

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

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The properties of a series of aliphatic and aromatic carboxylates and phenolate-mimicking functional groups of humic acid are discussed with regard to their behavior in aqueous solutions close to the surface. 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  $-\text{COOH}$ ,  $-\text{OH}$  (phenolic), and  $>\text{C}=\text{O}$  groups are the building blocks of humic acid.<sup>2,4</sup>

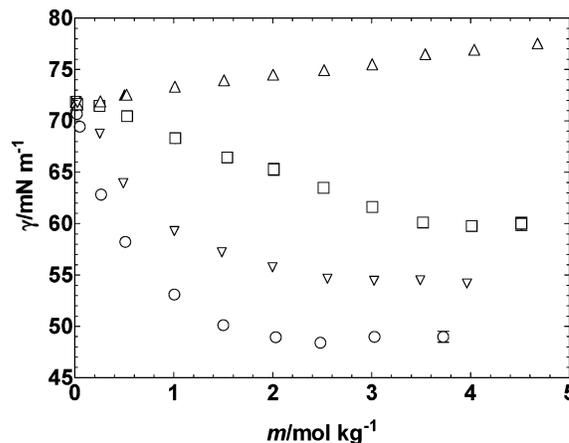
Humic acid has a good solubility in aqueous medium at  $\text{pH} > 2$ , and it is present in soil, fresh water, and seawater at varying concentration levels.<sup>5</sup> It exhibits surface activity and decreases the surface tension of water.<sup>4,6</sup> Due to its polyfunctionality, polydispersibility, and polyelectrolytic characters, humic acid (or humate) is expected to show a different behavior at the solid–solution and solution–vapor 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 surface 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 toward the bulk phase, similarly as observed, for example, 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.

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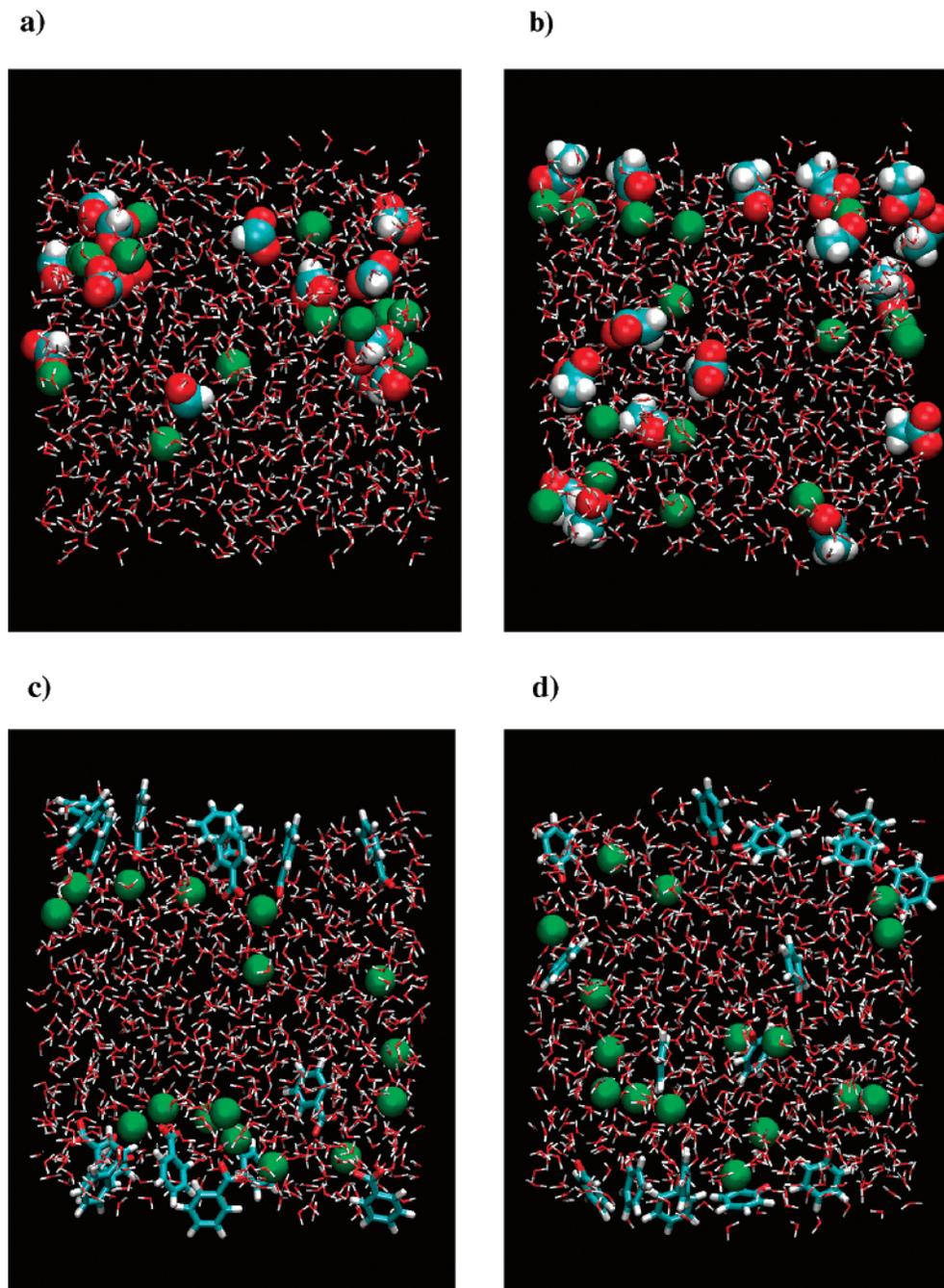


