Water Interaction with Laboratory-Simulated Fossil Fuel Combustion Particles

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To clarify the impact of fossil fuel combustion particles' composition on their capacity to take up water, we apply a laboratory approach in which the method of deposition of compounds, identified in the particulate coverage of diesel and aircraft engine soot particles, is developed. It is found that near-monolayer organic/inorganic coverage of the soot particles may be represented by three groups of fossil fuel combustion-derived particulate matter with respect to their Hansh's coefficients related to hydrophilic properties. Water adsorption measurements show that nonpolar organics (aliphatic and aromatic hydrocarbons) lead to hydrophobization of the soot surface. Acidic properties of organic compounds such as those of oxidized PAHs, ethers, ketones, aromatic, and aliphatic acids are related to higher water uptake, whereas inorganic acids and ionic compounds such as salts of organic acids are shown to be responsible for soot hydrophilization. This finding allows us to quantify the role of the chemical identity of soot surface compounds in water uptake and the water interaction with fossil fuel combustion particles in the humid atmosphere.

1. Introduction

The atmospheric importance of combustion-derived aerosols is primarily a result of their impact on the radiative balance and cloudiness related to global climate change.[1] Soot particles, also known as black carbon (BC), account for both the direct heating due to light absorption and indirect cooling because of the activation as cloud condensation nuclei (CCN) and ice nuclei (IN). Soot emission from transport systems is currently acknowledged to be the largest source of uncertainty in understanding the impact of fossil fuel burning on regional and global climate.[2] In this context, aircraft-generated IN have a special significance because they may allow ice nucleation at lower supersaturations than those required for homogeneous freezing, resulting in an increase in cirrus cloud coverage and changing their microphysical and optical properties.[3] The analysis of ice-nucleating aerosols sampled in cirrus clouds showed that they are dominated by carbonaceous particles.[4] However, there is considerable uncertainty regarding the quantitative estimate of the ice-nucleating ability of combustion-derived aerosols in the upper troposphere because it is difficult to obtain unambiguous evidence from in situ measurements for water uptake by BC aerosols and to identify the pathways from which they evolve into cloud formation.

Moreover, there is limited information on characteristics of soot exhausts from different combustion sources. Classical models of the composition of BC show them to be constructed of misaligned graphite platelets that form a nanoporous network that contains functional oxygenated groups.[5] However, chemical analysis of original combustion particles shows that soot not only addresses the properties of elemental carbon (EC) but also includes many varieties of organic carbon (OC) that together comprise an extremely complex structure.[6] The content of OC is known to vary with engine operating conditions and can represent 5−90% of the total mass of the particulate matter.[7] A comprehensive evaluation of organics present in diesel exhaust soot,[8] in motor vehicle soot,[9] and in aircraft engine combustor (AEC) soot[10] have pointed out the different classes of C_1 through C_{30} organic compounds. Motor vehicles can be regarded as one of the more serious sources of soot-associated polyaromatic hydrocarbons (PAHs) contributing most of the nanoparticle mass.[11] The evaluation of soot produced by light-duty diesel vehicles shows heavy alkanes constituting from 30 to 60% of the organic mass as a function of engine operating conditions.[12] Analysis by gas chromatographic mass spectrometry (GC/MS) facilitates the differentiation of particle-bound organics into fractions. Namely, 28 particulate-phase organic compounds are quantified in medium duty diesel exhaust, such as *n*- and branched alkanes, saturated cycloalkanes, aromatic hydrocarbons, *n*-alkanoic, alkanedioic, and aromatic acids.[8] Motor vehicle organic soot matter consists of alkanes, organic acids, PAHs, and oxygenated PAHs.[9] Some of organic compounds may consist of unburned lubrication oil and fuel. Recent GC/MS analysis of AEC soot[10] has shown the presence of many organic compounds similar to the composition of diesel soot fractionated in Schauer et al.[8] Moreover, alkens, benzene derivatives (alkilbenzenes), oxyalkanoic acids, ketones, esters, and phenols were identified.

The quantification of water uptake by soot particles, including aircraft-generated residuals, has been recently advanced in a number of laboratory studies[13,14] that suggest that the formation of a water film, extended over the surface of a particle, is a quantifiable measure that separates hygroscopic from nonhygroscopic soot. If soot particles are made mostly from EC, have a water insoluble organic coverage, or both, then they are classified as nonhygroscopic. Low water adsorption on some active sites is a typical mechanism of water interaction with hydrophobic soot. If the water film extended over the surface is formed because of water cluster formation on active sites and their confluence on the surface, then hydrophilic soot is assumed. Water uptake on hygroscopic soot significantly exceeds the formation of many surface layers; however, a number of important questions still remain, such as what features on the particle surface are responsible for active sites and water film formation and what surface OC compounds induce water

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uptake (phenomenon of hydrophilization) or retard water uptake (hydrophobization).

The determination of the surface requirements for water/ice nucleation at the microscopic level remains to be one of the most complex problems in understanding CCN and IN activation of BC aerosols in the atmosphere. It is assumed that soot aerosols may be incorporated into cloud droplets through the presence of water-soluble compounds.[15] The analysis of the chemical composition of atmospheric particles has shown the influence of organics on hygroscopic properties.[16] Inorganic and organic ions as well as three main classes of soluble organic compounds (neutral species, mono- and dicarboxylic acids, and polycarboxylic acids) were observed in fog and cloud droplets.[17] Published studies provide evidence of polar organic compounds taking up water[18] and thus increasing the cloud and fog formation ability of insoluble soot particles. Moreover, coating of internally mixed particles by sulfates and OCs may enhance their light adsorption in the atmosphere.[19] Hydrophilic coating reduces the lifetime and atmospheric loading of BC aerosols. Global climate models predict the significant aviation impact on cloudiness and climate assuming the high CCN activity of aircraft-generated soot.[20]

