

Ponderomotive forces, which are responsible for electroconvection, were investigated in relation to the properties of the liquid and the strength of the electric field of an infinite charged plate. The obtained solutions were used to obtain a parameter of the relative intensification of heat transfer in various dielectrics in an external electrostatic field.

It is a known fact that an electric field intensifies heat transfer to liquids and gases. The necessary conditions for the occurrence of electroconvection are gradients of the field strength and polarization coefficient of the medium close to the heat-transmitting surface, but it has been discovered experimentally [1] that a uniform electrostatic field also affects the free convection of a dielectric [1]. In the given case edge effects can be neglected and the field can be regarded as uniform everywhere, except for the region near the capacitor plates. Here the field is reduced owing to polarization of the medium resulting from orientation of molecules with permanent and (or) induced dipole moments, and also to separation of charges in the electric field of the surface. The liquid dielectrics used have a low, but nonzero, conductivity ($\sigma = 10^{-4} - 10^{-12} \Omega^{-1} \cdot \text{m}^{-1}$) and in this sense can be regarded as very weak electrolyte solutions. The pronounced effect of insignificant traces of impurities in the dielectrics on heat transfer, as observed by Senftleben [2], confirms this view. The characteristic length of the space-charge region on the surface lies in the range $1/\kappa = 10^{-8} - 10^{-4} \text{ m}$, which is usually much smaller than the region of variation of the electrostatic potential. It is in the shielding region, however, that the ponderomotive forces responsible for the additional convective flow of liquid are located.

The electrostatic field strength in a semiinfinite liquid with a prescribed potential on the plane boundary and a boundary charge screened by ions of opposite sign is calculated below as a model. The solutions obtained give the distribution of electrostrictive forces in the nonuniform temperature field of the liquid and their behavior in relation to the thermal change in gravitational forces and the similarity criteria, which characterizes the intensification of heat transfer in an electrostatic field. Since only the mechanism of polarization of the medium is considered, the results obtained can be extended to the case of a cylinder with radius greater than the shielding length and a heated liquid in an external electric field.

1. Let a plane charged surface $y=0$ form the boundary of a semiinfinite volume of a weak solution of binary electrolyte. We regard the mean concentration n_∞ of ions of each sign in unit volume as so small that the Debye shielding length $1/\kappa$ greatly exceeds the length of averaging of the electric field.

We find the dimensionless values of the total ion concentration, the space-charge density, and the strength and potential of the electrostatic field

$$n = \frac{n_+ + n_-}{2n_\infty}, \quad q = \frac{n_+ - n_-}{2n_\infty}, \quad \epsilon = \frac{eE}{\kappa kT}, \quad \varphi = \frac{e\Phi}{kT} \quad (1.1)$$

as functions of the dimensionless coordinate along a normal to the surface

$$\theta = \kappa y, \quad \kappa = (8\pi e^2 n_\infty / \epsilon_d kT)^{1/2} \quad (1.2)$$

Here E , Φ are dimensional values of the field strength and potential, n_+ and n_- are the concentrations of positive and negative ions, e is the absolute ion charge, kT is the temperature (in energy units), and ϵ_d is the dielectric constant.

Novosibirsk. Translated from *Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki*, No. 4, pp. 13-18, July-August, 1971. Original article submitted July 17, 1970.

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For simplicity we will assume the electrolyte symmetric (the moduli of the charge numbers $|z_+| = |z_-| = 1$) and the diffusion coefficients $D_1 = D = \text{const}$, which is approximately true for the commonest dissociating impurities at low concentration. Considering liquids and gas which either have high dielectric strength, or are indifferent to the charged surface, we neglect the current due to surface charge leakage

$$j_i = eD(z_i e n_i E / kt - \nabla n_i) = 0$$

This condition in conjunction with the Maxwell equations leads to the following system of equations:

$$q_\theta = n\varepsilon, \quad n_\theta = q\varepsilon, \quad \varepsilon_\theta = q, \quad \varphi_\theta = -\varepsilon \quad (1.3)$$

Whence, eliminating q and n , we obtain an equation for the field in the liquid

$$\varepsilon \varepsilon_{\theta\theta\theta} - \varepsilon_\theta \varepsilon_{\theta\theta} - \varepsilon^3 \varepsilon_\theta = 0 \quad (1.4)$$