**Figure 1.** Surface tension isotherms of aqueous sodium formate (triangles), sodium acetate (squares), sodium benzoate (inverted triangles), and sodium phenolate (open circles) at 298.15 K.

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, that is, 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. 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



**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.

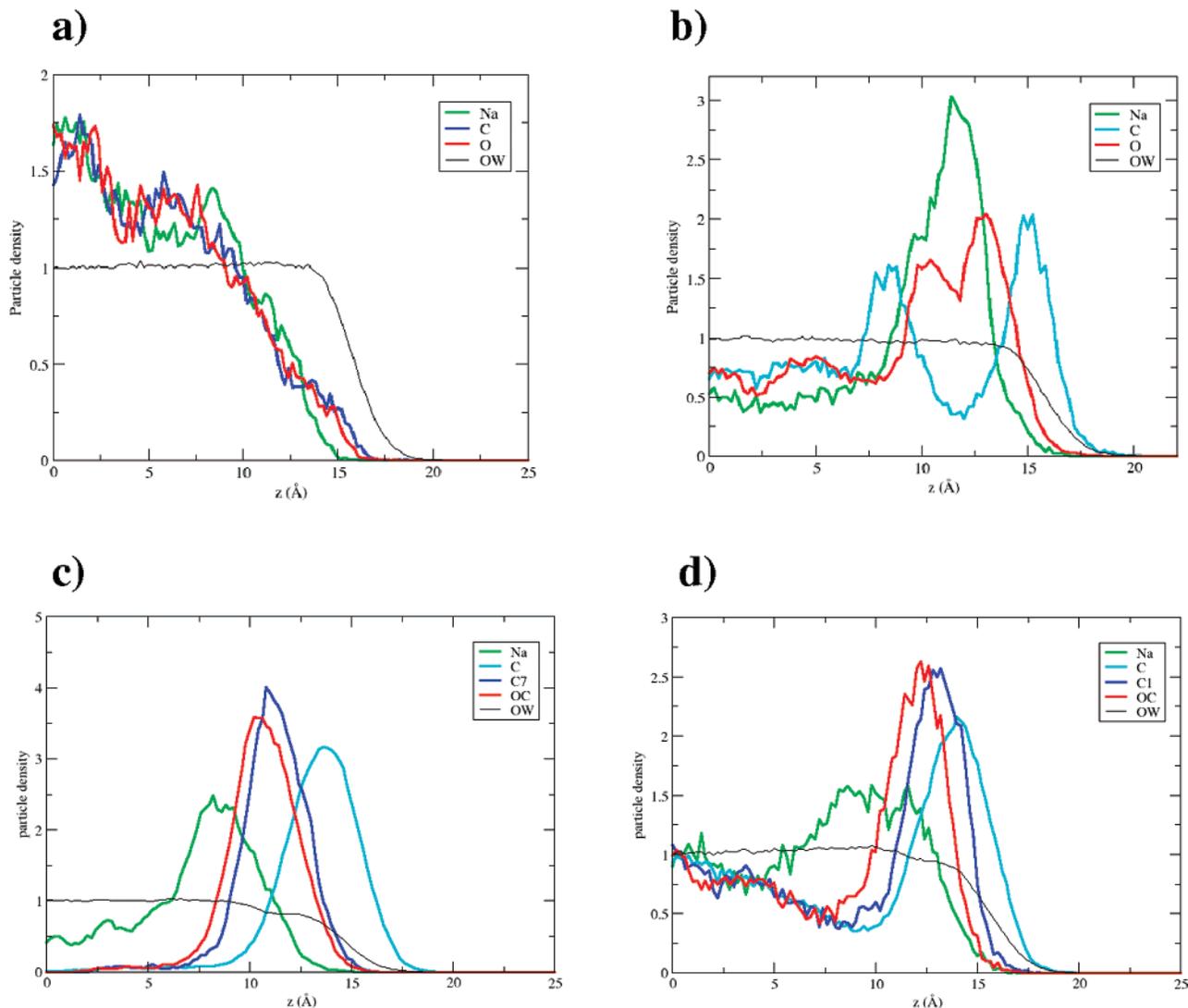
Chemie, India), and sodium phenolate trihydrate (>98%, Merck, Germany) were used without further purification. All solutions were prepared using double-distilled water. The surface tension,  $\gamma$ , of all solutions was measured with a Dynamic Contact Angle Meter and Tensiometer, DCAT-11 (Dataphysics, Germany) using the Wilhelmy platinum–iridium plate, type PT-11, of thickness 0.2 mm and area 3.98 mm<sup>2</sup> with an accuracy of  $\pm 1.5\%$  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 F32HP (Julabo, Germany) thermostat.

### III. Computational Details

Classical molecular dynamics simulations of sodium acetate (CH<sub>3</sub>COONa), sodium benzoate (C<sub>6</sub>H<sub>5</sub>COONa), sodium formate

(HCOONa), and sodium phenolate (C<sub>6</sub>H<sub>5</sub>ONa) solutions were performed in aqueous slabs. In order to construct the slab, a (tetragonal) prismatic box of  $30 \times 30 \times 100$  Å<sup>3</sup> was used. It contained 863 water molecules, and 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 nonbonded 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



**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.

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> Note that the small extent of reactivity of these ions to form organic acids and hydroxide (which cannot be described within the present force field) can be safely neglected for the purpose of this study. All molecular dynamics calculations were performed using the 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>

#### IV. 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 (~0.3%) 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 monoto-

nously 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>

The magnitude of surface propensity of sodium acetate, sodium benzoate, and sodium phenolate for the solution–vapor interface was examined by applying the Gibbs adsorption