During combustion, most of the sulfur in fossil (diesel, kerosene) fuel is oxidized to SO_2 and reacts with water to form sulfuric acid. Sulfuric acid makes up $\sim 1.2-5.3\%$ of the diesel particles mass at 40% engine load.[21] If water-soluble organic compounds and electrolytic inorganic substances (mainly sulfate, nitrate, chloride, and sodium) are present on a soot particle, then high water uptake may be predicted. For instance, the analysis of solute composition of diesel engine soot showed 0.19, 0.2, 1.6, and 0.57 wt % of SO_4^{2-}, Na^+, K^+, and Cl^-, respectively, totaling 3.5 wt % of soluble compounds.[22] They may form acidic and ionic species such as sulfuric acid and organic salts and impact the high CCN activity and hygroscopicity of diesel engine soot. Therefore, this type of soot shows significant growth of the particle diameter at subsaturation, a growth factor of 1.05 at 93% relative humidity (RH).[23]

Spectroscopic features of sulfate ions and organic sulfates have been obtained for aircraft engine-generated soot.[24,25] Sulfate ions, as much as 3.5 wt %, as well as 1.5 wt % of organic ions, such as acetate CH_3COO^-, formate $HCOO^-$, and oxalate $C_2O_4^-$, are extracted by water from AEC soot.[25] This is why the presence of low-molecular-weight organic acids, for instance, oxalic acid, may be expected to form on the surface of aviation soot, together with other organic compounds containing heteroatoms and sulfates that may provide the surface functionalities responsible for water uptake and the significant growth of the particle diameter; the growth factor is 1.22 at 93% RH.[13]

Different phenomena can occur if hydrophobic organic compounds form a surface film on the particles.[16] Low water uptake may occur because of adsorption on imperfections and structural defects. Nonpolar organic compounds do not generally take up water[18] and also may form films that lower the accommodation coefficient of water on the particles, thereby inhibiting absorption of water on the surface.

To demonstrate the effect of organic compounds on the hydrophilicity of soot particles, a laboratory approach applying the modification of BC particles by some organic compounds was developed in Dusek et al., Andrews and Larson, and Kotzik and Niessner.[26–28] It was found that coating with hexadecanol or benzo[*a*]pyrene efficiently suppressed the activation of CCN, whereas coating with ester, sodium salt, or azelaic acid increased the sensitivity of particle growth. Such a laboratory approach may be applied for studies of the effect of organic compounds

on the surface of combustion-derived particles. The majority of organic species found in combustion particles and the wide range of their individual properties significantly restrict the utility of such an approach. Recently, to resolve similar problems, a simplification of the representation of organic components in atmospheric particles was suggested in McFiggans et al.[29] Organic aerosol species were grouped into a relatively small number of representative compounds with respect to hygroscopicity that was then used to predict their behavior in the humid atmosphere.

This article presents an analysis of the impact on the ability of particles to interact with water of main classes of organic/inorganic compounds found in the covering of fossil fuel combustion soot. Water uptake measurements were performed on laboratory-simulated soot that are representative of carbonaceous aerosols emitted from transport sources (diesel, aviation) with respect to their composition. The role of chemical identity (molecular forms, polarity, and nature) and amount of oxygen-containing functionalities (aliphatic vs aromatic character) of the surface compounds is demonstrated. This representation is used to address the mechanism of water interaction with fossil fuel combustion particles in the humid atmosphere.

2. Laboratory Approach

Premixed flame soot, made in the laboratory and produced at various air/fuel combustion ratios by burning three fuels such as *n*-hexane, JP-8 (Jet fuel), and diesel, was analyzed by Jones[30] with GC/MS. The goal was to monitor the soot organic content dependent on combustion conditions. A correlation was found between the appearance of oxidized lower-weight aromatics with increased air/fuel ratio and an increase in soot particle hydration. A laboratory similar approach has been taken in the present study with the objective of finding the relationship between soot coverage composition and water uptake.

Because the chemical analysis of original combustion soot shows that it consists of EC with some fraction of OC on the surface, we assume that a laboratory-simulated soot substrate consisting of EC with an organic coverage is representative of original soot. The approach for producing the coverage by deposition of a given organic species on the EC substrate is described in Kiselev et al., Kovaleva and Shcherbakova, Vlasenko et al., and Esteve et al.[31–34] In our work, we use EC soot as a basis substrate and deposit organic compounds that are representative of those identified in the surface coverage of soot produced by fossil fuel burning.

Only small portions of the total particulate organic compound mass on soot produced by original combustion sources can be quantified as individual organic species.[9] Therefore, the composition of the resolved component in diesel soot ranges from 20 to 60% of alkanes, 20 to 30% of *n*-alkanoic and alkanedioic acids, 4 to 40% of PAHs, and less than 4% each of the benzoic acids, oxy-PAH, hopanes, steranes, and other compounds.[8] Therefore, we produced soot substrates by deposition of organic compounds from the main classes of organics identified in the surface coverage of soot produced by fossil fuel burning.

Acetylene soot (AS) and graphitized thermal soot (GTS) were chosen in our work as the basic EC substrate (EC soot) because of the pure EC composition and perfect homogeneous hydrophobic surface, as described in Kiselev et al.[35] and Greg and Sing.[36] AS soot is a commercially available material (Ukhta OPP) produced by acetylene exposure in an oxygen-free atmosphere. GTS soot was obtained from commercial thermal soot (Ukhta OPP) by high-temperature (3000 °C in the nitrogen flow) treatment. Three samples were produced by repeated graphitization procedure.

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TABLE 1: Main Classes of Organics Identified on Diesel and Aviation Soot and Their Representatives Chosen for Laboratory Simulation

class	alkanes	PAHs oxidized PAHs	aromatic acids	n-alkanoicacids	phenols
representative/formula	hexadecane $C_{16}H_{34}$	anthracene $C_{14}H_8O_2$ anthraquinone $C_{14}H_8O_2$ alizarine $C_{14}H_8O_4$	benzoic C_6H_5COOH phtalic $1,2\text{-}C_6H_4(COOH)$ trimellitic $1,2,4\text{-}C_6H_3(COOH)_3$	oxalic $HOOC-COOH$ stearic $C_{17}H_{35}COOH$	phenol C_6H_5OH
Hansch's parameter	8.536	4.304 3.669 1.285	1.848 1.034 0.921	−1.196 7.564	1.458

The main classes of organics identified in diesel and aviation soot are summarized in Table 1. Alkanes and PAHs represent the main classes of nonpolar organics, phenols and ketones are characterized as low-polar aromatic compounds, whereas aromatic and aliphatic acids relate to polar materials. "Representatives" are selected from each class of identified compounds, namely, hexadecane for alkanes, anthracene for PAHs, anthraquinon and alizarine for oxidized PAHs, benzoic, phtalic, and trimellitic acids for aromatic acids, oxalic and stearic acid for *n*-alkanoic acids, and phenol for phenols. (See Table 1.) Additionally, anthraquinon represents well the properties of polyaromatic ketones. The properties of ionic compounds and electrolytic inorganic substance in the soot coverage are represented by salt of carbonic acid, namely, sodium salt of benzoic acid (Na benzoate) and sulfuric acid.

