

Raman Spectroscopy and Molecular Dynamics Simulations of Aqueous Two-Phase Systems for the Purification of Phosphoric Acid:Supplementary Information

Guadalupe Falcon-Millan,^a J. Antonio Reyes-Aguilera,^b
Teresa A. Razo-Lazcano,^a A. Ramírez-Hernández,^{c,d}
Julio C. Armas-Perez^{*b} and M. Pilar Gonzalez-Muñoz^{*a}

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1 Molecular dynamics Simulations

Simulations were setup considering that all bonds involving hydrogens were constrained by using the LINCS algorithm[1]. The cutoff distance for the nonbonded interactions was set to 1.2 nm. Long-range electrostatics were accounted by using the Particle Mesh Ewald (PME) method with grid spacing of 0.16 nm. The long-range dispersion correction was applied for energy and pressure. As a first step, simulations in the canonical ensemble (NVT) were performed with simulations running for 20 ns for an initial equilibration. The density was set at values 20% lower than the reference density obtained in experiments to help equilibrate the sample. Subsequently, isobaric-isothermal (NPT) simulations were performed to reach a pressure of 1 bar. NPT simulations were run for 50 ns, long enough to reach the target pressure. Finally, a second series of NVT simulations were performed, these ran for a total time of 100 ns. The integration time step for all simulations was set at 1 fs. All systems were equilibrate at a temperature of 298 K and a pressure of 1 bar. For equilibration, the Berendsen barostat, with a coupling constant of 1 ps, was used, and temperature coupling was done by using the Berendsen thermostat with a coupling constant of 0.5 ps, which has been extensively used in molecular dynamics simulations. For simulations in the production stage, the Nosé-Hoover and Parrinello-Rahman were used as thermostat and barostat, respectively. The volume of the simulations box for each system was around 1000 nm³ and the shape of the simulation box was cubic.

In order to make a cross-validation between experimental data and simulations results for some solutions studied in this work, we proposed different experiments "in silico". Firstly, we carried out simulations for Na_2SO_4 molecules dissolved in water (TIP4P/2005 model was used in all solutions to represent water molecules) at various concentrations, describing molecular interactions using the Madrid-2019 force field which has been validated by Zeron *et. al.* [2] previously. For our validation, we compared density values obtained from simulations and calculated the relative error respect to experimental data measured by our group. In Figure 1 shows that the error associated for this first case is less than 5%.

Furthermore, we follow a similar procedure for a solution of PEG1000 at different molarities. For this case, we have compared with experimental data obtained from literature[3, 4, 5], as well as densities measured in our group. As it is shown in Figure 2, the comparison between the density obtained from the experiments and simulations is in good agreement with a relative error of less than 2% too. As a complement for this comparison, we simulated related systems, but we have included a fixed concentration of Na_2SO_4 in the solution. In Figure 3 shows experimental and simulation density results as a function of PEG polymer molarity. Experimental values were measured directly by our research group. In addition, we have included as an inset a plot with relative errors between experimental and simulation results. We found that even for the highest concentration of PEG1000, the relative error between them is less than 3%.

Later, a new cross validation data was made for a solution of H_3PO_4 at different concentrations. In Figure 4, we can see that there is an excellent agreement between real (reported by Egan *et. al* [6]) and calculate density values for H_3PO_4 solutions. Finally, it was verified that the force field used was suitable for a solution composed of a fixed molarity of PEG1000, Na_2SO_4 , and different concentrations of H_3PO_4 similar to reported in the experimental section. Figure 5 shows the comparison between the experimental and calculated densities. As we report in Table 1 in the main paper, the highest relative error value found it was 2.2%.

In Figures 6 and 7, we reported the number of contacts, as well as the minimum contact distance, calculated between carbon and oxygen atoms of PEG polymer-chains respect to different molecules present in the system. To obtain the normalized number of contacts reported in the supplementary material, the value calculated was divided by the product of the total number of PEG chains and the total number of molecules of the chemical species involved. Those results show that there are not important contributions from other types of interactions, even increasing concentration of H_3PO_4 .