The subscripts here denote the variable and order of the derivatives. If the medium is electrically neutral far from the surface

$$q, \varepsilon \rightarrow 0, \quad n \rightarrow 1 \text{ when } \theta \rightarrow \infty$$

and for a prescribed electrostatic potential on the surface (regarded as positively charged for definiteness) relative to infinity

$$\varphi(0) = \varphi_0 > 0, \quad \varphi(\infty) = 0$$

we obtain

$$\varphi = 2 \operatorname{lncth} \frac{\theta + \theta_0}{2}, \quad \varepsilon = \frac{2}{\operatorname{sh}(\theta + \theta_0)} \quad \left(\theta_0 = \operatorname{lncth} \frac{\varphi_0}{4} \right) \quad (1.5)$$

This solution can be obtained not only from the condition for zero ambipolar-diffusion ion flux, but also by the self-consistent field method. In fact, if, in accordance with the Debye-Hückel theory [3], we take the statistical ion distribution in the electrostatic field as

$$n_+ = n_\infty \exp(-\varphi), \quad n_- = n_\infty \exp \varphi \quad (1.6)$$

then the Poisson equation takes the form

$$\varphi_{\theta\theta} = \operatorname{sh} \varphi, \quad \varphi(\infty) = \varphi_\theta(\infty) = 0 \quad (1.7)$$

and gives the same relationship between field strength and potential as is given by equation (1.5)

$$\varepsilon = 2 \operatorname{sh} \varphi / 2 \quad (1.8)$$

In the immediate vicinity of the plate, however, these solutions have no physical sense in the case of a high degree of ionization of the liquid or in the case of a strongly charged surface. In the region of applicability of the obtained solutions the following two criteria must be satisfied.

Firstly, the mean distance between counterions must be not less than the distance specified by the condition for weakness of the Coulomb interaction of negative ions in comparison with their mean kinetic energy

$$n_-^{-1/2} \geq \delta = e^2 / \varepsilon_d k T$$

Secondly, the mean distance between positive ions must not be greater than the distance to the surface

$$n_+^{-1/2} \leq y$$

Using solutions (1.5), (1.6) we write the two criteria in the form

$$\operatorname{th} \frac{\theta + \theta_0}{2} \geq \max \left\{ \frac{\kappa \delta}{\sqrt{8\pi}}, \left(\frac{8\pi \kappa \delta}{\theta^3} \right)^{1/2} \right\} \quad (1.9)$$

We first investigate the first part of the inequality. It is valid in the region

$$\theta \geq \ln \left(\frac{\sqrt{8\pi} + \kappa \delta}{\sqrt{8\pi} - \kappa \delta} \operatorname{th} \frac{\varphi_0}{4} \right)$$

and, in particular, wherever $\theta \geq 0$, if the surface potential does not exceed the critical value

$$[\varphi_0] = \ln(8\pi / \kappa \delta) \quad (1.10)$$

We write this expression in another form, using the kinetic-theory relationship between the electrical conductivity σ and the ion mobility w [4]

$$\sigma = 2n_{\infty}ew, \quad w = eD / \epsilon_d kT$$

Then

$$\kappa = (4\pi\sigma / D)^{1/2}, \quad [\varphi_0] = \ln(2D / \sigma\delta^2) \quad (1.11)$$

and the values of the shielding lengths and critical potential can easily be estimated from tabulated parameters (the Schmidt number $S = \nu/D$ for most low-viscosity liquids with impurity conductivity is of the order of 10^3 , and for gases is close to unity). For instance, for dry air, regarded as a weakly ionized gas, the critical surface potential $[\varphi_0] \approx 30$, whereas for chemically pure, distilled, and sea (salinity 0.035) water $[\varphi_0] \approx 20, 10$, and 1 , respectively. The last, however, cannot be regarded as a weak electrolyte solution, since in this case the Debye length and the diameter of the water molecule are commensurable.

