

INTERFACIAL PROPERTIES OF SOOT PARTICLES IN DISPERSE SYSTEM STABILITY

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Abstract

This work is focused on the physico-chemical characterization of carbonaceous particulate emitted from controlled combustion sources and its effect on dynamic interfacial tension and surface dilational rheology of aqueous interfaces. Since large quantities of surfactants are introduced into wastewaters and water bodies by industrial activities, the properties of carbon particulate-laden liquid interfaces have been investigated in connection with the presence of surfactants. Aim of the work is to evidence the occurrence of synergetic effects between carbonaceous particulate and surfactants in the stability of water dispersions.

Two carbonaceous particulates have been selected as representative of aromatic and aliphatic soot. The carbonaceous particulate have been sampled from benzene and ethylene premixed laminar flames burning in fuel-rich condition and characterized in terms of micro and nanostructures and molecular weight distribution. Water-air (W/A) and water-hexane (W/H) interfacial properties of commercially available carbonaceous particles (carbon black) and real carbonaceous particulate have been investigated in presence of cetyl trimethylammonium bromide (CTAB), a widely used cationic surfactant. The dynamic surface/interfacial tension and the interfacial dilational rheological behaviour have been studied in relationship with their morphological properties evidenced by Atomic Force Microscopy (AFM). These results have been related also to foams stability for environmental purpose and, as perspective, to explore new techniques involving the set up of stable dispersion of carbon particulate for the synthesis of microporous materials to be employed in CO₂ capture.

Results and Discussion

Carbon particulates originated by combustion processes of benzene and ethylene (Cethylene and Cbenzene) have been studied from the interfacial properties point of view. The soot interfacial behaviour has been compared with a commercial furnace carbon black [1].

Combustion products were produced in well-controlled conditions by using premixed sooting laminar flames stabilized on a commercial water-cooled McKenna burner at atmospheric pressure. Ethylene and benzene were used as fuels to produce ethylene/O₂ (50.0/50.0, C/O=1, T_{max}=1650K) and benzene/O₂/N₂

(4.9/19.0/76.1, C/O=0.77, T_{max}=1835 K) flames. Cold gas velocity was 4 cm/s for both flames. Combustion products were isokinetically collected at 14 mm of height above the burner, corresponding to the end of soot formation region where flame-formed species reach their maximum concentration. Total particulate matter was recovered from the sampling line and extracted by dichloromethane (DCM) to separate the DCM-soluble species, containing polycyclic aromatic hydrocarbons (PAH), from the DCM-insoluble species (soot). Additional details about the sampling procedure and the analytical approach are reported elsewhere [2].

Benzene and ethylene soot microstructure [2] presented a significant degree of heterogeneity with big coalesced amorphous structures in which chain-like aggregates of small spherical primary particles are embedded. The contribution of amorphous structures appears to be lower in benzene soot. The primary particle dimension of the chain-like aggregates is 20-25 nm for benzene soot and 35-40 nm for ethylene soot. On the basis on dynamic light scattering (DLS) and size exclusion chromatography (SEC) evaluation, the hydrodynamic diameter of benzene soot (100 ±20nm) appears to be smaller with respect to the ethylene soot (150 ±20nm). Moreover SEC analysis indicates that ethylene soot is a polydispersion of particles < 20 nm and > 20 nm while benzene soot is narrow monodisperse (around 100 nm). Benzene and ethylene soot present different resistance toward oxidation as a consequence of the different microstructure and H/C content. The temperature of the maximum oxidation rate of benzene soot is 660°C (H/C = 0.059) and it is comparable to a commercial carbon black (690°C, H/C=0.039). Ethylene soot presents an oxidation rate comparable to the benzene soot (642 °C) and a higher content of H (H/C = 0.162) associated to the high number of carbon atoms edge sites accessible to oxidation. The comparable oxidation rate can be interpreted in terms of a higher surface of benzene accessible to oxidation with respect to ethylene soot.

The soot interfacial behaviour has been studied by means of measurements of the dynamic surface tension γ and of the dilational viscoelasticity (E) vs. frequency of the soot aqueous dispersions in the presence and absence of a cationic surfactant, CTAB ($C_{\text{CTAB}} = 10^{-4}\text{M}$ and $5 \cdot 10^{-4}\text{M}$). The interfacial properties have been investigated by a drop shape tensiometer (PAT1-Sinterface) [3] which is based on the acquisition of the drop profile and allows performing experiments of dynamic and equilibrium surface tension and of dilational viscous elasticity (E) vs. frequency (ν) in a low frequency range ($0.005 \text{ Hz} < \nu < 0.2 \text{ Hz}$).

The aqueous dispersions have been prepared by adding drop by drop the CTAB solution to the particle dispersion, in order to avoid the formation of aggregates. All the dispersions contain a constant amount of particles (0.1g/L) and, where CTAB is added, of roasted NaCl (1mM).

The interfacial tension measurements of the dispersions containing only the carbon particles show that both of them are not surface active, since the values of γ and E are similar to the ones of the pure solvent (72.5mN/m and 0mN/m, respectively).

