

# Propensities of Oxalic, Citric, Succinic, and Maleic Acids for the Aqueous Solution/Vapour Interface: Surface Tension Measurements and Molecular Dynamics Simulations

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## Abstract

Behaviour of oxalic, citric, succinic, and maleic acids at the air/water interface is characterized and quantified by surface tension measurements in a broad concentration range and molecular dynamics simulations in slab geometry employing a polarizable force field. The relative order of surface propensities of these atmospherically relevant acids is established in this study with results being also in a very good agreement with previous measurements.

## I. Introduction

Simple soluble organic (aliphatic and aromatic) acids are ubiquitous components of the biosphere and troposphere.<sup>1-8</sup> The composition and concentration of water-soluble organic acids in soil, water and troposphere vary and depend on many factors. Low molecular weight aliphatic organic acids (AOA) make an important contribution in the aquatic system.<sup>7,9</sup> These acids are produced by degradation of organic matter, as root exudates, and are also released by microbes.<sup>10-13</sup> The concentration of aliphatic monocarboxylic acids in soil (cultivated or forested) is higher ( $\leq 1$  mM) than that of dicarboxylic acids, the concentrations of which are  $\leq 50$   $\mu$ M.<sup>6</sup> In aquatic ecosystem the concentration of dissolved organic matter is  $\sim 100$  parts per million, which includes mono- and dicarboxylic acids, dicarboximides, pyridine carboxylic acids, sulfonic acid, and both aliphatic and aromatic hydrocarbons.<sup>5</sup> In the troposphere the most abundant dicarboxylic acids are oxalic acid ( $\sim 500$  ng m<sup>-3</sup>), followed by malic acid ( $\sim 60$  ng m<sup>-3</sup>), maleic acid ( $\sim 50$  ng m<sup>-3</sup>), and succinic acid ( $\sim 35$  ng m<sup>-3</sup>).<sup>8</sup>

The AOA are surface-active in nature and significantly affect the surface tension of aquatic system and of cloud droplets.<sup>14-19</sup> AOA play an important role in mobilizing metal micronutrient, enrichment of soil microorganism, and arresting and immobilizing harmful elements.<sup>13</sup> In addition, AOA in the troposphere significantly affect the aerosol particles, formation and growth of clouds and fog, having thus an impact also on climate change.<sup>3,4</sup> To this end, efforts are directed toward for understanding the climatic consequences of organics in the troposphere.<sup>20,21</sup>

To understand the role of AOA in the formation and growth of aerosol particle and condensation nuclei for cloud droplets, surface tensions of aqueous solutions of pure organic acids (mono- and dicarboxylic aliphatic acids and hydroxybenzoic acid) and mixtures thereof are needed for simulating the surface tension of real cloud and fog droplets.<sup>16,17,19</sup> Di- and tricarboxylic acids, e.g., citric, maleic, oxalic, and succinic acids are also ubiquitous in the troposphere and biosphere and their interfacial properties and propensities for the solution/vapour interface are essential parameters for understanding the water/cloud droplets formation. In our earlier publication<sup>22</sup> we examined the surface propensity of formate, acetate, benzoate, which are all anions of the corresponding monocarboxylic acids. The present AOAs with ionisable multicarboxylic groups and different molecular conformations may exhibit different surface propensities. Therefore, in this paper we report experimental surface tension measurements in conjunction with molecular dynamics (MD) simulations of aqueous solutions of these acids. Simulations allow for understanding of the microscopic picture of distributions and orientations of di- and tricarboxylic acids at the free solution surface, which can shed more light on the microscopic nucleation behaviour of the cloud/aerosol droplets.

## II. Material and Methods

Citric (> 99.5%, Qualigens Fine chemicals, India), Maleic (> 99.5 %, Merck, India), Oxalic (>99.5 %, BDH, India), and Succinic acids (> 99 %, sd fine-chem, India) were used without further purification. Each solution was prepared fresh using double-distilled water in mol.dm<sup>-3</sup> concentration unit. The surface tension,  $\gamma$ , of all solutions was measured with a Dynamic Contact Angle Meter and Tensiometer, DCAT-11 (Dataphysics, Germany) using the Wilhelmy platinum-iridium plate, type PT-11, of

thickness 0.2 mm and area 3.98 mm<sup>2</sup> with an accuracy  $\pm 1.5\%$  at 298.15 $\pm$ 0.02 K. The test solution was taken in a glass vessel (Duran, Germany) of 85 ml capacity and was placed in the receptacle. The temperature of the solution was maintained by circulating liquid through a receptacle from a RLS6D (Lauda, Germany) thermostat.

### III. Computational details

Classical MD simulations of citric, maleic, oxalic, and succinic acids solutions were performed in aqueous slabs. In order to construct the slab a (tetragonal) prismatic box of  $30 \times 30 \times 100 \text{ \AA}^3$  was used. It contained 863 water molecules and 16 - 64 citric, malonic, oxalic, or succinic acid molecules yielding approximately 1-4 molar solutions. Application of periodic boundary conditions at a constant volume with such a unit cell leads to an infinite slab with two water/vapour interfaces perpendicular to the z-axis.<sup>23</sup> The non-bonded interactions were cut off at 12  $\text{\AA}$  and long-range electrostatic interactions were accounted for using the particle mesh Ewald procedure.<sup>24</sup> All systems were first minimized (10,000 steps of steepest descent minimization) in order to avoid bad contacts and subsequently equilibrated for several hundreds of picoseconds before a 2 ns production run. All simulations were performed at 300 K with a time step of 1 fs within the canonical (constant volume) ensemble. All bonds involving hydrogen atoms were constrained using the SHAKE algorithm.<sup>25</sup> Geometries and energy data were saved for further analysis every 500 steps. Surface tensions were evaluated as  $\gamma = (1/2)L_z \langle P_{zz} - (P_{xx} + P_{yy})/2 \rangle$ , where  $P_{ii}$  are the diagonal components of the pressure tensor,  $L_z$  is the length of the simulation cell in the direction normal to the interface, the angular brackets denote time averaging, and the prefactor of 1/2 reflects the presence of two interfaces in the slab.

