}) than that of the α relaxation. Fig. 3c shows the temperature evolution of this second feature, as measured upon cooling from just below 233 K, the transition temperature between plastic and fully-ordered phases in pure SN. The intensity of the feature is always lower than that of the α peak and varies non-monotonically with temperature: it is completely absent above 233 K (not shown), temperature at which it suddenly appears in the loss spectrum, and it then decreases with decreasing temperature. The characteristic frequency of this loss feature, as extracted from a Debye fit (Eq. 3), is displayed in Fig. 3d. The origin of the loss feature is the spatial heterogeneity of the sample's conductivity and permittivity below 233 K: the partial phase transformation entails the appearance of fully-ordered crystallites with higher density, lower conductivity, and different static permittivity than the untransformed plastic matrix. Under an applied ac field, this heterogeneity leads to accumulation of ions at the boundaries between the two solid phases, resulting in a characteristic dipolar loss associated with space-charge effects[37,43] (sometimes referred to as Maxwell-Wagner-Sillars[30] relaxation). The phase boundaries are absent above 233 K, where the mixture is in a

homogeneous plastic phase, which confirms our identification of the loss feature. As visible in Fig. 1*c*, this loss is not observed in the $SN_{0.87}GN_{0.13}$ sample, at least above 170 K.

Given that the spectral position and shape of the loss feature of the nearly equimolar SN-GN mixture are very similar to those of the $SN_{0.93}GN_{0.07}$ sample, and considering that the Authors of Ref. 28 indicate a possible conductivity-related origin of this feature, it is likely that a partial phase separation leading to field-induced space-charge effects takes place in the nearly equimolar stoichiometry (where the miscibility of binary systems is usually lowest). From Fig. 3*b* it is clear that the σ_{dc} value for $SN_{0.93}GN_{0.07}$ near 233 K cannot be taken to be indicative of the (homogeneous) mixture; rather, in such mixture ion transport is limited to the plastic domains, which represent only a fraction of the total volume of the sample. This suggests that also the conductivity values reported in Ref. 28 may not be intrinsic to a homogeneous phase and that they may be actually limited by domain-boundary effects, which would rationalize why the Stokes-Einstein relation with σ_{dc} is not verified in the equimolar SN-GN mixture.[28] The above discussion indicates that the issue of phase separation is an important aspect of the phase behavior of succinonitrile-based mixtures, an aspect that has not been fully explored so far, and that as we will show in the following is also relevant for SN mixtures with lithium salts.

Given that succinonitrile has been proposed as basis material for novel solid-state electrolytes supporting Li-ion conduction,[14–18] it is interesting to study the molecular dynamics and conduction properties of SN-based systems upon doping with lithium salts. Fig. 4*a* displays low-temperature loss spectra acquired on the $SN_{0.89}GN_{0.11}$ plastic co-crystal. The sample exhibits a secondary relaxation at higher frequency (lower temperature) than the primary α process; this fast relaxation was reported also in the nearly equimolar mixture,[28,29] but its exact origin was not identified.[28] We refer to this relaxation as γ relaxation to maintain the nomenclature of Ref. 28.

As visible in the Arrhenius plot of Fig. 4*b*, the characteristic frequency f_γ of the fast relaxation (obtained by a fit of the dielectric loss data assuming a Havriliak-Negami profile, Eq.s 1 and 2) is fundamentally unchanged in the presence of Li^+ ions. Comparison with the data of Ref. 28 shows that it is also barely influenced by the stoichiometry. This entails that the γ relaxation is an intramolecular (conformational) dynamic process which is not affected by intermolecular interactions or by the presence of ions. The γ relaxation might correspond to transitions between different isomeric forms of the dinitrile species. Instead, the frequency f_α of the collective relaxation process is lower in Li-doped mixtures (especially at lower temperature), due to the stronger local interactions brought about by the presence of the Li^+ ions and the counter-ions.[6,44]

Fig. 4*c* shows a series of loss spectra acquired on the $SN_{0.87}GN_{0.13}$ mixture doped with $LiCF_3SO_3$. The spectra below 190 K are characterized by the presence (besides the α feature) of an intense space-charge relaxation, indicating that the sample is in a mixed solid phase at low temperature. The frequency of the space-charge relaxation is higher in $LiCF_3SO_3$-doped $SN_{0.87}GN_{0.13}$ mixture than in the $SN_{0.93}GN_{0.07}$ sample (Fig. 3); it should be noted that the pristine $SN_{0.87}GN_{0.13}$ mixture displays partial transformation to the fully ordered phase only below 170 K, and that no space-charge relaxation is visible in this sample (see Fig. 1). Similar results were obtained also in the $LiBF_4$-doped and $LiN(CF_3SO_2)_2$-doped $SN_{0.87}GN_{0.13}$ samples (not shown).

