Journal of Engineering Physics and Thermophysics, Vol. 75, No. 2, 2002

PHOTOEMISSION CHARGING OF A COLLECTIVE OF AEROSOL PARTICLES

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UDC 551.25:537.2

The photoemission charging of a collective of particles at normal atmospheric pressure and at lowered pressure of the air has been investigated. The dependences of the average initial charge of a droplet, the average equilibrium photoemission loss of charge by a droplet, and the equilibrium concentration of the electrons on the air pressure are presented as the basic experimental results. The process of photoemission charging of an aerodisperse system was theoretically described by solution of the equation of charge equilibrium of the average-radius particle with space charge. Comparison of the experimental and calculated results showed their satisfactory agreement.

The photoelectronic emission from aerosol particles which is caused by external radiation sources occurs in a number of applied problems of the physics of aerodisperse systems. In particular, photoemission in the atmosphere of the earth can cause an increase in the conductivity of the air and influence the thunderstorm activity of clouds [1]; it is also used for physicochemical analysis of aerosols [2].

In this work, the photoemission charging of a collective of particles at normal atmospheric pressure and at lowered pressure of the air has been investigated experimentally.

For this purpose we used a setup whose block diagram is shown in Fig. 1. The centrifugal aerosol generator 1 was located in the lower part of the setup. The aerodisperse system was produced from an aqueous solution of the dye "benzaldehyde green" of the triphenylmethane series with a mass concentration of 0.5%. The electronic work function was 4.413 eV [3]; the quantum yield from the photoactive reagent was equal to $\gamma = 3.22\cdot10^{-6}$ [3]. The average radius of the droplets was $\bar{r} = 13.8$ μm. The volumetric flow rate of the photoactive reagent W_{liq} in the aerosol generator varied from $4\cdot10^{-8}$ m^3/sec to $8\cdot10^{-8}$ m^3/sec with variation in the ambient-air pressure from $P = 0.67\cdot10^4$ Pa to $P_0 = 10^5$ Pa (Fig. 2). The volumetric flow rate of the air in dispersion was $W_{\text{air}} = 1.5\cdot10^{-3}$ m^3/sec. In the upper part of the setup, a DKSSh-500 lamp 5 with a UFS-5 light filter was located (Fig. 1). The intensity of radiation of the lamp in the air was $\phi_0 = 1.05\cdot10^{20}$ m$^{-2}\cdot$sec^{-1}. The maximum of the transmission band of the filter corresponded to the wavelength $\lambda = 210$ nm.

Droplets emit electrons under the action of the ultraviolet radiation of the lamp. In the air medium, the electrons form negative ions of oxygen which lose charge under the action of external UV radiation; therefore, the charge from the aerosol particles is transferred to the gaseous medium by the electrons. All the equipment within the region shown dashed in Fig. 1 was placed in an STBV-100 thermal vacuum chamber the air temperature in which was kept constant ($T = 300$ K). The samples of the aerosol were selected at a level of 0.5 m from the surface of the chamber floor.

An Obolenskii filter 7 (Fig. 1) was used to investigate the characteristics of the aerosol. When the liquid-droplet aerosol medium carrying an electric charge is pulled through the Obolenskii filter, the droplets of the liquid deposit on the porous material and, through a grid, give their charges to the internal cylinder connected with a current meter. By measuring the current formed by the deposited droplets with instruments 14 and 15 (Fig. 1) we can find the average charge which is carried by one droplet:

$$Q = \frac{I_{\text{f}}}{n_{\text{dr}} W_{\text{R}_1}} . \qquad (1)$$

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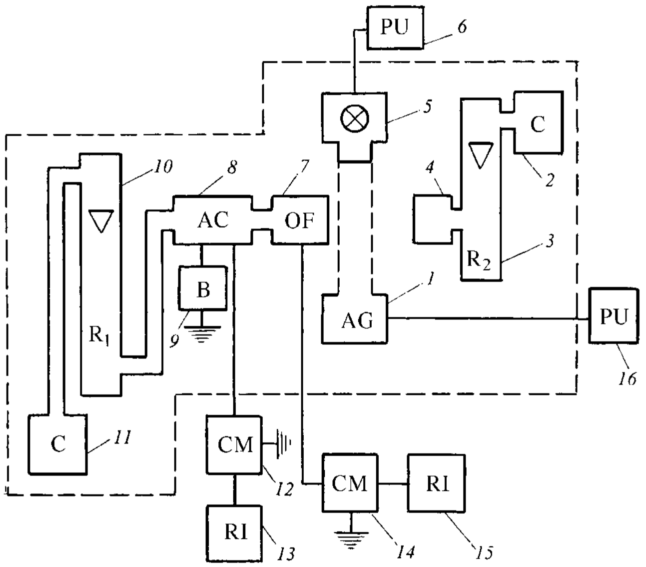


