ANALYSIS OF THE DIFFUSIVITIES OF H_2 AND O_2 IN LIQUID H_2O FROM EXPERIMENTAL MEASUREMENTS AND MOLECULAR SIMULATIONS

I. N. Tsimpanogiannis[1,*], O. A. Moultos[2]

[1] 6th km Harilaou-Thermi Rd, 57001 Thermi, Thessaloniki, GR,
Chemical Process & Energy Resources Institute (CPERI),
Centre for Research & Technology Hellas (CERTH)
[2] Engineering Thermodynamics, Process & Energy Department,
Faculty of Mechanical, Maritime and Materials Engineering,
Delft University of Technology, 2628CB Delft, The Netherlands
* i.n.tsimpanogiannis@certh.gr

ABSTRACT

The accurate knowledge of the intra-diffusivity of light gases (e.g., H_2, O_2) in liquid H_2O over a wide range of temperatures and pressures is important for the design and optimization of fuel cells and electrolyzers, and for controlling processes such as the air-water gas exchange. The three major routes that are followed for the measurement/estimation of diffusion coefficients are (i) experimental measurements, (ii) estimation through theoretical/semi-empirical models, and (iii) estimation through molecular simulations.

In this study, all available data from experimental measurements and molecular simulations for the intra-diffusivities of H_2 and O_2 in liquid H_2O, and for the self-diffusivity of pure H_2O are analyzed to examine the validity of the Stokes-Einstein (SE) relation. This analysis is motivated by the significant amount of work devoted through the years for improving the predictions of intra- and self-diffusivities in binary and multicomponent mixtures relevant to chemical and environmental processes. Here, we calculate the slopes s and t corresponding to the $\ln(D)$ *vs.* $\ln(T/\eta)$ and $\ln(D/T)$ *vs.* $\ln(1/\eta)$ plots, respectively, where D is the intra-diffusivity, η the viscosity, and T the temperature of the systems. Our results show that s and t deviate from unity for both cases that we consider in this study (i.e., experimental and simulation data). This means that the Stokes-Einstein relation is violated for the binary systems of H_2 and O_2 with H_2O, and for pure H_2O. Although prior studies mainly focused on re-evaluating the parameter A of the SE-based semi-theoretical/semi-empirical approaches expressed as $D = A\,(T/\eta)$, our results indicate that reliable predictions for the intra- and self-diffusivities can be achieved by improving the accuracy of the prediction of slopes s and t.

KEYWORDS: self-diffusivities, intra-diffusivities, molecular simulations, experimental measurements