A polarizable force field was employed in all MD simulations. For water, we used the POL3 model.<sup>26</sup> For the acid molecules we employed the general amber force field (GAFF) parameter set.<sup>27</sup> All MD calculations were performed using Amber 8 program.<sup>28</sup> Fractional charges for the anions were evaluated using the standard RESP procedure employing the Gaussian 03 package.<sup>29</sup>

## IV. Results and discussion

### *Experimental*

Surface tensions of all aqueous citric, maleic, oxalic and succinic acids solutions at 298.15 K are presented as functions of concentration in Figure 1. To exclude a possible effect of impurities we also measured the surface tension of aqueous solutions of a recrystallised and dried oxalic acid (data shown in Figure 1). The measured surface tension of these acids solutions are comparable within  $\pm 0.8\%$  of the literature data.<sup>14,17</sup> All four investigated acids behave like surface-active agents, but unlike typical surfactants, which decrease the surface tension of water by many fold at mM concentration or less.<sup>22,30</sup> The capacity of these acids to decrease surface tension of aqueous solutions are compared at  $\sim 0.5$  M and follows the order: oxalic acid < citric acid < succinic acid  $\sim$  maleic acid.

The measured surface tension ( $\gamma$ ) curves were fitted to the equation by Chuxi et al.,<sup>31</sup> which was parametrized for binary system<sup>14</sup>

$$\gamma = \gamma_2(1-x) + \gamma_1x - RTx(1-x) [A/(x+B(1-x)) + C/(Dx+(1-x))], \quad (1)$$

where  $\gamma_1$  and  $\gamma_2$  are the surface tensions of pure solute and solvent,  $A$ ,  $B$ ,  $C$ , and  $D$  are the adjustable parameters,  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $x$  is the mole fraction of a solute. This equation is applicable to entire concentration range, i.e., from pure solvent to pure solute. The molar concentration was converted to mole fraction using density data from literature.<sup>14,32</sup> We fitted the surface tension data to eq 1 taking  $\gamma_2 = 72.12 \text{ mN m}^{-1}$  for water (Figure 2). In both cases the fittings of eq 1 are excellent. The results of the fit (see Figure 2 and Table 1) are in a very good agreement (within  $\pm 0.25\%$ ) with the literature data.<sup>14,17</sup> However, our predicted surface tensions of pure acids (i.e., at  $x = 1$ ), are 9-17 % lower than the literature values<sup>14</sup> (except citric acid for which no literature data is available). This small deviation may be due to the limited concentration range investigated in the present study which ends well before the pure acid. Nevertheless, the estimated surface tensions of four aqueous acid solutions agree well with the measured data (Figure 2 and Table 1).

The surface propensities of the aqueous citric, maleic, oxalic, and succinic acids for the solution-vapour interface were evaluated using the Gibbs adsorption isotherm,  $dy = -RT\Gamma d(\ln a)$ , where  $\Gamma$  is the surface excess in  $\text{mol m}^{-2}$  and  $a$  is activity. The reported density values of citric, maleic, oxalic, and succinic acids<sup>14,33</sup> were used for interconversion of molar and molal concentrations. Activities of four acids were estimated using osmotic coefficients<sup>34,35</sup> following the reported procedure<sup>36</sup> and activity coefficient.<sup>37</sup> The surface excess was estimated to be  $0.06 \times 10^{-6}$ ,  $0.43 \times 10^{-6}$ ,  $1.01 \times 10^{-6}$ , and  $2.41 \times 10^{-6} \text{ mol m}^{-2}$  for oxalic, succinic, citric, and maleic acids, respectively. The results demonstrate that the maleic acid reduces the surface tension of water by greater extent, which may be due to the presence of  $-\text{C}=\text{C}-$ , than that of other three acids and

least in the case of oxalic acid. The corresponding area per molecule,  $A$  ( $\text{\AA}^2/\text{molecule}$ ) =  $(\Gamma N)^{-1}$ , where  $N$  is the Avogadro number was 69, 164, 386, and 2767  $\text{\AA}^2/\text{molecule}$  and follows the order: maleic acid < citric acid < succinic acid < oxalic acid.

### ***Computational***

Surface propensity and its effect on the decrease surface tension of environmentally relevant aqueous oxalic, citric, succinic, and maleic acid solutions was studied by MD simulations in slab geometry at varying acid concentrations. Figure 3 shows typical snapshots of these four acid solutions at 0.25 M, which demonstrate that the solute molecules are both soluble and surface active in water.

Surface behavior of the investigated acids was quantified using density profiles, i.e., averaged distributions of solute and solvent molecules across the slab (Figure 4). Oxalic acid, which is the smallest acid among studied acids, has a weak surface propensity. Its density profile exhibits both surface and bulk solvation, which is demonstrated by sizable signal both in bulk and surface areas (Figure 4a). Density profile shows that citric acid, which possesses three carboxylic groups, has a tendency to solvate in the bulk and in the subsurface where it exhibits a concentration peak (Figure 4b). This acid shows a low surface propensity due to strong interaction of the three carboxylic groups with water molecules via hydrogen bonds. At higher concentrations, citric acid molecules tend to strongly aggregate and form clusters. Succinic acid has a stronger hydrophobic character than oxalic and citric acids and preferably solvates within surface and subsurface areas (Figure 4c). The strongest surface propensity to the air/water interface among the investigated acids is observed

for maleic acid, the density profile of which is presented in Figure 4d. This is likely due to its different (from the other investigated acids) interactions and orientation at the surface due to the presence of the  $-C=C-$  bond resulting in a reduced ability to form strong hydrogen bonds with water molecules.

According to the Gibbs adsorption isotherm, surface or subsurface active agents decrease the surface tension of water. This is also born from MD simulations of the four organic acids under investigation and the degree of interfacial propensity roughly correlates with the reduction of surface tension (see Table 2 for calculated surface tension differences from neat water at 0.25 M). It should be noted that surface tension data from MD simulations are subjected to both systematic and statistical errors. The systematic error is due to force field deficiencies and finite size effects. Note that standard force fields give surface tension values of neat water within 60 mN/m from the experimental value.<sup>38</sup> From this point of view the performance of the POL3 model of water with surface tension of approximately 55 mN/m is rather satisfactory. The statistical error is due to finite length of simulations and low compressibility of water, leading to large pressure fluctuations. Also due to pairing and clustering of solutes simulations can suffer from non-ergodic effects.<sup>22</sup>

## **Conclusions**

Surface behaviour of aqueous solutions of atmospherically relevant citric, maleic, oxalic, and succinic acids was investigated by means of surface tension measurements at varying concentrations, complemented by molecular dynamics simulations in slab geometry with polarizable potentials. All these acids are water-

soluble, exhibiting at the same time propensity for the air/water interface. The relative order of surface propensities of these atmospherically relevant acids is oxalic acid < citric acid < succinic acid ~ maleic acid. There is a satisfactory agreement between results of MD simulations and surface tension measurements, the latter being in accord with previous experiments.<sup>22</sup>

The measured surface tension decrease as function of concentrations and fits to the data will prove valuable for atmospheric model calculations of aerosol particle formation and growth. Also, the behaviour of the investigated acids at the air/water interface is now understood at an atomistic level thanks to molecular dynamics simulations. Further laboratory studies and simulations shall be directed to aqueous mixtures of these compounds as they occur in atmospheric aerosols.

