Interactive comment on “Average molecular weight of surfactants in aerosols” by M. T. Latif and P. Brimblecombe

Anonymous Referee #1

Received and published: 12 November 2007

The paper reports a number of interesting observations about the nature of surfactants in atmospheric aerosol particles and the link between surfactants and humic-like substances (HULIS). The major fault in this paper is that the information is fragmented and it is difficult to find a common rational for the whole study. Clearly, the molecular weight measurements are only part of the work, which involves a suite of characterization techniques, including the determination of the "brown-coloured" substances, which are not accounted for by the title of the paper. The whole study looks very much a follow-up of the previous work from the same Authors (Latif and Brimblecombe, EST 2004). Overall, it is difficult to understand the results presented in this manuscript without having read carefully the EST paper. The reader has to refer to the past publication for many important experimental aspects (method for surfactant analysis, the
set of samples analysed, the standard materials used for the ozonolysis experiments),
so that the present manuscript is not fully self-consistent, but it is rather an extension
of the previous study. The Authors are invited to refocus their work, cutting all unnec-
essary information, reorganizing the paper, while including all supporting information
necessary for the comprehension of the results.

Major comments:

The estimation of the average molecular weight of a complex mixture of organic com-
ounds using ultrafiltration techniques can be challenging, especially when the chem-
ical nature of these compounds is poorly known. Because of potential molecular con-
formation effects and molecule-membrane interactions (Schafer et al., EST 2002), the
nominal pore sizes of the ultrafiltration membranes do not correspond to the actual
molecular mass of the fractionated material. Permeation coefficients to correct for
such effects are needed for quantitative ultrafiltration (Tadanier et al., EST 2000). The
Authors specify that the employed technique provides only nominal molecular weight
data, that is correct. However, the results obtained using different types of membranes
are not fully consistent. The MBAS measured in Norwich samples show a large high-
molecular weight fraction according to the separation on PL10 and PL30 membranes
(Figure 8a), while this fraction is considerably smaller based on separation on PL5
membranes (Figure 5a), which is illogical. In this reviewer’s opinion, the method em-
ployed in this study can provide information on the differences in molecular weight
distribution between samples fractionated in the same experimental conditions (as in
Fig. 5a and 5b), but it is not accurate in providing average molecular weight values in
absolute terms. It follows that the title of the paper is inappropriate.

In section 2.3, a surrogate acidity was calculated from the sum: 2nss[SO42-] +
nss[NO3-]. This is an error, since the bases have to taken into account, too.
For fine aerosol samples, the aerosol acidity can be expressed by the formula:
2nss[SO42-] + [NO3-] - [NH4+]. For PM10 or TSP samples, the calculation is more
problematic because nitrate can partition on coarse particles by displacement reac-
inations with Cl-. The paper by Ziemba et al. (J. Geophys. Res., V.112, D10S22, doi:10.1029/2006JD007605, 2007) provides a nice overview of the methods for describing aerosol acidity. Without subtracting the equivalents of ammonium in the sample, the simple sum 2nss[SO42-] + nss[NO3-] is NOT a surrogate of aerosol acidity.

Specific comments:

The whole introduction section is quite confused and can be considerably rationalised and shortened.

Introduction, page 13806, line 26 and followings: "it is clear that they are associated with the water soluble oxygenated and macromolecular polar organic substances..". This contradicts the list of alternative hypotheses (e.g., aliphatic hydrocarbons) reported in the following paragraph.

Last paragraph of page 13807: "Humic substances ..". The Authors might quote the paper by Graber and Rudich (Atmos. Chem. Phys. 6, 729-753, 2006) for a discussion on the similarities between aerosol complex organic components and the humic substances in soils and sediments.

Section 2.1. A table summarising the origin and type of the samples would greatly benefit the comprehension of the following discussion.

Section 2.6. It is not clear what the term "Brown Colourant" refers to. And why molecular size cut-offs of 10 and 30 KDa were used to separate it instead of the 5 KDa adopted for the surfactants? The occurrence of coloured organic compounds in the aerosol extracts should be clearly discussed in the Introduction, as well as the rational for the choice of the molecular size cut-offs in the experimental section.

Section 2.9. "soot exposure to ozone". This has nothing to do with the characterization of the aerosol samples. Please, clarify the scope of this section otherwise omit. Include "humic acid" in the title, and specify the source of the soot and humic acid materials.

Page 13811, line 13. What samples Figures 1a and 1b refer to? How much represen-
tative are these samples for the whole set? What is the minimum amount of sample (or DOC concentration) for which the a surface tension depression was observed?

Section 3.2 and Figures 2 and 3. I contest the use of surrogate acidity and expressed as H+ (nmol m-3) as it is derived here by the sum: 2nss[SO42-] + [NO3-] (see major comments). The observed positive correlations indicate, as correctly pointed out by the Authors, a link between surfactants and anthropogenic combustion sources, rather than with aerosol acidity. Since sulphate and nitrate make up aerosol mass mainly be gas-to-particle conversion, the surfactants might also originate from secondary sources rather than from direct vehicle emissions and biomass burning.

Page 13912, line 18. "It could be that surfactant only begins to appear in the aerosol system after DOC concentration exceeds 100 nmol m-3". Please, explain better. In this reviewer’s opinion, such threshold in DOC concentration indicates that the good correlation between surfactants and DOC found for pollution aerosol does not hold for background aerosol, in which both surfactants and DOC can be influenced by natural sources and ageing (e.g., oxidation) processes.

Section 3.5.2. This sub-section is rather obscure and should be reorganized. Based on the title of the sub-section, the discussion of the results of the UV-VIS measurements should anticipate those regarding the analysis of surfactants.

Caption of Figure 11. Replace "MBAS" with "EVAS".