

# **Propensity of Formate, Acetate, Benzoate, and Phenolate for the Aqueous Solution/Vapour Interface: Surface Tension Measurements and Molecular Dynamics Simulations**

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## **Abstract**

The properties of a series of aliphatic and aromatic carboxylates and phenolate mimicking functional groups of humic acid is discussed as far as their behavior in aqueous solutions close to the surface is concerned. Both surface tension measurements and MD simulations confirm that sodium formate behaves in accord with the classical theory of surfaces of electrolytes, whereas sodium acetate and, much more pronounced, sodium benzoate and sodium phenolate show a more hydrotropic behavior with surface active anions. Further to the surface tension data, the MD results suggest that these hydrotropes are highly oriented at the solution-vapor interface.

## I. INTRODUCTION

Humic acid, a supramolecule with polyfunctionality, polydispersibility, and polyelectrolytic character produced by microbial decomposition of mainly vegetative matter,<sup>1,2</sup> is widely distributed in the biosphere. The structure and the molecular weight of humic acid vary significantly depending on the source, with the acid from brown coal being more complex than that from soil, sediment, and water.<sup>3</sup> Structural details of humic acid are not fully elucidated yet. Nevertheless, structural analysis shows that condensed aromatic rings with COOH, OH (phenolic), and C=O groups are the building block of humic acid.<sup>2,4</sup>

Humic acid has a good solubility in aqueous medium at  $\text{pH} > 2$  and is present in soil, fresh water, and sea water at varying concentration levels.<sup>5</sup> It exhibits surface activity and decreases the surface tension of water.<sup>4,6</sup> Due to its polyfunctionality, polydispersibility, and polyelectrolytic characters humic acid (or humate) is expected to show a different behaviour at the solid-solution and solution-vapour interfaces. For example, humic acid and its model functional groups adsorb on metal oxides and oxy(hydroxides) and clay mineral surfaces in aqueous medium and form different types of surfaces complexes.<sup>7</sup> While at the solution–vapor interface, it is expected that the hydrophobic parts (i.e., the aromatic condensed ring) should be exposed to the vapor phase with the hydrophilic groups pointing towards the bulk phase, similarly as observed, e.g., in the aqueous magnesium acetate solution.<sup>8</sup> Moreover, in solution at  $\text{pH} > 2$  humate instantly forms complexes with dissolved polyvalent ions.<sup>9</sup> The above results indicate that humic acid or humate have interesting surface properties and they can behave differently at the interfaces and in the bulk solution.

Molecular dynamics simulations of humic acid or humate are hardly feasible due to their not fully resolved structure. An alternative way to proceed is to consider simpler organic carboxylate ions, such as benzoate, and phenolate. These can serve as model functional groups of humate, and their interfacial behavior can be compared to that of the smallest carboxylate anions, i.e., formate and acetate. To this end, we report in this paper surface tension measurements and molecular dynamics simulations of aqueous sodium acetate, benzoate, formate, and phenolate. To the best of our knowledge surface tension data of these carboxylates in a wide concentration range are not available in the literature. While providing integral information about the solution–vapor interface, surface tension does not give a microscopic picture of the distributions and orientations of the carboxylate anions at the surface. This is obtained from molecular dynamics simulations in slab geometry.

## II. EXPERIMENTAL

Sodium acetate (> 99.5%, Merck, India), sodium benzoate (> 99.5 %, Merck, India), sodium formate (> 99.5 %, Loba Chemie, India), and sodium phenolate trihydrate (> 98 %, Merck, Germany) were used without further purification. All solutions were prepared using double-distilled water. The surface tension,  $\gamma$ , of all solutions was measured with a Dynamic Contact Angle Meter and Tensiometer, DCAT-11 (Dataphysics, Germany) using the Wilhelmy plate with an accuracy  $\pm 0.01 \text{ mN m}^{-1}$  at  $298.15 \pm 0.02 \text{ K}$ . The temperature of the solution was maintained by circulating liquid through a receptacle from a F32HP (Julabo, Germany) thermostat.

