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A new model for phase equilibria of the ternary system $(H_2O - HI - I_2)$

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Abstract

A new thermodynamic model is proposed to describe the phase equilibria of the ternary system (H_2O -HI-I₂), known as the HI_x system and which represents the latent source of hydrogen for the Iodine – Sulfur thermochemical cycle. An homogeneous approach is adopted, for the first time, where the Peng-Robinson equation of state is combined, by means of MHV2 mixing rule, to UNIQUAC activity coefficient model supplemented with the solvation of hydrogen iodide by water, as proposed by Engels.

Keywords: Sulfur – Iodine cycle, HI_x system, Phase equilibria

1. Introduction

With the actual growth in energy demand, the decreasing of fossil resources and the perpetual increase of oil crude prices, together with limitations on the release of greenhouse gases, hydrogen produced from water splitting is a viable and long term candidate to supply our future energy needs.

The processes of massive hydrogen production from water that have the greatest likelihood of successful are electrolysis and thermo-chemical cycles. They are an environmentally attractive way to produce hydrogen without using fossil fuels.

Among hundreds of possible cycles, the Iodine-Sulfur (I-S) is a promising one, expected to become a major source of hydrogen production using high temperature heat from a nuclear reactor. The I-S thermodynamical cycle, depicted in figure 1, is divided into three sections, namely: (I) the Bunsen section, where water reacts with iodine and sulfur dioxide to produce two immiscible liquid acid phases: one phase containing mainly sulfuric acid and the other phase hydrogen iodide and iodine (known as HI_x section); (II) the sulfuric and (III) the hydrogen iodide acids concentration and decomposition sections, where intermediate products break down upon heating, releasing hydrogen and oxygen. Water, iodine and sulfur dioxide are recycled in the system [1].

Mathias [2] selected the thermodynamics of this cycle among challenging systems to be solved, especially, the ternary system H_2O -HI-I₂, involved in section III.

Indeed, the HI_x system is a strong electrolyte system, complex because of many phase behavior that occurs (vapor – liquid – liquid – solid) over the large range of pressure and temperature spanned in the process.

The present work focuses on the thermodynamic modelling of the HI_x system using experimental data available in literature with the aim of validating it, thereafter, on new experimental data of CEA (French Nuclear Energy Agency) under acquirement.



Figure1. Iodine - Sulfur thermochemical cycle scheme [1].

This paper is organized as follows. First, available literature experimental data are presented in detail. Then, a new model is presented and compared to former models and validated *vs* selected experimental data. Finally, conclusion and future works under investigation are mentioned.

2. Available experimental data

Before developing the model and parameters estimation procedure, it is necessary to collect and analyse available experimental data for the ternary system (HI-I₂-H₂O) and each binary subsystem (H₂O-HI), (H₂O-I₂) and (HI-I₂) (see table 1).

2.1. H_2O -HI binary

Total pressures of HI-H₂O binary mixtures have been measured by Wüster [3] and the mixing enthalpies by Vanderzee [4]. H₂O-HI mixture exhibits an azeotrope ($x_{HI} = 0.156$ at 126.50°C). For HI concentrations higher than the azeotrope the vapour phase is very rich in HI. Furthermore, for high temperatures (>200°C) HI dissociation in the vapour phase into H₂ and I₂ becomes significant. These experimental results have been used by Engels [5] to estimate the binary interaction parameters of the so called Engels solvation model using the Wilson activity coefficient model.

Atmospheric vapour liquid equilibrium curve of this system has been measured by Sako in 1985 [6] and earlier by Ducasse in 1926 [7]. These two authors measured both vapour and liquid equilibrium compositions at different temperatures. In 1963, Haase [8] gave at 25°C the isothermal vapour liquid equilibrium curve and showed that this system demixes into a liquid-liquid equilibrium above x_{HI} =0.346. Unpublished experimental data of Norman and O'Keefe found in the work of Neumann [9], confirm this fact and indicate the composition of the aqueous phase at five higher temperatures.

