

# DISSOLUTION AND SPECIATION OF ARSENIC OXIDES IN IONIC LIQUIDS

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## Abstract

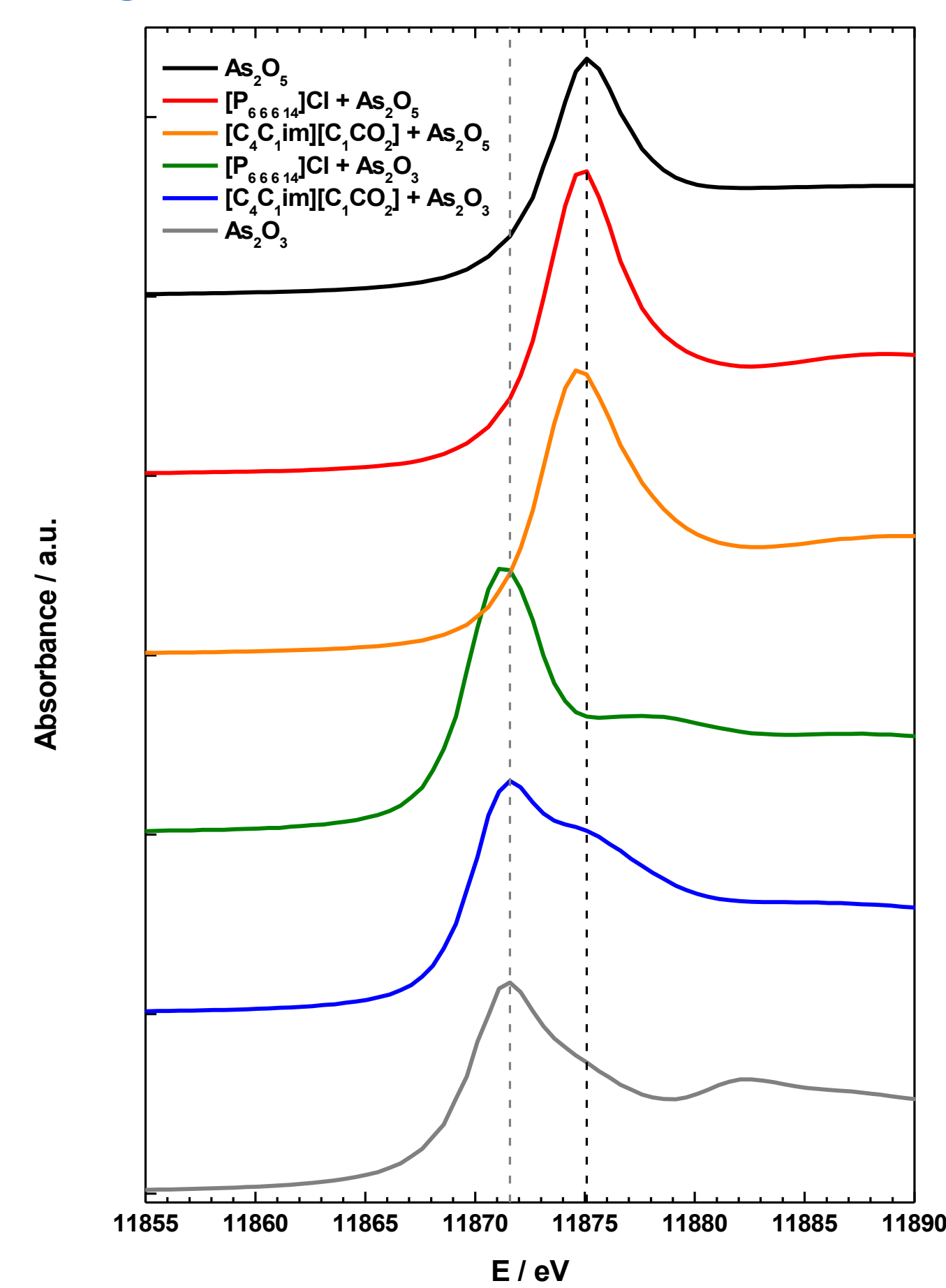
The solubility of arsenic(III) oxide and arsenic(V) oxide was screened in several ionic liquids. The best arsenic oxide solubility was observed in ionic liquids with basic anions, such as carboxylate. The solubility of arsenic(III) oxide and arsenic(V) oxide in ionic liquids with carboxylate anions decreases with increasing hydrophobicity of the cation or anion. The arsenic(III) oxide solubility in phosphonium and ammonium chlorides increased with increasing hydrophobicity of the ionic liquid cation. The arsenic species in the dissolved state was investigated for selected systems. In the arsenic(V) oxide solution, arsenic is most likely present as arsenate anions in all investigated ionic liquids. In the solutions of arsenic(III) oxide in ionic liquids with acetate as anion, an equilibrium of arsenite and arsenate was found. For phosphonium chlorides, the formation of an anionic complex between arsenic(III) oxide and the chloride anions of the ionic liquid is postulated. The results of the solubility screening and arsenic species in solution indicate different dissolution mechanisms for ionic liquids containing carboxylate anions or chloride as anion.

