On Control of Submicron Particles by Electric Field

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Abstract — The phenomena of the mass transfer of dispersed microparticles under the action of an external electrostatic field with the aim to control their motion, primarily, to separate them from the closed phase, are considered. The questions on the density of the particle mass flux and its physical parameters such as the forces moving the particles in the electric field, mass and partial concentration of dispersions, their dimensions and charges, as well as the influence of these parameters on the mass transfer regularities are discussed. It is presented a simple approach on the minimum of the potential energy of the "particle-surrounding ions" system when the problem on the particle charging in the ion field, say, of corona discharge is being solved. Particle potential energy stationary distributions of the mass concentration, particularly, the Boltzmann distribution has been obtained through analyzing a general expression for the mass flow density. It is presented the main convective diffusion equation which is revised to the case of an electric wind at corona discharge, as well as the simplest nonstationary equation for the residual concentration within the emitter zone of an electric filter which can be designed on the basis of the equation solution.

Index Terms — mass transfer, electric field, electric wind, charge and particle radius.

I. INTRODUCTION

The phenomena of heat transfer process enhancement in liquids and gases by electrostatic fields are well known [1-4]. Initially, some authors considered the information on these phenomena and similar ones to be rather sensational as it was implied the field action on the medium molecular thermal conduction itself. But later it emerged that the reason for the observed significant enhancement of heat transfer in liquid dielectrics and gases under the action of external electric fields are the electrohydrodynamic (EHD) phenomena, and, more precisely, electric convection [3, 5, 6], which is similar to the gravity natural one, but is caused by the electric nature forces which are collectively known in literature as ponderomotive ones [7]. These forces appear to be rather complicated depending on many factors such as if the medium as an ideal dielectric or real one with low conductivity, if the field is homogeneous or not, etc.

It is possible the field effect on the molecular thermal conductivity, however, it is not so far found experimentally. At the same time, the possibility of the electric field action on the process of mass transfer at the ion-molecular level has been proved experimentally [9] and analytically [10] through the investigations of the electrostatic field influence on the solubility of distilled water in sunflower oil. It has been considered the motion of molecules and ions due to diffusion, as well as owing to migration under the action of external electric forces of dipole nature acting on neutral molecules of water H_2O , and purely coulomb ones, acting on the ions of hydroxyl OH and hydroxonium H_3O^+ , the concentration of which in water is rather big and determines its pH-degree. The general conclusion is that purely coulomb mechanism of

charge transfer through the medium is responsible for the electric field effect on the solubility of water in oil. Consequently, one should keep this in view when searching for the possibilities to control mass transfer in general. It is not for nothing that when dielectric liquids [12] and gases [13] are cleaned from contaminants they are preliminary exposed to electric charging. In the case of gases this is usually achieved at the treatment of the dispersed medium within the corona charge field [13, 14]. It has been found that the corona discharge regularities also occur in dielectric (low conducting) liquids in the presence of highly nonhomogeneous fields. Therefore the methods of electric charging of particles in the corona discharge field are also used successfully in the case of electric cleaning (EC) of liquid dielectrics [15, 16].

The investigations of EC showed that its efficiency decreases with the reduction of the disperse particle dimensions and at present such liquid media, the dispersion degree of which is more than deciles of a micron, are exposed to EC. However, the onrush of nanotechnologies makes one give thought to the problems to control the motion of nanoparticles by external actions including the effects of electric fields. The authors of this article, referring to the EC sphere, decided to analyze the main regularities of mass transfer at EC at viewing angle of the application of the proven methods to the submicron level, including nano level. The above mentioned facts concerning the influence of the degree of dispersion on the EC effect show that no one can expect a high efficiency of the field action on the processes of our interest. Nevertheless, we think that it is early to exclude the existence of new approaches which can favor some positive improvements. In particular, the case in hand is the problem hydrodynamic aspects.

II. THE FORCES ACTING ON A PARTICLE IN THE EXTERNAL ELECTROSTATIC FIELD

In practice the most frequent is the case of the action on a particle of the force with purely coulomb nature

$$\mathbf{F}_{1} = q\mathbf{E}, \qquad (1)$$

where q is the particle charge; \mathbf{E} is the vector of the electric field strength in the particle location point. The difficulties in the case of formula (1) application are mainly connected with determination of the particle electric charge q, which is known to increase with the growth of the particle dimensions.