In our work, EC basic soot is covered by the representative organic/inorganic compound serving as a modifier. Although the hygroscopic effect will likely depend on the composition and structure of the multicomponent organic film on a original combustion particle, we limit the simulation to a single component film.

Adsorption modification is performed with the aqueous or organic solution dependent on the nature of the modifier and its solubility in a given solvent. The concentration of the modifier is chosen to be less than its solubility in the solution. For adsorption of hexadecane, heptane is used as a solvent, whereas anthracene and anthraquinon are deposited from benzene. For adsorption modification by alizarine, benzoic, and phtalic acids, ethanol is used. Oxalic and stearic acids are deposited from diethylic ether and chloroform, respectively. Phenol, trimellitic and sulfuric acids, alizarine red S, and benzoate Na produce the EC soot coverage from aqueous solutions. The consequence drying of the sample at $100-120$ °C in an oven removes the solvent. The homogeneous distribution of the modifier over the soot surface is achieved by careful mixing in a solution by evaporation of the solvent in an oven. The ratio of modifier to soot mass defines the thickness of the coverage. Variation of the solution concentration allows the deposition of organic matter from submonolayer to multilayers, that is, the production of up to $5-10\%$ of the OC coverage. For this purpose, the concentration of soot in the solvent is varied from 5 to 50%.

The BC surface can have acidic as well as basic properties. The acidic properties are caused by the presence of carboxyl groups and phenolic hydroxyl.[37] The acidity of a given functional group depends on its chemical environment, that is, the size and shape of polyaromatic layers, the presence and position of constituents, and the charge of neighboring groups. The reason for basic behavior of the carbon surface may be the π-basicity of graphene layers. The other is the pyrone-type structures on the edges of the polyaromatic layers. The concentration of basic sites decreases with increasing acidic character of the surface.[37] The surface functionalities such as carboxyl, hydroxyl, carbonyl, phenolic hydroxyl, anhydride, ethers, and quinone may create the hydrogen bonds of different strength impacting the extent of soot hygroscopicity.[38,39]

With the intent to demonstrate the impact of the acidity of functional groups on water uptake, we produce a suite of model soots by deposition of a nonpolar organic compound ("forefather") and of its derivatives containing functional groups of different polarity and ionic nature. The structure formulas of deposited compounds are shown in the scheme of Figure 1. Three-ring PAH, anthracene (1), is chosen as a forefather substrate. Its derivatives are created by deposition of anthraquinone (2) (contains additionally two quinone $=C=O$ groups), alizarine (3) (two phenolic hydroxyl $\equiv C-OH$ groups), and alizarine red S (4) (subsequent addition of the sulfoxide sodium $SO_3^-Na^+$ group).

Thermodesorption spectrometry is used to measure the specific surface area of EC and laboratory-simulated soot after low-temperature N_2 adsorption for both a reference sample having a known surface area and the sample of interest. Comparison of integral intensities of the thermodesorption spectra provides us with an estimate of the surface area with an accuracy 5%.

The amount of water uptake on soot was measured versus relative humidity (RH) in a controlled humidity desiccator using a gravimetrical method described by Kantro et al.[40] Those soots that were chosen as EC basic substrates, GTS and AS, were heated before adsorption measurements at 100 °C for 3 h to remove possible contaminations and chemisorbed water. We controlled the level of cleaning by repeatedly weighing the soot sample until the constant weight was attained. To save the deposited material on laboratory-produced soots, they were cleaned and dried in air at the water vapor pressure of 2×10^{-5} Torr, corresponding to RH $\approx 10^{-4}\%$. We achieved equilibrium water uptake during the adsorption measurements by repeatedly weighing the soot samples at a given RH until a
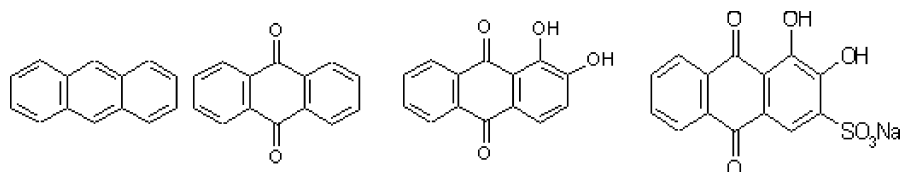
Figure 1. Organic compounds anthracene and its derivatives containing functional groups of different polarity.

constant value was attained. The accuracy of water uptake measurements is within 5−15%, dependent on the hydrophilicity of the sample. Reproducibility of results is proved by numerous repetitions of laboratory soot production and water uptake measurements.

For comparative analysis of the role of a given organic coverage in water uptake, absolute water uptake (the amount of water molecules, $N(H_2O)$, per unit of the surface area, nm^2) versus the RH is presented at $T = 295$ K. The values of absolute water uptake are calculated from gravimetric data, obtained in millimoles per gram, using the measured surface areas of bulk soot samples, obtained in meters squared per gram. It was found that the surface area of all modified soots in our study is within 8% of the value obtained for EC basic soot.

