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Конденсация пара на заряженных аэрозольных частицах, содержащих растворимые полимеры

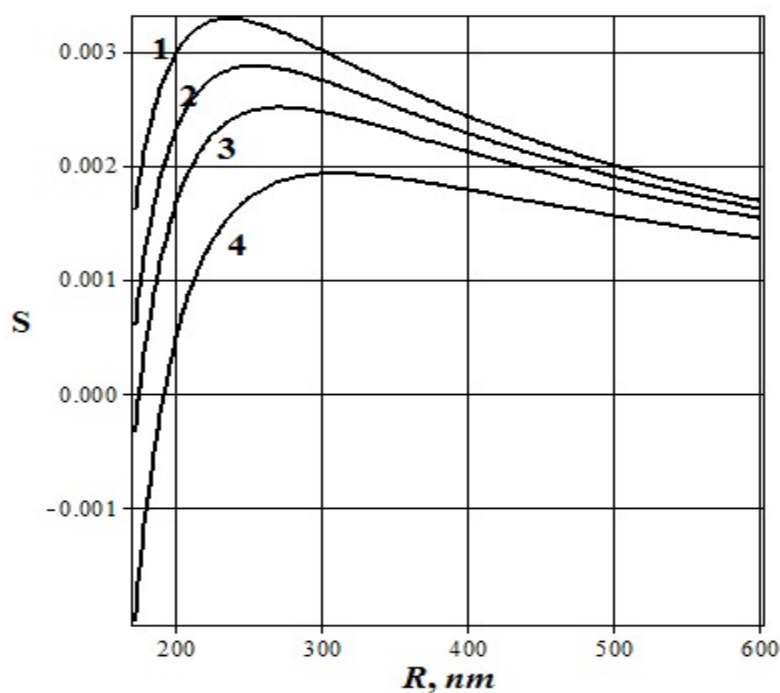
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Аннотация

Проведен теоретический анализ влияния нерастворимых поверхностно активных веществ (ПАВ) и растворимых высокомолекулярных полимеров, входящих в заряженную аэрозольную частицу на ее активацию путем адсорбции воды. Традиционная модель Кёлера дополнена теорией многослойной адсорбции Френкеля – Халси – Хилла и учтено влияние пленки ПАВ на поверхностное натяжение воды. Активность воды вычислялась по теории полимерных растворов Флори – Хаггинса. Получено окончательное выражение, позволяющее количественно определить зависимость критического перенасыщения от заряда, концентрации ПАВ и растворимого полимера, параметров многослойной адсорбции и активности.

Ключевые слова: аэрозольная частица, многослойная адсорбция, перенасыщение, поверхностно-активные вещества, полимерные цепи.



Зависимость перенасыщения S от радиуса капли при различных значениях параметра B теории многослойной адсорбции Френкеля – Халси – Хилла

Vapor Condensation on Charged Aerosol Particles Containing Soluble Polymers

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Abstract

A theoretical analysis of the effect of insoluble surfactants and soluble high-molecular polymers included in a charged aerosol particle on its activation by water adsorption has been carried out. The traditional Köhler model is supplemented by the theory of multilayer Frenkel–Halsey–Hill adsorption and the effect of the surfactant film on the surface tension of water is taken into account. The water activity was calculated using the theory of polymer solutions by Flory–Huggins. A final expression has been obtained that makes it possible to quantify the dependence of the critical supersaturation on the charge, the concentration of surfactants and soluble polymers, the parameters of multilayer adsorption and activity.

Keywords: aerosol particle, multilayer adsorption, supersaturation, surfactants, polymer chains

1. Introduction

Aerosol particles have the property of condensing water vapor on their surface, forming clouds and hazes, partially or completely dissolving in water. They have a cooling effect on the Earth's climate both directly, dissipating incoming solar radiation, and indirectly, acting as condensation nuclei, affecting the albedo of clouds. [1]. An unresolved problem today is the lack of understanding of the role of organic surfactants contained in aerosol particles on the physico-chemical processes during cloud formation, in particular, on the dependence of surface tension and activity of aerosol droplets on their size [2–3]. The role of the charge of aerosol particles in cloud formation has also not been studied. In addition, if an aerosol particle contains high-polymer inclusions, when they are dissolved in water, the simple Raoult's formula for calculating the activity of the solution is already unfair and a more complex theory should be applied [4, 5]. This paper is devoted to the theoretical study of the problems listed above.

