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Laboratory Simulation of the Interaction of Water Molecules with Carbonaceous Aerosols in the Atmosphere

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Abstract—A number of samples that simulate the chemical composition of carbonaceous aerosols emitted by transport into the atmosphere have been synthesized using the method of deposition of organic compounds and sulfuric acid, which are identified in the particulate coverage of diesel and aircraft engine soot particles, onto the surface of elemental carbon. The analysis of water adsorption isotherms allows one to estimate the influence of the surface chemistry of particles on the degree of their hygroscopicity. Water adsorption measurements show that modification of a particle surface by nonpolar organics (aliphatic and aromatic hydrocarbons) leads to the hydrophobization of a soot surface. The impact of polar oxygen-containing organic compounds (ethers, ketones, aromatic, and aliphatic acids) on adsorption capacity with respect to the water of samples that they modify substantially depends on the nature and composition of the hydrophobic part of the molecules. Among the ionic compounds organic acid salts have the most hydrophilization effect, which is comparable with the adsorption capacity of soot with sulfuric acid deposited on its surface. This observation allows one to quantitatively define how the nature of chemical compounds on soot surface influences water adsorption and to estimate the interaction of water molecules with fossil fuel combustion particles in a humid atmosphere.

Keywords: carbonaceous aerosols, hygroscopicity.
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INTRODUCTION

The constantly growing emissions from transport into the atmosphere have attracted more attention due to human impacts on the environment. It is believed that solid combustion products (soot particles) can change the radiation and chemical balance of the background atmosphere, produce cloud condensation nuclei (CCN) [1], and be harmful to human health [2]. The high CCN activity of carbonaceous aerosols can lead to changes in the microphysics of clouds and the initiation of additional cloudiness [3]. Hydrophilic soot particles with a sufficient number of oxygen-containing groups on the surface can be an effective center of ice nucleation upon precipitation of water vapor from gaseous phase [4], and by freezing of water drops with soot particle impurities [5]. However, the lack of data concerning the properties of emitting aerosols and their behavior in a humid atmosphere causes substantial uncertainty in making estimates of the climatic effects of transportation-related emissions into the atmosphere.

The recently developed conception for the determination of hydrophobic and hydrophilic carbonaceous aerosols in the atmosphere allows one to carry out quantitative analysis of hydration and water/ice nucleation processes on a soot particle surface [6, 4]. The comparative analysis of water adsorption onto soots of different compositions, from elemental carbon to complex compounds with large organic and water-soluble fractions shows the formation of a water film on the hydrophilic soot surface, which is necessary for the wetting of a particle and for overcoming the Kelvin barrier upon CCN formation. However, the issue of which substances and the extent to which they assist water uptake (hydrophilization of a surface) or, vice versa, they impede (hydrophobization of a surface) is not clear.

The degree of hygroscopicity of combustion particles and their capacity to form cloud condensation nuclei depend on the surface chemistry, the surface substances ability to form hydrogen bonds with water molecules, and the content of water-soluble matter. Soot particles emitted by different sources of combustion have a wide range of physicochemical properties, depending on the combustion conditions, and fuel type [7]. Normally, they consist of graphite microcrystallites (elemental carbon), with organic and inorganic compounds on a surface. Now we examine the characteristics of diesel soot (DS) from diesel fuel combustion in automobile engines [8] and aircraft soot, which is generated during aviation kerosene combustion in the combustion chamber of the gas turbine engine of

an aircraft (GTE) [9,10]. DS and GTE analysis carried out by gas chromatography–mass spectrometry has shown that many organic substances occur on the particle surface, i.e., alkanes, ethylenes, benzene derivatives, ethers, carboxylic acids, poly-aromatic hydrocarbons (PAHs), and phenols [11, 4]. In addition, on the particle surface large quantities of water-soluble substances occur. For DS, the content of water-soluble substances can reach 3.5% [12]. The main part of water-soluble substances is composed of inorganic sulfate (SO_4^{2-}), and chloride (Cl^-) anions, in addition to cations of ammonium (NH_4^+), sodium (Na^+) and potassium (K^+), which are capable of producing compounds on the particle surface that hydrophilize the particle surface and increase their ability to form CCNs. For GTE the fraction of water-soluble substances reaches 13.5% [9]. The high hygroscopicity level of aircraft soot is defined by its high concentration of organic and inorganic anions: sulfates, formates, acetates and oxalates.

