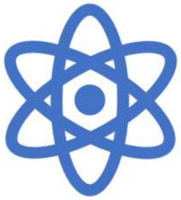
WG3 meeting

Tuesday, 27 February 2024

Milazzo, Italy

WG3: NECTAR for multicomponent solutions and complex matrices

Thermodynamic and chemical equilibrium data and speciation studies of real systems (e.g. natural waters, biological fluids, commercial products).



Classical procedures for the study of the equilibria in multicomponent systems (e.g. ionic liquids, mixed solvents, heterogeneous systems, etc.) are often inadequate when a high number of components is present in the matrix.

In this respect, there is an urgent need to update and adapt experimental procedures and computational approaches.

WG3 report

Oct 2019 – Feb 2024	
Collaborations activities	Around 15 active participants.
Networking activities:	2 NECTAR conferences organized by WG3 members; 10 STSMs by WG3 members; TS in calorimetry organized in Ljubljana
Dissemination and communication activities	8 with COST acknowledgement and 1 with „3 countries rule“ Two guidelines given at NECTAR web page
Participation at all NECTAR meetings	15 posters 20 oral presentations

WG3: NECTAR for multicomponent solutions and complex matrices defined in Brussels

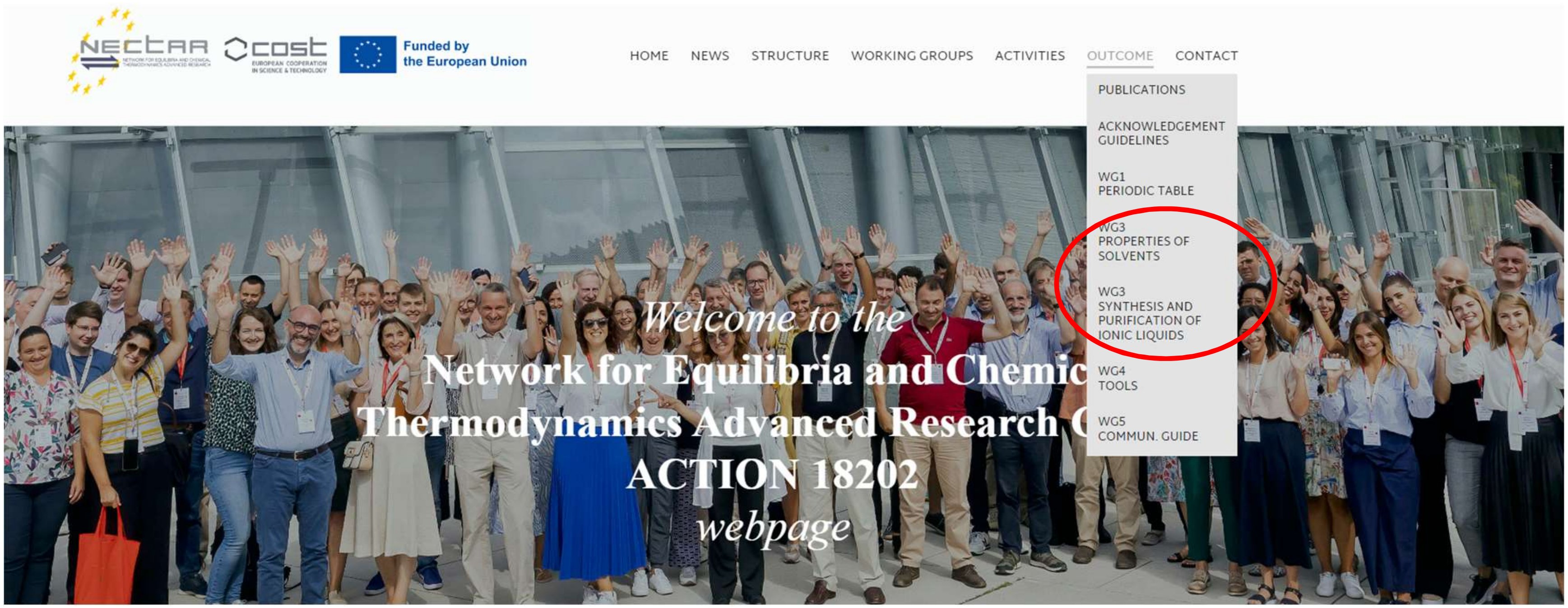
Complex materices	Speciation studies	Heterogeneous systems
• Task specific ionic liquids • Ionic liquids + molecular solvent	• Sulphur speciation • Critical elements • 3D metallacage complexes	• Sorbent materials • Nanoscale systems

