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Raman spectroscopic study of base catalyzed di- and trimerization of malononitrile in ionic liquids and water

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Abstract

Multivariate Curve Resolution (MCR) and Two-Dimensional Correlation Spectroscopy (2DCoS) have been employed to analyze the Raman spectra recorded from the reaction of malononitrile with KOH carried out in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate and water. In both cases the carbanion, which is formed by deprotonation of malononitrile, could be detected spectroscopically. When using the ionic liquid as solvent formation of the dimer was observed, whereas in aqueous solution a trimer was formed by a subsequent Michael addition. Based on the component spectra and concentration profiles obtained from MCR analysis the reaction intermediates as well as products could be identified. 2DCoS was very helpful in corroborating these results.

Keywords: 2D Correlation Spectroscopy; Multivariate Curve Resolution; Raman spectroscopy; Ionic liquids; Malononitrile

1. Introduction

In chemical research and technology there is a continued interest in Room Temperature Ionic Liquids (RTILs) for their interesting physico-chemical properties. RTILs are formed by organic cations and either organic or inorganic anions. Due to their ionic structure RTILs are characterized by a negligible vapor pressure even at elevated temperature. This important property is generally supplemented by non-flammability, good electrical conductivities as well as interesting solvating capabilities [1]. Therefore, RTILs have been used as solvents or co-solvents in chemical synthesis where they hold promise to substitute conventional organic solvents in certain applications. Frequently cited arguments, which support the use of RTILs in chemical synthesis, are their environmentally acceptable properties and their often advantageous influence on the course of reaction carried out in them [2–7].

In organic synthesis improved selectivity and recyclability of the reaction medium and catalysts have been reported [8–10]. Also in the field of biocatalysis the use of ionic liquids brought about advantages such as better yields and improved enzyme stability as well as enantioselectivity [5,7,11–14]. The reason for these interesting and promising properties of ionic liquids can most likely be understood if more information on the solvating characteristics of ionic liquids is available. In this context infrared and Raman spectroscopy are highly appropriate techniques because they allow in situ observation of chemical species present in ionic liquids as well as to measure resulting intermolecular interactions. Due to the non-destructive nature of these techniques also short living intermediates can be readily observed.

In this work the reaction between malononitrile and potassium hydroxide (KOH) in water and in 1-ethyl-3-methylimidazolium tetrafluoroborate (emimBF_4) has been

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studied by Raman spectroscopy. Malononitrile is a frequently used reagent in organic synthesis because of its exceptional reactivity due to its acid protons. Upon reaction with bases malononitrile, as well as other CH acids like malonate and cyanoacetic esters, form a carbanion acting as reactive intermediate. Malononitrile is therefore widely used in chemical synthesis especially in Knoevenagel condensations and Michael additions [15–19]. The ionic liquid emimBF_4 has been chosen as solvent because this ionic liquid already has found multiple use as reaction medium in organic chemistry [20–22]. For analysis of the in situ recorded Raman spectra and interpretation of the course of reactions observed in the solvents under investigation Two-Dimensional Correlation Spectroscopy as well as Multivariate Curve Resolution have been used.

2. Experimental

2.1. Reagents and instrumentation

All the chemicals used were purchased from Fluka (Steinheim, Germany), and they were of reagent grade. The RTIL used, 1-ethyl-3-methylimidazolium tetrafluoroborate (emimBF_4), was purchased from Solvent Innovation GmbH (Köln, Germany) and used without any pretreatment. Reaction was carried out by mixing 10 μl of malononitrile (1 M) in distilled water or pure RTIL and 5 μl of KOH (0.2 M) in distilled water. Solutions were hosted in a calcium fluoride plate where the reaction was monitored with a Confocal Raman Microscope LabRam HR800 (Jobin Ybon GmbH, Bernsheim, Germany). The instrument was equipped with a CCD detector. The 632.817 nm He–Ne laser was used as excitation source and the laser power was set to 14.5 mW. The resolution of the Raman system was set at 0.9 cm^{-1}. Each spectrum was recorded with a duration of 14 s.

