Cation coordination and hydrogen bonding in potassium and magnesium based-di-amidosil hybrids

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Abstract

Fourier transform mid-infrared and Raman spectroscopies were employed to elucidate the cation/alkyene chains, cation/cross-links, cation/anion interactions and hydrogen bonding occurring in amorphous di-amide cross-linked alkylene/siloxane hybrid materials (di-amidosil) doped with potassium and magnesium triflate (KCF$_3$SO$_3$ and MgCF$_3$SO$_3$), respectively. Materials with compositions $0 > n > 1$ (where $n$ expresses the molar ratio of carbonate oxygen atoms per guest cation) were investigated. The conformations (geometry) of the alkylene chains of the host-di-amidosil matrix are not affected by the presence of the guest salt in both dopant di-amidosil families. The K$^+$ and Mg$^{2+}$ ions coordinate to the carbonate oxygen atoms of the amide cross-links within the whole range of salt concentration considered, leading to the saturation of the cross-linkages, to a redistribution of the amide–amide hydrogen-bonded aggregates of the host matrix and, in the case of the K$^+$-doped sample with $n = 10$, to the formation of a new type of aggregate, stronger and more ordered than those detected at lower salt content. In both di-amidosil systems guest salt-additives leads to the increase of ionic associated species and to a concurrent decrease of the concentration of “free” anions.

1. Introduction

Sol–gel chemistry [1] is a remarkably versatile approach for the fabrication of organic–inorganic hybrid systems [2]. These advanced nanomaterials have attracted significant interest in the last few years due to the potential applications in many fields, such as, optics, magnetism and electrochemistry. The use of this synthetic route permits to combine at the nanoscale level the properties of organic materials (e.g., elastomeric nature) with the features of inorganic silica frameworks (e.g., thermal and dimensional stability) in a single multifunctional nanocomposite. The experimental conditions of the Sol–gel process and the chemical nature of the organic and inorganic components (functionality of the silane precursor and concentration of reagents) dictate the morphology, nanostructure and degree of organization of the hybrids. The nature of the interactions established between the organic and inorganic components are also important. The latter aspect allows distinguishing two major subclasses in the class of hybrid materials, known as class I and class II, depending on the establishment or not of covalent bonds between the organic and inorganic components, respectively.

Recently, we introduced a novel family of class II hybrid materials, named di-amidosils. In these di-amide cross-linked alkylene/siloxane hybrids the alkylene chains are bonded at both ends to the siloxane framework through amide (─CON(═O)─) groups [3]. The di-amidosil frameworks synthesized included 4 and 8 methylene repeat groups and were represented by the notations d-A(4) and d-A(8), respectively, where d corresponds to di and A represents the amide cross-link. Both hybrid networks are room temperature white light emitters, presenting an emission large, broad band in the blue/porphyrin-like blue spectral region. The origin of such broad band has been ascribed to the convolution of donor-acceptor pair (D–A) recombinations that occur in the NH groups of the amide linkages and in the siloxane nanodomains. The d-A(8) di-amidosil has a quantum yield of 5.4% [3].

Aiming at producing materials for optical applications we incorporated very recently europium triflate (Eu(CF$_3$SO$_3$)$_3$) into the d-A(8) di-amidosil host matrix [4]. Samples with 200 < $n$ < 8 were analyzed. The Fourier Transform infrared and Raman (FT-IR and FT-Raman, respectively) spectroscopic investigation performed provided evidences that: (1) The conformations of the alkylene chains of the host matrix in the doped materials (essentially gauche) are not affected by the presence of the salt; (2) The Eu$^{3+}$ ions are coordinated to the COO$^-$ groups of the amide cross-links over the whole range of salt concentration examined; (3) "Free" and weakly bonded triflate ions occur in all the samples analyzed and at $n = 8$ an ionic aggregate of unknown nature is formed. Photoluminescence (PL) data demonstrated that the doped hybrids are room temperature white light emitters, due to the convolution of the hybrid host emitting centers (amide cross-linkages and siloxane nanodomains) and the Eu$^{3+}$ intra-4f $^7$D$_{0}$ → $^7$F$_{2,4}$ transitions [4]. Another conclusion retrieved from PL results is that in the dinitrile di-amidosil with $n = 100$ the Eu$^{3+}$ ions occupy the same type of chemical local environment.

