Reprinted from JOURNAL OF COLLOID SCIENCE, Vol. 1, No. 3, May, 1946
Printed in U. S. A.

NEW ELECTROCAPILLARY PHENOMENA [1]

A. Frumkin

From the Institute of Colloid and Electrochemistry, Academy of Sciences, U.S.S.R., Moscow

Received April 26, 1946

When a metal comes in contact with a solution, chemical forces acting on the atoms of the metal and the ions of the solution give rise to a double layer of electrical charges which exerts a far-reaching influence on a number of physico-chemical properties of the metal, such as its surface energy, wettability, adsorptive properties and behavior in various electrode processes.

The subject of the present paper is the description and analysis of the influence of the double layer on what might, perhaps, be called the simplest physical properties of a metal: its dynamic behavior in the liquid state and mechanical hardness in the solid state. These phenomena have recently been investigated in the Institute of Colloid- and Electrochemistry of the Academy of Sciences of the U.S.S.R. by B. Levich and myself on the one hand, and by P. Rehbinder and co-workers on the other.

If a charged sphere of radius α is placed in an electric field of intensity E, then, as follows from elementary physical considerations, it will acquire a velocity equal to

$$U = \frac{2}{3}\frac{\epsilon E a}{\mu} \qquad (1)$$

where ϵ is the surface density of the charge and μ the viscosity of the medium. In the case of a liquid sphere this expression will have a slightly different numerical coefficient, which for a liquid sphere moving in a medium whose viscosity considerably exceeds that of the sphere itself becomes:

$$U = \frac{\epsilon E a}{\mu}. \qquad (2)$$

Inasmuch as the density of the charges spontaneously arising in the electric double layer is greater by many orders of magnitude than the density which can be attained by artificially charging the particle, one might expect that particles in an electrolyte solution subject to the action

---

[1] Address delivered on June 18, 1945 at the Jubilee session of the Chemistry Section of the Academy of Sciences of the USSR in celebration of the 220th anniversary of the Academy.

of an external electric field would acquire exceedingly high velocities. Actually, this is not so. The electrokinetic movement arising from application of a tangential electric field to the interface between a liquid and a foreign solid or liquid particle has long been known. It was discovered in 1807 by Reuss in Moscow, has since been the object of a great number of investigations, and has found applications in colloid chemistry, technology and biology. However, although the methods of investigating electrokinetic movement have progressed considerably since the time Reuss used a battery composed of 92 silver rubles and an equal number of zinc plates to create his electric field, no such large velocities as those mentioned above have ever been observed. Actually, the velocity of electrokinetic movement is very small and for $E = 1$ volt./cm. only amounts to several μ/sec. in aqueous solutions. The reason for this becomes apparent if one turns to the theory of electrokinetic movement developed especially by Helmholtz and Smoluchowski, and analyzes this movement in greater detail. The charges of the double layer, in contradistinction to those which we have placed on our sphere, are not free, the double layer containing equal amounts of charges of opposite sign which make up its two sheets. The electric forces acting on these sheets are equal in magnitude and opposite in sign. If the charge per unit surface area on the metal is ϵ, then that of the outer part of the double layer in the solution is $-\epsilon$, and the corresponding forces are ϵE and $-\epsilon E$, it being assumed that the field intensity is the same at small distances on both sides of the interface, as in the case of a dielectric particle. The points of application of these forces are separated by a very small distance equal to the thickness of the double layer d, *i.e.*, of the order of 10^{-7} cm. As a result, even small velocities of the relative motion of the particle and liquid suffice to give rise to large velocity gradients in the liquid near the particle surface and, hence, large viscous stresses which counterbalance the applied forces. For a particle whose dimensions are large compared with the thickness of the double layer the theory leads to the following expression for the velocity of the electrokinetic motion:

$$U = \frac{\epsilon E d}{\mu}. \qquad (3)$$

Inasmuch as $d \ll a$, this velocity is, in order of magnitude, much smaller than that of a particle carrying a free charge; for a particle of radius 10^{-2} cm. in a 0.1 N solution this ratio comprises 10^{-5}. The question arises as to whether or not it is possible to find conditions under which the high velocities which are ordinarily damped by the viscous stress in the double layer could be realized.

As far back as 1903 Christiansen (1) described another group of motions which can be observed when an electric current is passed through

a solution of an electrolyte containing a drop of mercury. Christiansen's explanation of the phenomena was as follows.

