



Study of the interactions of Sodium Thiocyanate, Potassium Thiocyanate and Ammonium Thiocyanate in water + *N,N*-dimethylformamide mixtures by Raman spectroscopy

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ARTICLE INFO

Article history:

Received 10 May 2007

Received in revised form 6 February 2008

Accepted 13 February 2008

Keywords:

Raman spectra

Dimethylformamide

Solvent effects

Thiocyanate salts

ABSTRACT

Raman spectra of water + *N,N*-dimethylformamide (DMF) mixtures and their solutions with NaNCS, KNCS and NH₄NCS were obtained. The bands of $\nu(\text{CO})$ stretching, $\delta(\text{OCN})$ bending, $r(\text{CH}_3)$ rocking and $\nu_{(\text{N}-\text{CH}_3)}$ stretching of the DMF molecule with and without salts were studied. The dependence of the vibration frequencies and Raman intensities of the bands on the composition of the mixed solvent was discussed. The change of the band frequencies as a result of the presence of the salts and the solvation of the cations by the solvent molecules was examined. The stronger cation solvation by the aprotic solvent molecules instead of the water molecules in DMF concentrated solutions was discussed. The $\nu(\text{CN})$ and $\nu(\text{CS})$ vibrations of the SCN⁻ ions were observed as a function of the cation present and the solvent composition. The presence of the SCN⁻ ions as “free”, contact ion pairs, or solvent separated pairs, was discussed.

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1. Introduction

The vibrational spectroscopy has been proved to be a valuable tool for the study of ionic solvation and association of electrolytes, as it is indicated by the reports that already have appeared [1–5]. The free molecules or ions and associated aggregates (ion pairs, clusters) interact differently with the incident radiation therefore each species has a characteristic band.

There have been also several publications regarding the solvation and ionic association of thiocyanate salts in various solvents using vibrational spectroscopy [6–11] but those in mixed solvents are still few. The study of electrolyte solutions of amides proved to be a valuable tool for obtaining information concerning the binding of the salts to peptide groups of proteins.

N,N-dimethylformamide (DMF) is the simplest disubstituted amide and has a peptide group with two basic centres, the oxygen of carbonyl and the nitrogen, which are in the same plane [12]. DMF is a polar solvent with dipole moment 3.8 D and dielectric constant 36.7 [13] consequently shows strong intermolecular interactions. Due to its strong electron-pair donating capacity ($\text{DN} = 26.6 \text{ kcal mol}^{-1}$) DMF behaves as a good cation solvator [14,15] but has restricted ability for anion solvation due to steric hindrance of the positive nitrogen atom. In the pure state shows

self-association, forming dimers or multiple molecules (clusters) [15–18].

The examination of the thermodynamic properties of the water–DMF solutions showed a high degree of association between the unlike molecules creating two- or three-dimensional networks [19–21]. The hydrogen bond between DMF–water molecules proves to be stronger than between the water molecules alone.

In the literature appears a number of reports concerning the Raman spectra of pure DMF [22], DMF + water [21,23,24] and DMF + water + electrolyte solutions [11,23].

As a continuation of our studies concerning the ion association of NaNCS, KNCS and NH₄NCS in DMF + water mixtures by both conductometric and viscometric methods [26,27] we apply Raman spectroscopy in these systems in order to study the solute–solute and solute–solvent interactions. We present detailed characteristic frequencies as a function of the solvent composition and we report the changes of these frequencies caused by various intermolecular interactions.

Our measurements were carried out in a series of DMF + water mixtures covering all concentration range and we were able to observe the variation of the strength of the bonds at the DMF + water mixtures. In the second part of this work we further investigate the change of Raman frequencies and intensities of these bands caused by Na⁺, K⁺ and NH₄⁺ thiocyanates in the same DMF–water mixtures. The solute–solvent interactions were examined also by means of the ν_{CN} and ν_{CS} stretching vibration bands. Although in the literature appear reports of Raman mea-

