

**NPL REPORT  
DEPC-MPE 031**

**Thermodynamic data for  
ionic liquids – needs and  
availability**

**A DINSDALE**

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## Thermodynamic data for ionic liquids – needs and availability

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### **ABSTRACT**

Ionic liquids (or low temperature molten organic salts) form potentially the basis of a new industrial technology that could revolutionise chemical processing as well as impact on many other industries. However so vast is the array of potential cations and potential anions that it has been estimated that these could produce over  $10^{12}$  ionic liquids. The field is one of great growth such that last year there were over 1500 publications containing the phrase “ionic liquid” in the title. Inevitably any report summarising the availability of information in this area is bound to be out of date as soon as it is produced – the intention is to update this report regularly.

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Approved on behalf of the Managing Director, NPL,  
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authorised by Director, Engineering and Process Control Division

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## 1 INTRODUCTION

Ionic liquids (or low temperature molten organic salts) form potentially the basis of a new industrial technology that could revolutionalise chemical processing as well as impact on many other industries. These liquids have a range of distinctive properties. Of particular importance is the melting point and its ability to dissolve various solutes. It is impossible to carry out measurements on all the ionic liquids of potential interest and so it is important to develop reliable models from which the properties of a new unstudied material can be predicted.

Melting points, solubilities and the way in which liquidus temperatures vary with composition are information displayed on the phase diagram. NPL has been at the forefront of the derivation of techniques for calculating phase diagrams from critically assessed thermodynamic data but thus far this approach has not been applied to ionic liquids. Because of the vast range of potential ionic liquids experimental work has been restricted to a limited set of cations and anions. Even for these experimental information in the literature concerning the thermodynamic properties is essentially limited to melting points, enthalpies of fusion, the activities of organic solvents dissolved in ionic liquids and certain phase diagram information e.g. miscibility gap between ionic liquids and water or ethanol and solubilities of gases such as H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>. While these in themselves are useful data, other important data such as the enthalpies of mixing between an ionic liquid and solutes are essentially non existent. Such data are key to the derivation of a full description of the thermodynamics of a system.

The purpose of this report is to review the published thermodynamic and phase diagram data for systems involving ionic liquids. At a later stage of the project selected measurements will be carried out at NPL to obtain a more detailed understanding of the thermodynamics of a small number of key systems using a mixture of dsc and rotation reaction calorimetry. At the same time molecular dynamics simulations is being used to compare predictions with our experimental data. The ultimate aim is to model all the available data for these selected systems in order to provide datasets able to reproduce all the experimental information and allow calculation of other properties such as the phase diagram.

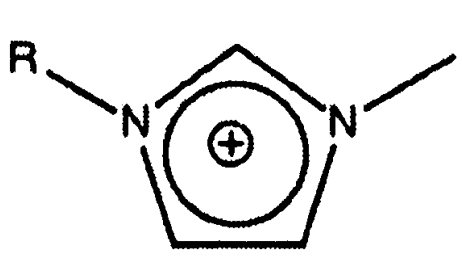
## 2 TERMINOLOGY

It has been estimated that the huge array of potential cations and potential anions could produce over 10<sup>12</sup> ionic liquids. Well developed and consistent terminology is therefore key to the identification of each ionic liquid. By and large the international community has adopted conventional abbreviations but their adoption is by no means universal. Most of the ionic liquids that have been the subject of major study are based on the three distinct families: substituted imidazolium, pyridinium and quaternary ammonium salts:

## 3 CATIONS

a) Imidazolium based cations in which the hydrogen atom bonded to two nitrogen atoms may be substituted by various groups typically alkyl. Recent innovations have used inorganic groups or even chains bound to solid state catalysts. The diagram below shows the hydrogen atom from one of the nitrogen atoms substituted by a methyl group

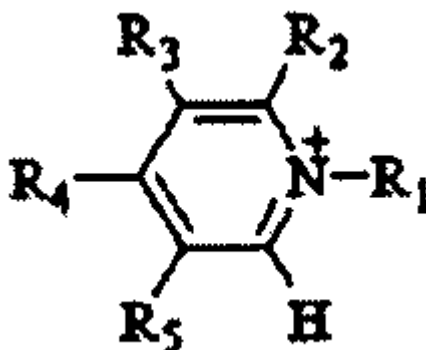
and the other substituted in same other way. The generic terminology for this class of cation is then [Rmim]. Where R is a specific group eg methyl, ethyl, butyl, hexyl the cation is then designated respectively as [mmim], [emim], [bmim], [hmim] etc.



1-R-methylimidazolium [Rmim]

In principle the hydrogen atoms normally bonded to the carbon atoms could also be substituted giving rise to the possibility of far greater complexity.

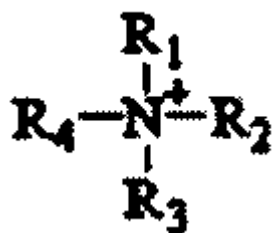
b) Pyridinium based cations in which the hydrogen atom bonded to the nitrogen of the six membered ring (labelled R<sub>1</sub> in the diagram below) can be substituted by various groups such as alkyl. This would be designated as [Rpy] or for specific examples [mPy], [ePy], [bPy] where the group R is methyl, ethyl or butyl respectively. The other R groups in the diagram below which are bonded to carbon atoms may also be substituted but again the terminology gets complicated.



Pyridinium

c) Quaternary ammonium

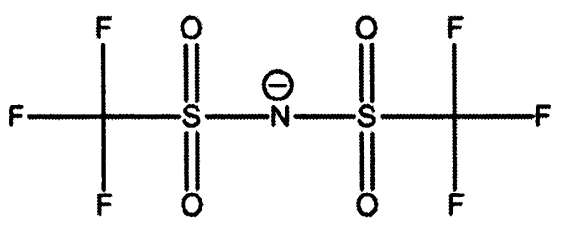
This is the simplest case where each of the four hydrogen atoms bonded to the nitrogen atom in an ammonium ion could be substituted by various groups such as alkyl. Therefore [m<sub>4</sub>N] would be the abbreviation for the tetramethyl ammonium ion. One important example of a quaternary ammonium based cation is choline (2-hydroxyethyl-trimethylammonium) where methyl forms three of the groups, the fourth being C<sub>2</sub>H<sub>4</sub>OH. Choline chloride based ionic liquids have been used by Abbott et al. with some success in specific industrial processes.



Quaternary ammonium

#### 4 ANIONS

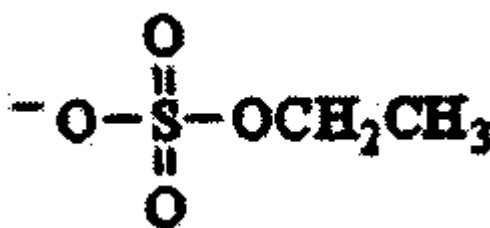
The type of anions used tend to have even greater variety. All tend to be monovalent and include simple anions like chloride, bromide, iodide to the very complicated docusate anion. Typically researchers have focussed on a limited number such as those given below:



bis(trifluoromethylsulfonyl)imide abbreviated to [BTI] or [NTf2]

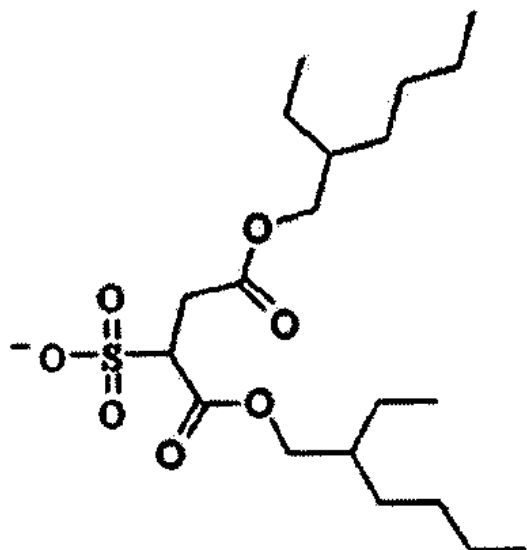
[PF<sub>6</sub>] : hexafluorophosphate

[BF<sub>4</sub>] : tetrafluoroborate

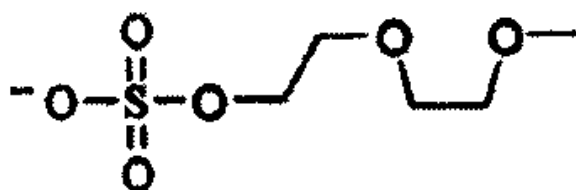
Ethyl sulfate [EtSO<sub>4</sub>]

[CH<sub>3</sub>-(OCH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>-O-SO<sub>3</sub>]

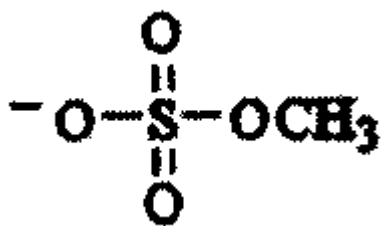
2-(2-methoxyethoxy) ethyl sulfate abbreviated to [MDEGSO<sub>4</sub>]



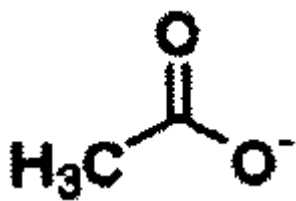
Docusate abbreviated to [doc]



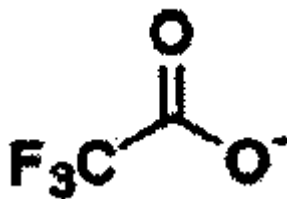
2-(2-Methoxy-ethoxy)-ethylsulfate abbreviated to [C<sub>5</sub>H<sub>11</sub>O<sub>2</sub>SO<sub>4</sub>]



Methyl sulfate abbreviated to [MeSO<sub>4</sub>]



Acetate [CH<sub>3</sub>CO<sub>2</sub>]

Trifluoroacetate [ $\text{CF}_3\text{CO}_2$ ]

Trifluormethanesulfonate [triflate]

## 5 WHY THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA ARE IMPORTANT

Thermodynamic properties and phase equilibria are intimately linked. Properties such as the melting point, the solubility of impurities and reagents and vapour pressures while they are all associated with phase equilibria, can be calculated if the thermodynamic properties of the various phases of the system are known. Moreover since thermodynamic properties are inherently fundamental they are well suited to modelling, correlations and extrapolations. The following are considered as key properties for ionic liquids:

- Melting point – knowledge of the melting point provides the information about the temperature range over which the liquid can be used. The temperature below which solid begins to precipitate varies as the liquid dissolves other materials such as gases, organic solvents, water or inorganic salts.
- Vapour pressure – ionic liquids themselves have extremely low vapour pressures but the vapour pressures of organic substances or simple inorganic materials such as  $\text{O}_2$  and  $\text{CO}_2$  can be very important properties for an industrial process.
- Solubility – Ionic liquids can be used as solvents for chemical reactions. They can also be used as a means of separating different types of materials eg aliphatic hydrocarbons from aromatic hydrocarbons. They can be used as the method for scrubbing gas streams or as a medium for carrying out electrochemical reactions.
- Energy storage - Ionic liquids have the potential for use as thermal storage materials because of their low melting points.