Under ordinary conditions the mercury surface in contact with the solution is positively charged. The double layer on the solution-mercury interface affects the magnitude of the interfacial tension making it less. When an electric current passes through the solution and the drop, as in an ordinary capillary electrometer, the initial positive charge of the mercury is decreased at the point where the current enters the drop while the interfacial tension increases here. At the point where the current goes from the drop to the solution the positive charge increases and the interfacial tension falls off. As a result a flow of the liquid arises along the surface in the direction of increasing interfacial tension, *i.e.*, opposite to the electric field as depicted in Fig. 1. Due to this movement the drop as a whole is repelled from the surrounding mass of liquid and migrates by a reaction movement in the direction of the field.

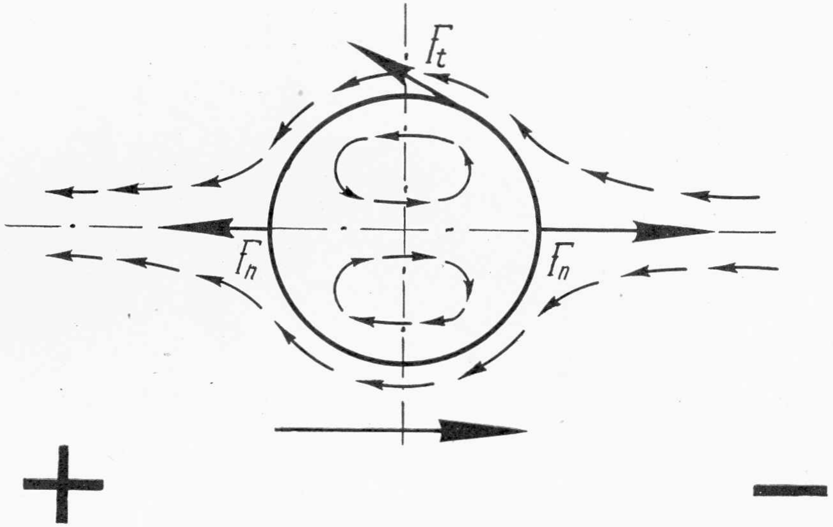

FIG. 1

Motion of a Mercury Drop in an Electrolyte Solution under the Influence of an Electric Field. The small arrows denote the direction of flow of the solution and the mercury at each point; the large arrow underneath the figure shows the direction of motion of the drop as a whole.

This qualitative explanation of the electrocapillary motion of the drop, as it is usually called, must, on the whole, be considered correct in the light of our present-day concepts. However, in such an interpretation, the relation between electrocapillary and electrokinetic movement is still not clear. In the subsequent literature these two groups of phenomena were usually treated completely independently; the few attempts to compare them (Craxford (2) Antweiler and Stakelberg (3)) did not, in the writer's opinion, throw sufficient light on the problem. Moreover, neither Christiansen nor the other authors gave a quantitative theory of electrocapillary movement. B. Levich and the present author have recently developed a quantitative theory of the dynamic behavior of charged metal surfaces (4) which makes an attempt to explain the relations between electrokinetic and electrocapillary movement and brings out some unexpected features of the latter. In the present communication the fundamentals of the theory are set forth, a detailed exposition is shortly to appear elsewhere.

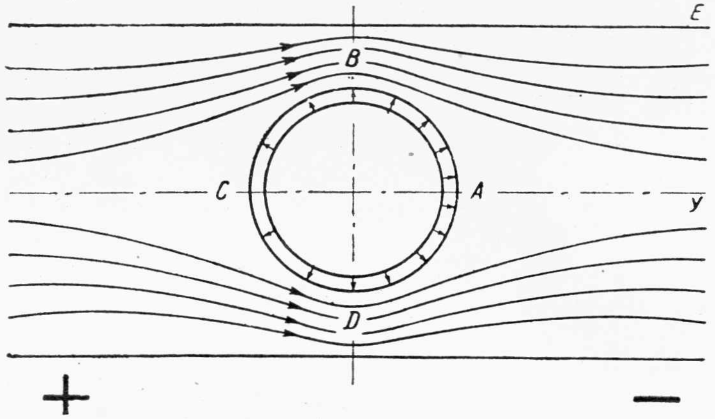

FIG. 2

Schematic Representation of the Double Layer of a Completely Polarizable Metal Particle in an External Electric Field. The arrows denote the direction of the lines of force.

