Mixtures of *m*-fluoroaniline with apolar aromatic molecules: phase behaviour, suppression of H-bonded clusters, and local H-bond relaxation dynamics

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ABSTRACT

We employ differential scanning calorimetry, IR spectroscopy, X-ray powder diffraction and dielectric spectroscopy to characterize binary mixtures of *m*-fluoroaniline (mFA), a rigid-molecule glass former, with two non-self-associating molecules containing benzene rings, namely *m*-xylene (mX) and a distyrene derivative (DS). The addition of mX suppresses the formation of H-bonded mFA clusters. While both mX and DS dilute the H-bond density of mFA, they have opposite effects on the glass transition temperature (T_g) and structural relaxation time of mFA, with mX acting as a plasticiser and DS as an antiplasticiser. While the mFA-DS mixtures can be studied in the supercooled liquid regime at DS molar mass fraction as high as 0.9 without undergoing phase separation, the mFA-mX mixtures remain homogeneous at low temperatures only up to a mX molar fraction of 0.5. All homogeneous mixtures display a structural relaxation which shifts according to the T_g of the mixture, and a secondary relaxation which remains virtually invariant with respect to that of pure mFA. For mX molar fraction higher than 0.5, the mixtures phase-separate into almost pure crystalline mX domains and a mFA-rich amorphous phase. Upon partial crystallization the structural relaxation time and T_g of the remaining amorphous fraction shift to larger values, consistent with the increased effective mFA concentration. At the same time, the secondary relaxation time undergoes a dramatic shift of more than two decades. These findings allow identifying the secondary relaxation in the rigid-molecule mFA glass former as a local reorientational motion of a *m*-fluoroaniline moiety around one of its H-bonds, a rotation that is strongly affected if the mobility of the H-bond sharing species is quenched by crystallization.

Table of Contents/Graphical Abstract Image

1. Introduction

Hydrogen (H) bonding is responsible for a number of important effects in both the liquid and solid states. In H₂O and other single component systems, the H-bond network is responsible for high melting and evaporation points. In the paradigmatic case of water, H-bonding also determines the anomalous density behaviour, the solvation properties, and the large heat capacity,^{1,2} and enables a particular type of charge transport known as Grotthuss proton shuttling and responsible for the dc conductivity of pure water and ice.^{3,4}

H-bonding in multicomponent or macromolecular systems leads to an even richer set of properties, which are in general harder to quantify or control. It is responsible for example for the large molecular dipole moment of the native form of biopolymers (*e.g.* DNA and protein helices) and for protein folding⁵ and molecular recognition.⁶ It plays a crucial role in determining the polymorphism of H-bonded systems,^{7,8,9,10} to the point that it can be exploited for the design of extended supramolecular structures (crystal engineering).¹¹ The Grotthuss mechanism is active in multicomponent systems such as some hydrates and water clathrates¹² and in surface hydration layers condensed onto low-conductivity materials.^{13,14}

In single-component H-bonded systems, macroscopic properties such as transition temperatures and enthalpies provide direct quantitative information about H-bonds, and spectroscopy allows the direct investigation of the structure and dynamics of the H-bond network. Such studies are less straightforward and in general less conclusive for multicomponent condensed phases, due to the more important role of heterogeneities and to the presence of different types of H-bonds formed by different donors and acceptor moieties. A prominent example is that of aqueous solutions, where solubility and solvation geometry depend in a crucial way on the subtle balance between enthalpic and entropic contributions to the free energy.¹⁵ A systematic study of multicomponent systems

as a function of concentration can in principle overcome these difficulties. Binary systems are, in this sense, the simplest systems where the effect of the heterogeneity on self-association and on the H-bond dynamics can be experimentally tested.^{10,16,17} Gathering quantitative information on the impact of H-bonding in binary systems is a crucial prerequisite to extend our understanding of the role it plays for the formation of complex molecular architectures and for the dynamics of biological processes.

The aim of this paper is to understand the impact of H-bonding on the physical properties of binary mixtures of small organic aromatic molecules, such as their phase behaviour, vibrational frequencies, relaxation dynamics, and glass-transition properties. In particular, we investigate the effect of the dilution of the density of H-bonding groups in a simple binary system composed of a self-associating molecule and an apolar molecule of similar structure but incapable of forming H-bonds except as very weak acceptor. The H-bonding molecule is *m*-fluoroaniline, whose molecular structure is shown as inset to Figure 1(b). Our choice is motivated by the fact that X-ray and neutron scattering experiments and Monte Carlo numerical simulations have shown the formation of H-bonded clusters in this molecular liquid,^{18,19} which furthermore displays, despite the rigid molecular structure, a rich relaxation dynamics that is accessible down to below the glass transition temperature.^{20,21}

