Novel organic solvents for the Bunsen Reaction

Marie L. Taylor[1], Peter Styring[1] and Ray W. K. Allen[1]
[1]Department of Chemical and Process Engineering, University of Sheffield, Mappin Street, Sheffield, S1 3JD, United Kingdom

Introduction

Hydrogen is an energy carrier that has the potential to be produced from renewable sources, with minimal (potentially zero) harmful emissions to the environment. There are many technologies (both proven and non-proven) for the production of hydrogen. Thermochemical cycles linked with nuclear heat are one of the most promising routes [Ewan and Allen 2005]. Of these cycles, the sulphur iodine (SI) cycle appears to have encouraged the most international excitement over the last decade.

The SI cycle was first developed by General Atomics (GA) in the early 70s. The cycle is characterised by the following reactions:

Equation 1: $I_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$

Equation 2: $H_2SO_4 \rightarrow \frac{1}{2}O_2 + SO_2 + H_2O$

Equation 3: $2HI \rightarrow H_2 + I_2$

Equation 1 is usually known as the Bunsen reaction. Here iodine reacts with sulphur dioxide and water to produce two acids, sulphuric acid (H_2SO_4) and hydriodic acid (HI). These acids are then decomposed, the H_2SO_4 decomposition produces an oxygen product (equation 2) and the HI decomposition produces hydrogen (equation 3). The overall result is a net input of water and a net output of hydrogen and oxygen. All other components are recycled.

For the Bunsen reaction, GA put forward a processing scheme where all reactants and products are fluids. The melting temperature of iodine is 387K so the Bunsen reaction was carried out at 393K. At this temperature the reaction is unfavourable, the free energy change being +82 kJ mol^{-1} (400K). GA showed that the two acid products formed in the Bunsen reaction could be separated by density if sufficient excess iodine was present [Norman et al. 1978]. This excess iodine helps to shift the reaction equilibrium forward and also causes the acids to spontaneously separate into two aqueous phases; a light phase containing the sulphuric acid and a heavy phase containing polyhydriodic acids, iodine, water and a number of protonated polyiodine complexes (known as the HI_x phase). The formation of these polyhydriodic acids in which iodide anions are solvated by molecular diiodine causes the phase separation to occur. The phase separation characteristics of the acids increase with increasing iodine concentration up until the iodine saturation point is reached [Sakurai et al. 2000].

An excess of water is also required for the reaction in order to shift the reaction equilibrium to the right, however this causes a significant change in the enthalpy due to acid dilution. These excesses of both water and iodine lead to a modified Bunsen reaction with a free energy change of -88 kJ mol^{-1} at 400K:

$$9I_2 + 16H_2O + SO_2 \rightarrow (2HI + 8I_2 + 10H_2O) + (H_2SO_4 + 4H_2O)$$

This modified reaction becomes thermodynamically favourable but is also very exothermic (ΔH = -90 kJ mol^{-1}) due to the large excess of water required. A further disadvantage is that this modified reaction causes complications with the HI separation and decomposition section due to the presence of a complex azeotrope.

The reduction of the large excesses of both water and iodine needed for phase separation is one of the key research challenges for future development of the SI cycle. Although promising results have been achieved using an electrochemical membrane reactor for the Bunsen reaction [Nomura et al. 2005] there is a problem when scaling up to commercial size. Therefore, alternative ways of reducing the large reactant excesses are currently under investigation. A small amount of work has been conducted in the past on the use of excess liquid sulphur dioxide and organic solvents in the Bunsen reaction, as a means of complexing and extracting the HI [De Beni et al. 1980]. The authors identified that liquid sulphur dioxide, being immiscible with sulphuric acid at low temperatures, dissolved HI well and therefore enabled acid separation. Both low boiling and high boiling molecular organic solvents were then employed as materials that were miscible with the sulphur dioxide and were capable of extracting the HI. Good results were achieved with the addition of high boiling organic solvents, in particular with tributyl phosphate (TBP). However, problems arose in then separating the HI from the solvent following water removal. On heating past 350K, the TBP began to degrade.

The aim of this work is to identify and examine possible solvents or groups of solvents that could be used effectively in the Bunsen reaction. Initial work on one potential group of solvents, ionic liquids, is reported here.