2. Physico-chemical model of aerosol activation and calculation results

Amphiphilic organic substances that practically do not mix with water (for example, long-chain fatty acids) form so-called Langmuir films (single-layer adsorption) on the water surface. In [6], based on the Gibbs adsorption equation, it was shown that a film of insoluble surfactants reduces the surface tension of water by

$$\Pi = \frac{k_B T}{\omega_w} \ln \left(1 + \frac{\omega_w}{\Omega_s - \omega_s} \right), \quad (1)$$

where k_B – Boltzmann's constant; T – absolute temperature; Ω_s – the area per molecule of the surfactant; ω_w and ω_s – the so-called areas of water molecules and surfactants, respectively.

Let's say on a hygroscopic aerosol particle with a dry radius R_d water vapor condenses. As a result, the radius of the wet aerosol particle increases to R (it is said that this is the radius of the drop). If p_s – saturated vapor pressure above a drop containing aerosol components dissolved in water, p_{0s} – the pressure of saturated vapor above the flat surface of pure water, the formula is valid [7, 8]:

$$\frac{p_s}{p_{0s}} = a_w a_q \exp(-\mathbf{A}\theta^{-\mathbf{B}}) \exp\left(\frac{2\gamma v_w}{k_B T R}\right) \quad (2)$$

Here, in addition to the traditional multiplier a_w – water activity, another dimensionless multiplier a_q has been added, related to the charge of the aerosol particle (see below). The supersaturation of the solution is defined as

$$S = \frac{p_s - p_{0s}}{p_{0s}} \quad (3)$$

Supersaturation dependence graphs S from the drop radius R are usually called Köhler curves. In (2) the third multiplier on the right takes into account multilayer adsorption according to the theory FHH ((Frenkel, Halsey, Hill [10]) and it is missing from the usual Köhler model [1, 3], the fourth multiplier determines the increase in saturated vapor pressure with a decrease in the drop radius R (the Kelvin effect). Here $v_w = M_w / N_A \rho_w$ – the volume per one molecule of water in a drop; ρ_w и M_w – mass density and molar mass of water. In (2), $\mathbf{A}$ и $\mathbf{B}$ – parameters of the adsorption potential of a multilayer adsorption isotherm in FHH theory. $\mathbf{A}$ characterizes the interaction between the surface of a solid particle and the first layer of adsorbate. The higher the value $\mathbf{A}$, the greater the amount of adsorbed water. $\mathbf{B}$ describes the interaction between the surface and subsequent layers of adsorbate (water). Small values $\mathbf{B}$ an increase in the force of attraction at large distances from the surface of the adsorbent (aerosol particle) is characterized [11]. The adsorption is most sensitive to the value of the parameter $\mathbf{B}$ (Fig.4).

$$\theta = \frac{R - \varepsilon^{1/3} R_d}{d_w} \quad (5)$$

– number of adsorbed monolayers of water; d_w – thickness of one monolayer; ε – total volume fraction of dissolved organic impurities in a dry aerosol particle; R_d – the radius of a dry aerosol particle.

$$\gamma = \gamma_w - \Pi \quad (6)$$

– the surface tension of the drop, taking into account the correction (1); γ_w – surface tension of pure water. In the case of even sufficiently dilute solutions of polymers with long chains, the simple Raoult's formula for solvent activity (water in our case) a_w is no longer fair and the well-known Flory – Huggins expression is used [4, 5, 12, 13]:

$$a_w = (1 - \phi) \exp \left[\left(1 - \frac{1}{f} \right) \phi + \chi \phi^2 \right] \quad (7)$$