Fig. 1. Block diagram of the experimental setup for investigation of the photoemission in a collective of droplets: 1) contrifugal aerosol generator (AG); 2 and 11) compressors (C); 3) rotameter RS-3A (R_2); 4) absolute filter; 5) DKSSh-500 lamp; 6 and 16) power units of the lamp and of the centrifugal generator (PU); 7) Obolenskii filter (OF); 8) aspiration capacitor (AC); 9) galvanic-cell battery (B); 10) rotameter RM-0.25 (R_1); 12 and 14) IMT-0.5 current meter (CM); 13 and 15) recording instruments (RI).

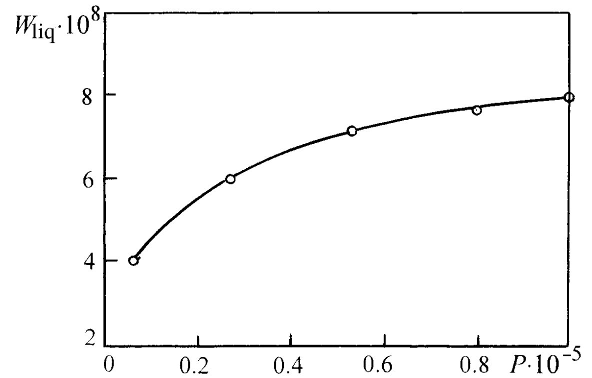


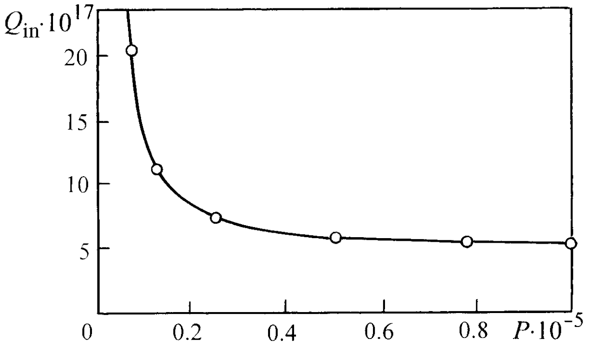
Fig. 2. Volumetric flow rate of the photoactive liquid W_{liq} in the centrifugal generator vs. pressure of the ambient air P. W_{liq}, m^3/sec; P, Pa.

The volumetric flow rate of the air passed through the Obolenskii filter was measured by rotameter 10 (Fig. 1). Pumping of the air through filter 7 was carried out by compressor 11. To determine n_{dr} the sample of the aerosol was aspired through filter 4 (Fig. 1); the concentration of the droplets was calculated from the formula

$$n_{dr} = \frac{m_2 - m_1}{\frac{4}{3} \pi \overline{r}^3 \rho W_{R_2} t} . \qquad (2)$$

The volumetric flow rate of the air passed through the filter 4 was measured by rotameter 3.

In the process of aspiration of the aerosol, the action of external UV radiation on the aerosol ceases. The electrons found in the air form the oxygen ions O_2^- the concentration of which is equal to the concentration of the electrons. The concentration of the oxygen ions was determined using the aspiration capacitor 8 (Fig. 1) located immediately behind the Obolenskii filter. The investigations showed that the velocity of the air flow influences the proc-



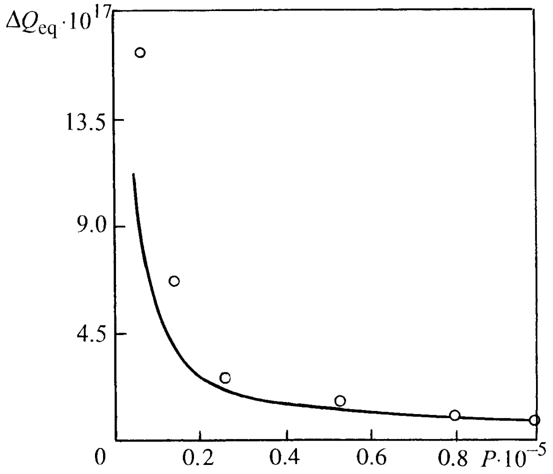


Fig. 3. Experimental dependence of the average initial charge of the droplet Q_{in} on the air pressure P for the aerosol of the aqueous solution of the dye benzaldehyde green with a mass concentration of 0.5%. Q_{in}, C; P, Pa.

