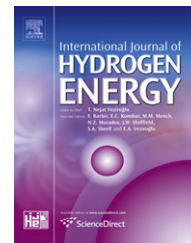


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# Improved solvation routes for the Bunsen reaction in the sulphur iodine thermochemical cycle: Part III—Bunsen reaction in molecular solvents

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## ABSTRACT

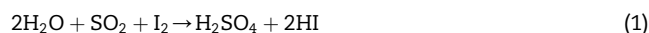
Operating the Bunsen reaction in a solvent has the potential to increase SI cycle efficiency and decrease operating costs. Analysing the solvent–acid mixtures produced is complicated as additional acid is formed when SO<sub>2</sub> comes into contact with water. Tri-*n*-butyl phosphate (TBP) is suitable for HI extraction; however, it is susceptible to acid catalysed dealkylation, resulting in solvent decomposition and the production of butyl iodide. Cyanex<sup>®</sup> 923 is found to be superior to TBP in the Bunsen reaction due to its high affinity for HI. Strong orange complexes between HI, SO<sub>2</sub> and the phosphoryl group in Cyanex<sup>®</sup> 923 are formed, giving good product separation, however severely hampering HI recovery. Washing the organic phase with water resulted primarily in the removal of H<sub>2</sub>SO<sub>4</sub>. HI could then be recovered either thermally or with a second wash step.

The Bunsen reaction in Cyanex<sup>®</sup> 923 remains far from optimised, however priority should be given to developing a more sophisticated analytical method in order to fully characterise the system.

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## 1. Introduction

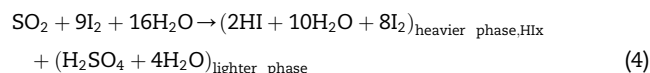
The Sulphur Iodine (SI) cycle has great potential for the massive scale production of hydrogen from water and has received much interest worldwide [1–4]. The cycle consists of three main reactions:



Reaction 1 is the Bunsen reaction in which sulphuric and hydriodic acids are produced. In reactions 2 and 3 these acids

are then decomposed, reaction 2 producing oxygen and reaction 3 producing hydrogen. The only inputs to the cycle are water and energy, the remaining components are recycled.

The Bunsen reaction is key to the cycle as excellent acid separation is required for the acid decomposition steps which follow. The Bunsen reaction is exothermic and high yields are therefore favoured by low temperatures. General Atomics proposed operating at 120 °C to avoid having solid iodine in the system (solidification point 113.7 °C), and using an excess of iodine and water (reaction 4) [1].



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The excess of iodine leads to phase separation between the two acids and the excess water gives reasonable reaction yields. Despite achieving two distinct acid phases which can be separated and then processed, the large excesses used also lead to complications downstream: evaporation of excess water incurs a high thermal burden; large amounts of iodine near to the solidification point tend to causing blockages; and the composition of the HIx phase is very near that of the HI–H<sub>2</sub>O azeotrope making separation difficult. Much work over the past decade has concentrated on ways to improve the Bunsen reaction, and in particular to reduce the excesses required. Part I of this work discussed the different options that have been considered [5], including: optimising the stoichiometry and phase separation characteristics [6], using an electrochemical cell [7,8], using a precipitating agent [9] and the use of solvents [9–12]. Using a solvent has potential to separate the acids at low cost and low energy demand. The ideal solvent for use in the Bunsen reaction would be hydrophobic, extract HI (and not H<sub>2</sub>SO<sub>4</sub>) and have a high solubility for both SO<sub>2</sub> and I<sub>2</sub>. In this way the reaction takes place in the solvent phase.

The properties of several common, commercially available ionic liquids (ILs) were assessed in part I to evaluate their suitability for use as solvents for the Bunsen reaction [5]. In particular, ILs with the [FAP]<sup>−</sup>, [Tf<sub>2</sub>N]<sup>−</sup> and [TMPP]<sup>−</sup> anions were tested for their HI extraction capability. The extraction of HI was found to involve the co-extraction of water, most probably due to the nature and strength of the HI aqueous azeotrope. None of the three families of ILs tested were found to be suitable for use in the Bunsen reaction, due to either poor HI extraction, the occurrence of hydrolysis or the presence of an ion exchange mechanism. Ionic liquids are designer solvents whose properties can be tailored based on the anion and cation used. Further ILs should be investigated before they are ruled out completely. Molecular solvents will not be susceptible to ion exchange and therefore are more likely to be suitable.

