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THE INFLUENCE OF ELECTRIFICATION UPON THE
SURFACE TENSION OF WATER AND MERCURY.¹

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THE investigations of Exner and Tuma,² Warburg,³ G. Meyer,⁴ Luggin,⁵ S. Meyer,⁶ Nernst,⁷ Behn,⁸ S. W. J. Smith,⁹ and many others have established beyond reasonable doubt that the electrocapillary phenomena occurring at the interface between a liquid metal and an electrolyte, in a capillary electrometer, for example, are due almost entirely to true alterations of surface tension resulting from the chemical changes of electrolysis. There are many other electrocapillary phenomena, however, which are undoubtedly caused largely, if not wholly, by the electrostatic forces that are developed by the presence of a charge upon the liquid surface. Thus when electrified, a soap bubble expands, a globule of mercury becomes more flattened, the wave pattern of a liquid jet issuing from an elliptical aperture becomes more elongated,¹⁰ etc., etc. In such cases the effect of electrification is usually similar to that which would be produced by a *diminution* of the surface tension. This

¹ A paper read before the American Physical Society, December 28, 1899.

² Wien. Ber. 97 IIa, p. 923, 1888.

³ Wied. Ann. 38, p. 321, 1889; *ibid.*, 41, p. I, 1890.

⁴ Wied. Ann. 45, p. 508, 1892; *ibid.*, 53, p. 845, 1894; et al.

⁵ Wien. Ber. 102 IIa, p. 913, 1893.

⁶ Wien. Ber. 105 IIa, p. 139, 1896.

⁷ Zeitschrift für Elektrochemie, 4, p. 29, 1897.

⁸ Wied. Ann. 61, p. 1897.

⁹ Proc. R. S. L. 64, p. 253, 1899.

¹⁰ Phil. Mag. Sept. 1882, p. 186.

fact is probably due to the universal employment of convex surfaces in such experiments; in the case of a concave charged surface a consideration of the electrostatic forces would lead us to expect an apparent increase in the strength of the surface film.

To determine whether, in addition to this electrostatic effect, there exists a true effect of electrification upon the surface tension of a liquid, investigations must obviously be made by methods which make the calculation of the purely electrostatic effect feasible, so that it may be eliminated from the total effect. Several earlier investigations bearing upon the existence and magnitude of a true change in surface tension produced by electrification, although quite inconclusive so far as such an effect is concerned, were reviewed by one of us in a recent paper.¹ This paper also described a new and more elaborate investigation of the same problem, and showed that the effect in question, if it exists at all, is much smaller than previously supposed. As the theory of the method used had not been fully developed at the time of publication, no more definite conclusion could then be drawn. To complete this theory, and by means of it to give the observations their final discussion, is the object of the present communication.

For a detailed account of the experiments, reference must be made to the paper already mentioned. It is sufficient to state here that the tension of the liquid surfaces, uncharged and charged to known electrical densities, was investigated by the method of capillary ripples, in a form capable of giving the surface tension of un-electrified water with an accidental error not greater than 0.05%.² When the liquids were electrically charged, either positively or negatively, the velocity of the capillary waves was found to be less than when the surface was unelectrified. In the case of water this observed change would correspond to a diminution in surface tension of about 4% for a surface density of 1.75 electrostatic units. For mercury the apparent change was not so great, being slightly less than 1% for a surface density of 2.33. It is to be observed, in accordance with what has been said above, that the results cited do not necessarily prove the existence of a *real* change in surface ten-

¹ Barnett, PHYSICAL REVIEW, 6, p. 257, 1898.

² Barnett l. c., p. 263.

sion; for the electrostatic forces acting upon a charged surface would cause a diminution in the velocity of capillary ripples even if the surface tension remained unaltered. In order to determine whether a real change in surface tension results from electrification, we must take account of the electrostatic forces in deriving the relation between surface tension and velocity.

To determine the velocity of capillary ripples we have the general equation¹

$$\frac{\delta p}{\rho} = -gh - \frac{d\varphi}{dt} \quad (1)$$

where ρ is the density of the liquid, h the displacement of the point considered above its equilibrium position, δp the resulting increment of pressure at the surface, φ the velocity potential, and g the acceleration of gravity.

