

COMMENTS

Comment on “Molecular Dynamics Simulation of the Liquid/Vapor Interface of Aqueous Ethanol Solutions as a Function of Concentration”

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Recently, Stewart et al. published a paper on molecular dynamics (MD) simulation of the liquid/vapor interface of aqueous ethanol solutions with various concentrations.¹ Their results provided us valuable information on the liquid/vapor interface of aqueous ethanol solutions. The authors compared the simulated surface tension with the experimental data and concluded that the combination of the OPLS all-atom (OPLS/AA) potential function for ethanol and the extended simple point charge (SPC/E) potential for water can both qualitatively and quantitatively describe the liquid/vapor interface of aqueous ethanol solutions with various concentrations. However, the agreement of the simulated and experimental surface tensions is not very good, especially in low concentrations, as shown in Figure 1. The simulated surface tensions are smaller than the measured values of pure water and pure ethanol, but larger than the measured values of water–ethanol solutions with mole fraction lower than 0.6. The authors argued that this departure is because these two potentials were not developed to work together. In fact this departure between the simulated and experimental surface tensions in ref 1 is mainly caused by the use of a “traditional definition” of concentration for the MD simulation system. Traditionally, in both experiments and MD simulations, concentration has been defined as the number of moles of solute A versus the total number of moles of solution (solute A + solvent B) in a given volume.³ Here we show the remarkable error caused by such a “traditional definition” of concentration in MD simulations and propose an alternative to define concentration in MD simulations of liquid solutions.

To compare the simulated and experimental surface tension, the simulated system and real macrosystem should have same concentrations in the interface and bulk phase. In an MD simulation system, due to the enrichment of the ethanol in the interface and the limited system size, the bulk phase concentration is remarkably different from the total average concentration, as shown in Figure 3 in ref 1. Moreover, the system size also affects the bulk phase concentration. For a specific average concentration, a larger size of the simulation system will decrease the influence of the enrichment of ethanol on the bulk phase concentration. In contrast, the volume of the interface in a real macrosystem is negligible compared to the volume of the bulk phase; therefore the enrichment of ethanol in the interface almost has no influence on the bulk phase concentration. Take a 1 cm³ cubic water–ethanol solution as an example, the thickness of the interface is about 1 nm, thus the volume of the interface is of the order of magnitude of 10⁻¹³ m³ and the volume of the bulk phase can be regarded as the total volume

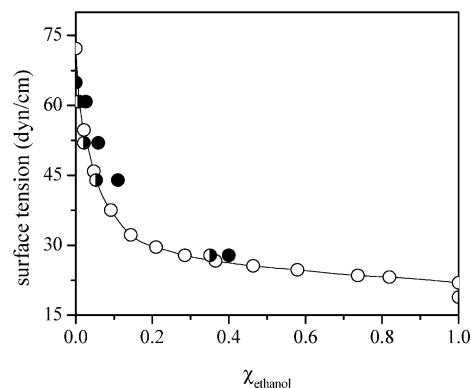


Figure 1. Surface tension of aqueous ethanol solutions as a function of ethanol concentration at 298 K. (χ is the mole fraction. The open circles are the experimental data.² The closed circles are the simulated values of Stewart et al.¹ The semi-open circles are the values calculated from those of Stewart et al. with concentration correction.)

of the solution, 10⁻⁶ m³. With the consideration that the enrichment of ethanol is more remarkable in low concentrations, we estimate the influence of the enrichment on the concentration of the bulk phase in a very low concentration, say mole fraction of 10⁻³. The total amount of the ethanol in the system is about 5.6×10^{-5} mol, and the amount of ethanol in the interface is of the order of magnitude of 10⁻⁸ mol. The above estimation shows that the bulk phase concentration in a real macrosystem is almost equal to the total average concentration as long as the average concentration is not extremely low (say, 10⁻⁵ mol).

From the above discussion, we can see that the influence of ethanol enrichment in the solution/vapor interface on the concentration of the bulk phase is much different for a simulation system than a real macrosystem. Thus, Figures 3A–D in ref 1 actually do not correspond to ethanol mole fractions of 0.026, 0.059, 0.11, and 0.40 as the authors claimed. Assuming that the MD simulation correctly predicts the enrichment of ethanol in the interface, a simulation system should correspond to a real macrosystem with the same concentration of the bulk phase as the simulation system. For a real macrosystem, the concentration of the bulk phase can be regarded as the total average concentration. We can calculate from the data points given by Stewart et al. that ethanol mole fractions of the bulk phase in Figures 3A–D in ref 1 are approximately 0.006, 0.022, 0.053, and 0.351. For comparison, the simulated surface tensions by Stewart et al. are plotted in Figure 1 with respect to the corrected concentration. The agreement of the simulated and experimental surface tension is remarkably improved. This result also shows that although SPC/E and OPLS/AA potentials were developed for H₂O and ethanol molecules, respectively, these two potentials do work well for predicting the surface tension of aqueous ethanol solutions with various concentrations.

References and Notes

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