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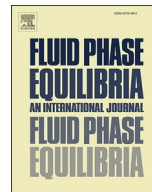
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## Corrigendum

## Corrigendum to “Molecular simulation of the vapor-liquid equilibria of xylene mixtures: Force field performance, and Wolf vs. Ewald for electrostatic Interactions” [Fluid Phase Equilib.] 485 (2019) 239–247

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Vapor-liquid equilibria of xylenes were computed using Monte Carlo simulations in the Gibbs ensemble. For binary mixtures, the predicted composition of the liquid phase is in agreement with experiments. The computed vapor phase densities of each isomer showed an effect on the predicted composition of the vapor phase of the mixture.

Unfortunately, the Monte Carlo code used to calculate the vapor-liquid equilibrium contained an error in the acceptance rule for molecule transfer in multi-component mixtures.

The Continuous Fractional Component (CFCMC) [1–3] algorithm in the Gibbs ensemble adds an extra molecule –the fractional molecule– per molecule type. In the CFCMC algorithm, trial moves are attempted to transform a fractional molecule of type  $a$  in box  $i$  to a whole molecule and, simultaneously, transform a molecule of type  $a$  in box  $j \neq i$  to a fractional molecule. These trial moves should be accepted according to Ref. [1]:

$$\text{acc}(o \rightarrow n) = \min\left(1, \frac{N_{j,a}}{N_{i,a} + 1} \exp[-\beta\Delta U]\right)$$

where  $N_{j,a}$  is the number of molecules of type  $a$  in box  $j$ ,  $N_{i,a}$  is the number of molecules of type  $a$  in box  $i$ , and  $\Delta U$  is the energy difference between the old and the new configuration.

Unfortunately, what was implemented (incorrectly) in the computer code is:

$$\text{acc}(o \rightarrow n) = \min\left(1, \frac{N_j}{N_i + 1} \exp[-\beta\Delta U]\right)$$

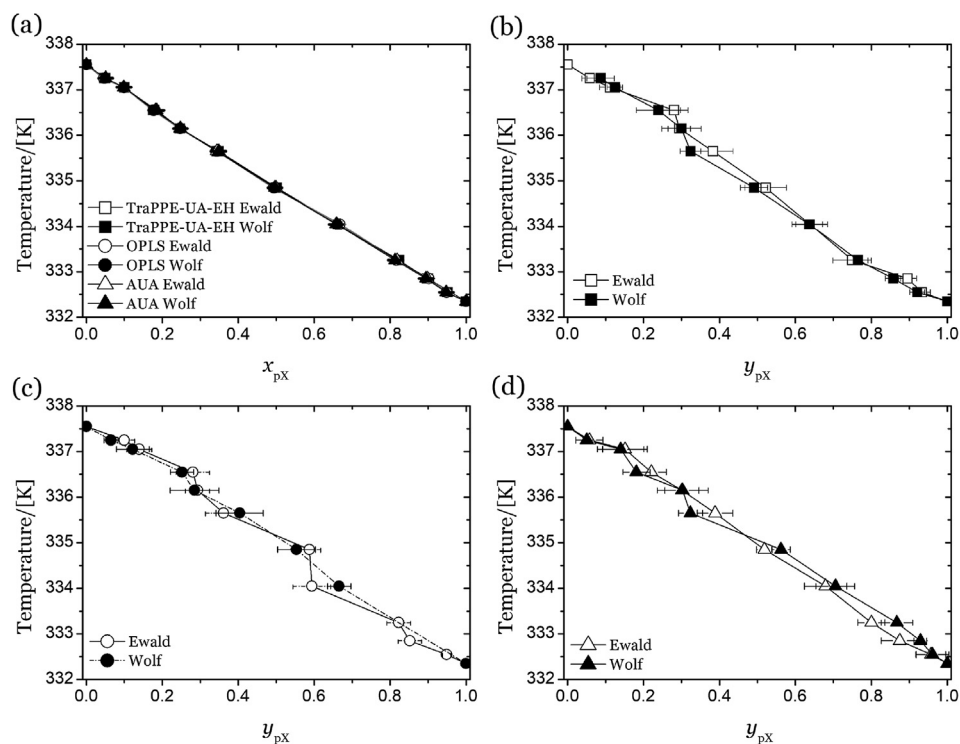
where  $N_i$  and  $N_j$  are the total number of molecules of all types in box  $i$  and  $j$ , respectively, and not only of type  $a$ . For the simulation of a single component,  $N_{j,a} = N_j$  and  $N_{i,a} = N_i$ . Therefore, the mistake in the acceptance rule only affects the simulations that include more than one component. As such, Figs. 1, Fig. 2, Fig. 3, Fig. 4, and Table 1 of the article are not affected by this error. This error was hard to detect for xylene isomers, as the boiling point of these isomers are close, and therefore  $N_{j,a}/N_{i,a}$  is close to  $N_j/N_i$ . The corrected code has been tested to yield the same results as the RASPA software [4,5] for various multi-component systems.