Let us consider more closely the forces acting on a metal particle in a medium through which an electric current is flowing. We shall limit ourselves to the simple case when the particle can be regarded as "completely polarizable," *i.e.*, when ions of the solution cannot become neutralized nor atoms of the metal ionized at the metal-solution interface. In this respect the metal particle behaves as if it were covered with a thin layer of a perfect insulator. A mercury drop in a potassium chloride solution from which all the dissolved oxygen has been removed can be considered as satisfying the condition of complete polarizability. If this condition is not satisfied, some corrections must be made in the relations deduced; these do not greatly affect their essential features, but weaken the observed effects. The distribution of the lines of force in the case of a completely polarizable positively charged particle is shown in Fig. 2 using the simplest model of a Helmholtz double layer in the form of a plate condenser. The current through the solution flows past the drop. Due to metallic conductance the potential inside the drop is everywhere constant, the external field merely causing a redistribution of the charges in the double layer. Under the influence of the external field the double layer becomes polarized so that the potential difference between metal and solution becomes greater on the right-hand side of the drop than on the left-hand side. Consider now the forces acting on a surface element ds at point B or D. The outer sheet of the double layer is subject to a force $-E_t \epsilon ds$, where E_t is the field intensity at the surface of the sphere (as is well known $E_t = \frac{3}{2}E$, where E is the intensity at a great distance from the drop); inside the metal, however, the field intensity is zero, hence the force on the inner sheet of the double layer is also zero and cannot counterbalance the force on the outer sheet, as in the case of a dielectric particle. As a result, a tangential force F_t arises as is shown in Fig. 1. On the whole, however, inasmuch as our sphere carries no free charges, the sum of the forces acting on it is zero and, therefore, the point of application of the forces acting in the opposite direction should be in another part of the sphere. This is easily seen if one considers the forces F_n normal to the surface at the points A and C. They are determined by the field intensity inside the double layer. The forces acting on the inner and outer sheets are opposite in sign. Since the curvature of the surface is slightly greater at the boundary of the inner sheet then, according to the equations of the field of a spherical condenser, the corresponding force is also slightly greater and the resultant of the forces of interaction between the charges is directed from the drop outward. Reverting to the usual terminology, one can say that the electric field, by decreasing the interfacial tension, reduces the Laplace pressure directed toward the center of the sphere. It is essential, however, that this force can be determined directly from the distribution of the electric field, without introducing the concept of interfacial tension, *i.e.*, by the same procedure as is used in the theory of ordinary electrokinetic movement. Since the density of the field of the double layer is greater on the right- than on the left-hand side of the drop, the components of the electric force normal to the surface for the surface elements near A and near C give a resultant force which coincides with the direction of the external field and is applied to the middle part of the drop. If one takes the sum of all the tangential and normal forces acting on the surface of a polarized metal drop, one gets, of course, zero. However, in contradistinction to the case of a non-conducting particle where this sum was zero for each surface element, here such a result holds only for the surface as a whole. On surface elements farther removed from the y-axis there is a predominance of the forces acting in the direction opposite to that of the field, while for the surface elements lying closer to the

y-axis there is a predominance of the forces acting in the direction of the field; the order of magnitude of these forces per unit surface area is $E\epsilon$, as was shown for the tangential force at the points B and D. In the case of a solid particle, these forces cannot affect the translatory motion of the particle as a whole, inasmuch as their sum is zero, and only give rise to strains in the particle. A different result is obtained for a liquid metal particle. The forces bring the liquid into motion which, as is easily seen, must take place as shown in Fig. 1. The viscous stresses for a drop of radius a in the surrounding medium and in the mercury are equal in order of magnitude to μ/a and μ'/a, where μ' is the viscosity of the mercury. The velocity of motion of the surface and, hence, the velocity of the movement of the particle as a whole due to reaction should therefore be equal, in order of magnitude, to $\epsilon Ea/(\mu + \mu')$. The complete hydrodynamic theory yields the more exact result:

$$U = \frac{\epsilon Ea}{2\mu + 3\mu'}, \tag{4}$$

i.e., U is of the same order of magnitude as for a drop carrying a free charge of density ϵ. In particular for a drop moving in a medium of comparatively high viscosity (like glycerine) for which $\mu \gg \mu'$,

