

STABILITY AND DISPERSION OF CONDUCTIVE DROPLETS IN A DIELECTRIC MEDIUM IN A UNIFORM ELECTRIC FIELD

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The problem of the analytic determination of the stability criterion for a charged droplet of conductive liquid is examined and experimental results relating to the dispersion of droplets from aqueous solutions of various compositions in a nonpolar medium in a uniform electric field are described. It is shown that the experiments and the theory are in satisfactory agreement.

It has been established [1] that unsatisfactory separation in the process of electrical dewatering of oils is associated with the possibility of additional dispersion of the water globules in a high-strength electric field. Consequently, the study of the stability and dispersion of water droplets in nonpolar media is of practical as well as theoretical interest. The solution of this problem may also be of value in other areas [2], for example, in atmospheric physics.

The electrical dispersion of water has been studied by numerous authors [3] in connection with the phenomenon of the electrical destruction of liquid surfaces in air.

Below, dispersion is analyzed with reference to an element of emulsion of the "water-oil" type, i. e., droplets of conductive liquid suspended in a nonpolar medium. In [4, 5] it was established that the particles of the dispersed phase of such emulsions are charged and in an electric field acquire directional motion.

Experiments [6], similar to that described by Millikan, have shown that the water particles of model emulsions have positive and negative charges, or may be uncharged.

It has also been found [1, 7] that when an uncharged droplet of conductive liquid is introduced into a uniform field of sufficient strength, it is deformed, acquiring the shape of an ellipsoid of revolution. Experiments also show that a charged particle likewise acquires a shape approaching that of an ellipsoid of revolution and moves along the field lines. Consequently, the problem reduces to that of a charged conductive ellipsoid introduced into a uniform electric field.

We assume that in the electric field the droplet has the shape of a prolate ellipsoid of revolution:

$$\frac{x^2}{a^2} + \frac{\rho^2}{b^2} = 1, \quad \rho^2 = y^2 + z^2,$$

where  $a > b$ , the direction of the x-axis being opposite to that of  $E_0$ . In the case in question the potential  $\varphi$  outside the droplet can be determined by integrating

the Laplace equation

$$\Delta\varphi = 0 \tag{1}$$

with the following conditions:

$$\varphi \Big|_s = \frac{q \operatorname{Arch} \frac{a}{b}}{4\pi\epsilon_0\epsilon \sqrt{a^2 - b^2}} \text{ [8]}, \quad \varphi \Big|_{\left| \frac{x}{a} \right| \rightarrow \infty} = -E_0x. \tag{2}$$

Using the prolate spheroidal coordinates  $\xi, \eta$  [8], we obtain the solution of (1) and (2) in the form

$$\begin{aligned} \varphi = & \frac{q}{8\pi\epsilon_0\epsilon ea} \ln \frac{\sqrt{\xi + a^2} + ae}{\sqrt{\xi + a^2} - ae} + \\ & + \varphi_0 \left[ \ln \frac{(1+e)\sqrt{\xi + a^2} - ae}{(1-e)\sqrt{\xi + a^2} + ae} + 2e \left( \frac{a}{\sqrt{\xi + a^2}} - 1 \right) \right] \times \\ & \times \left( \ln \frac{1+e}{1-e} - 2e \right), \end{aligned} \tag{3}$$

where

$$\varphi_0 = -E_0x = \mp E_0 \left[ \frac{(\xi + a^2)(\eta + a^2)}{a^2 - b^2} \right]^{1/2}$$

$$\text{and } e = \sqrt{1 - \frac{b^2}{a^2}}.$$

Using expression (3), we determine the electric force acting on unit surface of the droplet

$$\begin{aligned} \bar{F}_1 = & \frac{\epsilon_0\epsilon}{2} \left( \frac{d\varphi}{dn} \right)_{\xi=0}^2 \bar{n} = \\ = & \frac{\epsilon_0\epsilon}{2\mu} \left[ \frac{q}{4\pi\epsilon_0\epsilon r^3} + \frac{E_0x^3 \sqrt{(1-e^2)^3}}{r^2 n^{(x)}} \right]^2 \bar{n}, \end{aligned} \tag{4}$$

where

$$n^{(x)} = \frac{1-e^2}{2e^3} \left( \ln \frac{1+e}{1-e} - 2e \right) \text{ and } \mu = \frac{x^2}{a^4} + \frac{\rho^2}{b^4}.$$

Effects associated with the motion of the droplet are neglected.

