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Estimating the orientation component of stationary water dipoles in constant electric fields

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Abstract

The estimation is based on the proposed theoretical hypothesis explaining the experimentally registered process of increase in thickness of a water film at the internal surface of a hydrophilic capillary, under the effect of a constant electric field. The capillary is filled with two fluids (an aqueous solution and a nonpolar fluid—a gas or an organic liquid). The theoretical and experimental data are shown to be well consistent at a value of the orientation component in constant electric fields with a strength of 10^3–10^4 V/m estimated to be of the order of magnitude 0.6. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Film thickness; Capillary; Electric field; Water dipole orientation

1. Introduction

The present work is devoted to studying the experimentally established phenomenon of growth in thickness of a film of a polar electrolyte (water) between a nonpolar fluid (either a gas or a liquid) and a solid surface. The phenomenon occurs in the systems with a particular complicated geometric structure we studied (that will be described in detail below) under the effect of a constant or slightly alternating (upto 50 Hz without fail) external electric field. We deem that the specific geometric structure of the system (measuring cell) described below is not

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very significant from a fundamental, qualitative viewpoint. We used it, firstly, for carrying out specific quantitative calculations from our results, and secondly, because we had run experiments with this cell. Consequently, our conclusions may be applied to systems with another geometric structure, e.g. to classical first-order emulsions. The results currently at our disposal and characterising various aspects of the phenomenon, such as optical and electrical ones, led us to the assumption that this phenomenological macrophysical property of the given system is explained by the features of the molecular structure of water as a particular case of a liquid consisting of highly polar molecules.

The results of experiments for studying the electrical conductivity with respect to a direct current of a model first-order emulsion in a hydrophilic cylindrical capillary, were presented first by Tikhomolov et al. (1986). The system consisted of a quartz glass capillary filled with a current-conducting aqueous solution of an electrolyte (the “disperse medium”) and containing a nonpolar fluid (the “dispersed phase”) in its internal part. The fluid had the form of a column arranged along the capillary axis. The length of the column (l_c) exceeded the capillary diameter ($2\ r_k$) not more than 10 times. When the capillary was filled with fluids and owing to the natural hydrophilic nature of the glass, a thin film of water (“film”) remained between the side surface of the column and the enternal surface of the capillary. Its thickness in the equilibrium state (r_f) was 0.01–0.1 μm.

The experiments revealed that when the capillary is acted on by an external constant electric field (EEF) with an average strength along the capillary axis of $E_k = U_k/l_k = 0.1\text{–}4$ V/cm (where U_k is the voltage difference across the capillary ends, l_k is the length of the capillary), the thickness of the film increased by an order of magnitude and more.

In the new equilibrium state that set in under the effect of the EEF, the film generally[1] had a constant thickness along the axis of the capillary. This was established by optical observations. The synchronous optical observations correlated qualitatively with the electrical measurements (Tikhomolov et al., 1986; Krasikov and Tikhomolov, 1986). We must indicate here, however, that a change in the size and shape can be registered optically, but no measurements can be made.

It should be noted that these observations underlie the method of electrokinetic logging. It was tested when conducting industrial prospecting geophysical work at deposits by Tikhomolov et al. (1989). The development of this method, to date, was discontinued. One reason was the absence of developed parametric relations.

2. Theoretical statement of the problem and its decision

The theoretical solution of the problem is based on a model working system that is adopted in practically all scientific works devoted to the simulation of the behaviour of capillary porous bodies filled with two fluids (Bretherton, 1961; Astrachanzeva and Usiarov, 1974; Park and

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[1] At high values of E or prolonged action of the EEF, the local ability of the fluids sometimes led to the development of lens-shaped interlayers of water bounding on the film. This was registered optically and resulted in overstating the theoretical average film thickness at the initial stages of formation. An experiment was stopped when the development of such a “dimple” was discovered.

Homsy, 1984). Strictly theoretically, the only section of a film in the equilibrium state in the absence of an electric field, being the subject of discussion, is at the boundary of the "linking" of the hemisphere and cylinder. Diverse diametrically opposite concepts are advanced, but they are all based on their author's logic without any strict proof. However, at the order of magnitude of the values of thicknesses obtained in the experiment and of the length of a section discussed, its resistance cannot contribute substantially to the resistance of a capillary as a whole.