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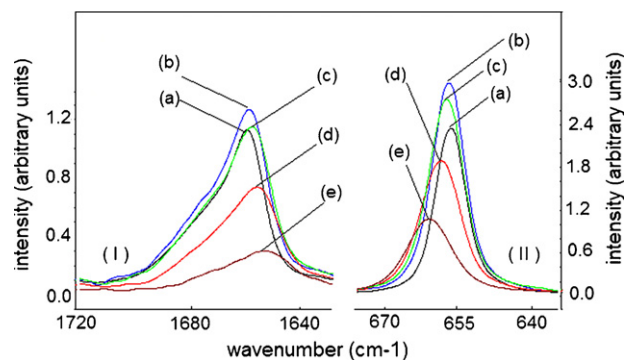


Fig. 1. Raman $\nu_{\text{C-O}}$ stretching (I) and δ_{OCN} bending (II) bands of various X_{DMF} in DMF–H₂O solutions. $X_{\text{DMF}} = 1.0$, (b) $X_{\text{DMF}} = 0.9$, (c) $X_{\text{DMF}} = 0.8$, (d) $X_{\text{DMF}} = 0.6$ and (e) $X_{\text{DMF}} = 0.3$.

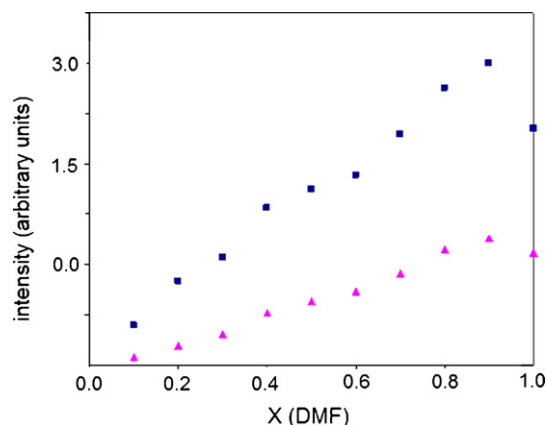


Fig. 2. Intensities of ν_{CO} and δ_{OCN} of various X_{DMF} in DMF–H₂O solutions.

measurements in DMF + thiocyanate solutions, there are not detailed Raman band studies concerning the influence of the DMF dilution in the DMF + water mixtures, on these specific functional groups.

2. Experimental

2.1. Materials

The *N,N*-dimethylformamide (Fluka, 99.8%) was used without further purification. The water was distilled, and the specific conductivity was found to be better than $0.40 \mu\text{S cm}^{-1}$ at 20°C . NaNCS (Fluka, >98.0%), KNCS (Merck, >98.5%) and NH₄NCS (Fluka, >99%), were dried to a constant weight at 110°C under atmospheric pressure. The DMF + water mixtures were prepared by mass ($\pm 0.0001 \text{ g}$). All salt solutions were prepared from a stock solution. Molar concentrations (3.0 mol dm^{-3}) were obtained from the salt and solution masses as well as the density values.

2.2. Raman measurements

The Raman spectra measurements were carried out on a Raman GX Spectrum FT Spectrometer equipped with a laser beam at the near IR region (1064 nm) and laser power 300 mW. A 10 mm silica cell was employed. The spectra were averaged over 400 scans. All spectra were obtained at room temperature with a resolution of 4 cm^{-1} .

3. Results and discussion

3.1. Raman spectra of DMF + water mixtures

The behaviour of the DMF molecules with the presence of H₂O was discussed in terms of the change of the Raman spectra of characteristic vibration bands, the ν_{CO} stretching, the r_{CH_3} in phase rocking, the $\nu_{(\text{N}-\text{CH}_3)}$ stretching and δ_{OCN} in-plane bending caused by the presence of water, from the corresponding values of the pure DMF. The assigned [22] frequencies are 1658, 1090, 864 and 657 cm^{-1} , respectively. In Figs. 1–3 are shown the bands obtained at various typical concentrations of DMF–water mixtures (expressed as DMF mole fractions, X_{DMF}).

The ν_{CO} band shifts to lower frequencies and the r_{CH_3} and δ_{OCN} to higher, following the DMF dilution. The $\nu_{(\text{N}-\text{CH}_3)}$ stretching remains unchanged throughout all solutions tested. These observations confirm the already published [28] results that the active centre to the hydrogen bonding between water and DMF is the carbonyl oxygen of the amide and that the free electrons of the N atom do not participate.