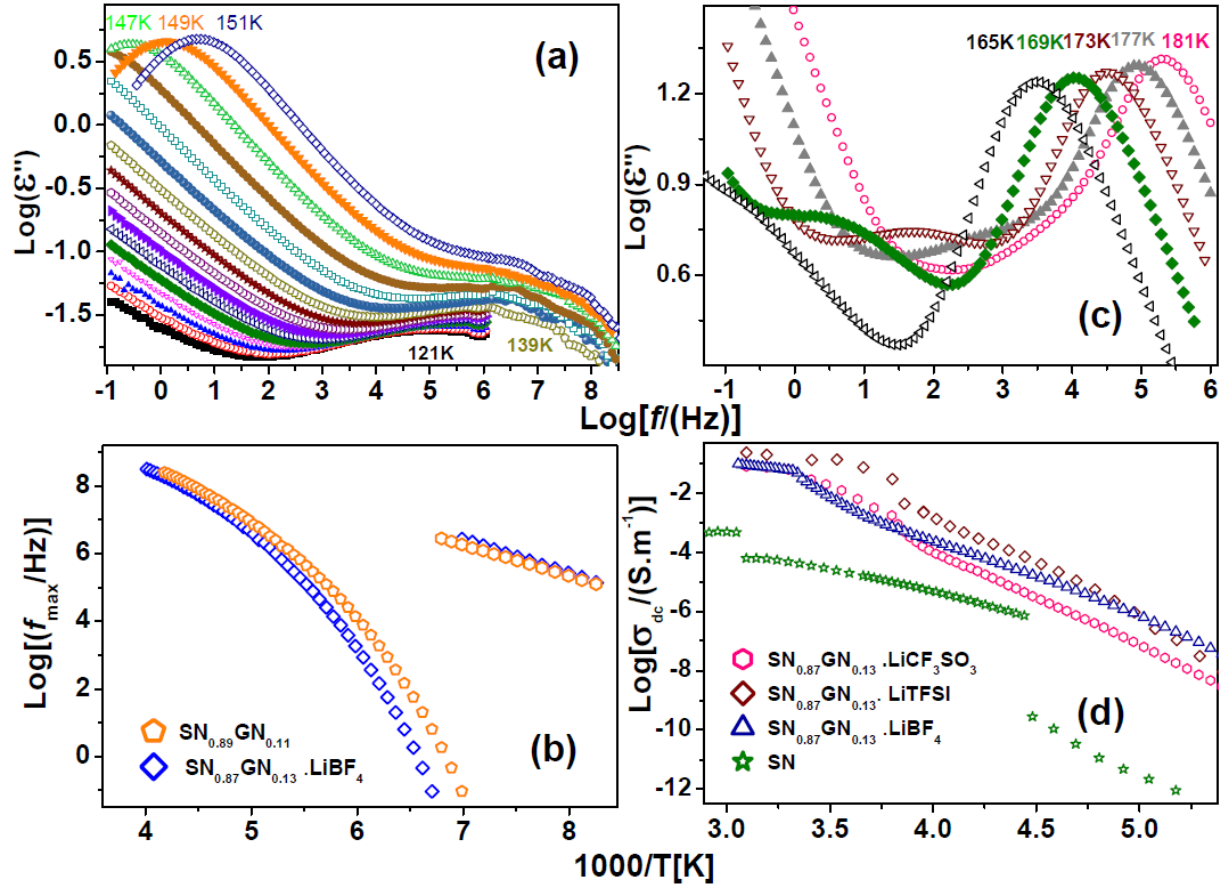**Figure 4.** (a) Dielectric loss spectra of the $SN_{0.89}GN_{0.11}$ plastic cocrystal, in the temperature range between 151 and 121 K, where a secondary (γ) relaxation is visible (at higher frequency than the α peak). (b) Arrhenius plot of f_α and f_γ for the same sample and for the $LiCF_3SO_3$-doped $SN_{0.87}GN_{0.13}$ mixture. (c) Loss spectra of the $LiBF_4$-doped $SN_{0.87}GN_{0.13}$ mixture between 181 and 165 K. (d) Arrhenius plot of the dc conductivity of the $SN_{0.87}GN_{0.13}$ sample doped with three different lithium salts, compared to that of pure SN.

