

# Effects of pH and Metals on the Surface Tension of Aqueous Humic Materials

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## ABSTRACT

Humic substances play an important role in the transport and fate of xenobiotic materials in the environment. Since most of the relevant interactions take place in aqueous media, it is of prime importance to understand the behavior of these natural polymers in solution. In this study, surface tension measurements were used to elucidate conformational and structural changes in dissolved humic and fulvic acids under different conditions of pH, ionic strength, and the presence of certain metal ions. The measurements showed that the amphiphilic character of the humic solutes, which determines their surface activity, varied significantly with pH and metal content. The charge of the metal ion added was found to have an important effect in rendering the humic material sufficiently amphiphilic to migrate to the surface. As cation concentrations were increased, the formation of micelle-like humic structures led to the restoration of higher surface tensions. Measurements with materials of different molecular size indicated that these structures could arise from both intermolecular aggregation and intramolecular coiling. Kinetic measurements showed that the evolution of surface tension values in humic acid solutions followed a course that was consistent with the migration of metal ions within the humic structure. This is thought to involve the formation and subsequent disintegration of hydrophobic domains as the metal-humate interactions change during a period of hours.

HUMIC ACID (HA) and fulvic acid (FA) are the products of the oxidative degradation, and subsequent polymerization, of plant and animal matter in the environment. The mechanism of formation of these substances is not well characterized, but both are known to be rich in aromatic, carboxylic, and phenolic functionalities. They also possess alkyl moieties, linking the various functional groups, and imparting a measure of flexibility to the polymer chains. The molecular features of the compounds are variable, depending on their age and origin. For this reason, HAs and FAs are operationally, rather than structurally, defined (Aiken et al., 1985). It is generally held that FA is the fraction of humus that is soluble at all pH values, whereas HA solubility decreases with decreasing pH, becoming entirely insoluble at pH < 2. A third component, humin, is insoluble at all pHs. A related feature distinguishing FAs from HAs is that the former have a lower molecular weight and greater functional group density. The molecular weight range commonly quoted for FA is 500 to 5000 daltons (Da), while it is >5000 Da for HA and can extend to values >1 000 000 Da (Aiken et al., 1985). Aqueous solutions of HA are generally polydisperse, with size ranges differing according to the origin—aqueous, terrestrial, or marine—of the material in question. The genesis of HA and FA has been shown to be a factor in the determination of molecular attributes such as acidity and size (Aiken et al., 1985; Senesi et al., 1989).

Among HAs, for instance, it is found that those of aqueous origin are smaller than those isolated from soil. A special case is Leonardite HA (LHA), which is found in association with lignite deposits and has a more condensed aromatic structure (Thorn et al., 1989; Engebretson and von Wandruszka, 1997).

The amphiphilic nature of HA, and to a lesser extent of FA, has given rise to the micellar (or detergent) model for these compounds (Wershaw, 1986, 1993). Other studies (Puchalski et al., 1992; Engebretson and von Wandruszka, 1994, 1996, 1997; Ragle et al., 1997; von Wandruszka et al., 1997; Yates et al., 1997) have indicated that the spontaneous aggregation of aqueous HAs can be intramolecular (involving a single polymer chain) or intermolecular (involving multiple chains). In the former case, it is thought that the humic polymers fold and coil in a manner that creates structured regions that can be likened to knots in a string. The interior of these assemblies is relatively hydrophobic, while the exterior is more hydrophilic. The structure is similar to that of a surfactant micelle, although it is constrained by the intramolecular nature of the arrangement, and the polydispersity of the material. The term *pseudomicelle* is therefore more appropriate to describe these structures. In analogy with synthetic surfactant micelles, the humic pseudomicelles contain sites for the sequestration of nonpolar solutes (Engebretson and von Wandruszka, 1994). A phenomenon similar to the pseudomicelle formation may also be achieved through intermolecular interactions, by the association of a number of humic polymers. The formation of both the intra- and intermolecular species depends on a range of solution conditions, including the concentration and nature of the HA, the pH, the temperature, and the nature and concentration of cationic species present in solution (von Wandruszka et al., 1997). It has been shown that metal ions, especially polyvalent ones, have a major influence on humic aggregation and the formation of pseudomicellar structures. This is thought to be due to the ability of the cations to both neutralize the negative charges on HA (reducing mutual repulsion), and engage in bridging interactions. The former gives the polymer the opportunity to assume a more contracted configuration, while the latter draws the chains together, enhancing the formation of hydrophobic "pockets."