$$U = \frac{1}{2}\frac{\epsilon Ea}{\mu},$$

i.e., the velocity acquired equals one-half the value for a liquid drop with a free charge of density ϵ. The above consideration shows that whereas, in the case of a non-conducting particle the influence of the external field on the charges of the double-layer gives rise to ordinary electrokinetic movement, in the case of a liquid metal drop it induces electrocapillary motions, which, due to the properties of the polarized double layer, make it possible to realize experimentally high values of the velocity corresponding, in order of magnitude, to the total charge of a sheet of the double layer. Although Christiansen's data cannot be utilized for a quantitative check of the relations derived, nevertheless they definitely show that the velocity of electrocapillary movement is greater than that of electrokinetic movement by several orders of magnitude. In this Institute I. Bagotzkaya recently made measurements of the deviations in an electric field of mercury droplets falling in water-glycerine solution of sodium chloride. These experiments, which are still in progress, give values of the mobility of the order of magnitude which follows from the theory here developed. Thus, for example, the mobility of a droplet of radius $a = 2.8 \times 10^{-2}$ cm. in a solution of viscosity $\mu = 2.5$ is 6×10^{-1}, whereas the ordinary electrokinetic mobility at the same viscosity would not have exceeded $\sim 3 \times 10^{-6}$ cm./sec. per volt/cm. The existence of such high mobilities in a viscous medium in which the rate of fall and the current density in the solution for a given field are small makes it possible to perform a number of interesting experiments with drops falling in an electric field. In addition to the effects described by Christiansen the following phenomena can be observed which have been investigated by I. Bagotzkaya. If the end of the capillary from which the mercury is dropping is placed between the electrodes, the application of an electric field greatly reduces the size of the drops formed; thus, a field of 8 volts/cm. caused a decrease in the diameter of the drops from 0.1 to 0.05 cm. It is possible in this manner to obtain very homogeneous, exceedingly small mercury droplets, which would be difficult to procure by other methods. If the solution in which the drops are falling is initially freed from oxygen by passing hydrogen through it, one can charge the drops positively or negatively, the charge communicated remaining practically constant throughout the time of fall, as evidenced by the rectilinear path of the drops in a homogeneous electric field. Positively charged drops are attracted to the cathode and, with a sufficiently strong field, strike it; the sign of the charge is then reversed and the drops bounce off the electrode as if reflected from it. This can be especially well observed with electrodes of platinized platinum. In a similar manner, negatively charged drops migrate toward the anode and, at certain values of the field, may reach it. In this case, however, an additional phenomenon is observed. The solution surrounding the anode is saturated with oxygen, so that the negatively charged drops can interact with the O_2 molecules and change their charge to positive before reaching the anode. This causes a change in the direction of motion and the drops recede from the anode, describing an arc, as depicted in Fig. 3. Under certain conditions, alternating changes in the sign of charge can be observed several times during the fall of one droplet.

It follows from equation (4) that the problem of determining the influence of the total charge on dynamic processes, which was formulated in the beginning of this communication, may be solved. If however, we attempted to get the greatest profit from this result and, following the procedure generally adopted in the study of electrokinetic phenomena, went over to highly dilute and weakly conducting solutions of electrolytes, in which it is easy to create comparatively strong fields, we should be somewhat disappointed. As the solution is diluted, the electrocapillary mobility falls off and finally approaches the ordinary electrokinetic values. This is the second interesting feature of these movements. The cause thereof becomes evident if we consider the motion of a mercury surface in a solution of electrolyte in the absence of an electric field, under the action of some other force, for example, gravity, as in the flow of mercury from a capillary. A mercury drop coming out of a capillary is shown in Fig. 4. If the surface of the mercury behaved say like a free water surface, then motions would arise in the mercury drop as denoted by the arrows in Fig. 4. These motions are directly related to the process of drop formation itself and, as Antweiler has shown, are actually observed when a drop of water flows out of a capillary. They must also be communicated to the solution, as shown in Fig. 4. However, such motions are not generally observed when mercury flows into an electrolyte solution. This follows in particular from the circumstance that the quantitative basis of polarographic analysis, the Ilkovič-Rideal-MacGillavry equation of the diffusion current of a dissolved substance to the surface of a growing drop, which was derived on the assumption that such motions are absent, is excellently borne out by experiment. In the derivation of this equation it is assumed that the drop grows similarly to a soap bubble or an inflated rubber balloon, *i.e.*, that all the motions take place normal to the surface. However, as was comparatively recently shown by Krjukova and Kabanov (5) tangential motions of the mercury surface caused by the flow process still do take place and radically affect the form of the polarographic curves if the mercury falls into a sufficiently concentrated solution (above 0.1 N KCl). These effects usually disappear in more dilute

