



Addressing solar power plant heat transfer fluid degradation: Experimental measurements of hydrogen transport properties in binary eutectic biphenyl/diphenyl ether

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ABSTRACT

High-temperature decomposition of receiver field heat transfer fluids (HTFs) can cause hydrogen build-up in the receiver annulus of Concentrating Solar Power (CSP) parabolic trough power plants. This build-up increases the receiver thermal losses and results in a decline in power output. Prior numerical work has shown that removal of hydrogen from the head space gas (HSG) in the plant expansion tanks can be an effective mitigation strategy. This approach requires a matching molar rate of hydrogen coming out of solution from liquid HTF into the HSG. Simulations show that the driving force introduced by removing hydrogen from the HSG results in sufficiently large hydrogen transport rates solely across the surface interface (with no active mixing or bubbling). However, uncertainties in Henry's Law Constant and especially mass transfer coefficient require obtaining experimental data to back up the simulations. This paper presents an experimental procedure and measured data for Henry's Law Constant and interface mass transfer coefficient for hydrogen absorbing in the binary eutectic mixture biphenyl/diphenyl ether as HTF. To the best of our knowledge, the experiment is the first of its kind to derive these two parameters in a relatively inexpensive, straightforward, and rapid manner, with moderate accuracy (about $\pm 15\%$ uncertainty). Measurements were taken at different temperatures, pressures, HTF mixing rates, HTF aging, and HSG compositions. The design of the experiment was based on literature review and numerical models simulating the transient and equilibrium behavior of the hydrogen/HTF system at laboratory-scale conditions. Values measured for Henry's Law Constant are around 400 bar/(mol/L), and they decrease slightly with increasing temperature. Both this magnitude and temperature dependency agree with correlations found in literature. The mass transfer coefficient measured for pure hydrogen dissolving in HTF ranges from 5×10^{-7} mol/(s·mbar·m²) (for 100 °C) to 4×10^{-6} mol/(s·mbar·m²) (for 293 °C). These values and strong temperature dependency agree with theoretical model predictions. HTF aging and mixing rate had negligible impact on the mass transfer coefficient. Lowering the hydrogen HSG pressure slightly increased the mass transfer coefficient (up to 10%). The presence of nitrogen significantly increased the mass transfer coefficient (up to 100%).

1. Introduction

As of January 2018, dozens of parabolic trough solar thermal power plants have been installed around the world for a total capacity of more than 4200 MW_e, the majority of which are in Spain and the United States; and 925 MW_e more are under construction (NREL, 2018). A known challenge is declining receiver efficiency over time caused by thermal degradation of the heat transfer fluids (HTFs) used in the receiver field (Moens and Blake, 2008). A commonly used HTF is the binary eutectic mixture of biphenyl (BP) and diphenyl ether (DPE), also known under the trademark names *Therminol VP-1* or *Dowtherm A*. At elevated temperatures (> 350 °C), the constituents BP and DPE slowly

decompose and form a wide array of products such as hydrogen gas and hydrocarbons including aromatics (Moens and Blake, 2008). The hydrogen gas penetrates through the steel wall of the receiver into the receiver annulus. After a few years, if the hydrogen absorption capacity of the getters installed in the annulus of the hottest receivers is exceeded, hydrogen pressure builds up, causing an increase in receiver thermal losses (Burkholder et al., 2008). The power output can decline by 10% to 20% (Burkholder et al., 2008; Glatzmaier et al., 2016), leading to tens of millions of dollars in lost revenue over the plant's lifetime, and highlighting the importance of hydrogen mitigation strategies to maintain design power production.

One possible mitigation strategy is removal of hydrogen from the

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Nomenclature	
Symbols	
A	liquid/gas interface area [m^2]
$c_{\text{H}_2,\text{HSG}}$	hypothetical hydrogen concentration in HTF in equilibrium with bulk gas-phase hydrogen partial pressure [mol/L]
$c_{\text{H}_2,\text{HTF}}$	actual hydrogen concentration in HTF [mol/L]
D	diffusion coefficient [m^2/s]
H	Henry's Law Constant [bar·L/mol]
k_g	gas-phase mass transfer coefficient [mol/($\text{s}\cdot\text{m}^2\cdot\text{mbar}$) or mol/($\text{s}\cdot\text{m}^2\cdot\text{bar}$)]
K_G	“gas-side” overall mass transfer coefficient [mol/($\text{s}\cdot\text{m}^2\cdot\text{mbar}$) or mol/($\text{s}\cdot\text{m}^2\cdot\text{bar}$)]
k_l	liquid-phase mass transfer coefficient [m/s]
K_L	“liquid-side” overall mass transfer coefficient [m/s]
N	molar rate [mol/s]
$p_{\text{H}_2,\text{HSG}}$	hydrogen partial pressure in the HSG [bar]
$p_{\text{H}_2,\text{HTF}}$	hypothetical hydrogen partial pressure in equilibrium with the bulk liquid-phase hydrogen concentration [bar]
Acronyms	
BP	biphenyl
DOE	Department of Energy
DPE	diphenyl ether
EERE	Energy Efficiency and Renewable Energy
HSG	head space gas
HTF	heat transfer fluid
NREL	National Renewable Energy Laboratory
NSO	Nevada Solar One
SETO	Solar Energy Technologies Office
UHP	ultra-high-purity
V/A	volume-to-area