Here ϕ – volume fraction of polymers in solution; f – the ratio of the volume of a polymer molecule to the volume of a water molecule; χ – the semi-empirical Flory – Huggins parameter, which takes into account the interaction of a solvent molecule with a polymer molecule. Formula (7) derived in the lattice model. In this model, a long-chain polymer molecule is divided into segments (submolecules), so that the volume of the segment is equal to the volume of a solvent (water) molecule. Each cell in the lattice can be occupied by either a water molecule or a polymer segment. By calculating the total number of polymer chain configurations, the mixing entropy is calculated. It's easy to guess that f is a number of segments in a polymer molecule (all polymer molecules have the same number of segments), and the volume fraction of the polymer substance in the solution is ϕ it coincides with the mole fraction of all segments in solution (the ratio of the number of segments in solution to the total number of water molecules and segments). It is clear that for "ideal" solutions ($f = 1, \chi = 0$) from (7), the Raoult's formula is obtained: $a_w = 1 - \phi$. According to [4]

the Flory – Huggins parameter χ depends on the volume fraction of the polymer in the solution ϕ according to the formula:

$$\chi = \frac{\psi}{(1-\nu\phi)^2} - \beta(1+2\phi) \quad (8)$$

Here ν , ψ и β – are constants. According to [4], with an increase in the volume fraction of the polymer in solution ϕ , the parameter χ increases slightly, remaining equal in magnitude to the order of unity (note that Huggins [13] considered χ as a constant). As a water-soluble polymer, let's take PEG (polyethylene glycol) and PAA (polyacrylic acid), for which the parameters ν , ψ , β are known [4]. The volume fraction of the polymer in the solution ϕ is calculated by the formula:

$$\phi = \frac{\varepsilon_p R_d^3}{R^3 - \varepsilon R_d^3} \quad (9)$$

Below, for the sake of certainty, black carbon will be considered as an aerosol particle. These particles may contain easily soluble polymers with a volume fraction ε_p , as well as insoluble surfactant fatty acids (stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ is considered for certainty) with a volume fraction ε_s . The total fraction of organic impurities in a dry aerosol particle is

$$\varepsilon = \varepsilon_p + \varepsilon_s \quad (10)$$

After activation (coating with water) of the aerosol particle, these substances dissolve in water. Soluble component (polymer) turns out to be in the volume of water, and the insoluble surfactant is on its outer surface at the boundary with air (the term insolubility in this case means that the surfactant will not be in the volume of the solution, but on the solution-air boundary). The number of molecules of insoluble surfactants is determined from the condition:

$$N_s = \frac{\varepsilon_s \frac{4}{3} \pi R_d^3 \rho_s N_A}{M_s} \quad (11)$$

Here ρ_s и M_s – density and molar mass of stearic acid.

Then the value Ω_s appearing in (1) is the area per surfactant molecule:

$$\Omega_s = \frac{4\pi R^2}{N_s} \quad (12)$$

Figure 1 shows the dependence of the surface tension of a drop γ in the presence of film of insoluble surfactant – stearic acid on its surface on the radius R . The calculation was carried out according to the formulas (1), (6), (11), (12). With a fixed volume fraction of stearic acid in a dry aerosol particle ε_s , the R_d increases help to reduce surface tension and increase the probability of activation of an aerosol particle. As the droplet size R decreases, the surface tension γ decreases due to a decrease in the parameter Ω_s (with constant R_d) and a corresponding increase of the surface concentration of surfactants.

Figure 2 shows dependence of the activity a_w of an aqueous polymer solution on the drop radius R calculated by formulas (7)–(9). Curves 1 and 2 are evaluated for polymer solutions of PAA (polyacrylic acid) and PEG (polyethylene glycol) respectively. Curve 3 corresponds to an "ideal" solution, the activity of which satisfies Raoult's law. The calculation shows that the Raoult's formula gives an underestimated value of the activity of an aqueous solution (especially especially at small R) of long-chain polymers and it should be replaced with the more accurate Flory – Huggins formula (7).