A laboratory method for the investigation of the surface compound influence on soot hygroscopicity, based on the deposition of organic compounds onto soot particles has been suggested in a number of papers [13, 14]. This kind of simulation of properties of particle combustion surface is complicated by the presence of the huge quantity of organic compounds found on their surface. To simplify this problem it was proposed in [15] to separate all organic components that are parts of original combustion aerosols into groups according to their hygroscopicity.

Within the present study the laboratory simulation of the interaction of water molecules with soot aerosols in the atmosphere has been shown.

The laboratory soot samples have been synthesized by the method of adsorptive modification with compounds found in the organic fraction of soot aerosols, which are emitted into the atmosphere by different types of transport. The relationship between gas adsorption and the chemical natures of various types of substances deposited on the soot surface has been determined. The developed approach allows one to define the correlation between soot particle properties and their behavior in a humid atmosphere.

EXPERIMENTAL

The laboratory simulation of solid combustion products was carried out by deposition of various organic compounds and sulfuric acid, which are present on soot original particles emitted by diesel and aircraft engines, onto elemental carbon. The method of adsorptive surface modification was used [16]. As a substrate for modification, graphitized thermal soot (GTS) prepared by high-temperature thermal soot treatment (at 2700–3000°C) consisting of elemental carbon was chosen. This kind of soot is a recognized test sample and has one of the most chemically and geometrically homogeneous nonpolar surfaces [17]. GTS particles 50–200 nm in size are polyhedrons, whose surface is formed by the basal face of graphite.

Table 1. The main classes of organic compounds contained in diesel and aircraft soots, and their representatives selected for laboratory simulation

Classes	Representative /formula
Alkanes	Hexadecane/$C_{16}H_{34}$
Aromatic acids	Benzoic/C_6H_5COOH Phthalic/1,2-$C_6H_4(COOH)_2$ Trimellitic/1,2,4-$C_6H_3(COOH)_3$
Carboxylic acids	Oxalic/HOOC–COOH Stearic/$C_{17}H_{35}COOH$
Phenols	Phenol/C_6H_5OH
PAHs	Anthracene/$C_{14}H_{10}$ Anthraquinone/$C_{14}H_8O_2$ Alizarin/$C_{14}H_8O_4$
Organic acid salts	Alizarin S/$C_{14}H_7O_4SO_3Na$ Sodium benzoate/C_6H_5COONa

Note: All formulas should be typed in the same way as they are written in Russian.

The main classes of organic compounds found in diesel and aircraft soot are listed in Table 1. Alkanes, and polyaromatic hydrocarbons are classes of nonpolar organic compounds; but phenols and ketones as well as aromatic and aliphatic acids are polar molecules; the polarity of oxygen-containing organic compounds strongly depends on their chemical composition. Representatives were selected from each class for deposition onto the GTS surface (Table 1). As representatives of ionic organic compounds sodium benzoate and sulfonic acid sodium salt (alizarin S) were deposited. In addition, samples modified by sulfuric acid, which is the most hygroscopic component of natural soot aerosols, were prepared for comparison.

Depending on the nature of the modifying agent and its solubility in a given volatile solvent, adsorptive modification was carried out from water or organic solutions. The solvent was then removed from the surface by gradual heating of the sample at 100–120°C. Homogeneous distribution of the modifier was reached by proper stirring of a solution until the complete evaporation of solvent was obtained. The varying of solution concentration enabled the precipitation of organic compounds with different deposited amounts: from fractions to several monolayers.

To estimate the influence of functional group nature on water adsorption, a number of laboratory soot samples was synthesized. These samples contained nonpolar compounds and their derivatives included distinct functional groups with different polarities or ionic