The variations of the ν_{CO} vibrations presented in Fig. 1(I) show an increasing broadness of the spectra with a gradual shifting to lower frequencies.

The deconvolution of the ν_{CO} spectra revealed a high intensity band (1658 cm^{-1}) and shoulder of lower intensity and higher frequency (ca. 1670 cm^{-1}).

We assign the 1658 cm^{-1} band to the free DMF and the 1670 cm^{-1} shoulder to dimers and clusters created by dipole–dipole interactions. With the increase of the water content the 1658 cm^{-1} band shifts to lower frequencies indicating [23,25,28] that the water molecules are connected through hydrogen bonding at the oxygen of the carbonyl of the DMF molecule. The double bond character of CO is lost and lower energy vibrations appear. The broadness of the ν_{CO} spectra shows an increasing population of the DMF–water clusters. The high frequency 1670 cm^{-1} band follows the same trend (shifting to lower frequencies, towards the 1658 cm^{-1} value) showing that the self associated DMF molecules are diminishing and remain as free DMF but of restricted population.

The deconvoluted spectra of the mixed solvent gave a number of shoulders with the increase of the water content ($X_{\text{H}_2\text{O}} < 0.6$) indicating the existence of different degrees of association and of the presence of particles of various kinds.

The in-plane bending δ_{OCN} , Fig. 1(II), of pure DMF shifts to higher wave numbers with the increase of the water content. The shifting confirms that the hydrogen bonding of the water molecules takes place through the carbonyl oxygen leading to a decrease of the motion of the OCN grouping and consequently to a higher energy

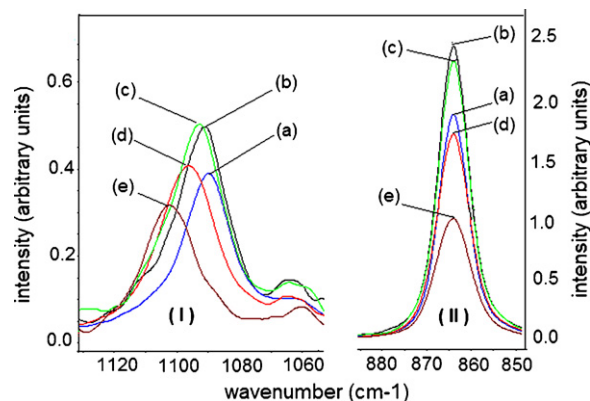


Fig. 3. Raman r_{CH_3} rocking (I) and $\nu_{(\text{N}-\text{CH}_3)}$ stretching (II) of various X_{DMF} in DMF–H₂O solutions. (a) $X_{\text{DMF}} = 1.0$, (b) $X_{\text{DMF}} = 0.9$, (c) $X_{\text{DMF}} = 0.8$, (d) $X_{\text{DMF}} = 0.6$ and (e) $X_{\text{DMF}} = 0.3$.

vibration. The deconvolution of the δ_{OCN} spectra showed no overlapping band.

In Fig. 2 are shown the intensities of δ_{OCN} bending and ν_{CO} stretching obtained at various mole fractions of DMF. A maximum value is observed for both vibrations at low water concentration which indicates the existence of a large population of species of the same kind. Indeed in low water concentration the water molecules are forming complexes, composed of two or three H_2O molecules for each DMF molecule [25].

It is already known [20,23] that the association of the H_2O and DMF molecules to creation of clusters is pronounced in this concentration region (in DMF rich solutions) where the bulk structure of H_2O is destroyed and where the DMF shows a strong structure breaking character. Because of the high ionic character of the carbonyl oxygen, hydrogen bonds are preferably formed between DMF– H_2O than between H_2O – H_2O molecules. It seems that at this low water concentration all the water molecules are “trapped” between the large number of DMF species forming complexes composed of two or three H_2O molecules for each DMF molecule.

It has already been shown [20,21] that have been observed maxima of the viscosity and the density values for water mixtures of *N,N*-disubstituted amides at the same solvent concentration. These maxima suggest a high degree of association between the water and the aprotic solvent dipoles and/or the formation of complexes between the solvent and the water molecules.