The model system is assumed to consist (Fig. 1) of a hydrophillic cylindrical capillary with a constant circular section (of radius r_k). In the central part of the capillary, the column of a non-polar fluid is placed. The column has a cylindrical form with a constant radius (r_c) and is limited at its ends by hemispheres of the same radius as the cylindrical part of the column. The remaining internal space of the capillary is filled with an aqueous solution of the electrolyte. The electrolyte, which is a wetting liquid forms a thin electrolyte layer between the external cylindrical surface of the column and the internal surface of the capillary. The thickness of the electrolyte layer is $r_f = r_k - r_c$.

In the absence of external force fields (including the EEF), the equilibrium value of r_f is determined by the balance of forces, namely, the capillary pressure at the side of the cylindrical part of the column, and all the possible components of the disjoining pressure existing in the film.

When the ends of the capillary (in which the indicated equilibrium was first established) are connected to an electrical circuit, in the region occupied only by the aqueous solution (III in Fig. 1) and in the water film on the boundary with the cylindrical surface of the column (I in Fig. 1), the strength E of the external electric field is constant in an axial direction. In other words, both, the field in (I) and (III) are homogeneous. The water in these regions, like any insulator, is polarised in the EEF. Like any highly polar substance, this is chiefly due to the orientation component — the orientation in the external field of the constant dipoles of the polar water molecules (Osipov and Minkin, 1965).

Without, for a while, touching the discussion part of the measure of orientation, we shall

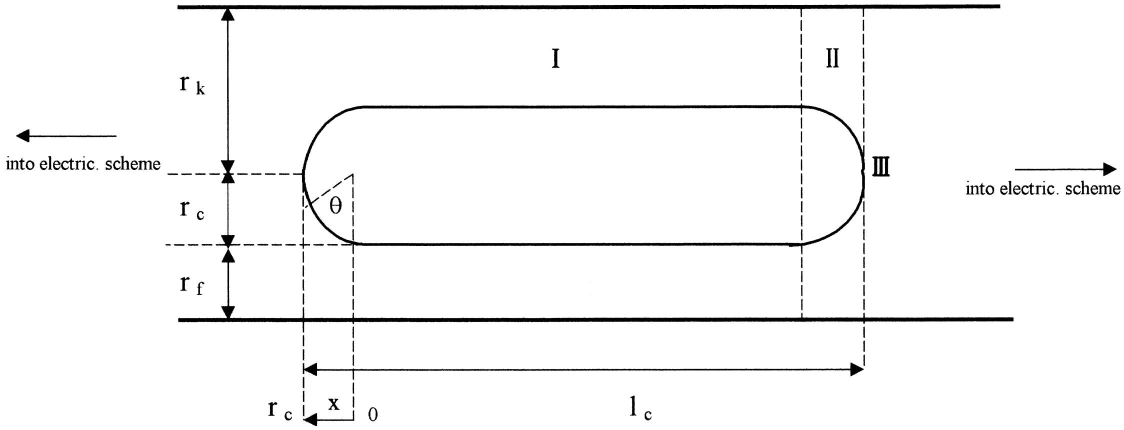

Fig. 1. Model of the working system — a capillary (the scale of r_k and r_f is not observed because r_k is much greater than r_f).

note that here the views of most of the authors, we know, converge. For example, according to Kirkwood's presentation (Kirkwood, 1939), the fraction of the orientation component of water polarization is 0.85. The other authors indicate a still greater fraction (Frenkel and Gubanov, 1940). Here, electrical forces that are identical in magnitude, but opposite in direction, act on the poles of H_2O dipoles, that differ in sign and are identical in value. We further consider a water molecule to be an integral physical system having definite electrical and geometric properties known from other data.

The situation is different with water dipoles in the region occupied by the electrolyte between the surface of the hemispheres and the internal surface of the capillary (II, Fig. 1). Orientation of the dipoles also occurs in this region, but here the force lines of the electric field are curved (i.e. the field is not homogeneous). Consequently, the electrical forces acting on the poles of a dipole do not compensate one another.

Assume that there are no other actions on a dipole in a system. Therefore, in accordance with the concepts of classical mechanics, a molecule acquires momentum in the direction of the increase in strength of the EEF. Owing to symmetry of the force fields, the motion of the dipoles at both sides of the column are directed from region III to I. The movement of water dipoles is actually equivalent to the existence of a water flow (the water flux). This water flux produces in region I an increased hydraulic pressure that acts on the cylindrical surface of the nonpolar fluid and displaces it in a direction normal to the axis of the capillary. The motion stops if a counteraction appears in the working system during the action of the EEF. Owing to the continuity of the water phase and the limited volume of the column, the overall motion of the molecules over all the dipoles of region II should increase the water film thickness and, accordingly, diminish the radius of the column. The latter signifies a growth in the capillary pressure. The consequence of the capillary pressure growth is the appearance of the water flow directed from region I to region III within the total ring of the film.

