Experimental study of the vapour-liquid equilibria of HI-I$_2$-H$_2$O ternary mixtures

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Abstract

In the framework of the massive production of hydrogen using the sulphur-iodine thermochemical cycle, the design of the reactive distillation column, chosen by CEA for the HIx section, requires the knowledge of the partial pressures of the gaseous species (HI, I$_2$, H$_2$O) in thermodynamic equilibrium with the liquid phase of the HI-I$_2$-H$_2$O ternary mixture in a wide range of concentrations up to 270°C and 50 bar. The experimental devices which enable the measurement of the total pressure and concentrations of the vapour phase (and thus the knowledge of the partial pressures of the different gaseous species) for the HI-I$_2$-H$_2$O mixture in the 20-250°C range and up to 35 bar are described. These devices are used to carry a large set of experiments investigating various mixtures with optical on-line diagnostics (FTIR for HI and H$_2$O, UV-visible for I$_2$). This leads to the determination of the concentrations in the vapour phase for many experimental conditions, results which are given in this paper. The experimental results obtained using both devices, a premiere as far as we know, will be used in the future to establish a new thermodynamic model which will allow the reliability of the evaluation of the iodine part of the iodine sulphur cycle to be increased.

Introduction

The search for new energetic vectors is of utmost importance due to the shortage of hydrocarbons and the high price reached by the oil barrel. Hydrogen appears to be a potential candidate if it can be massively produced at low cost. Among the various ways to achieve this goal, high-temperature electrolysis and thermochemical cycles, both using nuclear heat, are interesting solutions. Many studies have been devoted to thermochemical cycles since 1970 (Funk, 1976; Bamberger, 1978) and the most attractive one appears to be the iodine-sulphur one. Within the scope of studies on the massive production of hydrogen using this cycle (Norman, 1982; Vitart, 2008), the French atomic authority CEA has selected the more promising reactive distillation process (Roth, 1989; Belaissaoui, 2008) versus extractive distillation (O'Keefe, 1982) or electrodialysis (Miyamoto, 2000), in order to extract the hydrogen from the HIx phase produced by the Bunsen reaction. The scaling of this column, in which the distillation of the HIx phase and the decomposition of HI into hydrogen occur simultaneously, requires the knowledge of the vapour-liquid equilibrium, *i.e.* the partial pressures of the gas species HI, I$_2$, H$_2$O in thermodynamic equilibrium with the liquid phases of the corresponding HI-I$_2$-H$_2$O ternary mixtures (Engels, 1986; Doizi, 2007; Hodotsuka, 2008; Liberatore, 2008). In the liquid phase, the concentrations of the species vary in the intervals: $0.04 < [I_2] < 0.85$ and $0.03 < [HI] < 0.2$ for temperature between 20°C and 320°C and total pressures up to 50 bar.

Considering the severe experimental conditions, involving concentrated and corrosive media, our study was divided into two parts corresponding to two experimental devices. The first one, the low-pressure device, enables the study of vapour-liquid equilibria in a temperature range between 20°C and 140°C and for total pressures up to 2 bar. The second one, the high-pressure device enables the study of vapour-liquid equilibria in the process domain.

Based on the needs expressed, on the existing data and on the constraints imposed by the availability of hydriodic acid, an experimental campaign was carried around different groups of ternary compositions. These groups, characterised by their variable iodine and hydriodic acid contents, are represented in the ternary diagram of Figure 1.

This article describes the experimental devices and provides the experimentally determined values of the total pressures and vapour phase concentrations.