On the other hand, the droplet is acted upon by the capillary force

$$\bar{F}_2 = - \frac{1+a^2\mu}{a^2b^2\mu^{3/2}} a \bar{n}. \tag{5}$$

Starting from [9], we may assume that the droplet will be destroyed if the electric forces exceed the

capillary forces at some point of the surface. Expressions (4) and (5) show that this is most likely at one of the points  $x = \pm a$ . In this case, the charged droplet may be expected to be dispersed from the end turned toward the electrode whose sign is opposite to the sign of the droplet charge. In view of the symmetry of the field, an uncharged droplet should be dispersed from both ends simultaneously.

Consequently, if we neglect the force of gravity, the droplet stability condition can be represented by the inequality

$$\frac{\epsilon_0 \epsilon}{2\mu} \left[ \frac{|q|}{4\pi\epsilon_0 \epsilon r^3} + \frac{E_0 x \sqrt{(1-e^2)^2}}{r^2 n^{(x)}} \right] \Big|_{x=a} < \frac{(1+a^2\mu)\alpha}{a^2 b^2 \mu^{3/2}} \Big|_{x=a},$$

whence it is easy to obtain

$$E_0 < \frac{2n^{(x)}}{\sqrt[3]{1-e^2}} \sqrt{\frac{\alpha}{\epsilon_0 \epsilon r}} - \frac{|q| n^{(x)}}{4\pi\epsilon_0 \epsilon r^2 \sqrt[3]{1-e^2}}. \quad (6)$$

For the uncharged droplet ( $q = 0$ ), the stability condition will be

$$E_0 < \frac{2n^{(x)}}{\sqrt[3]{1-e^2}} \sqrt{\frac{\alpha}{\epsilon_0 \epsilon r}}. \quad (7)$$

The dispersion condition for this case is written

$$E_0 \geq E_0^{cr} = \frac{2n^{(x)}}{\sqrt[3]{1-e^2}} \sqrt{\frac{\alpha}{\epsilon_0 \epsilon r}}. \quad (8)$$

With the assumption  $e = \text{const}$ , expression (8) is analogous to that obtained in [3]. From expression (7), setting  $E_0 = 0$ , it is also possible to obtain the stability condition for a charged spherical droplet previously given by Rayleigh [8].

In our experimental investigation of this phenomenon, we dispersed individual droplets of various aqueous solutions. As the aqueous phase we took: 0.25 and 0.0025% solutions of the nonionogenic deemulsifier OP-10, a 1% sodium naphthenate solution, formation water from the Uzen deposit (pH = 8.8), and a 25% solution of chemically pure sodium chloride. The nonpolar medium was medicinal vaseline oil, purified on silica gel and filtered through a GIKI filter (maximum pore size  $1.68 \cdot 10^{-6}$  m).

The surface tension of these aqueous solutions at the boundary with the oil was measured by the modified method of droplet volume determination [10]. The droplet was formed in 180 sec. The measurements were made at temperatures corresponding to the conditions of the droplet dispersion experiments. The

surface tensions of the various systems are presented in Table 1.

Mechanical dispersion of the water in the oil was used for droplet formation. The required droplet was removed with a glass syringe and introduced into the interelectrode gap of a vertically mounted capacitor.

The stainless-steel electrodes of the capacitor employed had a polished inner surface. The distance between them was  $1,000 \cdot 10^{-2}$  m, the length and width of the plates were  $4.7 \cdot 10^{-2}$  and  $2.6 \cdot 10^{-2}$  m, respectively. Voltage was supplied to the capacitor plates from a high-voltage VS-20 rectifier. An S-96 kilovoltmeter was used to measure the voltage. The droplets were observed with a KM-6 cathetometer fitted with a camera and a micrometer scale.

The droplet could be kept in the interelectrode gap as long as desired, which was achieved by supporting it in an ascending flow of oil.

Preliminary experiments made it possible to determine the nature of the dispersion of charged and uncharged droplets. In these experiments, the voltage was applied in steps of 100–200 V. At a given value of the electric field strength ( $E_0$ ), the uncharged droplet always acquired a shape fairly close to that of an ellipsoid of revolution. Weakly charged droplets, moving toward the oppositely charged electrode, were similarly deformed. The uncharged deformed droplet remained in the field of view for a long time, until it acquired a charge.

When the capacitor plates were closed, the deformed ellipsoidal droplet was compressed into a sphere.

At  $E_0^{cr}$  the droplet was progressively deformed into an ellipsoid of revolution with noticeably increasing eccentricity. This stretching of the droplet usually ended in dispersion (Fig. 1a). The deformation time of droplets of systems 1 and 2 (on the order of a second) considerably exceeded that of the droplets of the other systems investigated. The observed development of deformation is determined by the time required for the electric field forces to counteract the forces of surface tension and viscous drag. The difference in droplet deformation times is primarily attributable to the significantly different values of the imposed field strengths.

Here, it is necessary to draw a special distinction between charged and uncharged droplets. When the critical field is switched on, the former deform non-uniformly with time (Fig. 1b) with the subsequent ejection of liquid from one side, which is determined by the presence of an excess charge  $q$ .