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## References:

1. Saxena, P.; Hildemann, L. M. *J. Atmos. Chem.* **1996**, *24*, 57.
2. Chebbi, A.; Carlier, P. *Atmos. Environ.* **1996**, *30*, 4233.
3. Jacobson, M. C.; Hansson, H. -C.; Noone, K. J.; Charlson, R. J. *Rev. Geophys.* **2000**, *38*, 267.
4. Glasius, M.; Lahaniati, M.; Calogirou, A.; Di Bella, D. *Environ. Sci. Technol.* **2000**, *34*, 1001.
5. Pizzarello, S.; Huang, Y.; Becker, L.; Poreda, R. J.; Nieman, R. A.; Cooper, G.; Williams, M. *Science* **2001**, *293*, 2236.
6. Strobel, B. W. *Geoderma* **2001**, *99*, 169.
7. Jonsson, A.; Ström, L.; Åberg, J. *Biogeochem.* **2007**, *82*, 153 and references therein.
8. Hsieh, L. -Y. ; Kuo, S. -C. ; Chen, C. -L. ; Tsai, Y. I. *Atmos. Environ.* **2007**, *41*, 6648.
9. Thurman, E. M. *Organic geochemistry of Natural Waters*. Martinus Nijhoff/Dr W Junk Publishers, **1985**, p. 497.
10. Jones, D. L. *Plant Soil.* **1998**, *205*, 25.
11. Gadd, G. M. *Adv. Microbial Physiol.* **1999**, *41*, 47.
12. Ryan, P. R.; Delhaize, E.; Jones, D. L. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **2001**, *52*, 527.
13. Haoliang, L.; Chongling, Y.; Jingchun, L. *Environ. Expt. Bot.* **2007**, *61*, 159.
14. Hyvärinen, A.-P.; Lihavainen, H.; Gaman, A.; Vairila, L.; Ojala, M. K.; Viisanen, Y. *J. Chem. Eng. Data* **2006**, *51*, 255.

15. Riipinen, I.; Koponen, I.K.; Frank, G. P.; Hyvärinen, A.-P.; Vanhanen, J.; Lihavainen, H.; Lehtinen, K. E. J.; Bilde, M.; Kulmala, M. *J. Phys. Chem. A* **2007**, *111*, 12995.
16. Facchini, M. C.; Decesari, S.; Mircea, M.; Fuzzi, S.; Loglio, G. *Atmos. Environ.* **2000**, *34*, 4853.
17. Topping, D. O.; McFiggans, G. B.; Kiss, G.; Varga, Z.; Facchini, M. C.; Decesari, S.; Mircea, M. *Atmos. Chem. Phys.* **2007**, *7*, 2371.
18. Shulman, M. L.; Jacobson, M. C.; Chawson, R. J.; Synovec, R. E.; Young, T. E. *Geophys. Res. Lett.* **1996**, *23*, 603.
19. Tuckermann, R.; Cammenga, H. K. *Atmos. Environ.* **2004**, *38*, 6135.
20. IPCC (Intergovernmental Panel on Climate Change), Basis, Summary for Policymakers; IPCC Secretariat: Geneva, Switzerland, 2007; [http://ipcc-wg1.ucar.edu/wg1/doc/WG1AR4\\_SPM\\_Approved\\_05Feb.pdf](http://ipcc-wg1.ucar.edu/wg1/doc/WG1AR4_SPM_Approved_05Feb.pdf).
21. IPCC (Intergovernmental Panel on Climate Change), Basis, Summary for Policymakers; IPCC Secretariat: Geneva, Switzerland, 2001; [http://www.grida.no/climate/ipcc\\_tas/wg1/index.htm](http://www.grida.no/climate/ipcc_tas/wg1/index.htm).
22. Minofar, B.; Jungwirth, P.; Das, M. R.; Kunz, W.; Mahiuddin, S. *J. Phys. Chem. C* **2007**, *111*, 8242.
23. Wilson, M. A.; Pohorille, A. *J. Chem. Phys.* **1991**, *95*, 6005.
24. Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. *J. Chem. Phys.* **1995**, *103*, 8577.
25. Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. *J. Comput. Phys.* **1977**, *23*, 327.
26. Caldwell, J. W.; Kollman, P. A. *J. Phys. Chem.* **1995**, *99*, 6208.
27. Wang, J. M.; Wolf, R. M.; Caldwell, J. M.; Kollman, P. A.; Case, D. A. *J. Comput. Chem.* **2004**, *25*, 1157.

28. Case, D. A. D., T. A.; Cheatham, III, T. E.; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Merz, K. M.; Wang, B.; Pearlman, D. A.; Crowley, M.; Brozell, S.; Tsui, V.; Gohlke, H.; Mongan, J.; Hornak, V.; Cui, G.; Beroza, P.; Schafmeister, C.; Caldwell, J. W.; Ross, W. S.; Kollman, P. A. *Amber 8*; University of California: San Francisco, 2004.
29. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, Gaussian, Inc., Wallingford CT, 2004.
30. Van Os, N. M.; Haak, J. R.; Rupert, L. Rupert, L. A. *Physicochemical Properties of Selected Anionic, Cationic and Nonionic Surfactants*, Elsevier: New York, 1993.31.  
 Chunxi, L.; Wenchuan, W.; Zihano, W. *Fluid Phase Equilib.* **2000**, *175*, 185.
32. Lineberger, C. E. *J. Am. Chem. Soc.* **1898**, *20*, 128.
33. Levin, B. J. *J. Phys. Chem.* **1955**, *59*, 640.

34. Robinson, R. A.; Smith, P. K.; Smith, E. R. B. *Trans. Faraday Soc.* **1942**, *38*, 63.
35. Kirsch, T.; Maurer, G. *Ind, Eng. Chem.* **1996**, *35*, 1722.
36. Sardroodi, J. J.; Ahmadian, S. M. S.; Pazuki, G. R.; Sadr, M. H.; Esmaili, M. *Comp. Coupling Phase Diagram Thermochem.* **2006**, *30*, 326.
37. Apelblat, A.; Dov, M.; Wisniak, J.; Zabicky, J. *J. Chem. Thermodynamics* **1995**, *27*, 347.
38. Garrett, B. C.; Schenter, G. K.; Morita, A. *Chem. Rev.* **2006**, *106*, 1355.