A difference is observed between the vibration frequencies of the in-plane methyl rocking (1090 cm^{-1} band) in the pure DMF and its water mixtures as it is shown in Fig. 3(I). The shift to higher frequencies by the water addition can be attributed to the increasing number of water molecules that are bound in the DMF clusters or complexes. As the species of DMF+water are composed of more water molecules, the in-plane rocking of the methyl group is hindered resulting to a higher energy vibration. Finally the $\nu_{(\text{N}-\text{CH}_3)}$ stretching (864 cm^{-1}) Fig. 3(II) does not change in position and shape but the intensity follows the same trend as in all spectra investigated in this work showing maximum magnitude at dilute DMF solutions. This result is expected as the nitrogen atom, due to steric hindrance, is not an active centre for the water molecules.

3.2. Raman spectra of the DMF + water + alkali thiocyanate solutions

3.2.1. Characteristic bands of the DMF molecule

The ν_{CO} stretching vibration in pure DMF and DMF+water solutions where examined when each of the Na^+ , K^+ and NH_4^+ thiocyanates was added.

The spectra are not symmetrical showing a shift to higher frequencies. The band shift depends on the charge density of the cation and as it is illustrated in Fig. 4(I) the greatest shift (ca. 9 cm^{-1}) is corresponding to DMF bound to Na^+ and the smallest (ca. 3 cm^{-1}) to DMF bound to NH_4^+ . The band frequencies in pure DMF are 1666 cm^{-1} for NaNCS and KNCS and 1662 cm^{-1} for NH_4NCS .

It is observed that the frequency is not depending on the water content for the DMF rich solutions but as the water content increases ($X_{\text{DMF}} < 0.6$) it shifts to lower values tending to these of the corresponding mixed solvent.

Thus, it is indicated that the cation is solvated through the carbonyl oxygen of the DMF and that due to the strong surface potential of the alkali ions the DMF molecule is attracted from its dimers or clusters. For the water rich solutions the cation is not solvated any more by the aprotic solvent. The small shift that has been observed for the NH_4^+ cation can be attributed to the small charge density of the NH_4^+ and the resultant restricted polarization of the DMF molecules.

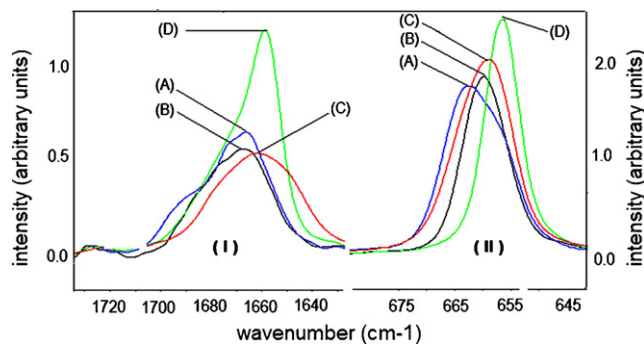


Fig. 4. Raman ν_{CO} stretching (I) and δ_{OCN} bending (II) of $X_{\text{DMF}} = 1.0$ in presence of thiocyanates (A): NaNCS, (B): KNCS, (C): NH_4NCS and (D): pure DMF.

The association constants (K_A) in the same solvent mixtures which vary [27] as $K_{A(\text{NaNCS})} > K_{A(\text{KNCS})} > K_{A(\text{NH}_4\text{NCS})}$ confirm the previous remark.

The bands in all cases are composite and by deconvolution it was showed that they are composed of several overlapping ones, thus indicating the presence of different kind of intermolecular interactions. More specifically it was observed that the high intensity components 1666 cm^{-1} for NaNCS and KNCS and 1662 cm^{-1} for NH_4NCS remain and several shoulders at higher wave numbers appear, the number of which increases with the water content of the mixture. The 1670 cm^{-1} shoulder is shown only in the more DMF concentrated solutions, thus indicating the existence of the DMF dimers and clusters, which are destroyed as the water content increases.

