Study of Water/Methanol-Ionic Liquid Interactions Using Mid-Infrarred Spectroscopy and Chemometrics

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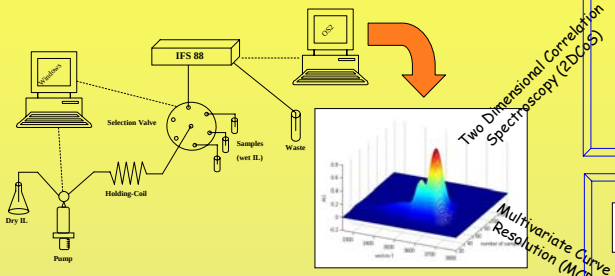
Ionic Liquids

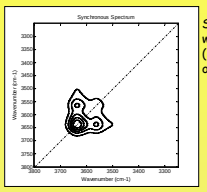
- **emimBF$_4$**: 1-ethyl-3-methylimidazolium tetrafluoroborate
- **bmimBF$_4$**:1-butyl-3-methylimidazolium tetrafluoroborate
- **bmimPF$_6$**: 1-butyl-3-methylimidazolium hexafluorophosphate



Automated preparation of a high number of water/methanol-IL mixtures and measurement of corresponding FT-IR spectra in a flow cell. Background: dry IL. Sample spectrum: recorded as injected sample (e.g. 6 % water in IL) is passing through the flow cell

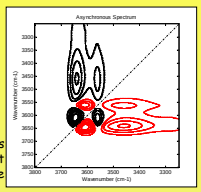
Data Matrix: X (m x n)

Correlation analysis:
- $S_{ww} = X^TX$ (synchronous map)
- $A_{ww} = X^THX$ (asynchronous map)



Spectral changes with the same rate (no information for our aim)

Spectral changes with different rate



Information about:
- Interactions (inter- and intra-molecular)
- Order in which the spectral changes occur

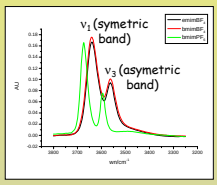
Data Matrix X (m x n) = $C \cdot S^T = C_1 \cdot S_1^T + C_2 \cdot S_2^T + C_3 \cdot S_3^T$

$X = C \cdot S^T + E = \Sigma C_k \cdot S_k^T + E$

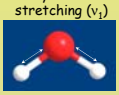
C = concentration profiles

S = spectra profiles

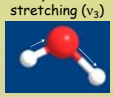
WATER



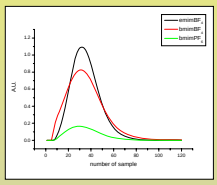
Symetric stretching (ν_1)



Asymetric stretching (ν_3)

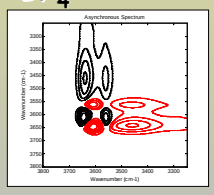


OH stretching spectra of selected concentration (*ca.* 0.55 % w/w) of water in the studied ionic liquids



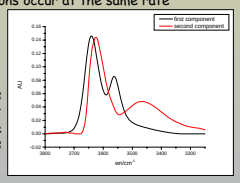
Flow profiles plotted at 3650 cm^{-1} for emimBF$_4$ and bmimBF$_4$ and at 3675 cm^{-1} for bmimPF$_6$

BF$_4^-$



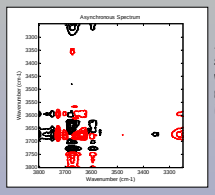
Maximum Value: 0.477

Asynchronous 2DCoS from concentration-dependent FT-IR spectral changes of water in emimBF$_4$ and bmimBF$_4$ where concentration was incresed from 0 to *ca.* 3 %. Lack of asynchronous peaks between 3650-3560 cm-1 and 3610-3460 cm^{-1} means that implicated interactions occur at the same rate



Spectra of individual interactions obtained by MCR. The first interaction corresponds to single water, while the second one is composed by cluster of it

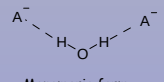
PF$_6^-$



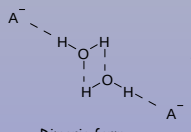
Maximum value: 0.004

Asynchronous 2DCoS from concentration-dependent FT-IR spectral changes of water in bmimPF$_6$ where concentration was increased from 0 to *ca.* 0.6 %. The maximum value makes it in the same range that noise. Therefore, only one interaction can be identified

