Estimation and correlation of multicomponent diffusivities in supercritical mixtures by the Multi Liu–Silva–Macedo model

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Molecular diffusion coefficient (D_{12}) is a transport property of chief importance for accurate modeling and design of rate-controlled processes, such as supercritical fluid extraction (SFE) and related equipment. SFE processes have been privileging the use of supercritical CO_2 mixed with a co-solvent since the fine tuning of the affinity of the solvent to the desired solutes can be optimized "à la carte", which also requires the knowledge of D_{12} values for each solute in a specific solvent mixture [1].
Currently, the experimental data for supercritical multicomponent systems are scarce and alternative schemes using equations for the prediction and correlation of this property are also lacking [2]. One relevant model for diffusivity estimation is that of Liu-Silva-Macedo [3,4], originally developed for self-diffusion coefficients (LSM) and later extended to binary tracer diffusion (TLSM) [3,5]. In this work, two model variants were devised from the original LSM and TLSM models, a purely predictive and a 1-parameter correlation which gave rise to the so-called Multi-LSM and Multi-LSM_{AD} archetypes, respectively. The latter models were then evaluated with 40 supercritical systems with a total of 817 experimental points retrieved from the literature.
The proposed models show an improved performance when compared with common literature models, namely the Wilke-Chang equation [6] and the 2-parameter correlation of Dymond–Hildebrand–Batschinski (DHB) [7]. The average absolute relative deviation (AARD) results indicate that the predictive Multi-LSM (AARD = 10.60 %) performs better than the Wilke-Chang equation (AARD = 15.22 %) and the Multi-LSM_{AD} correlation (AARD = 5.24 %) achieves a better result than the alternative DHB correlation (AARD = 13.06 %).Notwithstanding the good performance exhibited by the new models it is important to mention the size limitations of the database used in this studied. It would be important in the future to expand this database not only with data obtained through conventional experiments, such as the Taylor dispersion technique, but also with values calculated from the mean squared displacements computed from classical molecular dynamics (MD) simulation trajectories. The tremendous increase in the computational power and in the efficiency of the computational algorithms verified in the last decades makes MD an ideal complement for the study of D_{12}, especially when considering the difficulty and operation cost associated with more conventional techniques.

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