The phase composition diagram using the correct code is shown in Fig. 5. The observations based on the incorrect results remain. The composition of the liquid phase is not affected by the choice of force field or method for electrostatic interactions. For all the force fields, the correct vapor phase composition calculated with the Ewald and the Wolf methods are closer than in the incorrect simulations. In the incorrect results, the largest difference between vapor phase composition calculated with the Wolf and the Ewald method was 0.089 [mol/mol]. In the correct results, this difference is reduced to 0.067 [mol/mol].

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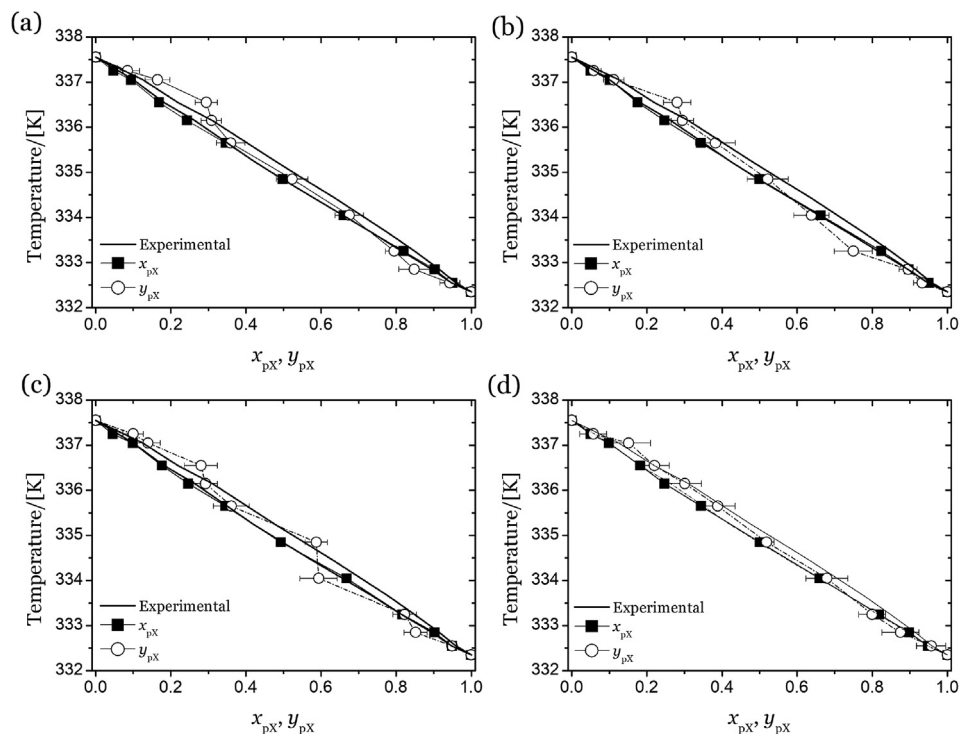
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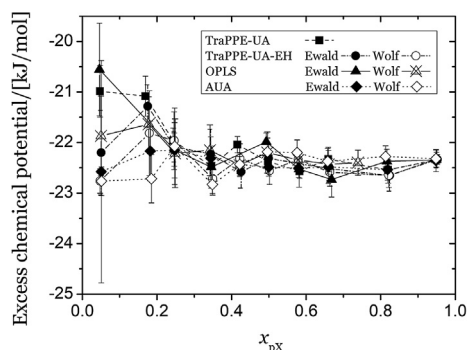
**Fig. 5.** Phase composition diagrams of the p-xylene/o-xylene binary mixture at 6.66 kPa using the Wolf and Ewald methods. (a) Liquid phase composition for TraPPE-UA-EH, OPLS and AUA force fields. Vapor phase composition for (b) TraPPE-UA-EH, (c) OPLS, and (d) AUA.  $x_{pX}$  is the mole fraction of pX in the liquid phase.  $y_{pX}$  is the mole fraction of pX in the vapor phase. Closed and open symbols represent the values using the Wolf and the Ewald method, respectively.