If δp is due to capillarity only, we have

$$\delta p = -T \frac{\partial^2 h}{\partial x^2}$$

T being the surface tension; and equation (1) becomes

$$\frac{T \partial^2 h}{\rho \partial x^2} = gh + \frac{d\varphi}{dt} \quad (2)$$

For the case of plane sine waves such as we have supposed, this gives for the velocity v

$$v^2 = \left(\frac{g}{k} + T \frac{k}{\rho} \right) \tanh kl$$

l being the depth of the liquid, λ the wave-length, and $k = \frac{2\pi}{\lambda}$.

In the experiments with which we are concerned the value of l was such that $\tanh kl$ differed from unity by less than one part in 2000, and we may put

$$v^2 = \frac{g}{k} + T \frac{k}{\rho}$$

with an error less than the experimental error.³

¹ Rayleigh, *Treatise on Sound*, Vol. II, § 353, Second edition.

² Rayleigh, *Treatise on Sound*, Vol. II, § 353, Second edition.

³ Barnett *l. c.*, p., 263.

If the wave frequency is n we have $v = n\lambda$, and the final expression for the surface tension becomes

$$T = \frac{\rho\lambda^2}{2\pi} \left(\lambda n^2 - \frac{g}{2\pi} \right). \quad (3)$$

When the surface of the liquid is charged, however, a pressure $-\frac{2\pi\sigma^2}{K}$ is developed in addition to that due to capillarity, σ being the electric surface density and K the dielectric constant of the medium above the waves. In order to obtain the whole increment of pressure, δp , resulting from the displacement h , it is therefore necessary to add to $-T \frac{\partial^2 h}{\partial x^2}$ a term $-\frac{2\pi}{K} (\sigma^2 - \sigma_0^2)$ where σ_0 is the surface density of the charge on the undistorted surface. In the place of equation (2) we have therefore, in this case,

$$\frac{T}{\rho} \frac{\partial^2 h}{\partial x^2} + \frac{2\pi}{K\rho} (\sigma^2 - \sigma_0^2) = gh + \frac{d\phi}{dt}. \quad (4)$$

The surface density σ at any point of the wave surface is a function of h whose form remains to be determined.

In the experiments already mentioned the surface of the liquid was made one coating of an air condenser, the other coating being formed of tinfoil supported on glass at a height of about 35 mm. above the surface. This arrangement was adopted in order to

Fig. 1.

obtain a more intense charge upon the liquid surface, and to make the electrical conditions definite, so that all the quantities involved should be capable of exact determination. To find the distribution of the charge over the wave surface under the conditions of the experiment, we may proceed as follows:

Let the axis of X be taken in the original level surface of the liquid, while the axis of Y is normal to the surface. Consider a

train of plane waves of amplitude b travelling in the direction of X . As the waves proceed a rearrangement of the charge occurs; but this takes place so rapidly that the electrical conditions are always the same as though the ripples were stationary. The surface being at a potential V_0 , while the plate AB is grounded, we have to determine the value of σ for all points along XX' .

For the region between the plates AB and the wave surface XX' , the electrical potential V is a function of x and y subject to the condition

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = 0. \quad (5)$$

It is clear that V , as a function of x , is periodic in the distance λ . With the origin as shown in the figure we may therefore write

$$V = A_0 + A_1 \cos kx + A_2 \cos 2kx + \dots \quad (6)$$

Since V must have the same value for $-x$ as for $+x$, none but cosine terms will appear in the expansion. The coefficients A_0 , A_1 , etc., are functions of y , but are independent of x .

Upon substitution in (5) we obtain

$$\frac{\partial^2 A_0}{\partial y^2} + \left(\frac{\partial^2 A_1}{\partial y^2} - k^2 A_1 \right) \cos kx + \left(\frac{\partial^2 A_2}{\partial y^2} - 4k^2 A_2 \right) \cos 2kx + \dots = 0.$$

Since this equation holds for all values of x the coefficients must vanish separately. Therefore,

$$\frac{\partial^2 A_0}{\partial y^2} = 0, \quad \frac{\partial^2 A_1}{\partial y^2} - k^2 A_1 = 0, \text{ etc.}$$

The solution of these equations leads to the following values for the coefficients in (6):

$$\begin{aligned} A_0 &= M_0 y + N_0 \\ A_1 &= M_1 \varepsilon^{ky} + N_1 \varepsilon^{-ky} \\ A_2 &= M_2 \varepsilon^{2ky} + N_2 \varepsilon^{-2ky} \\ &\text{etc.} \end{aligned}$$

The constants of integration are to be so chosen as to satisfy the boundary conditions, viz.: (1) For $y = a$, $V = 0$ for all values of x : (2) for $y = b \cos kx$, $V = V_0$.

