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# Improved solvation routes for the Bunsen reaction in the sulphur iodine thermochemical cycle: Part II – Molecular solvent properties

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## ARTICLE INFO

### Article history:

Received 11 July 2012

Received in revised form

10 September 2012

Accepted 5 October 2012

Available online 6 November 2012

### Keywords:

Sulphur iodine cycle

Bunsen reaction

TBP

DBBP

Cyanex® 923

Phosphine oxides

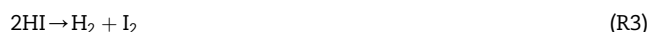
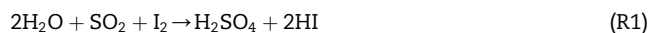
## ABSTRACT

Operating the Bunsen reaction in the presence of a molecular solvent has the potential to decrease the large excesses of water and iodine currently required and therefore to increase the efficiency of the sulphur iodine cycle. Tri-*n*-butyl phosphate (TBP) has been shown to extract HI into the solvent phase, however the TBP breaks down when treated thermally to recover the HI. Alternative solvents which also show a high extraction of HI, but that are stable in the presence of HI at high temperature, are needed. This paper investigates dibutylbutylphosphonate (DBBP) and Cyanex® 923 as alternatives to TBP. Both DBBP and Cyanex® 923 were shown to perform as well as or better than TBP against metrics including: HI extraction, H<sub>2</sub>SO<sub>4</sub> extraction, SO<sub>2</sub> solubility and I<sub>2</sub> solubility. Using TGA, thermal recovery of the HI was not successful from DBBP, as the solvent broke down in a similar way to TBP. Small amounts of HI were recovered through distillation of Cyanex® 923, however the yield was low. Partial success was achieved by backwashing the HI loaded Cyanex® 923 with water. Further work is needed to assess the performance of the actual Bunsen reaction in each of these solvents and to find ways of recovering the HI from the solvent.

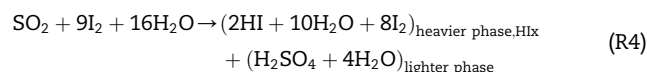
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## 1. Introduction

The sulphur iodine cycle is one of the most promising processes for massive scale hydrogen production from water [1]. The cycle consists of three key reactions as depicted in R1–R3.



Reaction 1 (R1) is the Bunsen reaction in which hydriodic acid and sulphuric acid are produced. General atomics suggested Bunsen reaction operation at 120 °C with large excesses of both water and iodine, as shown in R4, to enable phase separation of the two acid products and reasonable reaction yields.



Although two phases are produced, operation with such large excesses leads to problems downstream: evaporation of

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excess water incurs a high thermal burden; large amounts of iodine are prone to solidification due to operation very near to its melting point (113.7 °C); and the concentration of the HIx phase is very near the azeotrope causing separation difficulties. Much work has been carried out to investigate methods of reducing the large excesses used in order to increase cycle efficiency and bring it closer to commercialisation.

Part I of this paper [2] reviewed possible improvements to the Bunsen reaction, including optimising the stoichiometry and phase separation characteristics, using an electrochemical cell for the reaction, using a precipitating agent, operating with iodine as a limiting reagent and the use of solvents. The paper then concentrated on the use of ionic liquids as solvents. Tri-*n*-butyl phosphate (TBP) has been investigated by several groups as a potentially suitable solvent for the Bunsen reaction [3,4]. In the case of a solvent such as TBP, the reaction is conducted in excess SO<sub>2</sub> instead of excess iodine. Extraction of around 30% of the HI into the solvent phase was shown possible [2], however attempts to recover the HI from the solvent thermally failed as the TBP broke down [3]. Backwashing with large amounts of water was shown to be possible, however an extremely dilute solution (1.5%) is produced and this incurs a large energy penalty [4].

Several common, commercially available ionic liquids were investigated as potential solvents for the Bunsen reaction [2]. Extraction of HI was demonstrated, however co-extraction of water was shown to be necessary so the most hydrophobic ionic liquids only showed very limited extraction capability. Ionic liquids containing the [Tf<sub>2</sub>N]<sup>−</sup> anion showed comparable HI extraction to TBP, however they succumbed to an ion exchange process leading to loss of the ionic liquid into the aqueous phase. The extraction mechanism is thought to be very complex as both the solvent and acid are ionic in nature. It was concluded that without specifically tailoring an ionic liquid, it is unlikely that they will be successful in the Bunsen reaction.