Fig. 4. Experimental dependence of the average equilibrium photoemission loss of charge by the droplet ΔQ_{eq} on the air pressure P. The curve shows the calculation for the average radius of the droplet. ΔQ_{eq}, C; P, Pa.

ess of deposition of ions in the Obolenskii filter. However, for the flow rate of the aspired ionized air W_{R_1} = 10^{-3}–$2 \cdot 10^{-2}$ m^3/sec in the case of our geometric parameters of the Obolenskii filter and the aspiration capacitor the ions are not deposited in the Obolenskii filter, whereas the aspiration capacitor holds them completely.

Knowing the capacity of the aspiration capacitor, the flow rate of the air passing through it, and the mobility of the oxygen ions, we can find the potential difference which must be applied between the electrodes [4] for all the ions to be deposited on the electrode connected to the current meter:

$$U_{AC} = \frac{\varepsilon_0 W_{R_1}}{C_{AC} u_{O_2}} . \tag{3}$$

Under our conditions, $C_{AC} = 1.1 \cdot 10^{-11}$ F and $u_{O_2} \sim 10^{-4}$ m^2/(V·sec). In the case of such parameters one must apply a voltage of U_{AC} = 8–16 V between the electrodes of the aspiration capacitor; this voltage was produced by the galvanic-cell battery 9. The oxygen ions deviated in the electric field were deposited on the measuring electrode and produced the current I_{AC} recorded by the instruments 12 and 13 (Fig. 1). Knowing the flow rate of the air through the aspiration capacitor, one can determine the concentration of oxygen ions, which is equal to the concentration of the electrons in the thermal vacuum chamber:

$$n = \frac{I_{AC}}{e W_{R_1}} . \tag{4}$$

First we studied the value and sign of the charge of droplets produced by the centrifugal generator in the process of dispersion of the liquid without the action of UV radiation. The investigations showed that as a result of spraying of the solution of the dye "benzaldehyde green" with a mass concentration of 0.5% the droplets acquire a negative charge. The average initial charge of the droplet increases with decrease in the air pressure, which is caused, in all probability, by the reduction in the resistance of the ambient medium leading to a decrease in the time of separation of the droplet from the rotating cone of the generator. This in turn intensifies the process of charge separation in the bridge connecting the bulk of the liquid on the generator cone with the formed droplet. The process of photoelectronic emission from the droplet continues until the droplet attains equilibrium for which the flow of charge from the droplet is equal to the flow of charge to its surface from the ambient medium.

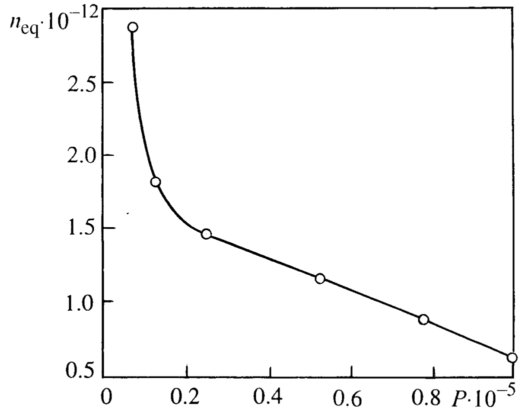


Fig. 5. Experimental dependence of the equilibrium concentration of the electrons n_{eq} on the air pressure P. n_{eq}, m^{-3}; P, Pa.

Since the average initial charge of the droplet changes, it is expedient to characterize the process of photoemission in the collective of droplets by the average equilibrium loss of charge by a droplet:

$$\Delta Q_{eq} = Q_{in} - Q_{eq}\,. \tag{5}$$

Figure 3 shows the average initial charge of a droplet as a function of the air pressure in the thermal vacuum chamber. Figure 4 shows the average equilibrium photoemission loss of charge by a droplet as a function of the air pressure in the thermal vacuum chamber. It follows from the given experimental results that ΔQ_{eq} increases as the pressure of the air in the thermal vacuum chamber decreases. This is explained by the increase in the luminous flux to the surface of the droplets since with decrease in the pressure in the thermal vacuum chamber the flow rate of the liquid in the centrifugal generator becomes lower and accordingly the concentration of droplets in the volume decreases, which leads to a growth in the radiation intensity.

Figure 5 gives the experimental dependence of the equilibrium concentration of the electrons n_{eq} in the volume of the thermal vacuum chamber on the air pressure P. The growth in this quantity with decrease in the pressure is caused by the increase in the photoemission loss of charge by the droplets.