### III. COMPUTATIONAL DETAILS

Classical molecular dynamics simulations of sodium acetate, sodium benzoate, sodium formate, and sodium phenolate 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, 16 - 64 sodium cations and acetate, benzoate, formate and phenolate anions, yielding approximately 1–4 molar solutions. Application of periodic boundary conditions at a constant volume with such a unit cell produces an infinite slab with two water–vapor interfaces perpendicular to the z-axis.<sup>10</sup>

The non-bonded interactions were cut off at 12 Å and long-range electrostatic interactions were accounted for using the particle mesh Ewald procedure.<sup>11</sup> All systems were first minimized (10,000 steps of steepest descent minimization ) in order to avoid bad contacts and 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 NVT ensemble. All bonds involving hydrogen atoms were constrained using the SHAKE algorithm.<sup>12</sup> Geometries and energy data were saved for further analysis every 500 steps.

A polarizable force field was employed in all MD simulations. For water, we used the POL3 model.<sup>13</sup> For the ions we employed the general amber force field (GAFF) parameter set.<sup>14</sup> All molecular dynamics calculations were performed using Amber 8 program.<sup>15</sup> Fractional charges for the anions were evaluated using the standard RESP procedure employing the Gaussian 03 package.<sup>16</sup>

### III. RESULTS AND DISCUSSION

#### *Experimental*

The surface tension isotherms at 298.15 K of aqueous sodium acetate, sodium benzoate, sodium formate, and sodium phenolate are depicted in Figure 1. The experimental surface tension of sodium formate at 0.5 mol kg<sup>-1</sup> and 298.15 K is in excellent agreement with previous data, while that of sodium acetate is ~ 2.2 % lower than the reported value at 0.5 mol kg<sup>-1</sup>.<sup>17</sup> A distinct feature in the variation of the surface tension isotherms with concentration can be noticed. Namely, surface tension of aqueous sodium formate monotonously increases with concentration (similarly to, e.g., aqueous alkali halide solutions), while for aqueous sodium acetate, and especially for sodium benzoate, and sodium phenolate the surface tension decreases (by up to ~17, 24, and 33%, respectively) up to certain concentration (3.4, 2.35, and 1.7 mol kg<sup>-1</sup>, respectively), after which the effect tends to saturate.

The decrease in surface tension with increasing solute concentration, especially the large one due to sodium benzoate and phenolate clearly demonstrates that these organic anions behave like surface-active agents, but not like typical surfactants (which provide much more pronounced decreases in surface tensions with a typical minimum around 10<sup>-2</sup> mol dm<sup>-3</sup> or less). A similar decrease in surface tension (20.25 mN m<sup>-1</sup>) is reported for dihydroxybenzoates, with a minimum at ~0.16 mol dm<sup>-3</sup>.<sup>18</sup> Contrary to surfactants, the leveling off of surface tension in the present systems is due to the onset of formation of loose aggregates and not due to micelle formation. According to the critical micellar solution, the concentration corresponding to minimum surface tension is termed 'minimum hydrotropy concentration' and the molecules showing such a behavior are known as hydrotropes.<sup>18,19</sup>

### *Computational*

The effect of increasing surface propensity in the series of formate, acetate, benzoate, and phenolate in the concentration range of 1-4 mol dm<sup>-3</sup> of their sodium salt solutions was investigated by MD simulations in slab geometry. Figure 2 shows typical snapshots of these four salts at 1 mol dm<sup>-3</sup>. We present side views of the unit cell with the solution/vapor interfaces at the top and bottom of each snapshot. The corresponding density profiles, i.e., histogrammed densities of sodium and the four carboxylate ions from the center of the slab to the solution–vapor interface are depicted in Figure 3.