Figure 1
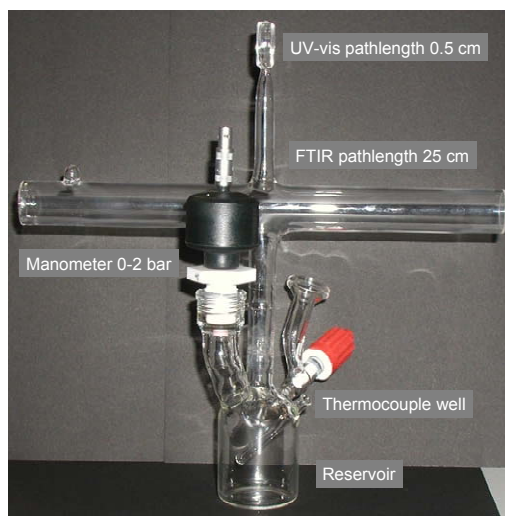
Initial choice of optical spectrometries

To measure the gas phase speciation, the choice of optical spectrometries was made. These "online" techniques allow concentration measurements (Hartmann, 2009) and then partial pressures measurements without altering the gas phase composition.

- Fourier Transform Infrared Spectrometry is used to measure H$_2$O and HI concentrations.

- UV visible spectrometry is used to measure I$_2$ concentration.

The choice of these spectrometries has been validated on cells containing pure samples (H$_2$O, HI, I$_2$) and HI-H$_2$O binary mixtures. They have been then implemented on the two experimental devices.

On the low-pressure device, the infrared measurements are performed using a Bruker Vector 22 FTIR spectrometer with a spectral resolution of 0.4 cm^{-1}. The major interest in this unit is the possibility to shift the infrared beam toward the outside of the apparatus and thus enable an "online" measurement. The IR configuration includes a Globar source, the Vector 22 interferometer with a KBr beam splitter and a nitrogen-cooled InSb detector. The entire optical path is under an inert nitrogen atmosphere for both the part outside the spectrometer and the Vector 22. The optical path length between the Globar source and the detector is longer than 1 m.

The UV visible measurements are performed using a commercial HR 2000 high-resolution fibre optic Ocean Optics spectrophotometer equipped with a halogen light source HL2000. The detector is a linear silicon CCD array. The spectral resolution measured with a Hg-Ar calibration lamp is better than 0.2 nm.

On the high-pressure device, the infrared measurements are performed using a Bruker Tensor 37 FTIR spectrometer. The IR configuration includes a NIR source, the Tensor 37 interferometer with a CaF2 beam splitter and a thermoelectrically-cooled InAs detector. The UV Visible measurements are made using a Varian Cary 300 spectrometer equipped with 600 μm core diameter optical fibres.

The two experimental devices

To contain the corrosive and concentrated mixtures, to allow gas phase speciation using optical spectrometries, two experimental devices were designed: a low-pressure one, and a high-pressure one.

The low-pressure device shown in Figure 1 is manufactured out of quartz and Pyrex, and features a reservoir containing the liquid mixture (+solid) to be studied. This reservoir is equipped with a total pressure gauge, a Teflon valve and a connector to introduce products. The pressure gauge used is the "EBRO VM 2000 ex" model operating within a guaranteed measurement range from 0 to 2 bar up to 125°C. K-type thermocouples and platinum resistance sensors are used to measure the temperature at different positions inside the oven. Two cells, with windows made of Suprasil quality quartz, are located in the upper part of the device and allow the optical measurement of the gaseous phase concentrations of HI, I$_2$ and H$_2$O. The first one, 250 mm long, is used for the measurement of HI and H$_2$O concentrations by infrared absorption spectrometry. The second one, 5 mm long, enables the determination of the I$_2$ concentration measurement by UV visible absorption spectrometry.

The high-pressure device is a microautoclave made of tantalum and located in a thermo-regulated oven as shown in Figure 2. It is a closed reactor with a constant volume of 140 cm^3. The total expected pressure is about 80 bars for a temperature close to 280°C. Tantalum has been chosen as the reference material for the internal part of the reactor in order to avoid corrosion from the products under study.

All connections between the different components of the reactor are sealed with 6 373 Kalrez O-rings. The associated instrumentation is composed of a set of 10 K-type thermocouples and a pressure gauge using a tantalum membrane.

The stabilisation in temperature and pressure is obtained after 6 hours. The major difficulties encountered were of technological nature and led to a special design of the tantalum valve and of the pressure gauge.