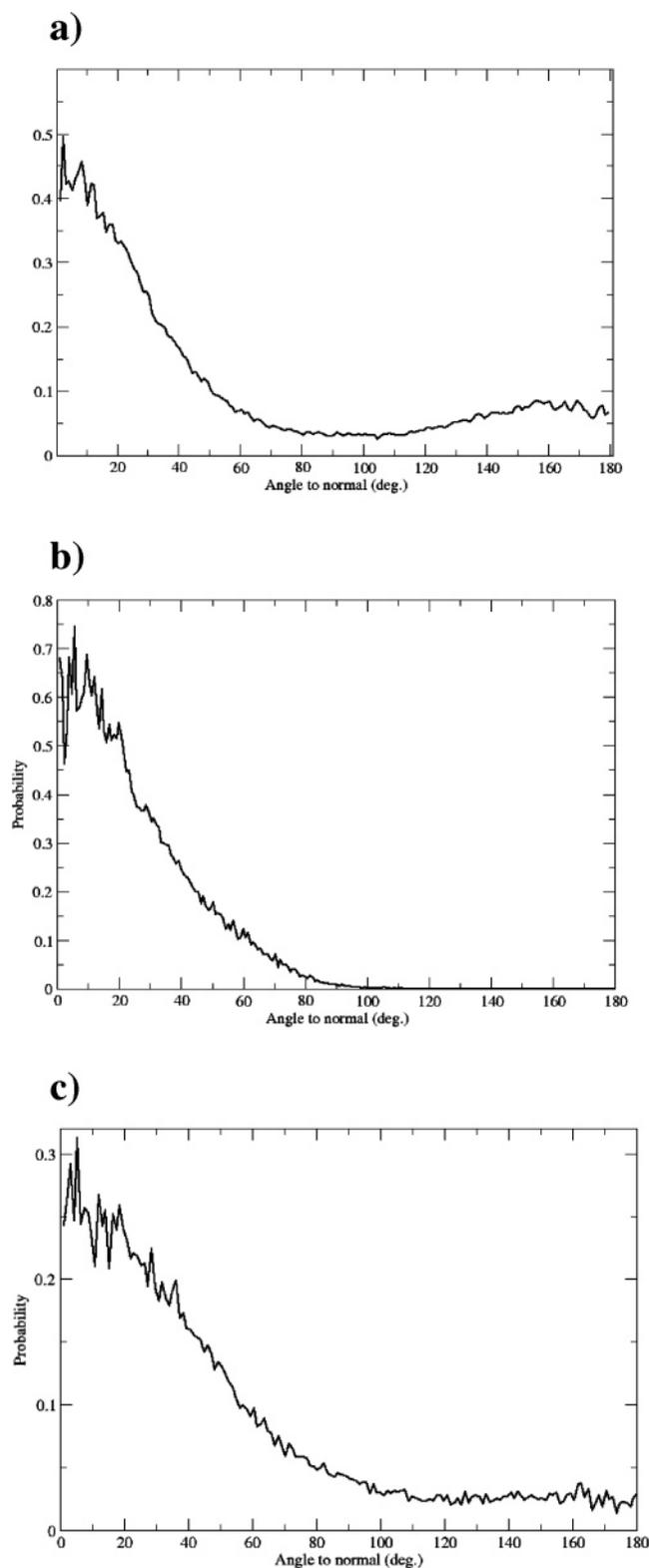
isotherms,  $d\gamma = -RTT d(\ln a)$ , where  $\gamma$ ,  $R$ ,  $T$ ,  $\Gamma$ , and  $a$  are the surface tension, gas constant, absolute temperature, surface excess in  $\text{mol m}^{-2}$ , and activity, respectively. The molal concentration was converted to molar concentration and subsequently to activity by using the reported density and activity coefficient values.<sup>20–21</sup> The surface excess ( $\Gamma$ ) for sodium acetate and sodium benzoate ( $1.83 \times 10^{-6}$  and  $2.12 \times 10^{-6} \text{ mol m}^{-2}$ ) was estimated from the linear plot of  $\gamma$  vs  $\ln a$  up to certain concentrations ( $3.52$  and  $2.55 \text{ mol kg}^{-1}$ , respectively) with corresponding area per molecule,  $A$  ( $\text{\AA}^2/\text{molecule}$ ) =  $(\Gamma N)^{-1}$ , where  $N$  is Avogadro's number,  $91$  and  $78$ , respectively. However, due to nonavailability of the reported activity coefficient data in the literature, to the best of our knowledge, for sodium phenolate, alternatively, we estimated the surface excess ( $\Gamma$ ) and the area per molecule ( $A$ ) from the linear plot of  $\gamma$  vs  $\ln c$  for comparison with that of acetate and benzoate, where  $c$  is the molar concentration, which are found to be  $3.02 \times 10^{-6} \text{ mol m}^{-2}$  and  $55 \text{ \AA}^2/\text{molecule}$ . The area per molecule ( $A$ ) for benzoate and phenolate are in good agreement with that of humate.<sup>22</sup> The surface excess shows that benzoate and phenolate adsorb at the solution–vapor interface relatively more than acetate.