2.2. Data analysis

Two-Dimensional Correlation Spectroscopy (2DCoS) and Multivariate Curve Resolution (MCR) are two complementary data analysis techniques for elucidation of spectral variations in evolving system. From a general point of view, 2DCoS spreads the one-dimensional spectra into a second spectral dimension with the same wavenumbers in both dimensions [23]. It provides both synchronous and asynchronous correlation maps. While the former represents the simultaneous or coincidental spectral changes, the latter one shows the correlation between bands changing with a different rate. Information on the temporal sequence of the events causing these changes can also be extracted when considering the signs of the asynchronous peaks. Thus, the asynchronous map gives useful information because it can help to identify overlapping bands in case they change at a different rate during the experiment. Raman spectra obtained were analyzed by MATLAB 5.3 software (The Maths Work Inc., Natick, MA, USA) on the basis of the freely available toolbox by Berry and Ozaki [24]. The mean spectrum of the data set was used as reference spectrum to construct correlation maps in 2DCoS.

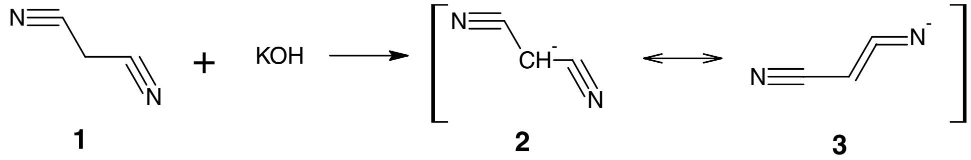
On the other hand, MCR decomposes the data set into the product of two smaller matrices containing concentration profiles and spectra of the modeled components that match best the recorded data set. The remaining spectral information not explained by the modeled concentration profiles and component spectra is captured in a residual data matrix. When performing MCR on the experimental data decision must be made as to how many components are to be modeled. Furthermore, it is necessary to come up with initial estimates for the spectra and/or concentration profiles prior to starting the iterative modeling process of MCR. For this task chemometric tools like principle component analysis (PCA), Evolving Factor Analysis (EFA) among others are used [25]. During the iterative modeling process constraints based on available physical and chemical knowledge may be applied. These constraints guide the iteration process to find chemically and physically meaningful results. Experimental data were treated by MATLAB 5.3 software (The Maths Work Inc., Natick, MA, USA) on the basis of the freely available toolbox by Tauler and de Juan [26].

As the concepts of 2DCoS and MCR are fundamentally different, the results they provide are complementary in nature. It is therefore useful to combine both techniques to obtain a complete picture of the process under study [27].

3. Results and discussion

Malononitrile, **1**, is a well-studied compound in organic chemistry. It is easily deprotonated by strong bases such as KOH [28,29]. This deprotonation yields a carbanion, that exists in resonant structures, **2** and **3** (see Scheme 1). Raman spectra recorded from the reaction between **1** and KOH in emimBF_4 are shown in Fig. 1. From the spectral changes observed, it gets clear that the reaction proceeded beyond simple deprotonation of **1**. From the deprotonation step itself, only two bands, one corresponding to both nitriles of **2** and the other to the single nitrile of **3**, should be expected. However, as a more complicated spectral pattern is observed it may be concluded that the reaction proceeds further with the carbanion as a plausible reactive intermediate. At the beginning of the reaction a band appeared at 2173 cm^{-1} with two further new bands arising at 2196 and 2158 cm^{-1}.

2DCoS was applied to the original data to identify kinetically correlated bands, as well as, bands belonging to different species. Synchronous and asynchronous maps are shown in Fig. 2. The synchronous map reflects the overall spectral changes. From the sign of the synchronous peaks it can be said that the band at 2173 cm^{-1} decreases when the bands at 2196 and 2158 cm^{-1} increase. A closer look at the synchronous correlation plot revealed that the synchronous peaks around 2273 cm^{-1} were slightly shifted.