The first condition requires that A_0 , A_1 , etc., should separately vanish for $y = a$. Therefore

$$\begin{aligned} M_0 &= -\frac{1}{a} N_0 \\ M_1 &= -N_1 \varepsilon^{-2ka} \\ M_2 &= -N_2 \varepsilon^{-4ka} \\ &\text{etc.} \end{aligned}$$

For the coefficient A_1 we therefore have

$$A_1 = N_1 (\varepsilon^{-ky} - \varepsilon^{-2ka+ky}).$$

Since the expression for V is to be used only in order to find the force at the surface of the liquid, and from this the value of σ , we are chiefly concerned with its value for points immediately above the surface. For such points y is small when compared either with a or with λ . The exponent of the second term of A_1 for points in the immediate neighborhood of the surface is therefore practically equal to $-2ka$. In the experiments upon water the value of a (distance between the liquid surface and the plate above) was about 4 cm., while λ was always less than 0.5 cm. In the experiments upon mercury, the value of a was about 3.4 cm., and that of λ less than 0.37 cm. In all cases the quantity $2ka$ is therefore greater than 100, and the second term in the expression for A_1 is entirely negligible. This is also true of the corresponding terms in A_2 , A_3 , etc. The expression for V therefore takes the form

$$V = -N_0 \frac{y}{a} + N_0 + N_1 \varepsilon^{-2ky} \cos kx + N_2 \varepsilon^{-2ky} \cos 2kx + \dots \quad (7)$$

For points on the wave surface, where $y = b \cos kx$, the potential is V_0 . Therefore for points on the surface

$$V_0 = N_0 - N_0 \frac{b}{a} \cos kx + N_1 \varepsilon^{-ky} \cos kx + N_2 \varepsilon^{-2ky} \cos 2kx + \dots$$

Remembering that the amplitude, b , of the ripples is extremely small, and that the y in the above expression can in no case exceed b , it is clear that the exponentials are practically equal to unity; and we have as a close approximation,

$$0 = N_0 - V_0 + \left(N_1 - \frac{b}{a} N_0\right) \cos kx + N_2 \cos 2kx + \dots$$

Since this relation holds for all values of x , the coefficients N_2, N_3 , etc., vanish, and

$$N_0 = V_0, \quad N_1 = \frac{b}{a} V_0.$$

The final approximate expression for V is therefore

$$V = V_0 \left(1 - \frac{y}{a} + \frac{b}{a} \varepsilon^{-ky} \cos kx \right) \quad (8)$$

and that for Y , the vertical component of the force at the surface, is

$$Y = - \frac{\partial V}{\partial y} = \frac{V_0}{a} (1 + kb \cos kx).$$

For waves of the extremely small amplitude used the horizontal component of the force is negligible in comparison with Y . Therefore,

$$\sigma = \frac{KV}{4\pi a} (1 + kb \cos kx).$$

Remembering that $\frac{KV}{4\pi a} = \sigma_0$, that $kb \cos kx$ is small, and that

$b \cos kx = y = h$, we have, finally,

$$\sigma^2 - \sigma_0^2 = 2kh\sigma_0^2 = \frac{4\pi\sigma_0^2}{\lambda} h$$

and equation (4) becomes

$$\frac{T}{\rho} \frac{\partial^2 h}{\partial x^2} = \left(g - \frac{8\pi^2\sigma_0^2}{K\lambda\rho} \right) h + \frac{d\varphi}{dt}. \quad (9)$$

Upon comparing this with equation (2) it appears that the effect of electrifying the surface is to alter the velocity of the waves in the same sense and to the same extent as would a diminution of the acceleration of gravity by $\frac{8\pi^2\sigma_0^2}{K\lambda\rho}$.

