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Experimental density-composition data and thermal expansion coefficient of HI-I_2-H_2O solution

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ABSTRACT

In thermochemical water-splitting iodine-sulfur cycle for hydrogen production, basic physico-chemical data of HI-H_2O-I_2 (HIx) solution are very important. Detailed and systematic studies on density/coefficient of thermal expansion (CTE) are in great need. In this work, the density values of 53 HIx samples with different compositions are measured at atmospheric pressure and temperatures ranging from 20 to 90 °C. HIx solution's density varies dramatically when changing HI or I_2 contents. Increasing either HI or I_2 concentration will cause increase of density. When heated, HIx's density decreases because of thermal expansion. With the help of density-temperature curves, the CTE values are calculated for HIx solutions of different compositions. It is found that increase of either I_2/HI or H_2O/HI will bring rise of HIx's CTE. Although the CTE value is relatively small, it is very sensitive to the change of composition. In the range of this work, the HIx's CTE value changes within 5.45E-4/ºC to 9.17E-4/ºC. Polynomial regression is conducted to model the relationship between CTE and the composition. The obtained approximate quadratic polynomial model has good accuracy to reproduce most of the experimental CTE values within a deviation of ±5%.

Introduction

As a clean energy carrier, hydrogen and its clean production have attracted great attention [1–3]. The Iodine–Sulfur thermochemical cycle (IS-cycle) is one of the most promising massive hydrogen producing methods [4–6]. It consists of three main reactions (three sections), i.e. Bunsen reaction (Bunsen section), sulfuric acid decomposition (sulfuric acid section) and hydriodic acid decomposition (HIx section), as described by Eqs. (1)–(3):

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \quad (1)$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2O_2 \quad (2)$$

$$2HI \rightarrow H_2 + I_2 \quad (3)$$

In Bunsen section, two kinds of acids, i.e. sulfuric acid and hydriodic acid are produced. With the existence excess I_2, Bunsen reaction products form two phases spontaneously. One phase is aqueous sulfuric acid and the other is so-called HIx, a mixture of hydrogen iodide, iodine and water. In sulfuric acid section, sulfuric acid phase is purified first and then H_2SO_4 is concentrated and decomposed to produce O_2, while other products, SO_2 and H_2O should be recycled to Bunsen

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Nomenclature

ρ	density, g/mL
t	temperature, °C
V	volume of HIx solution, ml
γ	volume thermal expansion coefficient (CTE), $°C^{-1}$
k	slope of the ρ-t curve, g/(ml °C)
p	significance level of variance analysis, dimensionless
R^2	correlation coefficient, dimensionless
$C_{H_2O/HI}$	H_2O/HI molar ratio, dimensionless
$C_{I_2/HI}$	I_2/HI molar ratio, dimensionless

section. Similarly in HIx section, HIx phase is purified and then HI is concentrated and decomposed to produce H_2, with I_2 recycled to Bunsen section.

Since proposed by General Atomics in mid 1970s, IS-cycle attracted considerable theoretical and experimental research for the process feasibility. Japan Atomic Energy Agency (JAEA) accomplished a demonstration of bench-scale IS process involving glassware at atmospheric pressure in 2004 [7]. Now it is in a process engineering stage in JAEA to use industrial materials for components [8]. Sandia National Laboratories (SNL), General Atomics Corporation (GA) and the French Commissariat à l'Energie Atomique (CEA) conducted laboratory-scale experiments to investigate IS-process as an International Nuclear Energy Research Initiative (INERI) project supported by the CEA and US DOE Nuclear Hydrogen Initiative [9]. In China, a 10NL-H_2/h IS-cycle facility was constructed in 2007 at INET (Institute of Nuclear and New Energy Technology) of Tsinghua University, and the close cycle demonstration were completed in 2009 [10,11]. In 2014, a bench scale IS-cycle facility with hydrogen production rate of 60NL/h was demonstrated at INET [12]. Research on IS-cycle are also very active in Korea. In 2013, a demonstration of electro-dialysis stack embedded HIx section was reported by Korea Institute of Energy Research (KIER) to be accomplished at H_2 producing rate of 10 L/h under pressurized conditions [13]. In the year of 2016, the H_2 producing rate of above HIx section was increased to the range of 18.3–50 L/h, depending on the operating conditions and HIx feed composition [14].