The supra-molecular spatial organization in liquid *m*-fluoroaniline is similar to that of *m*-toluidine, which consists of clusters centred about an amine group with the aromatic rings of the involved molecules pointing away from the central H-bonds.¹⁸ The clusters have a limited size due to the steric hindrance of aromatic rings: the typical separation between adjacent clusters, as determined experimentally, is about 12 Å, which corresponds to clusters of no more than 10 molecular units.¹⁹ The hydrophobic core of the molecules excludes the build-up of an extended H-bond network such as that of water

or other self-associating systems. The formation of *m*-fluoroaniline clusters likely results from the competition between the directional H-bond interaction of the amine and fluorine groups on one hand, and the effective repulsion between these functional groups and the hydrophobic aromatic benzenic rings. The aromatic rings, on the other hand, may also interact via attractive π - π interactions. Such competition between different types of specific interactions is known to give rise to a rich variety of self-assembled morphologies in the solid phase of H-bonding aromatic moieties.^{22,23}

The main experimental tools that we employ are calorimetry, IR spectroscopy, and dielectric relaxation spectroscopy. The latter technique is one of the most powerful techniques to investigate dipolar relaxation phenomena in glass forming systems. The most prominent dielectric relaxation feature in non-self-associating glass formers is the structural (α) relaxation, which displays an asymmetric and broad frequency profile and whose kinetic freezing is associated with the glass transition temperature.²⁴ On the other hand, in many H-bonded liquids such as water, monoalcohols, amines and peptides, the most intense dielectric loss feature has a symmetric and relatively narrow frequency profile, which is usually modelled with a Debye or Cole-Cole function (see Experimental section) and therefore dubbed “Debye-like” relaxation. The Debye-like relaxation is assigned to a cooperative H-bond network dynamics involving the rearrangement of H-bonds and a concomitant reorientation of the constituent molecules. While systems where H-bonding is the dominant interaction, such as water, exhibit only a Debye-like primary relaxation, whose kinetic freezing marks the glass transition,^{25,26,27,28} in many liquids where H-bond interactions are more diluted (such as monoalcohols with relatively long aliphatic chains) the Debye-like relaxation is spectrally separated from the structural α relaxation, which is observed at shorter characteristic times. In these latter systems, the Debye-like relaxation is ascribed to the formation of fluctuating H-bonded ring and chain

structures.^{29,30,31} In this respect, *m*-fluoroaniline is an atypical H-bonded liquid: rather than an intense Debye-like relaxation at low frequency, it displays a low-intensity, broad secondary relaxation feature at high frequency, referred to generically as “ β relaxation”, which has been associated with some internal dynamic process in the H-bonded clusters.²⁰

Here, we mix *m*-fluoroaniline with *m*-xylene, another aromatic benzene derivative without H-bonding functional groups (see inset to Figure 1(b)), and with a distyrene derivative, also characterized by benzenic rings and devoid of H-bond groups. Both types of binary mixtures exhibit a glass transition temperature intermediate between those of the pure components, and both a cooperative structural relaxation and the secondary relaxation process typical of pure *m*-fluoroaniline. Binary mixtures where *m*-xylene is the majority component undergo a phase separation into *m*-xylene-rich crystallites and *m*-fluoroaniline-rich amorphous regions. The secondary relaxation time is strongly influenced by the morphology of the sample: while in the homogeneous mixtures with either *m*-xylene or oligostyrene it is virtually unaffected compared to pure *m*-fluoroaniline,²⁰ in the phase-segregated, partially crystallized fluoroaniline-xylene mixtures it displays a dramatic shift by two or even three orders of magnitude. The spectral position, line shape, and intensity of the secondary relaxation, together with its strong sensitivity to the presence of domain boundaries, indicate that it is due to H-bonded dimers, whose dynamics is strongly affected when one of the molecules forming the dimer loses its mobility due to the direct interaction with a crystalline domain.

2. Experimental

m-fluoroaniline (mFA) and *m*-xylene (mX) were purchased from Aldrich Chemical Company with a purity of 99%. The distyrene derivative (DS, chemical formula $\text{CH}_3(\text{CH}_2)_3(\text{C}_6\text{H}_5)_2\text{H}$, molecular weight of 266 g mol⁻¹) was purchased from Polymer

Standards Service (Mainz, Germany). All three compounds are liquid at room temperature, and mFA_{1-x}mX_x mixtures with $0.25 \leq x \leq 0.95$ and a mFA_{1-x}DS_x mixture with $x = 0.9$ were prepared by simply mixing the appropriate amount of the pure materials, which were used as received without further purification.

Differential scanning calorimetry (DSC) thermograms were acquired using a Perkin-Elmer DSC-7 instrument equipped with a homemade liquid nitrogen low-temperature controller. Measurements were carried out in the range between 123 and 273 K, with a heating/cooling rate of 2 K min⁻¹. The same experimental procedure was applied to all concentrations under investigation: the sample was first cooled down from room temperature to around 123 K and then heated up again to room temperature. Fourier-transform infrared spectroscopy (FTIR) was performed on the liquid mFA–mX mixtures at room temperature (298 K) in the region of the NH stretching bands ($\lambda = 3150 - 3600$ cm⁻¹), using a Thermo Scientific Nicolet 6700 FT-IR spectrometer with a resolution of 0.01 cm⁻¹.