The surface tension of aqueous HA and FA solutions is a parameter with relevance to all types of aggregation of these substances. However, relatively few reports on this subject have appeared in the literature (Tschapek and Wasowski, 1976; Chen and Schnitzer, 1978; Ander-

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**Abbreviations:** Da, daltons; DDIW, doubly deionized water; FA, fulvic acid; HA, humic acid; IHSS, International Humic Substances Society; LHA, leonardite humic acid; LHACB, leonardite humic acid crude blend; LSLHA, Latahco silt loam humic acid; SRFA, Suwannee River fulvic acid; SRHA, Suwannee River humic acid.

son et al., 1995; Guetzloff and Rice, 1996). It has been shown that the surface tension decreases with increasing HA and FA concentration, but contradictory results have been presented on the dependence of surface tension on pH. One of the difficulties encountered in such measurements involves the concentration ranges considered. Results can vary significantly between humic solutions with concentrations in the grams per liter range (Guetzloff and Rice, 1996), and those in the milligrams per liter range. The pH of the aqueous solvent is also important: humic materials dissolve more readily in highly alkaline solutions ( $\text{pH} \geq 10$ ), but their conformational behavior and aggregation characteristics are strongly influenced by such conditions. These effects, together with those of ionic strength and the nature of the metal ions in solution, are evaluated through surface tension measurements in our study. To retain environmental relevance, the focus is on material dissolved at  $500 \text{ mg L}^{-1}$  in near-neutral solutions. For the metal addition studies a pH of 6 was used. These conditions are sufficient to produce surface tension effects of exponential magnitudes.

## MATERIALS AND METHODS

Studies were performed on Suwannee River humic acid (SRHA) and Suwannee River fulvic acid (SRFA), both purchased from International Humic Substances Society (IHSS; St. Paul, MN) and used as received. Leonardite humic acid (Horizon Ag Products, Kennewick, WA) was used in both its native state (Leonardite humic acid crude blend, LHACB) and extracted (LHA) forms. The LHA was extracted according to the procedure outlined by the IHSS (Hayes, 1985). Latahco silt loam humic acid (LSLHA) was extracted from a local soil in Northern Idaho (fine-silty, mixed, frigid Argiaquic Xeric Argialboll) according to the IHSS procedure. The soil was collected at a depth of 15 cm from a field kept at pasture for at least 20 yr. A full characterization of this HA has been reported previously (Engebretson and von Wandruszka, 1994). Reagent grade  $\text{NH}_4\text{OH}$ , reagent grade  $\text{HCl}$ ,  $1000 \text{ mg L}^{-1} \text{ Mg}$  standard,  $1000 \text{ mg L}^{-1} \text{ Na}$  standard, and  $\text{SmCl}_3$  were all used as received. All aqueous solutions of humic substances were prepared at  $500 \text{ mg L}^{-1}$  with doubly deionized water (DDIW) treated with a  $0.22\text{-}\mu\text{m}$  Millipore (Millipore Corp., Bedford, MA) filter system and brought to a minimum resistivity of  $16 \text{ M}\Omega \text{ cm}$ . All humic solutions were prepared by adding the appropriate mass of solute to a volumetric flask, adding DDIW, adjusting the solution pH to 9 with  $\text{NH}_4\text{OH}$ , sonicating for 1 h, and then adding DDIW to volume.