	Data type	Data number	Data source	Used	
				regression	validation
H ₂ O-HI	V-L	80	Wüster [3]	V	-
	V-L	38	Pascal [7]	-	\checkmark
	V-L	30	Sako [6]	-	\checkmark
	V-L	21	Haase [8]	-	\checkmark
	L-L	5	Neumann [9]	\checkmark	-
	L-L	1	Haase [8]	\checkmark	-
	H^{E}	13	Vanderzee [4]	no	no
H ₂ O-I ₂	L-L	10	Kracek [10]	Ŋ	-
	S-L	10	Kracek [10]	-	\checkmark
HI-I ₂	S-L	5	O'Keefe [11]	V	-
H ₂ O-HI-I ₂	V-L	280	Neumann [9]	V	-
	L-L	12	Norman [13]	no	no

Table 1. Experimental available data in literature for HI_x system and its binary sub-systems.

2.2. H_2O-I_2 binary

 H_2O - I_2 has been studied by Kracek [10] in 1931, who measured the solubility of iodine in water and put in evidence a miscibility gap lying between the solid-liquid equilibrium point at 112.3°C (close to the melting point of iodine) and an upper temperature of approximately 210°C. At 112.3°C, the light aqueous liquid phase contains 0.05 mole % of iodine and the heavy iodine liquid phase 98 mole % of iodine.

2.3. $HI-I_2$ binary

The only available data for $HI-I_2$ concerns the solubility of iodine in HI measured by O'Keefe and Norman [11] at five different temperatures. This work highlights that $HI-I_2$ solutions follow quite closely an ideal behavior.

2.4. H_2O -HI- I_2 ternary

Total pressure measurements for a [HI]/[H₂0] ratio up to 19% and various iodine concentrations are found in Neumann [9]. A synthesis of these results has been published by Engels *et al.* [12]. The liquid phase exhibits two miscibility gaps: one for low HI contents, due to the very low miscibility of I₂ in H₂O, and the second, found by Norman [13], for high HI contents and about 30% water/iodine concentration. The first one tends to disappear with increasing HI concentration, probably because of the formation of polyiodides ions like I₃⁻ [14].

All these data are reported in table 1. As highlited, some are used for model identification and others for validation.

3. Thermodynamic model

For modelling fluid-phase equilibria, a common practice is to use either a heterogeneous $(\gamma \cdot \phi)$ or a homogenous $(\phi \cdot \phi)$ approach [15].

- In the heterogeneous approach, vapour and liquid phases are handled differently. Reference state is perfect gas for the vapour phase and the fugacity coefficients φ (obtained from an equation of state (EOS)) are used to model real gas behavior. For the liquid phase, the reference state is ideal liquid and activity coefficients γ (derived from a model of molar excess Gibbs energy) are calculated to account for the non-ideality of the liquid phase.
- In homogeneous approach, the reference state, perfect gas, is the same for both vapour and liquid phases and fugacity coefficients φ are calculated from a unique EOS for all components in all fluid phases.

Until this work, all published models for the $(H_2O-HI-I_2)$ are derived from a heterogeneous approach:

- The Neumann model inspired by Engels's solvation model combines a modified NRTL model with the solvation of HI by H₂O (mH₂0 + HI → [(H₃0⁺, (m-1)H₂0), Γ]) put together to describe the non-ideality of the liquid phase. This model was used earlier by several authors [16, 17], to describe a reactive distillation column.
- Mathias and co-workers proposed to use an electrolyte model of Chen et al. [18] combining an asymmetric NRTL model with a Pitzer term.
- Whereas the vapour is assumed to behave like a perfect gas for these two models, Annesini et al. [19] use the RK EOS to calculate the gas phase fugacity and the electrolyte-NRTL activity coefficient model of Chen for the liquid phase.

We propose for the first time a HI_x system model following a homogeneous approach. Both phases are described by the same EOS: Peng Robinson with Boston Mathias alpha function (PR_{BM}). The MHV2 complex mixing rule is then used to better handle the non ideality of the liquid phase. This mixing rule includes an excess Gibbs energy model and we choose a combination of the UNIQUAC activity coefficient model with the solvation of HI by H₂O that we call UQSolv.

