Published in final edited form as:

Fluid Phase Equilib. 2018 ; 476 Pt A(25 November): 1–5. doi:10.1016/j.fluid.2018.04.001.

The Ninth Industrial Fluid Properties Simulation Challenge

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Abstract

The Ninth Industrial Fluid Properties Simulation Challenge aimed to test the ability of molecular modeling approaches to predict water/oil interfacial tension (IFT) at conditions of high temperature and pressure. In particular, the challenge featured water/oil IFT where the oil was n-dodecane, toluene, or a 50:50 n-dodecane/toluene blend at 1.825 MPa and temperatures in the range of 383 K to 443 K. Seven entries were received including approaches such as molecular dynamics (MD) and Monte Carlo (MC) simulations, COSMO-RS, and iSAFT, and they were judged by comparison to pendant drop tensiometer benchmark data. The quality of predictions varied among the entries between approximately 20 % and 70 % of the total points possible with the entries based on MD and MC having the highest scores in most cases. As is often the case in molecular modeling, predictions of the relative trends tended to be reliable even if the absolute values were not.

Keywords

interfacial tension; molecular modeling

1. Introduction

The Industrial Fluid Properties Simulation Challenge (IFPSC) is an open competition organized by employees of the National Institute of Standards and Technology and several companies (Dow Chemical, 3M Company, and United Technologies Research Center) with support from the Computational Molecular Science and Engineering Forum (CoMSEF) of the American Institute of Chemical Engineers (AIChE) and the Physical Chemistry Division

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Appendix A: Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.fluid.2018.04.001>.

of the American Chemical Society (ACS). The goals of the competition were to drive improvements in the practice of molecular modeling, formalize methods for the evaluation and validation of simulation results with experimental data, and ensure relevance of simulation activities to industrial requirements. The previous eight challenges held during the years 2001–2014 addressed various industrially relevant physical properties of small-molecule fluids such as adsorption in porous media, liquid-liquid and vapor-liquid equilibria, partition coefficients, viscosity, vapor pressure and heat of vaporization, heat of mixing, and density.^{1–8} Details of the previous challenges can be accessed at <http://fluidproperties.org>.

There is increasing interest in high temperature (T) and pressure (P) processing of emulsions. Typical conditions of interest are greater than 373 K and 0.1 MPa (pressurized process to maintain liquid state). Pendant drop tensiometer techniques are available for measuring interfacial tension (IFT) from droplet curvature at high T and P up to 473 K and 20 MPa (see Chaverot et al. as an example⁹), and water/oil IFT is of particular interest for the processing of oil sands to produce synthetic crude oil.¹⁰ Molecular simulations represent a promising computational tool for investigation in this area due to their potential to provide molecular-level insights into the physical mechanisms determining transport and phase behavior that can be difficult to probe experimentally, and molecular simulations have been used to study water/oil interfacial tension many times in the past.^{11–17} Well-designed and parameterized force fields (potential energy models used to describe intra- and inter-molecular interactions in molecular simulations) can be especially useful for predictions when they are transferrable (i.e., produce property predictions in good agreement with experiments) to different molecules, state points, and/or properties than those used to parameterize the models.

The ninth simulation challenge aimed to test the ability of molecular modeling approaches to predict water/oil IFT at high T and P.

2. Challenge

Challenge entrants were asked to make a total of 12 predictions of interfacial tension as summarized in Table 1 (3 oil phases and 4 temperatures). The pressure for all state points was 1.825 MPa.

Note that the oil blend was 50:50 on a mass basis. Details about purity of the chemicals and the experimental procedures used to measure IFT have been provided in the accompanying benchmark manuscript.

Any theory/modeling/simulation method was allowed as long as it is generally accepted to be a “molecular modeling” approach. For example, strictly empirical correlations were not considered for the challenge. The focus and goals of the IFPSC were to benchmark and promote molecular modeling and simulation methods. Use of any force field (or other model parameterization) previously published in the open literature prior to the announcement of the challenge was acceptable. Force fields (or other models) that had not been published previously could not be parameterized for this challenge using interfacial tension data for

both the same molecules and state conditions as the challenge problems. However, parameterization for the same molecules at different state points or different molecules at the same state conditions was acceptable. Here, “different state conditions” refers to low T and P, not high T and P at slightly different conditions from the challenge problems. Force fields (or other models) parameterized using any other published physical property data were allowed. The organizers suggested various related data sets from the literature that might be useful for parameterizing and/or validating the models.

Entries were scored by comparing the predicted interfacial tension values to the measured data. The comparison between predictions and experiment was performed both in terms of the IFT values and in terms of the IFT values relative to whichever one of the 12 IFT values that the entry predicted most accurately. The scores for the relative values contributed 2/3 of the total available points, and the raw IFT values contributed 1/3 of the total available points. Full credit was awarded for a prediction that agreed with the benchmark data within the experimental uncertainty (1 mN/m and 2.5 % for the absolute and relative predictions, respectively). A linear interpolation of partial credit was awarded for predictions with an absolute deviation that fell between a minimum threshold (the experimental uncertainty) and a maximum threshold (5 mN/m and 25 % for the absolute and relative predictions, respectively). No points were awarded for a prediction above the maximum deviation.