Out of these four systems the aqueous solution of sodium formate stands out as the only one where no surface activity is observed. The density profile of formate anion (as well as that of sodium) decays several Angstroms before the water signal, leaving an ion free surface layer (Figure 3a). This is a typical signature of bulk ion solvation expected for the small and weakly polarizable formate ion, which does not contain any hydrophobic group. At higher sodium formate concentrations extensive ion pairing is observed. This nonideal behavior is the strongest among the carboxylate salts investigated in this study.

Once the carboxylate anion carries a hydrophobic group its propensity for the solution/vapor interface becomes more pronounced. Already acetate, which bears a hydrophobic methyl group, shows surface activity with peak enhancement of about a factor of three compared to the bulk concentration (Figure 3b). Sodium counter-ions, which are *per se* repelled from the surface, show a subsurface peak, which is due to charge neutralization within the whole interfacial layer. The interfacial behavior of acetate in the present system is similar to that in aqueous magnesium acetate solution studied previously.<sup>8</sup>

The most surface-active behavior among the studied aqueous sodium carboxylates is exhibited by benzoate. The presence of the large hydrophobic benzene ring results in a strong segregation of benzoate to the surface (Figures 2c and 3c). Given the size of our simulation cell and sampling time benzoate anions actually do not spend enough time in the bulk interior to allow for a quantitative estimate of the surface/bulk segregation. Phenolate, which can be viewed as benzoate with the  $\text{COO}^-$  group replaced by  $\text{O}^-$  also shows an appreciable surface segregation (Figures 2d and 3d).

Figure 4 depicts orientational profiles of acetate, benzoate, and phenolate in the interfacial layer (formate is omitted since it does not penetrate to the surface). We plot the distribution of angles between the normal to the surface and the principal molecular axis (for acetate this coincides with the C-C bond, for benzoate the axis passes through the carboxylate carbon and the neighboring carbon of the benzene ring, while for phenolate it coincides with the O-C bond. For all three anions with a hydrophobic group the orientational distributions are highly non-isotropic with a strong peak at around  $0^\circ$ . This demonstrates a preferential orientation of these anions in the interface, with the charged group pointing into the aqueous bulk and the hydrophobic remainder of the molecular anion being exposed toward the vapor phase.

In order to relate directly to the experiment we have also attempted to evaluate the changes of surface tension upon adding either of the investigated salts. In the scope of molecular dynamics simulations, surface tension,  $\gamma$ , can be evaluated from the asymmetry of the pressure tensor  $p_{ii}$  employing a formula  $\gamma = \frac{1}{2} L_z \langle p_{zz} - (p_{xx} + p_{yy})/2 \rangle$ .<sup>20</sup> Here,  $z$  is the axis perpendicular to the surface,  $L_z$  is the length of the simulation box (prefactor of  $\frac{1}{2}$  accounts for the presence of two interfaces in the slab geometry) and averaging goes over the MD trajectory. The calculated values of surface tension are subjected to both systematic and statistical errors. The former is



mainly due to inaccuracies in the interaction potential and can amount to for standard force fields up to  $60 \text{ mN m}^{-1}$  (the present force field underestimates surface tension of water by some  $17 \text{ mN m}^{-1}$ ).<sup>21</sup> To partially circumvent problems with this systematic error we report here only differences in surface tension upon adding a particular salt. The statistical error due to large pressure fluctuations in an almost incompressible liquid amounts for the present simulations to  $1\text{--}2 \text{ mN m}^{-1}$ .

For sodium formate, MD simulations predict a slight increase in surface tension, which remains, however, for sub-molar concentrations within the statistical error (at larger concentrations the simulations suffer from non-ergodic effects due to extensive ion pairing). In contrast, surface tension of aqueous sodium acetate decreases with concentration (Table 1) indicating a net surface enrichment of ions. This decrease in surface tension and corresponding enhancement of ions at the surface is even stronger for the solutions of the more hydrophobic benzoate and phenolate anions (Tables 2 and 3). The present results are in a semi-quantitative agreement with the surface tension measurements reported above. The only significant discrepancy is that, unlike the measurements, calculations predict benzoate to be slightly more surface active than phenolate, which is likely due to small inaccuracies in the present empirical force field.