The predicted composition of the liquid phase is in excellent agreement with the experimental data. The correct simulations of the vapor phase compositions are closer to the experimental data than the incorrect simulations. The simulations with the incorrect acceptance rules showed an azeotrope behaviour that is not present in the correct simulations of the phase compositions.



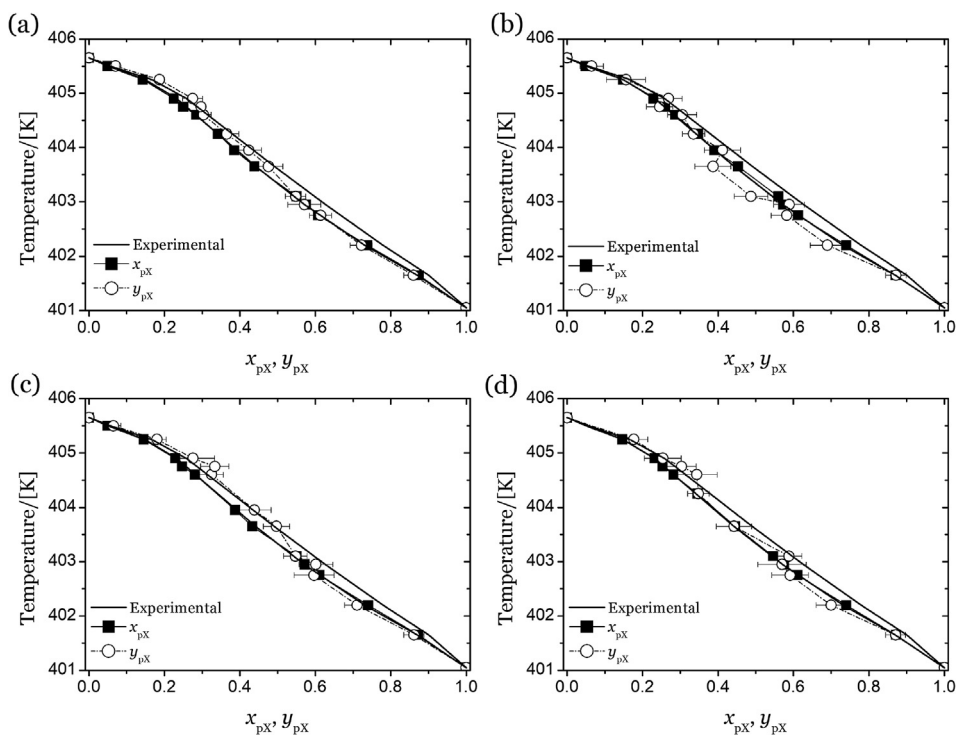
**Fig. 6.** Phase diagram of the p-xylene/o-xylene binary mixture at 6.66 kPa for (a) TraPPE-UA, (b) TraPPE-UA-EH, (c) OPLS, and (d) AUA, calculated using the Ewald method. Experimental data are from Llopis and Monton [6].  $x_{pX}$  (closed symbols) is the mole fraction of pX in the liquid phase.  $y_{pX}$  (open symbols) is the mole fraction of pX in the vapor phase.

The phase composition of the binary mixture and the excess chemical potential are not related. This is consistent with the observations from the incorrect simulations.



**Fig. 7.** Excess chemical potential ( $\mu_{pX}^e$ ) of p-xylene in the liquid phase of the pX/oX binary mixture at 6.66 kPa, as a function of the liquid phase composition for all force fields. The reference state for the excess chemical potential is the ideal gas. Closed and open symbols denote the use of the Ewald and the Wolf methods, respectively.

The predicted composition of the liquid phase is in excellent agreement with the experimental data. The correct simulations of the vapor phase compositions are closer to the experimental data than the incorrect simulations. The simulations with the incorrect acceptance rules showed an azeotrope behaviour that is not present in the correct simulations.



**Fig. 8.** Phase diagram of the p-xylene/o-xylene binary mixture at 81.3 kPa for (a) TraPPE-UA, (b) TraPPE-UA-EH, (c) OPLS, and (d) AUA, calculated using the Ewald method. Experimental data are from Parvez et al. [7].  $x_{pX}$  (closed symbols) is the mole fraction of pX in the liquid phase.  $y_{pX}$  (open symbols) is the mole fraction of pX in the vapor phase.

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