Surface tension measurements were taken with a Fisher Surface Tensiometer Model No. 21 (Fisher Scientific, Pittsburgh, PA), fitted with a 19-mm-diameter platinum-iridium ring. Samples were prepared for measurement by adding the appropriate amounts of acid or salt to 10 mL of humic solution and shaking for a period of 24 h on a reciprocating shaker. All metal-containing solutions were adjusted to pH 6.0 with  $\text{HCl}$  prior to salt addition, and the same acid was used in the pH studies. Solutions were placed in a shallow glass dish of 50 mm diameter, and the platinum-iridium ring was inserted in the middle of the container to avoid edge effects. The ring was raised through manual operation of the torsion mechanism, and the tension reading at the instant of surface detachment was noted. Kinetic measurements were performed after adding the appropriate amount of metal ion stock solution to 10 mL of humic solution, stirring for 1 min, and then taking

data at appropriate intervals. All measurements were taken in triplicate at a temperature of  $22^\circ\text{C}$ .

## RESULTS AND DISCUSSION

As with all surface active substances, the effect of HA and FA on surface tension depends on their tendency to accumulate at the water–air interface. This is dictated by their amphiphilic character (Hiemenz and Rajagopalan, 1997, p. 301), and therefore by the solution conditions that control it. Both pH and metal ion content have a major influence on the charge distribution and hydrophilicity of dissolved humic substances (von Wandruszka et al., 1997). These are therefore likely to be preeminent parameters in the determination of surface tension and the formation of pseudomicelles, since both are manifestations of the same solution properties. Error bars in the measurements described below did not extend beyond the plotting symbols used.

### pH Studies

Figure 1 shows that the surface tension–pH curves featured a minimum for all solutions, declining steeply from higher and lower pH values. The measured surface tension was greatest at high pH ( $>8$ ) in all cases, since the humic solute was highly anionic (and therefore very hydrophilic) under those conditions. The decrease in surface tension with decreasing pH reflects the gradual neutralization of acidic sites, which created amphiphilic species that migrated to the surface. The degree to which this occurred differed for different humic substances, being least pronounced for the fulvic acid, SRFA. This may be attributed to the high functional group density on these relatively small molecules, which allowed fairly extensive H bonding with the aqueous solvent throughout the pH range and hindered the development of a strong amphiphilic character. In all cases, the surface tension increased again in the low pH ranges where continued neutralization produced increasingly hydrophobic molecules with low surface activity. This was also accompanied by the onset of precipitation.

The surface tension variations observed with LHA were particularly strong, decreasing to a value below  $6.0 \times 10^{-2} \text{ N m}^{-1}$  at the minimum. This indicates that this HA was an especially effective amphiphile around pH 4, and may be viewed together with earlier results (Engebretson and von Wandruszka, 1996; Yates et al., 1997) indicating that LHA is less effectual in the formation of pseudomicelles than typical soil HAs. In combination, these observations suggest that partially neutralized LHA aggregates preferentially at the surface, and to a lesser extent in micelle-like aggregates. In contrast, LSLHA has been shown to have a pronounced tendency to form pseudomicelles (Engebretson and von Wandruszka, 1997; Ragle et al., 1997). Figure 1 shows that this HA produced a modest drop in surface tension at intermediate pH values, which may be considered to mean that both surface accumulation and micellar aggregation occurred to comparable extents in this case.

The crude humic acid (LHACB) behaved differently from the other humic substances, giving a moderate

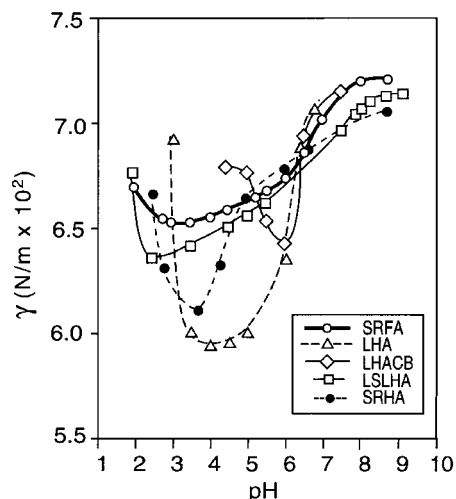


Fig. 1. Variation of surface tension with pH for 500 mg L<sup>-1</sup> humic acid and fulvic acid solutions. SRFA, Suwannee River fulvic acid; LHA, leonardite humic acid; LHACB, leonardite humic acid crude blend; LSLHA, Latahco silt loam humic acid; SRHA, Suwannee River humic acid.

decrease in surface tension at a relatively high pH (Fig. 1). This is undoubtedly due to the fact that this material was not deashed and contained a sizable proportion of metals (data not shown). This condition would be expected to leave only a small number of acidic moieties that may be deprotonated as the pH is raised. It therefore required a relatively high pH to render the bulk of the humic solute sufficiently ionized to impart a strong amphiphilic character to the molecules and achieve the maximum in surface activity.