Tri-*n*-butyl phosphate (TBP) has been investigated by several groups as a solvent for the Bunsen reaction [9,10]. Part II to this paper investigated TBP, and a range of other organic solvents, to evaluate their potential for use in the Bunsen reaction [13]. Extraction into TBP of around 30% of the HI in an azeotropic solution was found to be possible [5], however attempts to recover the HI thermally failed as the TBP broke down [14]. Backwashing the solvent with large amounts of water was found to successfully remove the HI from the TBP, however an extremely dilute solution (1.5 wt%) was produced which would incur a large energy penalty in downstream processing [9]. TBP is part of a trialkylorganophosphorus series, all the members of which contain a phosphoryl group. It is the oxygen of this phosphoryl group that forms a coordination bond with the protons from the acid and hence extracts the acid from the aqueous phase into the organic phase. Two other members of the Trialkylorganophosphorus series were selected for testing: dibutylbutylphosphonate (DBBP) and Cyanex<sup>®</sup> 923, a mixture of trihexyl and tri-octylphosphine oxides [13]. It would be expected that these two solvents could extract more HI than TBP due to the higher number of alkyl groups present which enhance the ability of the phosphoryl group to form coordination bonds. Solvents

were tested for their capability to extract HI and H<sub>2</sub>SO<sub>4</sub> and for their solubility to SO<sub>2</sub> and I<sub>2</sub>. Both DBBP and Cyanex<sup>®</sup> 923 were as good if not better than TBP on the basis of all four parameters tested. There were, however, some problems with the analysis. For both TBP and DBBP there were differences in the proton and iodide potentiometric titration results for the organic phase. Thermal recovery of HI from DBBP was unsuccessful as the solvent decomposed in a similar manner to TBP. Some success was achieved recovering HI thermally from Cyanex<sup>®</sup> 923, however only small amounts of acid were released. Recovery of HI from Cyanex<sup>®</sup> 923 by backwashing with water was somewhat successful. Although Cyanex<sup>®</sup> 923 showed potential for use in the Bunsen reaction, it was not tested in a real Bunsen reaction environment, in which the organic phase could contain SO<sub>2</sub>, H<sub>2</sub>O and residual iodine and H<sub>2</sub>SO<sub>4</sub>, as well as the HI. This paper investigates the use of Cyanex<sup>®</sup> 923 as a solvent under realistic Bunsen reaction conditions and revisits the recovery of HI. TBP is also investigated to allow a comparison between results. Further work is reported which aids understanding of the chemistry of the reactions occurring and the analysis problems experienced previously are addressed.

## 2. Experimental methods

The Bunsen reaction was initially performed on a small scale using TBP as a solvent in order to develop experimental and analytical procedures, to allow a comparison with literature and to develop a better understanding of the chemistry of the reaction mixtures. The reaction was then performed on a slightly larger scale using several solvents to further understand the chemistry of the reactions. An excess of sulphur dioxide was used in the reaction (along with the solvent) with the aim of reducing the excess water required. As iodine is the limiting reagent, a complete reaction should be indicated by the loss of colour from the solution.

The Bunsen reaction was then performed on a larger scale in both TBP and Cyanex<sup>®</sup> 923 to eliminate contamination errors. Following this the recovery of HI from the Cyanex<sup>®</sup> 923 was reassessed.

### 2.1. Materials

Two solvents are tested: TBP with a purity of greater than 99% (Sigma Aldrich), and Cyanex<sup>®</sup> 923 with a purity of 93% (remainder TBP, Cytech Industries Inc) which was dried prior to use to a water content of approximately 1.5 wt%. In addition, hexane and 1-octanol (Sigma Aldrich) are also used for observational tests. Iodine with a purity greater than 99.8% (Sigma Aldrich), sulphur dioxide with a purity of 99.99% (BOC) and deionised water are used in all experiments.

### 2.2. Method—preliminary experiments

Initial experiments using TBP were performed on a small scale for safety reasons. The amounts of reactant used (Table 1) were based on the experiments performed by De Beni et al. [14], however as a reaction temperature of 25 °C is used in this work, more solvent was needed in order to dissolve the

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