

The sixth industrial fluid properties simulation challenge †

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Abstract

The sixth industrial fluid properties simulation challenge was held in 2010. The contestants were challenged to predict mutual solubility in liquid-liquid equilibria (LLE) for the PROGLYDE DMM™ + water system at various temperatures and atmospheric pressure. The temperature-dependent balance of hydrophobic and hydrophilic interactions relevant to this system is also of great scientific and practical importance as a key driving force in phenomena like self-assembly and protein folding. Because the contestants were not given the experimental benchmark data until after they had submitted their predictions, this exercise represents a relatively rare opportunity to challenge experts in the field to make predictions without a priori knowledge of the correct answer nor the option to avoid publication of their predictions if they were especially poor in comparison to experiment. Seven groups accepted the challenge and used a variety of molecular modeling and simulation methods.

Keywords: liquid-liquid equilibria, industrial fluid properties simulation challenge, dipropylene glycol dimethyl ether, molecular modeling, molecular simulation, computational chemistry

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1. Introduction

During the decade since the Industrial Fluid Properties Simulation Challenge (IFPSC) was first organized in 2001, the challenge problems have focused on the calculation and prediction of a variety of physical properties of great significance to the chemical industry; liquid densities, viscosities, vapor-liquid phase boundaries, Henry's law constants, partition coefficients, and heats of mixing are some examples [1-6]. These challenges have been intended to drive improvements in the practice of molecular modeling, formalize methods for the evaluation and validation of simulation results with experimental data, and ensure the relevance of the academic community's simulation activities to industrial needs and requirements. The challenges have highlighted the promise and usefulness of molecular simulation for accurate physical property prediction while also illustrating some of its limitations. For example, despite the continued rapid increase in commonly-available computational power and algorithmic efficiency, atomistic simulations of moderately-complex chemical species still require large computational resources and significant time investment in many cases. A molecular simulation also presents the practitioner with many opportunities to make a trivial coding error or typo in an input file that can spoil the results of the simulation, and such difficulties occasionally trip up even the world's leading experts in these methods. Even when the simulations are set-up and run as intended, it is sometimes difficult to know ahead of time what level of accuracy can be expected for a given investment of (often significant) time and resources. For example, relatively-small changes to the details of the potential energy model that is used can have an unexpectedly-large impact on the simulation results [7]. These examples illustrate the fact that the IFPSC's vision for these modeling methods is not yet a reality: *"A robust, accurate, and easy-to-use set of modeling tools will be widely available for the prediction of physical properties of fluids and obtaining insight into the connections between molecular structure and properties. As a part of this tool set, molecular simulation will become a breakthrough technology that is widely accepted in the chemical industry and applied in conjunction with other predictive methods to meet the industry's evolving fluid property data needs."* With the potential impact of molecular simulations in industrial chemical and materials research and engineering even clearer now [8] than it was a decade ago, the IFPSC remains one of several activities that are needed to help make that vision into a reality [9].

Over the last 20+ years, studies of phase equilibria by molecular simulation have become relatively common, employing techniques such as Gibbs Ensemble Monte Carlo [10] and Grand Canonical Monte Carlo with histogram reweighting [11]. Typically, these methods have been used to study vapor-liquid equilibria in particular and to develop general, transferable force fields (potential energy models) that are reasonably accurate over a wide range of state conditions, molecular structures, and properties. Comparatively less attention has been paid to predicting liquid-liquid equilibria of realistic, moderately complex molecular fluids using the aforementioned methods, which tend to work best when the density difference between phases is sufficiently large. More commonly, molecular dynamics simulations have been used to study liquid-liquid systems, but those studies have typically focused on the details of the structure and interactions at the interface and not on predicting the bulk-phase compositions of the coexisting phases. Therefore, assessing the capability of molecular simulation methods and force fields to accurately predict liquid-liquid phase equilibria for practically-relevant and moderately-complex chemical systems is of interest in establishing more clearly the state-of-the-art capability in this application area.

Unlike most organic solvents, glycol ethers and glycol diethers exhibit an “inverse solubility” relationship with water. That is, in the range of normal process conditions they become more compatible as they are cooled and are completely miscible below the lower critical solution temperature (LCST). This behavior is typically rationalized in terms of a temperature-dependent balance between hydrophobic and hydrophilic interactions [12]. This balance of interactions in aqueous solutions is of great scientific and practical importance as a key driving force in phenomena like self-assembly and protein folding.

Glycol ethers are used in a wide range of product formulations and industrial processes. For example, they are used as solvents and co-solvents in both organic- and water-based formulations for applications such as cleaning solutions, paints, coatings, and inks. A variety of other novel applications have been proposed that take advantage of the inverse solubility behavior. Dipropylene glycol dimethyl ether (DPGDME) is unique among common propylene-oxide-based solvents in that it has no hydroxyl functionality. This means it is relatively inert and can be used in systems that are proton-sensitive (*e.g.*, water-based polyurethane coatings) [13]. Although mutual solubility data for liquid–liquid equilibrium (LLE) for a number of water + ethylene glycol ether and water + propylene glycol ether mixtures have been reported in the literature [12], the temperature-dependent, mutual solubility of the water + DPGDME system has not been reported previously. Data were only publicly-available at 298 K for the commercial product PROGLYDE DMM where the solubility of DPGDME in water is reported to be 35 wt % and of water in DPGDME to be 4.5 wt % [13].