To confirm if, as we suspect, the cation coordination process in the di-amidosil hybrid medium depends on the nature of the guest cation, we have decided in the present work to extend the analysis of the doped d-A8(B)-based hybrids to the analogue series doped with KCF$_3$SO$_3$ and MgCF$_3$SO$_3$. With this goal, we have employed FT-IR and FT-Raman spectroscopies to determine if the presence of the guest salt affects the alkylene chain conformations and their state of disorder and to elucidate the cation/amide cross-link and cation/anion interactions, as well as hydrogen bonding. We have complemented this spectroscopic analysis with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data.

2. Experimental section

2.1. Materials

Ethanol (CH$_3$CH$_2$OH, Merck), pyridine (py, Aldrich) and tetrahydrofuran (THF, Merck) were stored over
molecular sieves. Amberlyst A-21 Ion-Exchange Resin (Aldrich) was washed with THF and stored in an oven at 80 °C. Benzyl chloride (CICl=CHCH2Cl) (CICl, SC, Aldrich) and 3-methacryloyloxyethyltrimethoxysilane (ICh3,CHO, Silicate, APTES, Fluka), potassium tetratram (Aldrich, KCF4SO4) and magnesium trisulfate (Aldrich, Mg(SO4)2) were used as received. High purity distilled water (H2O) was used in all experiments.

2.2. Synthesis

The Kx+ and Mg2+ doped d-8(1)-based di-amidoxysil (Scheme 1) were prepared according to the method described in detail elsewhere [3,4]. Samples with $\infty > n > 5$ were produced as rigid films. Details of the synthetic procedure are indicated in the Table 1.

The Kx+ and Mg2+ containing di-amidoxysil have been identified on the basis of the notation proposed previously [4], i.e., d-A(81)(YCF5SO4), where Y = K (x = 1) and Mg (x = 2).

2.3. Experimental techniques

Samples for TGA were transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG-1000 thermobalance at a heating rate of 10°C min$^{-1}$ using high purity nitrogen as purging gas (20 cm$^3$ min$^{-1}$). Prior to measurement, the samples were vacuum-dried at 80°C for about 48 h and stored in an argon-filled glove box.

DSC measurements were obtained with a DSC131 Seitarm DSC. Disk sections with masses of approximately 10-20 mg were removed from the di-amidoxysil samples, placed in 40 µl aluminium cans and stored in a desiccator over phosphorous pentoxide for one week at room temperature under vacuum. After this drying treatment, the cans were hermetically sealed and the thermograms were recorded. Each sample was heated from 20 to 300°C at 10°C min$^{-1}$.

FT-IR spectra were acquired at room temperature using a Bruker FT20 spectrometer placed inside a glove-box with a dry argon atmosphere. The spectra were collected over the range 4000-400 cm$^{-1}$ by averaging 150 scans at a spectral resolution of 2 cm$^{-1}$. Solid samples (2 mg) were finely ground, mixed with approximately 175 mg of dried potassium bromide (Merck, spectroscopic grade) and pressed into pellets. Prior to recording the spectra, the pellets were first vacuum dried at 80-90°C for about 60 h, to reduce the levels of adsorbed water and solvent, and then transferred into a glove box.

The FT-Raman spectra were recorded at room temperature with a Bruker IFS-66 spectrometer equipped with a FRA-106 Ramans module and a near-infrared YAG laser with wavelength of 1064 nm. The spectra were collected over the range 3200-300 cm$^{-1}$ resolution at a resolution of 2 cm$^{-1}$. The accumulation time for each spectrum was 4 h.