Table 1

Values of the Surface Tension  $\alpha$  and the Constant  $k$  in Expression (9)

System	Designation of system	$\alpha \cdot 10^3$ , N/m	$k$
1	0.25% solution of OP-10	3.8	0.45
2	1% sodium naphthenate solution	4.3	0.46
3	0.0025% solution of OP-10	21.8	0.40
4	Formation water	47.0	0.42
5	25% sodium chloride solution	57.0	0.42

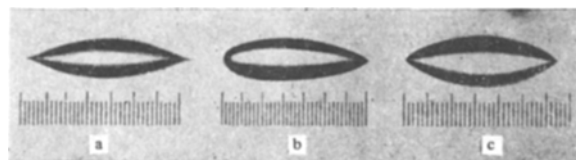


Fig. 1. Effect of the critical field on droplet deformation (scale division  $51 \cdot 10^{-6}$  m): a and b) dispersion of uncharged and charged droplets; c) shape of uncharged droplet after dispersion.

At the moment of dispersion the uncharged droplets have the configuration shown in Fig. 1a. As expected, liquid is ejected from both ends of the deformed droplet.

We note that when a field slightly exceeding the critical value is imposed, the droplets disperse with the ejection of very fine particles (Fig. 1a, b). Dispersion is accompanied by the formation of "miniature fountains," similar to those observed by previous investigators [3], at the points of maximum curvature of the droplet surface. If the imposed field exceeds  $E_0^{cr}$  by  $(2-3) \cdot 10^{-4}$  V/m, the dispersing droplets form distinguishable ( $r \approx 10^{-6}$  m) charged droplets. When the imposed field exceeds  $E_0^{cr}$  by more than  $5 \cdot 10^{-4}$  V/m, uncharged particles are dispersed with the formation of various droplets that separate from both ends. In the center we find the largest droplet, which is often uncharged. In all cases, the formation of very fine droplets ( $r < 10^{-6}$  m) is observed.

At small values of the surface tension  $\alpha$  at the phase interface, after dispersion the droplet retains its shape (Fig. 1c) for several minutes. Then it is compressed at one end, while an individual particle ( $r \approx 10^{-5}$  m) is ejected from the other. The process is alternately repeated, after which the droplet moves toward one of the electrodes. In this stage, it executes translational motion along the field lines, so that after liquid is ejected in one direction the droplet begins to move in the other, and so on. This was regularly observed in connection with concentrated solutions of OP-10 and sodium naphthenates.

After dispersion, droplets characterized by a large value of  $\alpha$  generally move toward one of the electrodes. Charged droplets behaved similarly. The particles ejected by the primary charged droplet always acquired a charge of the same sign as the droplet charge. The residue of the primary droplet tended to move in one direction, changing its previous direction of motion, while the dispersion products moved in the other.

It may be assumed that the alternating compression and ejection observed in connection with the droplets with small values of  $\alpha$  deformed into the configuration shown in Fig. 1c are determined by the acquisition of a charge due to primary dispersion products arriving from the electrodes. After this, the droplet is dispersed just as a charged droplet.

In all cases, the charge of the dispersion products is determined by the imposed field and the particle size.

In the experiments described, a marked scatter of the experimental data was observed for uncharged droplets, particularly for systems 3-5. This is evidently attributable both to changes in the value of  $\alpha$  determined by the time required to achieve absorption equilibrium at the phase interface, which was not checked in these experiments, and to its fluctuations during droplet formation. It may be that, in this case, the changes in  $\alpha$  are also determined by the adsorption and desorption of surface-active agents in the electric field. We also note that droplets with  $r \approx 300 \cdot 10^{-6}$  m or less were practically always charged.

This applies especially to systems 4 and 5. Weak electrification of the droplets was observed only for systems 1 and 2.

With this in mind, in the experiments to verify expression (8) the time between the moment of droplet formation and the application of the field was adjusted to 180 sec. A field of critical or near-critical strength was applied. This made it possible to use values of  $\alpha$  determined by the method described in [10] in the subsequent calculations.

The droplets without a charge were dispersed as before (Fig. 1a). The value of  $E_0^{cr}$  was determined by sampling several droplets similar in size. The graphs (Fig. 2) represent only those droplets dispersed either upon application of the critical voltage or after increasing the strength of the applied pre-critical field by  $(1-2) \cdot 10^{-4}$  V/m for systems with a small value of  $\alpha$  and by  $(2-3) \cdot 10^{-4}$  V/m for systems with a large surface tension coefficient. These experiments also showed that droplets of the same radius may be dispersed at different  $E_0^{cr}$ , which is attributable to fluctuations of  $\alpha$  under the conditions of droplet formation. However, in the experiments described these deviations did not exceed  $\pm 5\%$ .