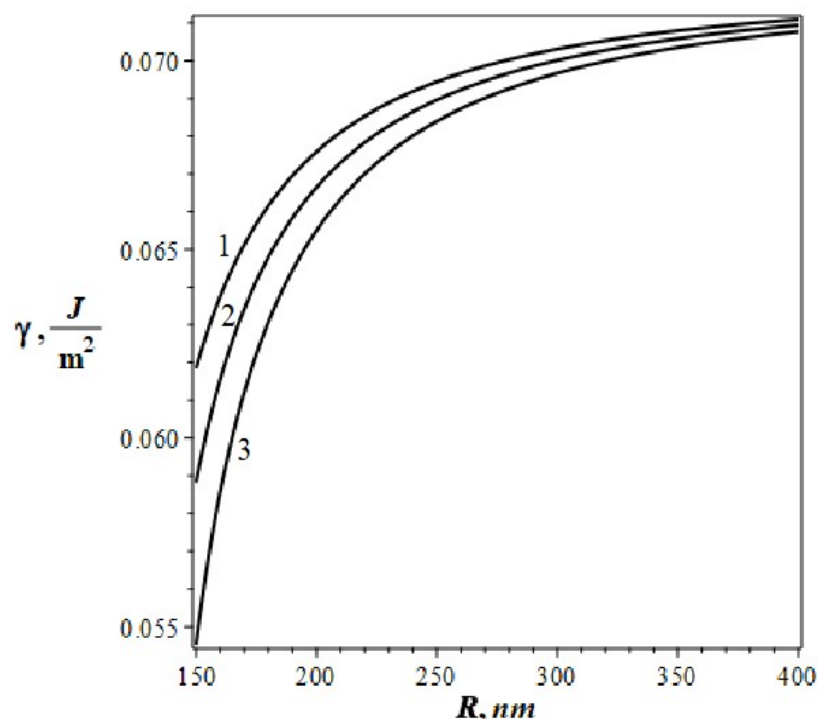


Fig. 1. Dependence of the surface tension of an activated aerosol particle (droplet) γ from its radius R if there is an insoluble film of surfactant on its surface (stearic acid). 1 – $R_d = 100$ nm ; 2 – $R_d = 105$ nm ; 3 – $R_d = 110$ nm ; Calculated parameters [7]: $T = 300$ K , $\gamma_w = 0.072$ J/m² , $\omega_w = 0.097$ nm² , $\omega_s = 0.32$ nm² , $M_s = 0.2845$ kg/mol , $\rho_s = 940$ kg/m³ , $\varepsilon_s = 0.05$

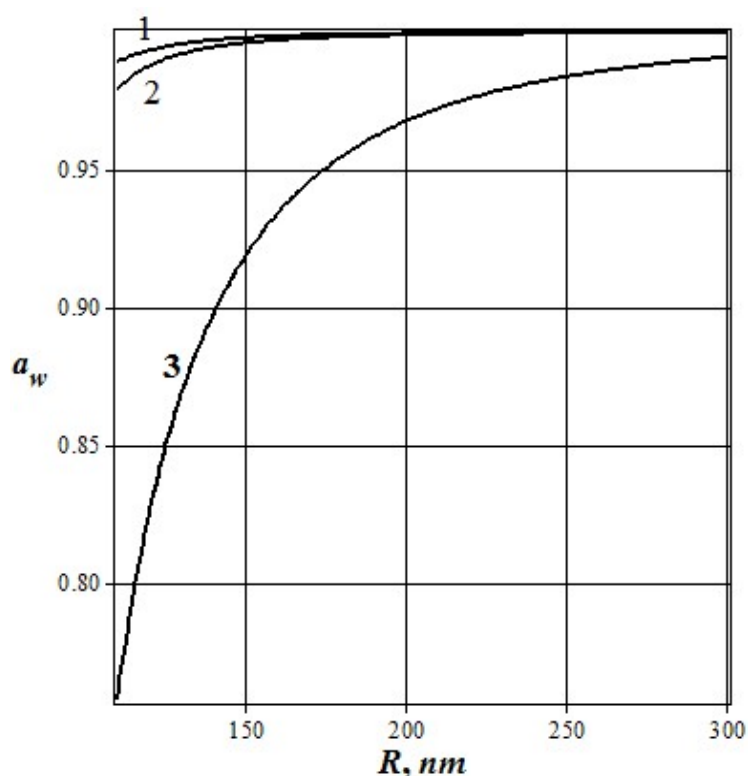


Fig. 2. Dependence of the activity a_w of an aqueous solution from the drop radius R . 1 – polyacrylic acid solution (PAA); 2 – polyethylene glycol solution (PEG); 3 – "ideal" solution ($f=1, \chi=0$), for which the Raoult's formula holds: $a_w = 1 - \phi$. Calculated parameters: $\varepsilon_p = 0.25$, $\varepsilon = 0.30$, $R_d = 100$ nm . The other parameters are the same as in Fig. 1. Curve 1: $f = 69.9$, $\psi = 9.02 \times 10^{-3}$, $\beta = -0.306$, $\nu = 0.922$; Curve 2: $f = 33.3$, $\psi = 8.86 \times 10^{-3}$, $\beta = -0.235$, $\nu = 0.942$. f, ψ, β, ν parameters, appearing in (8) are taken from [4]