## 6 WHAT SORT OF PROPERTIES ARE REQUIRED

Ultimately a full knowledge of all the thermodynamic properties are required. The most important properties are the melting points and enthalpies of fusion for the pure ionic liquid although information about the glass transition temperature, solid state transformations and the variation of heat capacity with temperature are also important. It has been shown recently that some ionic liquids can be distilled at low pressures. An understanding therefore of the nature of the gas phase in equilibrium with the liquid and the thermodynamic properties associated with its formation are also important. The standard enthalpy of formation of an ionic liquid is thought to be of minor importance.

However some interest has recently been shown in the study of phase diagrams between a pair of unrelated ionic liquids. Here the energetics associated with the double decomposition reaction whereby anions and cations are swapped is of interest.

For mixtures of ionic liquids or solutions of an organic solvent, water or a gas in the liquid, solubility and the way this changes with temperature is very important property. This is essentially phase diagram information although it can often be related directly to the thermodynamic properties of the ionic liquid solution. Other phase diagram information of interest would be compositions of the two liquid phases across a miscibility gap and the composition of the liquid in equilibrium with any solid phase. For most ionic liquids this second item is not likely to be appropriate but for it could be very important if the ionic liquid forms as a result of mixing between two higher melting solids such as a choline chloride and urea. In terms of thermodynamic properties the vapour above the ionic liquid can almost invariably be assumed to contain just the solute and so measurement of the vapour pressure can be related directly to the activity of the solute in the ionic liquid. The enthalpy of mixing between the components of the liquid phase is also an important property although in practice this has not been studied for systems involving ionic liquids. Enthalpy data are key to obtaining a good comprehensive model for the thermodynamic properties of ionic liquids.

## **7 WHAT PROPERTIES HAVE BEEN STUDIED**

The tables below summarise the measurement that have been reported to date. As the field of ionic liquids is one which is seeing such an explosion of activity these tables are inevitably out of date.

For pure ionic liquids the property most studied is the melting point. Coverage seems to be fairly good for the most common ionic liquids. The enthalpy of fusion and the heat capacity have been measured albeit to a lesser extent.

For solutions in ionic liquids the most common property measured is the activity coefficient at infinite solution, studied particularly for organic substances eg alkanes, alkenes, aromatics, alcohols. A number of these materials have been studied over the whole range of compositions usually by some sort of vapour pressure technique. There seems to be only one reported calorimetric work carried out to measure directly the enthalpies of mixing between an ionic liquid and another liquid (04reb/naj).

The solubility of certain gases eg  $H_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$  have been studied over a range of temperatures. The phase diagrams for a number of ionic liquid – organic liquid mixtures have been studied. Often the liquids are completely miscible but in some important systems eg involving water and alcohols, the phase diagram is characterised by a miscibility gap often centred about the 50% composition ionic liquid when expressed in terms of mass. Systems involving water are particularly important as ionic liquids are often difficult to get pure, water being a particularly common contaminant. A limited number of ternary systems have been studied involving an ionic liquid and two other substances e.g. water and an alcohol. A large co-solvent effect has been observed for such systems.

Some work has been carried out to characterise mixtures of ionic liquids. Where the ionic liquids are of the same family eg same cation or same anion, the phase diagrams seem fairly simple generally involving liquid and solid solutions. Recent work on mixtures of ionic liquids with different cations and different anions have shown significant tendency to demixing but this could be expected for reciprocal systems particularly where the double decomposition reaction is associated with a large change in Gibbs energy.

## 8 MODELLING

Various attempts have been made to correlate the melting points of ionic liquids with the nature of the cations and anions. Such attempts have shown valuable trends but also highlighted apparent anomalies (02kat/jai, 02kat/lom, 03eik/bre, 04gla, 05car/air).

The measured thermodynamic properties of mixing between ionic liquids and organic liquids have also been the subject of theoretical study. Some success has been achieved by using approaches like COSMO-RS (conductor-like screening model for real solvents) which provides a method for calculation of activity coefficients and phase equilibria of systems composed of volatile solvents and no-volatile ionic liquids (05jor/kri).

Attempts have also been made to study ionic liquids using a molecular dynamics approach. While this has achieved some success for the prediction of some properties it does not seem to have been used so far in the prediction of thermodynamic properties such as the enthalpy of fusion or enthalpies of mixing.

Tables 1 to 4, that follow, summarise published thermodynamic and phase diagram measurements for pure, binary and some ternary systems involving ionic liquids.

**Table 1** Studies of the thermodynamic properties of pure components

| Component                                | DfH | Cp          | Ttrans                                  | DHfus,<br>DHtrans |
|------------------------------------------|-----|-------------|-----------------------------------------|-------------------|
| [m <sub>4</sub> N][Cl]                   |     | 1962cha/wes |                                         | 1970mur/bre       |
| [e <sub>4</sub> N][Cl]                   |     |             | wel                                     |                   |
| [e <sub>4</sub> N][BF <sub>4</sub> ]     |     |             | 00ngo/lec                               |                   |
| [e <sub>4</sub> N][PF <sub>6</sub> ]     |     |             | 00ngo/lec                               |                   |
| [e <sub>4</sub> N][NTf <sub>2</sub> ]    |     |             | 00ngo/lec                               |                   |
| [e <sub>4</sub> N][Betl]                 |     |             | 00ngo/lec                               |                   |
| [e <sub>4</sub> N][Me]                   |     |             | 00ngo/lec                               |                   |
| [p <sub>4</sub> N][Cl]                   |     |             | wel                                     |                   |
| [p <sub>4</sub> N][Cl]                   |     |             | wel                                     |                   |
| [b <sub>4</sub> N][Br]                   |     |             | wel                                     |                   |
| [b <sub>4</sub> N][I]                    |     |             | wel                                     |                   |
| [b <sub>4</sub> N][Br <sub>3</sub> ]     |     |             | wel                                     |                   |
| [b <sub>4</sub> N][I <sub>3</sub> ]      |     |             | wel                                     |                   |
| [b <sub>4</sub> N][BF <sub>4</sub> ]     |     |             | wel                                     |                   |
| [b <sub>4</sub> N][PF <sub>6</sub> ]     |     |             | wel                                     |                   |
| [b <sub>4</sub> N][BPh <sub>4</sub> ]    |     |             | wel                                     |                   |
| [b <sub>4</sub> N][NTf <sub>2</sub> ]    |     |             | 00ngo/lec                               |                   |
| [b <sub>4</sub> N][Me]                   |     |             | 00ngo/lec                               |                   |
| [b <sub>4</sub> N][doc]                  |     |             | 05cro/mul                               | 05cro/mul         |
| [h <sub>4</sub> N][Cl]                   |     |             | wel                                     |                   |
| [o <sub>4</sub> N][Cl]                   |     |             | wel                                     |                   |
| [Dodec <sub>4</sub> N][Cl]               |     |             | wel                                     |                   |
| [et2Nic][EtSO <sub>4</sub> ]             |     |             | 05cro/mul                               | 05cro/mul         |
|                                          |     |             |                                         |                   |
| [mmim][BF <sub>4</sub> ]                 |     |             | 1999hol/sed                             | 1999hol/sed       |
| [mmim][MeSO <sub>4</sub> ]               |     |             | 06dom/pob                               | 06dom/pob         |
| [mmim][AlCl <sub>4</sub> ]               |     |             | 01hud/vis                               |                   |
| [mmim][NTf <sub>2</sub> ]                |     |             | wel                                     |                   |
|                                          |     |             |                                         |                   |
| [emim][Cl]                               |     |             | 00ngo/lec                               |                   |
| [emim][Br]                               |     |             | 00ngo/lec                               |                   |
| [emim][I]                                |     |             | 00ngo/lec                               |                   |
| [emim][BF <sub>4</sub> ]                 |     |             | 1999hol/sed,<br>00ngo/lec               | 1999hol/sed       |
| [emim][AlCl <sub>4</sub> ]               |     |             | 01hud/vis                               |                   |
| [emim][NO <sub>3</sub> ]                 |     |             | 01hud/vis                               |                   |
| [emim][NO <sub>2</sub> ]                 |     |             | 01hud/vis                               |                   |
| [emim][CH <sub>3</sub> CO <sub>2</sub> ] |     |             | 01hud/vis,<br>wel                       |                   |
| [emim][CF <sub>3</sub> CO <sub>2</sub> ] |     |             | wel                                     |                   |
| [emim][CF <sub>3</sub> SO <sub>2</sub> ] |     |             | wel                                     |                   |
| [emim][PF <sub>6</sub> ]                 |     | 03hol/rei   | 00ngo/lec,<br>01hud/vis,<br>1998gor/hol | 1998gor/hol       |
| [emim][AsF <sub>6</sub> ]                |     |             | 00ngo/lec                               |                   |

|                                                           |           |                                        |                                         |                           |
|-----------------------------------------------------------|-----------|----------------------------------------|-----------------------------------------|---------------------------|
| [emim][TfO]                                               |           |                                        | 01hud/vis                               |                           |
| [emim][NfO]                                               |           |                                        | 01hud/vis                               |                           |
| [emim][NTf <sub>2</sub> ]                                 |           |                                        | 00ngo/lec,<br>01hud/vis,<br>wel         |                           |
| [emim][Betl]                                              |           |                                        | 00ngo/lec                               |                           |
| [emim][Me]                                                |           |                                        | 00ngo/lec                               |                           |
| [emim][TA]                                                |           |                                        | 01hud/vis                               |                           |
| [emim][EtSO <sub>4</sub> ]                                | 06zhi/zhi | 06zhi/zhi                              |                                         |                           |
| [emim][N(CF <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> ] |           |                                        | 01hud/vis                               |                           |
|                                                           |           |                                        |                                         |                           |
| [eeim][NTf <sub>2</sub> ]                                 |           |                                        | wel                                     |                           |
|                                                           |           |                                        |                                         |                           |
| [pmim][BF <sub>4</sub> ]                                  |           |                                        | 1999hol/sed                             |                           |
| [pmim][Cl]                                                |           |                                        | 00ngo/lec                               |                           |
| [pmim][AlCl <sub>4</sub> ]                                |           |                                        | 01hud/vis                               |                           |
| [pmim][NTf <sub>2</sub> ]                                 |           |                                        | 00ngo/lec                               |                           |
| [pmim][PF <sub>6</sub> ]                                  |           |                                        | 00ngo/lec,<br>01hud/vis                 |                           |
|                                                           |           |                                        |                                         |                           |
| [ipmim][NTf <sub>2</sub> ]                                |           |                                        | 00ngo/lec                               |                           |
| [ipmim][I]                                                |           |                                        | 00ngo/lec                               |                           |
|                                                           |           |                                        |                                         |                           |
| [bmim][BF <sub>4</sub> ]                                  |           | 05gom/esp1                             | 1999hol/sed,<br>01hud/vis               |                           |
| [bmim][BPh <sub>4</sub> ]                                 |           | 03hol/rei                              |                                         |                           |
| [bmim][MeSO <sub>4</sub> ]                                |           |                                        | 06dom/pob                               | 06dom/pob                 |
| [bmim][Cl]                                                |           | 05zha/kam,<br>03hol/rei                | 01hud/vis,<br>03hol/rei1                | 05zha/kam                 |
| [bmim][I]                                                 |           |                                        | 01hud/vis                               |                           |
| [bmim][PF <sub>6</sub> ]                                  |           | 05gom/esp1,<br>04kab/blo,<br>03hol/rei | 01hud/vis,<br>1998gor/hol,<br>04kab/blo | 1998gor/hol,<br>04kab/blo |
| [bmim][NTf <sub>2</sub> ]                                 |           | 03hol/rei,<br>5gom/esp                 | 01hud/vis,<br>wel                       |                           |
| [bmim][AlCl <sub>4</sub> ]                                |           |                                        | 01hud/vis                               |                           |
| [bmim][MDEGSO <sub>4</sub> ]                              |           |                                        | 05cro/mul                               | 05cro/mul                 |
|                                                           |           |                                        |                                         |                           |
| [bbim][AlCl <sub>4</sub> ]                                |           |                                        | 01hud/vis                               |                           |
|                                                           |           |                                        |                                         |                           |
| [C5mim][BF <sub>4</sub> ]                                 |           |                                        | 1999hol/sed                             |                           |
|                                                           |           |                                        |                                         |                           |
| [hmim][BF <sub>4</sub> ]                                  |           |                                        | 1999hol/sed                             | 1999hol/sed               |
| [hmim][Cl]                                                |           |                                        | 01hud/vis                               |                           |
| [hmim][BF <sub>4</sub> ]                                  |           |                                        | 1999hol/sed,<br>01hud/vis               |                           |
| [hmim][PF <sub>6</sub> ]                                  |           | 03hol/rei                              | 1998gor/hol                             | 1998gor/hol               |
| [hmim][NTf <sub>2</sub> ]                                 |           | 05gom/esp                              |                                         |                           |
| [hmim][Br]                                                |           |                                        | 05cro/mul                               | 05cro/mul                 |