The corrected expression for the surface tension [see (3)] is, therefore,

$$T = \frac{\rho\lambda^2}{2\pi} \left(\lambda n^2 - \frac{g}{2\pi} \right) + \frac{2\lambda\sigma_0^2}{K}. \quad (10)$$

The *apparent* surface tension *i. e.*, the value of T obtained from (3) [or from (10) without taking into account the final term, which

gives the correction for electrostatic influences] is thus always less than the true surface tension by the amount $\frac{2\lambda\sigma_0^2}{K}$.

TABLE I.

Water.

V	λ	σ_0	$\frac{2\lambda\sigma_0^2}{74.3}$	T Apparent.	T Corrected.
0	0.496	0.00	0.00%	100.00%	100.00%
9000	.496	0.58	0.45	99.61	.06
12000	.495	0.77	0.79	99.29	.08
15000	.495	0.97	1.25	98.98	.23
18000	.494	1.17	1.82	98.37	.19
21000	.493	1.36	2.46	97.69	.15
24000	.492	1.56	3.22	96.94	.16
27000	.491	1.74	3.00	96.13	.13

TABLE II.

Mercury.

V	λ	σ_0	$\frac{2\lambda\sigma_0^2}{403.4}$	T Apparent.	T Corrected.
0	0.369	0.00	0.00%	100.00%	100.00%
9000	"	0.70	.09	99.92	.01
12000	"	0.93	.16	.88	.04
15000	"	1.17	.25	.83	.08
18000	"	1.39	.35	.75	.10
21000	"	1.63	.49	.61	.10
24000	"	1.87	.64	.44	.08
27000	"	2.09	.80	.25	.05
30000	"	2.33	.99	.08	.07

The experimental values of this apparent tension of water and mercury have been given for a number of different values of σ_0 in Tables IV. and V. of the paper referred to above, expressed in percentage of the values for $\sigma_0 = 0$.¹ By the use of equation (10) we are now able to apply the correction due to electrostatic influences. The results are given in Tables I. and II., expressed as before in percentage of the maximum values of T . These maximum values were $74.3 \frac{\text{dynes}}{\text{cms}}$ for water and $403.4 \frac{\text{dynes}}{\text{cms}}$ for mercury, respectively,

¹ Barnett, l. c., pp. 281-282.

which were obtained by making the following substitutions in (10):

$$K = 1, \quad g = 981, \quad n = 64.4, \quad \sigma_0 = 0$$

also, for water

$$\lambda = 0.496, \quad \rho = 0.998$$

and for mercury

$$\lambda = 0.369, \quad \rho = 13.54.$$

The final column of Table I. gives for the corrected surface tension of an electrified water surface values ranging from 0.06% to 0.23% higher than that of the uncharged surface, the average value being about $\frac{1}{4}\%$ higher; while the corresponding column of Table II. gives for the tension of an electrified mercury surface values from 0.01% to 0.10% higher than that for no electrification—the mean being about $\frac{1}{15}\%$ higher. The fact, however, that the very small variation follows no law in either case, being often less for high than for low electric surface densities, would indicate that it possesses no significance, and is due wholly to experimental errors. To make this evident, we shall examine the accidental error in measuring the “apparent” surface tension of water; what is said of the experiments upon water being true, with little alteration, for those upon mercury. As was shown in the paper already often quoted, a given percentage error in measuring λ produces in the computed value of T , under the conditions of the experiments, a percentage error about three times as great. More accurately, $\frac{\Delta T}{T} = 2.9 \frac{\Delta \lambda}{\lambda}$. An examination of figure 6 (*l. c.*) shows that in measuring λ the average departure from the mean (given by the curves) in each of the two measurements necessary was about $\frac{1}{20}\%$. The average accidental error in T is therefore about $\frac{1}{4}\%$; so that the small differences in the corrected value of the surface tension are all within experimental errors, and we may safely conclude that no effect of electrification upon the surface tension has been observed.

The complete investigation, therefore, while not excluding the possibility of discovering an effect of electrification upon surface tension by the use of improved methods and still more intense charges, itself gives no support to the view that such an effect exists.