PROGLYDE DMM ($C_8H_{18}O_3$) consists of three structural isomers (illustrated in Figure 1), two of which are the major components that occur in approximately equal amounts). A typical composition of PROGLYDE DMM is 50 % I, 47 % II, and 3 % III. CAS # 111109-77-4 can represent any of the three isomers or mixtures thereof.

2. The Challenge

The Sixth Industrial Fluid Properties Simulation Challenge was the following: for the PROGLYDE DMM + water system, compute the mutual solubility in liquid-liquid equilibria at temperatures of 283, 323, 333 and 353 K and atmospheric pressure. Because the contestants were not given the experimental benchmark data until after they had submitted their predictions, this exercise represents a relatively rare opportunity to challenge experts in the field to make predictions without a priori knowledge of the correct answer nor the option to avoid publication of their predictions if they were especially poor in comparison to experiment.

Any theory/modeling/simulation method could be used, but molecular modeling and simulation methods were especially encouraged. Any force fields (or other model parameterizations) previously published in the open literature prior to the announcement of this challenge were acceptable. Force fields (or other models) that had not been published previously could not be parameterized for this challenge using mutual solubility data for the water + PROGLYDE DMM system (except for the published data at 298 K). Force fields (or other models) were allowed to be parameterized using any other published physical property data. Participants were allowed to choose to model PROGLYDE DMM as only one of its constituent isomers or as a mixture of isomers.

Entries were scored by comparing the predicted composition of each phase (wt % PROGLYDE DMM) to the measured data. Full credit was awarded for a prediction that fell within the experimental uncertainty (5 %). A linear interpolation of partial credit was awarded for predictions with an absolute deviation above the minimum threshold and less than a maximum deviation of 25 %. No points were awarded for prediction above the maximum deviation. Each of the four state points were weighted equally (*i.e.* represented 25 % of the total points available).

Seven groups accepted the challenge and submitted entries to the competition. They included: 1) A. Vahid, F.S. Emami, E. Moharreri, and J. R. Elliott (University of Akron); 2) L. Zhao, C. Wu, and N. Huang (National Institute of Biological Sciences, Beijing, China; Washington University); 3) P. Bai and J.I. Siepmann (University of Minnesota); 4) J. Reinisch, A. Klamt, F. Eckert, and M. Diedenhofen (COSMOlogic); 5) T. Cheng, F. Li, J. Dai, and H. Sun (Shanghai Jiao Tong University); 6) S.-T. Lin, L.-H. Wang, W.-L. Chen, P.-K. Lai, and C.-M. Hsieh (National Taiwan University); and 7) T. Koddermann, K. N. Kirschner, J. Vrabec, M. Hulsmann, and D. Reith (Fraunhofer-Institut für Algorithmen und Wissenschaftliches Rechnen (SCAI); University of Paderborn).

3. Results and Discussion

In Figure 2 the predictions of the seven challenge entries are plotted and compared to the benchmark and supporting data measured by The Dow Chemical Company [14]. A variety of techniques were employed including approaches based on molecular dynamics (MD) and Monte Carlo (MC) simulations, COSMO methods, and a combination of MD with thermodynamic perturbation theory. The quality of the results also varied significantly. For the sake of clarity, the results are plotted again in Figure 3 but in this version include only the predictions of the top three entries and the benchmark data. These top three methods (two COSMO-based methods and one MC) made LLE predictions of remarkable accuracy for this system, especially in the high-temperature region. In general, it was important that they were able to “calibrate” their models using the publicly-available room-temperature data to be able to make such accurate predictions; the predictions tended to be much worse without that “calibration.” The molecular structures studied here are neither especially large nor exotic, yet predictions of their phase behavior by molecular modeling represent a very significant challenge (especially in the absence of any experimental data). Nevertheless, the ability to make such accurate predictions based on so little experimental data is certainly a remarkable accomplishment that would have significant industrial impact. For example, because elevated pressures would be required to collect this type of data at temperatures above 373 K, such experiments are more difficult than the ones described here. A modeling technique that could make quantitatively-accurate predictions at temperatures above 373 K would be highly desirable for this reason.

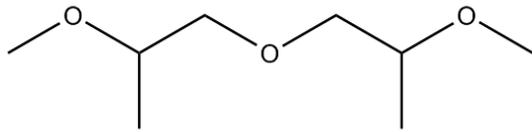
Five of the seven contestants were present at a special session at the American Institute of Chemical Engineers (AIChE) 2010 AIChE Annual Meeting in Salt Lake City. The session was sponsored by the Computational Molecular Science and Engineering Forum (CoMSEF; <http://comsef.org>) of the AIChE. At that session, the contestants presented their methods and predictions and discussed various aspects of this challenge problem. The challenge entries and the methods they used will be described in greater detail in individual articles in this journal issue.