If the particle is electrically neutral, it is also subjected to the action of the external electric field due to its polarity, the applied force being initially potential one [17]:

$$\mathbf{F}_2 = \nabla(\mathbf{P} \cdot \mathbf{E}), \tag{2}$$

where **P** is the electric dipole moment of the particle. From expression (2) it follows that the force appears only in the nonhomogeneous electric field, as $\mathbf{P} \sim \mathbf{E} = > \mathbf{P} \cdot \mathbf{E} \sim E^2$. Finally, there exists a class of media, for example, colloids, the particles of which have a double electric layer and, so called " ζ th potential" [18], consequently, some charge $c_1\zeta$. The force, which acts on the particle in such a case, is as following:

$$\mathbf{F_3} = c_1 \, \boldsymbol{\zeta} \cdot \mathbf{E}, \tag{3}$$

where c_1 is the proportionality constant.

The mass flows are determined by these three forces which can be also applied to the particle simultaneously. Assuming in (1) and (3) the coefficient at \mathbf{E} constant, note that all the forces are potential ones with the meaning of the potential energy W, which all three cases are given by the following formulas:

$$W_1 = q \cdot \varphi; \tag{4}$$

$$W_2 = -\mathbf{P} \cdot \mathbf{E} \,; \tag{5}$$

$$W_3 = c\zeta \cdot \varphi \,. \tag{6}$$

In formula (4) the particle charge does not depend on the coordinates. The same refers to the coefficient at φ in (6). Here φ means the electric potential through which the strength $\mathbf{E} = -\nabla \varphi$.

Proceed to the discussion of mass flows beginning with their density.

III. THE MASS FLOW DENSITY

This physical quantity is a vector and it is given by a well-known formula [19]:

$$\mathbf{i} = -\gamma D \cdot \nabla c + \gamma b \mathbf{F} \cdot c \,, \tag{7}$$

where c is the mass concentration of particles; γ is the medium density; D is the diffusion coefficient; b is the particle mobility coefficient by the force ${\bf F}$, in contrast to

 k_E by the field strength (see below). The force ${\bf F}$ is given by one of expressions (1)-(3) or through the potential energy according to the general formula:

$$\mathbf{F} = -\nabla W \tag{8}$$

by expressions (4) and (5).

The mobility coefficient can be calculated by the Stokes formula [19]

$$b = \frac{1}{6\pi\eta r}\,,\tag{9}$$

where r is the radius of the particles assumed spherical; η is the medium dynamic viscosity coefficient.

Please note that the mass flow given by formula (7) is through one with no allowance for the convective constituent which will appear below when the convective diffusion equation is generated.

The first summand in (70 is a diffusion one. In this case the diffusion coefficient can be calculated by the Einstein relation [19]

$$D = bkT$$

which in terms of (9) gives:

$$D = \frac{kT}{6\pi\eta r} \tag{10}$$

where k is the Boltzmann constant; T is the absolute temperature of the medium. The second summand in (7) is the flow density of the particles, caused by their motion under the action of external electrostatic forces (1)-(3). As is seen from (7) and (9) the radius of the particles decreasing, the flow of them must grow, but on the hand, when the radius increases all the coefficients at \mathbf{E} in the formulas for forces (1)-(3) also rise and possibly quicker than in the first degree, therefore, as a result the mass flow decreases with the growth of the particle dimensions, being practically observed.

Please note that the flow on the right side of (2) may have opposite directions but may also coincide depending on the direction of the second flow called a migration one. The second case may happen in the course of injection of one substance into another, for example, medically.

In the context of the mass transfer processes at the submicron level it is pertinent to note how the particle dimensions influence the transfer under the action of electric fields.

It follows from equation (7), formulas (9) and (10) that the decrease of the particle radius r results, in inverse proportion, in the growth of the mass flow \mathbf{I} , as $D \sim b \sim 1/r$, and it is real with respect to the mass concentration c. However, if we pass from this concentration c to partial one n, i.e. to the number of particles per volume unit, than, for the mass concentration determined by the following formula:

$$c \equiv \frac{m_1}{\gamma} = \frac{\gamma_0 \cdot V_0 \cdot n}{\gamma} = \frac{\gamma_0}{\gamma} \cdot \frac{4\pi r^3}{3} \cdot n,$$

where m_1 is the mass of all the particles per volume unit;

 γ_0 is the particle substance density; V_0 is the volume of the particles, we can make a conclusion that the density of the mass flow of the particles grows as the square of their radius. These notes equally refer to the both flows in right side of (7). However, there exist some specific features of the migration ("electric") flow mainly imposed by the electric charge q in the formula for force (1) to which we now restrict ourselves.

There are formulas to determine this charge, see, for example, [13]. All of them results in the growth of the particle charge when the radius increases. We suggest somehow another approach to derive a formula for the particle charge based on the principle of the system potential energy minimum, which is rather transparent and makes possible further generalizations.