Ionic liquids

In the last decade ionic liquids have emerged as excellent solvents in the area of green chemistry [Holbrey and Seddon 1999]. Ionic liquids are ‘non-volatile, non-flammable and thermally stable solvents and as such are very promising replacements for the traditional volatile organic solvents’ [Huddleston et al. 2001]. They are liquid at room temperature and are composed entirely of ions. The physical and chemical properties of these ionic liquids can be tailored by the choice of cation and/or anion [Brennecke and Maginn 2001] meaning that for any given application an optimum ionic liquid exists.

Ionic liquids are starting to be used in industrial separation methods and this is mainly due to their extremely low vapour pressure and thermal stability [Berthod et al. 2005]. Investigations have looked at the separation of metal ions, the separation of organic compounds, the separation of gases and the use of ionic liquids in analytical separation.

Ionic liquids have also been used in the field of acid extraction. Martak and Schlosser [2007] investigated the extraction of lactic acid with the ionic liquid trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate. The authors found that the ionic liquid was successful at extracting undissociated molecules of acid via a hydrogen bonding mechanism.

The work reported here focuses on whether the novel properties of ionic liquids can be utilised in the SI cycle as a solvent capable of extracting the HI into a second phase in the Bunsen reaction. For this to happen, major property requirements of the ionic liquid are that it must:

- Be immiscible with water
- Have a high selectivity for extracting HI
- Have a high thermal degradation temperature
- Have a high capacity for dissolving both iodine and sulphur dioxide

One of the first objectives of the experimental program was to identify those ionic liquids that are selective for HI via simple liquid-liquid extraction tests.

Experimental

Following a literature study and preliminary testing, nine ionic liquids were selected for further examination. In order to make a direct comparison to the work done by De Beni et al. [1980] TBP was also analysed for its extraction capability in the same environment and the results are presented with those of the ionic liquids.