Scheme 1.

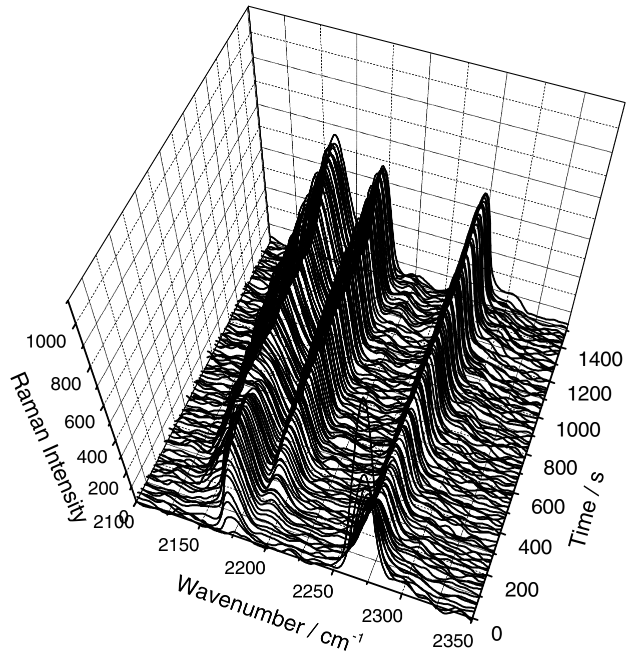


Fig. 1. Raman spectra taken during reaction time when emimBF_4 was used as solvent (reaction time 25 min, interval showed 1 min).

The correlation peak developed with 2173 cm^{-1} appeared at slightly lower wavenumber than the two peaks developed with 2196 and 2158 cm^{-1}. This could be indicative of more than one band contributing to the Raman intensity at 2273 cm^{-1}, but this point needed confirmation with the help of the asynchronous map. In the asynchronous map many peaks between the most significant bands in the system were observed. However, the lack of an asynchronous peak between 2196 and 2158 cm^{-1} bands was most indicative as it suggested that both belonged to the same process. Focusing the 2DCoS analysis only on the spectral region between 2250 and 2300 cm^{-1} (see Fig. 3) it got evident that at least two bands of different origin exist which must be attributed to different species. From these results three components could be identified; the reagent with a band at 2273 cm^{-1}, and two more species, one with a band at 2173 cm^{-1} and another one with two bands at 2196 and 2158 cm^{-1}. Furthermore, as can be deduced from Fig. 3, a reaction product showed a band close to 2273 cm^{-1} but

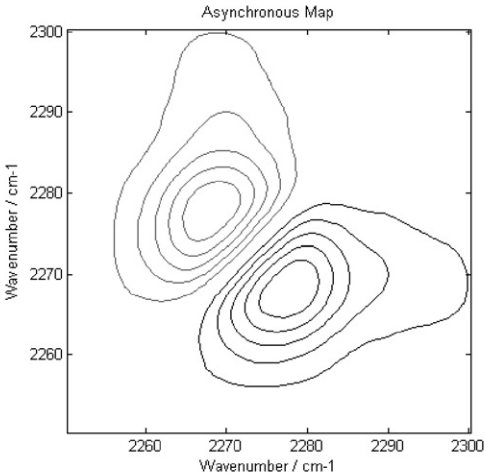


Fig. 3. Asynchronous correlation map obtained from 2DCoS of the reaction carried out in emimBF_4 focused in the region 2250–2300 cm^{-1}.