It is clear from the graphs that at a given value of  $\alpha$ ,  $E_0^{cr} = f(r)$  is satisfactorily described by the expression

$$E_0^{cr} = k \sqrt{\frac{\alpha}{\epsilon_0 \epsilon r}}, \quad (9)$$

where  $k$  and  $\alpha$  are constants.

The observed experimental deviations (curves 4 and 5, Fig. 2) from relation (9) on the interval  $r$  ( $150-350$ )  $\cdot 10^{-6}$  m, which do not exceed 20%, must evidently be attributed primarily to the presence of a free charge on the dispersed droplets.

Values of the coefficients  $k$  calculated from expression (9) using the experimental data obtained are presented in Table 1.

An analysis of photomicrographs of the droplets at the moment of dispersion leads to the results presented in Table 2. It is clear from Table 2 that,

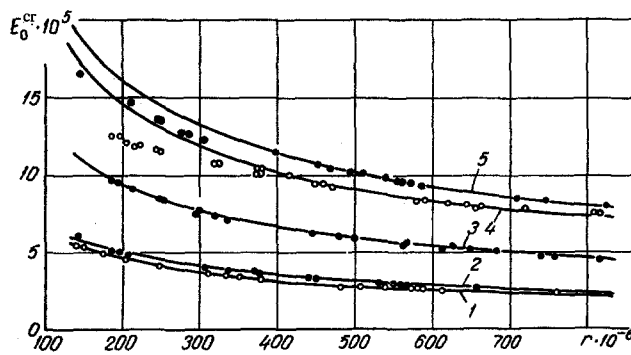


Fig. 2. Critical field strength  $E_0^{cr}$  (V/m) as a function of the radius  $r$  (m) of the dispersed droplets for various systems: 1-5) at  $\alpha$  equal to 3.8; 4.3; 21.8; 47;  $57 \cdot 10^{-3}$  N/m, respectively. The circles represent experimental points, the curves calculations based on (9).

Table 2  
Values of the Parameter  $e$  at the Moment  
of Droplet Dispersion

System 1			System 3			System 5		
$r \cdot 10^6, \text{m}$	$b/a$	$e$	$r \cdot 10^6, \text{m}$	$b/a$	$e$	$r \cdot 10^6, \text{m}$	$b/a$	$e$
182	0.31	0.951	349	0.32	0.947	194	0.28	0.960
						206	0.30	0.954
205	0.30	0.954	382	0.31	0.951	245	0.30	0.954
240	0.30	0.954	473	0.29	0.957	300	0.32	0.947
360	0.29	0.957	557	0.31	0.951	367	0.31	0.951
372	0.30	0.954	670	0.31	0.951	376	0.32	0.947
						425	0.31	0.951
						545	0.31	0.951

within the limits of error of the experiment, the eccentricity  $e$  at the moment of dispersion, calculated from the  $a$  and  $b$  determined from the usual relations, can be assumed equal to 0.952 on the investigated interval of  $r$  for all the systems investigated.

Substitution of the numerical value of  $e$  into inequalities (7) and (8) makes it possible to determine the value of the expression preceding the radical, namely, 0.43.

Clearly, the experimental values of the coefficient  $k$  for the investigated system (Table 1) satisfactorily coincide with 0.43.

Obviously, we may conclude that the applicability of expression (7) as a criterion of droplet stability in an electric field has been experimentally demonstrated.

Expression (7) contains parameters that are easily determined experimentally. Accordingly, it can be used for practical calculations, in particular, for calculating the technical parameters of the electrical dewatering of oils.

#### NOTATION

$x, y,$  and  $z$  are Cartesian rectangular coordinates;  $\xi, \eta$  are prolate spheroidal coordinates;  $r$  is the droplet radius;  $a$  and  $b$  are the semiaxes of the ellipsoid of revolution;  $e$  is the eccentricity of the ellipsoid of revolution;  $n^{(x)}$  is the coefficient of depolarization of the ellipsoid along the  $x$ -axis;  $\bar{n}$  is the outward normal to the surface of the ellipsoid of revolution;  $\alpha$  is the surface tension at the phase interface;  $E_0$  and  $\varphi_0$  are, respectively, the strength and potential of the external homogeneous field;  $E_0^{CT}$  is the critical field strength

causing dispersion of the droplet;  $q$  is the droplet charge;  $\varphi$  and  $\varphi_s$  are the potentials outside and at the surface of the charged droplet, respectively;  $\epsilon = 2.2$  is the relative dielectric constant of the medium;  $\epsilon_0 = 8.85 \cdot 10^{-12}$  F/m is the absolute dielectric constant of free space;  $k$  is a constant.

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