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MOTION OF AN ELECTROLYTE–GAS INTERFACE IN AN ELECTRICAL FIELD

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UDC 537.84

The article discusses the phenomenon of the motion of an electrolyte–gas interface, first observed on electrical levels. It gives a comparative characterization of the phenomena, for purposes of practical use, with a solution of problems of control by the position of a liquid–liquid interface.

While the mechanics of a liquid has been rather well studied at the present time, the problem of effective control by the position of a liquid has not yet been solved. It is a question here not of mechanical

Miass. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 6, pp. 25-28, November-December, 1975. Original article submitted July 16, 1974.

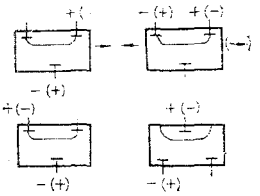

Fig. 1

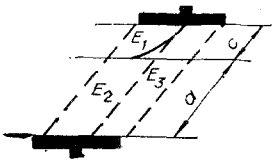

Fig. 2

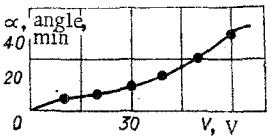

Fig. 3

control, which has well-known shortcomings (slow action, large weight, large overall dimensions), but of control by the position of the distributed masses of liquids using the forces of an electrical field. A number of recently discovered effects [1-7] makes this possible in principle; however, their technical realization is difficult in view of the special requirements (a high transformation coefficient of the controlling signal, small overall dimensions and weight, safety in operation, reliability). The reason for this consists in the characteristic conditions for the existence of a motion of the liquid field: a) the presence of strong constant or variable fields; b) the use of suspensions or pure dielectric liquids.

The effect of the motion of an electrolyte–gas interface, observed on electrical levels, offers a relatively great possibility for practical use [8].

The special characteristics of the experiment are the following: A voltage of direct (up to 50 V) or alternating current (frequency from 20 Hz to 10 MHz and an amplitude up to 60 V) was fed to electrodes of rectangular configuration, soldered into a cylindrical glass ampoule (at its lower and upper parts), filled with an electrolyte (a 2%-solution of lithium in ethanol) and containing a gas cavity. Under these circumstances, there is observed a motion of the interface in the direction shown by the arrow in Fig. 1.

As a result of a number of experiments, the following special characteristics were brought out:

1) When a field (either constant or variable) is set up between oppositely arranged electrodes, the motion of the gas cavity is always directed toward a position of the symmetrical arrangement of the cavity with respect to an axial line connecting the centers of the electrodes. When the field is set up between the upper electrodes, the motion of the cavity is directed preferentially toward the side of the electrode with a negative polarity.

2) Measurement of the value of the continuous current between the electrodes (with a fully established motion of the cavity) shows that, in the case of a negative polarity of the upper electrode, the current, falling exponentially, in the course of time becomes practically equal to zero (the value of the current 30 min after the feeding of a voltage of 50 V to the electrodes was 6 μA). However, in the case of a positive polarity, there is a relatively large residual current.

From the results of the experiments it can be concluded that the probable mechanism of the phenomenon, due to the tendency of the electrical system to go over into a state with a minimal energy, is complicated to a considerable degree by interaction between the field and the diffusional covering of the double layer, forming at the interface between the media.

From the equation of the balance of the mechanical energy and the electrical energy expended it follows that

$$-\Delta W_{\text{м}}=\Delta W_{\text{e}},$$

where ΔW_M and ΔW_e are defined by the expressions

$$\Delta W_{\text{м}}=mgh; \tag{1}$$

$$\Delta W_{\text{e}}=\frac{\varepsilon}{8\pi}\int E^2(\gamma)\,dV, \tag{2}$$

here m is the mass of the liquid; g is the acceleration due to gravity; h is the height of the raising of the center of mass of the liquid; ε is the dielectric permittivity; E is the intensity of the electrical field; V is the volume; γ is the conductivity of the electrolyte.