The in-plane bending δ_{OCN} bands of the alkali thiocyanate solutions ($659\text{--}662\text{ cm}^{-1}$) and of the pure DMF are presented in Fig. 4(II). The bands are sharp and symmetrical and show a shift from the corresponding solvent band to higher frequencies, which is cation dependent as was in the case of the ν_{CO} stretching. The wave numbers vary as: $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+$ and in any case remain unchanged for each salt throughout all the solvent mixtures tested.

We can conclude from the previous remarks that in the DMF rich solutions, the DMF and not the water molecules dominate in the cation solvation spheres.

As it is shown in Fig. 5 the deconvolution of the δ_{OCN} spectra of NaNCS in solutions rich in DMF gave two overlapping bands appearing at 664 cm^{-1} and at 657 cm^{-1} . We assign the high frequency band, to the DMF molecules bound to the cation at the first coordination sphere. The low frequency shoulder is assigned

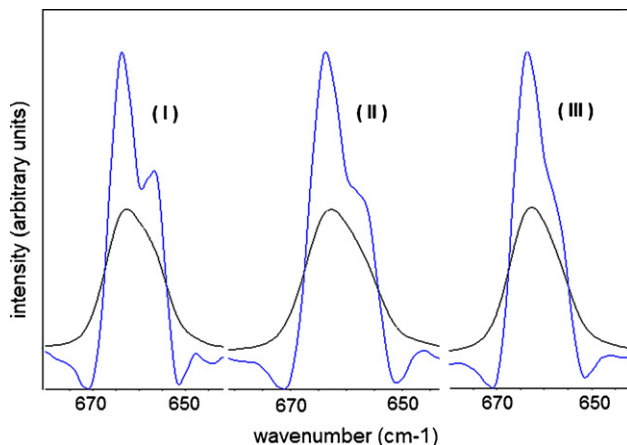


Fig. 5. Deconvoluted spectra of δ_{OCN} of NaNCS in DMF– H_2O solutions: (I) $X_{\text{DMF}} = 1.0$, (II) $X_{\text{DMF}} = 0.9$ and (III) $X_{\text{DMF}} = 0.8$.

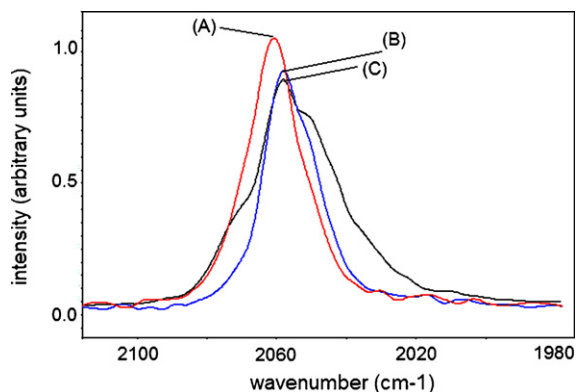


Fig. 6. Raman spectra of ν_{CN} in $X_{\text{DMF}} = 1.0$ of (A) NaNCS, (B) KNCS and (C) NH_4NCS .

to the DMF molecules bound to the second coordination sphere of Na^+ (probably further connected through hydrogen bonding to water molecules) and to the DMF molecules weakly interacting with the thiocyanate anion. The 664 cm^{-1} component dominates as the water content of the NaNCS solutions increases ($X_{\text{DMF}} < 0.7$) showing that the Na^+ does not behave as a structure maker in the water rich solutions.

No overlapping bands were found for all KNCS and NH_4NCS solutions examined. The existence of only one band in these solutions indicates that solvation occurs mostly at the first coordination sphere of the cation. The original and the deconvoluted spectra of the NaNCS solutions are showed in Fig. 5.

The band frequency of the r_{CH_3} in-plane rocking is found at ca. 1001 cm^{-1} not depending on the salt dissolved or the composition of the solvent mixture.

As it was expected there was not a frequency shift of the $\nu_{(\text{N}-\text{CH}_3)}$ (864 cm^{-1}) vibration for all solution mixtures examined. The intensity follows the same trend with the water increase showing a peak at $X_{\text{DMF}} = 0.9$.