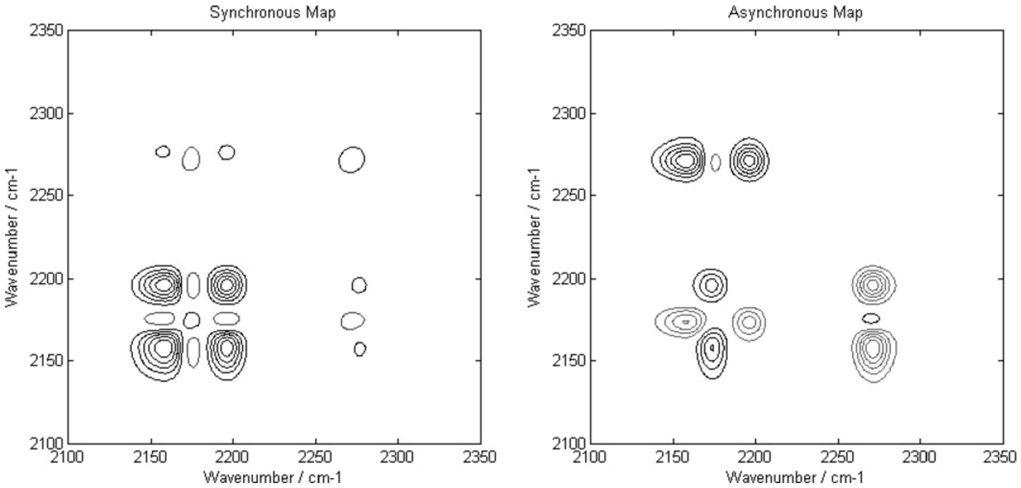


Fig. 2. 2DCoS analysis of the reaction in emimBF_4 in the region 2100–2350 cm^{-1}.

slightly shifted to higher wavenumber. A principle component analysis of the data also suggested that the data set could be modeled using three components. The data set was subsequently analyzed with MCR to obtain the pure spectra and the concentration profiles of the components involved in the reaction. EFA was used to generate the initial estimates of the three components. Unimodality of concentration profiles and non-negativity of spectra and concentration profiles were applied as constraints. MCR results for this system are shown in Fig. 4, where concentration profiles (a) and pure spectra (b) can be seen. The first component corresponds to the reagent (species **1**) with its band at 2273 cm^{-1}. The second component is an intermediate species which is formed very fast at the beginning of the reaction. This species showing bands at 2273 and 2173 cm^{-1} can be attributed to the carbanion **2**, a reactive intermediate. The final product of the reaction shows bands at 2273, 2196 and 2158 cm^{-1}. As described in the literature [28], self-condensation of malononitrile can occur in the presence of a strong base, as KOH, forming a dimer, known as 2-amino-1,1,3-tricyanopropene, **4**. The formation of the dimer **4** follows the Thorpe type reaction shown in Scheme 2. According to Carboni the infrared spectrum of **4** has three bands in the nitrile region at 2370, 2217 and 2197 cm^{-1} which are related to unconjugated and conjugated nitrile groups, respectively [30]. These three bands corresponded with the Raman bands in solution obtained with MCR at 2273 (unconjugated nitrile group), 2196 and 2158 cm^{-1} (conjugated nitrile groups).

To study the influence of the reaction media on the process, the same reaction was carried out in a conventional solvent, like water. The spectra obtained (Fig. 5) were analyzed as before. When the reaction is performed in water, the experimental spectra are similar to those obtained in emimBF$_4$, with bands slightly shifted due to the change of the media but a new band centered at 2228 cm^{-1} was observed. In Fig. 6 the 2D correlation maps are shown.