To evaluate complex band FT-IR and FT-Raman envelopes and to identify underlying spectral components, the iterative least-squares curve-fitting procedure in the PeakFit software was used extensively throughout this study. The best fit of the experimental data was obtained by varying the frequency, bandwidth and intensity of the bands and by employing Voigt band shapes. A linear baseline correction with a tolerance of 0.2% was employed. The statistical errors of the curve-fitting procedure were less than 0.02.

3. Results and discussion

3.1. Morphology and thermal properties

The DSC curves show that the d-A(81)KCF5SO4 and d-A(81)MgCF5SO4 xerogels with $n > 5$ are entirely amorphous (Fig. 1).

The TGA curves of selected Kx+-doped di-amidoxysil with $n > 5$ (Fig. 2) reveal that these materials start to decompose at about 280-290°C. From approximately 340-370°C the rate of mass loss increases dramatically (Fig. 2). In the salt-rich Kx+-based sample with $n = 5$ degradation takes place in two stages: the first stage begins at 300°C and the second one is initiated at 485°C (Fig. 2).

In the case of the di-amidoxysil doped with MgCF5SO4 and $n > 5$, thermal decomposition starts at about 240-270°C and proceeds with a progressive mass loss. Beyond 350-370°C the process is significant for more than 5% weight loss. At $n = 10$ and 5, a second stage of degradation is visible in the TGA curves at temperatures higher than approximately 420°C (Fig. 2).

3.2. Polymer chain conformations and state of disorder

In this section we will examine the FT-Raman spectra of the d-A8(1)KCF5SO4 and d-A8(1)MgCF5SO4 di-amidoxysil in the region that includes the CH2 symmetric and asymmetric stretching modes ($\nu$CH2 and $\nu$CH3, respectively). This high-frequency region (3000-2000 cm$^{-1}$) is extremely useful to evaluate alternations of the polymer chain conformations and of their state of disorder in the presence of increasing amounts of guest salt.

The FT-Raman spectra of the d-A8(1)KCF5SO4 and d-A8(1)MgCF5SO4 compounds in the CH2 and CH3 regions are presented in Figs. 3a and b, respectively.

The frequency, intensity and frequency width at resonance height of the Raman $\nu$CH2 and $\nu$CH3 bands are sensitive to the gauche/trans conformer ratio, of order of the alkylene chains and to the intermolecular interactions occurring between the chains [5,6]. Shifts of these events to higher wavenumbers indicate an increase in the conformational disorder of the systems (i.e., an increase in the proportion of gauche conformations) [5,6]. In the Raman spectrum of alkylene chains in the crystalline state (all-trans conformations) the $\nu$CH3 mode is manifested as a strong band in the 2864-2878 cm$^{-1}$ interval, whereas the $\nu$CH2 mode gives rise to bands at 2930 cm$^{-1}$ (sym. medium) and 2850-2844 cm$^{-1}$ (trans) [7-9].

The FT-Raman $\nu$CH2 region of the K+/$\text{Mg}^{2+}$-doped di-amidoxysil hybrids with 100 $\geq n \leq 5$ exhibit two prominent bands centered at 2924/2926 and 2892/2894 cm$^{-1}$ and a shoulder at 2862/2863 cm$^{-1}$ (Fig. 3a/Fig. 3b). The events at 2924/2926 and 2892/2894 cm$^{-1}$ are ascribed to the $\nu$CH2 fundamental and to the Fermi resonance between the $\nu$CH3 fundamental with the many overtones of the CH2 bending vibrations, respectively, and are characteristic of disordered alkylene chains [7-9]. The intense 2892/2894 cm$^{-1}$ feature is associated with the CH2 stretching mode of alkylene chains in the amorphous state [7-9].

These results indicate that the alkylene chains of the di-amidoxysil samples examined are fully disordered and adopt gauche conformations over the whole range of salt concentration considered. Thus, the spectroscopic data obtained

1. PeakFit is a product of Jandel Corporation, 2591 River Boulevard, Sun Rafael, CA 94901, USA.
demonstrate that the addition of KCF$_2$SO$_3$ and 
MgCF$_2$SO$_3$ to d-A(8h) affects, neither the conformations of the alkyne chains, nor their state of disorder.