3. Results

3.1. Water Uptake on Elemental Carbon Soot. The fundamental theory of water adsorption on BCs assumes that because of low dispersion energy between water molecules and graphite platelets, there is a strong dependence on the presence of hydrophilic sites, so-called primary adsorption sites.[41,42] Graphitized soot is proposed in the literature as the reference hydrophobic material; it possesses a homogeneous surface with a very small fraction of hydrophilic heterogeneities known as residual active sites.[43−45] The edges of the graphene planes and in-plane carbon vacancies may be available for interaction with reactive molecules.[46] Young[43] et al. measured its amount to be about 1/1500 of the value that would be expected in the case of the nearest water molecular packing on the solid surface (a statistic monolayer of water ML). At 95% RH, only about 1/30 of water ML is adsorbed on graphitized soot, and a small increase in adsorption is observed at highest RH because of capillary condensation into interparticle cavities.[44,45]

GTS was produced and chosen for our study. It demonstrates the perfect polyhedron structure of primary particles arising because of graphitization of the soot surface under high-temperature exposure (near 3000 °C).[13] The graphitization procedure remove organics, oxygen, and other impurities from the soot surface;[36] therefore, it leads to the formation of a chemically and geometrically homogeneous surface made from basis planes of graphite. But some hydrophilic heterogeneities probably arise from traces of oxygen-containing functionalities, such as those that might be expected on the structure defects and at the edge atoms of graphite planes.[43,46] The presence of heterogeneities such as phenolic and carboxyl groups is attractive for water adsorption.[47,48] These functionalities may also be responsible for chemisorptions of some organic and ionic species as well as for heterogeneous mono- and bimolecular reactions on the graphite surface.[49]

The isotherm of water adsorption on one sample of GTS soot is shown in Figure 2 The measured surface area of 6 m^2/g is assumed. Adsorption on GTS at low RH was so limited that we could not estimate the number of residual active sites. A small increase in adsorption near 2 H_2O per nm^2 is observed at 96% RH, probably because of small cluster formation on some residual active sites.[45] The maximum of the GTS soot adsorption capacity, near 5.5 H_2O per nm^2, is reached at saturation. For comparison, the value of one ML of water, 10 H_2O per nm^2, can be calculated assuming an effective molecular cross-section area for the water molecule of 0.105 nm^2. Two other GTS soot samples, produced by the repeated graphitization procedure, appear to have a more homogeneous surface and therefore slightly less water adsorption, as will be presented below in Figures 5 and 6.
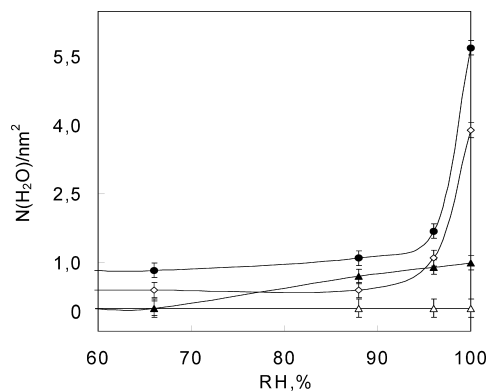
Figure 2. Isotherms of water adsorption on EC soot with hexadecane coverage of 2 (▲) and 12 nm^{-2} (△) and with anthracene coverage of 12 nm^{-2} (◇). The isotherm of EC soot is indicated by ●. The curves are to guide the eye.
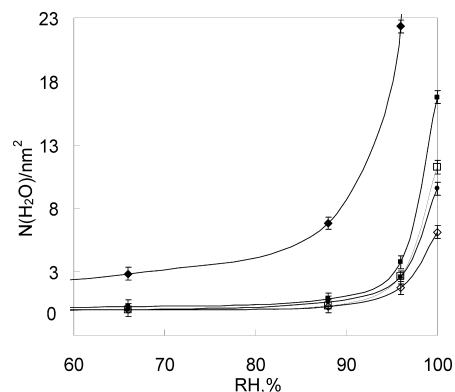
Figure 3. Isotherms of water adsorption on model soots with organic compounds containing functional groups of different polarity and ionic nature shown in Figure 1. Symbols mark the experimental data for deposited anthracene (◇), anthraquinone (□), alizarine (■), and alizarine red S (◆). Coverage is 0.3 nm^{-2}. The isotherm of EC soot is indicated by ●.

AS has surface structure and adsorption capacity very similar to those of GTS soot; however, the surface area of AS, 80 m^2/g, is larger than GTS. That is why this soot was recommended by Kiselev et al.[35] for replacement of GTS soot in adsorption studies requiring substrates with higher surface area. The AS isotherm of water adsorption is shown in Figure 3. Maximal uptake on AS soot is higher than that on GTS soot, near 9 H_2O per nm^2 because of the impact of more-developed mesoporosity relating to higher surface area. Both GTS and AS soot represent EC soot in our study.

3.2. Effect of Hydrophobization by Alkanes. Representative organic compounds serving as organic modifiers may be separated into two groups. The first one, alkanes and PAHs, contains only C and H atoms; therefore, their interaction with water is assumed to be very weak and should produce a hydrophobic coverage. Oxygen-containing hydrocarbons, that is, acids, salts, phenols, and quinines, of the second group are characterized by diphilicity (or amphiphilicity) because they are composed of two parts, namely, a polar functional group and a nonpolar hydrocarbon radical. The polar functional group is hydrophilic in nature and may form the hydrogen bond with water molecules. The hydrophilic properties of diphilic molecules and their solubility in water depend on the mass ratio of hydrophilic and hydrophobic parts of the organic molecule. The structure and composition of the hydrophilic part play a significant role.

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In general, the surface modification by some layers decreases the adsorption potential of the surface for the interacting molecules because of the increasing distance from the surface. Therefore, the chemical nature of the covering molecules becomes dominate. In the case of interaction with water molecules, the surface coverage decreases the number density of the active residual adsorption centers on the EC surface because of their occupation by a modifier. Therefore, we may assume that the polarity of the modified surface should be mostly determined by the chemical nature of deposited molecules, but their impact depends on the total coverage.

Alkanes, made from $-(CH_2)-$ chains with no polar functionalities, are nonpolar insoluble organic compounds. We may assume that their deposition on the surface of EC soot should decrease the influence of residual sites but cannot provide new active sites for the water adsorption. This is confirmed by water uptake measurements on soot covered by hexadecane. Figure 2 shows the water isotherms obtained for pure GTS soot and GTS soot covered by hexadecane. Error bars show one standard deviation of the range of amount of water adsorbed at a given RH. One sees that at saturation, EC soot with the hexadecane coverage of 2 nm^{-2} exhibits five times less adsorption than the original EC soot. Such coverage corresponds to an equivalent amount of $\sim$2 ML of hexadecane, assuming an effective molecular cross-section area of 1.07 nm^2, as presented in Gregg and Sing.[36] It is found that nearly 12 nm^{-2} of the hexadecane coverage (near 12 ML) is needed to approach the total hydrophobization of the EC surface. (See Figure 2.) Therefore, we may conclude that there is a quite strong interaction of water molecules with residual adsorption sites that requires a large thickness of the layer to minimize the role of the EC surface.