- Task Specific ILs: Chelating ILs, Pharmaceutically Active ILs, Zwitterionic ILs, Surface Active ILs (RS, SI, CZ)
- Mixtures of ILs and MS (aqueous solutions): determination of the thermodynamic parameters, equilibrium constants, evaluation of the interactions experimentally and using MD especially NCI, interactions of drugs or biologically active substances (RS, SI)
- Speciation studies: Sulphur speciation of free and incapsulated drugs Raloxifene and Tizanidine and method developing (DK), speciation of supramolecular self-assembled 3D metallacage complexes (DE), extraction of critical elements using ionic liquids (RS), heterogeneous equilibria (MD)

Task

- Defining recommended experimental and data analysis procedures and guidelines for an accurate speciation of systems in complex matrices such as ionic liquids, mixed solvents, systems containing surfactants or sorbent materials.
- Release first guidelines on interactions in non-aqueous systems

Guidelines



Funded by the European Union
HOME
NEWS
STRUCTURE
WORKING GROUPS
ACTIVITIES
OUTCOME
CONTACT
PUBLICATIONS
ACKNOWLEDGEMENT GUIDELINES
WG1 PERIODIC TABLE
WG3 PROPERTIES OF SOLVENTS
WG3 SYNTHESIS AND PURIFICATION OF IONIC LIQUIDS
WG4 TOOLS
WG5 COMMUN. GUIDE
Welcome to the
Network for Equilibria and Chemic
Thermodynamics Advanced Research C
ACTION 18202
webpage

Ionic liquids – guidelines for synthesis and purification

Funded by the European Union

HOME NEWS STRUCTURE WORKING GROUPS ACTIVITIES OUTCOME CONTACT

Synthesis and purification of Ionic Liquids

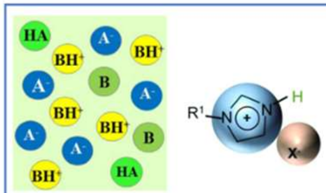
This guide outlines methods for synthesizing and purification of protic, aprotic and zwitterionic ionic liquids, including alternative and cleaner approaches. The synthesis of ionic liquids involves several steps, including identification of the reagents, choosing the appropriate solvent and optimizing the reaction conditions. The guideline for synthesizing these liquids requires understanding the basic principles of ionic liquid synthesis, selecting the right reactants based on the desired properties and conducting the reaction under proper conditions. The steps involved include selecting the cation and anion, selecting the solvent, reaction optimization and purification. Each of these steps is critical to ensure the successful synthesis of high-quality ionic liquids that meet the desired specifications.

Synthesis of Ionic Liquids

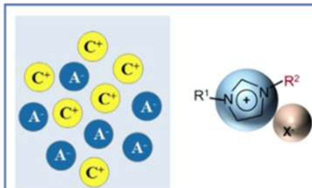
Purification and Challenges

SYNTHESIS AND PURIFICATION OF IONIC LIQUIDS

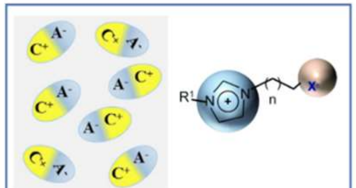
Synthesis of Ionic Liquids



Protic



Aprotic



Zwitterionic

Synthesis and purification of Ionic Liquids

Synthesis of Ionic Liquids

Protic Ionic Liquids (PILs)