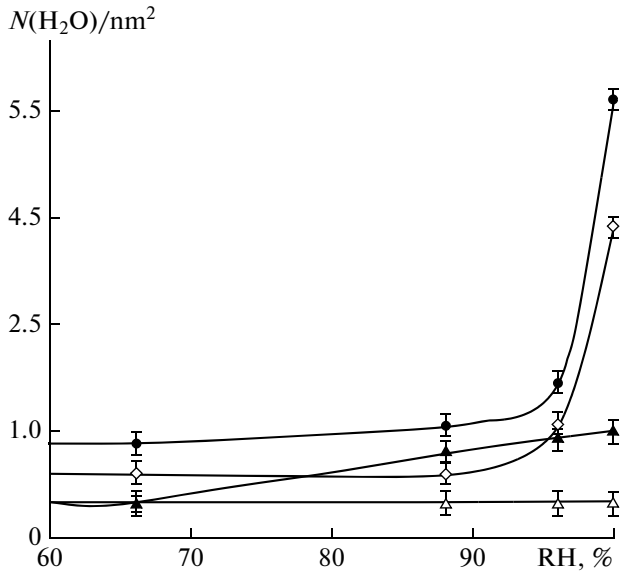

Fig. 1. The isotherms of water adsorption on GTS soot with hexadecane coating of 2 nm^{-2} (▲) and 12 nm^{-2} (△); and with anthracene, of 12 nm^{-2} (◇). The isotherms of water adsorption on unmodified GTS in this and the following figures are marked with the sign (●).

natures deposited on the GTS. A polyaromatic hydrocarbon, anthracene, was selected as a nonpolar substance. Anthracene derivatives, viz., anthraquinone, which contains two quinone groups; alizarin (1,2-dioxyanthraquinone), which contains two extra hydroxyl groups; and alizarin S, which is a sulfonic acid sodium salt (1,2-dioxy-3-sulfoanthraquinone) were deposited onto the GTS surface as well.

The value of water adsorption depending on the relative humidity (RH) was measured by a gravimetric technique at $T = 22°C$ [18]. The accuracy of measurement of water adsorption was from 5 to 15%, depending on the sample's hygroscopicity. Before measurements, the samples were dried under a water vapor pressure of 2×10^{-5} torr. The specific surface area of soots was determined by nitrogen adsorption using the thermal desorption method.

RESULTS AND DISCUSSION

1. The Hydrophobization of the Soot Surface

Due to the weak dispersion interaction of polar water molecules with carbon adsorbents the primary adsorption depends on the presence of active sites (functional groups) on their surface [17]. The GTS surface contains negligible amounts of residual hydrophilic sites, which are mainly located on the lateral edges of flat basal faces of graphite, which forms the microstructure of the particles; this allowed increasing water molecule adsorption when the relative humidity was more than 95% [19]. The isotherm of water molecule adsorption on GTS is shown in Fig. 1. The water molecule adsorption is insignificant in the initial region and then increases up to 5.5 molecules per nm^{-2} at saturation, which does not even reach the value of one statistical water monolayer (around 10 molecules/nm^{-2}) calculated according to assumption that the cross-sectional area of a water molecule is 0.105 nm^{-2} [20].

The organic covering of soot particles, which occurs as a result of adsorptive modification, decreases the dispersion capacity of the carbon matrix because of it creates a distance between adsorbate molecules and the adsorbing surface. In addition, the modifier molecules, which screen the most active sites of the surface, dramatically reduce its residual inhomogeneity. In this case the adsorption properties of modified samples must depend mainly on the nature of the modifier molecules. Hydrophobic substances, alkanes, and PAHs consist only of carbon and hydrogen atoms. Consequently, their interactions with water molecules are either almost absent or are negligible, thus, one can assume that the deposition of this type of compound leads to surface hydrophobization.

In Fig. 1 the isotherms of GTS surfaces with deposited hydrophobic substances, namely, hexadecane (alkane) and anthracene (PAH) are presented. When the deposition of hexadecane is 2 nm^{-2} (~2 monolayers) in depth, the adsorption of water in saturated vapor is about five time less in comparison to the adsorption on GTS. An increase of the hexadecane quantity to 12 nm^{-2} (~12 monolayers) enhances the decrease in GTS surface dispersion capacity and almost completely hydrophobizes it. An anthracene deposition of the same 12 nm^{-2} (~9 monolayers) does not hydrophobize the GTS surface completely, probably, because of the ability of π-electrons in the PAH aromatic ring to form weak hydrogen bonds with water molecules [21].

2. The Effect of the Nature of Anthracene Derivative Functional Groups

The oxygen-containing functional groups of organic compounds are substantial centers for the formation of hydrogen bonds with water molecules. To estimate the contribution of various functional groups to the hydrating properties of soot, water adsorption experiments were carried for a number of samples obtained by deposition of anthracene and its derivatives containing polar quinone, =C=O; hydroxyl, ≡C–OH; and ionic sulfoxy groups, $-SO_3$.