|                                            |  |  |                         |             |
|--------------------------------------------|--|--|-------------------------|-------------|
| [hmim][TNf <sub>2</sub> ]                  |  |  | 05cro/mul               | 05cro/mul   |
| [hmim][BF <sub>4</sub> ]                   |  |  | 05cro/mul               | 05cro/mul   |
|                                            |  |  |                         |             |
| [hpmim][BF <sub>4</sub> ]                  |  |  | 1999hol/sed             |             |
|                                            |  |  |                         |             |
| [omim][BF <sub>4</sub> ]                   |  |  | 1999hol/sed             |             |
| [omim][Cl]                                 |  |  | 01hud/vis               |             |
| [omim][PF <sub>6</sub> ]                   |  |  | 1998gor/hol             | 1998gor/hol |
| [omim][PF <sub>6</sub> ]                   |  |  | 01hud/vis               |             |
| [omim][TNf <sub>2</sub> ]                  |  |  | 05cro/mul               | 05cro/mul   |
| [omim][BF <sub>4</sub> ]                   |  |  | 05cro/mul               | 05cro/mul   |
| [omim][Br]                                 |  |  |                         | 05cro/mul   |
|                                            |  |  |                         |             |
| [C9mim][BF <sub>4</sub> ]                  |  |  | 1999hol/sed             |             |
| [C10mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
| [C11mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
| [C12mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
| [C13mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
| [C14mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
| [C15mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
| [C16mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
| [C18mim][BF <sub>4</sub> ]                 |  |  | 1999hol/sed             | 1999hol/sed |
|                                            |  |  |                         |             |
| [hmmim][TNf <sub>2</sub> ]                 |  |  | 05cro/mul               | 05cro/mul   |
| [perfluoro-hmim][TNf <sub>2</sub> ]        |  |  | 05cro/mul               | 05cro/mul   |
| ECOENG 500                                 |  |  | 05cro/mul               | 05cro/mul   |
|                                            |  |  |                         |             |
|                                            |  |  |                         |             |
| [emmim][CF <sub>3</sub> SO <sub>2</sub> ]  |  |  | wel                     |             |
| [emm5im][CF <sub>3</sub> SO <sub>2</sub> ] |  |  | wel                     |             |
|                                            |  |  |                         |             |
| [ipmim][PF <sub>6</sub> ]                  |  |  | 00ngo/lec,<br>01hud/vis |             |
| [dmeim][Cl]                                |  |  | 00ngo/lec               |             |
| [dmeim][Br]                                |  |  | 00ngo/lec               |             |
| [dmeim][PF <sub>6</sub> ]                  |  |  | 00ngo/lec               |             |
| [dmeim][NTf <sub>2</sub> ]                 |  |  | 00ngo/lec               |             |
| [dmeim][Betl]                              |  |  | 00ngo/lec               |             |
| [dmpim][Cl]                                |  |  | 00ngo/lec               |             |
| [dmpim][PF <sub>6</sub> ]                  |  |  | 00ngo/lec               |             |
| [dmpim][NTf <sub>2</sub> ]                 |  |  | 00ngo/lec               |             |
| [dmpim][Betl]                              |  |  | 00ngo/lec               |             |
| [H2m3im][Cl]                               |  |  | 00ngo/lec               |             |
| [m5im][I]                                  |  |  | 00ngo/lec               |             |
| [m5im][PF <sub>6</sub> ]                   |  |  | 00ngo/lec               |             |
| [m5im][NTf <sub>2</sub> ]                  |  |  | 00ngo/lec               |             |
| [                                          |  |  |                         |             |

|                                |  |  |             |             |
|--------------------------------|--|--|-------------|-------------|
| C12-py][PF <sub>6</sub> ]      |  |  | 1998gor/hol | 1998gor/hol |
| [C14-py][PF <sub>6</sub> ]     |  |  | 1998gor/hol | 1998gor/hol |
| [C16-py][PF <sub>6</sub> ]     |  |  | 1998gor/hol | 1998gor/hol |
| [C18-py][PF <sub>6</sub> ]     |  |  | 1998gor/hol | 1998gor/hol |
| [C12-3-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [C14-3-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [C16-3-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [C18-3-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [C12-4-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [C14-4-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [C16-4-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [C18-4-Mepy][PF <sub>6</sub> ] |  |  | 1998gor/hol | 1998gor/hol |
| [empty][EtSO <sub>4</sub> ]    |  |  | 05cro/mul   | 05cro/mul   |
| [bpy][Br]                      |  |  | 05cro/mul   |             |
| [bmpy][Br]                     |  |  | 05cro/mul   |             |
| [bmpy][TNf <sub>2</sub> ]      |  |  | 05cro/mul   | 05cro/mul   |
| [bmpy][BF <sub>4</sub> ]       |  |  | 05cro/mul   | 05cro/mul   |
| [bmmpy][Br]                    |  |  | 05cro/mul   |             |
| [bDMApy][Br]                   |  |  | 05cro/mul   |             |
| [b2Nic][TNf <sub>2</sub> ]     |  |  | 05cro/mul   | 05cro/mul   |
| [hpy][TNf <sub>2</sub> ]       |  |  | 05cro/mul   | 05cro/mul   |
| [hmpy][Br]                     |  |  | 05cro/mul   | 05cro/mul   |
| [hmpy][TNf <sub>2</sub> ]      |  |  | 05cro/mul   | 05cro/mul   |
| [hmmpy][TNf <sub>2</sub> ]     |  |  | 05cro/mul   | 05cro/mul   |
| [hemmpy][TNf <sub>2</sub> ]    |  |  | 05cro/mul   |             |
| [hpeepy][TNf <sub>2</sub> ]    |  |  | 05cro/mul   | 05cro/mul   |
| [hDMApy][Br]                   |  |  | 05cro/mul   |             |
| [hDMApy][TNf <sub>2</sub> ]    |  |  | 05cro/mul   | 05cro/mul   |
| [hmDMApy][Br]                  |  |  | 05cro/mul   |             |
| [hmDMApy][TNf <sub>2</sub> ]   |  |  | 05cro/mul   | 05cro/mul   |
| [h(mPiP)py][Br]                |  |  | 05cro/mul   |             |
| [h(mPiP)py][TNf <sub>2</sub> ] |  |  | 05cro/mul   |             |
| [ompy][TNf <sub>2</sub> ]      |  |  | 05cro/mul   | 05cro/mul   |

**Table 2 Studies of the thermodynamic properties of binary systems involving an ionic liquid**

| System                                                   | $\gamma^\infty_i / H_i$ | $\gamma_i$ | Phase Equil                      | Other |
|----------------------------------------------------------|-------------------------|------------|----------------------------------|-------|
| [mmim][NTf <sub>2</sub> ]-benzene, toluene               | 02kru/was,<br>04kat/kru |            |                                  |       |
| [mmim][NTf <sub>2</sub> ]- cyclohexane                   | 02kru/was,<br>04kat/kru |            |                                  |       |
| [mmim][NTf <sub>2</sub> ]- n-alkanes                     | 02kru/was               |            |                                  |       |
| [mmim][NTf <sub>2</sub> ]-CO                             |                         |            | 04ohl/dys                        |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]- acetone        | 04kat/gem               |            |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]- benzene        | 04kat/gem               |            |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]- toluene        | 04kat/gem               |            |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]- cyclohexane    | 04kat/gem               |            |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]- n-alkanes      | 04kat/gem               |            |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]-acetone         |                         | 05kat/gme1 |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]-methanol        |                         | 05kat/gme1 |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]-ethanol         |                         | 05kat/gme1 |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]-tetrahydrofuran |                         | 05kat/gme1 |                                  |       |
| [mmim][Me <sub>2</sub> PO <sub>4</sub> ]-water           |                         | 05kat/gme1 |                                  |       |
| [mmim][MeSO <sub>4</sub> ]-water                         |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-methanol                      |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-ethanol                       |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-propanol                      |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-butanol                       |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-pentanol                      |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-hexan-1-ol                    |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-heptan-1-ol                   |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-octan-1-ol                    |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-nonan-1-ol                    |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-decan-1-ol                    |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-dipropyl ether                |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-dibutyl ether                 |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-MTBE                          |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-MTAE                          |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-pentan-2-one                  |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-pentan-3-one                  |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-hexan-2-one                   |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-heptan-2-one                  |                         |            | 06dom/pob                        |       |
| [mmim][MeSO <sub>4</sub> ]-cyclopentan-2-one             |                         |            | 06dom/pob                        |       |
| [mmim][BF <sub>4</sub> ]-CO                              |                         |            | 04ohl/dys                        |       |
|                                                          |                         |            |                                  |       |
| [emim][NTf <sub>2</sub> ]- alcohols                      | 02hei/kul,<br>03dav/let |            | 03hei/leh,<br>05hei/leh<br>05hei |       |
| [emim][NTf <sub>2</sub> ]- propan-1-ol                   |                         |            | 2005hei/leh                      |       |
| [emim][NTf <sub>2</sub> ]-butan-1-ol                     |                         |            | 05hei/leh                        |       |
| [emim][NTf <sub>2</sub> ]- t-butanol                     | 05hei/mar1              |            |                                  |       |
| [emim][NTf <sub>2</sub> ]- pentan-1-ol                   |                         |            | 05hei/leh                        |       |