**Computational.** The effect of increasing surface propensity in the series of formate, acetate, benzoate, and phenolate in the concentration range of  $1\text{--}4 \text{ mol dm}^{-3}$  of their sodium salt solutions was investigated by MD simulations in slab geometry. Figure 2 shows typical snapshots of these four salts at  $1 \text{ mol dm}^{-3}$ . 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 3 compared to the bulk concentration (Figure 3b). Sodium counterions, 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> Preliminary calculations on aqueous acetic acid show that the protonated form has a significantly higher surface propensity as can be expected for a neutral species.

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  $\text{COO}^-$



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

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

**TABLE 1: Changes in Surface Tension of Sodium Acetate, Sodium Benzoate, and Sodium Phenolate Solutions Compared to That of Neat Water**

concentration (mol dm <sup>-3</sup> )	$\Delta\gamma$ (mN m <sup>-1</sup> ) sodium acetate	$\Delta\gamma$ (mN m <sup>-1</sup> ) sodium benzoate	$\Delta\gamma$ (mN m <sup>-1</sup> ) sodium phenolate
1	-2	-5	
1.5			-4
2	-3		
3.5		-15	-14
4	-8		

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°. 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. This is qualitatively seen already from the density profiles showing the carboxylate carbon atoms deeper in the aqueous phase than the aliphatic or aromatic carbons (Figure 3).

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  $\gamma = \frac{1}{2}L_z < p_{zz} - (p_{xx} + p_{yy})/2 >$ .<sup>23</sup> Here,  $z$  is the axis perpendicular to the surface,  $L_z$  is the length of the simulation box (prefactor of 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 for standard force fields up to 60 mN m<sup>-1</sup> (the present force field underestimates surface tension of water by some 17 mN m<sup>-1</sup>).<sup>24</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 1–2 mN m<sup>-1</sup>.

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 (Table 1). The present results are in a semiquantitative 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.

## V. 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

imply that the model functional groups, like carboxylate, phenolate, and similar ones are primarily responsible for the surface-active properties of humic acid.