High-resolution X-ray powder diffraction (XRPD) profiles were recorded on selected mFA–mX mixtures at several temperatures after quenching to 120 K, using a vertically mounted INEL cylindrical position-sensitive detector (CPS120). The latter was used in the Debye-Scherrer geometry (transmission mode), enabling simultaneous recording of the diffraction intensity over a 2θ -range between 4° and 120° (angular step ca. 0.029° (2 θ)). The generator voltage and current were set to 35 kV and 35 mA, respectively, and monochromatic Cu-K α 1 radiation ($\lambda = 1.54056$ Å) was selected using a Ge(111) crystal monochromator. Temperature control was achieved with a liquid-nitrogen 700 series Cryostream Cooler by Oxford Cryosystems operating from 90 to 500 K with a temperature accuracy of 0.1 K. The initially liquid mixtures were placed into 0.5 mm-

diameter Lindemann capillaries which were continuously rotated perpendicularly to the X-ray beam during data collection to minimize possible effects of preferred orientations.

The frequency and temperature dependence of the complex dielectric permittivity of the samples was determined using broadband dielectric spectroscopy. The measurements were performed with two different setups sensitive to different frequency ranges, namely a capacitor connected via electrical contacts to a Novocontrol Alpha analyzer (10^{-2} to 10^7 Hz), and a smaller capacitor mounted at the end of a coaxial waveguide in reflection geometry and connected to a HP4291 impedance analyser (10^6 to 10^9 Hz). Temperature control of the sample was achieved using the Novocontrol Quatro Cryosystem employing N_2 gas flow from a liquid nitrogen dewar and a resistive Pt sensor (PT100) in thermal contact with one of the capacitor plates. The liquid mixtures were loaded into stainless steel capacitors specially designed for liquid samples, with the parallel-plate electrodes separated by 50 μm thick silica spacers. The temperature interval of the measurements was between 114 and 253 K, with ± 0.1 K stability.

BDS experiments yield the complex permittivity of a sample as a function of frequency. The imaginary permittivity spectra $\epsilon''(\omega)$ (the so-called loss spectra) were fitted as the sum of distinct spectral components, each representing a different dipolar relaxation process (primary, secondary, and, in mixed-phase samples, space-charge relaxations), plus a conductivity background, visible only well above the glass transition temperature of the mixtures. Each relaxation loss was modelled as the imaginary part of a phenomenological Havriliak-Negami function, whose analytical expression is:^{32,33}

$$(1) \epsilon_{HN}''(\omega) = \frac{\Delta\epsilon}{(1 + (i\omega\tau_{HN})^c)^d}.$$

Here, $\Delta\epsilon$ is the so-called dielectric strength (intensity) of the relaxation, the exponents c and d are shape parameters related to the slopes of the loss peak in logarithmic

representation,²⁴ and τ_{HN} is a fitting parameter from which the characteristic time τ at which the imaginary part of the permittivity is maximum is obtained as:

$$(2) \tau = \tau_{HN} \left(\sin \frac{c\pi}{2+2d} \right)^{-1/c} \left(\sin \frac{cd\pi}{2+2d} \right)^{1/c}.$$

By fitting the data using Eq. 1 we found that while the structural relaxation associated with the glass transition had a Havriliak-Negami line shape, the secondary and the space-charge relaxations were best described as the imaginary part of a Cole-Cole function,^{34,35} which is a special case of the Havriliak-Negami function (Eq. 1) with $d = 1$ and $c \neq 1$. The Cole-Cole function reduces to the well-known Debye function if $c = 1$. While the imaginary part of the Havriliak-Negami function has an asymmetric line shape, that of the Cole-Cole function is symmetric, and for this model function the parameter τ_{HN} coincides with the time τ at which the imaginary permittivity is maximum.

3. Results and discussion

3.1 Characterization by FTIR and DSC

As mentioned in the introduction, addition of m-xylene (mX) to m-fluoroaniline (mFA) leads to a reduction in the density of the H-bonding groups of mFA and thus to a dilution of the H-bond network. Figure 1(a) shows the FTIR spectra of the N-H stretch mode in binary mixtures with different mX concentration. The frequency of this mode is modified when the hydrogen atom of the amino group participates in a H-bond. It may be observed that both the symmetric and the asymmetric stretching mode are considerably modified at high mX molar fraction (i.e., in correspondence with a strong reduction of the aggregate population). In particular, while for each (symmetric and asymmetric) stretching mode two different FTIR bands are observed in pure mFA, corresponding to aggregated and non-aggregated mFA molecules, at high mX content the component due to the H-bond-induced clusters is missing. This is visualized in Figure 1(b), which shows the relative

weight of the monomer mFA component in the FTIR spectrum as a function of the molar fraction of m-xylene (x). Such ratio tends to unity as the molar fraction of mX increases. We thus conclude that the addition of mX leads to a suppression of the H-bonded clusters in the liquid mixtures, as may be expected. This behaviour is similar to that of alkane solutions in tert-butanol, where concentration-dependent aggregation occurs.³⁶

Figure 1. (a) FTIR absorption spectra of binary mFA–mX mixtures in the region of the N-H stretching bands, for different mX concentrations. (b) Ratio of the area of the

component due to the mFA monomers to the total area (monomers plus clusters), for both N–H stretching modes (symmetric and asymmetric).