**Table 1** Numerical values of the parameters of Eq. 1.

Acid	$\gamma_1$ (mN m <sup>-1</sup> )	$\gamma_2$ (mN m <sup>-1</sup> )	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	Std dev in $\gamma$
Oxalic	44.87	71.94	-0.2801	0.1172	2.669	11.87	0.16
Citric	47.30	72.15	-0.1769	0.0788	2.419	13.97	0.32
Succinic	45.20	72.01	-0.2455	0.0786	3.128	12.40	0.09
Maleic	44.37	71.97	-0.1310	0.0418	3.335	24.16	0.30

**Table 2** Calculated changes in surface tension of 0.25 M acid solutions compared to pure water.

<i>Acid</i>	$\Delta\gamma_1$ (mN m <sup>-1</sup> )
Oxalic	-1.1 ± 1.0
Citric	-2.1 ± 0.3
Succinic	-1.7 ± 1.6
Maleic	-4.2 ± 0.8

**Figure captions:**

**Figure 1** Surface tension isotherms vs molarity of citric, maleic, oxalic acid, and succinic acid at 298.15 K. Full symbols are values for the corresponding acids from Refs 17 and 14.

**Figure 2.** Surface tension isotherms vs mole fraction of citric acid, maleic acid, oxalic acid, and succinic acid at 298.15 K. Symbols are experimental and the solid lines are theoretical values from Eq 1.

**Figure 3.** Typical snapshots of slabs of 0.25 M aqueous solutions of (a) oxalic acid, (b) citric acid, (c) succinic acid, and (d) maleic acid. The two solution/vapor interfaces are at the top and bottom of the snapshots. Color coding: C – cyan, O – red, and H - white.

**Figure 4.** Density profiles of water oxygen, and the carbon and oxygen atoms of (a) oxalic acid, (b) citric acid, (c) succinic acid, and (d) maleic acid.