Here it is worth noting that some measurable and prominent effect of the surface modification by alkane is observed only at the highest relative humidities, a phenomenon that will be observed for many other modifiers, as discussed below. Therefore, this range of RH will be presented in all of the Figures of this article. Most likely, at the highest RH, the clusters may grow, indicating the effect of modifiers more prominently or capillary condensation that helps to increase uptake.

It is found that the same large coverage of 12 nm^{-2} of anthracene (corresponding to $\sim$9 ML)[50] is not enough for total hydrophobization of the EC surface. As one sees in Figure 2, EC soot with such coverage of anthracene still demonstrates some measurable water adsorption. The π-electrons in the PAH aromatic rings likely form the weak hydrogen bound with water molecules.

3.3. Impact of Surface Functionalities. Oxygen-containing functional groups of a modifier, assuming they act as primary adsorption site, are proposed to increase the water interaction with the modifier coverage because of the hydrogen bond formation. But the different strength of the hydrogen bond may alter the impact. This effect is demonstrated by water uptake measurements on a suite of model soots with organic compounds containing functional groups of different polarity, including ionic ones. In the first series of measurements, we deposit a low concentration of molecules, 0.3 nm^{-2}, that corresponds to about 0.2 to 0.35 ML[50,51] to observe the effect of new active sites in competition with residual ones of EC soot. Isotherms of water adsorption on model soots with anthracene, anthraquinon, alizarine, and alizarine S coverages of 0.3 nm^{-2} are plotted in Figure 3. Deposition of the forefather substrate, anthracene, leads to 30% less water adsorption than on EC soot. This hydrophobization effect was discussed above. The presence of two quinone groups in the anthraquinon coverage induces the
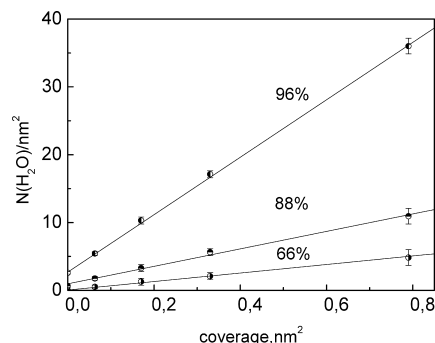

Figure 4. Water adsorption on model soot versus coverage of sodium salt of sulfoacid at various relative humidities: 66, 88, and 96%.

increase in water uptake up to the capability of original EC soot. The isotherm of model soot with anthraquinon is very similar to one of EC soot. It is likely that a number of new active sites, induced by quinine groups, are similar to the amount of residual sites of EC soot. Two additional phenolic hydroxyl groups in the alizarin modifier double the number of active sites, consequently leading to a slight increase in water uptake up to 1.7 times at saturation. We should probably take into account the possibility for limitation of the water adsorption on the alizarin coverage due to the intermolecular hydrogen bounds between $=O$ and $-OH$ groups in the alizarin molecule.

In comparison with weakly polar functional groups of organic compounds discussed above, the ionic sulfoxide group in sodium salt provides a prominent effect. This organic salt increases the water adsorption one order of magnitude at saturation. (See Figure 3.) Moreover, the water adsorption on EC soot with the alizarine red S coverage is found to be significantly higher than that on EC soot over the total RH range, a feature of hydrophilic BCs having a significant number of strong active sites on the surface.[36]

In the second series of measurements, the variation of the coverage with ionic sulfoxide groups up to a monolayer allows us to analyze the impact of a number of active sites. Figure 4 shows the water adsorption at three values of RH for the different alizarine red S content up to 0.8 nm^{-2}. The solid lines show the linear fit of experimental points denoted by symbols with a high correlation of r^2 near 0.998. The linear dependence of the water adsorption on the modifier coverage assumes a proportional increase in a number of active sites.

Variation of the coverage up to a monolayer of weakly polar aromatic compounds containing quinone groups does not change the water adsorption ability of EC soot, whereas phenolic hydroxyl groups have a small hydrophilization effect. The alizarine coverage of one order of magnitude higher than the one shown in Figure 3 changes the water adsorption up to 1.7 times only at saturation. It is likely that the oxygen-containing derivatives of anthracene have a large hydrophobic part whose influence can not be overpowered by hydrophilic functional groups. Therefore, nonionogenic oxygen-containing PAH derivatives found in the organic coverage of fossil fuel burning soots may not always significantly impact the hygroscopic nature of the soot particles.

3.4. Effect of Hydrophilization by Organic Acids. Carboxyl groups COOH of organic acids are assumed to impact the water interaction with soot more than other oxygen-containing polar functionalities because of their ability to form the strongest hydrogen bond.[52] The activity of these sites is determined by the impact of the hydrocarbon part of organic acid that significantly affects the strength of the H-bond in OH
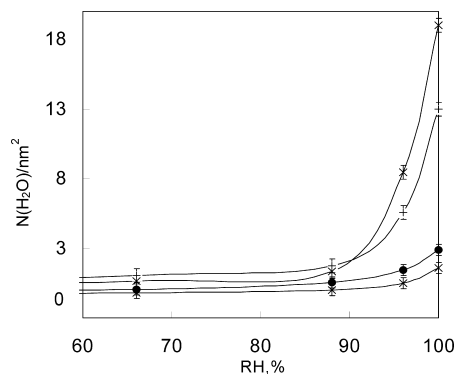
Figure 5. Isotherms of water adsorption on EC soot with deposited benzoic ($\times$), phtalic ($+$), and trimellitic acids ($*$). Coverage is 3.5 nm^{-2}. Isotherm of EC soot is indicated by ●.