|                                                         |                                                                    |                         |                                                     |  |
|---------------------------------------------------------|--------------------------------------------------------------------|-------------------------|-----------------------------------------------------|--|
| [emim][NTf <sub>2</sub> ]- 1-hexanol                    | 05hei/mar1                                                         |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- methanol                     | 05hei/mar1                                                         | 05kat/gme               |                                                     |  |
| [emim][NTf <sub>2</sub> ]- ethanol                      |                                                                    | 05kat/gme               |                                                     |  |
| [emim][NTf <sub>2</sub> ]- 2-propanol                   |                                                                    | 05kat/gme1              |                                                     |  |
| [emim][NTf <sub>2</sub> ]- ethylene glycol              | 05hei/mar1                                                         |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- 1-4-butanediol               |                                                                    |                         | 05hei/leh                                           |  |
| [emim][NTf <sub>2</sub> ]- water                        |                                                                    | 05kat/gme1              | 05hei/leh                                           |  |
| [emim][NTf <sub>2</sub> ]-alkenes, alkynes              | 05dee/let                                                          |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- chloromethanes               | 02hei/kul                                                          |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- chloroform                   | 05hei/mar1                                                         |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- acetone                      | 02hei/kul,<br>02kru/was                                            | 05kat/gme1              |                                                     |  |
| [emim][NTf <sub>2</sub> ]- acetonitrile                 | 02hei/kul                                                          |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- MTBE                         | 02hei/kul                                                          |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- TAME                         | 02hei/kul                                                          |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]- benzene                      | 02hei/kul,<br>02kru/was,<br>03dav/let,<br>04kat/kru                | 04kat/kru               | 05hei/leh                                           |  |
| [emim][NTf <sub>2</sub> ]- toluene                      | 02hei/kul,<br>02kru/was,<br>03dav/let,<br>04kat/kru,<br>05hei/mar1 | 04kat/kru               |                                                     |  |
| [emim][NTf <sub>2</sub> ]- cyclohexane                  | 02hei/kul,<br>04kat/kru                                            | 04kat/kru,<br>05kat/gme |                                                     |  |
| [emim][NTf <sub>2</sub> ]- cyclohexene                  |                                                                    | 05kat/gme               |                                                     |  |
| [emim][NTf <sub>2</sub> ]- n-alkanes                    | 02hei/kul,<br>02kru/was                                            |                         |                                                     |  |
| [emim][NTf <sub>2</sub> ]-nonan-1-al                    |                                                                    | 04ver/vas               |                                                     |  |
| [emim][NTf <sub>2</sub> ]-4-methyl-<br>benzaldehyde     |                                                                    | 04ver/vas               |                                                     |  |
| [emim][NTf <sub>2</sub> ]-nonan-2-one                   |                                                                    | 04ver/vas               |                                                     |  |
| [emim][NTf <sub>2</sub> ]-4-phenylbutan-2-<br>one       |                                                                    | 04ver/vas               |                                                     |  |
| [emim][NTf <sub>2</sub> ]-nonanal                       |                                                                    |                         | 05hei/mar1                                          |  |
| [emim][NTf <sub>2</sub> ]-CO                            |                                                                    |                         | 04ohl/dys                                           |  |
| [emim][NTf <sub>2</sub> ]-CO <sub>2</sub>               | 05cam/bec                                                          |                         | 04cam/sco,<br>04sco/cam,<br>05kim/cho,<br>05cam/bec |  |
| [emim][NTf <sub>2</sub> ]-C <sub>2</sub> H <sub>4</sub> | 05cam/bec                                                          |                         | 04cam/sco,<br>04sco/cam,<br>05cam/bec               |  |
| [emim][NTf <sub>2</sub> ]-ethene                        | 05cam/bec                                                          |                         | 05cam/bec                                           |  |
| [emim][NTf <sub>2</sub> ]-propane                       | 05cam/bec                                                          |                         | 05cam/bec                                           |  |
| [emim][NTf <sub>2</sub> ]-propene                       | 05cam/bec                                                          |                         | 05cam/bec                                           |  |
| [emim][NTf <sub>2</sub> ]-isobutane                     | 05cam/bec                                                          |                         | 05cam/bec                                           |  |
| [emim][NTf <sub>2</sub> ]-butane                        | 05cam/bec                                                          |                         | 05cam/bec                                           |  |
| [emim][NTf <sub>2</sub> ]-1-butene                      | 05cam/bec                                                          |                         | 05cam/bec                                           |  |
| [emim][NTf <sub>2</sub> ]-1,3-butadiene                 | 05cam/bec                                                          |                         | 05cam/bec                                           |  |

|                                                      |                           |            |                                       |  |
|------------------------------------------------------|---------------------------|------------|---------------------------------------|--|
| [emim][NTf <sub>2</sub> ]-methoxybenzene             |                           | 05vas/ver  |                                       |  |
| [emim][NTf <sub>2</sub> ]-<br>(hydroxymethyl)benzene |                           | 05vas/ver  |                                       |  |
| [emim][NTf <sub>2</sub> ]-1,2-ethanediol             |                           | 05vas/ver  |                                       |  |
| [emim][NTf <sub>2</sub> ]-1,4-butanediol             |                           | 05vas/ver  |                                       |  |
| [emim][NTf <sub>2</sub> ]-dimethyl adipate           |                           | 06vas/ver  |                                       |  |
| [emim][NTf <sub>2</sub> ]-ethyl benzoate             |                           | 06vas/ver  |                                       |  |
| [emim][NTf <sub>2</sub> ]-benzylamine                |                           | 06vas/ver  |                                       |  |
| [emim][NTf <sub>2</sub> ]-tetrahydrofuran            |                           | 05kat/gme1 |                                       |  |
| [emim][PF <sub>6</sub> ]-water                       |                           |            | 02won/che                             |  |
| [emim][PF <sub>6</sub> ]-alcohols                    |                           |            | 04dom/mar                             |  |
| [emim][PF <sub>6</sub> ]-CO <sub>2</sub>             |                           |            | 03sha/pet                             |  |
| [emim][BF <sub>4</sub> ]-CO                          |                           |            | 04ohl/dys                             |  |
| [emim][BF <sub>4</sub> ]-CO <sub>2</sub>             |                           |            | 05cos/tou,<br>05kim/cho               |  |
| [emim][EtSO <sub>4</sub> ]- alkenes, alkynes         | 02kru/was                 |            |                                       |  |
| [emim][EtSO <sub>4</sub> ]- benzene, toluene         | 02kru/was,<br>2004kat/kru | 04kat/kru  |                                       |  |
| [emim][EtSO <sub>4</sub> ]- cyclohexane              | 02kru/was,<br>04kat/kru   | 04kat/kru  |                                       |  |
| [emim][EtSO <sub>4</sub> ]- n-alkanes                | 02kru/was                 |            |                                       |  |
| [emim][triflate]-CO <sub>2</sub>                     |                           |            | 04cam/sco,<br>04sco/cam               |  |
| [emim][triflate]-C <sub>2</sub> H <sub>4</sub>       |                           |            | 04cam/sco,<br>04sco/cam               |  |
| [emim][dca]-CO <sub>2</sub>                          | 05cam/bec                 |            | 04cam/sco,<br>04sco/cam,<br>05cam/bec |  |
| [emim][dca]-C <sub>2</sub> H <sub>4</sub>            | 05cam/bec                 |            | 04cam/sco,<br>04sco/cam,<br>05cam/bec |  |
| [emim][dca]-ethene                                   | 05cam/bec                 |            | 05cam/bec                             |  |
| [emim][dca]-propane                                  | 05cam/bec                 |            | 05cam/bec                             |  |
| [emim][dca]-propene                                  | 05cam/bec                 |            | 05cam/bec                             |  |
| [emim][dca]-isobutane                                | 05cam/bec                 |            | 05cam/bec                             |  |
| [emim][dca]-butane                                   | 05cam/bec                 |            | 05cam/bec                             |  |
| [emim][dca]-1-butene                                 | 05cam/bec                 |            | 05cam/bec                             |  |
| [emim][dca]-1,3-butadiene                            | 05cam/bec                 |            | 05cam/bec                             |  |
| [emim][tosylate]-hexane                              | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-heptane                             | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-octane                              | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-nonane                              | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-cyclohexane                         | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-benzene                             | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-toluene                             | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-ethylbenzene                        | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-m-xylene                            | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-o-xylene                            | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-1-hexene                            | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-1-hexyne                            | 06mut/jau                 |            |                                       |  |
| [emim][tosylate]-1-heptyne                           | 06mut/jau                 |            |                                       |  |

|                                                          |                         |           |                                                 |  |
|----------------------------------------------------------|-------------------------|-----------|-------------------------------------------------|--|
| [emim][tosylate]-2-butanone                              | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-2-pentanone                             | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-1,4-dioxane                             | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-methanol                                | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-ethanol                                 | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-1-propanol                              | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-2-propanol                              | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-2-methyl-1-propanol                     | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-1-butanol                               | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-ether                                   | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-chloroform                              | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-dichloromethane                         | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-tetrachloromethane                      | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-acetonitrile                            | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-1-nitropropane                          | 06mut/jau               |           |                                                 |  |
| [emim][tosylate]-thiophene                               | 06mut/jau               |           |                                                 |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-ethane          | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-ethene          | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-propane         | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-propene         | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-isobutane       | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-butane          | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-1-butene]       | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-1,3-butadiene   | 05cam/bec               |           | 05cam/bec                                       |  |
| [emim][CF <sub>3</sub> SO <sub>3</sub> ]-CO <sub>2</sub> | 05cam/bec               |           | 05cam/bec                                       |  |
|                                                          |                         |           |                                                 |  |
| [e2mim][NTf <sub>2</sub> ]- alcohols                     | 02kru/was               |           |                                                 |  |
| [e2mim][NTf <sub>2</sub> ]- benzene, toluene             | 02hei/kul,<br>02kru/was |           |                                                 |  |
| [emmim][NTf <sub>2</sub> ]-CO                            |                         |           | 04ohl/dys                                       |  |
| [bmmim][NTf <sub>2</sub> ]-CO                            |                         |           | 04ohl/dys                                       |  |
|                                                          |                         |           |                                                 |  |
| [bmim][Cl]-water                                         |                         |           | 01hud/vis                                       |  |
| [bmim][I]-water                                          |                         |           | 01hud/vis                                       |  |
| [bmim][NTf <sub>2</sub> ]- alcohols                      | 05vas/ver               | 05ver/saf | 03naj/esp,<br>05hei/leh,<br>04cro/aki,<br>05hei |  |
| [bmim][NTf <sub>2</sub> ]-methanol                       | 05hei/mar               |           |                                                 |  |
| [bmim][NTf <sub>2</sub> ]-ethanol                        | 05hei/mar               |           |                                                 |  |
| [bmim][NTf <sub>2</sub> ]- cyclohexanol                  | 05hei/mar               |           | 05hei/leh                                       |  |
| [bmim][NTf <sub>2</sub> ]- 1,2-hexanediol                |                         |           | 05hei/leh                                       |  |
| [bmim][NTf <sub>2</sub> ]- 1,3-cyclohexadiene            | 05hei/mar               |           | 05hei/leh                                       |  |
| [bmim][NTf <sub>2</sub> ]- benzene                       | 05hei/mar               |           | 05hei/leh                                       |  |
| [bmim][NTf <sub>2</sub> ]- propan-1-ol                   | 05hei/mar               |           | 05hei/leh                                       |  |
| [bmim][NTf <sub>2</sub> ]-propan-2-ol                    | 05hei/mar               |           |                                                 |  |
| [bmim][NTf <sub>2</sub> ]- butan-1-ol                    | 05hei/mar               |           | 05hei/leh                                       |  |
| [bmim][NTf <sub>2</sub> ]-isobutanol                     | 05hei/mar               |           | 05reb/naj                                       |  |