## Discussion

The dissolution of metals in ionic liquids and the understanding of their speciation is of great importance to catalytic reactions, metal ion batteries, solar cells, electroplating and in the formation of new materials. Metal oxides, due to their high lattice energies, are generally hard to dissolve e.g. in organic or aqueous solvents. However, it has been reported, that several metal oxides have a high solubility in ionic liquids and deep eutectics. The driving force for the dissolution can be the formation of a complex, e.g. with the carboxylate group of a functionalized ionic liquid cation, with heterogeneous carbenes formed *in situ* of imidazolium based ionic liquids, with the deep eutectic anion or with an organic complexing agent, or by forming halometalates.

Here, the dissolution of arsenic oxides in ionic liquids is investigated. Arsenic is a heavy metalloid, is very toxic and causes several diseases such as blackfoot disease or cancer. Several studies have demonstrated that arsenic can be extracted very efficiently from water using several ionic liquids based on ammonium or phosphonium cations. After extraction of soil samples in imidazolium-based ionic liquids, only arsenic(III) was found, although arsenic(V) was the dominant oxidation state. This indicates that the ionic liquid does not only extract and dissolve the arsenic species, but can also affect the oxidation state. So far, little is known about the speciation of arsenic within an ionic liquid. However, knowledge of the speciation of metal ions in ionic liquids is of importance for understanding the extraction processes and is of advantage for the optimization of such systems.