Figure 6. Isotherms of water adsorption on EC soot with deposited phenol (Δ), stearic acid (▲), and oxalic acid ($\bigcirc$). Coverage is 3.5 nm^{-2}. Isotherm of EC soot is indicated by ●.

and $-$COOH groups. Moreover, the molecular form, that is, chemical composition and geometry of the molecule (aliphatic vs aromatic character), plays a dominant role in this case. To demonstrate this impact, water uptake measurements on a number of soots with deposited aromatic acids containing one, two, and three carboxyl groups are performed. For this series of measurements, we cover the surface by modifiers at the same number density 3.5 nm^{-2}. These layers correspond to ~1.9, 2.3, and 2.5 ML of benzoic,[53] phtalic, and trimellitic acids,[54] respectively.

Figure 5 shows the isotherms of water adsorption on soots with benzoic, phtalic, and trimellitic acid coverage. One sees that the impact of one carboxyl functional group of benzoic acid is negligible, even less than one of the residual active sites of the EC surface. It seems that in this case the impact of the hydrophobic hydrocarbon part of the molecule is dominant. At saturation, increasing the number of carboxylic groups in aromatic phtalic and trimellitic acids leads to an increase in the water adsorption in comparison with benzoic acid, up to 1 and 2 ML of water, respectively. Moreover, the ability of carboxyl acids to build intermolecular hydrogen bonds may lead to the dimer association between carboxyl groups, and these bonds may play some role in the limitation of the interaction with water.[55]

A comparison of the water adsorption on EC soot covered by phtalic acid with soot covered by oxalic acid of the same coverage demonstrates the role of a molecular form of acid (aliphatic vs aromatic character) because the oxalic acid molecule has two carboxyl groups but is aliphatic in character. The oxalic acid molecule does not contain any methyl groups and is easily dissociated because of the polarized $-$OH bond. Therefore, it forms the strongest hydrogen bond with a water molecule between oxygen-containing molecules studied in this work.

Figure 6 shows the high water adsorption on EC soot of oxalic acid with 3.5 nm^{-2} coverage (1 ML). It approaches up to 1.4 ML of water at 96% RH, whereas the phtalic acid coverage demonstrates only 0.1 ML of water. (See Figure 5.) Moreover, the effect of hydrophilization of the EC surface by oxalic acid may be observed because significant water uptake is seen over the total range of the RH. Even three carboxylic groups of aromatic trimellitic acid cannot provide the same hydrophiliza- tion effect as oxalic acid made. (See Figure 5.) Its high water uptake correlates to the ability of oxalic acid molecules to form the crystallite hydrates (COOH)$_2$·2H$_2$O easily.[56]

The long aliphatic chain limits the hydrophilic effect of acid, as can be observed in Figure 6 for stearic acid with one carboxylic group. Lengthening of the hydrophobic hydrocarbon
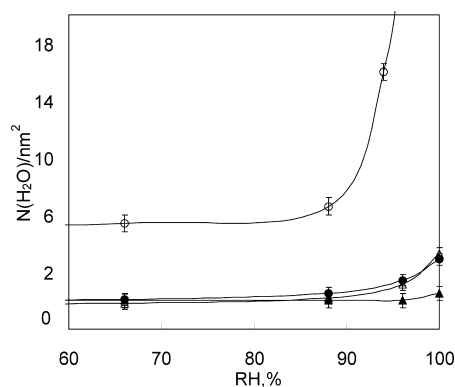
part of the acid molecule leads to the reduction of the number density of active sites on the unit of the surface, to the decrease in the polarity of $-$OH bound in a carboxyl group, and therefore to the decreased probability of the hydrogen bound formation. Therefore, the coverage by stearic acid leads to almost hydro- phobization of the EC surface.

Phenol, possessing the properties of a very weak acid, was also included in our analysis. The isotherm of water adsorption on EC soot with phenol coverage of 3.5 nm^{-2} is shown in Figure 6. Its deposition, corresponding to ~1.4 ML,[57] cannot lead to water uptake higher than one on the residual active sites of EC soot. One sees in Figure 6 that at 96% RH, the water adsorption is 1.3 times less on EC soot with the phenol coverage than on EC soot. Therefore, we should conclude that the presence of a very weak acid leads to the effect of hydrophobization of the EC surface.

It is worth noting the strong difference between water interaction with phenol and oxalic acid soot coverage. Both of these organic matters are soluble in water, but the acidity of phenol is significantly less than that of oxalic acid, and the impact of the coverage of these two acids on the water adsorption is strongly different (Figure 6). Therefore, we may conclude that the acidity of organic compounds is the dominant characteristic in determining the water adsorption.

To quantify the effect of the molecular form of an organic acid and its strength, we analyzed the water uptake by soot with a given acid coverage with respect to the correlation with characteristics of this acid, namely, the acidity constant pK and solubility in water. For comparison, we included the strongest inorganic acid, sulfuric acid. The dependences of the water adsorption on pK and solubility of deposited acids are presented for different relative humidities in Figure 7a,b, respectively. Low-solubility benzoic acid with the highest pK has a negligible effect on water uptake. But the lower the value of pK, the stronger the acid, and we observe the increasing amount of water adsorbed on soots with phtalic, trimellitic, and oxalic acid coverage in correlation with their acidity constants. Similar behavior is found in the dependence on the acid solubility.

3.5. Effect of Hydrophilization by Ionic Compounds and Inorganic Acids. Our studies show that organic acids on the surface of hydrophobic EC soot, except oxalic acid, weakly impact the hydrophilization of its surface because low water adsorption is observed up to 96% RH, not exceeding 1 ML of water. Significantly higher water adsorption may be seen on modified soot surfaces with deposited ionic compounds such as salts of carbonic acids. Above, we observed this effect by analyzing the impact of ionic surface functionalities such as
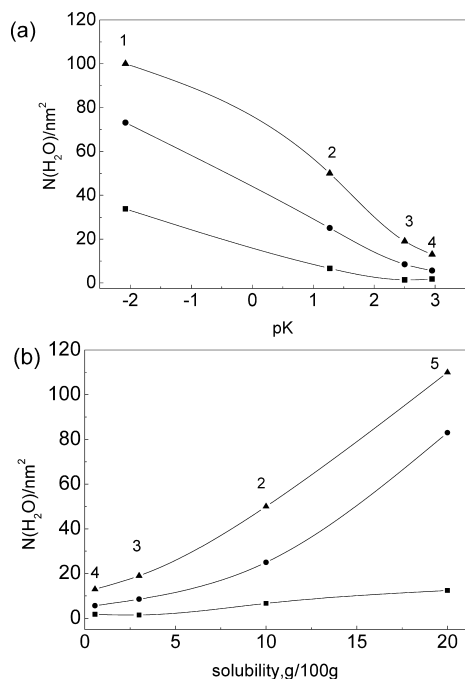
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(a)