#### **IV. CONCLUSIONS**

Both surface tension measurements and MD simulations show that acetate, and in particular benzoate, and phenolate have a strong propensity for the solution-vapor interface, in contrast to formate which is repelled from the aqueous surface. In addition, MD simulations

indicate a strong orientation of acetate, benzoate, and phenolate at the interface, which can be probed by surface selective spectroscopic techniques. These findings can help to understand more in detail the surface active behavior of humic acid, for which, according to the present results, mainly the aliphatic and aromatic moieties with carboxylic and phenolic groups seem to be responsible.

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**Table 1:** Change in surface tension of sodium acetate solutions compared to neat water.

Concentration (mol dm <sup>-3</sup> )	$\Delta\gamma$ (mN m <sup>-1</sup> )
1	-2
2	-3
4	-8

**Table 2:** Change in surface tension of sodium benzoate solutions compared to neat water.

Concentration (mol dm <sup>-3</sup> )	Surface tension (mN m <sup>-1</sup> )
1	-5
3.5	-15

**Table 3:** Change in surface tension of sodium phenolate solutions compared to neat water.

Concentration (mol dm <sup>-3</sup> )	$\Delta\gamma$ (mN m <sup>-1</sup> )
1.5	-4
3.5	-14

## Figure Captions

**Figure 1:** Surface tension isotherms of aqueous sodium formate (triangles), sodium acetate (squares), sodium benzoate (inverted triangles), and sodium phenolate (open circles) at 298.15 K.

**Figure 2:** Typical snapshots of slabs of 1 M aqueous solutions of sodium a) formate, b) acetate, c) benzoate, and d) phenolate. The two solution/vapor interfaces are at the top and bottom of the snapshots. Color coding: Na - green, C -cyan, O - red, H - white.

**Figure 3:** Density profiles of water oxygen, sodium and the carbon and oxygen atoms of a) formate, b) acetate, c) benzoate, and d) phenolate. Color coding: Na - green, carboxylate O - red, carboxylate C – blue, aliphatic or aromatic C – cyan, and water O – black.

**Figure 4:** Orientational profiles of anions in the interfacial layer. a) acetate, b) benzoate, and c) phenolate.

Figure 1:

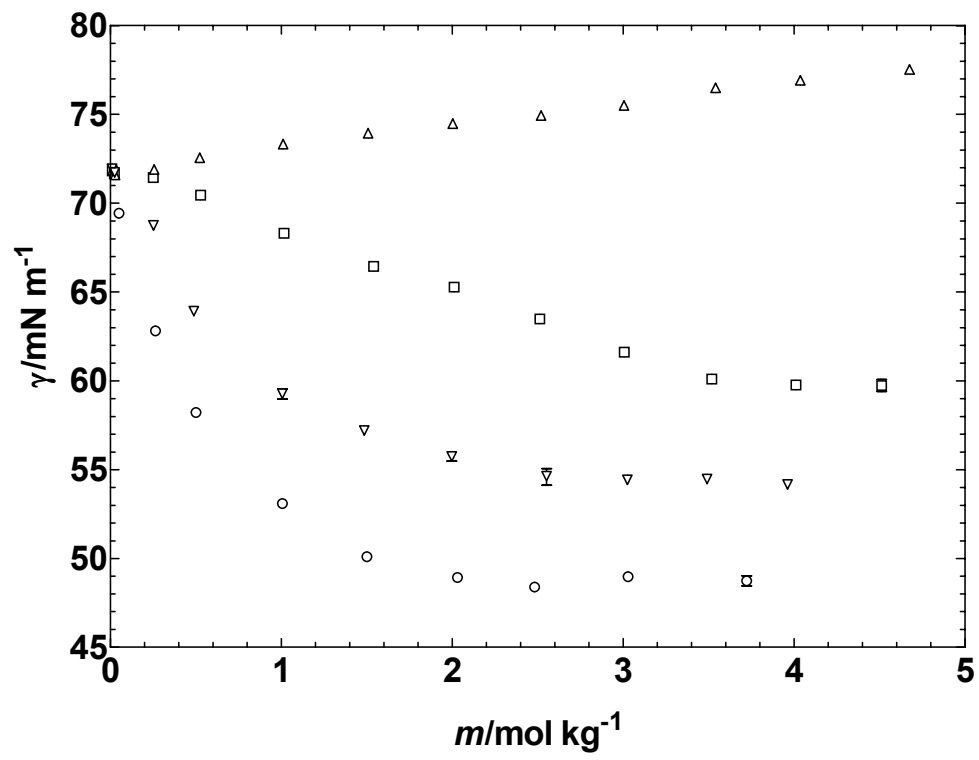
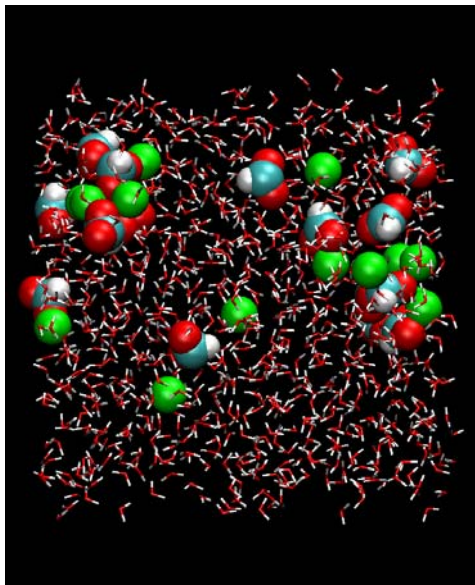


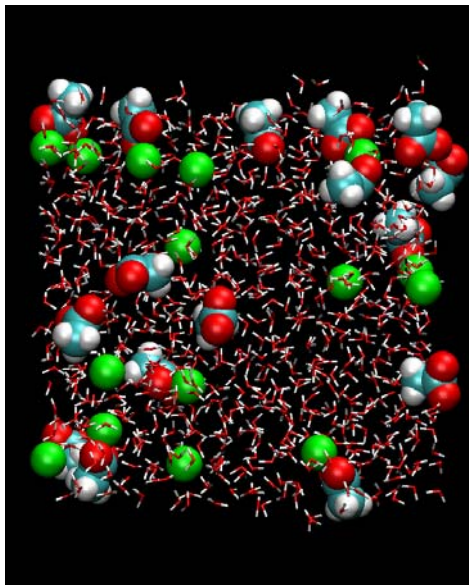


Figure 2:

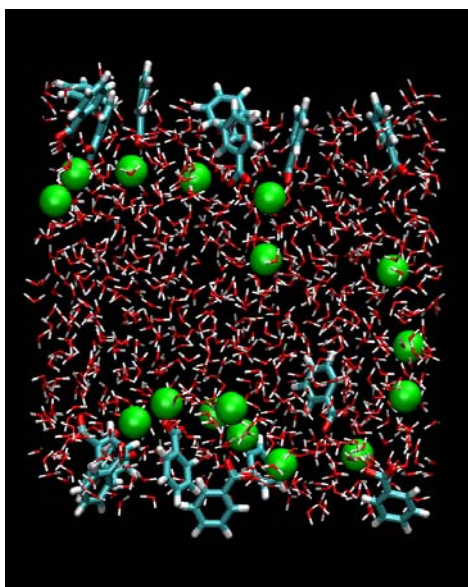
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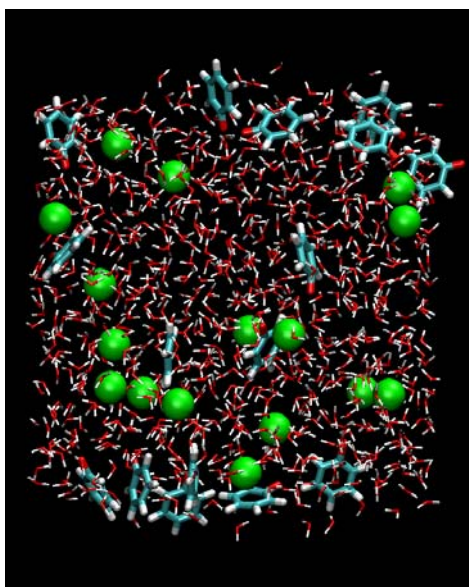
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c)