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## References and Notes

- (1) Hatcher, P. G.; Spiker, E. C. In *Humic Substances and Their Role in the Environment*; Frimmel, F. H., Christman, R. F., Eds.; Wiley: Chichester, 1988; p 59.
- (2) Stevenson, F. J. *Humus Chemistry: Genesis, Composition, Reactions*, 2nd ed.; John Wiley and Sons: New York, 1994.
- (3) *Humic Substances II: In Search of Structure*; Hayes, M. H. B., MacCarthy, P., Malcolm, R. L., Swift, R. S., Eds.; John Wiley and Sons: Chichester, 1989.
- (4) Beckett, R. In *Surface and Colloid Chemistry in Natural Waters and Water Treatment*; Beckett, R., Ed.; Plenum Press: New York, 1990; p 3.
- (5) Kramer, J. R.; Brassard, P.; Collins, P.; Clair, T. A.; Takats, P. In *Organic Acids in Aquatic Ecosystems*; Perdue, E. M., Gjessing, E. T., Eds.; John Wiley and Sons: Chichester, 1990; p 127.
- (6) Quagliotto, P.; Montoneri, E.; Tambone, F.; Adani, F.; Gobetto, R.; Viscardi, G. *Environ. Sci. Technol.* **2006**, *40*, 1686.
- (7) (a) Nordin, J.; Persson, P.; Laiti, E.; Sjöberg, S. *Langmuir* **1997**, *13*, 4085. (b) Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; MacCarthy, J. F. *Geochim. Cosmochim. Acta* **1995**, *59*, 219. (c) Evanko, C. R.; Dzombak, D. A. *Environ. Sci. Technol.* **1998**, *32*, 2846. (d) Vermeer, A. W. P.; van Riemsdijk, W. H.; Koopal, L. K. *Langmuir* **1998**, *14*, 2810. (e) Vermeer, A. W. P.; Koopal, L. K. *Langmuir* **1998**, *14*, 4210. (f) Evanko, C. R.; Dzombak, D. A. *J. Colloid Interface Sci.* **1999**, *214*, 189. (g) Das, M. R.; Mahiuddin, S. *Colloids Surf., A—Physicochem. Eng. Aspects* **2005**, *264*, 90. (h) Tipping, E. In *Organic Acids in Aquatic Ecosystems*; Perdue, E. M., Gjessing, E. T., Eds.; John Wiley and Sons: Chichester, 1990; p 209.
- (8) Minofar, B.; Vacha, R.; Wahab, A.; Mahiuddin, S.; Kunz, W.; Jungwirth, P. *J. Phys. Chem. B* **2006**, *110*, 15939.
- (9) Stevenson, F. J. *Humus Chemistry: Genesis, Composition and Reaction*, 2nd ed.; John Wiley and Sons: New York, 1994; p 378.
- (10) Wilson, M. A.; Pohorille, A. *J. Chem. Phys.* **1991**, *95*, 6005.
- (11) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. *J. Chem. Phys.* **1995**, *103*, 8577.
- (12) Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. *J. Comput. Phys.* **1977**, *23*, 327.
- (13) Caldwell, J. W.; Kollman, P. A. *J. Phys. Chem.* **1995**, *99*, 6208.
- (14) Wang, J. M.; Wolf, R. M.; Caldwell, J. M.; Kollman, P. A.; Case, D. A. *J. Comput. Chem.* **2004**, *25*, 1157.
- (15) Case, D. A.; D., T. A.; Cheatham, T. E., III; 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.
- (16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; 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.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.
- (17) Morgan, J. L. R.; McKirahan, W. W. *J. Am. Chem. Soc.* **1913**, *35*, 1759.
- (18) Macinnis, J. A.; Macneil, S. L.; Burke, S. E.; Palepu, R. *J. Surf. Sci. Technol.* **2000**, *16*, 77.

(19) Bauduin, P.; Renoncourt, A.; Kopf, A.; Touraud D.; Kunz, W. *Langmuir* **2005**, *21*, 6769.

(20) *International Critical Tables of Numerical Data. Physics. Chemistry and Technology*; Washburn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. VI.

(21) *Handbook of Chemistry and Physics*, 66th ed.; West, R. C., Ed.; CRC Press: Boca Raton, FL, 1985; p D-252.

(22) Terashima, M.; Fukushima, M.; Tanaka, S. *Colloids Surf., A—Physicochem. Eng. Aspects* **2004**, *247*, 77.

(23) Zhang, Y.; Feller, S. E.; Brooks, B. R.; Pastor, R. W. *J. Chem. Phys.* **1995**, *103*, 10252.

(24) Garrett, B. C.; Schenter, G. K.; Morita, A. *Chem. Rev.* **2006**, *106*, 1355.