Cases where $\varphi_0 \gg 4$ are of practical interest, since the dimensionless electrostatic potential is referred to $kT/e = 0.03$ V ($T = 300^\circ\text{K}$), and the obtained values of $[\varphi_0]$ are less than the technical criteria for strong surface charge. Investigating inequality (1.9) further, we find that in the region $\theta < 1$ of surface charge shielding the last part of the inequality is decisive for liquids with mean ion concentration $n_{\infty} \ll \delta^{-3}$, i.e., for practically all liquid dielectrics. Hence, the region of applicability of the solutions of (1.5) and (1.8) is uniquely defined and its dimensionless limit θ_* is a weak function of the degree of ionization of the medium

$$\theta \geq \theta_* = 2(\pi\kappa\delta)^{1/2} \sim 0.1 \quad (1.12)$$

and the potential φ_* at the limit is much less than the surface potential

$$\varphi_* = 2\ln\text{cth}(\pi\kappa\delta)^{1/2} \ll \varphi_0$$

We write the field potential in the immediate vicinity of the surface in the form of three terms of a McLaurin series

$$\varphi = \varphi_0 + \varphi_{\theta}(0)\theta + 1/2\varphi_{\theta\theta}(0)\theta^2 \quad \text{when } \theta \ll 1$$

and, combining the solutions for the potential and its derivative at the limit θ_* , we determine the field strength and space-charge density

$$\begin{aligned} \epsilon_0 &= -\varphi_{\theta}(0) = \frac{2}{\theta_*} \left(\varphi_0 - 2\ln\text{cth}\frac{\theta_*}{2} - \frac{2}{\text{sh}\theta_*} \right) \\ q_0 &= -\varphi_{\theta\theta}(0) = \frac{2}{\theta_*^2} \left(\varphi_0 - 2\ln\text{cth}\frac{\theta_*}{2} - \frac{2\theta_*}{\text{sh}\theta_*} \right) \end{aligned} \quad (1.13)$$

We note that the last terms containing hyperbolic functions can be neglected, since with the restrictions adopted earlier,

$$\epsilon_0 > \varphi_0 (\pi\kappa\delta)^{-1/2} > (2\pi)^{-0.3} \varphi_0 > 1$$

and we can regard the potential distribution in the shielding region as parabolic,

$$\varphi = \varphi_0 (1 - \theta / \theta_*)^2 \quad (1.14)$$

This generally adopted operation of "sewing together" the solutions is less accurate than the method of asymptotic combination [5], but requires less information about the physicochemical effects on the charged surface. The indicated method, however, can be used in a particular case for determination of the mean strength $\langle \epsilon \rangle$ of the field within the limits of the surface charge shielding length. The internal solution for the potential can be written in dimensional form $\Phi = \Phi_0 - \gamma E$ ($\theta \leq 1$) which does not contain either δ or $1/\kappa$ as a characteristic length, and the external solution is a one-term expansion $\varphi = \epsilon$ of Eq. (1.14) in the region $\theta \geq 1$. Combining their limits when $\theta \rightarrow 1$ and $\theta \rightarrow 0$, respectively, we obtain $\langle \epsilon \rangle = \varphi_0$, which follows, in particular, also from Eq. (1.13).

2. When the medium is in mechanical and thermal equilibrium the molecules are acted on not only by gravitational forces $f_g = \rho g$, but also by ponderomotive forces directed towards the charged surface, irrespective of the sign of the charge and with space density

$$f_e = -\frac{\kappa_1}{2} \nabla E^2, \quad \kappa_1 = \frac{\epsilon_d - 1}{4\pi} = \frac{\rho N}{M} \left(\beta + \frac{p_0^2}{3kT} \right) \quad (2.1)$$

Here κ_1 and β are the polarization coefficients of the medium and an individual molecule, ρ and M are the density and molecular weight, p_0 is the constant component of the dipole moment of the molecules, and N is the Avogadro number. Outside the shielding region the ponderomotive forces are small

$$f_e = \kappa\kappa_1 E^2 \text{cth}(\theta + \theta_0), \quad \theta > \theta_*$$

Hence, we can regard them with reasonable accuracy as localized in the layer $\theta \leq \theta_*$ with mean density

$$\langle f_e \rangle = 1/2 \kappa\kappa_1 E_0^2 \quad (2.2)$$

When the thermal equilibrium of the medium is distributed, the increment of these forces is

$$\Delta f_e = - \left[\frac{\partial \langle f_e \rangle}{\partial T} \right]_{T=T_0} \Delta T = \langle f_e \rangle \left[\alpha + \frac{1}{2T_0} \left(1 + \frac{2}{1 + 3\beta k T_0 p_0^{-2}} \right) \right] \Delta T \quad (2.3)$$

In differentiating expression (2.2) we take account not only of the variation of the Debye length $1/\kappa$ and the polarization coefficient κ_1 with the liquid temperature T , but also the thermal expansion

$$\rho = \rho_0 (1 - \alpha \Delta T), \quad \alpha = - \frac{1}{\rho_0} \left[\frac{\partial \rho}{\partial T} \right]_p, \quad \Delta T = T_0 - T \ll T_0$$

Here ρ_0 and T_0 are the parameters of the liquid on the body surface (at $y=0$).