Let initially neutral spherical low conducting particle with radius R is surrounded by N_0 ions with radius r_0 , charge q_0 and N ions pass to the particle. Then the total energy of the system is as follows:

$$U = (N_0 - N) \cdot \frac{q_0^2}{8\pi\varepsilon_0\varepsilon r_0} + \frac{q_0^2 \cdot N^2}{8\pi\varepsilon_0\varepsilon R}$$

Putting to zero the N-derivative of this function, we obtain the following formula for the particle charge:

$$Q = N \cdot q_0 = (R/d) \cdot q_0$$

where $d=2r_0$ is the ion diameter. The simplicity of this formula apparently shows that it may be used with the aim of estimations but not rigorous calculations. Assuming (for the nanoparticles) $R\sim 10^{-8}$ M, $r\sim 10^{-10}$ M, we obtain $Q\sim 10^2\, q_0$ – a realistic value.

Subsequently we consider the stationary states ($\partial/\partial t = 0$), among which the Boltzmann equilibrium one

3.1. Boltzmann distribution. This distribution is obtained at I = 0 which means the dynamic equilibrium between the diffusion flow (the first summand in (7) and migration one at the expense of electrostatic forces (the second summand in (7)). Besides, it is implied $\gamma = const$, b = const, with the meaning of independence on the coordinates. Equating the right side of (7) to zero, we obtain the following homogeneous equation:

$$-D \cdot \nabla c + b \mathbf{F} \cdot c = 0$$
.

the solution of which in terms of (8) is as follows:

$$c = c_0 \cdot e^{-W/(k \cdot T)}. \tag{11}$$

For the particular case of equilibrium in the field of gravity forces with the potential energy of the particles $W=m_0\cdot g\cdot z$, where m_0 is a single particle mass we obtain a well-known distribution

$$c = c_0 \cdot e^{-(m_0 \cdot g \cdot z)/(k \cdot T)}$$

Similarly, substituting into (11) the expressions for potential energies (4)-(6), we receive the corresponding electric distributions for the cases of electric forces, respectively:

$$c = c_0 \cdot e^{-(q \cdot \varphi)/(k \cdot T)}, \tag{12}$$

supposing $\varphi_0 = 0$ corresponds to the concentration C_0 .

Thus, positively charged particles will accumulate near the grounded electrode, where $\varphi_0 = 0$, and negatively charged ones will gather far from it.

For the case of ideal particles we have from (5)

$$c = c_0 \cdot e^{(\mathbf{P} \cdot \mathbf{E})/(k \cdot T)}, \tag{13}$$

And, as the vector of the dipole moment \mathbf{P} is nearly always parallel to the vector of the electric field strength \mathbf{E} , it follows from distribution (13) that dielectric particles (at q=0) should gather into the region of high field strengths. The case of force (6) is similar to (4) and the distribution has the following form:

$$c = c_0 \cdot e^{-(c_1 \zeta \cdot \varphi)/(k \cdot T)}$$

3.2. Generalization of the Boltzmann distribution in the case i = const, F = const. Here there happens the preponderance of one of the flows in the right side of (7) over another. Namely, if the resulting flow i is directed against the particle concentration gradient, than the diffusion process predominates, and vice versa.

The concentration distribution in this case is found from nonhomogeneous equation (7) as the sum of the general solution (11) of the homogeneous equation, discovered above, and a particular solution of the nonhomogeneous one which with an accuracy to the constant multiplier is \mathbf{i} . Thus,

$$c = c^* \cdot \exp[-W/(k \cdot T)] + \mathbf{i}/(\gamma b\mathbf{F}), \quad (14)$$

where the division of two vectors in (14) is admissible as they are supposed collinear. Besides, $\boldsymbol{\mathcal{C}}^*$ is a new arbitrary constant and is found from the following condition:

$$c|_{\mathbf{W}=0} = c^* + \mathbf{i}/(\gamma b\mathbf{F}) = c_0.$$

Hence

$$\Rightarrow c = c_0 \cdot e^{-\frac{W}{kT}} + \frac{\mathbf{i}}{\gamma b \mathbf{F}} \cdot (1 - e^{-\frac{W}{kT}}). \tag{15}$$