References

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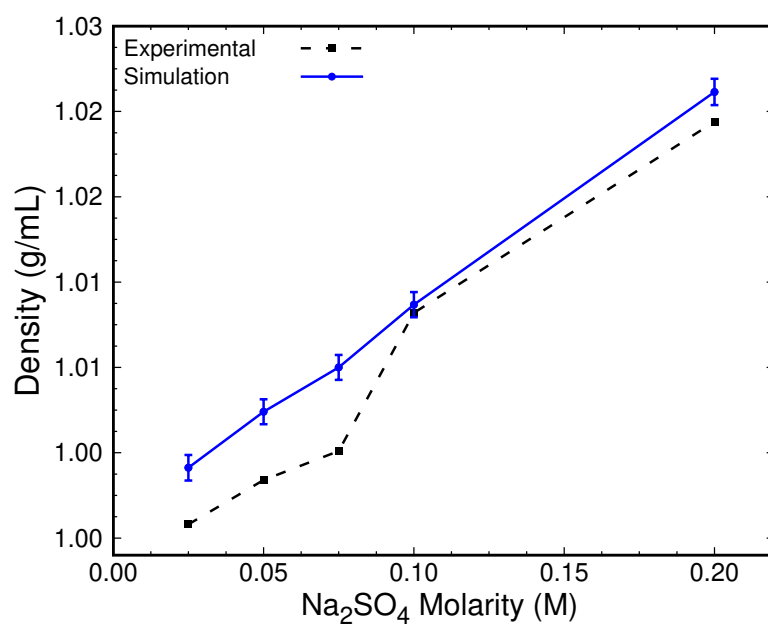


Figure 1: Comparison of density values of Na₂SO₄ dissolved in aqueous solution obtained from experimental data (dashed line, squares) and molecular dynamics simulations (solid line, circles), as a function of Na₂SO₄ molarity.

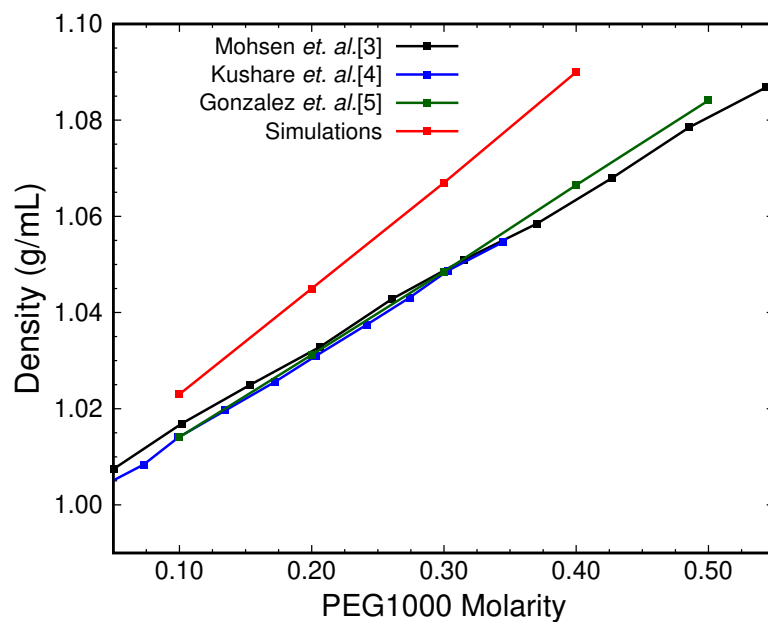


Figure 2: Comparison of density values for an aqueous solution of PEG polymer. Experimental data were obtained from Gonzalez-Tello *et. al.*[3] (black), Kushare *et. al.*[5] (blue) and Mohsen *et. al.*[4] (green). Densities values obtained from MD simulations are shown in red, as a function of PEG1000 Molarity.