The experimental programme

Five composition groups were studied in the low-pressure device, four composition groups in the high-pressure device as shown in Figure 3. The choice of the composition of the ternary mixtures was made in order to be representative of the different part of the reactive distillation column from bottom to top.

The concentration range for iodine is between 4% and 85%. For a fixed iodine content, at least three different HI concentrations were realised around the total pressure minimum.
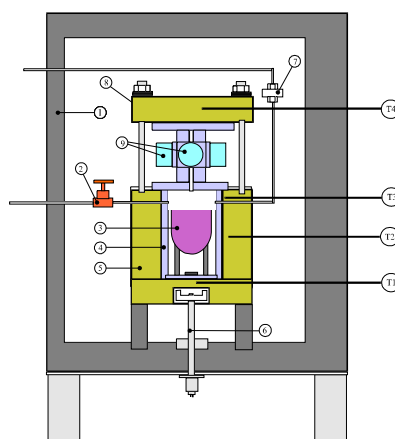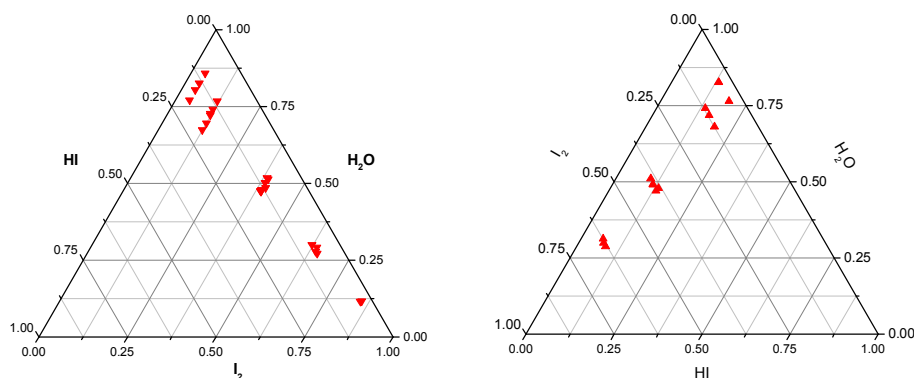
Figure 2

Figure 3: Compositions studied in the low-pressure and in the high-pressure device

Experimental results with the low-pressure device

The concentrations which have been studied in the low-pressure device are summarised in Table 1.

The total pressure versus HI concentration for the different iodine contents are summarised in Figure 4 at 130°C. A good agreement (position and value) is observed with the results published in the literature.

For partial pressures (see Figure 5), a good agreement is found on the left of the total pressure minimum. On the right, HI content higher than calculated is observed in the vapour phase using Prophy thermodynamic model (Prosim, n.d.).

Experimental results with the high-pressure device

Fourteen experiences were realised on the high-pressure device describing the behaviour of the distillation column ranging from 4% to 65%.

- For 63% iodine content, corresponding to the bottom of the column, three HI concentrations, 8.2, 7.2 and 6.3%, were studied (see Figure 6).

A good agreement between Prophy calculations and experimental results is observed for H_2O. HI and I_2 concentrations are underestimated.

- For 39% iodine content, corresponding to the entrance of the column, three HI concentrations, 13.5, 11.5 and 10%, were studied (see Figure 7).

A good agreement between Prophy calculations and experimental results is observed for HI and H$_2$O. I$_2$ concentration is underestimated.

- For 12% iodine content, corresponding to the top of the column, three HI concentrations, 19.5, 16.1 and 13.8% were studied (see Figure 8).

A good agreement between Prophy calculations and experimental results is observed for HI and H$_2$O. I$_2$ concentration is underestimated, and H$_2$ formation is observed for high HI concentration.

- For 4% iodine content, at low HI concentration, a good agreement for H$_2$O and HI is observed.

- At HI high concentration, Hi concentration decreases versus time due to hydrogen formation.

Conclusions

The experimental study presented in this paper provides new data on liquid-vapour equilibrium of HI-I$_2$-H$_2$O mixtures at high temperature and pressure (Doizi, 2009; Larousse, 2009). These results are important to improve the modelling of the distillation column used in the SI cycle.