|                                                |                         |            |                                       |  |
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| [bmim][NTf <sub>2</sub> ]-secbutanol           | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-tertbutyl alcohol    | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- pentan-1-ol         | 05hei/mar               |            | 05hei/leh                             |  |
| [bmim][NTf <sub>2</sub> ]-tert-pentanol        | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- hexan-1-ol          | 05hei/mar               |            | 05hei/leh                             |  |
| [bmim][NTf <sub>2</sub> ]-heptan-1-ol          | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-propanal             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-2-propanal           |                         | 05kat/gme1 |                                       |  |
| [bmim][NTf <sub>2</sub> ]-butanal              | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-pentanal             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-hexanal              | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-octanal              | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- 1-hexanal           | 05hei/mar               |            | 05hei/leh                             |  |
| [bmim][NTf <sub>2</sub> ]- methyl caproate     |                         |            | 05hei/leh                             |  |
| [bmim][NTf <sub>2</sub> ]- 2-hexanone          |                         |            | 05hei/leh                             |  |
| [bmim][NTf <sub>2</sub> ]- water               |                         | 05kat/gme1 | 01hud/vis,<br>05hei/leh,<br>05reb/naj |  |
| [bmim][NTf <sub>2</sub> ]-CO                   |                         |            | 04ohl/dys                             |  |
| [bmim][NTf <sub>2</sub> ]-1-pentane            | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-hexane             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-heptane            | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-octane             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-nonane             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-decane             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-undecane           | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-dodecane           | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-pentene            | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-hexene             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-heptene            | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-octene             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-nonene             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-decene             | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-undecene           | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-1-dodecene           | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-methyl propanoate    | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-methyl butanoate     | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-methyl pentanoate    | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-methyl hexanoate     | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-methyl heptanoate    | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- alkenes, alkynes    | 02kru/was,<br>05vas/ver |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- acetone             | 05hei/mar               | 05kat/gme1 |                                       |  |
| [bmim][NTf <sub>2</sub> ]- acetonitrile        | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- N-methylpyrrolidone | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- 1,4-dioxane         | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]- benzene, toluene    | 02kru/was               | 04kat/kru  |                                       |  |
| [bmim][NTf <sub>2</sub> ]-toluene              | 05hei/mar               |            |                                       |  |
| [bmim][NTf <sub>2</sub> ]-ethyl benzene        | 05hei/mar               |            |                                       |  |

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| [bmim][NTf <sub>2</sub> ]-propyl benzene    | 05hei/mar               |           |                                                                                                 |  |
| [bmim][NTf <sub>2</sub> ]-butyl benzene     | 05hei/mar               |           |                                                                                                 |  |
| [bmim][NTf <sub>2</sub> ]-pentyl benzene    | 05hei/mar               |           |                                                                                                 |  |
| [bmim][NTf <sub>2</sub> ]-cyclohexane       | 02kru/was,<br>05hei/mar | 04kat/kru |                                                                                                 |  |
| [bmim][NTf <sub>2</sub> ]-cyclohexene       | 05hei/mar               |           |                                                                                                 |  |
| [bmim][NTf <sub>2</sub> ]-n-alkanes         | 02kru/was,<br>05hei/mar |           |                                                                                                 |  |
| [bmim][Br] - trifluoroethanol               |                         | 04kim/shi |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ] - trifluoroethanol |                         | 04kim/shi |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ] - water            |                         |           | 01hud/vis,<br>01ant/mag,<br>02won/che,<br>04reb/naj,<br>02naj/esp<br>05cer/tro                  |  |
| [bmim][BF <sub>4</sub> ] - alcohols         |                         |           | 04cro/aki                                                                                       |  |
| [bmim][BF <sub>4</sub> ]-CO                 |                         |           | 04ohl/dys                                                                                       |  |
| [bmim][BF <sub>4</sub> ] - CO <sub>2</sub>  | 05cam/bec               |           | 03hus/maj,<br>05cam/bec                                                                         |  |
| [bmim][BF <sub>4</sub> ] - O <sub>2</sub>   |                         |           | 03hus/maj                                                                                       |  |
| [bmim][BF <sub>4</sub> ]-ethane             | 05cam/bec               |           |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ]-ethene             | 05cam/bec               |           |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ]-propane            | 05cam/bec               |           |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ]-propene            | 05cam/bec               |           |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ]-isobutane          | 05cam/bec               |           |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ]-butane             | 05cam/bec               |           |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ]-1-butene           | 05cam/bec               |           |                                                                                                 |  |
| [bmim][BF <sub>4</sub> ]-1,3-butadiene      | 05cam/bec               |           |                                                                                                 |  |
| [bmim][PF <sub>6</sub> ]-water              |                         |           | 01hud/vis,<br>01ant/mag,<br>02won/che,<br>04reb/naj,<br>02naj/esp<br>05naj/ser                  |  |
| [bmim][PF <sub>6</sub> ]-alcohols           |                         |           | 03wu/mar                                                                                        |  |
| [bmim][PF <sub>6</sub> ]-ethanol            |                         |           | 05reb/naj,<br>05naj/ser                                                                         |  |
| [bmim][PF <sub>6</sub> ]-CO                 | 04ohl/dys               |           | 05kum/kam1                                                                                      |  |
| [bmim][PF <sub>6</sub> ]-CO <sub>2</sub>    | 05cam/bec               |           | 1999bla/han,<br>03kam/tum,<br>04cam/sco,<br>04sco/cam,<br>05cam/bec,<br>05kim/cho,<br>05naj/ser |  |
| [bmim][PF <sub>6</sub> ]-H <sub>2</sub>     |                         |           | 06kum/kam1                                                                                      |  |
| [bmim][PF <sub>6</sub> ]-CH <sub>4</sub>    |                         |           | 02ant/mag,<br>03kam/tum                                                                         |  |

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| [bmim][PF <sub>6</sub> ]-C <sub>2</sub> H <sub>4</sub> | 05cam/bec               |  | 02ant/mag,<br>03kam/tum,<br>04cam/sco,<br>04sco/cam,<br>05cam/bec |  |
| [bmim][PF <sub>6</sub> ]-C <sub>2</sub> H <sub>6</sub> | 05cam/bec               |  | 02ant/mag,<br>03kam/tum,<br>05cam/bec                             |  |
| [bmim][PF <sub>6</sub> ]-propane                       | 05cam/bec               |  | 05cam/bec                                                         |  |
| [bmim][PF <sub>6</sub> ]-propene                       | 05cam/bec               |  | 05cam/bec                                                         |  |
| [bmim][PF <sub>6</sub> ]-isobutane                     | 05cam/bec               |  | 05cam/bec                                                         |  |
| [bmim][PF <sub>6</sub> ]-butane                        | 05cam/bec               |  | 05cam/bec                                                         |  |
| [bmim][PF <sub>6</sub> ]-1-butene                      | 05cam/bec               |  | 05cam/bec                                                         |  |
| [bmim][PF <sub>6</sub> ]-1,3-butadiene                 | 05cam/bec               |  | 05cam/bec                                                         |  |
| [bmim][PF <sub>6</sub> ]-O <sub>2</sub>                |                         |  | 05kum/kam1                                                        |  |
| [bmim][PF <sub>6</sub> ]-Ar                            |                         |  | 02ant/mag,<br>03kam/tum                                           |  |
| [bmim][SbF <sub>6</sub> ]-CO                           |                         |  | 04ohl/dys                                                         |  |
| [bmim][CF <sub>3</sub> CO <sub>2</sub> ]-CO            |                         |  | 04ohl/dys                                                         |  |
| [bmim][OcOSO <sub>3</sub> ]- 2-butanone                | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 1,4-dioxane               | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 2-pentanone               | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 1-ethanol                 | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 1-propanol                | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 2-propanol                | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 2-methyl-1-propanol       | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 1-butanol                 | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- ether                     | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- chloroform                | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- dichloromethane           | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- acetonitrile              | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- 1-nitropropane            | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- ethylbenzene              | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- m-xylene                  | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- o-xylene                  | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- thiophene                 | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]-n-pentane                  | 05let/mar               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]-n-hexane                   | 05let/mar,<br>06mut/jau |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]-n-heptane                  | 05let/mar,<br>06mut/jau |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]-n-octane                   | 05let/mar,<br>06mut/jau |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]- nonane                    | 06mut/jau               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]-hex-1-ene                  | 05let/mar,<br>06mut/jau |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]-oct-1-ene                  | 05let/mar               |  |                                                                   |  |
| [bmim][OcOSO <sub>3</sub> ]-hex-1-yne                  | 05let/mar,<br>06mut/jau |  |                                                                   |  |

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| [bmim][OcOSO <sub>3</sub> ]-hept-1-yne              | 05let/mar,<br>06mut/jau |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-oct-1-yne               | 05let/mar               |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-cyclopentane            | 05let/mar               |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-cyclohexane             | 05let/mar,<br>06mut/jau |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-cycloheptane            | 05let/mar               |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-benzene                 | 05let/mar,<br>06mut/jau |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-toluene                 | 05let/mar               |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-carbon<br>tetrachloride | 05let/mar,<br>06mut/jau |  |           |  |
| [bmim][OcOSO <sub>3</sub> ]-methanol                | 05let/mar,<br>06mut/jau |  |           |  |
| [bmim][triflate] - alcohols                         |                         |  | 04cro/aki |  |
| [bmim][NO <sub>3</sub> ]-CO <sub>2</sub>            |                         |  | 01bla/gu  |  |
| [bmim][MeSO <sub>4</sub> ]-dipropyl ether           |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-dibutyl ether            |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-MTBE                     |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-MTAE                     |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-pentan-2-one             |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-pentan-3-one             |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-hexan-2-one              |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-heptan-4-one             |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-water                    |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-methanol                 |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]- ethanol                 |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-butanol                  |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-propanol                 |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-butanol                  |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-pentanol                 |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-hexanol                  |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-heptanol                 |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-octanol                  |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-nonanol                  |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-decanol                  |                         |  | 06dom/pob |  |
| [bmim][MeSO <sub>4</sub> ]-undecanol                |                         |  | 06dom/pob |  |
| [bmim][DEGSO <sub>4</sub> ]-pentane                 | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-hexane                  | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-heptane                 | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-octane                  | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-hex-1-ene               | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-oct-1-ene               | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-hex-1-yne               | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-hept-1-yne              | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-oct-1-yne               | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-cyclopentane            | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-cyclohexane             | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-cycloheptane            | 05let/dom               |  |           |  |
| [bmim][DEGSO <sub>4</sub> ]-benzene                 | 05let/dom               |  |           |  |