The thermal behaviour of the mixtures, as determined by DSC measurements, is shown in Figure 2. The samples behaved differently according to their composition: for a molar fraction of mX lower than $x < 0.75$, only the characteristic step-like feature signalling the glass transition is visible in the DSC thermograms (Figure 2(a)). This shows that the binary mixtures sufficiently rich in mFA can be supercooled down to the glass transition without undergoing crystallization neither upon cooling nor in the subsequent heating. For a molar composition $x \geq 0.75$, during the heating above T_g the recrystallization and melting processes are observed (in the DSC thermograms, recrystallization takes place ca. 50 K below the melting point). Dashed lines in Figure 2(a) indicate the determinations of the characteristic temperatures. In the schematic phase diagram displayed in Figure 2(b), a typical melting point depression with respect to pure *m*-xylene ($x = 1$) is observed with increasing *m*-fluoroaniline concentration, a typical feature of (eutectic) binary equilibrium phase diagrams. The liquidus lines, calculated by means of the Schröder-Van Laar equation³⁷ assuming zero solid-state solubility, are shown as bold red or blue lines. The red line is calculated assuming the melting temperature of mFA reported in Ref. 38, and the blue one that of Ref. 39.

The glass transition could be reliably detected only for an mX molar concentration up to $x = 0.75$, as for higher mX content the glass transition occurred at lower temperature, at the very limit of the measuring range of our DSC setup (see however the BDS results in the next section). The characteristic temperatures obtained from the DSC thermograms are summarized in Table 1 for all studied concentrations. The thermal evolution of the calorimetric glass transition T_g is depicted with open diamonds in Figure 2(b). The data

indicate a roughly linear dependence, with T_g decreasing with increasing mX concentration (mX has a lower glass transition temperature than mFA, which results in a plasticizing effect^{40,41} on *m*-fluoroaniline).

Figure 2. (a) DSC thermograms of the mFA_{1-x}mX_x binary mixtures with $x = 0.50$ (blue) and $x = 0.75$ (green). Dashed lines indicate the determinations of T_g , T_r and T_m . (b) Equilibrium and non-equilibrium phase diagram of the mFA–mX binary system. The red

and blue lines correspond to the liquidus calculated assuming two different melting temperatures for mFA (see the text for details). The horizontal dashed lines mark the position of the eutectic temperature in both cases. The closed and open circles correspond, respectively, to the melting and crystallization temperatures, obtained from the DSC thermograms. Diamonds correspond to the T_g obtained with DSC; the T_g values for the pure compounds are those of Ref. 39. Crosses and black triangles correspond to the kinetic T_g calculated from dielectric measurements on the α and α^* relaxations, respectively. The oblique dashed line is a linear fit. For values see Table 1.

x	T_m [K]	T_r [K]	T_g DSC [K]	T_g BDS [K]
0	229 [ref. 38], 220 [ref. 39]		173 [ref. 39]	171.7
0.25			163.0	164.7
0.50			155.0	155.2
0.65				147.7
0.75	220.4	175.0	142.3	141.2
0.90	227.2	181.3		
1	232.0	180.6	125.5 [ref. 39]	

Table 1. Melting (T_m) and recrystallization (T_r) temperatures of the $mFA_{1-x}mX_x$ mixtures, and their glass transition temperature obtained from calorimetry (T_g DSC) and dielectric spectroscopy (T_g BDS).

3.2 BDS characterization

Figure 3 displays selected low-temperature isothermal loss spectra acquired on three distinct mX molar fractions ($x = 0.25$, 0.75 and 0.90) between 117 and 237 K. All spectra of the $x = 0.25$ and $x = 0.75$ mixtures are characterized, at sufficiently low temperature,

by a prominent primary relaxation loss, followed by a secondary loss of much lower intensity at higher frequency (or lower temperature). The spectra of the $x = 0.9$ sample are characterized by the presence of a third relaxation process besides the former two, which is visible at frequency lower than that of the primary (α) relaxation and corresponds to an interfacial space-charge relaxation (see e.g. the spectrum at 201 K in Figure 3(c)). Such relaxation, known as Maxwell-Wagner-Sillars polarization, is due to the fact that the $x = 0.9$ sample is actually a phase-separated, partially crystalline sample, as we show later on.

The observation of a secondary loss in mixtures of rigid molecules incapable of internal conformational dynamics is intriguing. For mX molar fractions between 0 and 0.50 (see Figure 3(a)), the loss curves follow a behaviour similar to that of pure mFA, with an α relaxation whose intensity and spectral position are functions of the m-xylene content, and a weaker secondary β relaxation whose spectral position is barely affected by the composition of the mixture and matches approximately that of the β relaxation observed in ambient-pressure studies on pure mFA.^{42,43} This entails that the origin of the β relaxation in the binary mixtures (at least with x up to 0.50) is the same as that of pure mFA. The spectral line shape undergoes a smooth evolution between one spectrum and the next, without any abrupt change of the frequency nor intensity of the relaxation with increasing temperature, which indicates that the mixtures remain as homogeneous as they are in the liquid state.