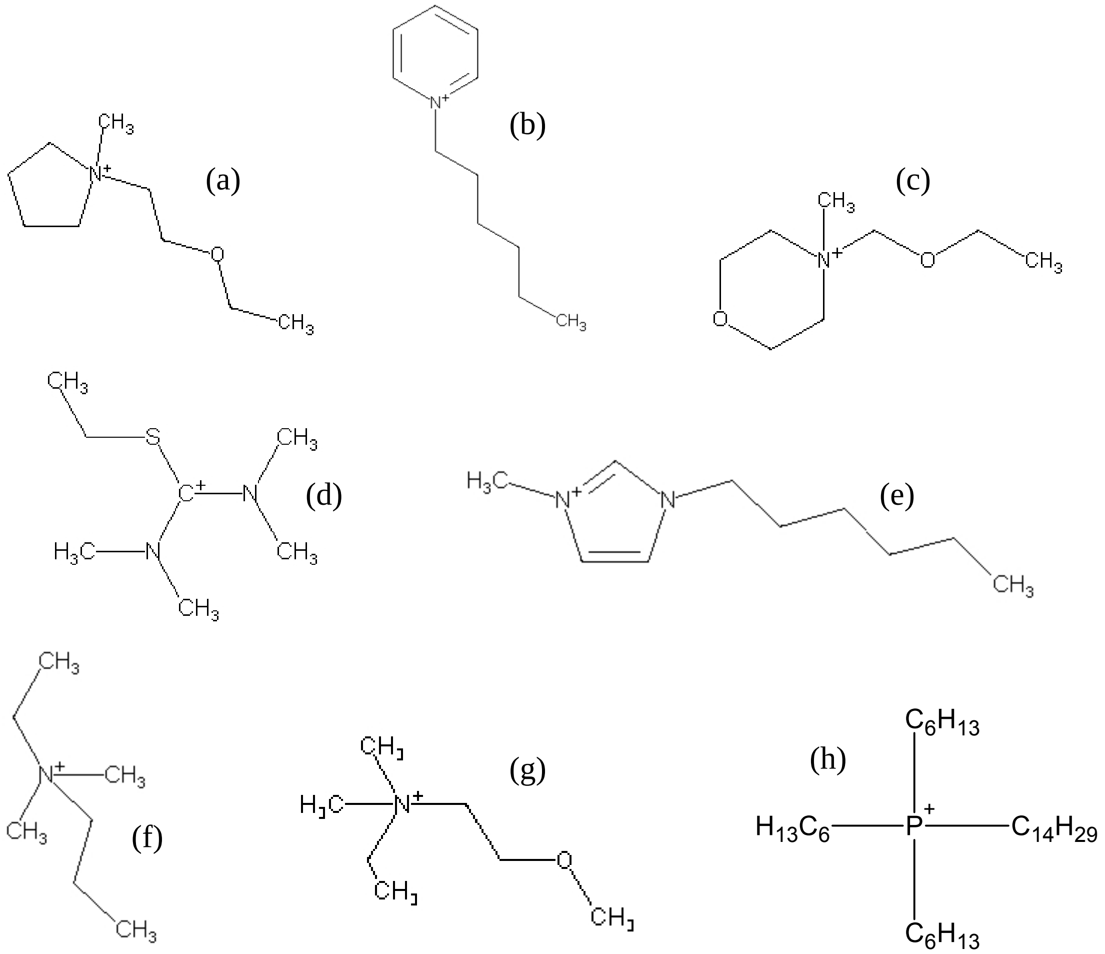

Figure 1. Ionic liquid cations: (a) 1-(2-ethoxyethyl)-1-methylpyrrolidinium ((eOe)mpl); (b) n-hexylpyridinium (hpyr); (c) N-Ethoxymethyl-N-methylmorpholinium ((eOm)mmo); (d) S-Ethyl-N,N,N',N'-tetramethylisothiouronium (Sem$_4$iso); (e) 1-hexyl-3-methylimidazolium (hmim); (f) Ethyl-dimethyl-propylammonium (Nemmp); (g) N-ethyl-N,N-dimethyl-2-methoxyethylammonium (Nemm(mOe)); (h) trihexyltetradecylphosphonium (P$_{666,14}$)

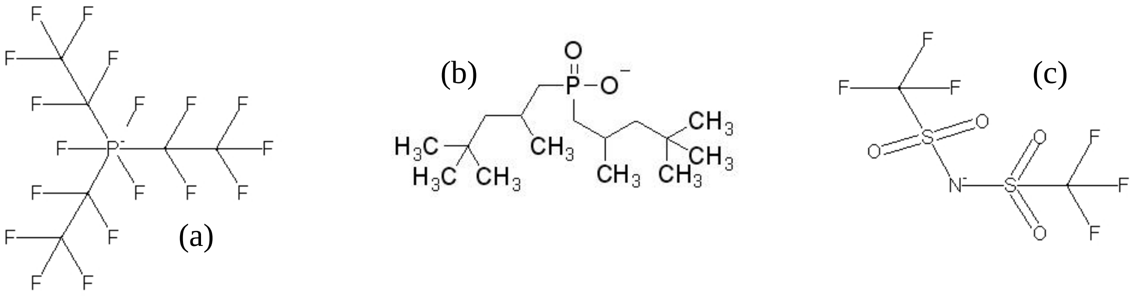

Figure 2. Ionic liquid anions: (a) tris(pentafluoroethyl)trifluorophosphate (FAP); (b) bis(2,4,4-trimethylpentylphosphinate (TMPP); (c) bis(trifluoromethylsulphonyl)imide (Tf_2N)

Figures 1 and 2 show the molecular structure of a selection of ionic liquid cations and anions. The ionic liquids used in the experiment are listed in table 1. All ionic liquids except the n-hexylpyridinium bis(trifluoromethylsulphonyl)imide were available commercially and were used as received. The n-hexylpyridinium bis(trifluoromethylsulphonyl)imide was synthesised and verified by ^1H NMR prior to use.

Table 1. Ionic liquid selected for HI extraction tests

	Ionic liquid
1	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [hmim][FAP]
2	1-(2-Ethoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulphonyl)imide [(eOe)mpl][Tf_2N]
3	Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate [$P_{666,14}$][FAP]
4	N-Ethoxymethyl-N-methylmorpholinium bis(trifluoromethylsulphonyl)imide [(eOm)mmo][Tf_2N]
6	S-Ethyl-N,N,N',N'-tetramethylisothiouronium tris(pentafluoroethyl)trifluorophosphate [Sem_4iso][FAP]
8	Ethyl-dimethyl-propylammonium bis(trifluoromethylsulphonyl)imide [Nemmp][Tf_2N]
9	N-Ethyl-N,N-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulphonyl)imide [Nemm(mOe)][Tf_2N]
11	Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate [$P_{666,14}$][TMPP]
14	n-hexylpyridinium bis(trifluoromethylsulphonyl)imide [hpyr][Tf_2N]

Equal volumes of each of the ionic liquids were mixed with unstabilised azeotropic HI solution for one hour. Following this the mixtures were left to settle for a minimum of 12 hours. Samples of both the aqueous and organic phases were analysed for iodine, acid and iodide content using potentiometric titrations. An iodide balance and a proton balance allowed independent determination of the mass of both phases. ^1H NMR spectra were obtained for each of the pure ionic liquids and also for the aqueous and organic phases following extraction. This allowed any chemical interaction between the acid and the ionic liquid to be observed.