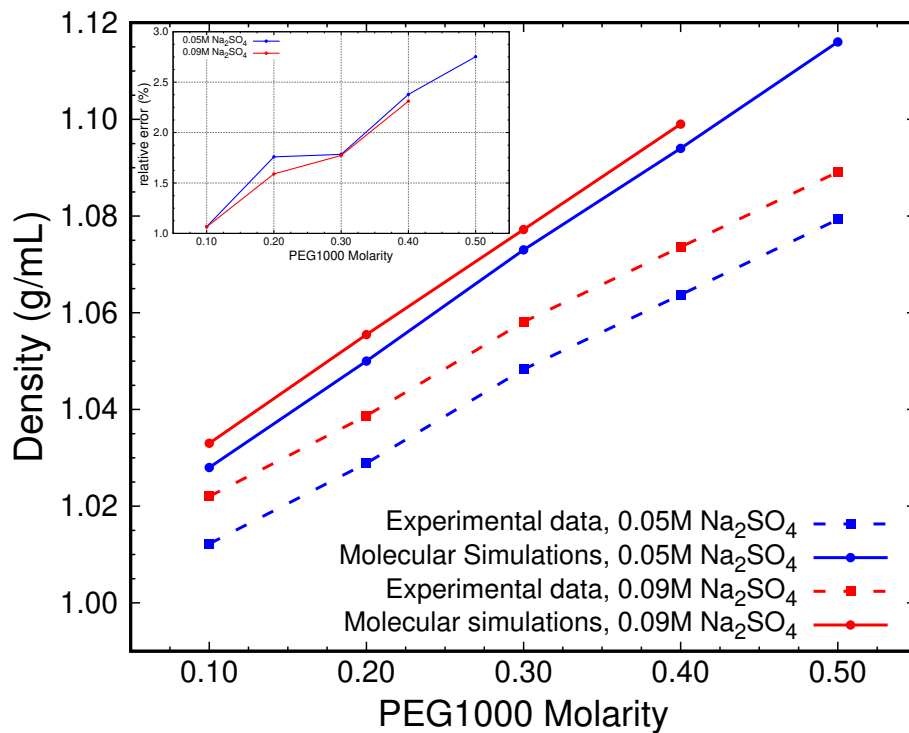


Figure 3: Comparison of density values for an aqueous solution of PEG1000 and a fixed concentration of 0.05M (blue) and 0.09M (red) Na₂SO₄ obtained from experimental data (dashed line, squares) and molecular dynamics simulations (solid line, circles), as a function of PEG1000 Molarity.

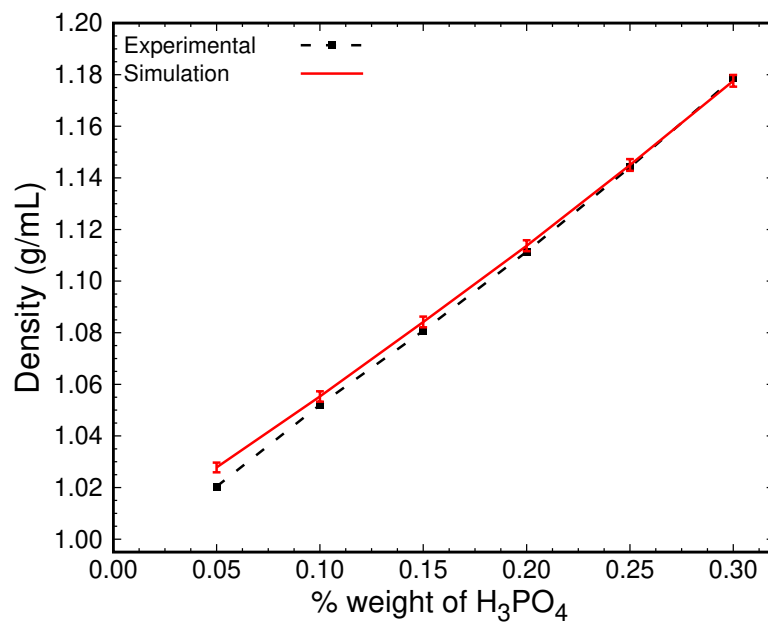


Figure 4: Comparison of density values for an aqueous solution of H₃PO₄ from experimental data obtained from Egan *et. al.*[6] (dashed line, squares) and molecular simulations (solid line, circles), as a function of H₃PO₄ concentration.

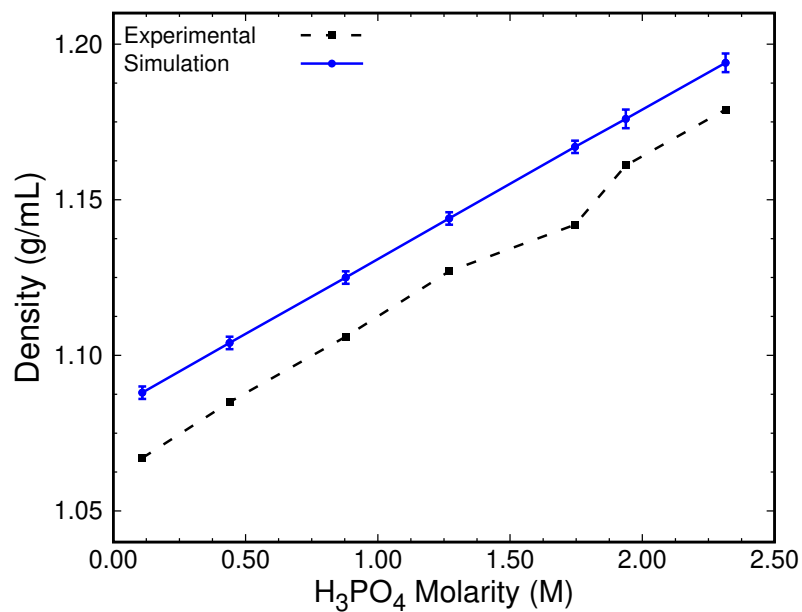


Figure 5: Comparison of density values for an aqueous solution with fixed concentration of PEG1000 and sodium sulfate (at 0.33M and 0.09M respectively) obtained from experimental data (dashed line, squares) and molecular simulations (solid line, circles), as a function of H₃PO₄ molarity.