In theoretical description of the process of photoemission charging of the aerodisperse system, we used the boundary-sphere method [5–7]. The particle of average radius $\bar{r}$ was surrounded by a concentric sphere; the concentric sphere was at a distance equal to $l = (l_{O_2} + l_e)/2$ from the particle surface, i.e., to the average between the mean free path of the oxygen ion l_{O_2} and the mean free path of the electron l_e. These parameters are interrelated as $l_e = 4\sqrt{2}\,l_{O_2}$ [8]. Under normal conditions, $l_{O_2} = 6\cdot 10^{-8}$ m [9]. The space bounded by the particle surface and the boundary sphere will be called the kinetic zone. It is assumed that within this zone the electrons and the oxygen ions move without mutual contacts, colliding just with the boundary sphere and the particle surface. The electrons colliding with the molecules of nitrogen do not form ions and are elastically scattered [10], after which a part of the scattered flow of the electrons can return to the particle surface and be captured by it. The other part of the flow goes beyond the boundary sphere and participates in the diffusive transfer of charge. The electrons colliding with the molecules of oxygen form the negative ions of O_2, since in the oxygen molecule the energy of electron affinity is positive and the process of adhesion of an electron to it is energy-profitable [10]. A part of the oxygen ion goes beyond the boundary sphere and participates in the diffusive transfer of charge. The remaining ions of oxygen move to the surface of the particle, giving it their negative charge. The evaluations of [11] show that photodestruction of the oxygen ions within the kinetic zone is improbable; therefore, the flow of them from the boundary sphere to the particle surface will exist.

Based on the boundary-sphere model we obtained the equation of charge equilibrium of a particle with the space charge surrounding it [11]:

$$F(Q)\,I = \pi(\bar{r} + l)^2\, e n_{eq}\,[\bar{v}_{O_2} - \Psi(Q)]\exp\left[-\frac{Qu}{4\pi D(\bar{r} + l)\,\varepsilon_0}\right]. \tag{6}$$

The expression on the left-hand side of Eq. (6) determines the flow of charge from the particle surface. The right-hand side determines the flow of charge to the particle. The saturation photocurrent from the surface of a particle of average radius $\bar{r}$ is determined from the formula

$$I = \pi\overline{r^2}\, e\gamma\,\phi \,. \tag{7}$$

We find the intensity of radiation in a collective of particles, knowing the intensity of radiation in the air and taking into account the attenuation of the radiation flux in fog (this attenuation is determined by the Bouguer law [12]):

$$\phi = \phi_0 \exp\,[-\,\alpha\pi\overline{r^2}\, n_{\mathrm{dr}}Z]\,. \tag{8}$$

The attenuation coefficient of radiation α depends on the parameter $2\pi\bar{r}/\lambda$. For our situation, $\alpha = 2$. The concentration of droplets in the fog produced by the centrifugal generator in the thermal vacuum chamber was calculated using the expression

$$n_{\mathrm{dr}} = \frac{W_{\mathrm{liq}}}{\frac{4}{3}\pi\,\overline{r^3}\,W_{\mathrm{air}}}\,. \tag{9}$$

The calculations of the concentration of aerosol droplets carried out using formula (9) were compared to the results obtained according to formula (2). The comparison of the numerical values showed their good agreement accurate to 5%. The characteristic distance at which the radiation flux is attenuated Z will be evaluated by the distance from the lamp to the outlet of the centrifugal generator $H = 0.8$ m. Since the position of the aerosol particle at all points between the lamp and the generator outlet is equally probable, $Z = H/2$. With account for formula (8), expression (7) will take the form

$$I = \pi\,\overline{r^2}\, e\gamma\,\phi_0 \exp\,[-\,\pi\overline{r^2}\, n_{\mathrm{dr}}H]\,. \tag{10}$$

The function of the negative charge of the particle $F(Q)$ determines the attenuation of the photoemission current from the particle by scattering of the photoelectrons by the molecules of nitrogen at the boundary sphere. The explicit form of this function has been determined in [1]. On the right-hand side of Eq. (6), $\bar{v}_{\mathrm{O}_2} = (8kT/\pi m_{\mathrm{O}_2})^{1/2}$ is the average velocity of the oxygen ions. The function of the negative charge of the particle $\Psi(Q)$ determines the retardation of the flow of oxygen ions from the boundary sphere to the particle surface [11]:

$$\Psi\,(Q) = \frac{el}{(2m_{\mathrm{O}_2}kT)^{1/2}\,\pi^{3/2}\,\varepsilon_0\overline{r^2}}\left(Q^{1/2} - \frac{\bar{r}\,e^{1/2}}{2l}\right)^2 . \tag{11}$$