At $\mathbf{1} = 0$ from (15) there follows particular case (11) – the Boltzmann distribution. Within the region of small potential energies (W = 0) the distribution is close to the initial one– c_0 . At large ones ($W \to \infty$)

the distribution of concentrations becomes such without regard for diffusion and $\mathbf{F} = \text{const.}$ Usually this corresponds to the far regions of the processes. For

illustrative purposes we apply formula (15) to the field of gravitation:

$$c = c_0 \cdot e^{-\frac{m_0 g z}{k \cdot T}} + \frac{\mathbf{i}}{\gamma b \mathbf{F}} \cdot (1 - e^{-\frac{m_0 g z}{k \cdot T}}). \quad (16)$$

This distribution corresponds to the continuous fall of particles from high altitudes under the gravity forces keeping below (at z=0) a constant concentration c_0 =const and constant flow of particles at the high altitudes z. Similar physical situations may be observed in electric fields. The constant multiplier at brackets (15) we denote c_{∞} (in the meaning of $W \to \infty$). Then instead of formula (15) one can write:

$$c = c_0 \cdot e^{-\frac{W}{kT}} + c_{\infty} \cdot (1 - e^{-\frac{W}{kT}}),$$
 (17)

where c_{∞} is given by the following formula:

$$c_{\infty} = \mathbf{i}/(\gamma b\mathbf{F}),\tag{18}$$

In this case it is implied that $i \sim F$.

All the distributions obtained above are stationary ones, i.e. independent of time. Boltzmann distribution (11) is an equilibrium one from the viewpoint of the dynamic balance between the diffusion and migration processes. Generally, the mass transfer processes are covered by the convective diffusion equations, which, along with the diffusion equation itself, include the equations of hydrodynamics and in our case those of electrohydrodynamics.

IV. EQUATIONS OF DIFFUSION

The main equation of convective diffusion has the following form [19]:

$$\gamma \left(\frac{\partial c}{\partial t} + \mathbf{v} \nabla c \right) = -\nabla \mathbf{i} \,, \tag{19}$$

where \mathbf{v} is the hydrodynamic velocity, and the mass flow density is given by formula (7). For incompressible medium (19) can be rewritten in the form:

$$\gamma \frac{\partial c}{\partial t} = -\nabla [-\gamma D \cdot \nabla c + \gamma c (b\mathbf{F} + \mathbf{v})]. \quad (20)$$

It is seen that the account for the liquid motion amounts to the addition to the through velocity

$$\mathbf{u} \equiv b \cdot \mathbf{F}$$

of the hydrodynamic velocity **v.**Denoting the total velocity

$$\mathbf{w} \equiv \mathbf{u} + \mathbf{v}$$

and assuming velocity **u** constant from (20) we obtain:

$$\frac{\partial c}{\partial t} = D \cdot \nabla^2 c + \mathbf{w} \cdot \nabla c.$$

Under the conditions of electric convection, and in the case of corona discharge – of electric wind (EW) the hydrodynamic velocity **v** has a one-dimensional jet character and its value is as follows [20]:

$$\upsilon = c_2 \cdot \frac{v}{d} \cdot \left(\frac{jd^3}{k_E \cdot \gamma v^2}\right)^{1 \to 0,5} \tag{21}$$

where $v=\eta/\gamma$ is the kinematic viscosity; k_E is the mobility of the ions of the corona electrode sign; d is the characteristic size of the corona electrode; c_2 is the coefficient of proportionality, $c_2 \sim 1$. The exponent decreases from l to 0.5 as EW develops from laminar flow to turbulent one.

If the case is of EC usually the working space of an electrofilter (EF) consists of two zones: emitter one where the particles are imposed to charging and the liquid is put into electroconvective mixing collecting zone with the arranged traps of dispersed particles. In the course of the EF operation the concentrations in both regions are nearly constant, when the process begins they are the same, nearly equal to the initial ne c_0 , then in the first the concentration decreases, and in the collecting one it increases. The transition between the zone is in the form of a narrow boundary mass transfer layer with some thickness δ . On one side of the layer the concentration is assumed equal to the average value across the emitter zone volume $-\overline{c}$, from where the cleaned liquid is filtered out. On the other side it is assumed equal to the average value in the collecting part. It is shown in works [20, 21] that integration over the emitter volume, i.e. averaging it is possible to obtain approximately a linear equation in the following simplest form:

$$\frac{d\,\overline{c}}{dt} = A \cdot \overline{c} + B \,. \tag{22}$$

The expression for the coefficients A and B contain all possible physical parameters of the process, and depending on the relation between them one can get a large number of particular cases of the solution of equation (22) [21].

Thus, it has reviewed the simplest analytical approaches to the solution of the problems of separation of heterogeneous media with the help of electric fields from the viewpoint of application of these approaches to the questions emerging in practice and theory of the transfer of submicron particles in heterogeneous media.

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