Optical online diagnostics have been used to determine the concentrations in the vapour phase. The results show that, for global compositions close to the azeotrope, the thermodynamic model correctly predicts concentrations of HI and H$_2$O up to temperatures of about 260°C, while improvements must be made to better represent the iodine concentration in the vapour phase.

For compositions with HI concentrations higher than the azeotropic one, it was pointed out that the model cannot converge on finite solutions for temperatures higher than 150°C. Moreover, HI dissociation into hydrogen and iodine has to be accounted for in high-HI and low-I$_2$ compositions.

Table 1: Concentrations studied in the low-pressure device

Compounds introduced			Total P	[H$_2$O] & [HI]	[I$_2$]
The analysis of the pertinence of the number of significant figures is undergoing evaluation					
I$_2$ = 3.98%	- HI = 13.43%	- H$_2$O = 82.58%	X	X	X
I$_2$ = 4.04%	- HI = 10.06%	- H$_2$O = 85.90%	X	X	X
I$_2$ = 3.95%	- HI = 15.63%	- H$_2$O = 80.42%	X	X	
I$_2$ = 4.02%	- HI = 18.91%	- H$_2$O = 77.08%	X	X	X
I$_2$ = 12.09%	- HI = 15.19%	- H$_2$O = 72.72%	X	X	X
I$_2$ = 12.28%	- HI = 15.5%	- H$_2$O = 72.22%	X	X	X
I$_2$ = 12.11%	- HI = 13.82%	- H$_2$O = 74.07%	X	X	X
I$_2$ = 12.49%	- HI = 17.85%	- H$_2$O = 69.66%	X	X	X
I$_2$ = 12.45%	- HI = 20.16%	- H$_2$O = 67.40%	X	X	
I$_2$ = 11.94%	- HI = 11.25%	- H$_2$O = 76.82%	X	X	X
I$_2$ = 39.11%	- HI = 9.57%	- H$_2$O = 51.32%	X	X	
I$_2$ = 38.61%	- HI = 9.65%	- H$_2$O = 51.74%	X	X	X
I$_2$ = 38.75%	- HI = 11.02%	- H$_2$O = 50.24%	X	X	
I$_2$ = 39.74%	- HI = 11.67%	- H$_2$O = 48.58%	X	X	X
I$_2$ = 39%	- HI = 13.11%	- H$_2$O = 47.90%	X	X	X
I$_2$ = 39%	- HI = 13.56%	- H$_2$O = 47.45%	X	X	X
I$_2$ = 38.83%	- HI = 13.59%	- H$_2$O = 47.58%	X	X	
I$_2$ = 38.96%	- HI = 13.625%	- H$_2$O = 47.41%	X	X	
I$_2$ = 49.18%	- HI = 9.11%	- H$_2$O = 41.71%	X	X	X
I$_2$ = 63.95%	- HI = 6.94%	- H$_2$O = 29.11%	X	X	X
I$_2$ = 62.11%	- HI = 7.9%	- H$_2$O = 29.99%	X	X	X
I$_2$ = 64.97%	- HI = 7.79%	- H$_2$O = 27.25%	X	X	X
I$_2$ = 64.25%	- HI = 7.95%	- H$_2$O = 27.81%	X	X	X
I$_2$ = 85.37%	- HI = 2.99%	- H$_2$O = 11.64%	X	X	X
I$_2$ = 85.01%	- HI = 3.45%	- H$_2$O = 11.54%	X	X	X
I$_2$ = 84.5%	- HI = 3.44%	- H$_2$O = 12.06%	X	X	X
I$_2$ = 84.66%	- HI = 3.27%	- H$_2$O = 12.07%	X	X	X