Acknowledgments

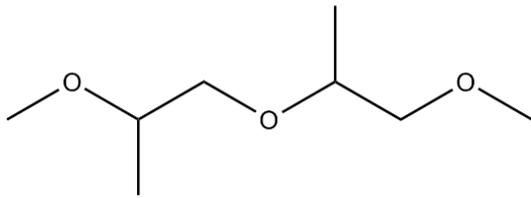
We would like to thank the Computational Molecular Science and Engineering Forum (CoMSEF) of the American Institute of Chemical Engineers and the Physical Division of the American Chemical Society (ACS) for their institutional support. We would like to thank the 3M Company, BP Amoco, The Dow Chemical Company, DuPont, Exxon Mobil, and Mitsubishi Chemical Corporation for financial support. We would like to recognize the contribution from The Dow Chemical Company in establishing the benchmark data, and the anonymous committee of academic modeling experts who served as external judges for the challenge. Finally, we would like to thank all the participants for their willingness to commit considerable time and resources to this Challenge and for participating in the valuable discussions during the challenge symposium at the AIChE annual meeting.

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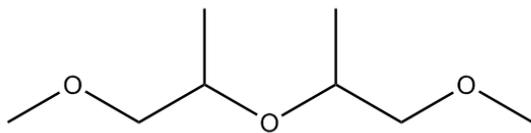
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(Isomer I, CAS # 63019-84-1)



(Isomer II, CAS # 89399-28-0)



(Isomer III)

Figure 1 The three structural isomers of PROGLYDE DMM.

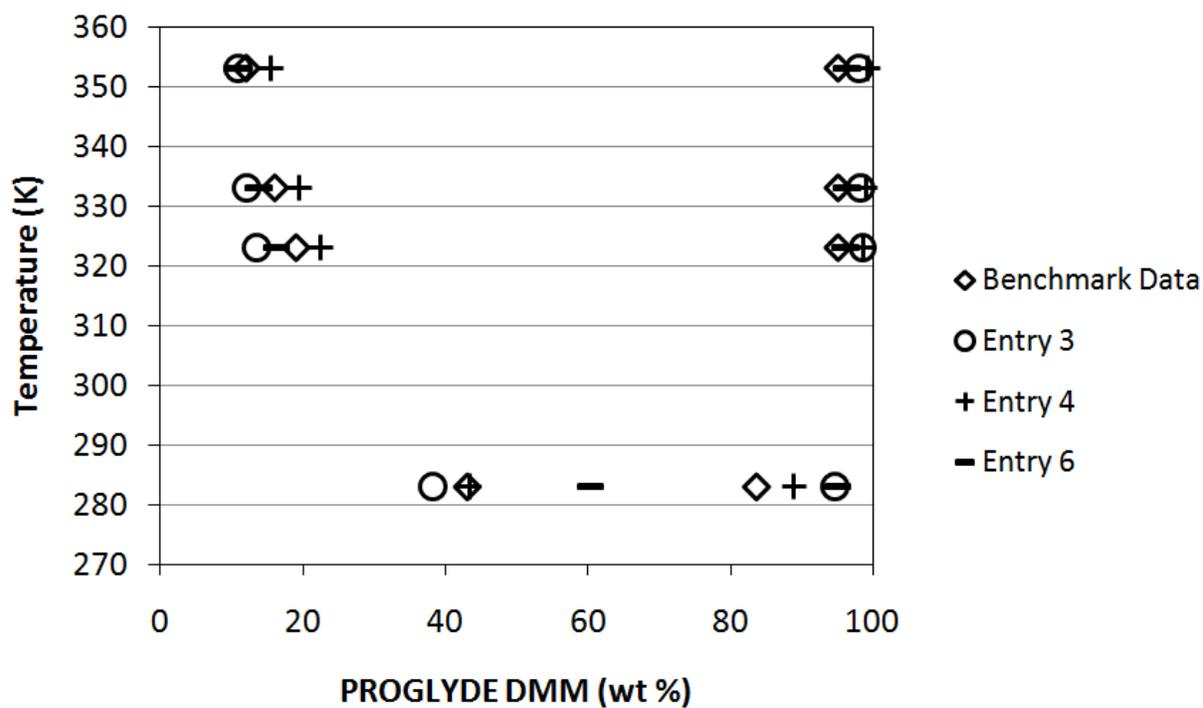


Figure 3 Mutual solubility in liquid-liquid equilibria for the PROGLYDE DMM + water system with compositions expressed as weight % PROGLYDE DMM. The diamonds represent the benchmark experimental data, and the other symbols represent the predictions of the top three challenge entries.