Figure 1

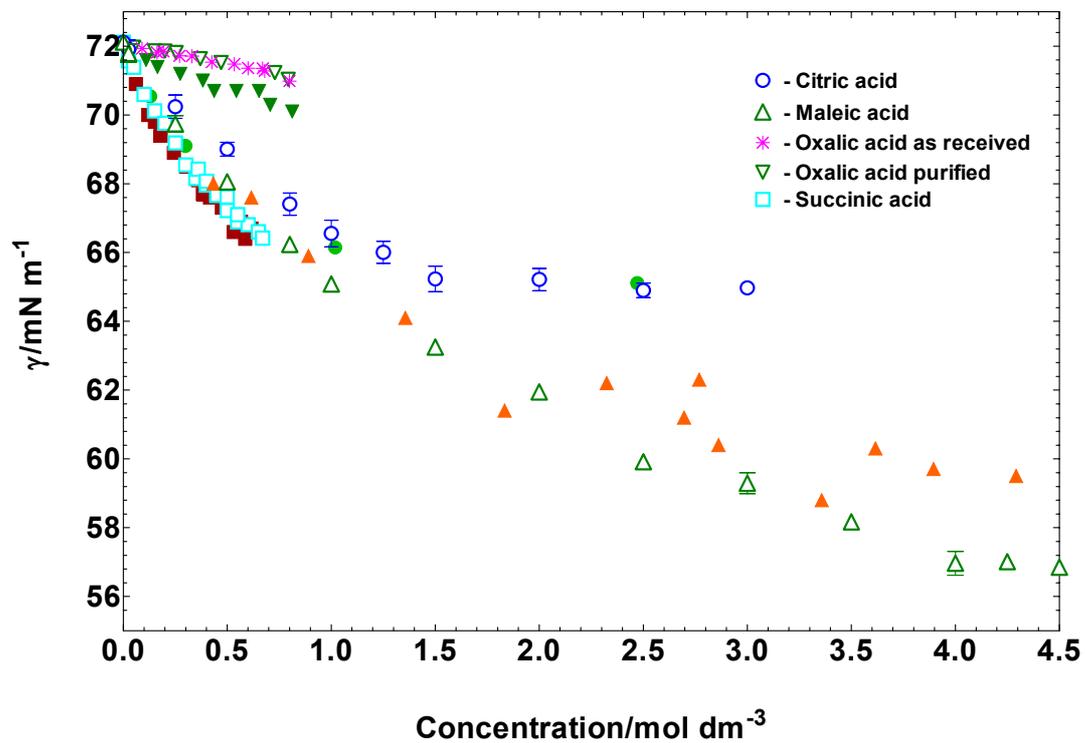


Figure 2

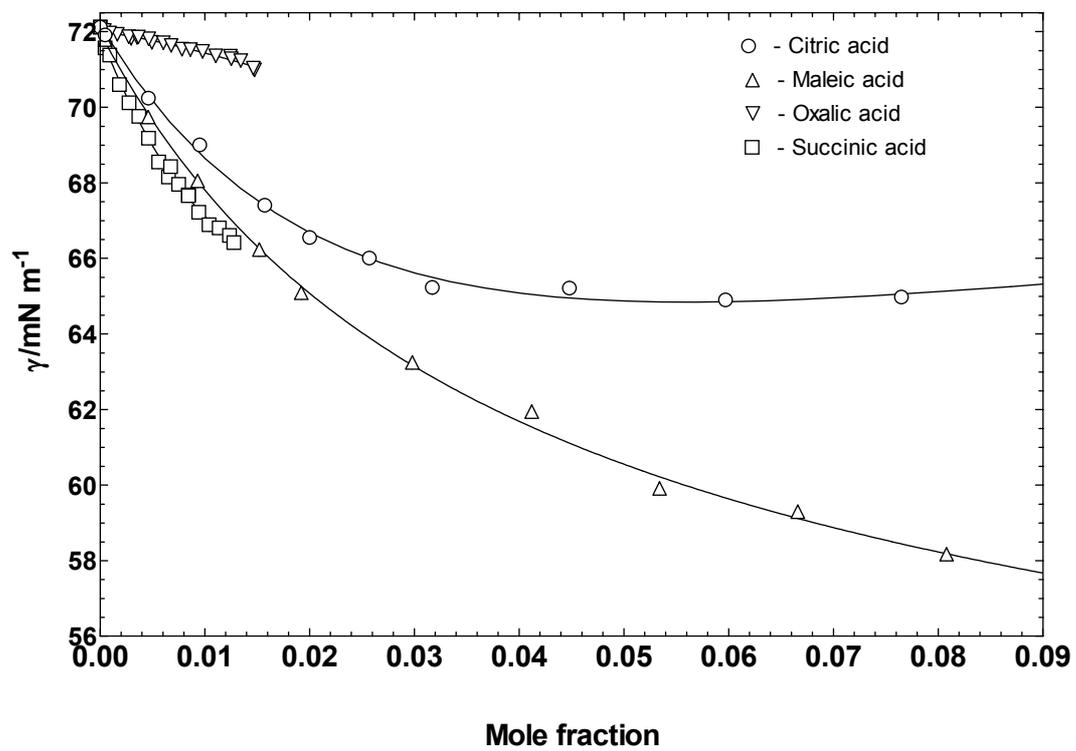


Figure 3a