The r_{f} value at equilibrium in the presence of EEF depends completely on the balance of the two flows indicated above. This is the "flow" version of our presentation of the mechanism resulting in thickening of the water film in the system under consideration. Theoretically, this scheme of movement represented in terms of flow may be described also in the "force" version, i.e. as the action of two forces producing these flows. Further we designate the first force as "electric", and the second one as "the force originating from development of capillary pressure" or "capillary pressure force".

In commencing the theoretical derivation of the force underlying the motion of the dipoles, we shall give first of all, the number of simple constructions (Fig. 1). They are based meanwhile on a description of the intense parameters of molecular media generally adopted in classical physics. They are expressed in terms of a mean statistical quantity that is constant in an infinitely small unit of volume of the medium.

We use the "direction of flow around a hemisphere" as the co-ordinate where the changes in the parameters are estimated in the process being considered:

$$x = r_{\mathrm{c}} \sin\theta = (r_{\mathrm{k}} - r_{\mathrm{f}}) \sin\theta. \tag{1}$$

In accordance with the above, the relation between the x-component of the strength of the EEF and the geometric parameters of region II is written in the form:

$$E_x = \frac{\mathrm{d}(I \cdot R)}{\mathrm{d}x} = I\frac{1}{\chi\pi(a^2 + x^2)} \tag{2}$$

where I is the current; R is the electrical resistance; χ is the conductivity of the solution; $\pi a^2 = \pi(r_\mathrm{k}^2 - r_\mathrm{c}^2)$ is the cross-section of the film ring in region I. The value of I being the flow of the charges in the absence of concentration (charge) polarization[2], does not depend on the site in the aqueous solution, i.e. it is not a function of x. According to the proposed physical picture of the cause of film thickening, we are interested not in E, but in its increment dE (the differential, having in view our proceeding from the tenets of classical physics):

$$\mathrm{d}E_x = \frac{I}{\chi\pi} \cdot \mathrm{d}\left(\frac{1}{a^2 + x^2}\right). \tag{3}$$

Now let us go over to a description of the medium with consideration of its molecular structure. For this purpose, we shall arbitrarily single out a hollow region in II. We shall determine its size by the radius of the sphere whose volume equals the mean statistical volume of the medium falling to the share of each molecule with consideration of the existing concepts of the structurisation of specific liquids (water here). We place a molecule of water at the centre of the sphere. It is characterised by the distance between the poles of the dipole, d_dip and the charge e_dip. Since in the systems we are solving here, the force characteristics of the external electrical field acting on a molecule are determined mainly by the ohmic losses of the medium (and not by the dielectric ones as indicated by Onsager (Frenkel and Gubanov, 1940; Onsager (1936)), we shall put the singled out space into a continuous medium characterised by the electrical conductivity of the solution χ.

In an external constant electric field, the electrical vector of a dipole of a molecule of a polar substance (water) strives to orient itself in a direction tangential to that of the vector of the external electric field. Let us assume that owing to the entropy factor, the directions of the dipole vector and that of the external field fail to coincide and form an angle γ. The efficiency of the action of the external field on the dipole of a molecule is determined geometrically by the mean value of the projection of the constant dipole moment of the molecule onto the direction of the external field, i.e. by the expression $E_\mathrm{ef} = E_x \cos\gamma$. Statistically, the efficiency of action of the external field on a dipole is proportional to the correlation (w) of the turning of the dipole moment in the direction of the external field (Frenkel and Gubanov (1940)). We can thus write that

$$w = \cos\gamma. \tag{4}$$

The electrical force (df_1) acting in region II on the dipoles in the volume of a water ring having a thickness equal to the characteristic dimension of the space of a water molecule ($d_{\mathrm{H_2O}}$) is:

$$\mathrm{d}f_1 = e_\mathrm{dip}\frac{\rho_M N_A}{M}\pi\left(a^2 + x^2\right)d_{\mathrm{H_2O}}\frac{I}{\chi\pi}\mathrm{d}\left(\frac{1}{a^2 + x^2}\right)\frac{d_\mathrm{dip}}{d_{\mathrm{H_2O}}}\cos\gamma. \tag{5}$$

Here $e_\mathrm{dip}\rho_M N_A/M$ is the mean statistical density for one of the poles of the dipole in unit

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[2] At the thicknesses realised in the experiments, no concentration polarization should appear (Tikhomolova, 1993).

volume of water, e_{dip} is the charge of a pole of a H_2O dipole (with an accuracy to the sign −, the charge of an electron), ρ_M is the density of H_2O, M is the molecular mass of H_2O, $\pi(a^2+x^2)d_{H_2O}$ is the volume of the indicated ring, $\frac{I}{\chi\pi}\mathrm{d}(\frac{1}{a^2+x^2})$ is the difference of the strengths on the surfaces confining the ring, and d_{dip} is the distance between the poles of a dipole in a molecule of H_2O (in the following, the value of d_{dip} is adopted equal to 0.43×10^{-10} m).