|                                                                                                         |           |           |           |  |
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| [bmim][DEGSO <sub>4</sub> ]-toluene                                                                     | 05let/dom |           |           |  |
| [bmim][DEGSO <sub>4</sub> ]-CCl <sub>4</sub>                                                            | 05let/dom |           |           |  |
| [bmim][DEGSO <sub>4</sub> ]-methanol                                                                    | 05let/dom |           |           |  |
|                                                                                                         |           |           |           |  |
| [mbPy][BF <sub>4</sub> ]-alcohols                                                                       | 02hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-chloromethanes                                                                 | 02hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-acetone                                                                        | 02hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-acetonitrile                                                                   | 02hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-MTBE                                                                           | 02hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-TAME                                                                           | 02hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-benzene, toluene                                                               | 01hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-cyclohexane                                                                    | 01hei/kul |           |           |  |
| [mbPy][BF <sub>4</sub> ]-n-alkanes                                                                      | 01hei/kul |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-n-pentane                                                                     | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-n-hexane                                                                      | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-n-heptane                                                                     | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-n-octane                                                                      | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-cyclopentane                                                                  | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-cyclohexane                                                                   | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-benzene                                                                       | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-1-pentene                                                                     | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-1-hexene                                                                      | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-1-heptene                                                                     | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-1-octene                                                                      | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-2-butanone                                                                    | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-2-pentanone                                                                   | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-ethanol                                                                       | 05kat/gme |           |           |  |
| [mbPy][NTf <sub>2</sub> ]-2-propanol                                                                    | 05kat/gme |           |           |  |
|                                                                                                         |           |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- alcohols                                                                   | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- alkenes, alkynes                                                           | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- chloromethanes                                                             | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- acetone                                                                    | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- MTBE                                                                       | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- TAME                                                                       | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- benzene, toluene                                                           | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- cyclohexane                                                                | 04kat/gem |           |           |  |
| [N-ePyr][NTf <sub>2</sub> ]- n-alkanes                                                                  | 04kat/gem |           |           |  |
| [ePy][NTf <sub>2</sub> ]-CO                                                                             |           |           | 04ohl/dys |  |
| [bPy][NTf <sub>2</sub> ]-CO                                                                             |           |           | 04ohl/dys |  |
| [Hpyr][CH <sub>3</sub> OC <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> ]- alcohols                       | 04kat/gem |           |           |  |
| [Hpyr][CH <sub>3</sub> OC <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> ]- benzene, toluene               | 04kat/gem |           |           |  |
| [Hpyr][CH <sub>3</sub> OC <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> ]- cyclohexane                    | 04kat/gem |           |           |  |
| [Hpyr][CH <sub>3</sub> OC <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> ]- n-alkanes                      | 04kat/gem |           |           |  |
| [Hpyr][C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]- benzene, toluene |           | 04kat/kru |           |  |

|                                                                                                   |           |           |                         |  |
|---------------------------------------------------------------------------------------------------|-----------|-----------|-------------------------|--|
| [Hpyr][C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> SO <sub>4</sub> ]-cyclohexane |           | 04kat/kru |                         |  |
| [hPy][NTf <sub>2</sub> ]-CO                                                                       |           |           | 04ohl/dys               |  |
| [oPy][NTf <sub>2</sub> ]-CO                                                                       |           |           | 04ohl/dys               |  |
| [C <sub>7</sub> H <sub>7</sub> Py][NTf <sub>2</sub> ]-CO                                          |           |           | 04ohl/dys               |  |
| [emPy][NTf <sub>2</sub> ]-CO                                                                      |           |           | 04ohl/dys               |  |
| [bmPy][NTf <sub>2</sub> ]-CO                                                                      |           |           | 04ohl/dys               |  |
| [C <sub>7</sub> H <sub>7</sub> mPy][NTf <sub>2</sub> ]-CO                                         |           |           | 04ohl/dys               |  |
|                                                                                                   |           |           |                         |  |
| [omim][Cl]- alkenes, alkynes                                                                      | 03dav/let |           |                         |  |
| [omim][Cl]- benzene, toluene                                                                      | 02hei/leh |           |                         |  |
| [omim][Cl]- n-alkanes                                                                             | 02hei/leh |           |                         |  |
| [omim][BF <sub>4</sub> ]- alcohols                                                                | 05hei/mar |           |                         |  |
| [omim][BF <sub>4</sub> ]-pentan-1-ol                                                              |           |           | 05hei/kla,<br>04wag/sta |  |
| [omim][BF <sub>4</sub> ]- alkenes, alkynes                                                        | 05hei/mar |           |                         |  |
| [omim][BF <sub>4</sub> ]- benzene, toluene                                                        | 05hei/mar |           |                         |  |
| [omim][BF <sub>4</sub> ]- n-alkanes                                                               | 05hei/mar |           |                         |  |
| [omim][BF <sub>4</sub> ]-CO <sub>2</sub>                                                          |           |           | 01bla/gu                |  |
| [omim][BF <sub>4</sub> ]-water                                                                    |           |           | 01ant/mag               |  |
| [omim][PF <sub>6</sub> ]- alcohols                                                                |           |           | 03wu/mar                |  |
| [omim][PF <sub>6</sub> ]-CO <sub>2</sub>                                                          |           |           | 01bla/gu                |  |
| [omim][PF <sub>6</sub> ]-water                                                                    |           |           | 01hud/vis,<br>01ant/mag |  |
| [omim][Cl]-water                                                                                  |           |           | 01hud/vis               |  |
| [omim][NTf <sub>2</sub> ]- n-pentane                                                              | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- n-hexane                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- n-heptane                                                              | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- n-octane                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- 1-pentene                                                              | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- 1-hexene                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- 1-heptene                                                              | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- 1-octene                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- cyclopentane                                                           | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- cyclohexane                                                            | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- cyclopentene                                                           | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- cyclohexene                                                            | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- benzene                                                                | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- toluene                                                                | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- m-Xylene                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- o-Xylene                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- p-Xylene                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- methanol                                                               | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- ethanol                                                                | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- 1-propanol                                                             | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]- water                                                                  | 05kat/gme |           |                         |  |
| [omim][NTf <sub>2</sub> ]-CO                                                                      |           |           | 04ohl/dys               |  |
|                                                                                                   |           |           |                         |  |
| [Hmim][NTf <sub>2</sub> ]- alcohols                                                               | 05let/mar |           |                         |  |
| [Hmim][NTf <sub>2</sub> ]- alkenes, alkynes                                                       | 05let/mar |           |                         |  |

|                                                         |                          |           |                                                     |  |
|---------------------------------------------------------|--------------------------|-----------|-----------------------------------------------------|--|
| [Hmim][NTf <sub>2</sub> ]-1-pentene                     | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-1-hexene                      | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-1-heptene                     | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-1-octene                      | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-cyclohexene                   | 05kat/gme                | 05kat/gme |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]- chloromethanes               | 05let/mar1               |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]- benzene                      | 05let/mar1,<br>05kat/gme |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]- toluene                      | 05let/mar1,<br>05kat/gme |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-m-Xylene                      | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-p-Xylene                      | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]- n-alkanes                    | 05let/mar1               |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-n-pentane                     | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-n-hexane                      | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-n-heptane                     | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-n-octane                      | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-cyclopentane                  | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-cyclohexane                   | 05kat/gme                | 05kat/gme |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-acetone                       | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-2-butanone                    | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-2-pentanone                   | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-methanol                      | 05kat/gme                | 05kat/gme |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-ethanol                       | 05kat/gme                | 05kat/gme |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-1-propanol                    | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-2-propanol                    | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-tetrahydrofuran               | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-diisopropyl ether             | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-ethyl tert-butyl ether (ETBE) | 05kat/gme                |           |                                                     |  |
| [Hmim][NTf <sub>2</sub> ]-Methyl ter-amyl ether (TAME)  | 05kat/gme                |           |                                                     |  |
| [hmim][NTf <sub>2</sub> ]-CO                            |                          |           | 04ohl/dys                                           |  |
| [Hmim][NTf <sub>2</sub> ]-CO <sub>2</sub>               |                          |           | 04bal/cul,<br>04aki/mel,<br>05kim/cho,<br>06kum/kam |  |
| [hmim][BF <sub>4</sub> ]- alcohols                      |                          |           | 03wag/sta,<br>04wag/sta,<br>04cro/aki               |  |
| [hmim][BF <sub>4</sub> ]-CO                             |                          |           | 04ohl/dys                                           |  |
| [hmim][BF <sub>4</sub> ]-CO <sub>2</sub>                |                          |           | 04sha/pet,<br>05kro/sha,<br>05kim/cho,              |  |
| [hmim][BF <sub>4</sub> ]-pentane                        | 03let/sok1               |           |                                                     |  |
| [hmim][BF <sub>4</sub> ]-hexane                         | 03let/sok1               |           |                                                     |  |
| [hmim][BF <sub>4</sub> ]-heptane                        | 03let/sok1               |           |                                                     |  |
| [hmim][BF <sub>4</sub> ]-octane                         | 03let/sok1               |           |                                                     |  |
| [hmim][BF <sub>4</sub> ]-cyclopentane                   | 03let/sok1               |           |                                                     |  |
| [hmim][BF <sub>4</sub> ]-cyclohexane                    | 03let/sok1               |           |                                                     |  |
| [hmim][BF <sub>4</sub> ]-hex-1-ene                      | 03let/sok1               |           |                                                     |  |

|                                                                                         |            |  |             |           |
|-----------------------------------------------------------------------------------------|------------|--|-------------|-----------|
| [hmim][BF <sub>4</sub> ]-hept-1-ene                                                     | 03let/sok1 |  |             |           |
| [hmim][BF <sub>4</sub> ]-oct-1-ene                                                      | 03let/sok1 |  |             |           |
| [hmim][BF <sub>4</sub> ]-hex-1-yne                                                      | 03let/sok1 |  |             |           |
| [hmim][BF <sub>4</sub> ]-hept-1-yne                                                     | 03let/sok1 |  |             |           |
| [hmim][BF <sub>4</sub> ]-oct-1-yne                                                      | 03let/sok1 |  |             |           |
| [hmim][BF <sub>4</sub> ]-benzene                                                        | 03let/sok1 |  |             |           |
| [hmim][BF <sub>4</sub> ]-methanol                                                       | 03let/sok1 |  |             |           |
| [hmim][BF <sub>4</sub> ]-cycloheptane                                                   | 03let/sok1 |  |             |           |
| [pmim][PF <sub>6</sub> ]- alcohols                                                      |            |  | 03wu/mar    |           |
| [hxmim][PF <sub>6</sub> ]- alcohols                                                     |            |  | 03wu/mar    |           |
| [hxmim][PF <sub>6</sub> ]-water                                                         |            |  | 01hud/vis   |           |
| [hmim][PF <sub>6</sub> ]-methanol                                                       | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-pentane                                                        | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-hexane                                                         | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-heptane                                                        | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-octane                                                         | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-cyclopentane                                                   | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-cyclohexane                                                    | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-cycloheptane                                                   | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-cyclooctane                                                    | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-hex-1-ene                                                      | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-hept-1-ene                                                     | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-oct-1-ene                                                      | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-hex-1-yne                                                      | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-hept-1-yne                                                     | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-oct-1-yne                                                      | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-benzene                                                        | 03let/sok  |  |             |           |
| [hmim][PF <sub>6</sub> ]-CO <sub>2</sub>                                                |            |  | 05kim/cho   |           |
| [hxmim][Cl]-water                                                                       |            |  | 01hud/vis   |           |
| [hpmim][PF <sub>6</sub> ]- alcohols                                                     |            |  | 03wu/mar    |           |
| [1-hexyl-oxymethyl-mim][BF <sub>4</sub> ]-<br>n-alkanes                                 |            |  | 05dom/mar   |           |
| [1-hexyl-oxymethyl-mim][NTf <sub>2</sub> ]-<br>n-alkanes                                |            |  | 05dom/mar   |           |
| [C12mim][Cl]-alcohols                                                                   |            |  | 03dom/bog   |           |
| [C7H7mim][NTf <sub>2</sub> ]-CO                                                         |            |  | 04ohl/dys   |           |
|                                                                                         |            |  |             |           |
| [emim][NTf <sub>2</sub> ]-[C10mim][NTf <sub>2</sub> ]                                   |            |  |             | 05lop/cor |
| [bmim][NTf <sub>2</sub> ]-[C10mim][NTf <sub>2</sub> ]                                   |            |  |             | 05lop/cor |
| [hmim][NTf <sub>2</sub> ]-[C10mim][NTf <sub>2</sub> ]                                   |            |  |             | 05lop/cor |
| [omim][NTf <sub>2</sub> ]-[C10mim][NTf <sub>2</sub> ]                                   |            |  |             | 05lop/cor |
| [bmim][NTf <sub>2</sub> ]-[omim][NTf <sub>2</sub> ]                                     |            |  |             | 05lop/cor |
| [emim][NTf <sub>2</sub> ]-[omim][NTf <sub>2</sub> ]                                     |            |  |             | 05lop/cor |
| [hmim]{PF <sub>6</sub> }-[C16-py][PF <sub>6</sub> ]                                     |            |  | 1998gor/hol |           |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-n-pentane       |            |  | 05dom/mar   |           |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-n-hexane        |            |  | 05dom/mar   |           |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-n-heptane       |            |  | 05dom/mar   |           |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-n-octane        |            |  | 05dom/mar   |           |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-<br>cyclohexane |            |  | 05dom/mar   |           |

|                                                                                       |  |  |           |  |
|---------------------------------------------------------------------------------------|--|--|-----------|--|
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-benzene       |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-toluene       |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-ethylbenzene  |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-o-xylene      |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ]-m-xylene      |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-n-hexane     |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-n-heptane    |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-cyclohexane  |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-benzene      |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-toluene      |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-ethylbenzene |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-o-xylene     |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-m-xylene     |  |  | 05dom/mar |  |
| [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ]-p-xylene     |  |  | 05dom/mar |  |