3.3. Cation coordination and hydrogen bonding

In this section we will examine in detail the spectral signa-
tures of the d-A(8h)YCF$_2$SO$_3$ di-amidolys as a func-
tion of salt content in specific regions of the FT-IR and 
FT-Raman spectra that permit to gain insight into the 
Y$^{+}$/Amide and Y$^{+}$/CF$_2$SO$_3$ interactions.

3.3.1. Cation/amide interactions and hydrogen bonding

The assessment of the strength of the hydrogen bonds established between the amide cross-links and of the role of the amide linkages in the coordination of the K$^+$ and Mg$^{2+}$ ions in the d-A(8h) system will be investigated here 
by means of a thorough analysis of the Amide I and Amide II regions (1600-1600 cm$^{-1}$ and 1600-1500 cm$^{-1}$, respectively) of the FT-IR spectra of the two series of 
diamidolys. As the d-amidolys host network provides a sin-
gle type of coordinating site (the carbonyl oxygen atoms of 
amide groups), the analysis of the modifications undergone 
by the Amide I and Amide II bands upon salt addition are 
fundamental to determine to what extent the guest cations 
bind to the carbonyl oxygen atoms of the amide linkages in 
in addition to interacting with the triazole oxygen atoms.

The FT-IR spectra of selected K$^+$ and Mg$^{2+}$-doped 
diamidolys samples in the Amide I and Amide II spectral 
regions are depicted in Figs. 4a and b, respectively. 
The results of the curve-fitting performed in the 
1800-1800 cm$^{-1}$ interval of the d-A(8h)KCF$_2$SO$_3$/
d-A(8h)MgCF$_2$SO$_3$ di-amidolys are displayed in Fig. 5
(Fig. 6). The composition dependence of the areas of the 
resolved components of the Amide I band of the two series of 
samples is reproduced in the inset of Fig. 5/(inset of Fig. 6).

The Amide I mode (or carbonyl stretching mode) is a very 
complex vibration that receives a major contribution from the 
C=O stretching vibration [19]. As this vibration mode is sensitive to the specificity and magnitude of hydro-
gen bonding, this band is often resolved into several dis-

tinct components, that correspond to different 
C=O environments (aggregates). As the absorption coefficients of 
C=O groups involved in different aggregates can be dif-

erent and are unknown, it is not possible to compare 
itensity values of different spectral components. Therefore 
only the changes undergone by each component represent 
concentration variations of each type of aggregate [10][11].

The Amide II mode, essentially due to the N-H in-
plane bending vibration, is sensitive to chain conformation 
and intermolecular hydrogen bonding [12], providing val-
uable information about the distribution of hydrogen bond 
strengths [10][13].

Amide I region. Fig. 4 demonstrates that the addition of 
K$^+$ and Mg$^{2+}$ ions to the d-A(8h) matrix gives rise to several 
structural modifications in the Amide I and Amide II regions, 
specially at high salt concentration, a solid proof that the 
alkaline and alkaline-earth ions coordinate to the carbonyl 
oxgen atoms of the amide cross-links within the whole 
range of salt concentration. We note that, while in the 
dilute K$^+$ and Mg$^{2+}$-doped compounds with n $\geq$ 20 dop-
ing equals in the disappearance of the 1754 cm$^{-1}$ compo-
nent and in a certain amount of band redistribution, in 
the case of more concentrated samples (n $\leq$ 20) the spectral 
modifications are more marked (Figs. 4a and b, respec-
tively). This is particularly evident in the FT-IR spectrum of 
d-A(8h)KCF$_2$SO$_3$ as manifested by the drastic change suffered by the band profile (Fig. 4a).