The addition of CTAB reduces the γ values and leads to a decrease of the dilational viscoelasticity increasing C_{CTAB} , as shown in Figure 1.

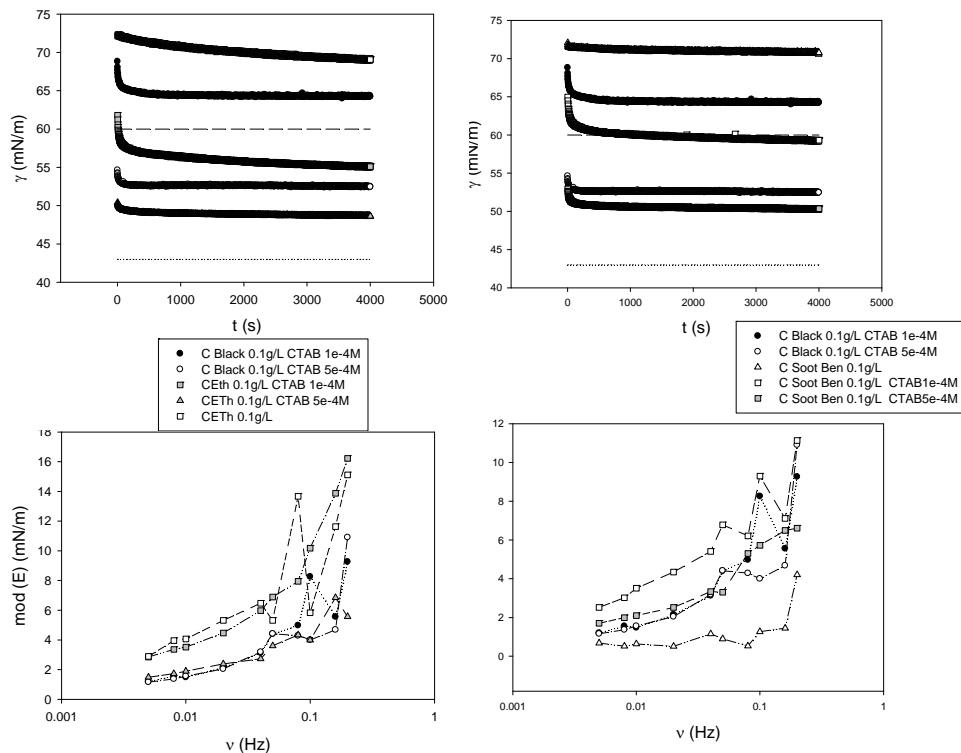


Figure 1. Dynamic surface tension and viscoelasticity modulus of Cethylene and Cblack (left) and Cbenzene and Cblack dispersions (right) with different C_{CTAB} (left); The dotted lines indicate the g equilibrium values for $C_{CTAB} = 1e-4M$ and $C_{CTAB} = 5e-4M$ aqueous solutions.

The interfacial tensions of the different kinds of particles, at constant CTAB concentration (Figure 2), evidence the fact that Cethylene mostly interacts with the surfactant molecules, since it results to be the most active at the interface. Anyway, the samples from a real industrial process are characterized by lower values of γ with respect to the commercial carbon black particles. It is interesting to notice that the presence of particles increases the surface tension values of the dispersions containing $5 \cdot 10^{-4} M$ of CTAB with respect to the value of the CTAB solution. A different behaviour is observed with the lowest C_{CTAB} . In fact, Cbenzene dispersion behaves as the surfactant solution, while the presence of Cethylene and Cblack varies the γ trends in comparison with the solution, with a γ reduction and increase respectively.

From the rheological point of view the viscoelasticities of the different systems are all comparable to each other.