The dc conductivity of pure SN and of SN-polymer mixtures increases significantly upon doping with lithium salts, due to the higher ion density.[13–18] The same is true also for the binary nitrile mixtures studied here, as visible in Fig. 4*d*, which shows the dc conductivity of the $SN_{0.87}GN_{0.13}$ sample doped with three different lithium salts ($LiBF_4$, $LiCF_3SO_3$, and

LiN(CF$_3$SO$_2$)$_2$) compared with that of pure SN. The Li-doped mixtures exhibit all a kink at a temperature similar to or lower than that of the onset of the liquid-to-plastic transition in the SN-GN mixtures (see Fig. 3a). This kink is due to the fact that the Li-ion conductivity is generally lower in a (partially) plastic crystalline phase than in the liquid. For all Li-salt doped samples we observed the breakdown of the Walden and Stokes-Einstein relation, as reported for the LiBF$_4$-doped mixture in Ref. 6, which is indicative of a decoupling between small-ion diffusion and nitrile reorientations when the conductivity is dominated by Li$^+$ ions. This shows that the correlation between conductivity and molecular rotational dynamics is only present in the undoped materials, where conduction is dominated by self-diffusion of ionized molecules. If charge transport in the undoped mixtures were mediated by the simple drift of atomic or diatomic ions though the interstitial voids, one would expect the same lack of correlation between ion drift and rotational dynamics. In other words, the validity of the Stokes-Einstein relation only in the undoped co-crystals rules out that the ionic conduction of pristine mixtures is due to H$^+$ or OH$^-$ ions, confirming our interpretation of the anomalously high ionic conductivity of nitrile cocrystals as due to self-diffusion.

As a final remark, we point out that the SN$_{0.93}$GN$_{0.07}$ sample doped with LiBF$_4$ could be partially supercooled from the liquid phase without transforming completely into a solid phase (not shown). The possibility of supercooling SN-GN mixtures was reported in Ref. 29, but only at very high GN content, while the undoped SN$_{0.93}$GN$_{0.07}$ sample undergoes a transition to the plastic phase and even partial crystallization at lower T, as discussed above. The possibility of partially supercooling the Li-doped sample suggests that the stronger ionic interactions and/or the presence of the third molecular component (the BF$_4^-$ counterions) is able to partially preserve the liquid state. This result and Fig. 4c show that if a specific SN mixture is to be considered for

electrolyte applications, the issue of phase separation induced by Li-ion doping should be investigated.

Conclusions.

We employed scanning calorimetry and dielectric spectroscopy to probe the plastic cocrystals formed by succinonitrile with glutaronitrile and acetonitrile. The samples display a tendency to phase-segregate: the liquid-to-plastic transition takes place across a wide temperature interval, and the transition from the plastic phase to the fully-ordered low temperature phase sometimes leads to the formation of succinonitrile-rich domains surrounded by a plastic matrix. Stable and homogeneous plastic-crystalline phases appear to form only when adding to succinonitrile specific (low) amounts of glutaronitrile. These solid mixtures display self-diffusion of a minority of neutral and ionized molecules, which give rise to an exceptionally high ionic conductivity at room temperature. The succinonitrile-glutaronitrile plastic samples are found to obey the Walden and Stokes-Einstein rules typical of liquid electrolytes, which is a wholly unexpected feature for a plastic-crystalline phase. In detail, the ratio $f_\sigma / (f_\alpha k_B T)$ is a temperature-independent constant equal to approximately 10^{15} J^{-1} for all studied succinonitrile-glutaronitrile mixtures.

The Stokes-Einstein relations break down in the samples doped with lithium salts, which confirms that the rotation-drift correlation is only valid when charge transport is dominated by self-diffusion of bulky molecular ions, while the motion of smaller atomic ions is decoupled from the molecular dynamics. Doping with lithium boosts the ion conductivity and slows the collective molecular dynamics of the mixtures, while leaving unaffected the fast relaxation dynamics associated with intramolecular (configurational) changes. Given that all mixtures are partially liquid at room temperature, they cannot be employed as solid-state Li+-ion electrolytes.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

ABBREVIATIONS

SN succinonitrile; GN glutaronitrile; AN acetonitrile; DSC differential scanning calorimetry; VFT Vogel-Fulcher-Tammann; SC space charge.

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