The Amide I envelopes of the K$^+$/Mg$^{2+}$-doped di-
amidolys with n $\geq$ 20 exhibit two broad bands centred at 
approximately 1733/1735 and 1650/1648 cm$^{-1}$, respectively (Fig. 4a/Fig. 4b). The 1735 cm$^{-1}$ event was decomposed into two components at 1733 and 1714/1710 cm$^{-1}$ (Fig. 5/Fig. 6), ascribed to disordered amide-amide aggreg-
ates (D1 and D2, respectively) in which the hydrogen bonds between the N-H and C=O groups are very weak 
and weak, respectively [3]. The broad band at 1650/
1648 cm$^{-1}$ produced by the K$^+$/Mg$^{2+}$-doped d-A(8h)-based 
compounds with n $\geq$ 20 was resolved into three compo-
nents at 1679/1675, 1632/1648 and 1623/1618 cm$^{-1}$ 
(Fig. 5/Fig. 6). These features are attributed to the absorp-
tion of C=O groups in ordered amide-amide aggregates 
with increased hydrogen bond strength (O1, O2 and O3, 
respectively) [3].

The new Amide I event observed at 1615 cm$^{-1}$ in FT-IR 
spectrum of d-A(8h)KCF$_2$SO$_3$ (Fig. 5) is indicative of the 
ocurrence of a new ordered amide-amide aggregate, 
considerably stronger that those found in the more 
diluted samples. In the Amide I envelope of the 
d-A(8h)MgCF$_2$SO$_3$ materials with n $\leq$ 10 band redistrib-
ution is more marked than that observed in the less 
consentrated samples (Fig. 6).

The results retrieved from the Amide I region of the K$^+$/ 
Mg$^{2+}$-doped xerogels with n $\leq$ 20 may be correlated with a 
massive coordination of the cations to the carbonyl 
groups of the amide linkages of the hydrogen-bonded amide-
amide aggregates of d-A(8h) [3]. While for K$^+$ doping this 
process involves a considerable breakdown of the ordered 
O2 structures (Fig. 5), in the presence of Mg$^{2+}$ ions the 
main consequence is a remarkable increase of the propor-
tion of aggregates O3 (Fig. 6).

The plots shown in the inset of Fig. 5/(inset of Fig. 6) 
allow to gain better insight into the modifications the 
hydrogen-bonded aggregates of d-A(8h) are subject to as 
the KCF$_2$SO$_3$/MgCF$_2$SO$_3$ concentration is progressively 
raised.

The component characteristic of non-bonded C=O groups 
(1754 cm$^{-1}$) in the K$^+$-doped d-A(8h)-based series 
disappears upon salt addition (n = 80), the amount of dis-
ordered D1 amide-amide aggregates suffers a slight 
increase, whereas the proportion of the disordered D2 
and ordered O1 ones remains practically unchanged. In 
addition, the fraction of the most ordered O3 associations 
decreases slightly, whereas that of the ordered O2 ones 
increases rapidly (inset of Fig. 5). Between 80 $\leq$ n $\leq$ 40 
the only changes worth mentioning are a marked decrease 
of the proportion of the disordered D1 aggregates at the 
expanse of a slight increase of the amount of D2 and O2 
associations (inset of Fig. 5).

In the Mg$^{2+}$-doped di-amidolys with n $\geq$ 20, while the 
fraction of non-bonded C=O groups (1754 cm$^{-1}$) is null, 
the proportion of the disordered D1 and D2 and ordered 
O1 aggregates remains practically constant (inset of 
Fig. 6). In contrast, the proportion of ordered O2 and 
O3 structures suffers an increase at n = 100 (inset of 
Fig. 6). Upon inclusion of more salt (n $\leq$ 100), the fraction 
of O2 structures grows significantly and in parallel that 
of the O3 aggregates decreases (inset of Fig. 6). At n = 5 the 
significant change is, no doubt, the increase of the 
amount of O3 associations (inset of Fig. 6).