3.2.2. Characteristic bands of the SCN^- anion

Generally the linear thiocyanate ion has three Raman bands [29–32]. A CN out of phase stretch (2050 cm^{-1}) a bending degenerate band (480 cm^{-1}) and a CS in phase band (735 cm^{-1}). These frequencies change according to the coordination mode, showing whether the complexes are N– or of S– bonded. An increase in the 2050 cm^{-1} together with an increase in the 735 cm^{-1} vibration and a steady value of the 480 cm^{-1} band, indicates the presence of N–bonded complexes while an S– coordination implies an increase of the 2050 cm^{-1} band and a decrease of both 480 and 735 cm^{-1} bands.

In the present work, the spectra of the solutions examined showed two bands at about 2060 and 735 cm^{-1} which are assigned to the CN out of phase and to the CS in phase stretching, respectively. As it was found an increase of both frequencies (ca. $8\text{--}10\text{ cm}^{-1}$ for ν_{CN} – and ca. $10\text{--}17\text{ cm}^{-1}$ for ν_{CS}) for all solutions studied, thus it can be concluded that the complexes created here are N– bonded.

The ν_{CN} stretching region in the DMF–water solutions gave the spectra that are presented in Fig. 6. As it is illustrated the change of cation did not affect the high intensity band. More particularly, the NaNCS solution gave a high intensity symmetrical band at 2060 cm^{-1} the KNCS a high intensity band at 2058 cm^{-1} and a shoulder at 2050 cm^{-1} and the NH_4NCS a main band at 2058 and shoulders at 2050 and 2070 cm^{-1} . In all cases the frequency of the dominating bands was independent of the solvent composition but the appearing broadness became more distinct with the increase of the water content.

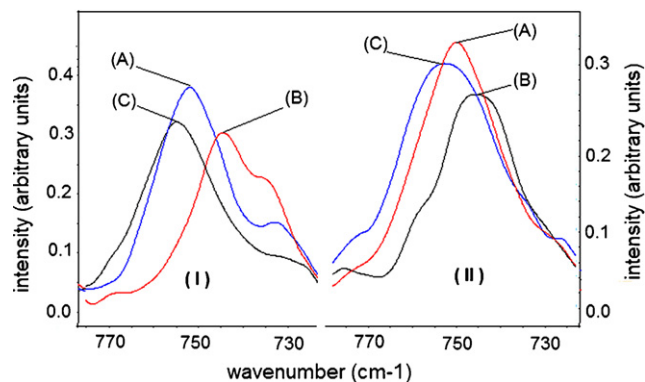


Fig. 7. Raman spectra of ν_{CS} of (A) NaNCS, (B) KNCS, (C) NH_4NCS . In: (I) $X_{\text{DMF}} = 1.0$ and (II) $X_{\text{DMF}} = 0.7$.

By deconvolution it was confirmed that all spectra were composed of several overlapping bands the number and the intensities of which, were depending on the water content of the solvent mixture. Particularly the NaNCS gave in pure DMF a high intensity symmetrical band at 2060 cm^{-1} and bands of lower intensity at 2070 and 2050 cm^{-1} . With the dilution new bands appear at 2074 and 2044 cm^{-1} . The KNCS gave a 2058 cm^{-1} high intensity and a 2050 cm^{-1} lower intensity band. With the dilution additional bands appear at 2074 , 2070 and 2044 cm^{-1} .

The NH_4NCS provides the most complex spectra in neat DMF and in diluted solutions as well. It gives a high intensity band at 2058 and smaller bands at 2074 , 2070 , 2050 and 2044 cm^{-1} . It is obvious that different kinds of association take place between the SCN^- ions, the cations and the solvent molecules.

We assign the dominating bands (2060 and 2058 cm^{-1}) to contact ion pairs [30,32] and the lower frequency band (2050 cm^{-1}) to “free” solvated SCN^- ions and/or to ions at the second coordination sphere.

Indeed, DMF is a very good cation solvator and the SCN^- can be found at the outer coordination sphere creating solvent separated pairs, coexisting in the solution with the contact anion pairs. These two kinds of species are present in all solvent mixtures. Their concentration is decreasing with the solvent dilution as it is showed by the decrease of the intensities of the corresponding bands and it seems that entities comprising H_2O molecules are developed. The higher frequency components (2074 and 2070 cm^{-1}), the intensity of which is increased with the water content of the solution, were assigned to SCN^- ions solvated by the water molecules [30] and to triple and multiple ions.