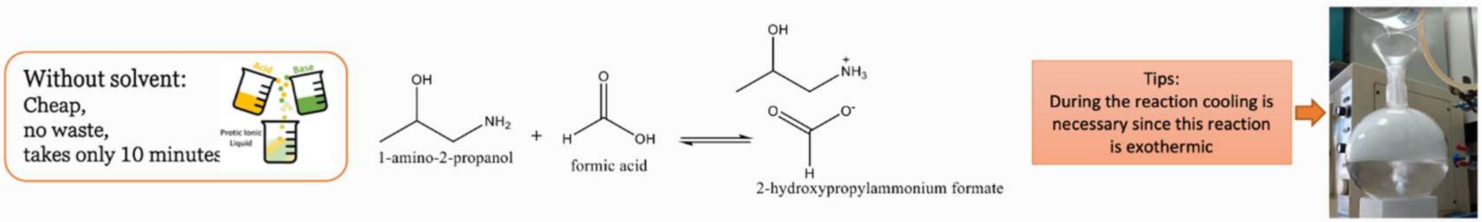
Protic ionic liquid (PIL) is a subclass of ionic liquid that has a protonated cation and can be synthesized through a neutralization reaction which involves transferring a proton from a Brønsted acid to a Brønsted base.

$$B + A \rightarrow HB^{+} + A^{-}$$

- PILs are a good conductor of protons and ions.
- Water may be used as a solvents or titration can be performed without any solvent. Example
- Complete proton transfer between the acid and base must occur for optimal production.
- The cation on which the proton resides determines the proton activity of the IL.
- To achieve this, there must be **a high pKa difference** between the acid and base.
- In aqueous solutions, **a difference greater than 10** is sufficient for more than **99% proton transfer**.
- Various factors, such as the physical and chemical properties of the base and acid determine the extent of proton transfer and ionicity of the IL.
- A highly recommended procedure is to determine an acid-base titration curve for the two components dissolved in water.
- The equivalence point and pH at the end point confirm the purity of the IL after synthesis and any subsequent handling procedures.
- Diluting an IL sample in water to the standard concentration confirms the previously determined equivalence point pH.

Synthesis and purification of Ionic Liquids

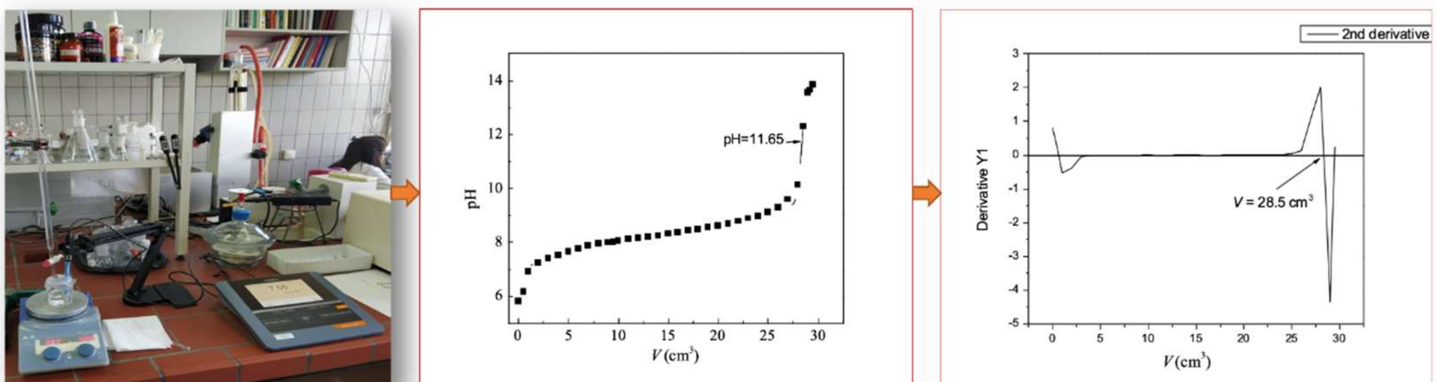
Example:



(Click to close)

- The cation on which the proton resides determines the proton activity of the IL.
- To achieve this, there must be **a high pKa difference** between the acid and base.

Titration curve:

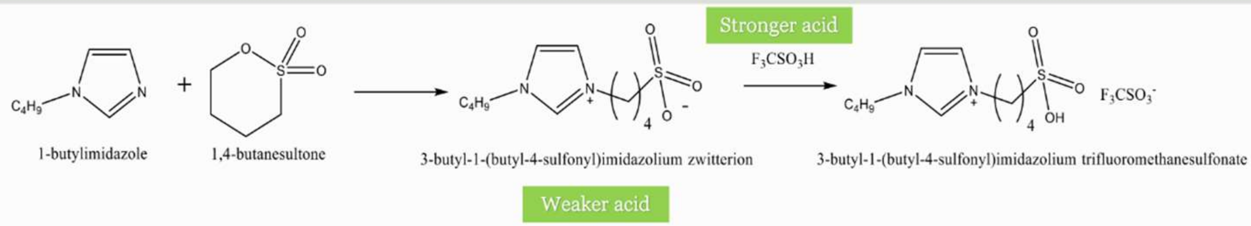


(Click to close)

- The equivalence point and pH at the end point confirm the purity of the IL after synthesis and any subsequent handling procedures.
- Diluting an IL sample in water to the standard concentration confirms the previously determined equivalence point pH.