The isotherms of water adsorption on GTS surfaces, when the surface content of anthracene, anthraquinone, alizarin, and alizarin S is 0.3 molecules/nm^{-2} (~0.2–0.35 monolayer) are shown in Fig. 2. At saturation the water adsorption on soot modified by anthracene is 1.5 times less than that on GTS. The deposition of anthraquinone increases the water adsorption up to the value of the original GTS. The number of active sites introduced by the two quinon groups may be approximately equal to the number of residual active sites on the

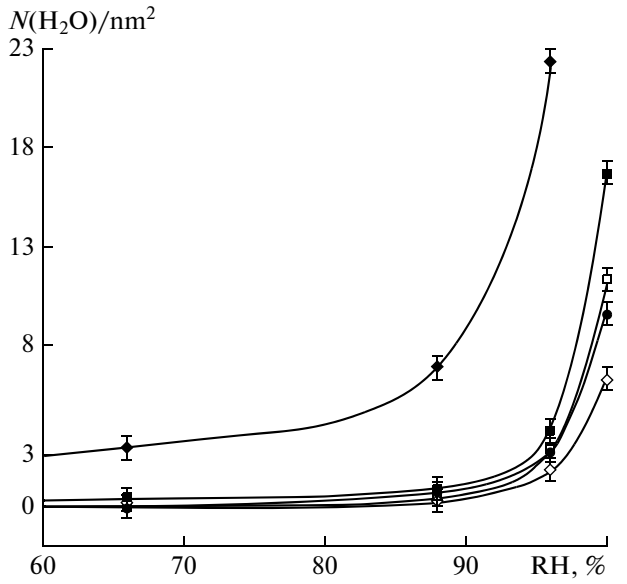

Fig. 2. The isotherms of water adsorption on GTS with organic acids containing functional groups of various ionic natures and polarities deposited on its surface. The following signs correspond to respective compounds: (◇) to anthracene, (□) to anthraquinone, (■) to alizarin, and (◆) to alizarin S. The deposited layer is 0.3 nm^{-2}.

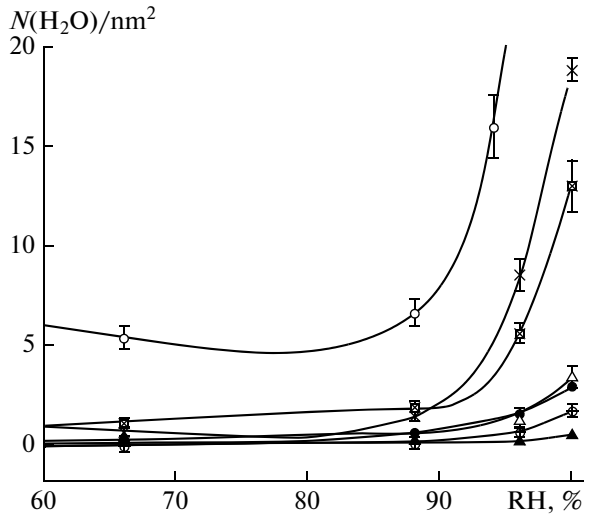

Fig. 3. The isotherms of water adsorption on GTS with (⊕) benzoic, (⊗) phthalic, (*) trimellitic, (▲) stearic, (○) oxalic acids, and (△) phenol coatings. The deposited layer is 3.5 nm^{-2}.

GTS surface. The polar modifier, alizarin, which contains two extra phenol hydroxyl groups, enhances the water adsorption at saturation by approximately 1.7 times. But the most considerable contribution to water adsorption increase is made by an ionic substance, sulfonic acid sodium salt (alizarin S). This compound raises the adsorption by an order of magnitude and the water adsorption on this sample is substantially higher than on GTS, even at a relative humidity of ~60%. Thus, the water adsorption of the investigated modified soots can be arranged in the following order: Anthracene < GTS < Anthraquinone < Alizarin ≪ Alizarin S.