All spectra were fitted as described in the experimental section in order to extract quantitative information about the relaxation times and dielectric strength of the relaxation processes. The relaxation times of non-phase-separated, homogeneous mixtures (with x up to 0.65) are displayed as Arrhenius plot in Figure 4. The β relaxation times could be fitted with an Arrhenius law, except for the high temperature data of pure

mFA, for which a cross-over is observed at 195 K, as already reported in previous studies.^{20,21} In contrast, the primary α relaxation displays a non-simply activated behaviour. We define as customary a kinetic arrest temperature as the temperature at which the relaxation time of the α relaxation reaches a value of 100 s ($\log(\tau_\alpha) = 2$). This temperature is reported in the last column (labelled T_g BDS) of Table 1, where it can be observed that it matches the calorimetric T_g of the corresponding mixture. We therefore conclude that the α dielectric loss of the mixtures is the structural relaxation associated with their glass transition.

Figure 3. Selected isothermal dielectric loss spectra of three $mFA_{1-x}mX_x$ mixtures: (a) $x = 0.25$ between 237 and 177 K every 6 K; (b) $x = 0.75$ between 197 and 125 K every 6

K; (c) $x = 0.90$ between 201 and 129 K every 6 K. Solid lines correspond to fits and dotted lines to fit components; the latter are shown only for few spectra (183 and 117 K in (a); 163 and 125 K in (b); 201, 165 and 129 K in (c)).

The shift of the α relaxation towards shorter times as the mX molar fraction increases is indicative of the plasticizing effect of mX on mFA. In systems where the intermolecular interactions are dominated by H-bonding, such as water or methanol, the primary relaxation has a narrow, symmetric line shape. In contrast, the α loss in mFA and its mixtures with mX is rather broad and clearly asymmetric, as in non-self-associating glass formers; this indicates that there is not a single dominant intermolecular interaction in the mFA–mX binary system.

As for the origin of the secondary β relaxation, the fact that it is unaffected by the mX content while the α relaxation is (*i.e.*, the lack of a plasticizing effect on the secondary process) allows discarding the initial assignment⁴³ of the secondary relaxation of *m*-fluoroaniline as a Johari-Goldstein relaxation.⁴⁴ In fact, Johari-Goldstein relaxations are closely related to the structural relaxation and their characteristic time scales with that of the α process.^{45,46} That the β relaxation is not of the Johari-Goldstein type is consistent also with the fact that the Coupling Model^{47,48} does not apply to our data, as visible in Figure 4.

Figure 4. Relaxation times as a function of reciprocal temperature for the α (closed symbols) and β (open symbols) relaxations of homogeneous $mFA_{1-x}mX_x$ mixtures with x between 0 and 0.65. For $x = 0.65$, only data below the recrystallization temperature are shown, where the supercooled liquid mixture is still homogeneous (see the text). The star represents the glass transition temperature of pure mX (after Ref. 39), and centre-dotted symbols the predicted secondary relaxation times using the Coupling Model.

BDS experiments measure the change in macroscopic polarization under an applied electric field. Rigid molecules such as mFA and mX do not possess any internal degrees of freedom that might result in conformational isomerism, and thus cannot display any dipolar conformational relaxation.^{49,50} Having discarded also a Johari-Goldstein process, the only possible origin of the secondary dielectric relaxation in mFA and mFA – mX mixtures is either the variation of polarization brought about by the breaking and reformation of H-bonds, or the motion of next-neighbour molecules reorienting around

their mutual H-bond, or else a more cooperative dynamics of the H-bond network as a whole. A recent dielectric study of pure mFA under an applied hydrostatic pressure argued that the β relaxation of this compound originates from a local dynamics inside H-bonded clusters.²⁰ The fact that our α and β relaxation times converge to the same value at high temperature suggests that the β process is a local motion which also takes place as an intermediate step of the α relaxation process: as the temperature is increased, the character of the α relaxation becomes less and less cooperative and thus more representative of the local dynamics around a single H-bond than that of a whole cluster.

In order to gain more insight on the exact origin of the secondary relaxation we look at the results for phase separated samples. For x equal to 0.65 and 0.75 (Figure 3(b)), one can follow the evolution of the α and β peaks with temperature only up to approximately 165 K. Because the samples were initially quenched from the liquid phase, they tend to retain, at least at low temperature (lower than 165 K) a homogeneous amorphous character. However, an increase of the temperature from this low temperature metastable state provides sufficient thermal energy for the sample to phase-separate (Figure 2(a)). When this happens, the primary α relaxation fades away and a new relaxation, which we will refer to as α^* , becomes visible at higher frequencies (shorter times); the effect can be clearly visualized by comparing the loss spectra of the $x = 0.75$ sample at 161 and 167 K (Figure 3(b)). At the same time the β relaxation undergoes a dramatic shift to lower frequency, or, more correctly, its intensity vanishes and a new secondary relaxation, which we label as β' , appears at lower frequency.