Example:

- the Bronsted acidic IL, 3-butyl-1-(butyl-4-sulfonyl)imidazolium trifluoromethanesulfonate, can be synthesized over two steps.
- First, 1-butylimidazole reacts with 1,4-butanesultone to generate the zwitterion.
- Second, the zwitterion is acidified by adding trifluoromethanesulfonic acid, which protonates the zwitterion to form the trifluoromethanesulfonate anion.
- The low pKa of the acid helps to transform the sulfonate group into a sulfonic acid, making the reaction successful.



(Click to close)

These zwitterionic liquids are similar to ILs but cannot migrate in an electric field. They help ensure that the Li^+ ions can transport smoothly in the electrolyte.

The reaction involves the nucleophile 1-methylimidazole reacting with 1,3-propanesultone. The sultone undergoes ring opening at the α-carbon to produce the zwitterion with >98% yield. Zwitterionic ILs can act as Bronsted acids. This property makes them useful as catalysts and solvents. Example.

II. Properties of solvent

Properties of solvents

Below is a list of some of the most commonly used solvents. Clicking on each of them will take you to a list with the following properties: melting point, boiling point, dielectric constant, dynamic viscosity, dipole moment, donor number, acceptor number, empirical solvent polarity parameter (E_T), and normalized E_T^N.

If not denoted differently, data are taken from the book J. M. G. Barthel, H. Krienke, W. Kunz, Physical Chemistry of Electrolyte Solutions, Modern Aspects, Springer, 1998.

List of Solvents

Find the solvent...

- Acetone
- Acetonitrile
- Benzene
- 1-Butanol
- γ-Butyrolactone
- Carbon tetrachloride
- Chloroform
- Cyclohexane
- Diethylene glycol
- Diethyl carbonate
- Dimethyl sulfoxide
- 1,4-Dioxane
- Ethanol
- Ethyl acetate

Solvent

Melting point (1 atm) =

Boiling point (1 atm) =

Dielectric constant (25 °C) =

Dynamic viscosity (25 °C) =

Density (25 °C) =

Dipole moment (in the gas phase) =

Donor number (+info)=

Acceptor number (+info)=

$E_T(30)$ (+info)=

E_T^N (+info)=

PROPERTIES OF SOLVENTS

Below is a list of some of the most commonly used solvents. Clicking on each of them will take you to a list with the following properties: melting point, boiling point, dielectric constant, dynamic viscosity, dipole moment, donor number, acceptor number, empirical solvent polarity parameter (E_T), and normalized E_T^N.

If not denoted differently, data are taken from the book J. M. G. Barthel, H. Krienke, W. Kunz, Physical Chemistry of Electrolyte Solutions, Modern Aspects, Springer, 1998.

List of Solvents

Find the solvent...

- Acetone
- Acetonitrile
- Benzene
- 1-Butanol
- γ-Butyrolactone
- Carbon tetrachloride
- Chloroform
- Cyclohexane
- Diethylene glycol
- Diethyl carbonate
- Dimethyl sulfoxide
- 1,4-Dioxane
- Ethanol

Acetone

Melting point (1 atm) = **-94.7 °C**

Boiling point (1 atm) = **56.29 °C**

Dielectric constant (25 °C) = **20.56**

Dynamic viscosity (25 °C) = **0.303 mPa·s**

Density (25 °C) = **0.7844 kg·dm^{-3}**

Dipole moment (in the gas phase) = **2.69 D**

Donor number (+info)= **17.0 kcal·mol^{-1}**

Acceptor number (+info)= **12.5**

$E_T(30)$ (+info)= **42.2 kcal·mol^{-1}**

E_T^N (+info)= **0.35**

(Click to clear)