3. The Hydrophilization of the Soot Surface. the Influence of the Chemical Composition of Organic Acids and Salts

Among oxygen-containing functional groups contained in organic compounds, –COOH (carboxylic acids) can form strong hydrogen bonds with water molecules, so these groups should make the most considerable contribution to the adsorption capacity of water in comparison to other oxygen-containing groups [22]. However, the ability of carboxyl groups to interact with water molecules depends on the hydrocarbon part of an organic acid molecule; this has a significant effect on the polarity of –OH and –COOH groups. The effect of carboxyl group quantity, when the hydrocarbon part is constant, for a series of aromatic acids, namely, benzoic (one group), phthalic (two groups), and trimellitic (three groups) acids has been studied. The deposition of these modifiers is 3.5 nm^{-2} or ≈1.9, 2.3, and 2.5 monolayers for benzoic, phthalic, and trimellitic acids, respectively. The water adsorption isotherms for the given series are presented In Fig. 3. Apparently, the presence of one carboxyl group in benzoic acid hardly influences the hygroscopicity of soot and even slightly reduces water adsorption on GTS. In this case the decrease in surface adsorption capacity after modification is probably not compensated by the surficial occurrence of occasional carboxyl groups, that is, the contribution of the hydrophobic part of a molecule, which is quite small, to the interaction is dominant. An increase in carboxyl groups leads to a rise of adsorption capacity. The adsorption is increased by up to one monolayer by phthalic acid deposition; trimellitic acid increases it by up to two monolayers. This fact confirms the idea that the adsorption of water molecules depends on the quantity of primary active sites [23].

The comparison of water adsorption on GTS surfaces modified by phthalic and oxalic acids, which have two carboxyl groups in their compositions, when the deposition quantity of 3.5 nm^{-2} remains the same, shows the role of an acidic molecule structure (Fig. 3). An oxalic acid molecule has two carboxyl groups, no methylene groups, and readily dissociates due to its strongly polarized –O–H bonds, producing $–COO^-$ anions (the dissociation constant, $pK_a = 1.27$ is given in Table 2). This is why it produces the strongest hydrogen bonds with water molecules, among the organic acids studied in the present work; one can observe a significant growth of water adsorption over the whole RH range. In the case of phthalic acid deposition, a noticeable water adsorption occurs only at RH ~90%. Obviously, the reason for this difference is that there is a substantial hydrophobic part (aromatic

Table 2. Solubility in water, S, g/100g of water, dissociation constant, pK_a, at 20°C, and the quantity of adsorbed water molecules at RH = 96%

Modifier	S, g/100 g	pK_a	$N(H_2O)/nm^2$
Oxalic acid	10	1.27	25
Trimellitic acid	3	2.5	8.5
Phthalic acid	0.57	2.95	5.7
Benzoic acid	0.27	4.18	0.5
Stearic acid	0.03	8.5	0.2
Phenol	6.7	10	1.1

ring) in a phthalic acid molecule, and a smaller number of active sites ($pK_a = 2.95$) produced by the deposition mentioned above in comparison to oxalic acid. The deposition of trimellitic acid containing three carboxyl groups also cannot hydrophilize the GTS surface in the manner observed for the GTS surface with deposited oxalic acid, whose adsorption value at saturation is ~5 monolayers of water (Fig. 3).

The presence of stearic acid, which is a monobasic carboxyl acid of the aliphatic series, on the GTS surface decreases its adsorption capacity (see Fig. 3). The long-chain hydrophobic part of this acid is the cause of polarity suppression for –OH bonds on the carboxyl group, and of a decrease in active site concentration per surface unit. Since stearic acid has very weak acidic properties ($pK_a = 8.5$), its deposition on a surface leads to almost complete hydrophobization of the GTS surface.

Phenol deposition, which also has very weak acidic properties ($pK_a = 10$), at the same quantity does not stimulate an increase in water adsorption in comparison to adsorption on residual active sites of GTS. According to Fig. 3, one can see that at RH = 96% the water adsorption on GTS coated with phenol is 1.3 times less than on the original soot.

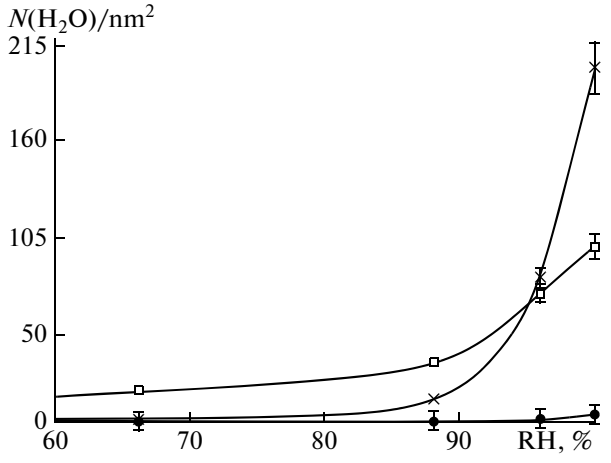

Fig. 4. The isotherms of water adsorption on GTS coated with (□) sulfuric acid, and (×) sodium benzoate. The deposited layer is 3.5 nm^{-2}.