The last term $(d_{\mathrm{dip}}/d_{H_2O})$ considers that the density of distribution of the dipoles in the ring is statistically lower than that of the H_2O molecules (the distance between dipole poles is smaller than the size of water molecules and, moreover, of the space).

Let us write the addends of the balance of two aforesaid forces acting on the whole film-ring surface, in accordance with our presentation on phenomenon mechanism.

The electrical force acting on all the dipoles in each region II is:

$$F_{\mathrm{el}}=\int_{a^2}^{r_{\mathrm{k}}^2}\left[\frac{I}{\chi}d_{\mathrm{dip}}e_{\mathrm{dip}}\frac{\rho_M N_A}{M}\right](a^2+x^2)\mathrm{d}\left(\frac{1}{a^2+x^2}\right)\cos\gamma=\frac{I}{\chi}d_{\mathrm{dip}}e_{\mathrm{dip}}\frac{\rho_M N_A}{M}\ln\frac{r_{\mathrm{k}}^2}{r_{\mathrm{k}}^2-r_{\mathrm{c}}^2}w$$

$$=\frac{I}{\chi}d_{\mathrm{dip}}e_{\mathrm{dip}}\frac{\rho_M N_A}{M}\ln\frac{r_{\mathrm{k}}^2}{r_{\mathrm{k}}^2-(r_{\mathrm{k}}-r_{\mathrm{f}})^2}w. \tag{6}$$

The force determined by the development of capillary pressure with a cylindrical surface is:

$$F_{\mathrm{k}}=\left(\frac{\sigma}{r_{\mathrm{c}}}\right)\pi\left(r_{\mathrm{k}}^2-r_{\mathrm{c}}^2\right)=\frac{\sigma}{r_{\mathrm{k}}-r_{\mathrm{f}}}\pi\left[r_{\mathrm{k}}^2-(r_{\mathrm{k}}-r_{\mathrm{f}})^2\right], \tag{7}$$

where σ is the interface tension of the boundary of two fluids. The formula represents the capillary pressure force as the product of the capillary pressure at the cylindrical form of the interface of two phases and of the surface of the film ring.

Consequently, proceeding from the basic concepts of the forces acting in the system, we obtain those, which underlie the equilibrium thickness of a film in a capillary included in the circuit of an EEP, we obtain:

$$w\frac{e_{\mathrm{dip}}\rho_M N_A I d_{\mathrm{dip}}}{M\chi}\ln\frac{r_{\mathrm{k}}^2}{r_{\mathrm{k}}^2-(r_{\mathrm{k}}-r_{\mathrm{f}})^2}=\frac{\sigma\pi}{r_{\mathrm{k}}-r_{\mathrm{f}}}\left[r_{\mathrm{k}}^2-(r_{\mathrm{k}}-r_{\mathrm{f}})^2\right]. \tag{8}$$

However, since the electric field parameter in the formula, i.e. the current, depends on the specific structure of the conducting channel, it is not correct to insert into a theoretical formula the current that is registered in an experiment. In practice, the structure of a film in the absence of an electric field may differ initially from that of model one. The reasons are the formation of dimples in the absence of electric field and the development of various changes due to fluctuation effects (Burrill and Woods, 1973; Tikhomolov et al., 1986; Krasikov and Tikhomolov, 1986). The exclusion of the current I from the derivatives with respect to x in deriving the formula does not contradict this tenet. The magnitudes of the current vary with a different structure, but in any case for any structure, no matter what the current is, it is constant over the entire conducting channel. The parameters of the electric field must be selected so as to single out the geometric structure of the channel of the aqueous solution conducting the current in an explicit form, corresponding to the theoretical model. It is easy to meet this requirement by representing the current as the result of dividing the voltage drop across the ends of the entire capillary (U_k) = const by the resistance, also of the entire capillary, $(R_\mathrm{k}) = f(r_\mathrm{k})$. With the adopted model of the system, the resistance of the capillary consists of the resistances of three consecutively located parts, namely, the part outside the column (the total of both sides of the latter), the part accommodating both meniscuses (also in sum), and the part where the water film is limited by the cylindrical part of the column surface. The corresponding formula was already given earlier (Tikhomolov and Voznaya, 1989):

$$R_\mathrm{k} = \frac{2}{\chi\pi\sqrt{r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2}}\mathrm{arctg}\frac{(r_\mathrm{k} - r_\mathrm{f})}{\sqrt{r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2}} + \frac{l_\mathrm{c} - 2(r_\mathrm{k} - r_\mathrm{f})}{\chi\pi\left[r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2\right]} + \frac{l_\mathrm{k} - l_\mathrm{c}}{\chi\pi r_\mathrm{k}^2}. \tag{9}$$