3. Results and Discussion

Seven entries employing a variety of different methods were received from: a) Andersson, Eckert, Reinisch, Klamt, and Stipp (U. Copenhagen, COSMOlogic, U. Regensburg – COSMO-RS); b) Papavasileiou, Moulton, and Economou (National Center for Scientific Research, Greece; Texas A&M at Qatar – molecular dynamics); c) Herdes, Ervik, Mejías, and Müller (U. Bath, NTNU, U. Concepcion, Imperial College – molecular dynamics); d) Mu and Chapman (Rice - iSAFT); and e) Wang, Haghmoradi, and Chapman (Rice – density gradient theory); f) Chen, Xue, Harwood, Chen, and Siepmann (Minnesota – Monte Carlo); and g) Shen and Sun (Shanghai Jiao Tong U., Jilin U. – molecular dynamics). Most of these teams presented their work at the IFPSC session (sponsored by CoMSEF) at the 2016 AIChE Annual Meeting in San Francisco. The predictions for IFT were compared to the benchmark values in Figure 1, Figure 2, and Figure 3. Most of the entries (with the exception of Siepmann et al.) overpredicted the IFT of n-dodecane. For toluene, the entries from Andersson et al. and Müller et al. were closest to the benchmark, and Siepmann et al. and Müller et al. were closest for the blend. The slopes of linear fits to the IFT versus T data are plotted in Figure 4. Of the three oils, n-dodecane showed the strongest T-dependence (steepest slope). Several of the entrants predicted the correct trend in terms of the T-dependence. A summary of the scores for the challenge entries is given in Table 2. The second column contains the total scores for each entry (out of a maximum possible of 36). The third and fourth columns break down the scores into contributions from the absolute (1/3 of the total) and relative (2/3 of the total) comparison to the benchmark data. The remaining columns further breakdown the contributions from the three oils. Note that the total relative contribution to the scores for each of the entries was greater than twice the absolute contribution to the score. Molecular modeling approaches often do a good job of predicting relative trends in physical property data for a series of structures or state

conditions even if they do not predict quantitatively accurate absolute values because the underlying physical mechanisms are accurately described by the simulations. Herdes and Müller (pictured in Figure 5) and coworkers were named Champions of the Ninth Industrial Fluid Properties Simulation Challenge. Siepmann and coworkers were honored for their second-place performance.

Looking to the future, the Tenth Industrial Fluid Properties Simulation Challenge was announced at the 2017 AIChE annual meeting and will challenge molecular modelers to predict the pressure-dependence of viscosity for a short, branched alkane. See <http://fluidproperties.org> for more details.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The organizers of the Industrial Fluid Properties simulation challenge would like to thank Dow Chemical for providing the benchmark experimental data for the 9th Challenge. We also thank the American Chemical Society Green Chemistry Institute Chemical Manufacturers Roundtable and the Sustainable Separation Processes: Accelerating Industrial Application of Less Energy-Intensive Alternative Separations initiative (AltSep) for financial support. We also thank the Computational Molecular Science and Engineering Forum (CoMSEF) of the American Institute of Chemical Engineers for sponsoring the IFPSC session at the AIChE annual meeting and the Physical Chemistry Division of the American Chemical Society for managing our finances.

References

1. Case F; Chaka A; Friend DG; Furip D; Golab J; Johnson R; Moore J; Mountain RD; Olson J; Schiller M; Storer J, The first industrial fluid properties simulation challenge. *Fluid Phase Equilib.* 2004, 217 (1), 1–10.
2. Case F; Chaka A; Friend DG; Furip D; Golab J; Gordon P; Johnson R; Kolar P; Moore J; Mountain RD, The second industrial fluid properties simulation challenge. *Fluid Phase Equilib.* 2005, 236 (1–2), 1–14.
3. Case FH; Brennan J; Chaka A; Dobbs KD; Friend DG; Furip D; Gordon PA; Moore J; Mountain RD; Olson J; Ross RB; Schiller M; Shen VK, The third industrial fluid properties simulation challenge. *Fluid Phase Equilib.* 2007, 260 (2), 153–163.
4. Case FH; Brennan J; Chaka A; Dobbs KD; Friend DG; Gordon PA; Moore JD; Mountain RD; Olson JD; Ross RB; Schiller M; Shen VK; Stahlberg EA, The fourth industrial fluid properties simulation challenge. *Fluid Phase Equilib.* 2008, 274 (1–2), 2–9.
5. Case FH; Chaka A; Moore JD; Mountain RD; Olson JD; Ross RB; Schiller M; Shen VK; Stahlberg EA, The fifth industrial fluid properties simulation challenge. *Fluid Phase Equilib.* 2009, 285 (1–2), 1–3.
6. Case FH; Chaka A; Moore JD; Mountain RD; Ross RB; Shen VK; Stahlberg EA, The sixth industrial fluid properties simulation challenge. *Fluid Phase Equilib.* 2011, 310 (1–2), 1–3.
7. Ross RB; Ahmad R; Brennan JK; Frankel KA; Moore JD; Moore JD; Mountain RD; Shen VK; Schultz NE; Siderius DW; Smith KD; Thommes M, The seventh industrial fluid properties simulation challenge. *Fluid Phase Equilib.* 2014, 366, 136–140.
8. Schultz NE; Ahmad R; Brennan JK; Frankel KA; Moore JD; Moore JD; Mountain RD; Ross RB; Thommes M; Shen VK; Siderius DW; Smith KD, The Eighth Industrial Fluids Properties Simulation Challenge. *Adsorpt. Sci. Technol* 2016, 34 (1), 3–12.
9. Chaverot P; Cagna A; Glita S; Rondelez F, Interfacial Tension of Bitumen–Water Interfaces. Part 1: Influence of Endogenous Surfactants at Acidic pH. *Energy Fuels* 2008, 22 (2), 790–798.