Suggested interactions



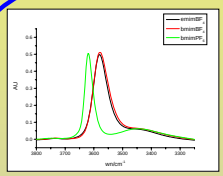
Monomeric form



Dimeric form

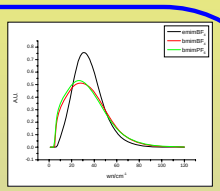
A^- : Anion (BF_4^- or PF_6^-)

METHANOL



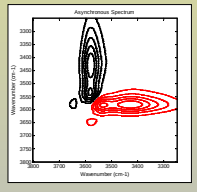
Stretching vibration. Only one band

OH stretching spectra of selected concentration (*ca.* 4 % w/w) of methanol in the ionic liquids



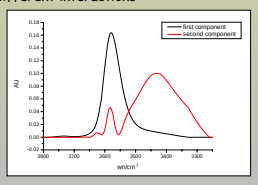
Flow profiles plotted at 3580 cm^{-1} for emimBF$_4$ and bmimBF$_4$ and at 3620 cm^{-1} for bmimPF$_6$

BF$_4^-$



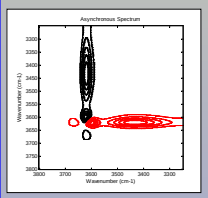
Maximum value: 0.193

Asynchronous 2DCoS from concentration-dependent FT-IR spectral changes of methanol in emimBF$_4$ and bmimBF$_4$ where concentration was increased from 0 to *ca.* 4 %. Both peaks are correlated asynchronously, which means they belongs at different interactions



Spectra of individual interactions obtained by MCR. The first interaction corresponds to monomer of methanol, while the second one corresponds to cluster of methanol interacting with the ionic liquids.

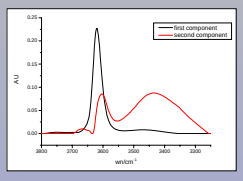
PF$_6^-$



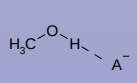
Maximum value: 0.163

Asynchronous 2DCoS from concentration-dependent FT-IR spectral changes of methanol in bmimPF$_6$ where concentration was increased from 0 to *ca.* 4 %. Both peaks are correlated asynchronously, which means that they belong at different interactions

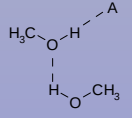
Spectra of individual interactions obtained by MCR. The first interaction corresponds to monomer of methanol, while the second one coresponds to cluster of methanol interacting with the ionic liquid.



Suggested interactions



Monomeric form



Dimeric form

A^- : Anion (BF_4^- or PF_6^-)

CONCLUSIONS

- Two types of cluster can be identified in both cases, water and methanol.
  - ✓Water or methanol in **monomeric** form are the major species observed.
  - ✓At higher concentrations, water-water or methanol-methanol **dimers** associated via hydrogen bonding can be found.
  - ✓ However in bmimPF$_6$, the most hydrophobic ionic liquid studied, only monomeric water can be identified, due to the low amount of water that can be dissolved.
- Anions of ionic liquids are major responsible for the interaction with water/methanol molecules. Anions interact with water and methanol monomers via hydrogen bonding giving the characteristics spectral features observed.
- Different cations provided different SIA profiles. That is, diffusion (which is related to viscosity of ionic liquids) is strongly dependent on the cation.

REFERENCES

1. I. Noda, A. E. Dowrey, C. Marcott, G. M. Story, Y. Ozaki, "Generalized Two-Dimensional Correlation Spectroscopy", Appl. Spectrosc. 54 (2000) 236A
2. R. Tauler, B. Kowalski, S. Fleming, "Multivariate Curve Resolution Applied to Spectral Data from Multiple Runs of an Industrial Process", Anal. Chem. 65 (1993) 2040
3. J. Diewok, M. J. Ayora Cañada, B. Lendl, "Two Dimensional Correlation Spectroscopy and Multivariate Curve Resolution in Analyzing pH-dependent Evolving Systems Monitored by FT-IR Spectroscopy – A comparative Study", Anal. Chem. 74 (2002) 4944