Assuming that there is no surface density of the charges at the interface, taking account of the geometric relationships (Fig. 2), expressions (1), (2), depending on the magnitude of the shift of the interface x and the angle of inclination of the ampoule α, and neglecting edge effects, have the form

$$\Delta W_{\text{м}} \simeq -\frac{1}{32}\rho g l_{\text{a}}^3 b_{\text{C}} \alpha^2,$$

$$\Delta W_{\text{e}} = \frac{3}{8\pi}\left[\frac{1}{\varepsilon}E_1^2 V_c(x) + E_2^2(\gamma)\,V_d(x) + E_3^2(\gamma)\left(V_{cd}(x) - V_{cd}^*\right)\right],$$

where

$$\left.\begin{aligned} V_c(x) &\approx \frac{2}{3} b_{\text{C}} h_{\text{C}} x \\ V_d(x) &\approx \frac{1}{3}\left(3\pi r_{\text{a}}^2 - 2 b_{\text{C}} h_{\text{C}}\right) x \\ V_{cd}(x) &\approx \pi r_{\text{a}}^2 (l_{\text{e}} - x) \\ V_{cd}^* &\approx \pi r_{\text{a}}^2 l_{\text{e}} \end{aligned}\right\} \quad 0 \leqslant x \leqslant l_{\text{e}}. \tag{3}$$

Here ρ is the specific weight; l_{a} is the length of the ampoule; l_{e} is the length of the electrode; r_{a} is the radius of the ampoule; h_{C} is the height of the cavity; b_{C} is the width of the cavity. The total increment of the energy with the replacement $x = k_\alpha \alpha$ (k_α is the mechanical coefficient of transformation of the ampoule) is determined by formulation of the expression

$$\Delta W(\alpha) = \frac{\varepsilon k_\alpha}{8\pi}\left[\frac{2}{3\varepsilon} b_{\text{C}} h_{\text{C}} E_1^2 + \frac{1}{3}\left(3\pi r_{\text{a}}^2 - 2 b_{\text{C}} h_{\text{C}}\right) E_2^2(\gamma) - \pi r_{\text{a}}^2 E_3^2(\gamma)\right]\alpha - \\ - \frac{1}{32} l_{\text{a}}^3 b_{\text{C}} \rho \alpha^2.$$

Due to the motion of the cavity, the system goes over into a new steady state, characterized by a minimum of the energy with given initial conditions:

$$\frac{d[\Delta W(\alpha)]}{d\alpha} = 0.$$

From this we can determine the connection between the angle of inclination of the ampoule and the sustaining field:

$$\alpha = \frac{2\varepsilon k_\alpha}{\pi l_{\text{a}}^3 b_{\text{C}} \rho}\left[\frac{2}{3\varepsilon} b_{\text{C}} h_{\text{C}} E_1^2 + \frac{1}{3}\left(3\pi r_{\text{a}}^2 - 2 b_{\text{C}} h_{\text{C}}\right) E_2^2(\gamma) - \pi r_{\text{a}}^2 E_3^2(\gamma)\right]. \tag{4}$$

Expression (4) can be corrected, taking into consideration the existence, at the phase interface, of the field of the double layer of charges, with the intensity [9]

$$E^* = \frac{4\pi C(\varphi - \psi_1)}{\varepsilon_0 \varepsilon}$$

(φ is the potential of the electrode; C is the capacitance of the double layer; ψ_1 is the thermodynamic potential);

$$\alpha = \frac{2\varepsilon k_\alpha}{\pi l_{\text{a}}^3 b_{\text{C}} \rho}\left[\frac{2}{3\varepsilon} b_{\text{C}} h_{\text{C}} E_1^2 + \frac{1}{3}\left(\pi r_{\text{a}}^2 - 2 b_{\text{C}} h_{\text{C}}\right) E_2^2(\gamma) - \pi r_{\text{a}}^2 E_3^2(\gamma) + \frac{\pi C^2 b_{\text{C}}^2 \delta_c l_{\text{a}}^3 \rho}{\varepsilon^2 \varepsilon_0^2}(\varphi - \psi_1)^2\right]. \tag{5}$$

Assuming the intensities of the fields of the individual sections (γ = const) to be proportional to the applied voltage U, from expression (5) we obtain $\alpha \simeq kU^2$. However, as the experimental dependence shows (Fig. 3), in the initial and final sections, α has the form

$$\alpha \simeq kU^n \quad (n \leqslant 1).$$

Such a divergence of the results can be explained, specifically, by the existing dependence of the conductivity of the electrolyte on the value of the voltage applied to the electrodes (this comes out particularly clearly in experiments with a direct current). From the physical aspect, the basis of this dependence is obviously the interaction between the field and a relatively mobile diffusion covering of the double layer of charges at the interface between the media.

Thus, it has been experimentally established that the efficiency of control by the position of an electrolyte–gas interface is considerably higher (by several orders of magnitude) than that of the existing method of control using a dielectric liquid.

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