Figure 4: Total pressure vs. [HI] molar for various [I₂] molar
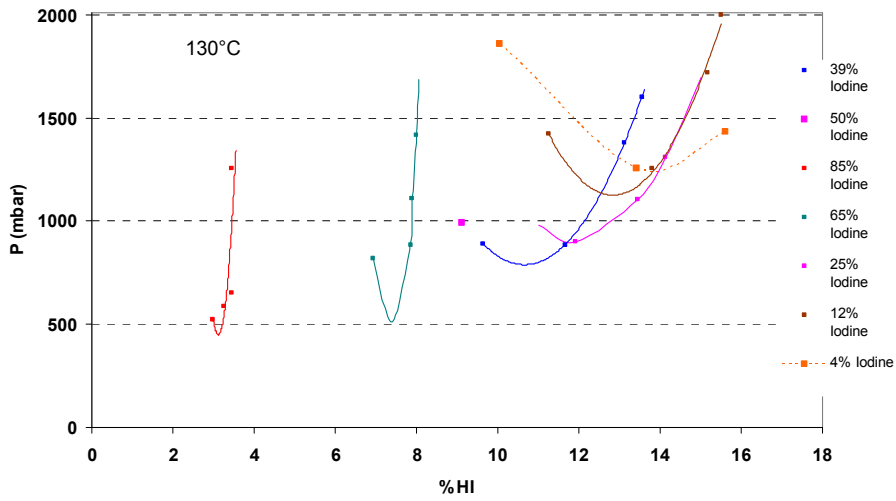
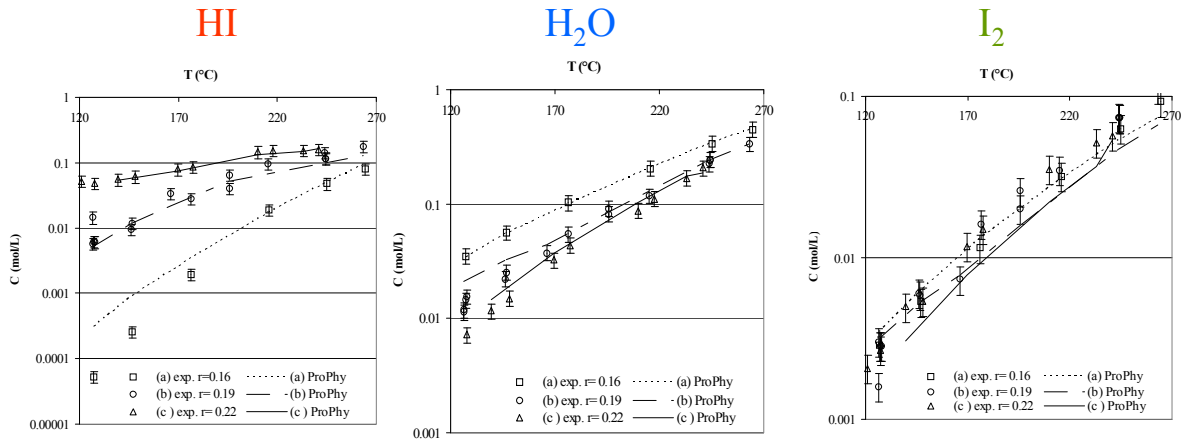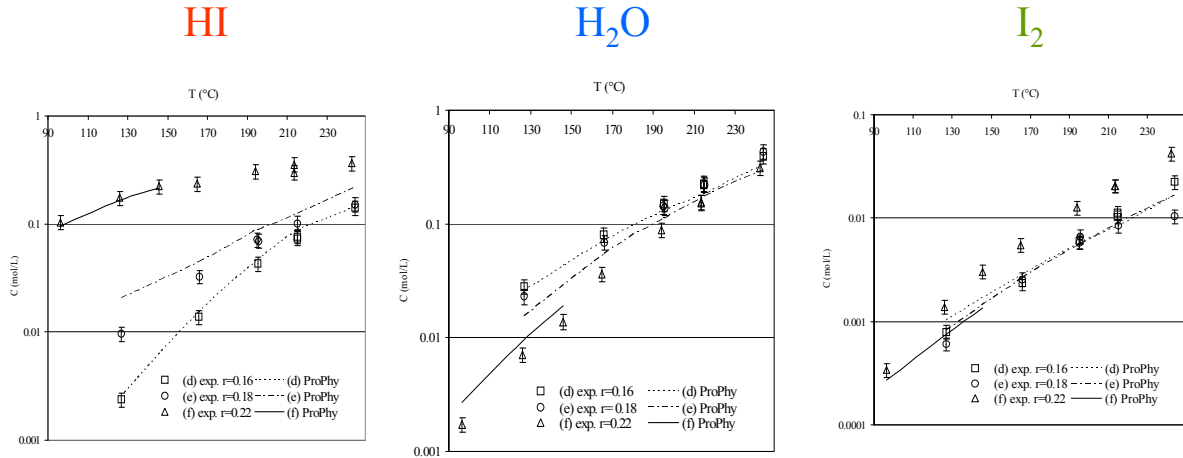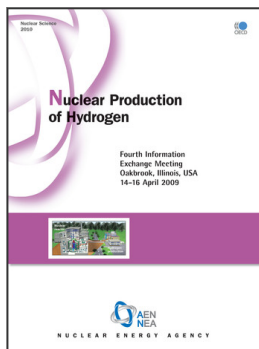**Figure 5**