Results – HI extraction

Table 2. Amount of protons and iodide (I^-) ions extracted by the ionic liquids

Ionic liquid	**% Protons extracted into organic phase ± 0.3**	**% Iodide ions extracted into organic phase ± 0.3**
1 [hmim][FAP]	0.3	0.5
2 [(eOe)mpl][Tf_2N]	22.5	11.7
3 [$P_{666,14}$][FAP]	0.4	0.7
4 [(eOm)mmo][Tf_2N]	26.5	15.2
6 [Sem_4iso][FAP]	1.3	1.5
8 [Nemmp][Tf_2N]	16.7	7.2
9 [Nemm(mOe)][Tf_2N]	21.2	9.8
11 [$P_{666,14}$][TMPP] **- run 1** **11** [$P_{666,14}$][TMPP] **- run 2**	18.0 14.7	19.3 23.6
14 [hpyr][Tf_2N]	10.8	4.7
TBP	-	15.9

Table 2 shows the % protons and % iodide ions extracted by each of the ionic liquids. The data is presented based on ions rather than molecular HI so as to show the significant difference in the amounts of protons and iodide ions extracted by the Tf_2N ionic liquids. The TBP was found to extract 15.9 wt% of the HI in the same environment. In all cases (except that of IL 11) the mass balances based on the proton and the iodide agreed to within 5%. Looking at the results, it is clear that the ionic liquids can be split into three general groups for analysis according to their anions:

Tris(pentafluoroethyl)trifluorophosphate (FAP) ionic liquids (ILs 1, 3 and 6) - The extraction of protons and iodide ions for the FAP ionic liquids show that very little of the HI from the aqueous phase is extracted when compared to that of the TBP result. It is hypothesised that this may be due to the general mechanism of extraction of most hydrohalic acids. Many authors have documented the extraction of hydrochloric acid by TBP, and with it the co-extraction of water molecules. Kertes [1960] demonstrated the presence of two well defined species in the TBP-HCl-H_2O system, the first forming at low initial acid concentrations with the composition $[(TBP)_2\cdot HCl\cdot(H_2O)_6]$ and the second forming at higher initial acid concentrations with the composition $[TBP\cdot HCl\cdot(H2O)_3]$. Stoyanov [1993] goes on to describe the molecular state of these species at different initial acid concentrations. Baldwin et al. [1959] state that for HI, hydrobromic acid and hydrochloric acid water is co-extracted into TBP at an approximate ratio of four water molecules per acid molecule. The co-extraction of water with hydrohalic acids has been observed with other organic solvents such as trialkyl phosphine oxides [Mrnka et al. 1974, Alguacil and Lopez 1996] and methyl isobutyl ketone [Widmer 1970]. During the work done on the Bunsen reaction with solvents De Beni et al. [1980] observed co-extraction of water. The authors attributed this to the strength of the HI aqueous azeotrope.

Water co-extraction has also been observed when extracting acids into ionic liquids [Martak and Schlosser 2007]. It is therefore highly likely that the extraction of HI into ionic liquids will involve the co-extraction of water.

The anion is generally used to control the water miscibility of the ionic liquid (although the cation can also influence the hydrophobicity) [Huddleston et al. 2001]. The water uptake of a selection of ionic liquids containing the three anions under investigation is shown in table 4:

Table 4. Comparison of water uptake by ionic liquids containing Tf_2N, FAP and TMPP anions. [a] Ignat'ev et al. [2005] [b] Cyphos 104 data sheet

Ionic liquid	**Water uptake (ppm)**
1-hexyl-3-methylimidazolium Tf2N	10670[a]
1-hexyl-3-methylimidazolium FAP	2030[a]
1-butyl-3-methylpyrrolidinium Tf2N	14800[a]
1-butyl-3-methylpyrrolidinium FAP	3500[a]
Trihexyl(tetradecylphosphonium) TMPP	206000[b]

It is clear that the order of hydrophobicity for the anions is FAP > Tf_2N > TMPP. Of the three groups, the FAP ionic liquids extract significantly less HI than the Tf_2N and TMPP ionic liquids. If HI is only extracted in a hydrated form then it would be expected that ionic liquids containing FAP anions would extract the least amount out of the three. Unfortunately, the water content of the organic phase could not be measured directly using Karl Fisher analysis due to the presence of iodine.