In order to exclude the potential for ion exchange processes to occur the solvent must be molecular by nature. As discussed previously [2], potential solvents for the Bunsen reaction must: be hydrophobic, be capable of extracting HI from an aqueous solution, have a low affinity for sulphuric acid, and have a high solubility for both sulphur dioxide and iodine. In order for a concentrated hydriodic phase to be produced, the solvent must have: a high thermal degradation temperature, a high level of stability towards HI at high temperature and a large liquid range and low vapour pressure. This paper considers the suitability of advanced molecular solvents for use in the Bunsen reaction. The extraction of HI and H<sub>2</sub>SO<sub>4</sub> as well as the solubility of I<sub>2</sub> and SO<sub>2</sub> are considered. The recovery of HI from the resultant organic phase is also investigated.

The use of the most promising solvents in the Bunsen reaction is presented in a separate paper [5].

## 2. Identification of potential molecular solvents

Considerable work has been performed investigating the extraction (or co-extraction) of acids into molecular solvents.

Much of the work has been carried out in relation to hydrometallurgical processes, as solvents are commonly used to extract metals from aqueous acidic solutions. Amines and ammonium salts have been shown to be fairly successful at extracting a number of mineral acids from aqueous solutions [6–8]. The extent of extraction and the nature of the complexes formed depend heavily on the acid and its concentration in the aqueous phase, however, recovery of the acid from these organic solvents is generally not straightforward (in comparison to e.g. TPB). Alamine<sup>®</sup> 336, a water insoluble tri-octyl/decyl amine, was found to extract a large proportion of hydrochloric acid from an aqueous solution [8]. However, problems arose during acid recovery when stripping of the acid extracted into the solvent phase with water was not possible and sodium hydroxide had to be used. If this process was used in the Bunsen reaction, it would result in the formation of sodium iodide and water and it would be virtually impossible to recover the hydriodic acid. Alamine<sup>®</sup> 336 was therefore not considered further. Aliquat<sup>®</sup> 336 is a water insoluble quaternary ammonium salt that was shown to be an effective extractant of hydrochloric acid (better than TBP but worse than Alamine<sup>®</sup> 336) [8]. An HI extraction test performed with Aliquat<sup>®</sup> 336 revealed analysis problems with the organic phase [9]. The analysis of the aqueous phase showed a disproportionate amount of proton and iodide ions suggesting that Aliquat<sup>®</sup> 336 succumbs to an ion exchange process. It has therefore not been considered further.

TBP is part of a trialkylorganophosphorus series, as shown in Fig. 1. All of the species contain a phosphoryl group and it is the oxygen of this group that is responsible for forming a coordination bond with the protons from the acid, hence extracting it from the aqueous phase into the organic phase. As well as the phosphoryl group, each species contains three other groups, either alkyl (R) or alkoxy (OR) groups. Alkoxy groups are electron withdrawing whereas alkyl groups are electron releasing. The alkyl groups therefore enhance the ability of the phosphoryl group to form coordination bonds. Phosphine oxides would therefore be expected to extract more acid than TBP. The thermal stability of the organophosphorus series increases from left (phosphate) to right (phosphine oxide) due to the increasing alkyl groups. The increased thermal stability of phosphine oxides is advantageous in the context of the Bunsen reaction as it means there is more potential for hydriodic acid recovery by thermal means. Phosphine oxides are mainly used in the hydrometallurgy industry for the extraction of metals from aqueous acidic solutions, however at high acidities it has been found that the extraction of acid can compete favourably with the extraction of the metals [10]. Cyanex<sup>®</sup> 923 is a mixture of trihexyl and trioctylphosphine oxides and has been shown to extract both hydrochloric and sulphuric acids [8,10], therefore it will be

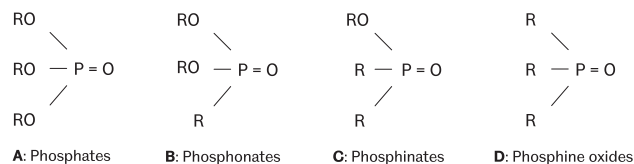


Fig. 1 – Trialkylphosphorous series.

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