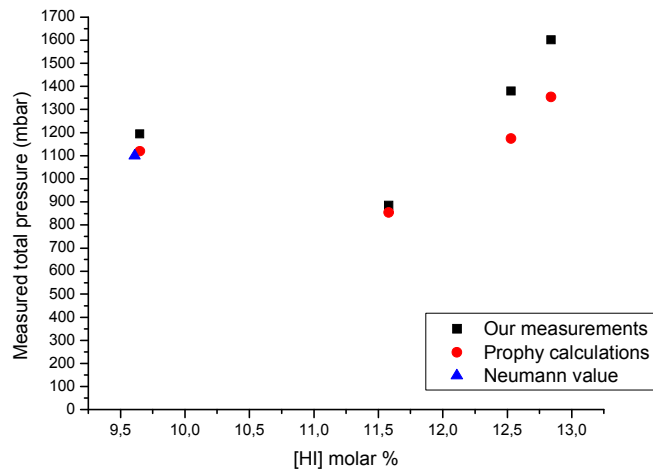
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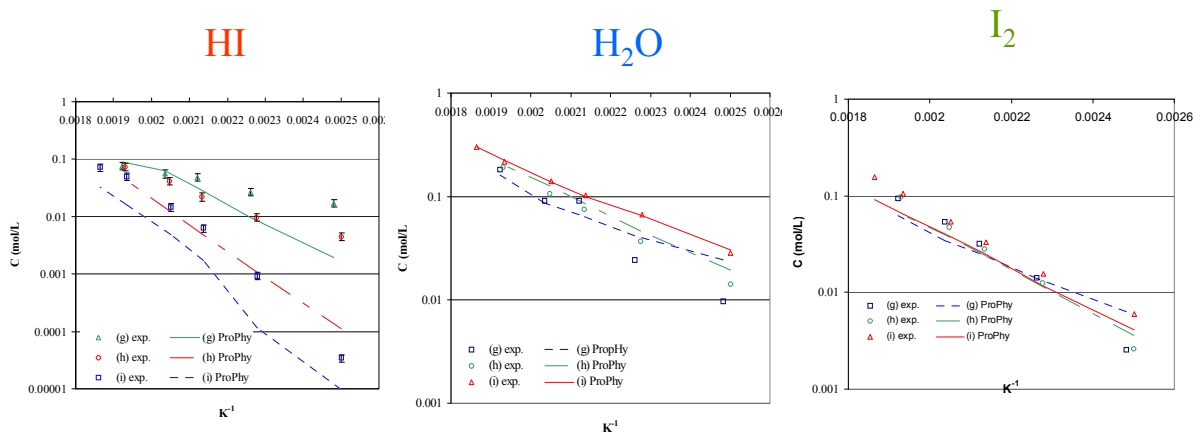
Figure 7

Figure 8

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