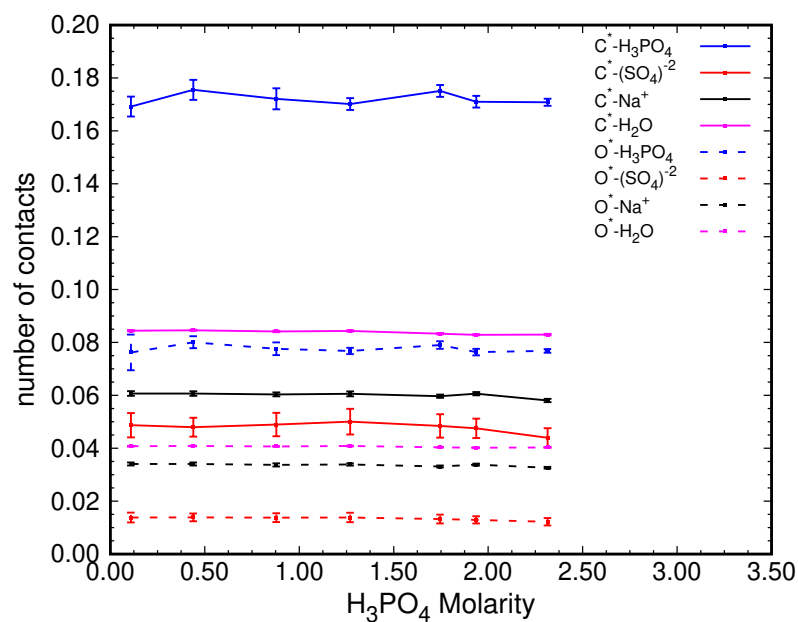


Figure 6: Number of contacts between carbon (solid lines) and oxygen (dash lines) atoms of PEG polymer chains and the different molecules present in the system: H_3PO_4 (blue), SO_4^{2-} (red), Na^+ (black) and H_2O (magenta), as a function of H_3PO_4 molarity.

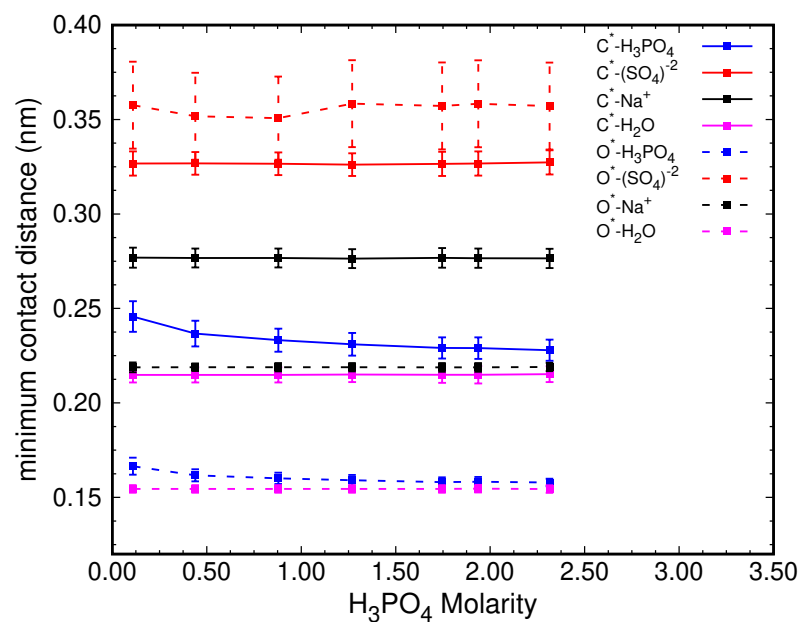


Figure 7: Minimum contact distance between carbon (solid lines) and oxygen (dash lines) atoms of PEG polymer chains and the different molecules present in the system: H₃PO₄ (blue), SO₄⁻² (red), Na⁺ (black) and H₂O (magenta), as a function of H₃PO₄ molarity.