Where l_c is the length of the column including the meniscuses, l_k is the length of capillary, and χ is the conductivity of the solution. The first addend at the right reflects the resistance in the region of the meniscuses, the second, that of the water ring in the cylindrical part of the column, and the third, outside the column. Inserting in expression (8), instead of I the voltage U_k as being independent of the structure of the conducting channel in the explicit form, and R_k as the right-hand side of formula (9), we obtain the final expression of the formula derived in accordance with the proposed physical concepts of the cause of the growth in film thickness and the mechanism reflecting the equilibrium state of the film under current:

$$\begin{aligned} &U_\mathrm{k} w \frac{e_\mathrm{dip}\rho_M N_A d_\mathrm{dip}}{M\left[r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2\right]} \ln \frac{r_\mathrm{k}^2}{r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2} : \left\{ \frac{2}{\sqrt{r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2}}\mathrm{arctg}\frac{r_\mathrm{k} - r_\mathrm{f}}{\sqrt{r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2}} \right. \\ &\left. + \frac{l_\mathrm{c} - 2(r_\mathrm{k} - r_\mathrm{f})}{r_\mathrm{k}^2 - (r_\mathrm{k} - r_\mathrm{f})^2} + \frac{l_\mathrm{k} - l_\mathrm{c}}{r_\mathrm{k}^2} \right\} \\ &= \frac{\sigma}{r_\mathrm{k} - r_\mathrm{f}}. \end{aligned} \tag{10}$$

In terminating our theoretical treatment, we shall attract attention to the last formula containing two variables whose values are unknown a priori. One of them is the required r_f and the second is w. The impossibility of inserting a definite value of w is due to the extremely discussible nature of a general question of fundamental science — the measure of the orientation of a H_2O molecule in water (a liquid) when a constant electric field acts on the latter.

A reply on the value of w can be obtained in principle, by using for comparison, values of r_f calculated independently in a way not related to the proposed concept. This can be done on the basis of a formula representing Ohm's law for the resistance of capillary as a whole (R_k) in terms of the resistance of individual parts of the current-conducting channel having a complicated structure. Numerical values of R_k can be obtained from experiments consisting of measurement of volt–ampere curves $(R_\mathrm{k} = U_\mathrm{k}/I)$.

In our calculations by the formula of Ohm's law in the present study, we used the same model system as in the theoretical derivation. It is obvious that formula (9) is the corresponding formula for calculations. To stress that the value of r_f calculated in the given variant is not associated with the theoretical hypothesis, but reflects the phenomenon of thickening per se, we shall further use the superscript "e" in the relevant value of r_f obtained experimentally (r_f^e). Like the theoretical value, the experimental one may contain an error because of the lack of correspondence of the real and model structure, but this is not connected with the physical postulates on the mechanism of the thickening of the film under a current.

The value of w can be determined in two ways. (It should be noted that according to control calculations relating to individual cases, the values are very close.) In the first one, the value of r_f^e found from resistance measurements is inserted into formula (10). Here w is the only unknown quantity. The second way, which we use below, consists in the following. It is first assumed that $w = 1$, i.e. that the axes of all the dipoles are oriented strictly in the direction of the external electric field strength. The corresponding value of the thickness calculated here will be designated below by r_f^t. The particular form of expression (10) is now as follows:

$$U_\mathrm{k}\frac{e_\mathrm{dip}\rho_M N_A d_\mathrm{dip}}{M\left[r_\mathrm{k}^2-\left(r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}\right)^2\right]}\ln\frac{r_\mathrm{k}^2}{r_\mathrm{k}^2-\left(r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}\right)^2}:\left\{\frac{2}{\sqrt{r_\mathrm{k}^2-\left(r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}\right)^2}}\mathrm{arctg}\frac{r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}}{\sqrt{r_\mathrm{k}^2-\left(r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}\right)^2}}\right.$$

$$\left.+\frac{l_\mathrm{c}-2\left(r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}\right)}{r_\mathrm{k}^2-\left(r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}\right)^2}+\frac{l_\mathrm{k}-l_\mathrm{c}}{r_\mathrm{k}^2}\right\}$$