The width of the kinetic zone of a particle depends on the air pressure in the thermal vacuum chamber $l = l_0\frac{P_0}{P}$. The equilibrium concentration of the electrons and the charge of the particle are interrelated by the condition of conservation of the total charge in the system:

$$en_{\mathrm{eq}} = (Q_{\mathrm{in}} - Q_{\mathrm{eq}})\, n_{\mathrm{dr}}\,. \tag{12}$$

The experimental conditions were such that the average initial charge on the droplet depends on the air pressure in the thermal vacuum chamber. The flow rate of the photoactive reagent in the aerosol generator and hence the concentration of droplets in the thermal vacuum chamber are also related to the air pressure. This leads to the dependence of the radiation intensity on the pressure. Taking into account the distinctive features of the experiment, we presented the main calculated result (Fig. 4) in the form of the dependences of the equilibrium photoemission loss of charge by a droplet of average radius on the pressure of the air. The comparison of the experimental and calculated results shows their satisfactory coincidence. It should be noted that the experimental values of the average equilibrium loss of charge by the droplet (Fig. 4) can be understated. This is explained by the systematic error which is introduced into the measurements by the Obolenskii filter, since not all the droplets deposited on the filter come into electrical contact with the measuring system.

The results of this work can be used in creating the equipment of photoemission analysis of aerodisperse systems and contribute to a better understanding of the physics of atmospheric aerosols,

NOTATION

γ, quantum yield from the photoactive reagent; $\overline{r}$, average radius of the droplets, m; $\overline{r^2}$, average square of the droplet radius, m^2; $\overline{r^3}$, average cube of the droplet radius, m^3; W_{liq}, volumetric flow rate of the photoactive reagent, m^3/sec; W_{air}, volumetric flow rate of the air in the aerosol generator, m^3/sec; W_{R_1}, volumetric flow rate of the air passed through the Obolenskii filter and the aspiration capacitor, m^3/sec; W_{R_2}, volumetric flow rate of the air passed through filter 4, m^3/sec; P and P_0, pressure of the air in the thermal vacuum chamber and normal atmospheric pressure respectively, Pa; ϕ_0 and ϕ, intensity of radiation in the air and in the aerodisperse system respectively, $m^{-2}\cdot sec^{-1}$; λ, wavelength corresponding to the maximum of the transmission band, nm; T, temperature of the air in the thermal vacuum chamber, K; Q, average charge carried by one droplet, C; e, electron charge, C; ΔQ_{eq}, average equilibrium loss of charge by the droplet, C; Q_{in} and Q_{eq}, average initial charge of the droplet and average equilibrium charge of the droplet respectively, C; I_f, current that is produced by the liquid phase deposited on the Obolenskii filter, A; I_{AC}, current of the aspiration capacitor, A; I, saturation current from the surface of the average-radius droplet, A; n_{dr}, concentration of the droplets of the photoactive liquid in the volume of the thermal vacuum chamber, m^{-3}; n and n_{eq}, concentration of the electrons in the volume of the thermal vacuum chamber and their equilibrium concentration, m^{-3}; m_1 and m_2, mass of the clean filter and of the filter with a deposited dispersed phase, kg; $\rho = 10^3$ kg/m^3, density of the substance of the droplet; t, aspiration time, sec; U_{AC}, potential difference between the electrodes of the aspiration capacitor, V; C_{AC}, capacity of the aspiration capacitor, F; u_{O_2}, mobility of the oxygen ions, $m^2/(V\cdot sec)$; ε_0, electric constant, F/m; l, width of the kinetic zone; l_0, the same, for $P = P_0$, m; l_{O_2} and l_e, mean free path of the oxygen ion and of the electron respectively, m; α, attenuation coefficient of radiation; Z, characteristic distance of attenuation of radiation, m; H, distance from the lamp to the outlet of the centrifugal generator, m; $F(Q)$, function of the negative charge of a particle determining the attenuation of the photoemission current from the particle due to the scattering of photoelectrons by the molecules of nitrogen on the boundary sphere; $\overline{v}_{O_2}$, average velocity of the oxygen ions, m/sec; k, Boltzmann constant, J/K; m_{O_2}, mass of the oxygen ion, kg; $\Psi(Q)$, function of the negative charge of a particle determining the retardation of the flow of oxygen ions from the boundary sphere to the particle surface, m/sec. Subscripts: liq, liquid; R_1 and R_2, rotameters; air, air; AC, aspiration capacitor; in, initial; eq, equilibrium; e, electron; O_2, oxygen; dr, droplet.

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