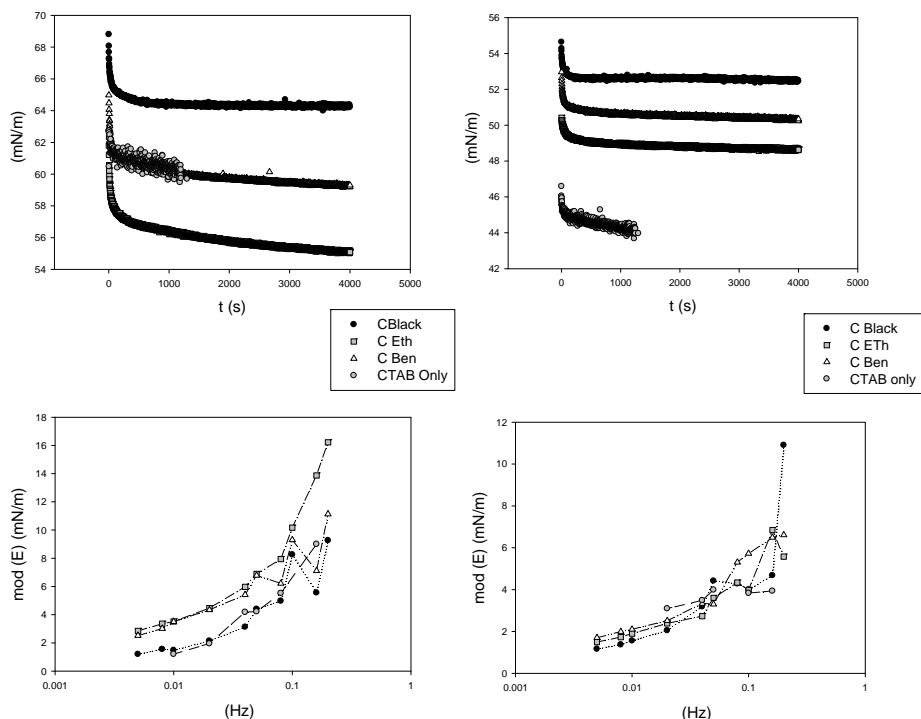


Figure 2. Dynamic surface tension and viscoelasticity modulus of carbonaceous particles at constant CCTAB = 1e-4M (left) and CCTAB = 5e-4M (right).

Interesting information on particle behaviour may be deduced by the capability of the dispersions to form stable disperse systems, such as foams. The results are summarized in Table 1.

Foams have been obtained insufflating an Argon gas flow through a porous glass disc inside a glass column. Carbon particles alone, being not surface active at water/air interface, do not allow the formation of any stable foams. The addition of CTAB to the particles gives rise to stable disperse systems only for the highest surfactant concentration. The destabilization time of the foam in the presence of ethylene soot is comparable to the one of the pure surfactant. This means that the stability of the foam is not ascribable to the presence of the solid particles. While, the presence of the other kind of particles reduces the foam life time, with respect to the pure CTAB [4,5].

The behaviour and features of these real particulates are comparable to the ones of commercial carbon black particles [1]. Even in this latter case, a stable foam is formed with the highest CTAB amount and its destabilization time is higher in comparison with the foams obtained with soot from ethylene and benzene.

The different foam life times are not explained by the interfacial properties of the systems at water/air interface. In fact, the dilational viscoelasticities of the samples

are all comparable to each other. While from the surface tension point of view, γ values decrease increasing the surfactant concentration, which may favour the foam formation, but not the foam stabilization. The different foam stabilization may be ascribable to the presence of carbon particles at the fluid interface, which act as a steric barrier, preventing the bubble coalescence and, hence, increasing the foam life time.

Table 1. Formation and stability of foams from 0.1g/L carbonaceous particle aqueous dispersions.

System	Foam Formation
Carbon Black	NO
Carbon Black + CTAB = 1e-4M	NO
Carbon Black + CTAB = 5e-4M	YES (t = 2h 30min)
Cbenzene	NO
Cbenzene + CTAB = 1e-4M	NO
Cbenzene + CTAB = 5e-4M	YES (t = 1h 20min)
Cethylene	NO
Cethylene + CTAB = 1e-4M	NO
Cethylene + CTAB = 5e-4M	YES (t = 2h)
CTAB = 1e-4M	NO
CTAB = 5e-4M	YES (t = 2h)

The AFM study of the ethylene and benzene soot was performed using a Veeco Nanoscope III (Digital Instrument, Santa Barbara, CA). This allows a sample up to about 1 cm^2 to be fitted in the operational stage with a maximum scanning area of about $12\text{ }\mu\text{m}$ and a Z resolution of about $4\text{ }\mu\text{m}$ for imaging. It has been used in air in contact mode with minimum force using a SiN probe. In order to evaluate the interfacial properties of the carbon particles, measurements with a colloidal probe have been carried out. This technique was performed utilizing probes with different surface behavior: silica (hydrophilic) and polystyrene (hydrophobic). All the samples have been prepared by evaporation of the corresponding dispersions in acetone.

In CBlack aggregates, particles can be found of an average diameter of 15-20 nm with a more frequent spherical symmetry [2]. Benzene and ethylene soot (Figure 3) present bodies of cylindrical geometry with diameters 80-100 nm and height on the order of 10 nm. Ethylene soot shows similar results with higher presence of

aggregates. In addition, from the study of the interaction with hydrophobic and hydrophilic particles (polystyrene and SiO_2) by means of the colloidal probe technique Cbenzene and Cethylene show a characteristic mostly hydrophobic with an adhesion to the SiO_2 particle practically negligible while on the other side with the polystyrene probe (hydrophobic) the adhesion is more remarkable.

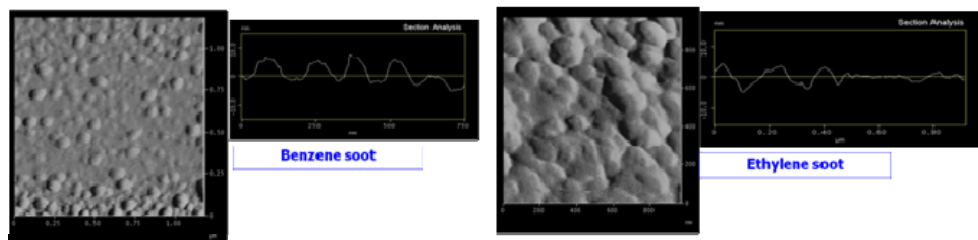


Figure 3. AFM images of ethylene and benzene soot.

Acknowledgments

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