$$=\frac{\sigma}{r_\mathrm{k}-r_\mathrm{f}^\mathrm{t}}. \tag{11}$$

By using formula (11), we find the corresponding value of r_f^t. The value of w is now found by the expression:

$$w=\frac{r_\mathrm{f}^\mathrm{e}}{r_\mathrm{f}^\mathrm{t}}. \tag{12}$$

For illustrating the value of $r_\mathrm{f}^\mathrm{t} = f(U_\mathrm{k})$ obtained by formula (11), Fig. 2 presents a curve calculated for the system octane–KCl with the geometric characteristics $r_\mathrm{k} = 126$ μm and $l_\mathrm{c} = 1 \times 10^3$ μm. The solution of Eqs. (11) and (9) in the explicit form relative to r_f^t and r_f^e involves considerable difficulties. We used a numerical method of iterations in a computer with standard applied algorithms and programs.

3. Results of the experiments

Let us now describe the experimental part of the work. We varied the radius of the capillary (40–170 μm), the length of the column (10–20) r_k, the composition of the electrolyte (KCl, NaCl), and the nature of the nonpolar fluid (octane, air). The length of the capillary in all the experiments was 25 cm. The concentration of the electrolyte was 0.1 M (its conductivity was $\mathrm{Ohm}^{-1} \times \mathrm{m}^{-1}$). The prolonged establishment of equilibrium in the system in the absence of a current was indicated in Tikhomolov and Voznaya (1989). When an EEF is applied, new equilibrium sets in that in principle is not connected with the initial equilibrium without a current. This is why in our experiments, we did not wait for equilibrium to set in, in the initial system, but nevertheless, began to apply the field in 25–30 min after the capillary was filled with fluids. During this time, the period of rapid changes in the geometric parameters of the films terminated. In Fig. 2, we plotted the relation $r_f^e = f(U_k)$ in the form of points and curve 2 approximating them (the correlation coefficient is 0.95) as an illustration of the general typical curves obtained in our experiments. The geometric characteristics of the system which curve 2 relates to, are identical to those in the model calculations of $r_f^t = f(U_k)$ shown in Fig. 2 by curve 1. The scatter of the results relating to the systems of the given sampling is very small when U_k exceeds 3 V; at lower values of U_k, the scatter is great and irregular, but the average values are close to those obtained at "high" voltages.

To separate the authentic laws of the change in the parametric relations obtained from the experiments with the use of formula (9) and calculated by formula (11), we treated the experimental results statistically. We analysed 26 experimentally obtained volt–ampere relations with 15–20 measurements in each. We compared the results of calculating r_f^e and r_f^t for each of the relations. We set the geometric characteristics of the model cell when calculating r_f^t that were identical to the experimentally measured actual ones in each of the experiments when determining r_f^e. We separated the 26 experiments into three samples differing in general features of nature of the nonpolar fluid and the composition of the electrolyte.

The first sample included systems with the fluids octane and a KCl solution (Table 1). We obtained the dimensions in μm. The second sample included systems from octane and an NaCl solution (Table 2). The third sample included systems of air and a KCl solution (Table 3): Calculations showed that the electric field strength in the region of the meniscuses (II) for all the samples was 2–2.7 × 10^3 V/m at $U_k = 3$ V and 5–6 × 10^3 V/m at $U_k = 25$–40 V. We thus

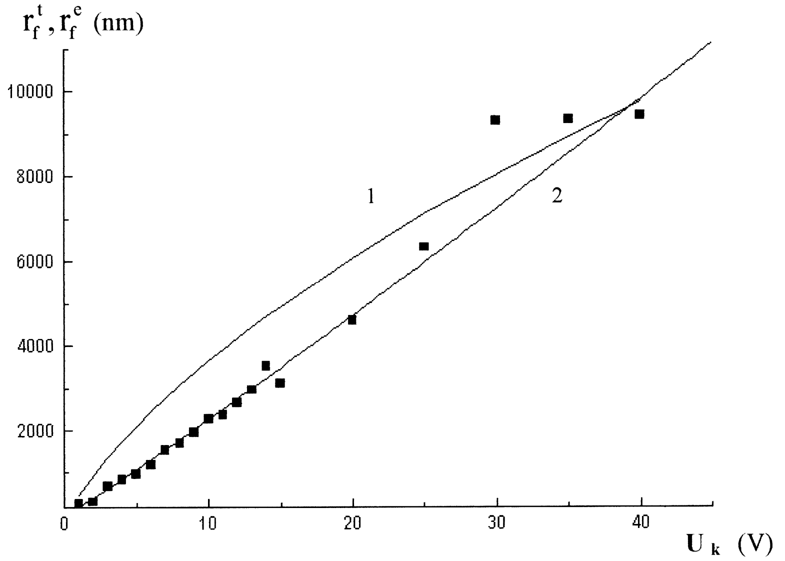

Fig. 2. Plots of r_f^t (curve 1) and r_f^e (the dots are experimental results approximated by curve 2) vs. U_k.