## XANES

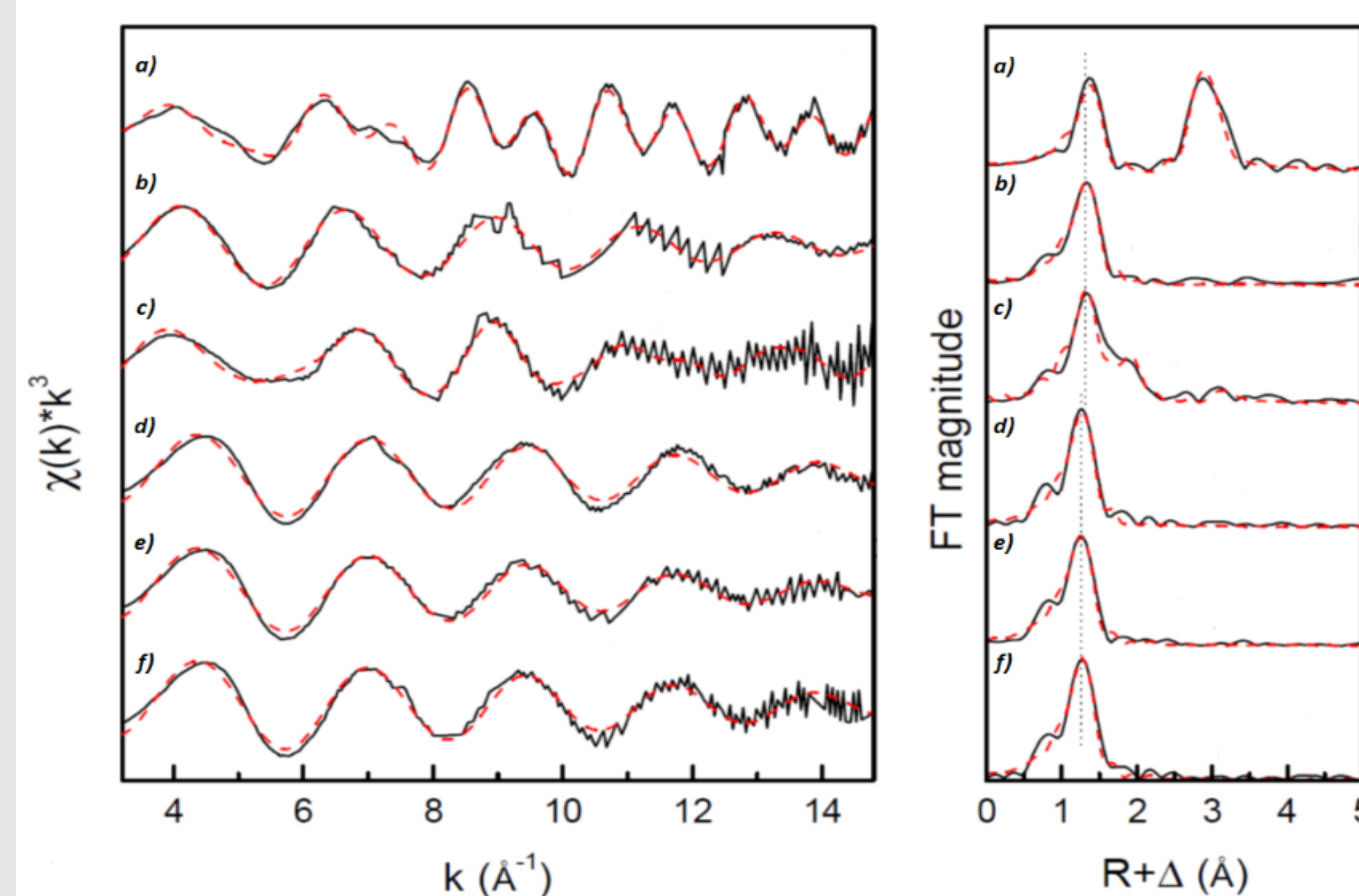


XANES spectra of arsenic(III) oxide solutions in [P<sub>6,6,6,14</sub>][Cl] (orange), [P<sub>2,2,2,8</sub>][C<sub>1</sub>CO<sub>2</sub>] (green), [C<sub>4</sub>py][C<sub>1</sub>CO<sub>2</sub>] (blue) and [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] (violet). For comparison the XANES of solid arsenic(III) oxide (grey, bottom) and arsenic(V) oxide (black, top) are included.

The arsenic(III) oxide solubility in phosphonium and ammonium chlorides increases with increasing hydrophobicity of the ionic liquid cation. The investigations of arsenic(III) oxide solution in [P<sub>6,6,6,14</sub>][Cl] indicates anionic complex formation between arsenic(III) oxide and the chloride anions of the ionic liquid.

The hydrophilic nature of the arsenate, but at the same time hydrophobic nature of the ionic liquid cation, is most likely the reason for the observed trend. The arsenic(V) oxide solubility in phosphonium chlorides decreases with increasing hydrophobicity of the ionic liquid cation. The solubility of arsenic(III) oxide and arsenic(V) oxide in ionic liquids containing carboxylates as anionic species decreases with increasing hydrophobicity of the ionic liquid cation or anion. The arsenic(III) oxide solubility further decreases with decreasing amounts of water (at a water content below 20 mol% in [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>]). The analytical investigations of arsenic(III) oxide in [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>], [C<sub>4</sub>py][C<sub>1</sub>CO<sub>2</sub>] and [P<sub>2,2,2,8</sub>][C<sub>1</sub>CO<sub>2</sub>] indicate that arsenic exists as an equilibrium between arsenite and arsenate ions. In the solutions of arsenic(V) oxide only arsenate anions are present.

## EXAFS



Left:  $k^2$ -weighted normalized  $\chi$  function and right: Fourier transforms of the  $\chi$  function of a) monoclinic arsenic(III) oxide, b) As<sub>2</sub>O<sub>3</sub> dissolved in [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>], c) As<sub>2</sub>O<sub>3</sub> dissolved in [P<sub>6,6,6,14</sub>][Cl], d) solid As<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O (n = 3-5), e) As<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O (n = 3-5) dissolved in [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>], and f) As<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O (n = 3-5) dissolved in [P<sub>6,6,6,14</sub>][Cl]. The black solid lines are experimental data and the red dashed lines represent the theoretical fit of the data.