The effect of the phase separation on the dielectric response is best visualized in Figure 5. Panel (a) shows the comparison between the loss spectra of all studied samples at $T = 171$ K. While for x up to 0.5 a single structural relaxation is present, for $x = 0.65$ two intense relaxations are observed, indicative of a mixed-phase sample. A similar behaviour

is observed for $x = 0.75$, while for larger mX molar fractions only the α^* relaxation is visible at all temperatures. The frequency shift of the secondary relaxation is clear in the comparison of the loss spectra acquired at 143 K after quenching the mixtures, shown in the Figure 5(b): the spectral position of the secondary relaxation for $x > 0.75$ is totally changed with respect to the homogeneous mixtures with $x < 0.75$.

Figure 5. Comparison of the dielectric loss spectra at 171 K (a) and 143 K (b) for different mX molar fractions.

Another effect of the macroscopic phase separation that is typically observed with dielectric spectroscopy, is the emergence of Maxwell-Wagner-Sillars space-charge relaxations which are due to the sample heterogeneity, namely, to the difference in the static permittivity and dc conductivity values of the different phases.²⁴ All phase-separated samples displayed a relaxation feature at significantly lower frequency than both structural relaxations (in fact, at lower frequency than the α relaxation of pure mFA). The feature was barely visible in the phase-separated sample with average mX molar fraction of $x = 0.65$, while it became more intense with increasing mX molar fraction (see Figure 3(b)). In the following we focus mainly on the molecular processes and not on this interfacial space-charge relaxation.

Our temperature-dependent XRD characterization of the $x = 0.75$ sample (Figure 6(a)) shows that phase separation occurs by formation of crystalline domains isostructural to mX, with the rest of the sample remaining in the amorphous state (supercooled liquid or glassy, depending on the temperature). Since part of initially homogeneous mixture phase separates into crystallites that are almost pure in mX, the remaining amorphous mFA–mX domains are correspondingly richer in *m*-fluoroaniline. In Figure 6(a) it is observed that even right after quenching the liquid mFA_{0.25}mX_{0.75} down to 120 K, the sample already contains a small fraction of crystalline material; this fraction increases as the sample temperature is increased to 180 K, where the amorphous (bump-like) background is significantly reduced in intensity and the diffraction peaks become more prominent. All diffraction peaks could be assigned to crystalline *m*-xylene, as visible from the comparison of our spectra with that of a mX polycrystalline sample measured at 4 K.⁵¹ This shows that the two compounds do not form a solid solution within a significant concentration range, as may be expected from the lack of H-bonding groups in the mX

species. The samples with $x > 0.75$ always displayed the maximum phase separation also right after quenching from the liquid state (not shown).

All primary (α , α^*) peaks were fitted with a Havriliak-Negami function (Eq. 1), while for both secondary (β and β') relaxations, and for space-charge relaxations, when present, the best fit was obtained with a Cole-Cole line shape (Eq. 1 with $d = 1$). The Cole-Cole exponent c of the space-charge relaxation was between 0.8 and 1, in agreement with the expectation for a Maxwell-Wagner-Sillars polarization process.²⁴ The Arrhenius plot of the relaxation times of all samples is shown in Figure 6(b). The space-charge relaxation could only be fitted in the samples with $x > 0.65$.

Both α and α^* relaxations exhibit non-Arrhenius temperature dependence. It may be observed that the α^* relaxation of the $x = 0.9$ sample is almost perfectly overlapped with the α relaxation of the homogeneous $x = 0.25$ mixture. This observation, together with the fact that only (part of) the mX fraction crystallizes, allows concluding that the α^* relaxation is the structural relaxation of the mFA-rich amorphous domains present in the phase-separated samples. The same conclusion can be reached by looking at the dielectric and calorimetric glass transition temperature of phase-separated samples (filled triangles in Figure 2(b), and inset to Figure 6(b)), which lies in between those of pure mFA and that of the homogeneous mFA_{0.5}mX_{0.5} mixture. The above discussion implies in particular that the mFA_{0.1}mX_{0.9} liquid mixture phase-separates upon cooling into amorphous domains with a composition close to mFA_{0.75}mX_{0.25} and representing roughly 13% (=10/75) of the sample, and mX crystallites occupying the remaining 87%. The phase separation of the samples with $x \geq 0.65$ obviously leads to the suppression of the α peak of the homogeneous mixture of high mX content.

Figure 6. (a) XRPD patterns of the mFA_{0.25}mX_{0.75} sample right after the quench to 120 K (green) and after a subsequent heating to 180 K (red). For comparison purposes we show also the diffraction pattern of pure crystalline mX at 4.5 K (blue), retrieved from Ref. 51. (b) Relaxation times as a function of reciprocal temperature for the α (filled symbols), α* (half-filled symbols), β (open symbols), β' (centre-dotted symbols), and space-charge (MWS, strike-through symbols) relaxations observed in the mFA–mX

binary system. The star represents the glass transition temperature of pure mX. Inset: kinetic glass transition temperature T_g for both the α (filled symbols) and α^* (open symbols) relaxations. Vertical lines represent the associated error bars.