Table 1
The parameters of the systems in the experiments with fluids octane and KCl-solution

r_k	126	108	68	44	126	126	64	114	157	143
l_c	1000	1000	950	2600	1000	1500	1250	550	1250	1250

see that the value of E_m, in particular, did not depend practically on the composition and depended only slightly on U_k.

The results of calculating the average values by formulas (9)–(11) for all the samples are presented in Figs. 3 and 4 showing plots of r_f^e and w versus U_k.

4. Discussion

We shall note what we presume to be the most fundamental conclusions issuing from an analysis of the above actual data and presented in the figures.

1. The values of w with a good approximation do not depend on U_k.
2. The values of w do not practically depend on the geometric characteristics of systems.
3. The average values of r_f^e for the samples and r_f^t for a model having geometric characteristics equal to those of the average ones, and the physical parameters equal to those used in the experimental sample are of the same order of magnitude and differ in magnitude by not over two or three times.
4. The values of r_f^e are always lower than those of the r_f^t corresponding to them. This indicates that the error in estimating r_f with the aid of r_f^t is systematic. The difference does not virtually depend on the nature of the nonpolar fluid and depends only slightly on the composition of the electrolyte in the studied systems. The ratio $r_f^e : r_f^t$ (i.e., w or $\cos\gamma$) to a first approximation is a constant quantity, estimated to be 0.3 for small values of U_k and 0.6 for large ones.

It is quite obvious that with our given physical construction of the model, the indicated systematic error can be explained by the failure to consider a number of probable effects, e.g. associated with motion (including with the flow), the manifestation of forces of viscous friction, or by the failure to consider specific details of the geometric structure of the conducting channel with definite values of the electrical resistance of the system. However, on the basis of the logic of the model solution, the practical experience obtained in the experiments, and analogy of the matter on the similarity of the data we revealed when analysing published information on the problem of the polarization of dipole dielectric liquids, we presumably

Table 2
The parameters of the systems in the experiments with fluids octane and NaCl-solution

r_k	67	59	132	67	74	59	59	50	132	46
l_c	2350	1500	2350	950	1170	1660	4000	1660	2320	1480

Table 3
The parameters of the systems in the experiments with fluids air and KCl-solution

r_k	123	68	150	119	104	117
l_c	1400	1800	2350	1750	1600	2550

found the most probable culprit responsible for the actually observed discrepancy of the values of r_f^e and r_f^t. It is the influence of the entropy factor on the orientation of the dipole molecules.

Since a comparative analysis of the most well known theories are of interest to us only in the light of our results, let us consider in greater detail some aspects of the correspondence of our results to the classical tenets of the theories of polarization of the dipole dielectrics. It should be noted that the values of $w = \cos\gamma = 0.4$–0.6 we obtained here at a strength of the EEF of 3000–5000 V/m, are interpreted by us according to their physical meaning as the average value of the projection of the constant dipole moment of a water molecule in the direction of the strength vector of the EEF. The obtained values of w, in our opinion, coincide well with the results of Kirkwood obtained when calculating the permittivity of water by analyzing his model. He estimates the orientation parameter $\cos\gamma$ to be 0.4–0.5 and interprets it according to its geometrical meaning as a projection.

At the same time, we must note that the values of w we obtained are inscribed much more poorly into the theoretical concepts of Debye–Onsager (Onsager, 1936; Debye, 1935; Frenkel and Gubanov, 1940). From the practical viewpoint, the latter result is lawful, in our opinion. In particular, it was indicated (Frenkel and Gubanov, 1940) that the application of the theories of Debye, Onsager, and the combinations created on their basis with liquids consisting of polar