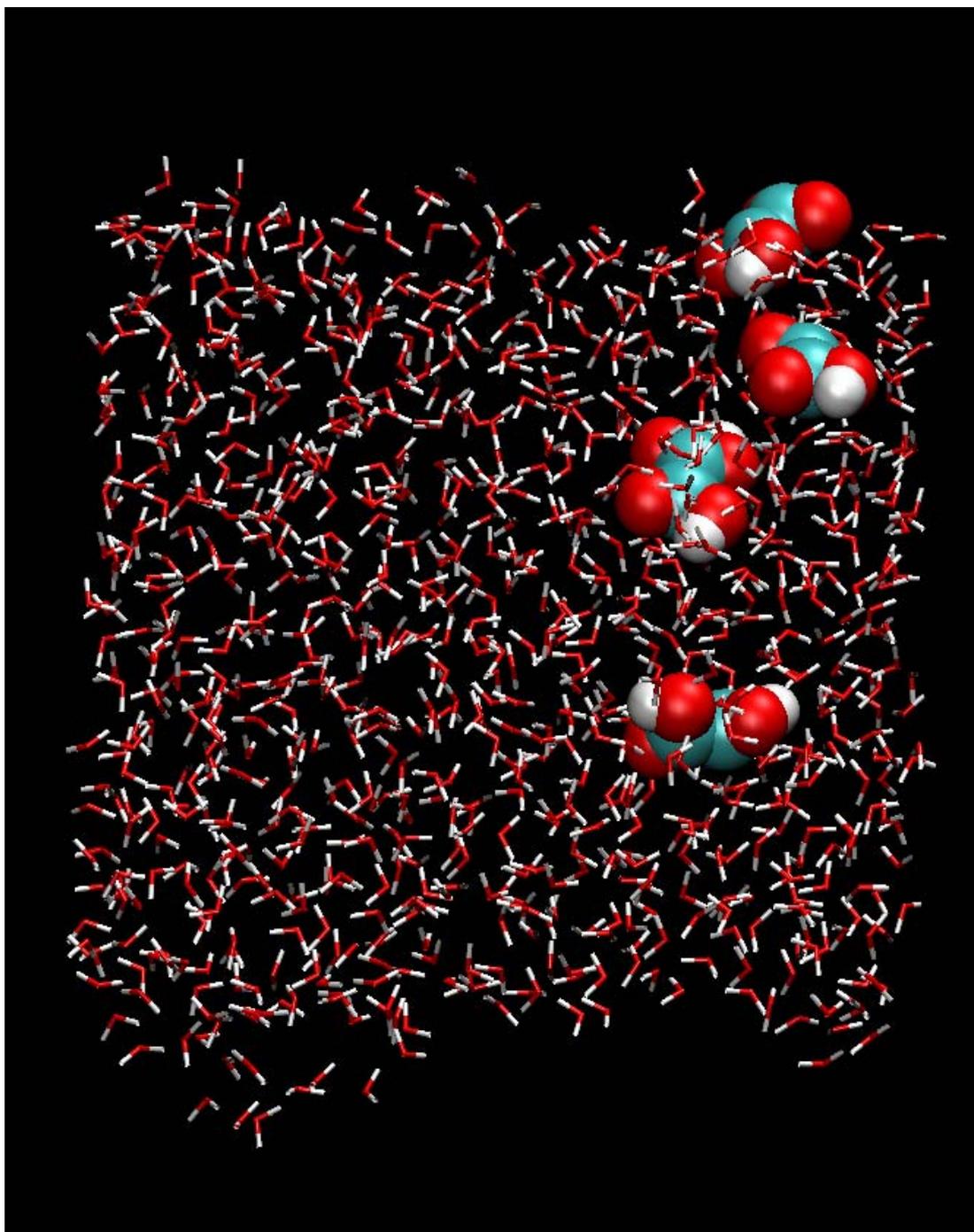


Figure 3b

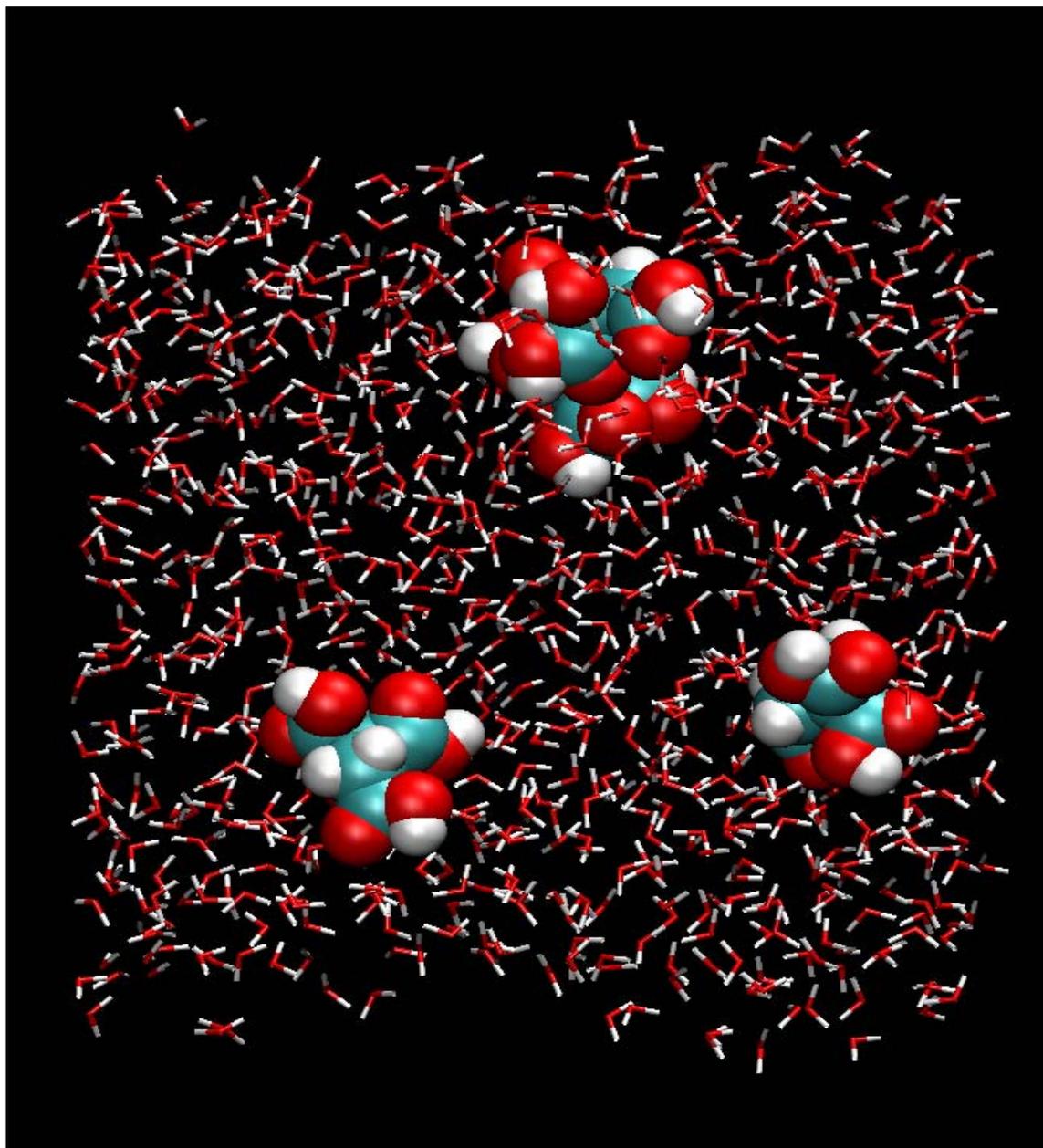


Figure 3c

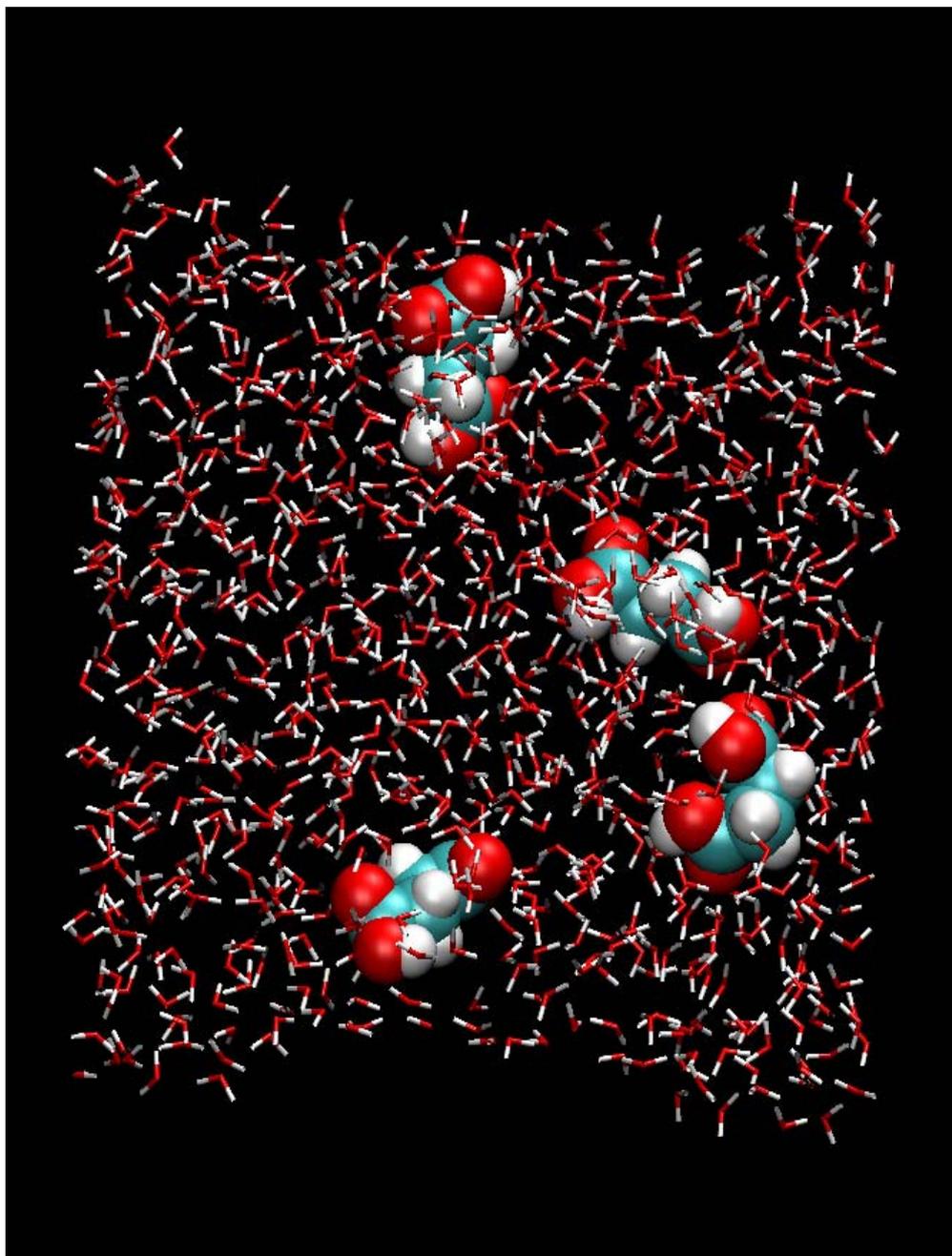