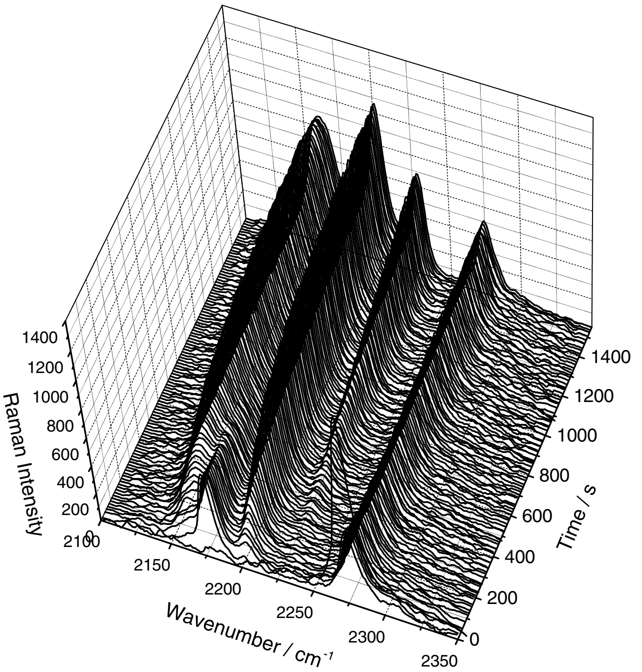


Fig. 5. Raman spectra taken during reaction time when water was used as reaction medium (final time 25 min).

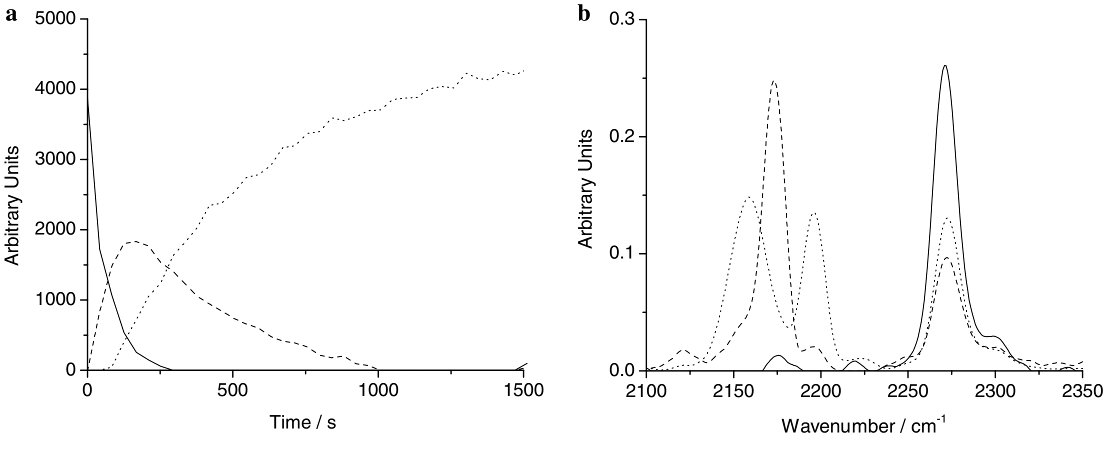
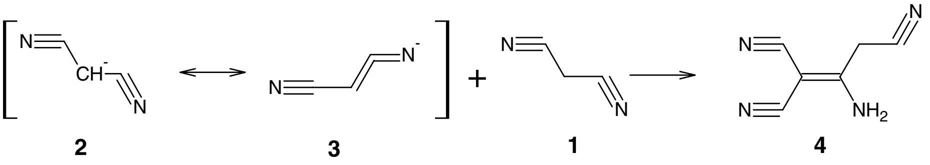


Fig. 4. Concentration profiles (a) and pure spectra (b) obtained by applying MCR to the data obtained using emimBF$_4$ as reaction medium.



Scheme 2.

