

## Predictive Capability of Equations of State for Investigating Effect of Isomeric Structures of Branched Cyclic Hydrocarbons on Densities at Elevated Temperatures and Pressures

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The increasing consumption of global oils has led to the necessity of pursuing and recovering unconventional resources such as ultradeep reservoirs beneath the deep sea. High-pressure density data are one of the critical fundamental properties for the design and optimization of the processes related to safe exploration, recovery and purification of such oils in sedimentary basins approximately 6100 meters or more underground, at which the temperature and pressure can reach 523 K and 240 MPa, respectively. The significant effects of high-pressure density data have been clearly stated in a recent report from National Energy Technology Laboratory (NETL) of Department of Energy (DOE) [1]. The NETL report also stated that high-pressure density data play an important role as a fundamental database in the modeling studies given that oil companies presently are using equations of state (EoS) based on lower temperature and pressure database that lead to unsatisfactory density predictions at extreme temperatures and pressures [1].

Wu and coworkers [2-10] have been making continuous efforts on the high-pressure density determination as well as the development and examination of a variety of EoS for density predictions at extreme conditions since 2010. A recent work by Wu et al. [4] provides a new insight into the strengths and limitations of three widely used EoS by studying the performance of the EoS applied to the solution properties of several cyclic isomers at high temperatures and pressures, which have not been considered in the previous published literature. Wu et al. investigated the isomeric structural effect on the experimental high-pressure densities for methylcyclohexane (methylC6) and four branched C6 cyclic isomers, ethylcyclohexane

(ethylC6), *cis*-1,2-dimethylcyclohexane (*cis*-1,2), *cis*-1,4-dimethylcyclohexane (*cis*-1,4), and *trans*-1,4-dimethylcyclohexane (*trans*-1,4), followed by a detailed discussion of the density modeling with the Peng-Robinson (PR) EoS, high-temperature, high-pressure volume-translated (HTHP VT) PR EoS, and perturbed-chain statistical associating fluid theory (PC-SAFT) EoS.

In the work by Wu et al. [4], density data were experimentally determined for methylC6 and the four cyclic isomers, ethylC6, *cis*-1,2, *cis*-1,4, and *trans*-1,4 at temperatures up to 525 K and pressures up to 275 MPa, which extends the current database for cyclic hydrocarbons, especially considering that no literature data above the atmosphere pressure have been reported before for *cis*-1,4 and *trans*-1,4. The structural differences of the four isomers were reflected in the ordering of the densities, of which *cis*-1,2 has the largest densities and *trans*-1,4 has the smallest densities over the studied temperature and pressure range. The authors ascribed the density difference to the packing of the isomers.

Another goal of the work by Wu *et al.* was to determine if it was possible for the EoS models including PR EoS, HTHP VT-PR EoS, and PC-SAFT EoS to mimic the trends observed for the density ordering for the four cyclic isomers. Density predictions with the PR EoS and HTHP VT-PR EoS required knowledge about the critical temperature,  $T_c$ , the critical pressure,  $P_c$ , and the acentric factor,  $\omega$  for each studied compound, which were obtained from literature [11]. PC-SAFT EoS predictions required knowledge about the number of segments,  $m$ , the temperature-independent segment diameter,  $\sigma$ , and the interaction energy,  $\varepsilon$ , which were taken directly

from literature for methylcC6 and ethylcC6 [12] and were estimated with group-contribution method proposed by Tihic et al. for *cis*-1,2, *cis*-1,4, and *trans*-1,4 [13]. The HTHP VT-PR EoS provides modest improvements over the PR EoS, but neither of these equations is able to account for the isomer structural effect on the densities. The PC-SAFT EoS gives better density predictions than PR and HTHP VT-PR EoS, but cannot fully account for the effect of isomer structural differences, either. In the final section of the paper, given that the PC-SAFT pure-component parameters were not reported before for *cis*-1,2, *cis*-1,4, and *trans*-1,4, these parameters were obtained either by sole fitting to experimental high-pressure density data or by fitting to the combination of density data and literature vapor pressure data, which is very useful and provides a fundamental database for future modeling researchers to develop a more accurate group-contribution method to take into account the isomeric structural effects.

In summary, the recent work by Wu et al. [4] extended the density database and investigated the EoS predictive capabilities of capturing the isomeric structural effects on densities of several cyclic hydrocarbons at extreme temperatures and pressures. Such a study is not only useful in engineering applications by providing new experimental data and examining the performance of several EoS, but also provides new insights for future researchers to develop more accurate models to account for the structural effects. One of the most important challenges in this area is the scarcity of the experimental thermodynamic property data at extreme conditions especially for isomers. Wu's work gives a new direction by investigating the high-pressure densities of cyclic isomers, but more work needs to be done to generate more thermodynamic data for a variety of isomers for the development of more accurate thermodynamic models in the future.

## Reference

- [1] D. Tapriyal, R. Enick, M. McHugh, I. Gamwo, B. Morreale, High Temperature, high pressure equation of state density correlations and viscosity correlations, in, National Energy Technology Laboratory (NETL), Pittsburgh, PA, and Morgantown, WV (United States), National Energy Technology Laboratory, 2012, pp. 112.
- [2] Y. Wu, B. Bamgbade, K. Liu, M.A. McHugh, H. Baled, R.M. Enick, W.A. Burgess, D. Tapriyal, B.D. Morreale, Fluid Phase Equilib., 311 (2011) 17-24.
- [3] Y. Wu, B.A. Bamgbade, H.O. Baled, R.M. Enick, W.A. Burgess, D. Tapriyal, M.A. McHugh, Liquid Densities of Xylene Isomers and 2-Methylnaphthalene at Temperatures to 523 K and Pressures to 265 MPa: Experimental Determination and Equation of State Modeling. Ind. Eng. Chem. Res., In press (2013) <http://dx.doi.org/10.1021/ie400805y>.
- [4] Y. Wu, B.A. Bamgbade, W.A. Burgess, D. Tapriyal, H.O. Baled, R.M. Enick, M.A. McHugh, J. Phys. Chem. B, 117 (2013) 8821-8830.
- [5] Y. Wu, K. Liu, B.A. Bamgbade, M.A. McHugh, Fuel, 111 (2013) 75-80.
- [6] K. Liu, Y. Wu, M.A. McHugh, H. Baled, R.M. Enick, B.D. Morreale, J. Supercrit. Fluids, 55 (2010) 701-711.
- [7] H. Baled, R.M. Enick, Y. Wu, M.A. McHugh, W. Burgess, D. Tapriyal, B.D. Morreale, Fluid Phase Equilib., 317 (2012) 65-76.
- [8] B.A. Bamgbade, Y. Wu, W.A. Burgess, M.A. McHugh, Fluid Phase Equilib., 332 (2012) 159-164.
- [9] W.A. Burgess, D. Tapriyal, B.D. Morreale, Y. Wu, M.A. McHugh, H. Baled, R.M. Enick, Fluid Phase Equilib., 319 (2012) 55-66.
- [10] B.A. Bamgbade, Y. Wu, H.O. Baled, R.M. Enick, W.A. Burgess, D. Tapriyal, M.A. McHugh, J. Chem. Thermodyn., 63 (2013) 102-107.

- [11] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, The Properties of Gases and Liquids, 3rd Edition, McGraw Hill, New York, USA, 1977.
- [12] J. Gross, G. Sadowski, Ind. Eng. Chem. Res., 40 (2001) 1244-1260.
- [13] A. Tihic, G.M. Kontogeorgis, N. von Solms, M.L. Michelsen, L. Constantinou, Ind. Eng. Chem. Res., 47 (2008) 5092-5101.