Figure 3d

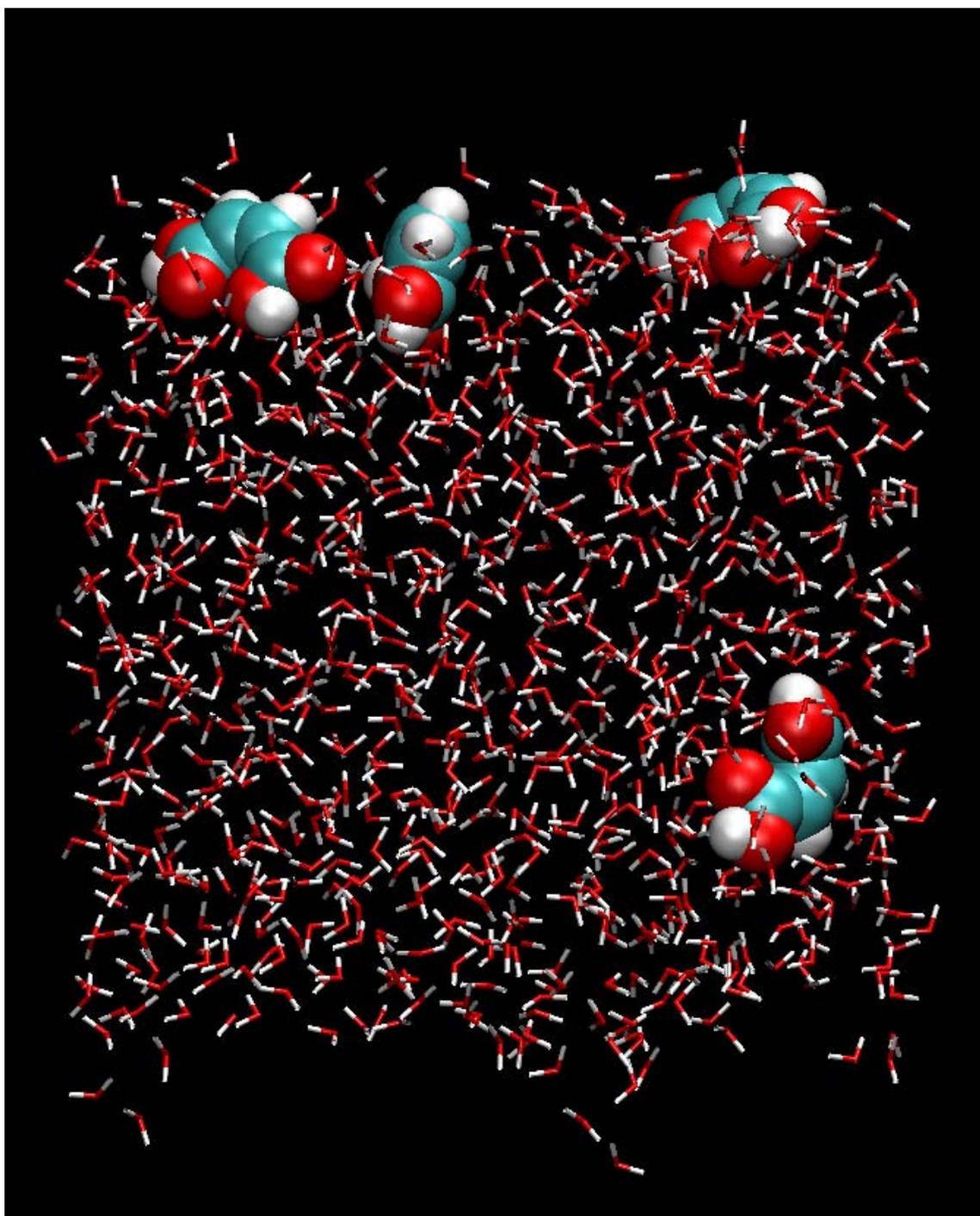


Figure 4a

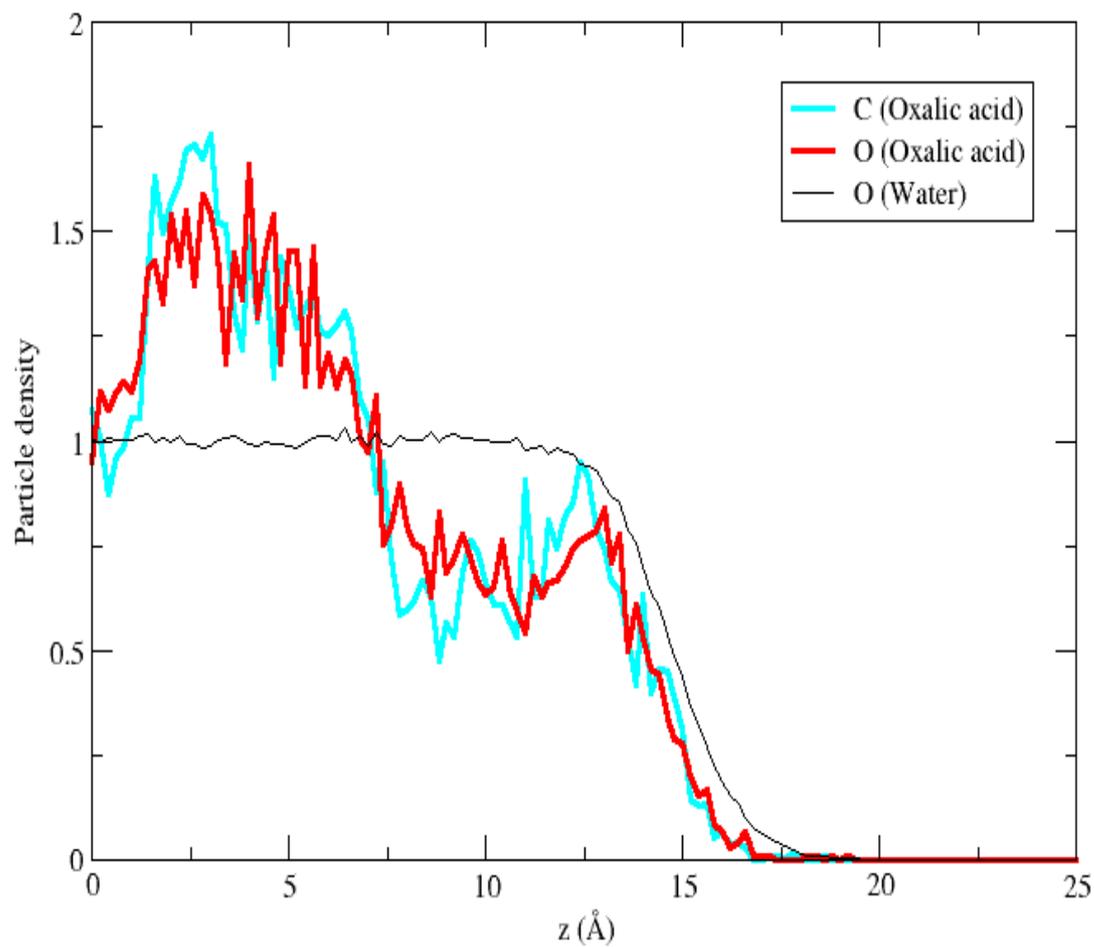