The values of the kinetic arrest temperature (dielectric T_g) extrapolated from the fits of the α and α^* relaxations are summarized in Table 2. The table also reports the corresponding fragility index m , defined as^{52,53} $m = \frac{d(\text{Log}\tau_\alpha)}{d(T_g/T)} \Big|_{T=T_g}$.

The fragility values indicate that pure mFA and its homogeneous mixtures are relatively fragile glass formers. The fragility index decreases slightly with increasing mX content, which entails that the dynamic correlation decreases with decreasing H–bond density. This experimental result can be associated with the lower number and the smaller size of the H-bonded clusters as the mX content increases.

X	$T_g(\alpha)$ [K]	$T_g(\alpha^*)$ [K]	$m(\alpha)$	$m(\alpha^*)$	$E_a(\beta)$ [K]	$E_a(\beta')$ [K]
0	171.7±0.4		87±1		3304±12	
0.25	164.7±0.2		79±2		4036±7	
0.50	155.2±0.8		80±2		4179±5	
0.65	147.7±0.2	167.8±0.5	78±3	84±2	4190±90	
0.75	141.0±1.0	168.4±0.4	72±2	89±2	4270±80	4470±120
0.90		163.0±1.0		80±1		4190±20
0.95		161.7±0.4		81±2		4070±40

Table 2. Dielectric glass transition temperature (T_g) and fragility index m for the α and α^* relaxations, and values of the activation energy (E_a) of the β and β' relaxations, of all mFA–mX samples studied.

In Figure 6(b) both secondary processes associated with H-bonding follow a simply-activated behaviour. The characteristic time of this secondary relaxation is observed to decrease by two or three orders of magnitude in the phase-separated, partially crystallized mFA-mX samples. As mentioned in the introduction, several H-bonding liquids (e.g., certain monoalcohols, amines, and amides) display, in addition to the structural α relaxation, a slower and more intense relaxation appearing at lower frequency, which arises from the formation and disruption of fluctuating H-bonded structures such as chains of rings and is often referred to as “Debye process” due to the line shape of its loss curve.^{30,31,54,55} In our case, the spectral position, line shape, and intensity of the β and β' relaxations are opposite to those of a Debye process: both secondary relaxations have a Cole-Cole profile with a value of the c exponent lower than 0.4, and they have a higher characteristic frequency and lower intensity than the α relaxation. This implies that the secondary relaxation in *m*-fluoroaniline cannot have the same origin as the one commonly believed to apply to the Debye-like relaxation, namely in terms of the dynamics of extended chain or ring structures. Such possibility is also excluded by the fact that the β' relaxation is observed also at very low mFA content, where the mFA molecules are too diluted in the sample to form such extended H-bond structures.

In view of this, the most likely rationalization of the secondary relaxation is that this process is due to some internal dynamics of a H-bonded dimer, that is, a relaxation process involving only two adjacent molecules. This interpretation is consistent with the dramatic shift in the frequency of the secondary process when one of the molecules loses its mobility due to the direct interaction with a crystalline domain (either because it becomes part of a solid solution isostructural to the mX crystalline domain, or because it is in direct contact with one).

It is interesting to note that the liquid phase of 1-methylindole, a rigid aromatic heterocyclic molecule that does not self-H-bond, displays, besides the structural and Johari-Goldstein relaxations, also a secondary relaxation attributed to the rotation of the molecules in the plane defined by the heterocycles, which is less hindered by interactions with next-neighbour molecules (and is thus less cooperative) compared to the structural relaxation.^{56,57,58} The phenomenology of mixtures of 1-methylindole with less polar aromatic molecules is very similar to that of the homogeneous mixtures of mFA, with a β relaxation that does not undergo any shift with respect to the pure compound while the α displays plasticising effects.⁵⁷ An interpretation of the β relaxation in terms a free rotation about an axis passing through the centre of the aromatic ring cannot hold for either *m*-fluoraniline or its mixtures, because free rotation of the mFA moieties is hindered by the formation of H-bonds, and the mFA moieties have a less marked two-dimensional character than 1-methylindole, so that an in-plane rotation does not have necessarily lower hindrance than a three-dimensional reorientational motion. However, the mFA molecule could display partially hindered, small-angle reorientations around an H-bond to which it participates, and since the molecule has a nonzero dipole moment, such reorientation would result in a change in the macroscopic dipole moment of the sample and be therefore detectable by dielectric spectroscopy.²⁴

Further insight on this issue can be gained studying mixtures with low mFA content that remain homogeneous also upon cooling. This is the case of the mFA mixture with the distyrene derivative (DS). Figure 7(a) shows selected dielectric loss spectra of the mFA_{0.1}DS_{0.9} mixture. Three separate relaxation processes are visible: a structural relaxation at lower frequency, the secondary β relaxation at higher frequency, and a third relaxation at intermediate frequencies. The Arrhenius plot of the three relaxation times is displayed in Figure 7(b). Contrary to mX, DS has a higher glass transition temperature

than mFA, and, as visible in Figure 7(b), it has an antiplasticising effect⁴¹ on its structural (α) relaxation: the α relaxation time of the mFA_{0.1}DS_{0.9} sample is intermediate between those of the pure components, as is the extrapolated dielectric T_g , which is 12 K higher in the mixture than in pure mFA.