**Table 3 Ternary Systems studied**

| System                                                              | $\gamma_i^\infty$ | $\gamma_i$ | Phase Diagram |           |
|---------------------------------------------------------------------|-------------------|------------|---------------|-----------|
| [emim][NTf <sub>2</sub> ] – acetone – 2 propanol                    |                   | 05dok/gme  |               |           |
| [emim][NTf <sub>2</sub> ] – 2 propanol - water                      |                   | 05dok/gme  |               |           |
| [emim][I <sub>3</sub> ]-toluene-heptane                             |                   |            |               | 00sel/mck |
| [bmim][NTf <sub>2</sub> ] – acetone – 2 propanol                    |                   | 05dok/gme  |               |           |
| [bmim][NTf <sub>2</sub> ] – 2 propanol - water                      |                   | 05dok/gme  |               |           |
| [bmim][NTf <sub>2</sub> ]- isobutanol-water                         |                   |            | 05reb/naj     |           |
| [bmim][I <sub>3</sub> ]-toluene-heptane                             |                   |            |               | 00sel/mck |
| [hmim][BF <sub>4</sub> ]-1-hexene - ethanol                         |                   |            |               | 04let/red |
| [hmim][PF <sub>6</sub> ]-1-hexene - ethanol                         |                   |            |               | 04let/red |
| [emim][NTf <sub>2</sub> ]- propan-1-ol-water                        |                   |            |               | 05hei/leh |
| [emim][NTf <sub>2</sub> ]- butan-1-ol-water                         |                   |            |               | 05hei/leh |
| [emim][NTf <sub>2</sub> ]- pentan-1-ol-water                        |                   |            |               | 05hei/leh |
| [emim][NTf <sub>2</sub> ]-<br>[bmim][NTf <sub>2</sub> ]-n-hexane    | 05kat/gme         |            |               |           |
| [emim][NTf <sub>2</sub> ]-<br>[bmim][NTf <sub>2</sub> ]-n-heptane   | 05kat/gme         |            |               |           |
| [emim][NTf <sub>2</sub> ]-<br>[bmim][NTf <sub>2</sub> ]-n-octane    | 05kat/gme         |            |               |           |
| [emim][NTf <sub>2</sub> ]-<br>[bmim][NTf <sub>2</sub> ]-1-pentene   | 05kat/gme         |            |               |           |
| [emim][NTf <sub>2</sub> ]-<br>[bmim][NTf <sub>2</sub> ]-2-butanone  | 05kat/gme         |            |               |           |
| [emim][NTf <sub>2</sub> ]-<br>[bmim][NTf <sub>2</sub> ]-2-pentanone | 05kat/gme         |            |               |           |
| [emim][NTf <sub>2</sub> ]-<br>[bmim][NTf <sub>2</sub> ]-water       | 05kat/gme         |            |               |           |
| bmim][NTf <sub>2</sub> ]-1-butanol-water                            |                   |            | 05naj/reb     |           |
| bmim][NTf <sub>2</sub> ]-1-butanol-water-CO <sub>2</sub>            |                   |            | 05naj/reb     |           |
| [bmim][PF <sub>6</sub> ]-water-ethanol                              |                   |            | 02naj/esp     |           |
| [omim][Cl]-methanol-C <sub>7</sub> H <sub>16</sub>                  |                   |            | 03let/dee     |           |
| [omim][Cl]-methanol-C <sub>16</sub> H <sub>34</sub>                 |                   |            | 03let/dee     |           |
| [omim][Cl]-ethanol-C <sub>7</sub> H <sub>16</sub>                   |                   |            | 03let/dee     |           |
| [omim][Cl]-ethanol-C <sub>12</sub> H <sub>26</sub>                  |                   |            | 03let/dee     |           |
| [omim][Cl]-ethanol-C <sub>16</sub> H <sub>34</sub>                  |                   |            | 03let/dee     |           |

**Table 4 Summary of content of papers**

| Reference    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
|--------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1962cha/wes  | Heat capacities of tetramethyammonium chloride and bromide determined by low-temperature adiabatic calorimetry up to 350 K. Values for the entropy at 298.15 K were given.                                                                                                                                                                                                                                                                                     |
| 1970mur/bru  | Temperature of transition of tetramethyammonium chloride measured to 262-5 C with an associated enthalpy of 9896 J mol <sup>-1</sup> . The authors found that the substance sublimed before melting. It was found that tetramethyammonium bromide does not undergo a solid state phase transformation. The high value for the enthalpy of transition implies significant disordering and this may be taken as an approximate value for the enthalpy of fusion. |
| 1997lee/lee  | Study of transition temperatures and enthalpies of transition for a variety of benzimidazolium and imidazolium salts showing liquid crystal behaviour.                                                                                                                                                                                                                                                                                                         |
| 1998gor/hol  | Review of data for a variety of dialkyl imidazolium and alkylpyridinium salts with hexafluorophosphate anion.                                                                                                                                                                                                                                                                                                                                                  |
| 1999hol/sed  | General review of ionic liquids and their properties and potential.                                                                                                                                                                                                                                                                                                                                                                                            |
| 1999hol/sed1 | Properties of [Rmim][BF <sub>4</sub> ] salts. The salts with short alkyl chain lengths are liquids at room temperatures and form glasses on cooling. Longer chain salts are low melting solids which show a large liquid crystal formation over a range of temperatures. The paper gives value for liquidus temperatures, liquid crystal transformations and, in many cases, the enthalpies associated with these transitions.                                 |
| 99wel        | Review of ionic liquids field.                                                                                                                                                                                                                                                                                                                                                                                                                                 |
| 00ngo/lec    | Melting and freezing points for a range of pure ionic liquids. Also studied decomposition of ionic liquids by TGA.                                                                                                                                                                                                                                                                                                                                             |
| 01abb/cap    | Freezing points of mixtures of a quaternary ammonium chloride and MCl <sub>2</sub> (M=Zn, Sn) in a molar 1:2 ratio. The authors found that lowering the symmetry and inclusion of a functional group reduces the freezing point. More detailed results are presented for mixtures of choline chloride and zinc chloride.                                                                                                                                       |
| 01ant/mag    | Presentation of the miscibility gap and vapour liquid equilibria in three ionic liquid – water systems. The ionic liquids selected are: [bmim][PF <sub>6</sub> ], [omim][PF <sub>6</sub> ] and [omim]BF <sub>4</sub> .                                                                                                                                                                                                                                         |
| 01hud/vis    | Study of the effect of water on properties of imidazolium based ionic liquids. Hydrophilic anions (eg chloride and iodide) produce ionic liquids that are completely miscible with water. The paper contains a number of references to melting point determinations.                                                                                                                                                                                           |
| 02kat/jai    | Use of melting points of imidazolium based ionic liquids to develop predictive tools to aid in the development of new ionic liquids. The authors list the melting points for a large number of imidazolium bromides and benzimidazolium bromides.                                                                                                                                                                                                              |
| 02kat/lom    | Correlation of the melting points of 126 pyridinium bromides. The experimental values are not tabulated.                                                                                                                                                                                                                                                                                                                                                       |
| 02naj/esp    | Studies of the phase equilibria in the ternary [bmim][PF <sub>6</sub> ]-water-ethanol system. The system shows a surprising mixed solvent effect where a mixture of water and ethanol suppresses the miscibility gap.                                                                                                                                                                                                                                          |

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| 02sha/bre  | Monte Carlo simulations on [bmim][PF <sub>6</sub> ]. Although the title of the phase states thermodynamic properties those covered by the paper are the molar volume, cohesive energy density, isothermal compressibility, cubic expansion coefficient and liquid structure. The force field was developed through a combination of ab initio calculations and literature parameters values. The level of agreement between calculation and experiment was considered to be good. |
| 03eik/bre  | Correlation of the melting points of various quaternary ammonium ionic liquids. Few experimental values are given.                                                                                                                                                                                                                                                                                                                                                                |
| 03hol/rei  | Measurement of the heat capacity of [bmim][NTf <sub>2</sub> ], [bmim][Cl], [bmim][PF <sub>6</sub> ], [emim][PF <sub>6</sub> ], [hmim][PF <sub>6</sub> ] and [bmim][Bph <sub>4</sub> ].                                                                                                                                                                                                                                                                                            |
| 03hol/rei1 | Study of the polymorphism of [bmim] halides. The authors obtained two different crystal structures of [bmim][Cl] on crystallising from the melt. The melting points were determined by dsc.                                                                                                                                                                                                                                                                                       |
| 03let/dee  | Studies of ternary phase diagrams between [omim][Cl], an alkanol and an alkane at 298.2 K.                                                                                                                                                                                                                                                                                                                                                                                        |
| 03let/sok  | Measurement of the activity coefficients at infinite dilution for a variety of organic solutes in [hmim][PF <sub>6</sub> ].                                                                                                                                                                                                                                                                                                                                                       |
| 03let/sok1 | Measurement of the activity coefficients at infinite dilution for a variety of organic solutes in [hmim][BF <sub>4</sub> ].                                                                                                                                                                                                                                                                                                                                                       |
| 04for/pri  | Review of some of the properties of ionic liquids.                                                                                                                                                                                                                                                                                                                                                                                                                                |
| 04kab/blo  | Detailed measurement of the heat capacity, temperature and enthalpy of fusion and density of [bmim][PF <sub>6</sub> ].                                                                                                                                                                                                                                                                                                                                                            |
| 04ohl/dys  | Study of the solubility of CO in 37 ionic liquids using high pressure <sup>13</sup> C NMR spectroscopy.                                                                                                                                                                                                                                                                                                                                                                           |
| 04reb/naj  | Comprehensive review and analysis of experimental thermodynamic and phase data between [bmim][BF <sub>4</sub> ] and water. The paper also reports calorimetric measurements of the enthalpy of mixing, apparently the only example of such measurements on ionic liquid systems.                                                                                                                                                                                                  |
| 04ver/vas  | Vapour liquid equilibria for a variety of aldehydes and ketones in [emim][NTf <sub>2</sub> ] using a transpiration technique. The authors derived activity coefficients.                                                                                                                                                                                                                                                                                                          |
| 05cam/bec  | Experimental study and modelling of the solubility of hydrocarbons at low pressures in 5 ionic liquids [bmim][PF <sub>6</sub> ], [bmim][BF <sub>4</sub> ], [emim][NTf <sub>2</sub> ], [emim][CF <sub>3</sub> SO <sub>3</sub> ] and [emim][dca].                                                                                                                                                                                                                                   |
| 05cer/tro  | Study and analysis of data for the miscibility gap in the [bmim][BF <sub>4</sub> ]-water system.                                                                                                                                                                                                                                                                                                                                                                                  |
| 05cro/mul  | Melting points, transition temperature and heat capacities for a wide range of pyridinium based ionic liquids. These properties are also compared with data for a number of imidazolium and quaternary ammonium based salts.                                                                                                                                                                                                                                                      |
| 05dok/gme  | Study of vapour – liquid equilibria in ternary systems involving the ionic liquids [emim][NTf <sub>2</sub> ] and [bmim][NTf <sub>2</sub> ] with acetone, 2 –propanol and water. Measurements were carried out and the results correlated using the Wilson, NRTL and UNIQUAC models.                                                                                                                                                                                               |
| 05dom/mar  | Studies of the miscibility gaps involving two ionic liquids with a variety of aliphatic and aromatic hydrocarbons. The ionic liquids are: [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][BF <sub>4</sub> ] and [C <sub>6</sub> H <sub>13</sub> OCH <sub>2</sub> mim][NTf <sub>2</sub> ].                                                                                                                                                                                   |
| 05gom/esp  | Experimental studies on [bmim][NTf <sub>2</sub> ] and [hmim][NTf <sub>2</sub> ] in order to measure to density and the speed of sound. The results were interpreted in terms of compressibilities, expansivities and heat capacities.                                                                                                                                                                                                                                             |