(b)

Figure 7. Water adsorption on EC soots with sulfuric (1), oxalic (2), trimellitic (3), phtalic acid (4), and Na benzoate (5) coverages versus (a) acidity constant pK and (b) solubility of modifier. Coverage is 3.5 nm^{-2}. RH: 88 (■), 96 (●), and 100% (▲).
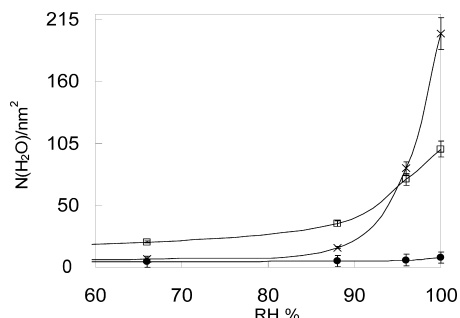

Figure 8. Isotherms of water adsorption on EC soot with deposited sulfuric acid (□) and Na benzoate (×). Coverage is 3.5 nm^{-2}. Isotherm of EC soot is indicated by ●.

those of sodium salt of sulfoacid. Here we would like to demonstrate the effect of the surface modification by a salt of carbonic acid, namely, sodium salt of benzoic acid (Na benzoate).

Figure 8 shows the isotherm of the water adsorption on EC soot with deposited Na benzoate of the same coverage of 3.5 nm^{-2}, like we used for organic acids. For Na benzoate, this coverage corresponds to ∼2 ML (because its structure is similar to benzoic acid). Such coverage strongly changes the surface chemistry of EC soot. Significant increase in the water adsorption is observed at RH > 60%. It is 60 and 170 times higher at 96% RH than the adsorption on EC soot and on EC soot modified by benzoic acid, respectively. (See Figure 5.) Therefore, strengthening the energy of intermolecular interactions due to the formation of hydrogen bond of water molecules with adsorbed organic ions is observed.[38]

It is worth noting that the organic ionic modifier, salt of carbonic acid, may increase the ability of the EC surface to adsorb water similar to sulfuric acid, one of the most hygroscopic inorganic matters. Figure 8 shows the isotherm of the water adsorption on EC soot with deposited sulfuric acid of the same coverage, 3.5 nm^{-2}, corresponding to 0.8 ML. One

sees the significant hydrophilization effect by sulfuric acid. It is high over the total RH range (not shown in this Figure). A similar effect was observed because of the modification by sodium salt of sulfoacid with the same coverage.

4. Discussion

The analysis of water uptake on soots with different coverages shows the largest effect of hydrophilic/hydrophobic properties of organic compounds on the surface. Therefore, the systematic analysis and classification of the extent of hydrophilicity of the coverage matter is fruitful; however, the acidity constant pK may relate to hydrophilic properties only in the framework of one class of organic matter, acids.

The most widely used empirical parameter for estimation of hydrophilicity of many organic molecules and their ability to create the hydrogen bond is the Hansch's parameter. It is defined as a coefficient of distribution of the organic matter in the system *n*-octanol/water, $P_{ow} = C_o/C_w$, where C_o and C_w are the number densities of organic matter in *n*-octanol and in water, respectively.[58,59] The quantitative relation between the structure of the molecule and its activity, QSAR, suggests that any property of organic matter, P, may be taken as a function of three intermolecular interactions, namely, stereometric, electrostatic, and hydrogen bond formation[60]

$$P = f(\alpha, \sum q, \sum C) \qquad (1)$$

where α is the molecular polarizability relating to stereometric interaction, q is the charge responsible for electrostatic interaction, and C is the hydrogen bound factor. In the QSAR approach, the relation for the Hansch's parameter

$$\log P_{ow} = 0.267\alpha - \sum C_a \qquad (2)$$

is used where C_a is an acceptor factor of the hydrogen bond. The higher the polarizability of the organic matter, the higher is its number density in *n*-octanol. An increase in the acceptor ability of hydrogen bond leads to an increase in the number density of organic matter in water. Equation 2 is obtained on the basis of the analysis of 2850 monofunctional organic compounds by fitting the calculated log P_{ow} to experimental data.[61] In this way hydrophobicity values for 35 small, simple, "basic" fragments have been obtained as well as values for 185 larger fragments characterizing the intramolecular hydrogen bonding contribution to log P_{ow} and charge interactions. Moreover, Hansch's parameter is found to be inversely proportional to the solubility in water[62] and is related to the acidic constant, pK, of OC acids and with sorption characteristics.[63] Therefore, QSAR methodology for log P_{ow} calculation is able to process many organic molecules is and useful for classification of the extent of the molecular hydrophilicity.

In this work, the internet web-based program for interactive calculations of the hydrophilic parameter of the basic structural molecule substituent is used.[64,65] Hansch's parameters for organic modifiers are presented in Table 1. For ionic compounds, namely, alizarine red S and Na benzoate, we have obtained −0.681 and −1.561, respectively.