### Metal Ion Studies

Figure 2 shows the results obtained by adding Mg<sup>2+</sup> to HA and FA solutions (pH 6). Increasing Mg<sup>2+</sup> concentrations affected surface tension readings in a similar manner as decreasing pH. This agrees with previous studies that have shown that cations enhance pseudomicelle formation (Wershaw, 1993; Engebretson and von Wandruszka, 1994; Yates et al., 1997). However, there are notable differences in the details of the curves in Fig. 1 and 2. First, the response of SRFA surface tension to Mg<sup>2+</sup> not only reached the lowest value among the humic substances, but did so in a relatively abrupt fashion (decreasing  $\approx 9 \times 10^{-3}$  N m<sup>-1</sup> for an Mg<sup>2+</sup> concentration increase of  $< 4 \times 10^{-5}$  M). This indicates that the FA aggregates formed with Mg<sup>2+</sup> had a strong amphiphilic character, probably because intermolecular binding of FA by metal ions rendered the carboxylic sites involved less capable of H bonding. The relatively non-polar regions thus produced—before the equivalent amount of cations was added and some functional groups were still unaffected—imparted increased surface activity to the fulvic assembly. The influence of Mg<sup>2+</sup> on LHA surface tension may appear to be relatively small in Fig. 2 ( $< 2 \times 10^{-3}$  N m<sup>-1</sup> in the initial drop) in comparison with the pH effect ( $> 1.2 \times 10^{-2}$  N m<sup>-1</sup>), but it should be noted that the concentration axis begins at  $1.0 \times 10^{-5}$  M metal ion. The value at the

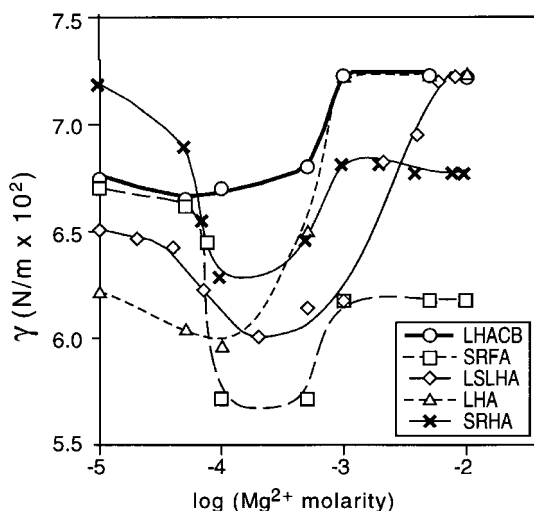


Fig. 2. Variation of surface tension with Mg<sup>2+</sup> concentration for 500 mg L<sup>-1</sup> humic acid and fulvic acid solutions (pH 6). LHACB, leonardite humic acid crude blend; SRFA, Suwannee River fulvic acid; LSLHA, Latahco silt loam humic acid; LHA, leonardite humic acid; SRHA, Suwannee River humic acid.

zero concentration point (which cannot be displayed on this log axis) can be gleaned from Fig. 1, at a pH value slightly above 6. Thus it is clear that the LHA surface tension actually decreased from an initial value of  $\approx 6.7 \times 10^{-2}$  N m<sup>-1</sup> when Mg<sup>2+</sup> was added. As was the case with the results obtained with decreasing pH, the minimum in the LHA curve here occurred sooner than it did with the other extracted humic substances. A similar observation was made with LHACB, which reached a minimum at a relatively high pH, and also did so at a low Mg<sup>2+</sup> concentration. This must again be attributed to the metal ions present in the crude material.

