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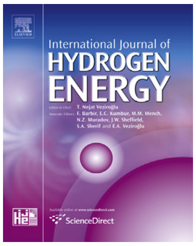

Short Communication

A unique approach to the vapour phase of the HI_x feed of the sulfur iodine thermochemical cycle: A Raman spectroscopy study

V.H. Ramos-Sanchez [a,b,*], R. Jeans [b], R.H. Elder [c], G. Zaragoza-Galán [a], R. Devonshire [b]

[a] Cuerpo Académico de Química Aplicada y Educativa, Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Nuevo Campus Universitario, Circuito Universitario, Chihuahua, Chih C.P. 31125, Mexico
[b] High Temperature Science Laboratories, Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK
[c] Department of Chemical and Biological Engineering, University of Sheffield, Sheffield S1 3JD, UK

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ABSTRACT

The Sulfur Iodine cycle has great potential for large scale hydrogen production from water. The HI_x processing stage (Section III) of the cycle exhibits the major challenges. Among them, experimental vapour liquid equilibrium data is scarce, mainly due to inherent hurdles to monitor the system under operating conditions of this section, *i.e.* temperature, acidity, and corrosion. Until now, UV–Visible and FTIR spectroscopies are the online monitoring techniques of choice, however due their selection rules, there is no experimental spectroscopic evidence of H_2 during direct decomposition of HI_x. Bearing this in mind, here we demonstrate the feasibility of exploiting two different Raman spectroscopic techniques as *in situ* monitoring tools, to gain substantial knowledge on the mechanisms of hydrogen production in Section III. Whereas resonance Raman spectra revealed the occurrence of $HI\cdot(H_2O)_3$ in the vapour phase; coherent anti-Stokes Raman spectra of H_2 allowed us to estimate kinetic data such as the activation energy for HI decomposition of a given hyper-azeotropic ternary mixture (*i.e.* x_{HI}: 0.144; x_{I_2}:0.308; x_{H_2O}:0.548) is 149.15 kJ/mol.

Introduction

Thermochemical water splitting offers a way of converting heat and renewable electricity into hydrogen, an energy carrier that can be easily transported and stored. The Sulfur family of thermochemical cycles have received the most interest over the last decade due to their potential for efficient, massive scale hydrogen production. The sulfur iodine (SI) cycle consists of three reactions (1)–(3), the net result of which is the splitting of water – all other components are recycled.

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* *Corresponding author*. Cuerpo Académico de Química Aplicada y Educativa, Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Nuevo Campus Universitario, Circuito Universitario, Chihuahua, Chih C.P. 31125, Mexico. Tel.: +52 614 2366000.
E-mail address: vramos@uach.mx (V.H. Ramos-Sanchez).

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Feasibility of the SI cycle has been proven through bench testing [1,2] with levels of production of hydrogen reported at General Atomics integrated loop of 60 L/h [3], and recent facilities designed to produce 100 L/h at the Institute of Nuclear and New Energy Technology [4]. When operated with an excess of iodine and water, the two acids produced in the Bunsen reaction (reaction (1)) spontaneously phase separate. These acids are separated and then decomposed to given hydrogen and oxygen products. Processing of the HI_x phase ($HI-H_2O-I_2$), comprising HI_x separation and HI decomposition, is identified, and generally accepted, as the most expensive and energy consuming stage within the process, primarily due to its slow rate and complexity due to the presence of an azeotrope.

$$2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI \tag{1}$$

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2 \tag{2}$$

$$2HI \rightarrow H_2 + I_2 \tag{3}$$

Depending on the specific engineering approach taken, HI_x separation and HI decomposition can be carried out independently, or combined in a single step. Extraction using phosphoric acid [1], reactive distillation [5] and electroelectrodialysis [6], have all been considered for HI_x processing. At this point, breaking of the hydroiodic acid azeotrope, which ranges from $x_{HI} = 0.156$ (1 bar; 125 °C) [7] to $x_{HI} = 0.133$ (22 bar; 245 °C) [8], is vital to allow distillation of the aqueous solution. Analogous to the hydroiodic acid, the $HI-I_2-H_2O$ ternary system also exhibits a pseudoazeotrope. The vapour pressure of this acid phase is mainly driven by the presence of iodine, rather than by the temperature of the stream [8]. In fact, it is only at very low iodine concentrations that temperature plays an influential role in the vapour pressure of the system. This behaviour can only be explained by the formation of iodine containing species such as polyiodides or iodine aquo-complexes, as reported in previous specialised studies focused on the liquid phase of HI_x, which coincidentally used Raman spectroscopy as an analysis tool [9–12].