Although the mechanism of extraction is not fully understood, it is clear that only negligible amounts of acid are taken up by the organic phase meaning that they are unsuitable for use in the Bunsen reaction.

Bis(trifluoromethylsulphonyl)imide (Tf_2N) ionic liquids (ILs 2, 4, 8, 9 and 14)- The results for this group of ionic liquids are slightly more complex. There are significant differences in the acid content values depending on whether it is based on the proton or the iodide analysis. In each case only approximately half the amount of iodide ions, when compared to protons, are extracted into the organic phase. The mechanism of extraction with regard to the Tf_2N ionic liquids appears to differ to that of the FAP ionic liquids (water co-extraction aside). Looking at the organic phases, it can be seen that more protons are present than corresponding anions and vice versa in the aqueous phase. In order that electroneutrality be maintained throughout the system this must mean that there is transfer of ionic liquid ions between the phases. As the HI is extracted into the organic phase in its dissociated form the protons are free to pair with either the iodide ions or the anions of the ionic liquid. Similarly the iodide ions can pair with the protons or the ionic liquid cations. Of the Tf_2N ionic liquids tested none of the cations are hydrophobic in nature. Therefore, if a pairing between an iodide ion and an ionic liquid cation occurs it is free to transfer into the aqueous phase.

This ion exchange mechanism has been observed previously. Work has been undertaken to examine the extraction of metal ions from acidic nitrate media by ionic liquids [Dietz and Dzielawa 2001]. The authors observed that the extraction of strontium from aqueous nitrate media, did not involve nitrate ion coextraction, indicating a cation exchange mechanism taking place. The effect of increasing the hydrophobicity of the cation was investigated [Dietz et al. 2003] and a decrease in cation exchange was observed when the length of the alkyl chain on the cation was increased from C5 to C10. However, further work by the authours revealed that multiple mechanisms can take place, and that ionic liquid loss to the aqueous phase can still occur even with these more hydrophobic cations [Dietz and Stepinski 2005].

In summary, it is expected that the Tf_2N ionic liquids also extract HI with a co-extraction of water. Due to their more hydrophilic nature (when compared to the FAP ionic liquids) they are able to extract more acid and this is seen in the extraction results. However, as the system is entirely ionic, an equilibrium exists in the organic phase between HI, $[H][Tf_2N]$, [Cation][I] and $[Cation][Tf_2N]$, of which the [Cation][I] is free to transfer into the aqueous phase. Observation of the ^1H NMR spectra of the aqueous phases following extraction with the Tf_2N ionic liquids does indeed show the presence of the organic cation in all cases.

Obviously, a loss of the cation to the aqueous phase severely compromises the integrity of the solvent. Unless a process can be found whereby there is no loss of the solvent it is unliklely that the Tf_2N solvents will be suitable for the Bunsen reaction.

Bis(2,4,4-trimethylpentylphosphinate) (TMPP) ionic liquids (IL 11) - The results for the bis(2,4,4-trimethylpentyl)phosphinate ionic liquid tested show discrepancies in the component balances. The potentiometric analysis of the organic phase for both protons and iodide ions exhibit two equivalence points, suggesting that there is a more complex chemical interaction occurring than seen with the previous two groups of ionic liquids. Further work is needed to determine what is happening in this mixture, however significant amounts of both protons and iodide ions are extracted when compared to the TBP.

Conclusions

The results presented in this paper show that a great deal of further work is needed if ionic liquids are to be considered for use in the Bunsen reaction of the sulphur iodine cycle. Unlike more traditional molecular solvents, the extraction mechanism is potentially far more complex as the entire system, both solvent and acid, is ionic by nature. It is hypothesised that the extraction of HI by these solvents involves the co-extraction of water molecules, most probably due to the nature and strength of the HI aqueous azeotrope. The extremely hydrophobic nature of the FAP ionic liquids means that negligible amounts of acid are taken into the organic phase therefore making them unsuitable. The Tf_2N ionic liquids, whilst extracting significant quantities of acid succumb to a cation exchange process, leading to solvent loss to the aqueous phase. The TMPP ionic liquid shows some promise however further work is needed to determine the complex processes taking place in the mixture. Current investigations are now focussing on more traditional molecular solvents with the aim of avoiding the cation exchange process which occurs in some ionic liquids.

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Alguacil F. J. and Lopez F. A. (1996) The extraction of mineral acids by the phosphine oxide Cyanex 923, *Hydrometallurgy*, **42(2)**, 245-255.