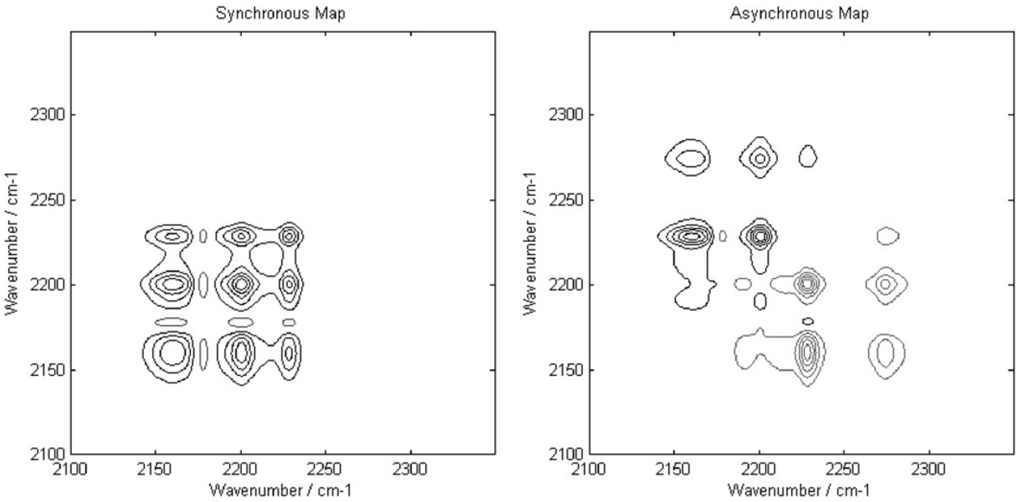


Fig. 6. 2DCoS analysis of the reaction in water in the region 2100–2350 cm^{-1}.

Similarly with the emimBF$_4$ system, the asynchronous map contained many correlations between the most significant bands, but no correlation between 2201 and 2161 cm^{-1}. The synchronous map showed correlations between all bands with the remarkable exception of the band at 2274 cm^{-1}. This observation could be explained in two ways. Either there was only one process taking place involving that band, or it is assumed that in case this reaction is carried out in water the unconjugated nitrile band does not change its position. To investigate this spectral region in more detail a second 2D analysis was carried out this time focusing on the spectral region between 2250 and 2300 cm^{-1} (Fig. 7). The appearance of an asynchronous peak in this study now indicated that, as in the case of using the ionic liquid as solvent, more than one process involving the 2274 cm^{-1} band took place during reaction. Considering the additional band at 2228 cm^{-1}, it could be assumed that a minimum of four components were involved in the reaction. Analysis of the data using PCA also suggested that the spectral variance could be explained by four components. For analysis of the data set by multivariate curve resolution again evolving factor analysis was applied to generate initial estimates. As in the emimBF$_4$ system, unimodality to concentration profiles and non-negativity to concentration profiles and pure spectra were applied as constraints. The obtained component spectra with the corresponding concentration profiles are shown in Fig. 8. The three first components reassemble those obtained from the reaction in emimBF$_4$. The presence of a fourth component whose appearance coincides with the disappearance of the third component clearly indicates that in water the reaction advanced further than in the ionic liquid. The fourth component most likely is 2-cyanomethyl-1,1,3,3-tetracyanopropene, **5**, a trimer of **1**, which forms by Michael addition between the carbanion and the dimer **4** (Scheme 3) that is accompanied by elimination of NH$_3$.

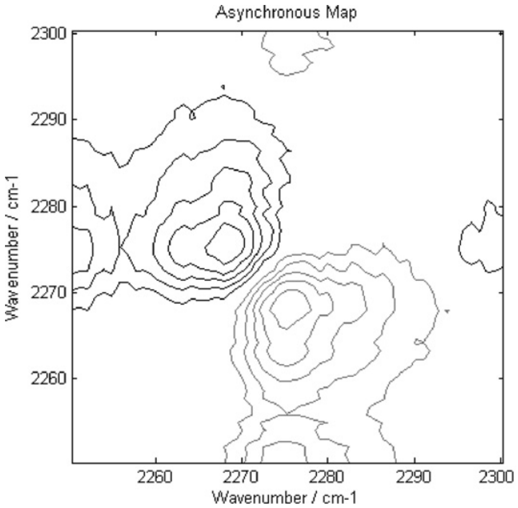


Fig. 7. Asynchronous correlation map obtained from 2DCoS of the reaction carried out in water focused in the region 2250–2300 cm^{-1}.