Despite being proven technically feasible at bench scale [1]; the General Atomics original process design for the SI cycle exhibited a shortcoming in the phosphoric acid reconcentration stage due to its high energy demand, poor efficiency and introduction of an additional component. However, early work considering reactive distillation at the RWTH Aachen University suggested that hydrogen was readily dissociated from the HI_x phase at temperatures higher than 170 °C, through total vapour pressure measurements of a hydroiodic acid solution (57 wt%) containing iodine traces [8]. Further experiments proved the viability of reactive distillation, using the HI_x stream directly from the Bunsen section (composition x_{HI}:0.110; x_{I_2}:0.390; x_{H_2O}:0.500). The minimum operating conditions of the reactive distillation were found to be 22 bar and 262 °C [5].

An accurate picture of the VLE behaviour of the $HI-I_2-H_2O$ system is essential for detailed design and optimisation of the HI_x processing section of the SI cycle. In order to accomplish such a picture, total vapour pressures of the ternary system for a wide range of temperatures and compositions [8], and more recently partial pressures, have been reported [13–15]. Such harsh environment has inherently imposed the need of using optical online techniques to achieve monitoring of this system [16]. Complementarily, much of the work in recent years has been focused on understanding hydrogen production through predictions and models of the VLE of HI_x. For instance Hadj-Kali et al. proposed a new thermodynamic model based on a very good collection of previous experimental data as well as taking into considerations some of the relevant features of the previous models reported until then [17]. On the other hand, Zhang et al. developed an integral kinetic model based on experimental data obtained at high temperature (500–1000 °C), which detailed viable routes for HI decomposition in presence and absence of molecular iodine [18,19]. Empirical models have been developed based on artificial neural network and such approach seems to be consistent with experimental data, and even have offered predicted scenarios not yet evaluated experimentally [20].

Despite recent efforts, the VLE data available is still not enough to describe a wide range of experimental conditions. This paper reports the first VLE measurements carried out *in situ* by resonance Raman spectroscopy (RRS) and coherent anti-Stokes Raman spectroscopy (CARS) on the $HI-H_2O$ and $HI-I_2-H_2O$ systems. The first ever optical spectroscopic evidence of hydrogen in the vapour phase of the HI_x Processing Stage of the Sulfur–Iodine Thermochemical Water Splitting Cycle is presented. Although preliminary, these results exhibit the capability of Raman spectroscopy to overcome the natural obstacles imposed by the chemical nature of the system in order to obtain kinetic data.

Experimental

Sample preparation

Samples of the $HI-H_2O$ binary system (hydroiodic acid 67 wt %) and the $HI-I_2-H_2O$ ternary system were prepared according to the methodology described elsewhere [12]. Ampoules, manufactured from GE214 fused quartz, consisting of a dual cylindrical shape formed from an ≈50 mm length of tubing with an outer diameter (OD) of 10.5 mm and an inner diameter (ID) of 6.0 mm; and an ≈60 mm length of tubing with an outer diameter (OD) of 18 mm and an inner diameter (ID) of 15.2 mm were produced and fused coaxially. These sample containers were prepared initially with one end, the thinner, formed into a closed hemispherical shape and the other end, the thicker, attached coaxially to a 100 mm length of GE214 tubing with 4 mm OD and 2 mm ID used for connection via a compression fitting to a vacuum line manifold (Figure S1, *see Supplementary Information*). Cleaning, preparation and sealing of ampoules was identical to that described by Ramos-Sanchez et al. [12], with the exception that, in the present work, most samples were dosed with a known pressure of nitrogen to be used as internal standard, which in such case were finally sealed with a known sub-atmospheric pressure of 65 mbar of nitrogen (N_2). This N_2 allowed validating the total vapour pressure estimations based on the CARS spectra here presented.