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| 05gom/esp1 | Experimental studies on [bmim][BF <sub>4</sub> ] and [bmim][PF <sub>6</sub> ] in order to measure to density and the speed of sound. The results were interpreted in terms of compressibilities, expansivities and heat capacities.                                                                                                                                                                                                                                                                                                                                           |
| 05hei      | Summary of thermodynamic studies on ionic liquid – non aqueous solvent mixtures.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
| 05hei/kla  | Measurement of liquid-liquid phase equilibria in the [omim][BF <sub>4</sub> ]-pentan-1-ol system between 282 and 292 K. A miscibility gap was identified with an upper critical solution temperature of 292 K. Their demixing temperature is about 3K higher than the value obtained by 04wag/sta1.                                                                                                                                                                                                                                                                           |
| 05hei/leh  | Studies of the liquid – liquid phase equilibria between a) [emim][NTf <sub>2</sub> ] and propan-1-ol, butan-1-ol and pentan-1ol with and without small additions of water, and b) [bmim][NTf <sub>2</sub> ] and cyclohexanol and 1,2-hexanediol between 275 K and 345 K. The authors also qualitatively examined a number of other solutes with those two ionic liquids for degrees of miscibility.                                                                                                                                                                           |
| 05hei/mar  | Measurement of the activity coefficients at infinite dilution of a number of alcohols, hydrocarbons, esters and aldehydes in [bmim][NTf <sub>2</sub> ].                                                                                                                                                                                                                                                                                                                                                                                                                       |
| 05hei/mar1 | Measurement of activity coefficients and heats of dilution of a number of high boiling organic solvents in [emim][NTf <sub>2</sub> ] between 298 and 323 K. Transpiration techniques were used to determine the composition of the vapour phase across the whole composition of the binary systems. Detailed results were given for nonanal solutions in [emim][NTf <sub>2</sub> ]. Also the authors reported that a titration calorimeter was used to measure enthalpies of dilution. Results were reported for infinite dilution and compared with other experimental data. |
| 05jor/kri  | Detailed article showing background to COSMO-RS and it ability to make predictions of thermodynamic properties and phase equilibria for systems involving ionic liquids.                                                                                                                                                                                                                                                                                                                                                                                                      |
| 05kat/gme  | Study of vapour liquid equilibria at 353 K for a variety of systems involving 6 ionic liquid. The authors used the experimental data to derive values for the activity coefficients at infinite dilution. The results were correlated with data for other systems in order to generate group interaction parameters. Experimental and modelled results were compared with predictions from COSMO-RS.                                                                                                                                                                          |
| 05kat/gme1 | Measurement of the vapour liquid equilibria between various organic compounds and three ionic liquids [emim][NTf <sub>2</sub> ], [bmim][NTf <sub>2</sub> ] and [mmim][(CH <sub>3</sub> ) <sub>2</sub> PO <sub>4</sub> ].                                                                                                                                                                                                                                                                                                                                                      |
| 05kim/cho  | Studies of the solubility of CO <sub>2</sub> in 6 ionic liquids: [bmim][PF <sub>6</sub> ], [hmim][PF <sub>6</sub> ], [emim][BF <sub>4</sub> ], [hmim][BF <sub>4</sub> ], [emim][NTf <sub>2</sub> ] and [hmim][NTf <sub>2</sub> ].                                                                                                                                                                                                                                                                                                                                             |
| 05kum/kam  | Measurement of the solubility of CO in [bmim][PF <sub>6</sub> ] between 293 and 373 K up to pressures of 10 MPa.                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
| 05kum/kam1 | Measurement of the solubility of oxygen in [bmim][PF <sub>6</sub> ] between 293 and 373 K up to pressures of 9.1 MPa. The solubility is reported to be very low.                                                                                                                                                                                                                                                                                                                                                                                                              |
| 05lac/szy  | Studies of the miscibility gap in binary systems between mixed [C <sub>m</sub> mim][NTf <sub>2</sub> ] and various mixed CH <sub>x</sub> Cl <sub>4-x</sub> . The authors show that various types of miscibility gaps are observed ie some with upper consolute temperature, some with lower consolute temperature and others with closed loops.                                                                                                                                                                                                                               |
| 05let/dom  | Measurement of the activity coefficients at infinite dilution of a variety of organic solutes in [bmim][DEGSO <sub>4</sub> ].                                                                                                                                                                                                                                                                                                                                                                                                                                                 |

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| 05let/mar  | Measurement of activity coefficients at infinite dilution in [bmim][O <sub>2</sub> SO <sub>3</sub> ] at 298.15, 313.15 and 328.15. The solutes were hydrocarbons and methanol. The authors conclude that this ionic liquid should not be considered as a solvent for separation of alkanes and aromatics.                                                                                 |
| 05lop/cor  | Determination of the excess molar volumes in six binary systems between ionic liquids.                                                                                                                                                                                                                                                                                                    |
| 05min/kam  | C <sub>p</sub> , Δ <sub>fus</sub> H, Δ <sub>evap</sub> H of ([bmim][Cl])                                                                                                                                                                                                                                                                                                                  |
| 05naj/reb  | Studies of the miscibility gap in the system [bmim][NTf <sub>2</sub> ]-1-butanol-water and [bmim][NTf <sub>2</sub> ]-1-butanol-water-CO <sub>2</sub> system.                                                                                                                                                                                                                              |
| 05naj/ser  | Studies of the miscibility gap between [bmim][PF <sub>6</sub> ] and supercritical carbon dioxide, water and ethanol. No data are given.                                                                                                                                                                                                                                                   |
| 05reb/lop  | Distillation of [C10mim][NTf <sub>2</sub> ] and [C12mim][NTf <sub>2</sub> ] ionic liquids and prediction of critical temperatures and boiling temperatures from measured surface tension data.                                                                                                                                                                                            |
| 05reb/naj  | A general review of experimental and theoretical work carried out on ionic liquids at Oeiras and Lisbon. Much of the work discussed relates to study of the miscibility gap between ionic liquids and alcohols and water.                                                                                                                                                                 |
| 05vas/ver  | Measurement of the activity coefficients of various ethers and alcohols in [emim][NTf <sub>2</sub> ] using a transpiration technique.                                                                                                                                                                                                                                                     |
| 05zha/kam  | Measurement of the thermodynamic properties of [bmim][Cl] by thermogravimetric and differential thermal analysis. The results were interpreted in terms of the heat capacity and enthalpy of fusion.                                                                                                                                                                                      |
| 06abb/cap  | Discussion of the application of hole theory in order to understanding the viscosity and other thermophysical properties of deep eutectic solvents. The paper also has some discussion of the phase diagram between EtNH <sub>3</sub> Cl and hydrogen bond donors such as urea, acetamide, trifluoroacetamide.                                                                            |
| 06abb/cap1 | Solubility of metal oxides from electric arc furnace dust in deep eutectic solvents. Solubilities of a range of oxides are given in a 1:2 choline chloride:urea solution at 60 C. Cu <sub>2</sub> O, PbO <sub>2</sub> and SnO were particularly soluble.                                                                                                                                  |
| 06dom/pob  | Solubilities of binary mixtures between either [mmim][MeSO <sub>4</sub> ] or [bmim][MeSO <sub>4</sub> ] and alcohols, ethers or ketones between 270 K to the boiling temperature. There is complete miscibility between [mmim][MeSO <sub>4</sub> ] and water and alcohols up to heptan-1-ol up to 310 K and between [bmim][MeSO <sub>4</sub> ] and water and alcohols up to undecan-1-ol. |
| 06ear/esp  | Experimental demonstration that some ionic liquids can be distilled between 200-300 C at low pressures                                                                                                                                                                                                                                                                                    |
| 06end/abe  | Review of field of application of ionic liquids up to the end of 2005. Some information about thermodynamic properties and thermal stability but not comprehensive by any means.                                                                                                                                                                                                          |
| 06esp/gue  | Study of the densities and derived thermodynamic properties of phosphonium based ionic liquids – trihexyltetradecylphosphonium chloride, trihexyltetradecylphosphonium acetate, trihexyltetradecylphosphonium [NTf <sub>2</sub> ].                                                                                                                                                        |
| 06kum/kam1 | Measurement of the solubility of H <sub>2</sub> in [bmim][PF <sub>6</sub> ] between 313 and 373 K and pressures up to 9Mpa.                                                                                                                                                                                                                                                               |
| 06mut/jau  | Use of gas chromatography for determination of thermodynamic properties of ionic liquids. The activity coefficient at infinite dilution was measured for 29 polar and non-polar compounds in [bmim][octyl sulphate] at 323.15, 333.15 and 343.15 K, and [emim][tosylate] at 323.15 K. The solutes were alkanes, alkenes, alkynes, cycloalkanes, aromatics and alcohols.                   |

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| 06red     | Brief review, applications. Highlights the need for physicochemical and thermodynamic properties, especially liquid temperature range, heat capacity and thermal stability. He refers to measurements of heat capacity and enthalpies of fusion and vaporisation made on [bmim][Cl]. He points out that lowering the viscosity by adding a cosolvent makes it necessary to characterise binary and ternary systems. |
| 06vas/ver | Measurement of the of vapour liquid equilibrium between various esters and benzylamine in [emim][NTf <sub>2</sub> ] using the transpiration technique between 298 and 318 K. The results were used to derive activity coefficients.                                                                                                                                                                                 |

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