As is known, a charged aerosol particle with an adsorbed layer of water has significantly lower electrostatic energy than in the dry state due to the high dielectric constant of water, so the charge promotes to the condensation of water vapor [14]. The multiplier a_q in (2) has the well-known form [15, 16] (in SI units):

$$a_q = \exp\left(-\frac{v_w}{k_B T} \frac{(eN)^2}{32\pi^2 R^4 \varepsilon_0}\right) \quad (13)$$

Here e is the elementary charge; N – the number of elementary charges; ε_0 – the electric constant.

Substituting (7) and (13) into (2) for oversaturation S we obtain the final expression:

$$S = (1 - \phi) \exp\left(-\frac{v_w}{k_B T} \frac{(eN)^2}{32\pi^2 R^4 \varepsilon_0}\right) \exp\left[\left(1 - \frac{1}{f}\right)\phi + \chi\phi^2\right] \exp(-\mathbf{A}\theta^{-\mathbf{B}}) \exp\left(\frac{2\gamma v_w}{k_B T R}\right) - 1 \quad (14)$$

Using (14), and (5), (8), (9) it is possible to build a dependence of supersaturation S on the drop radius R . The maximum value $S = S_{\max} = S_{cr}$ is called the critical supersaturation (the appropriate radius $R = R_{cr}$). When the partial pressure of vapor in the atmosphere p satisfies the inequality $\frac{p - p_{0s}}{p_{0s}} > S_{cr}$, the aerosol particle is activated, i.e. vapor condensation on it at any value of R . The calculations in Fig. 3 shows that as the charge of the droplet eN increases, the critical supersaturation decreases significantly, which contributes to vapor condensation.

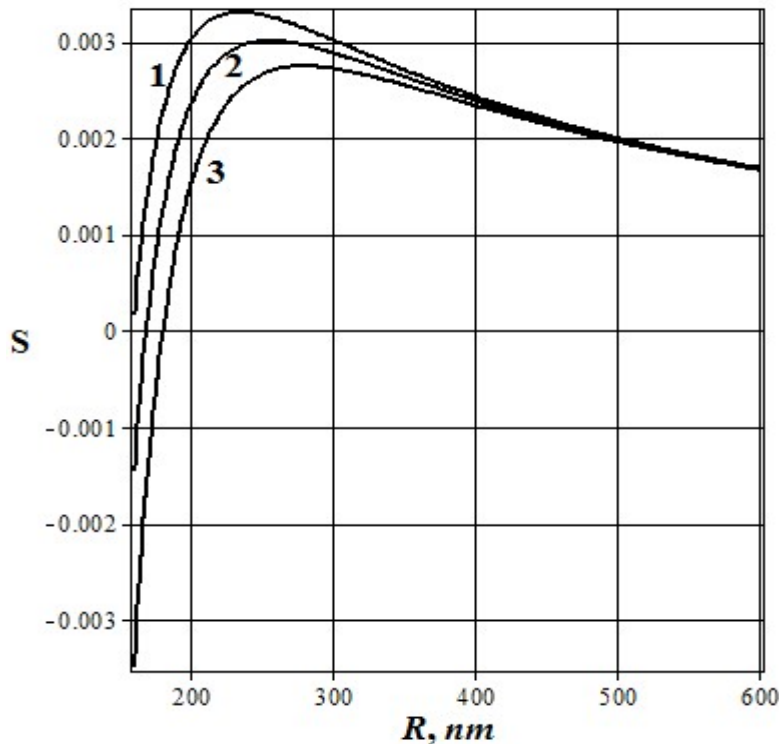


Fig. 3. Dependence of supersaturation S on the drop radius R at different charge eN values. Polyacrylic acid (PAA) was chosen as the soluble polymer. Calculated parameters: $\mathbf{A}=12$, $\mathbf{B}=1.93$ [7], $R_d=120$ nm, $d_w=0.289$ nm. The other parameters are the same as in Fig. 2. 1 – $N=0$; 2 – $N=4000$; 3 – $N=6000$