Baldwin W. H., Higgins C. E. and Soldano B. A. (1959) The distribution of monovalent electrolytes between water and tributyl phosphate, *Journal of Physical Chemistry*, **63(1)**, 118-123.

Berthod A., Ruiz-Angel M. J. and Huguet S. (2005) Nonmolecular solvents in separation methods: Dual nature of room temperature ionic liquids, *Analytical Chemistry*, **77**, 4071-4080.

Brennecke J. and Maginn E. (2001), Ionic liquids: innovative fluids for chemical processing, *AIChE Journal*, **47(11)**, 2384-2389.

Cytec data sheet, Cyphos® IL 104 phosphonium ionic liquid: Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate.

De Beni G., Pierini G. and Spelta B. (1980) The reaction of sulphur dioxide with water and a halogen. The case of iodine: reaction in presence of organic solvents, *International Journal of Hydrogen Energy*, **5**, 141-149.

Dietz M. L. and Dzielawa J. A. (2001) Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: implications for the 'greenness' of ionic liquids as diluents in liquid-liquid extraction, *Chemical Communications*, **20**, 2124-2125.

Dietz M. L., Dzielawa J. A., Laszak I., Young B. A. and Jensen M. P. (2003) Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids, *Green Chemistry*, **5(6)**, 682-685.

Dietz M. L. and Stepinski D. C. (2005) A ternary mechanism for the facilitated transfer of metal ions into room-temperatures ionic liquids (RTILs): implications for the 'greenness' of RTILs as extraction solvents, *Green Chemistry*, **7**, 747-750.

Earle M. J., Esperanca M. S. S., Gilea M. A., Canongia Lopes J. N., Rebelo L. P. N., Magee J. W., Seddon K. R. and Widegren J. A. (2006) The distillation and volatility of ionic liquids, *Nature*, **439**, 831-834.

Ewan B. C. and Allen R. W. K. (2005) A figure of merit assessment of the routes to hydrogen, *International Journal of Hydrogen Energy*, **30**, 809-809.

Giaconia A., Caputo G., Ceroli A., Diamanti M., Barbarossa V., Tarquini P. and Sau S. (2007) Experimental study of two phase separation in the Bunsen section of the sulfur-iodine thermochemical cycle, *International Journal of Hydrogen Energy*, **32**, 531-536.

Holbrey J. and Seddon K. (1999), Ionic liquids, *Clean Products and Processes*, **1**, 223-236.

Huddleston J., Visser A., Reichert W., Willauer H., Broker G. and Rogers R. (2001) Characterisation and comparison of hydrophillic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, *Green Chemistry*, **3**, 156-164.

Ignat'ev N. V., Welz-Biermann U., Kucheryna A., Bissky G. and Willner H. (2005) New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions, *Journal of Fluorine Chemistry*, **126**, 1150-1159.

Kertes A. S. (1960) Solute-solvent interaction in the system hydrochloric acid-water-tri-n-butyl phosphate, *Journal of Inorganic and Nuclear Chemistry*, **14**, 104-113.

Martak J. and Schlosser S. (2007) Extraction of lactic acid by phosphonim ionic liquds, *Separation and Purification Technology*, **57**, 483-494.

Mrnka M., Jedinakova V. and Sladkovska J. (1974) The extraction of HCl by TDPO in benzene, *Journal of Radioanalytical Chemistry*, **21**, 87-95.

Nomura M., Okuda H., Kasahara S. and Nakao S-I (2005) Optimisation of the process parameters of an electrochemical cell in the IS process, *Chemical Engineering Science*, **60**, 7160-7167.

Norman J., Mysels K., O'Keefe D., Stowell A. and Williamson D. (1978) Water splitting: The chemistry of the I_2-SO_2-H_2O reaction and the processing of the H_2SO_4 and HI products, *Miami international conference on alternative energy*, **8**, 3495-3526.

Sakurai M., Nakajima H., Amir R., Onuki K. and Shimizu S. (2000) Experimental study on side-reaction occurrence condition in the iodine-sulfur thermochemical hydrogen production process, *International Journal of Hydrogen Energy*, **25**, 613-619.

Stoyanov E. S. (1993) Molecular state of hydrochloric acid and its tribuyl-phosphate extracts, *Journal of Structural Chemistry*, **34(5)**, 714-721.

Widmer H. M. (1974) Solvation effects and ion association in solvent extraction systems. I. The thermodynamics of hydrochloric acid in the water-methyl isobutyl ketone system, *Journal of Physical Chemistry*, **74(17)**, 3251-3262.