The field strength on the surface is constant owing to the absence of temperature fluctuations on the wall and is

$$E_0 = \Phi_0 \left[\frac{\pi (8\kappa_\infty e)^2}{\epsilon_d k T} \right]^{1/2} \quad (2.4)$$

In the usual method of experimental investigation of electroconvection the heated body is in an external electric field and, hence, the field strength E_0 can be calculated in the usual way if the characteristic length of the body is much greater than the shielding length.

The thermal increment of the ponderomotive forces (2.3) is independent of the charge polarity and, as distinct from the change in gravitational forces $\Delta f_g = \rho_0 g \alpha \Delta T$, is always directed against the temperature gradient in the medium and creates an additional convective flow. The degree of intensification of heat transfer in an electrostatic field is characterized by the ratio of these forces

$$V = \frac{\Delta f_e}{\Delta f_g} = v E_0^2, \quad v = \frac{\kappa (\epsilon_d - 1)}{8\pi \rho g} \left[1 + \frac{1}{2\alpha T_0} \left(1 + \frac{2}{1 + 3\beta k T_0 p_0^{-2}} \right) \right] \quad (2.5)$$

The expression in the square brackets is $1 + 1/\alpha T_0$ on the average, since for dipoleless molecules it is $1 + 1/2\alpha T_0$, and for molecules with preferred orientational polarization it is $1 + 3/2\alpha T_0$. Using Eq. (1.11) we can write the parameter v , which unifies the properties of the liquid, in a form convenient for approximate calculations

$$v \cong \frac{\epsilon_d - 1}{4\rho g} \left(1 + \frac{1}{\alpha T_0} \right) \left(\frac{\sigma S}{\pi v} \right)^{1/2} \quad (2.6)$$

Hence, we obtain the following results. The intensification of heat transfer in an electric field increases with increase in the polarity of the molecules and dielectric constant and with reduction of the viscosity, molecular weight, and compressibility of the medium, other conditions being equal.

Heating of nonpolar liquids leads to an increase in the parameter v due to reduction of the viscosity and electric resistance, whereas polar liquids show an opposite tendency due to disturbance of orientational order. Finally, the effect of electroconvection is more pronounced in liquids than in gases, in view of the considerable difference in the values of the Schmidt number and bulk expansion coefficient.

Multiplying the ratio of the thermal increment of the ponderomotive forces to the Stokes resistance to motion of the liquid mole by the Reynolds and Prandtl numbers we obtain the electroconvection analogs of the Grashof and Rayleigh numbers

$$G_e = GV, \quad R_e = RV$$

The usual power relationship between the Nusselt number and the Rayleigh number in free-convection theory

$$\text{Nu} = \text{const } R^n \quad (n = 0.12 - 0.33)$$

can be extended to the case of electroconvection. We assume the additivity of the convective fluxes due to volume forces of gravitational and electroconstrictive origin. We obtain the equation for heat transfer in an electrostatic field

$$\text{Nu}_e = \text{const} (R + R_e)^n = \text{Nu} (1 + V)^n \quad (2.7)$$

The relationship between the relative increase in the heat transfer coefficient and the strength of the electrostatic field as the latter increases varies from quadratic

$$\text{Nu}_e / \text{Nu} - 1 \rightarrow n\nu E_0^2 \text{ when } E_0 \rightarrow 0$$

to a weaker relationship

$$\text{Nu}_e / \text{Nu} - 1 \rightarrow (\nu E_0^2)^n \text{ when } E_0 \rightarrow \infty$$

which illustrates the saturation of electroconvection observed by Senftleben. Equation (2.7) can be used to estimate the "threshold" value of the electrostatic field at which intensification of heat transfer becomes appreciable. In fact, where $E_0 = \nu^{-1/2}$ and in the indicated range of values of n we can expect an increase in the heat transfer coefficient in an electrostatic field by 10–25%, which is close to the error of the corresponding experiments.

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