10. Nowbahar A; Whitaker KA; Schmitt AK; Kuo T-C, Mechanistic Study of Water Droplet Coalescence and Flocculation in Diluted Bitumen Emulsions with Additives Using Microfluidics. *Energy Fuels* 2017, 31 (10), 10555–10565.
11. Natália M; Cordeiro DS, Interfacial Tension Behaviour of Water/Hydrocarbon Liquid-Liquid Interfaces: A Molecular Dynamics Simulation. *Mol. Simul* 2003, 29 (12), 817–827.
12. Wang H; Carlson E; Henderson D; Rowley RL, Molecular Dynamics Simulation of the Liquid-liquid Interface for Immiscible and Partially Miscible Mixtures. *Mol. Simul* 2003, 29 (12), 777–785.
13. Rivera JL; McCabe C; Cummings PT, Molecular simulations of liquid-liquid interfacial properties: Water–n-alkane and water-methanol–n-alkane systems. *Phys. Rev. E* 2003, 67 (1), 011603.
14. Nicolas JP; de Souza NR, Molecular dynamics study of the n-hexane–water interface: Towards a better understanding of the liquid–liquid interfacial broadening. *J. Chem. Phys* 2004, 120 (5), 2464–2469. [PubMed: 15268387]
15. Jorge M; Cordeiro MNDS, Molecular Dynamics Study of the Interface between Water and 2-Nitrophenyl Octyl Ether. *J. Phys. Chem. B* 2008, 112 (8), 2415–2429.
16. Zhang J; Dong Z; Zhang Y; Wang M; Yan Y, Effects of the Methane Content on the Water– Oil Interface: Insights from the Molecular Level. *Energy Fuels* 2017, 31 (7), 7026–7032.
17. Jian C; Poopari MR; Liu Q; Zerpa N; Zeng H; Tang T, Reduction of Water/Oil Interfacial Tension by Model Asphaltenes: The Governing Role of Surface Concentration. *J. Phys. Chem. B* 2016, 120 (25), 5646–5654. [PubMed: 27268710]

Figure 1. Benchmark and predicted IFT values for water/n-dodecane at various temperatures (uncertainty estimated to be 1 mN/m for the benchmark data and approximately 0.5–3 mN/m for the various prediction methods).

Figure 2. Benchmark and predicted IFT values for water/toluene at various temperatures (uncertainty estimated to be 1 mN/m for the benchmark data and approximately 0.5–3 mN/m for the various prediction methods).

Figure 3. Benchmark and predicted IFT values for water/50:50 n-dodecane/toluene at various temperatures (uncertainty estimated to be 1 mN/m for the benchmark data and approximately 0.5–3 mN/m for the various prediction methods).

Figure 4. Slopes of linear fits to the IFT vs T data (uncertainties in the slopes estimated to be approximately 0.01–0.04 for the various methods).

Figure 5.
Champions of the ninth simulation challenge: Carmelo Herdes and Erich Müller

Table 1.

Summary of oils and state conditions included in the challenge

oil	T (K)
n-dodecane	383, 403, 423, 443
toluene	383, 403, 423, 443
50:50 (wt/wt) n-dodecane:toluene blend	383, 403, 423, 443

Table 2

Summary of the scores for the challenge entries

Entry	total	absolute	relative	dodecane absolute	toluene absolute	blend absolute	dodecane relative	toluene relative	blend relative
Müller	26.0	7.4	18.5	0.1	3.6	3.7	2.5	2.9	3.9
Siepmann	22.4	6.7	15.7	2.7	0.1	3.9	3.3	0.7	3.8
Sun	19.7	2.5	17.2	0.8	1.7	0.0	3.3	3.3	2.0
Andersson	17.5	3.8	13.7	0.0	3.6	0.2	1.0	3.9	2.0
Chapman (iSAFT)	17.4	0.4	17.0	0.0	0.4	0.0	2.9	3.0	2.6
Economou	14.5	1.2	13.3	0.0	1.2	0.0	2.0	3.2	1.4
Chapman (DGT)	8.3	1.3	7.0	0.6	0.3	0.4	3.4	0.0	0.1