The 2040 cm^{-1} band can be assigned to contact dimer ion pairs [30,32].

In the present work, the stretching vibrations of ν_{CS} in pure DMF were found as follows: Dominating bands at 752 cm^{-1} (NaNCS), 745 cm^{-1} (KNCS), 755 cm^{-1} (NH_4NCS) and shoulders at 733 , 736 and 734 cm^{-1} , respectively (Fig. 7(I)). The high frequency most intense band is assigned to contact ion pairs (Me^+NCS^-) and the lower frequency to “free” solvated SCN^- anions [33].

Upon dilution irrespective of the cation present, the high intensity bandshape broadens (Fig. 7(II)) reflecting the different kinds of interaction that appear in the solution. The deconvolution of the spectra showed that the high intensity band remains at the same frequency not affected of the increase of the water content of the solution but at the same time several bands of lower intensity appear.

In Fig. 8 is illustrated the effect of the solvent dilution on the ν_{CN} and ν_{CS} spectra.

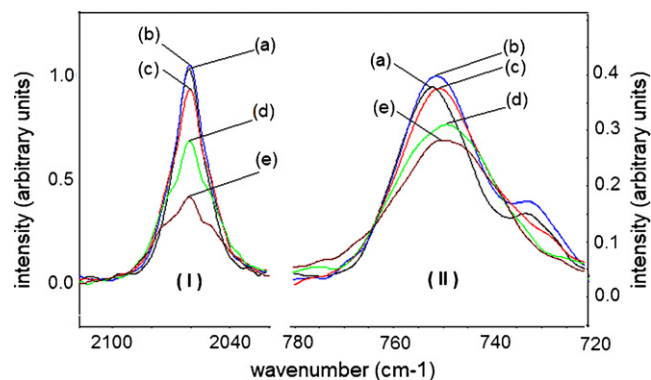


Fig. 8. Raman spectra of ν_{CN} : (I) and ν_{CS} : (II) of NaNCS in DMF + water solutions. (a) $X_{\text{DMF}} = 1.0$, (b) $X_{\text{DMF}} = 0.9$, (c) $X_{\text{DMF}} = 0.8$, (d) $X_{\text{DMF}} = 0.6$ and (e) $X_{\text{DMF}} = 0.3$.

It must be noted that the dominating bands of both stretching regions ν_{CN} and ν_{CS} showed a maximum intensity magnitude at DMF rich solutions. An increased population of the contact ion pairs seems to dominate at this region a conclusion that is in accordance with that made previously, concerning the enhanced creation of DMF + water clusters at this solvent concentration.

4. Conclusion

The active centre of DMF is the oxygen atom as it is shown by the decrease of ν_{CO} , and the increase of δ_{OCN} band frequencies. A maximum value of the intensities appearing at ca. $X_{\text{DMF}} = 0.8$ and the increase of the half width indicate the existence mainly of DMF + H₂O species at this solvent concentration.

In the thiocyanate salts and in DMF rich solutions the species that are present are comprised of contact ion pairs as well as solvent separated pairs. The NaNCS solutions show the presence of solvation at the second coordination sphere. A loose solvation of the NH₄⁺ is appearing due to the smaller surface potential of the ion in comparison with the other two alkali ions following that this salt is mostly found as contact ion pairs.

The 735 cm⁻¹ band of the ν_{CS} showed the presence of free SCN⁻ anions or anions solvated by DMF. With the increase of the water ($X_{\text{DMF}} < 0.6$) the cations seem not to be any more solvated by DMF and the DMF is preferably attracted by the H₂O molecules creating dimmers and clusters. The intensity of the ν_{CN} main band is decreased with the dilution and new bands as shoulders appear in lower and higher wavenumbers showing that a variety of species are present in the mixture.

Acknowledgments

The authors wish to thank Professor K. Viras, Department of Chemistry, University of Athens for helpful discussions. This work was partially supported by the University of Athens (Grant: 70/4/3345).

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