According to the calculation in Fig. 4, as the parameter $\mathbf{B}$ of the theory of multilayer adsorption FHH increases, the critical supersaturation S_{cr} increases, which is associated with a decrease in the attractive potential between the aerosol particle and the water layers.

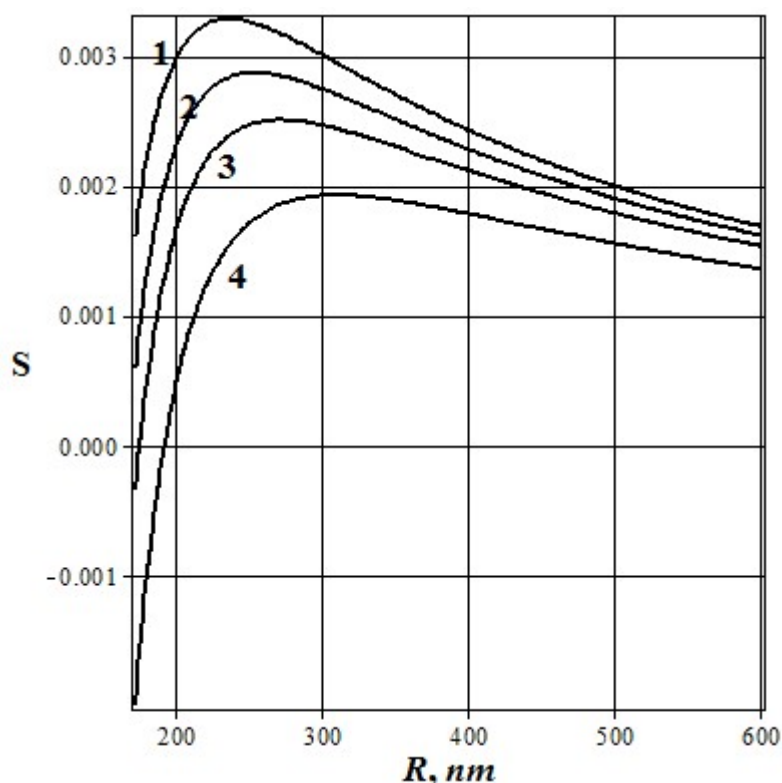


Fig. 4. Dependence of supersaturation S on the drop radius R for different B parameter of FHH theory of multilayer adsorption. $N=1000$. The other parameters are the same as in Fig. 3.
 1 – $B=1.93$; 2 – $B=1.6$; 3 – $B=1.5$; 4 – $B=1.4$

3. Conclusions

Model for the activation of an aerosol particle has been proposed which simultaneously takes into account several factors that are essential for the condensation of water vapor on them:

1. Dependence of the surface tension of the solution on the curvature (Kelvin effect);
2. Reduction of the surface tension of the droplet in the presence of insoluble surfactants.
3. Multilayer adsorption (FHH model);
4. The effect of the droplet charge;
5. When high-molecular polymers are dissolved in water, the decrease in the activity of the solution is calculated not by the simple Raoult's formula as usual, but on the basis of the Flory – Huggins theory.

The calculations performed have quantitatively confirmed all qualitative considerations:

1. Insoluble surfactants reduce supersaturation;
2. The Raoult's formula gives an underestimated value of water activity;
3. Charge reduces supersaturation;
4. With a decrease in the parameter B of the theory of multilayer adsorption FHH, the supersaturation of the solution decreases.
5. Accurate supersaturation calculation requires knowledge of the parameters of the adsorption potential of a multilayer isotherm in the theory of FHH – A and B , as well as knowledge of Flory – Huggins parameter χ , which takes into account the interaction of a solvent molecule with a polymer.

These parameters are most often found experimentally and their values can be found in the literature.

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