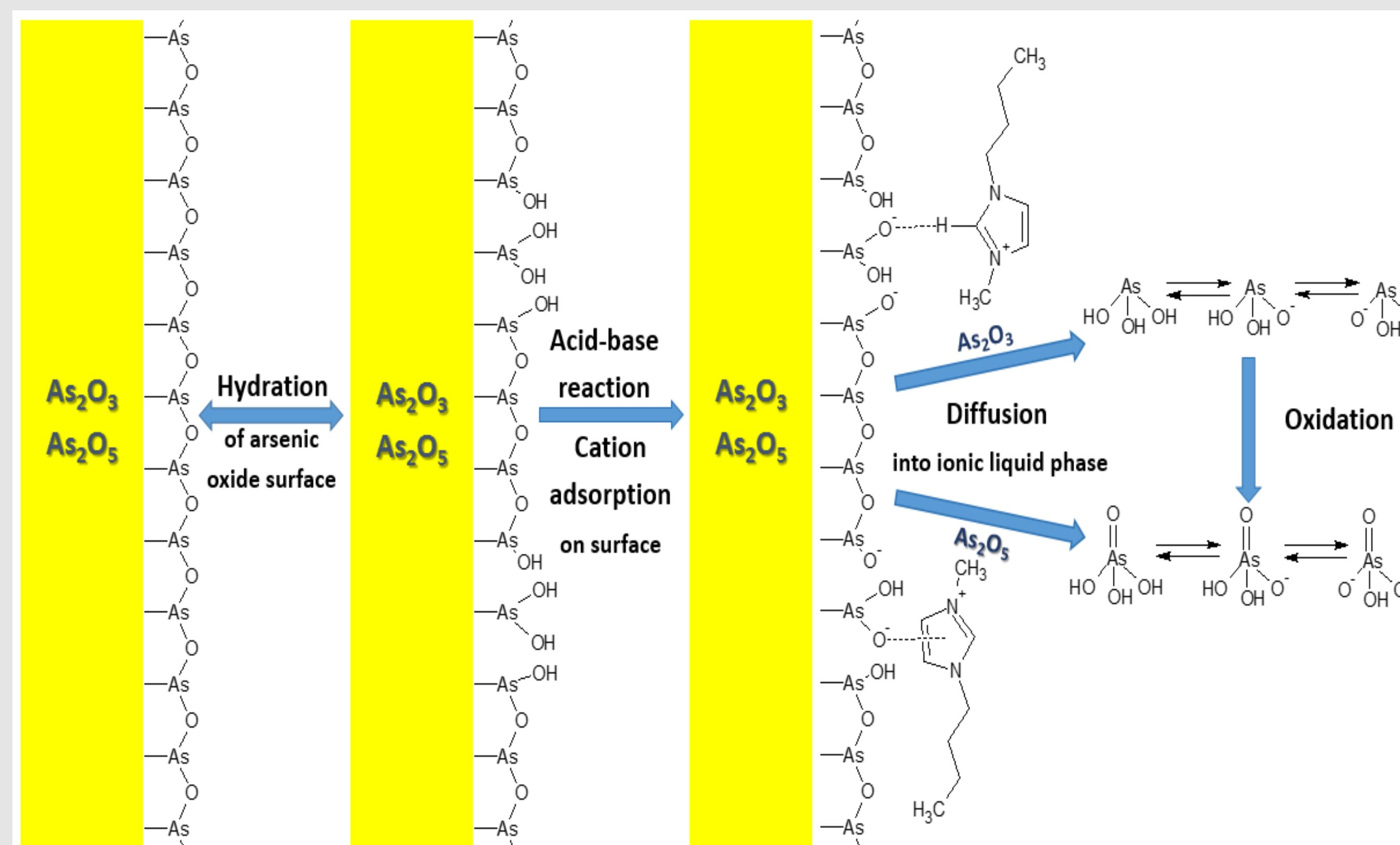


Illustration of the proposed dissolution mechanism of arsenic(III) and arsenic(V) oxide into ionic liquids containing carboxylate as anion, here [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] as representative.

## XAS measurements @ DUBBLE

Arsenic K-edge (11.867 keV) X-ray absorption spectra (XAS) of solid arsenic(III) oxide, arsenic(V) oxide and their solutions in [P<sub>6,6,6,14</sub>][Cl], [P<sub>2,2,2,8</sub>][C<sub>1</sub>CO<sub>2</sub>], [C<sub>4</sub>py][C<sub>1</sub>CO<sub>2</sub>] and [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] with a concentration of approximately 5 mol% arsenic at room temperature were collected at the Dutch-Belgian Beamline (DUBBLE) at the European Synchrotron Radiation Facility (ESRF). The energy calibration was done using Au foil (L<sub>III</sub>, 11.919 keV). Several scans were collected for each sample to check for reproducibility of the data and were averaged to improve the signal-to-noise ratio. EXAFS data extraction and data fitting was performed using the programs WinXAS, EXAFSPAK and the Artemis suite. Theoretical phase and amplitude functions were calculated using FEFF 8.2 based on the crystal structure of As<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>5</sub>.

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