Figure 9 shows the correlation between the Hansch's parameter for all modifiers used in our study and water uptake at the coverage near 1 to 2 ML. The smaller the Hansch's parameter the more hydrophilic is a given molecule, and the higher is the water adsorption of soot with a given coverage. In Figure 9,
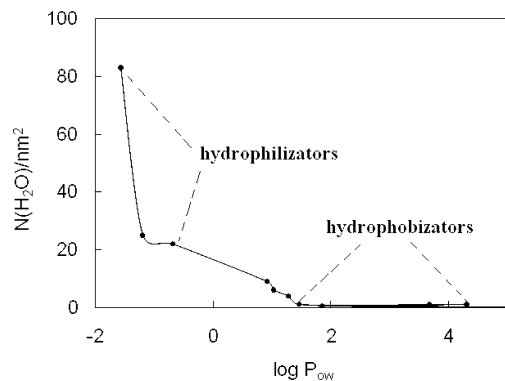
Figure 9. Correlation between the Hansch's parameter of the modifier and water adsorption on soot with a given organic coverage at 96% RH. Coverage is 3.5 nm^{-2}.

we may clearly distinguish three groups of modifiers. The first one is characterized by log P_{ow} from ~1.28 and higher. The coverage of these molecules either leads to the decrease in water adsorbability of the surface or does not change its water uptake. We call this group the hydrophobizators. Alkanes, phenols, PAHs, and some low-polar oxygen-containing derivatives of these organics with large hydrophobic part, including weak monobasic aromatic and aliphatic acids, belong to hydrophobizators. The second group is characterized by log P_{ow} from ~0.9 up to ~1.28. In this case, the covered soot surface becomes relatively hydrophilic and may adsorb water up to 1 ML. Polybasic aromatic acids comprise the second group. For ionic compounds and oxalic acid, log $P_{ow} \approx$ <0; they produce the hydrophilic coverage, which may adsorb water more then 1 ML. Therefore, we refer to this third group as hydrophilizators. Good correlation between the Hansch's parameter of the coverage molecules and water uptake of soots allows the recommendation of this parameter for description and prediction of hygroscopic properties of organic/inorganic matter on the soot particles in the atmosphere.

5. Conclusions

Main organic/inorganic components that are representatives of diesel motor and aviation engine soot coverage were deposited on the surface of EC soot to simulate water uptake of original combustion residuals and to determine how differences in soot composition impact the water−soot interaction. It was found that one of the fundamentals of the basic organic chemistry that the structure defines the molecular properties also relates to the water interaction with organic coverage on the surface; that is, the molecular structure of organic coverage determines the water uptake. The presence of aliphatic and aromatic hydrocarbons leads to hydrophobization of the soot surface. The thicker the layer of those fractions, the less is the ability of soot to take up water. Hydroxyl and quinine groups in oxidized aromatic hydrocarbons, carboxylic groups in long-chain aliphatic acids, and phenols build weak hydrogen bonds with water molecules; therefore, they slightly change the water adsorption of the EC surface. Only acids with rather strong carboxylic groups (with high acidity constants) may impact water uptake.

The ability of organic and inorganic acids to increase the hydrophilic properties of the soot surface correlates with their acidity constant and solubility. Increasing a number of carboxylic groups in mono-, di-, and three-carboxylic acids provides the prominent hydrophilization effect. A factor of 15 higher water uptake is demonstrated by the monolayer coverage of

strong aliphatic dicarboxyl (oxalic) acid in comparison with the coverage of aromatic dicarboxyl acid (phtalic acid); it proves the role of a molecular form of acid (aliphatic vs aromatic character).

The most effective hydrophilization agent in the soot coverage is organic/inorganic ions in ionic organic compounds such as sodium salt of sulfoacid or benzoic acid as well as inorganic acid such as sulfuric acid. Linear dependence of the water adsorption on ionic sulfoacid groups is related to the proportional increase in a number of active sites, whereas the variation of the coverage up to a monolayer of weakly polar aromatic compounds containing quinine and phenolic groups does not change the water adsorbability of EC soot significantly.

The quantification of the role of main classes of surface compounds in the soot coverage leads to the conclusion that sulfate, alkaline, and organic ions measured in the water-soluble fraction of AEC soot play a significant role in its hygroscopicity. These ions may originate from polar and ionic organic/inorganic compounds such as dicarboxylic acids, salts of organic acids, or sulfuric acid. These compounds form the water-soluble AEC soot coverage effectively absorbing water, and thus AEC soot takes up water as much as 8 ML at saturation[25] and even more.[13,14] Therefore, ionic organic/inorganic compounds in the soot coverage are responsible for hydrophilization of the particle surface.

However, long-chain ($C_{20}-C_{30}$) classes of alkens and benzene derivatives (alkilbenzenes) are also found in the soot coverage of aircraft engine soot. Therefore, we may conclude that the hydrophobization effect is due to the presence of such compounds in the soot particle coverage. Moreover, oxygen-containing PAH derivatives found in the organic coverage of soot produced from burning fossil fuel may not always significantly impact the hygroscopic nature of the soot particles. The finding of Saxena et al.[16] has shown that (1) the total water adsorbed by atmospheric particles is less than the amount of water expected to be adsorbed by inorganics alone, and (2) the decrease in water adsorption is caused by the presence of organics. Similar conclusions were inferred for the CCN activation of particles generated from aircraft engines.[24] The mechanism by which this decrease takes place may be explained in the framework of our findings: at the same coverage, all organic compounds, including the strongest acids, take up water less than ionic salts and inorganic acids. In light of this evidence, we can not assess whether the observed extent of soot hygroscopicity can be explained by the presence of inorganics alone, whereas hydrophobic and relatively hydrophobic compounds inhibit water uptake.

In McFiggans et al.,[29] it was proven that the simplification of the representation of organic components of atmospheric particulates is a productive approach for emission and chemistry models predicting the behavior of ambient particulates in the moist atmosphere. Here we continue this approach and suggest the soot complexity reduction by abstraction from detailed speciation of each individual component. Our observations indicate that although particle coverages are not identical in composition, they can be grouped into major compositional tendencies. The soot particle organic/inorganic coverage may be represented by three groups of fossil fuel combustion-derived particulate matter with respect to their Hansh's coefficients related to hydrophilic properties. This reasonable description is sufficient to describe the water behavior on soot in atmospheric systems by a number of representative scenarios reflecting various water uptake by soot particles advanced by the concept of quantification.[14] Therefore, the QSAR approach

relating the structure of the molecule to its properties and assuming the Hansh's coefficients as a measure of molecular hydrophilicity suggests a key parameter for studies of the environmental fate of combustion particles in the atmosphere. The enhanced knowledge on soot composition and its water uptake opens new scenarios as far as cloud condensation and ice nucleation on soot exhaust from transport systems are concerned.

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