In spite of the simple principle, IS-cycle is a complicated close process. It is very difficult to realize closed-loop continuous hydrogen production. Recent years, great efforts have been devoted to the kinetics of the three main reactions [15–19], catalyst development [20–22], flowsheet/modelling studies [23], performance assessment [24], and so on. By now, one of the challenges is that lots of separating units such as gas separator, liquid-liquid phase separator, distillation column and electrodialysis cell etc. are required for the streams in the process. The streams are especially complex in the HIx section [25]. Basic physico-chemical data of HI-I_2-H_2O solution (HIx) in the HIx section are found to be very important, though this solution involves mainly three components, i.e., HI, I_2, and H_2O. These three substances make up a highly non-ideal system. In our previous work, thermodynamic properties of HIx are estimated and applied in the process simulation & design [26]. Density data, together with coefficient of thermal expansion (CTE) of HIx, are not only necessary for CFD, and also found to be very useful in the case where volume of the solution must be appointed. For example, volume flow rates must be calculated using density data, when setting a diaphragm pump to transport HIx. Additionally, the design and arrangement of HIx's containers such as tanks, pipes are in great need of CTE data. Because of the high corrosiveness of HIx solution, coated or lined materials are often used in the containers. For the selection of all above materials, including structure materials, coating or lining layers, the CTE data are necessary.

Like other physico-chemical data, density data have further uses. Kubo et al. [27] proposed a novel estimation technique for compositions of Bunsen reaction solutions in IS cycle, using the density values measured from the diphase equilibrium reaction products as inputs, including the density of HI-I_2-H_2O phase (containing a small amount of H_2SO_4). In our previous research [28], density data coupled with voltage signals were used for the composition determination of HIx solution, applying Gibbs phase rule.

As mentioned above, density and CTE are of great importance for the IS-cycle research and operation. Unfortunately, to the best of our knowledge, there is no detailed and systematic report on density and CTE data for HIx solutions. Furthermore, there are especially no related data reported for hyper-azeotropic HIx solutions shown in documents. This study is aiming at establishing a density/CTE databank of HIx solutions. HIx samples of different compositions are prepared in this work. With the help of electro-electrodialysis (EED) technique [29,30], hyper-azeotropic HIx samples, i.e. HI-I_2-H_2O solutions with HI concentration higher than that in the azeotropic HI-H_2O solution, are also secured. Density values of the samples are measured using an oscillating U-tube density meter at atmospheric pressure and temperatures ranging from 20 to 90 °C. Consequently, the CTE values are calculated. The relationship among density/CTE, composition and temperature of HIx solution is discussed.

Experimental

Chemicals

Hypo-azeotropic hydriodic acid (~56 wt%) and iodine (>99.9 wt %) were purchased from Beijing Leadersh Chemical Co. Ltd. Analytical pure Sodium thiosulfate, sodium hydroxide and potassium iodide (all from Guangdong Xilong Chemical Co. Ltd.) are used as received for titration methods to analyze the HI and I_2 contents in certain HI-I_2-H_2O solutions.

Preparation and density measurement of the HI-I_2-H_2O solutions

Azeotropic hydriodic acid is prepared in lab by distillation of above commercial hypo-azeotropic hydriodic acid. This azeotropic hydriodic acid (HI-H_2O) is titrated to determine the composition at the molar ratio HI: H_2O = 1:5.360. Consequently, a series of HIx, i.e. HI-I_2-H_2O solutions of certain

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