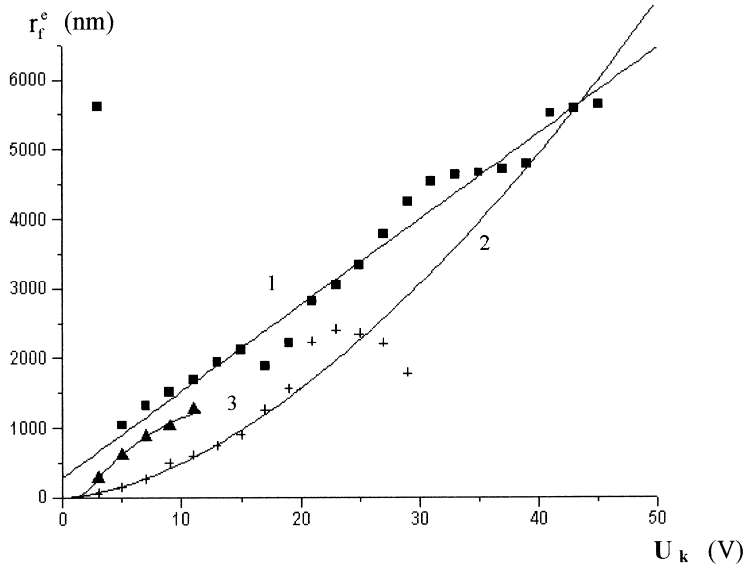

Fig. 3. Plots of r_f^e vs. U_k. The dots are experimental results, the curves are their approximations. Curve 1 and squares are the system octane–KCl solution, curve 2 and crosses are octane–NaCl solution, curve 3 and triangles are air–KCl solution.

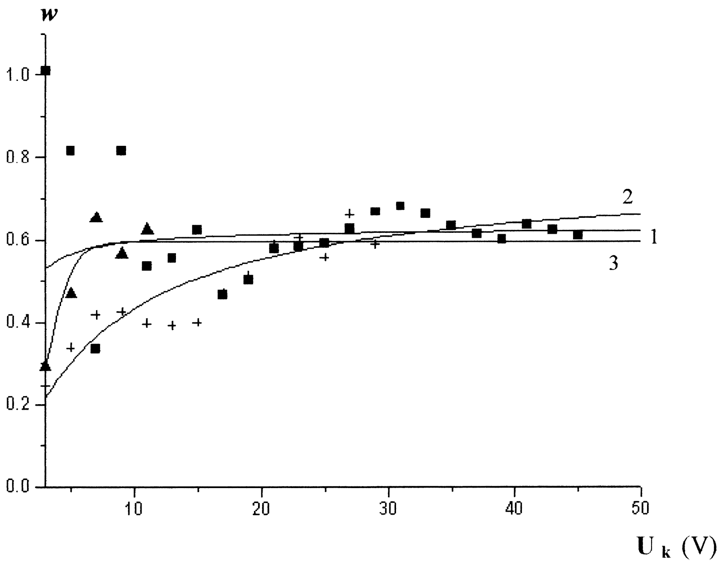

Fig. 4. Plot of w vs. U_k. The dots are experimental results, the curves are their approximations. For the notation see Fig. 3.

molecules, gives appreciably poorer results in calculations of the basic characteristic parameters of electrical properties (e.g. the values of permittivity).

Since Debye's views were subjected to evolution, strictly speaking, any of Debye's models corresponding to the result obtained, is worse than Kirkwood's. For objectiveness, we must note that in Debye's theory the physical meaning of the entropy factor is transparent and definite, namely, it signifies the molecular–thermal motion of the molecules. In Kirkwood's theory, this factor is abstract and imbedded in the theory regardless of the forces determining it. Nevertheless, both the theories contain semiempirical features. Both the local field in the Onsager–Debye theories and the height of the potential barrier in Kirkwood's theory can be determined only experimentally. They are, in essence, empirical correction factors to analytical relations. Proceeding from these considerations and from the experimental data described earlier, we must state that:

1. The phenomenological phenomenon we are studying, cannot be described on the basis of Debye's theory
2. The cause is apparently the incorrect concepts in the indicated theoretical works of the thermal motion of molecules in liquids. The latter statement evidently coincides with later views of Debye (1935) himself.

5. Conclusions

The following are the main conclusions of our work:

- The closeness of the film thickness values calculated on the basis of our hypothesis to the thickness values obtained by an independent method points to the correctness of the hypothesis on the cause of the increase in the thickness of a water film under the effect of an external electric field. Moreover, in a more general plan, result points to the correctness of the hypothesis on the development of a pressure gradient in highly polar liquids when an inhomogeneous electric field acts on them.

- The found value of $w (= \cos \gamma)$ is interpreted as the projection of the orientation of the vector of the dipole moment of water molecules in the direction of the EEF due to the entropy factor. The value of w is very close to Kirkwood's parameter, which in essence characterises the same property in highly polar liquids — the cause of the orientation effect in constant electric fields.

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