Amide I1. The Amide II band of the d-A(8h)KCF$_2$SO$_3$ 
and d-A(8h)MgCF$_2$SO$_3$ di-amidolys with n $\geq$ 20 was 
decomposed into a pair of peaks at 1562/1557 and 1532/ 
1538 cm$^{-1}$, respectively (Fig. 5/Fig. 6), suggesting the pre-

sence of hydrogen-bonded aggregates with two average 
hydrogen bond strengths. Although these bands persist in
the FT-IR spectrum of the d-A(9b)KCF$_3$SO$_4$ di-amidoxyl, a new component emerges at 1585 cm$^{-1}$ (Fig. 5). This feature is tentatively correlated with the development of the Amide I band at 1605 cm$^{-1}$ (Fig. 5). We note that both components (i.e., 1605 and 1585 cm$^{-1}$) are purely superimposed in the borderline that is usually established to distinguish the Amide I region from the Amide II region.

3.4. Cation-anion interaction

As mentioned above, in the two sets of doped di-amidoxyls studied in the present work, the triflate oxygen atoms are, apart from the oxygen atoms of the carbonyl groups of the amidoxyl links, the second type of coordinating site available for the guest K$^+$ and Mg$^{2+}$ ions.

To inspect the chemical surrounding experienced by the triflate ions at increasing salt content in both series of materials we analysed the FT-IR and FT-Raman spectra in the diagnostic region characteristic of the symmetric stretching vibration mode of the SO$_3$ group (v$_{SO_3}$) since this vibration mode is very sensitive to coordination effects.

The components isolated in the FT-IR/FT-Raman v$_{SO_3}$ band profiles of representative K$^+$ and Mg$^{2+}$-doped di-amidoxyls are depicted in Figs. 7a and b, respectively. Figs. 8a and b show the composition dependence of the area of the resolved components of the d-A(8s)KCF$_3$SO$_4$ and d-A(8s)MgCF$_3$SO$_4$$_3$ xerogels with n ≤ 20, in the FT-IR and FT-Raman v$_{SO_3}$ envelopes, respectively.

The FT-IR/FT-Raman v$_{SO_3}$ band of the K$^+$-doped d-A(8)S-based samples with n ≥ 10/20 was decomposed into three components: one intense event at 1032 cm$^{-1}$ and two shoulders at 1038 and 1029 cm$^{-1}$ (top/bottom of Fig. 7a). The FT-IR/FT-Raman v$_{SO_3}$ regions of the salt-rich xerogels with n = 5 (top/bottom of Fig. 7a) were decomposed into the same components: three bands at 1052, 1038 and 1032 cm$^{-1}$ and two shoulders at 1045 and 1026 cm$^{-1}$.

In contrast, the FT-IR v$_{SO_3}$ envelope of the d-A(8b)MgCF$_3$SO$_4$$_3$ samples with n ≥ 20 was resolved into only two components: a band at 1032 cm$^{-1}$ and a shoulder at 1028 cm$^{-1}$ (top of Fig. 7b). Upon introduction of more guest salt (n = 5) the FT-IR v$_{SO_3}$ band profile changes drastically as a result of the new events at 1051, 1045 and 1038 cm$^{-1}$ (top of Fig. 7b). In the case of d-A(8b)MgCF$_3$SO$_4$$_3$ a new component develops at 1051 cm$^{-1}$ in the FT-IR spectra (top of Fig. 7b). The FT-Raman v$_{SO_3}$ envelope of the d-A(8a)MgCF$_3$SO$_4$$_3$ samples with n ≥ 20 was decomposed into a band at 1032 cm$^{-1}$ and two shoulders at 1037 and 1026 cm$^{-1}$ (bottom of Fig. 7b).

At n = 10 a weak band emerges at approximately 1000 cm$^{-1}$ in the FT-Raman spectrum (bottom of Fig. 7b). With the increase of salt concentration (n = 5) the intensity of the shoulders detected in the dilute materials increases and a new band appears at 1043 cm$^{-1}$ (bottom of Fig. 7b).