The effects of metal ions other than Mg<sup>2+</sup> on the

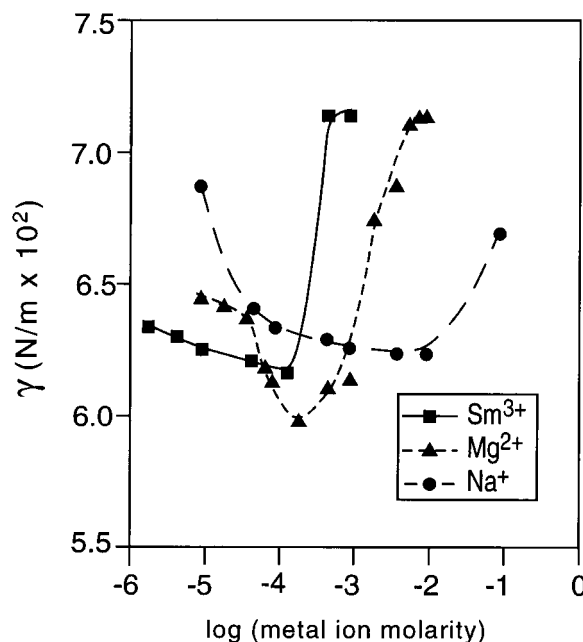


Fig. 3. Variation of surface tension of 500 mg L<sup>-1</sup> Latahco silt loam humic acid (LSLHA) solutions (pH 6) with metal concentration.

surface tension of HA and FA solutions are shown in Fig. 3. It can be seen that the curve for  $\text{Na}^+$  resembles the one obtained with changing pH (Fig. 1), which is not surprising in view of the inability of the monovalent Na ion to undergo bridging interactions with humic materials. On the other hand,  $\text{Sm}^{3+}$  produced a surface tension minimum at a relatively low concentration, followed by a sharp rise above  $\approx 10^{-4} M \text{Sm}^{3+}$ . This bears out results obtained with a fluorescent probe (Ragle et al., 1997), from which it was concluded that Sm is especially effective in the creation of pseudomicellar humic aggregates. Each cation demonstrated a unique progression of surface tension behavior for LSLHA. A higher charge on the metal ion produced (i) a lower surface tension at a lower metal concentration, (ii) an earlier attainment of the minimum, and (iii) a steeper subsequent rise. This trend is consistent with the proposed mechanism—the higher the charge on the metal ions, the fewer are needed to produce amphiphilic humic species that partition to the surface. Likewise, subsequent humic aggregation and pseudomicellization are more effective with more highly charged ions, leading to abrupt withdrawal of the polymers from the surface and a prompt restoration of the surface tension.

A complicating factor in the interpretation of surface tension measurements of FA and HA solutions is related to the polydispersity of these compounds. It is conceivable that smaller fragments of a HA such as LSLHA readily accumulate at the surface, while the longer chains of the same compound have a greater tendency to form pseudomicelles. This may be the reason why this HA shows both a decrease in surface tension (as discussed above) and clear evidence of pseudomicelle formation, as indicated by fluorescence enhancement studies (Engebretson and von Wandruszka, 1994, 1996, 1997).

### Kinetic Studies

Recent work on the kinetics of metal–HA interactions in aqueous solution (Wahlberg and Staffan, 1996; Eng-

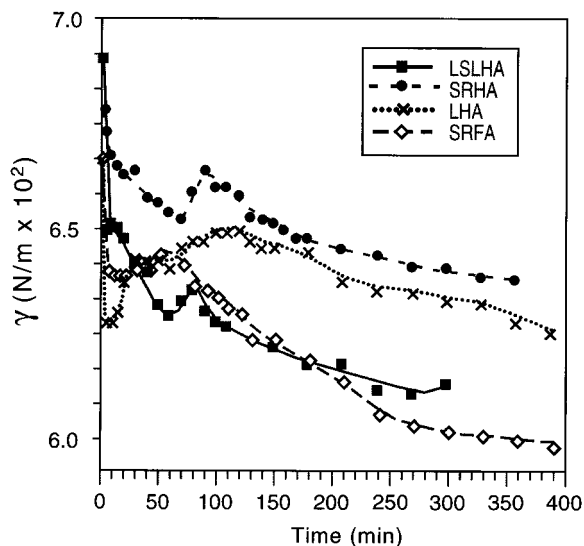


Fig. 4. Variation of surface tension with time for  $500 \text{ mg L}^{-1}$  humic acid and fulvic acid solutions (pH 6) in the presence of  $1.0 \times 10^{-4} M \text{Mg}^{2+}$ . LSLHA, Latahco silt loam humic acid; SRHA, Suwannee River humic acid; LHA, leonardite humic acid; SRFA, Suwannee River fulvic acid.

