U.S. National Committee to IAPWS

2016 Report on Activities of Potential Interest to IAPWS

Communicated from the Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO:

- In a collaboration with the Ruhr University of Bochum (Germany), we continue to work on an IAPWS project for an equation of state for the thermodynamic properties of heavy water. A preliminary equation has been developed, and will be refined and augmented soon by some new data for the ideal-gas heat capacity and for the second and third virial coefficients.
- Work is beginning on a related IAPWS project to develop new transport property correlations for heavy water.
- In collaboration with researchers at Fondazione Bruno Kessler (Italy), Nicolaus Copernicus University (Poland), and the University of Delaware (USA), two state-of-the-art flexible model for the water pair potential have been used to calculate second virial coefficients $B(T)$ for both H_2O and D_2O. Calculations for the third virial coefficient $C(T)$, which also utilize state-of-the-art 3-body potentials, are in progress. The calculations use the path-integral Monte Carlo method, which fully accounts for both intermolecular and intramolecular quantum effects. The results so far agree with experimental data, but cover a wider range of temperatures. The effect of molecular flexibility is found to be significant in comparison to the uncertainty of the calculations and of the experimental data, implying that the rigid models often used for water are insufficient if the best quantitative accuracy for virial coefficients is desired.

Communicated from the University of Maryland, College Park

- Research is predicting a new type of fluctuation-induced pressure in confined liquid layers subjected to a temperature gradient. Estimates of the magnitude of these non-equilibrium pressures in a layer of liquid water have been presented.

T.R. Kirkpatrick, J.M. Ortiz de Zarate, and J.V. Sengers, Phys. Rev. E 93, 012148 (2016); ibid. 93, 032117 (2016).

- Additional publications of potential interest

Water: A Tale of Two Liquids, Gallo, P; Arnann-Winkel, K; Angell, CA; Anisimov, MA; Caupin, F; Chakravarty, C; Lascaris, E; Loerting, T; Panagiotopoulos, AZ; Russo, J; Sellberg, JA; Stanley, HE; Tanaka, H; Vega, C; Xu, LM; Pettersson, LGM. CHEMICAL REVIEWS 116 (13) 7463-7500 DOI: 10.1021/acs.chemrev.5b00750 pub. JUL 13 2016

Hydrophobicity and thermodynamic response for aqueous solutions of amphiphiles, Zemankova, K; Troncoso, J; Cerdeirina, CA; Romani, L; Anisimov, MA. CHEMICAL PHYSICS 472, 36-43 DOI: 10.1016/j.chemphys.2016.02.020 pub. JUN 15 2016

Two-state thermodynamics and the possibility of a liquid-liquid phase transition in supercooled TIP4P/2005 water, Singh, RS, Biddle, JW; Debenedetti, PG; Anisimov, MA. JOURNAL OF CHEMICAL PHYSICS 144 (14) Article Number: 144504, DOI: 10.1063/1.4944986 pub. APR 14 2016

Mesoscale solubilization and critical phenomena in binary and quasi-binary solutions of hydrotropes, Robertson, AE; Phan, DH; Macaluso, JE; Kuryakov, VN; Jouravleva, EV ; Bertrand, CE; Yudin, IK; Anisimov, MA FLUID PHASE EQUILIBRIA 407, 243-254 SI DOI: 10.1016/j.fluid.2015.06.030 pub. JAN 15 2016

Communicated from the ASME Research & Technology Committee on Water and Steam in Thermal Systems

- The *Consensus on Pre-Commissioning Stages for Cogeneration and Combined Cycle Power Plants* document, which serves to inform, educate and assist the reader in adequately considering and planning for the many major activities involved in the design, construction and start-up of cogeneration and combined cycle power plants, is nearly ready for release and publication by ASME.

The Water Technology Subcommittee is working on an update to the ASME "brown book," *Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers*; this ASME publication provides a consensus of proper current operating practices for the control of feedwater and boiler water chemistry in the operation of industrial and institutional, high duty, primary fuel fired boilers. These practices are aimed at minimizing corrosion, deposition, cleaning requirements, and unscheduled outages in the steam generators and associated condensate, feedwater, and steam systems. The publication will be an expansion as well as a revision of the operating practice consensus documents previously issued by the Committee in 1994 to include advances in boiler design and water treatment technology.

Communicated from Scripps Institution of Oceanography

- Scripps continues involvement in SCOR Working Group (WG-145) that will — in part — address the need for a suitable activity coefficient model for seawater that can be used to further the goal of establishing a suitable seawater pH definition that is metrologically traceable. This group met in February 2016 in New Orleans, and Scripps and University of East Anglia, UK have put in a joint proposal to the UK-NERC (and US-NSF) to work on developing the proposed Pitzer-type model, combining both an evaluation of pre-existing data, as well as the measurement of additional new data that is needed to meet the goal.

Communicated from OLI Systems

- **Aqueous solution chemistry of rare-earth elements**

OLI Systems continued its research on the properties of aqueous solutions of rare-earth elements within the framework of the Department of Energy's Critical Materials Institute. OLI Systems provides simulation tools for other members of the institute. In a recently completed project, a thermodynamic model of rare earth elements in the presence of complexing agents (i.e., citrates, gluconates, and acetates) has been established. This model has been utilized to rationalize the stripping of rare-earth cations adsorbed on bacterial cells using lanthanide binding tags. This work has been published in:

Park, D., Reed, D., Yung, M., Eslamimanesh, A., Lencka, M., Anderko, A., Fujita, Y., Riman, R.E., Navrotsky, A., Jiao, Y., "Bioadsorption of Rare Earth Elements through Cell Surface Display of Lanthanide Binding Tags," *Environmental Science & Technology*, 50 (2016) 2735-2742.

A comprehensive analysis of the thermodynamic behavior of rare earth chlorides is nearing completion.

- **Amines**

A major effort has been devoted to developing a comprehensive model for the phase behavior of amines and corresponding amine hydrochlorides in aqueous systems. The amines considered in this work are used as neutralizers in the power generation and refining industries. The model has been described for selected amines in the following paper:

M.M. Lencka, J.J. Kosinski, P. Wang, and A. Anderko, "Thermodynamic modeling of aqueous systems containing amines and amine hydrochlorides: Application to methylamine, morpholine, and morpholine derivatives," *Fluid Phase Equilibria*, 418 (2016) 160-174

- **Other topics**

A model has been developed for various sodium phosphates in aqueous environments. The model is valid for temperatures up to 350 C and includes speciation, solid-liquid equilibria, vapor-liquid equilibria and liquid-liquid equilibria at high temperatures. The liquid-liquid equilibrium shows a lower critical end point and is strongly dependent on the Na/P ratio.

Work has been completed on modeling the behavior of actinides (U, Np, Pu, Am, Cm) at the most important oxidation states in the presence of acids, bases, carbon dioxide, carbonates, chlorides, nitrates and other salts. The model predicts the solubility and speciation of actinides in wide ranges of concentrations, ranging from dilute solutions that are relevant to the environmental fate of radionuclides to very concentrated solutions in nitric acid, which are used in nuclear fuel processing. Also, a model has been developed for predicting the behavior of lead species, including various lead silicates, molybdate, tungstate and acetate, formate and nitrate.

Work is in progress on simulating the behavior of calcium, magnesium, and zinc silicates in aqueous systems. This project is motivated primarily by the need to predict phenomena associated with SAGD (steam-assisted gravity drainage) processes.

In a separate project, work is ongoing on modeling the solubility of scale-forming minerals in oil and gas production. These minerals include $BaSO_4$, $CaCO_3$, $CaSO_4$, ZnS, and PbS.