The faster secondary relaxations of the mFA_{0.1}DS_{0.9} mixture exhibits roughly the same relaxation times and activation energy as pure mFA (Figure 7(b)), and can therefore be identified with the local H-bond β relaxation. Concerning the relaxation intermediate between the α and β processes, since the DS derivative is apolar and mFA is rigid, the only possible origin of this process is the Johari-Goldstein relaxation mentioned previously, which is a local process involving reorientation of the whole molecules as the structural relaxation, but less cooperative in character. The Johari Goldstein relaxation of pure mFA has been observed in a high-pressure dielectric study²⁰ that showed that while mFA displays a local H-bond relaxation at ambient pressure, it displays only a Johari-Goldstein relaxation under an applied moderate hydrostatic pressure. The results of Figure 7 are interesting because both processes are observed in the same sample in the same frequency window, which allows concluding that the two processes can be present simultaneously and confirms the existence of a non-Johari-Goldstein relaxation in mFA-containing samples. Our results further show that characterization of mixtures can be a powerful tool for identifying the origin of dielectric relaxation processes.^{40,59,60,61}

Figure 7. Selected dielectric spectra (a) and Arrhenius plot of the relaxation times of the primary and of both secondary relaxations (b) of the mFA_{0.1}DS_{0.9} mixture. In (b) the structural relaxation of pure mFA and pure DS are also shown for comparison. Inset to (b): schematic of a possible motion contributing to the secondary relaxations. The vector $\vec{p}$ indicates the direction of the molecular dipole moment, which changes in the relaxation process.

The most important aspect of Figure 7(b) is the fact that the β relaxation time in mFA_{0.1}DS_{0.9} is virtually unchanged with respect to pure mFA, despite the fact that the mixture contains only 10% of *m*-fluoroaniline. This shows that the dramatic shift of this relaxation in the mX case (β' relaxation) is exclusively due to the formation of crystalline domains. While the samples with similarly high mX molar fractions only exhibited the β' relaxation, the mFA_{0.25}mX_{0.75} sample displayed both β and β' relaxations. The simultaneous observation in partially crystallized mFA–mX samples, of a structural relaxation similar to that of homogeneous mixtures, and of a strongly modified β' relaxation strongly suggest that the latter relaxation is due to the H-bond dynamics taking place near the periphery of the amorphous domains. For $x = 0.75$, the amorphous domains are large enough to display both an unperturbed β relaxation stemming from the bulk of the domain, and a dramatically modified surface β' relaxation. For larger x , the amorphous domain size and thus the bulk contribution are negligible. We can therefore tentatively assign the ambient-pressure secondary relaxations to the rotation of mFA molecules around the H-bond that they form either with a next neighbour molecule in the supercooled liquid fraction (β process), or belonging to a crystalline domain (β' process). A cartoon description of what these local molecular relaxations could look like is displayed in the inset to Figure 7(b).

4. Conclusions

We have investigated the occurrence of H-bond induced clusters and secondary relaxation dynamics in a mixture of *m*-fluoroaniline with a distyrene derivative, which contains benzenic rings and no H-bonding groups, and several mixtures of *m*-fluoroaniline with *m*-xylene, another aromatic compound with only hydrogen and methyl sidegroups. Different *m*-xylene concentrations were probed by means of calorimetry, IR

spectroscopy, X-ray diffraction and dielectric spectroscopy. FTIR results unambiguously shows the suppression of the H-bond cluster size with increasing *m*-xylene molar fraction. At *m*-xylene concentrations higher than 0.65 the mixtures phase-separate into crystalline nuclei of a solid solution almost pure in *m*-xylene, and amorphous *m*-fluoroaniline-rich domains.

Addition of *m*-xylene results in a shorter relaxation time (faster dynamics) of the cooperative structural α relaxation associated with the glass transition. The fragility, and therefore the dynamic correlation, is found to decrease slightly with increasing *m*-xylene content, likely due to the lower number of hydrogen bonds. Two different secondary processes, β and β' , are observed in homogeneous and phase-separated samples, respectively. The common Arrhenius behaviour and same activation energy indicate that their microscopic origin is the same as in pure *m*-fluoroaniline. The fact that the β' relaxation has a characteristic time that is longer by two orders of magnitude than that of the β process shows that the local H-bond dynamics is dramatically influenced by the mobility of the immediate neighbourhood of the given *m*-fluoroaniline molecules. We thus assign both relaxations to a local dipolar dynamics involving rotation about the hydrogen bond formed by a *m*-fluoroaniline molecule with one of its nearest neighbours.

The dilute mixture of *m*-fluoroaniline with the apolar distyrene derivative exhibits three relaxations: a structural dynamics slower than pure *m*-fluoroaniline, the β relaxation, and a genuine Johari-Goldstein relaxation at intermediate frequencies. This allows distinguishing clearly between the two types of processes, and confirms the local H-bond character of the β relaxation.

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