bretson and von Wandruszka, 1997, 1998) has shown that these associations form slowly and evolve in periods that may extend from hours to days. One of the concepts developed in these studies was that the initial interaction between metal ions and dissolved humic materials is largely coulombic in nature and is most effective in pseudomicelle formation. The typical time scale for the completion of this process was  $\approx 1 \text{ h}$  (Engebretson and von Wandruszka, 1998). However, with time the metal ion migrates within the humic structure, eventually finding a thermodynamically most favored coordination site. Stable associations are formed there, probably involving inner sphere complexes (with alkaline earth and transition metals). The consequence of this process is that the electrostatically induced humic pseudomicelles disintegrate in a period of several hours (Engebretson and von Wandruszka, 1998).

Figure 4 shows the kinetics of surface tension development in humic solutions after a single addition of  $\text{Mg}^{2+}$ , bringing its concentration to  $1.0 \times 10^{-4} M$  (see the minima of the curves in Fig. 2). The surface tension decreased rapidly after the salt was added, reaching a minimum in 10 min (LHA) to 60 min (SRHA). It then increased, reaching a local maximum after 1 to 2 h, followed by a sustained decrease for the remainder of the measurement period. The initial sequence of events indicates the formation of amphiphilic species and their migration to the surface. While this process only took a matter of minutes for all humic solutions, there were distinct differences between the individual compounds. These differences cannot be fully explained at this time. However, the ensuing rise and subsequent extended drop in surface tension can be interpreted based on previous kinetic work using fluorescent probes (Engebretson and von Wandruszka, 1998). It is likely that the approximately hour-long period during which the surface tension rose corresponds with the electrostatically induced aggregation and pseudomicelle formation. This resulted in more compact structures, which reduced the amphiphilic character of the individual molecules and prevented them from accumulating along the air-water interface due to the hydrophilic exterior of the pseudomicelle. However, this was a transient state that gradually disappeared as the metal ions formed stable complexes and the humic structure “unfolded” again (vide supra). The result of this final conformational

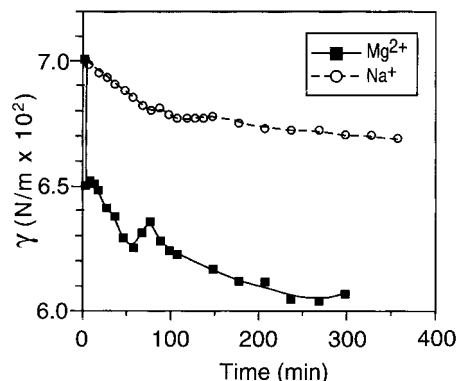


Fig. 5. Variation of surface tension with time for  $500 \text{ mg L}^{-1}$  Latahco silt loam humic acid (LSLHA) solutions (pH 6) in the presence ( $1.0 \times 10^{-4} M$ ) of  $\text{Mg}^{2+}$  or  $\text{Na}^+$ .

change was the steady decrease in surface tension shown in Fig. 4. The fact that this happened with both HAs and FAs, must again be ascribed to the formation of micelle-like structures by either intra- or intermolecular processes in dissolved humic materials. In light of this argument, monovalent cations should produce this effect to a much lesser extent, or not at all, since they are less able to induce pseudomicelle formation. This is borne out by the curves in Fig. 5, which show that the addition of  $\text{Na}^+$  led to an essentially smooth decrease in the surface tension of an LSLHA solution, showing little evidence of the intermediate rise obtained with  $\text{Mg}^{2+}$ .

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