Figure 4b

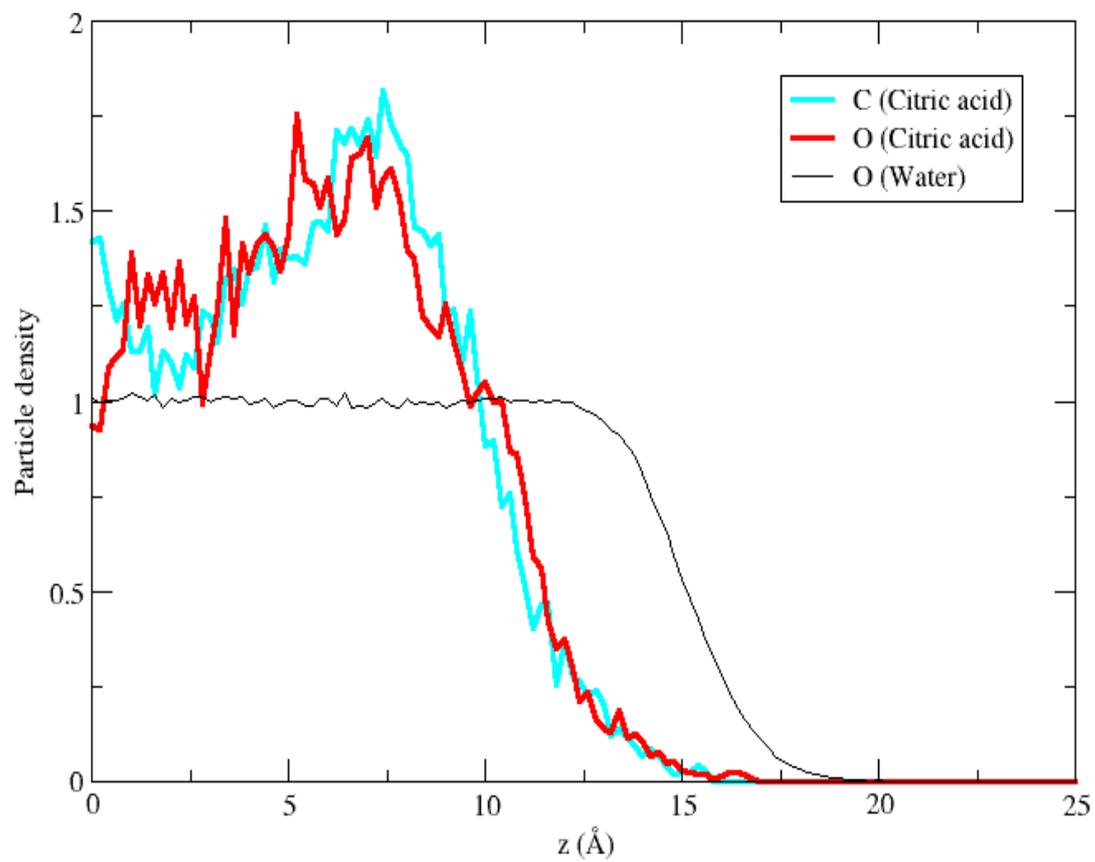


Figure 4c

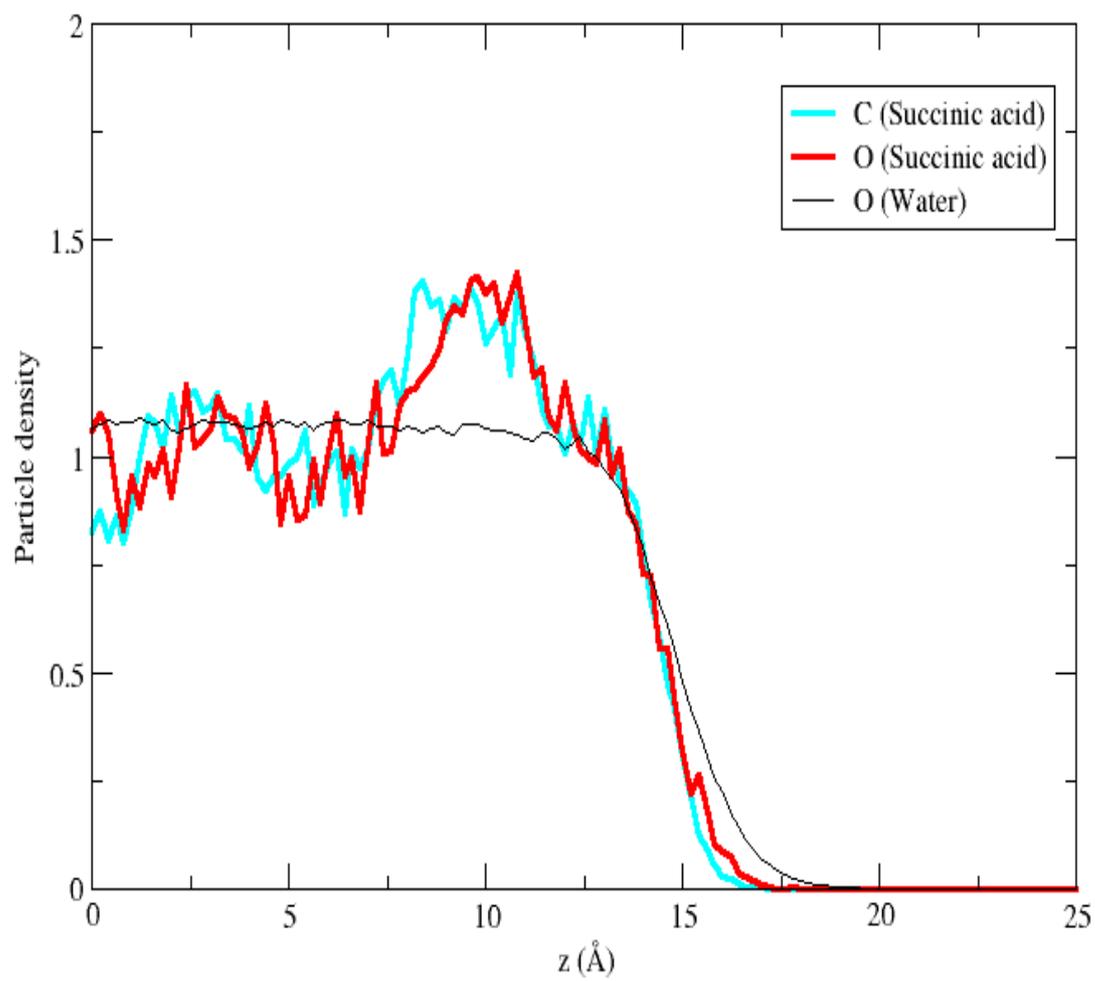


Figure 4d