The v$_{SO_3}$ band at 1032 cm$^{-1}$ is assigned to "free" ions [14]. The contribution of "cross-link separated ion pairs" to the 1032 cm$^{-1}$ band cannot be, however, discarded [15]. The shoulders found at 1028/1026 cm$^{-1}$ and at 1038/1037 cm$^{-1}$ are associated with weakly coordinated triflate ions [15]. The event at about 1045/1043 cm$^{-1}$ is tentatively ascribed to contact ion-pairs. The 1052/1051 and 1069 cm$^{-1}$ features are tentatively attributed to the formation of ionic aggregates of unknown nature.

Close analysis of the FT-IR and FT-Raman spectra of the d-A(8)sKCF$_3$SO$_4$ samples (top and bottom of Fig. 8a, respectively) allows to infer that the vibration of the five v$_{SO_3}$ modes present is manifested differently in infrared and Raman scattering. This means that the vibration of each of these modes imposes changes of different magnitude in the dipole moment and in the polarizability of the species in question. This effect is particularly evident in the case of the FT-IR components located at 1032 and 1045 cm$^{-1}$, whose counterparts in the FT-Raman spectrum are much weaker. In the FT-IR spectra of the Mg$^{2+}$-based analogues, the component at 1031 cm$^{-1}$ (n = 5) (top of Fig. 8b) has no counterpart in the FT-Raman spectrum (bottom of Fig. 8b).

The presence of KCF$_3$SO$_4$Mg(CF$_3$SO$_4$)$_3$ in the d-A(8)S di-amidoxyl hybrid medium has the following major consequences:

1. At n ≥ 20, all the amide cross-links are saturated, but the K$^+$ (or Mg$^{2+}$) ions disturb the amide-amide aggregates moderately. We have found evidence of a certain amount of aggregate redistribution, but globally the strength of hydrogen bonding remains the same, as manifested in Fig. 5 (Fig. 6).

2. At n ≤ 20 the interaction of the K$^+$ ions with the C=O groups is such that one amide-amide aggregate, stronger than those formed in the non-doped host matrix, develops. Fig. 8a (Fig. 8b) demonstrates that at n ≤ 10, ionic association increases abruptly at the expense of a marked reduction of the concentration of "free" triflate ions.

Comparison of the spectral data obtained in the present work with the results derived from our previous study of the d-A(8)sEu(CF$_3$SO$_4$)$_3$, di-amidoxyls [4] leads us to conclude that the amide-amide aggregates of the salt-free network are more perturbed by the inclusion of Eu(CF$_3$SO$_4$)$_3$ than by the incorporation of KCF$_3$SO$_4$ or MgCF$_3$SO$_4$$_3$. In fact, the growth of a new hydrogen-bonded aggregate appears much earlier in the presence of the guest lanthanide ion than in the presence of the K$^+$ ion (n = 20 [4] and 10, respectively). With these ions, the cation/amide interaction leads to the formation of the same amide-amide association, an indication that hydrogen bonding is of the same order of magnitude and consequently independent of cation nature and concentration. In contrast, when Mg$^{2+}$ ions are added to d-A(8)s, no new hydrogen-bonded associations grow. These findings give support to the explanation that in the d-A(8)a medium the Eu$^{3+}$ ions are the species that exhibit the greatest tendency to bond to the carbonyl oxygen atoms of the amide cross-links, followed by the K$^+$ ions. The Mg$^{2+}$ ions have clearly less affinity for the C=O groups than Eu$^{3+}$ and K$^+$.

Taking into account the latter conclusions, we would expect to find a very low proportion of coordinated triflate ions within the d-A(8)sEu(CF$_3$SO$_4$)$_3$ medium. The FT-IR [16] and FT-Raman spectra of the Eu$^{3+}$-doped di-amidoxyls confirmed the presence of a remarkably low degree of ionic association in the materials, even in salt-rich samples [4].