In the literature different trimers have been described too, [28] but due to the similarity between the spectrum of the third and the fourth components there is a strong indication that under these experimental conditions indeed **5** is being formed. According to results from MCR analysis, the pure spectrum for the trimer matches almost exactly the spectrum of **4** with the difference of the additional band at 2228 cm^{-1}. In **4** and **5** the unconjugated nitrile is centered at 2274 cm^{-1}. The conjugated nitriles give rise to two bands at 2201 and 2161 cm^{-1} due to the hindered rotation at the carbon double bond. The additional band (2228 cm^{-1}) present in **5** may be assigned to both nitriles near to the carbanion as they probably cannot be spectroscopically distinguished in solution.

4. Conclusions

In situ reaction monitoring using Raman spectroscopy provided high quality spectra of the base catalyzed

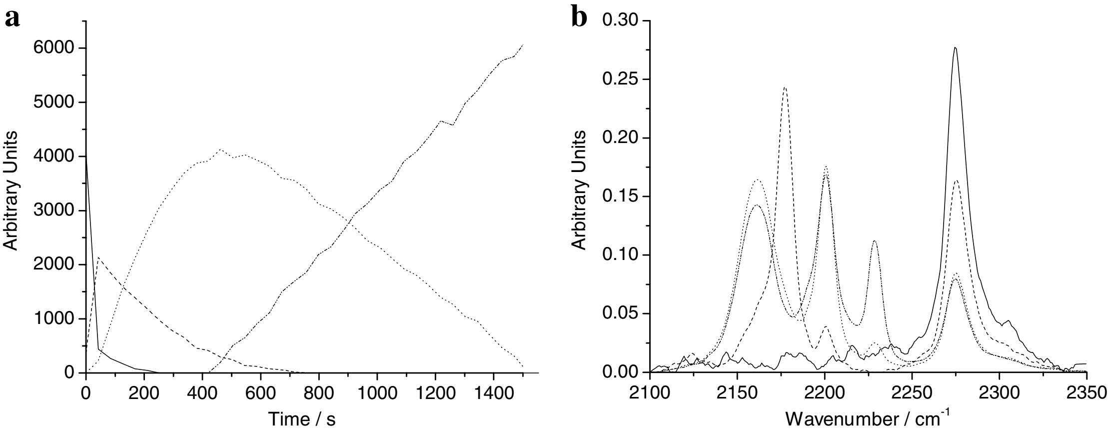
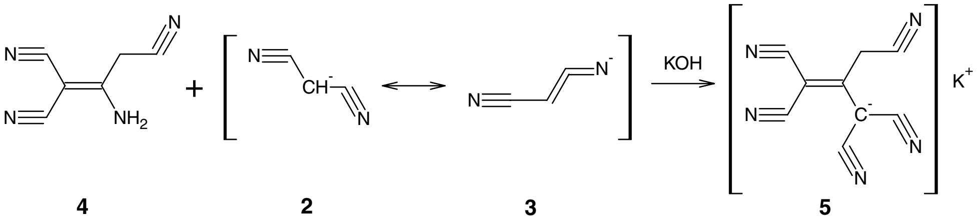


Fig. 8. Concentration profiles (a) and pure spectra (b) obtained by applying MCR to the data obtained using water as reaction medium.



Scheme 3.

di- and trimerization of malononitrile in an ionic liquid and water, respectively. Due to the strongly overlapping bands chemometric techniques had to be employed for assignment of the spectral bands to the individual species present in the reaction. In this particular study well-defined species including substrate, intermediates as well as reaction products could be assumed. Analysis of these data sets by MCR appeared to be most appropriate and powerful. This is because MCR is based on the assumption that the complex spectral data result as the superposition of the spectra of individual species according to their concentration at a given reaction time. During this process complementary analysis of the data using 2DCoS was useful. Meaningful correlations arising from well-resolved peaks were obtained. In addition the strength of 2DCoS in resolving strongly overlapping bands was evident also in this application. In particular the asynchronous correlations found in the restricted spectral area between 2250 and 2300 cm^{-1} were important to support the results obtained from MCR analysis.

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