Thus, one can conclude that the presence of molecules with weakly acidic properties (carboxyl acids and phenol) that have a massive hydrophobic part preferentially hydrophobizes the GTS surface, despite the presence of active sites, such as carboxyl groups.

It follows from the comparison of data on water adsorption with such physicochemical characteristics of organic acids as solubility in water and pK_a, that good correlation between the hydrophilic properties of soots modified by these acids and the mentioned parameters is observed. In Table 2 the dissociation constants, pK_a, and solubility in water for a series of modifiers is compared with the number of water molecules adsorbed at RH = 96%. One can see a growth of the adsorption for carboxyl acids with increasing solubility and decreasing pK_a in the following series of acids: stearic, benzoic, phthalic, trimetillic, and oxalic acids. It is interesting to compare the adsorption on soots modified by oxalic acid and phenol. Phenol, which has an –OH group in its composition, is a very weak acid. Although these compounds have similar values of solubility in water, the strength of oxalic acid is significantly higher than that for phenol. Oxalic acid substantially hydrophobize the GTS surface, while phenol inhibits water adsorption in comparison to the original GTS. It follows from the comparison of phenol with benzoic acid, whose molecules have the same hydrophobic part, an aromatic acid, that phenol, which is weaker than benzoic acid, but is much more soluble in water, contributes to the greater water uptake by modified GTS than benzoic acid. The correlation violation for benzoic acid and phenol indicates the important role of not only the nature of a molecule's hydrophobic part, but also the nature of oxygen-containing functional groups in water adsorption.

The adsorption capacity of GTS with deposited organic acids, except oxalic acid, does not exceed one monolayer at RH levels up to 96%. A substantially higher adsorption capacity should occur for GTS with deposited ionic compounds on its surface, for instance, the salts of carboxylic acids. A similar effect has already been observed for sulfonic acid sodium salt (alizarin S) (see Fig. 2). The isotherm of water adsorption on GTS with deposited sodium benzoate layer of 3.5 nm^{-2} (2 monolyers) is shown in Fig. 4. It is clear that the deposition of this compound hydrophilizes the surface considerably. In spite of the fact that the considerable growth of adsorption on GTS with sodium benzoate coating starts only at RH values > 60%, at RH > 80% the water adsorption is more than on GTS with an oxalic acid coating. At RH = 96% the water adsorption on GTS with a sodium benzoate coating is maximal (60 times higher than on the original GTS and 170 times higher than on GTS with a benzoic acid coating). In this case, an increase in the intermolecular interaction energy, which is due to the

formation of hydrogen bonds between water molecules and organic ions, is observed [21]. It is important to note that an ionic organic modifier increases the ability of the GTS surface to adsorb water and it behaves almost like sulfuric acid, which is one of the most hygroscopic inorganic compounds. For comparison reasons, the isotherm of GTS with a deposited sulfur acid layer of 3.5 nm^{-2} (~0.8 mololayer) is presented in Fig. 4. The presence of sulfuric acid hydrophilizes the GTS surface, even at low RH values.

CONCLUSIONS

The laboratory modification of the graphitized soot surface with organic compounds and sulfuric acid identified in diesel and aircraft soots was carried out with the purpose of simulating the composition of aerosols from transport emissions and their capacity to adsorb water. It was shown that the presence of aliphatic and aromatic hydrocarbons on soot surfaces leads to a hydrophobization effect. Weakly polar aromatic compounds contain quinone and hydroxyl groups; long-chain aliphatic acids with carboxyl groups form weak hydrogen bonds with water molecules as well, thus not significantly changing the adsorption value of the soot surface. The capacity of organic acids to hydrophilize a surface correlates with their acidic dissociation constants and their solubility in water. An increase in the quantity of carboxyl groups for mono, bi, and tri carboxylic acids leads to an increase in the adsorption capacity of particles. Organic anions in ionic organic compounds, such as salts of organic acids (carboxylic and sulfonic acids) make the most contribution to the hydrophilicity of surface particles, which is comparable with the contribution of sulfuric acid.

Summarizing the role of the main compound classes found on original soot surfaces, one can conclude that sulfuric acid and organic anions that have been found in the water-soluble fraction of aircraft soot make the most contribution to its hygroscopicity.

The results allow us to clarify uncertainties in the description of the climatic consequences of emissions from various types of transportation, helps in the determination of the soot aerosol contribution, and it enables us to identify the ability to form CCNs and ice nucleation centers in the atmosphere.

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