Compared to the heterogeneous approach, a homogeneous one with a complex mixing rule adds EOS accurate prediction of VLE at high pressure and temperature, esp. above $T_{crit,HI}=150,7^{\circ}C$; a reference state valid for all compositions, unlike the asymmetric electrolyte convention for HI; handling of liquid non ideal behavior via the excess Gibbs energy model.

Model development is achieved within Simulis Thermodynamics, a ProSim[™] thermophysical properties calculation server available as a MS-Excel add-in and CAPE-OPEN compliant component [20].

4. Model Identification and results

The methodology adopted to estimate model parameters consists in dealing separately with each binary subsystem before refining the parameters of the ternary system.

For the first step, only UNIQUAC binary interaction parameters were regressed for both H_2O-I_2 and $HI-I_2$. Then, for the H_2O-HI binary, hydrogen iodide solvation by water is considered and the solvation parameters are simultaneously regressed with the UNIQUAC binary interaction parameters between H_2O , HI and the solvation complex. As it can be seen in figure 2, the H_2O-I_2 mixture is highly non ideal with L-L equilibrium exhibited above the eutectic temperature (112,3 °C). Both Neumann's and UQSolv (UNIQUAC + solvation) match correctly the experimental equilibrium curve in the iodine phase. But our model remains better for the aqueous phase. In addition, our

prediction of solid iodine solubility in water at low temperatures is very good.

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Figure 2. Experimental and calculated H₂O - I₂ liquid-liquid and solid-liquid equilibrium curves

At low pressure, heterogeneous and homogeneous approaches together join. It is why, concerning H_2O -HI binary, interaction parameters are fitted at low pressures using the heterogeneous approach (UQSol + PR_{BM}) on the basis of the experimental vapor – liquid equilibrium data of Wüster [3] and liquid – liquid equilibrium data of Haase [8] and Neumann [19]. At high pressure, those parameters are used within the MHV2 mixing rule for the PR_{BM} EOS.

Identification is performed on all experimental data, except those on the right side of azeotrope where experimental uncertainty is high because of difficulties to assess the experimental liquid composition and because of HI vapor decomposition observed.

Figure 3 shows the model prediction *versus* experimental liquid – vapor equilibrium data for the binary system H₂O-HI at atmospheric pressure. Obviously, our model accurately represents experimental results in the domain of database used for identification (x_{HI} <17%) but with a noteworthy discrepancy on the right of the azeotrope where the experimental data are still uncertain.



Figure 3: Water - Hydrogen iodide isobaric liquid - vapor equilibrium curve at P=1atm.

Another significant achievement of the proposed model is the quantitative prediction of the liquid – liquid equilibrium above $x_{HI}=0.36$ as expected by experiment [8, 9].

For the ternary system, keeping constant both the binary interaction parameters regressed for each binary system and the solvation parameters of hydrogen iodide by water, the ternary L-V equilibrium data are fitted by estimating the interaction between iodine and the solvation complex. The resulting model provides a fair description of the V-L equilibrium behaviour with an absolute average error lower than 9% and a maximum error less than 45% (resp. 9.6% and 64% for Neuman's model). However, L-L equilibrium remains to be validated, especially in the region of the ternary diagram between water and hydrogen iodide.

5. Conclusion

The highly non ideal HI_x system has been modeled by an homogeneous approach based on the Peng-Robinson equation of state with MHV2 complex mixing rule including UNIQUAC activity coefficient model and a solvation equilibrium of HI by H₂O. This approach is well suited for expected process temperature and pressure conditions that may be high and probably higher than the HI critical temperature (150,7°C). The resulting model (PR_{BM} + MHV2 + UQsolv) successfully represents most of the liquidvapor, liquid-liquid, liquid-solid, liquid-liquid-vapor experimental data available from the literature. The largest discrepancy is found for high HI concentration mixtures where experimental data are sparse and uncertain.

Improvements are under investigation including polyiodide ions formation and HI decomposition in iodine and hydrogen for the vapor phase rich in HI.

At the same time, an experimental campaign for acquiring vapor – liquid – equilibrium data for the ternary system has been launched by CEA, with the aim of enhancing the thermodynamic knowledge of the phase equilibrium.

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