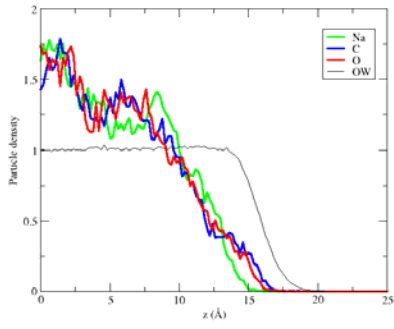


d)

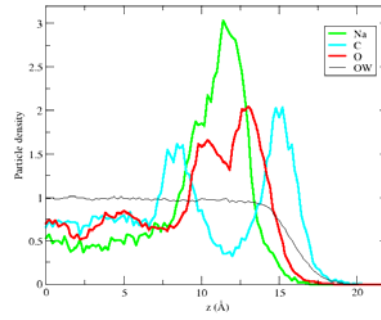


**Figure 3:**

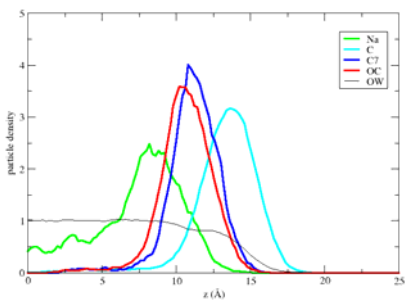
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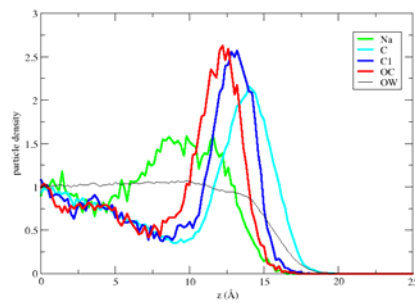
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**c)**

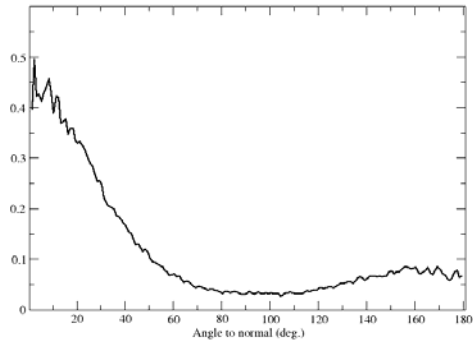


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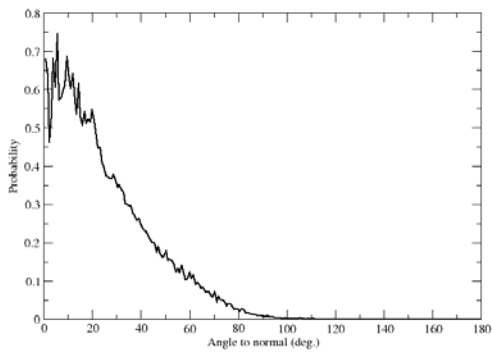


**Figure 4:**

**a)**



**b)**



**c)**