HTF in the expansion tanks. Previous work by Glatzmaier (2009), Glatzmaier et al. (2016), and Kuckelkorn et al. (2015) predicted that purging hydrogen from the expansion tanks at a sufficiently high rate will limit receiver thermal losses and power output decline over the lifetime of the plant. The system envisioned by Glatzmaier (2017) removes the hydrogen from the headspace gas (HSG) through a membrane separator. Steady-state purging requires an equal rate of hydrogen transferring out of the HTF solution into the HSG replacing the removed hydrogen. Beckers and Glatzmaier (2017) developed analytical and numerical models to estimate the hydrogen mass transfer rate across the HTF-HSG liquid/gas interface. For the Nevada Solar One (NSO) Plant expansion tank geometry and conditions, with *Therminol VP-1* as HTF, the model suggests that passive removal (i.e., hydrogen mass transfer solely across the surface interface) is sufficient to meet moderate hydrogen removal rates of 1.7×10^{-4} mol/s/tank. To meet more aggressive removal rates (up to 2×10^{-4} mol/s/tank), a diffused aeration system—which has additional mass transfer across the liquid/gas interface of injected bubbles—is likely necessary. Moderate removal rates are sufficient to ensure design power output over a 30-year lifetime starting with new or slightly degraded receivers. Aggressive removal rates are necessary to restore heavily degraded receivers (by reversing hydrogen transport out of the annulus into the HTF) and to restore the plant output to its design capacity.

The model predicts that passive removal is likely sufficient to meet moderate removal rates. However, uncertainty in the values of two model parameters—the Henry's Law Constant and, particularly, the mass transfer coefficient—precludes definite conclusions. To lower the uncertainty and confirm (or disprove) the model results, a laboratory-scale test was developed to obtain experimental data for these two parameters. The experiment is based on investigating the absorption of hydrogen into the HTF (in this study *Therminol VP-1*) by measuring the decline of hydrogen pressure over time. The procedure allows one to obtain both the mass transfer coefficient (from transient behavior) and Henry's Law Constant (from equilibrium conditions) using the same test in one experimental run. The setup is, to a first approximation, a scaled-down version (about 50,000 times in terms of interface area) of an actual NSO expansion tank, about 50% filled with HTF and the remaining half with HSG. To the best of our knowledge, this experiment and procedure are the first of its kind to derive these two parameters in a relatively inexpensive, straightforward, and rapid manner, with moderate accuracy (about $\pm 15\%$ uncertainty). The experiment and measurement results are presented in this paper.

The Henry's Law Constant is a fundamental property of a liquid/gas system and is of importance in several applications (e.g., soda carbonization or wastewater treatment (Crittenden et al., 2012)). Henry's Law states that the amount of gas dissolved in a liquid is proportional to its partial pressure in the gas phase (Cussler, 2009). The proportionality

factor is typically referred to as Henry's Law Constant. Despite its name, its value ranges widely among different liquid/gas systems; even for the same system, it usually strongly depends on temperature (Sander, 2015). Various types of Henry's Law Constant are in use even though they all represent the same equilibrium condition: a different value is obtained depending on the units chosen, whether the parameter is non-dimensionalized or not, and whether the numerator or denominator represents gas partial pressure or liquid concentration. Henry's Law Constant has been carefully measured for several liquid/gas systems (e.g., $\text{H}_2\text{O}/\text{CO}_2$), an extensive database of which is maintained by Sander (2015).

Various methods have been developed to measure Henry's Law Constant, usually grouped into static and dynamic methods (Fendinger and Glotfelty, 1988; Dewulf et al., 1995; Staudinger and Roberts, 1996; Özer, 2005; Fang et al., 2006). The static methods rely on direct measurement of gas and liquid concentrations of a component in a closed system under equilibrium conditions. Different variations exist such as the single-equilibration technique, multiple-equilibration technique, and variable-headspace technique, all discussed in detail by Staudinger and Roberts (1996). Dynamic techniques rely on relative concentration changes in one phase, and they are typically more accurate and can measure lower Henry's Law Constants (as defined in Section 2) than the static techniques. Examples of dynamic methods are the gas-stripping, wetted-wall column, and fog-chamber techniques. The magnitude of Henry's Law Constant and maximum allowable uncertainty, cost, and lead time determine which method is applicable. In this study, the maximum allowable cost and lead time are low, acceptable uncertainty is up to 20% (moderate accuracy), and Henry's Law Constant is relatively high. As a result, a simple and straightforward hydrogen equilibrium pressure measurement (single-equilibration technique) is combined with a mass balance on the closed system (to calculate hydrogen concentration in the HTF). Highly accurate measurements of Henry's Law Constant were not necessary for this study because previous experimental data were available (Kuckelkorn et al., 2015), and the impact of Henry's Law Constant on the performance of the hydrogen mitigation unit is limited. The latter is a result of competing effects: a higher Henry's Law Constant (more volatile gas component) increases the mass transfer rate of hydrogen from HTF into HSG in the expansion tanks, but also results in higher hydrogen partial pressures (and higher thermal losses) in the receiver annulus.

Unlike Henry's Law Constant, the mass transfer coefficient is not a fundamental physical property of the liquid/gas system but depends on the application. For example, it is a function of the geometry of the setup and whether the fluid is static or being mixed. One approximate method is to measure the diffusion coefficient, which is an underlying parameter in the mass transfer coefficient and is a fundamental property of a gas/gas or liquid/gas system. Various techniques have been

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