4. Conclusions

In the present work, we investigated amorphous di-amidoxyls doped with a wide range of KCF$_3$SO$_4$ and MgCF$_3$SO$_4$$_3$ concentration (n ≥ n ≥ 20). The studies carried out provided evidence that the amide/amide chains in
both doped di-amidoxal series adopt essentially gauche conformations, demonstrating that the polymer chains of the host di-amidoxal matrix are not affected by the presence of the guest salt at any salt content. The calcium bond to the carbonyl oxygen atoms of the amide cross-links within the whole range of salt content. The concentration of "free" CP$_2$SO$_4$ ions decreases progressively with the incorporation of guest salt in both systems, while those of the weakly coordinated triflate ions, contact ions pairs and higher aggregates grows.

Acknowledgement

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References

Table 1
Details of the synthetic procedure of the d-A(β-naphthoyl)PSC(SO₃) and
nω-A(β-naphthoyl)PSC(SO₃) d-enaminals

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>d-A(β-naphthoyl)PSC(SO₃)</th>
<th>nω-A(β-naphthoyl)PSC(SO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>React until</td>
<td>0.2 mol</td>
<td>0.2 mol</td>
</tr>
<tr>
<td>2</td>
<td>Intermediate</td>
<td>0.6 g</td>
<td>0.6 g</td>
</tr>
<tr>
<td>3</td>
<td>Product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Product</td>
<td></td>
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Fig. 1. DSC curve of the d-A(β-naphthoyl)PSC(SO₃) and nω-A(β-naphthoyl)PSC(SO₃) d-enaminals.

Fig. 2. TGA curves of selected d-A(β-naphthoyl)PSC(SO₃) and nω-A(β-naphthoyl)PSC(SO₃) d-enaminals.
Fig. 3. FT-Raman spectra in the $\nu_C$CH$_2$ and $\nu_C$CH$_3$ modes of the d-$\text{AO}_{2}$.KCF$_3$SO$_3$ (a) and d-$\text{AO}_{2}$.MgCF$_3$SO$_3$ (b) di-anion/diol. The frequencies indicated represent the average value of the frequencies of all the samples considered.

Fig. 4. FT-IR spectra in the Amide I and Amide II region of the d-$\text{AO}_{2}$.KCF$_3$SO$_3$ (a) and d-$\text{AO}_{2}$.MgCF$_3$SO$_3$ (b) di-anion/diol. The frequencies indicated represent the average value of the frequencies of all the samples considered.
Fig. 5. Curve-fitting results in the Amide I and Amide II of the d-$\text{Al}_{13}$KCF$_5$SO$_4$ di-aminals. The frequencies indicated represent the average value of the frequencies of all the samples considered. Inset: Soft concentration dependence of the integral intensity of the different spectral components resolved in the Amide I region of d-$\text{Al}_{13}$KCF$_5$SO$_4$ di-aminals. The lines drawn are just guides for the eyes.

Fig. 6. Curve-fitting results in the Amide I and Amide II of the d-$\text{Al}_{13}$MgCF$_5$SO$_4$ di-aminals. The frequencies indicated represent the average value of the frequencies of all the samples considered. Inset: Soft concentration dependence of the integral intensity of the different spectral components resolved in the Amide I region of d-$\text{Al}_{13}$MgCF$_5$SO$_4$ di-aminals. The lines drawn are just guides for the eyes.
Fig. 7. Curve-fitting of FT-IR (top) and FT-Raman (bottom) ν3SO2 region of selected δ-Δ3RbKCF·SO3 (a) and δ-Δ3RbMgCF·SO3 (b) disamidolos. The frequencies indicated represent the average value of the frequencies of all the samples considered.

Fig. 8. Salt concentration dependence of the integral intensity of the different spectral components resolved in the FT-IR (top) and FT-Raman (bottom) of the δ-Δ3RbKCF·SO3 (a) and δ-Δ3RbMgCF·SO3 (b) disamidolos. The lines shown are just guides for the eyes.