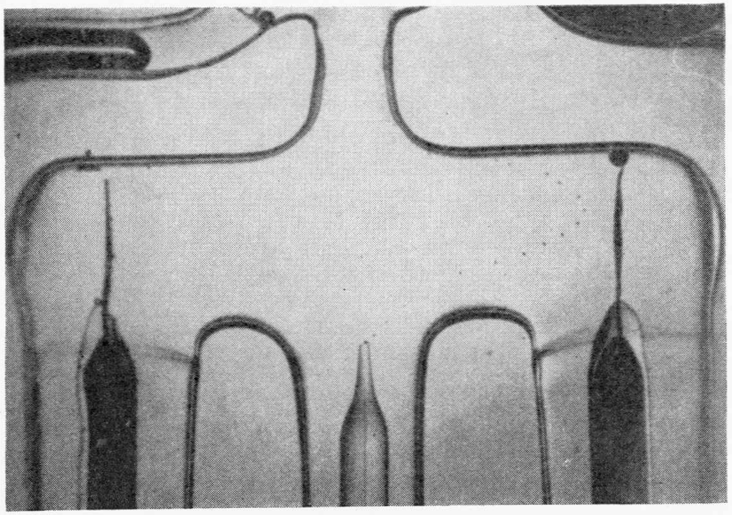

FIG. 3

Motion of Negatively Charged Mercury Drops in an Electric Field. The drops move toward the anode but, upon approach, the sign of their charge is reversed due to the action of dissolved oxygen and they change the direction of their motion.

solutions. In such systems, under certain conditions, as is well known, one can observe motions of the surface due not to the process of flow but to the inhomogeneity of the electric field of the polarizing current. These motions, which play an important rôle in polarography, should not be confused with the phenomena here described.

How can this influence of the concentration on the dynamic properties of the surface be explained? Let us examine what happens to the charges of the double layer during the motion of the surface. As is evident from Fig. 4, the flow of the liquid carries the charges to the upper part of the drop where, consequently, the charge density increases. As a result, an electric field is set up between the upper and lower parts of the drop which retards the motion of the surface. The direction of the field is shown by the double arrows in Fig. 4. This field induces an electric current in the solution which equalizes the potential difference and decreases the accumulation of charges. In sufficiently conducting solutions the potential differences are almost completely equalized and the described

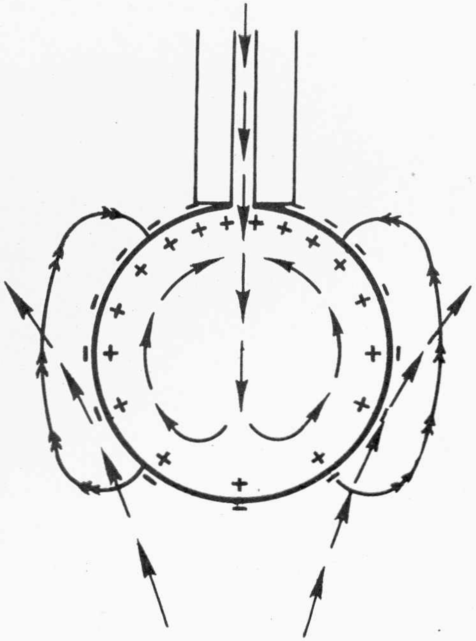

FIG. 4

Emergence of a Mercury Drop from a Capillary. The single arrows show the direction of flow of the mercury and of the solution; the double arrows—the direction of the lines of force of the electric field.

motion of the surface can develop without hindrance. On the contrary, in dilute, weakly conducting solutions, the induced potential differences almost completely stop the tangential motion and the drop actually grows like an inflating rubber balloon.

A quantitative analysis of the problem shows that the mode of motion depends on the magnitude of the dimensionless coefficient $\frac{\epsilon^2}{\kappa(2\mu+3\mu')}$, where κ is the electrical conductivity of the solution. If $\frac{\epsilon^2}{\kappa(2\mu+3\mu')} \ll 1$, *i.e.*, in the case of a weakly charged surface or well conducting solution, the damping effect is absent. If $\frac{\epsilon^2}{\kappa(2\mu+3\mu')} \gg 1$, damping sets in and the tangential motions disappear. T. Krjukova was recently able to confirm these conclusions by direct observations of the velocity of motion of the solution near the surface of growing mercury drops over a wide range of concentrations and potentials. She showed, in particular, that whereas in a normal potassium chloride solution these motions are observable at all potentials, in a 10^{-4} N KCl solution they can be observed only for very small charges in the immediate neighborhood of the electrocapillary zero and practically disappear at a distance of 0.2 volt from this point. The application of the theory to the case of falling drops also brings forth a number of interesting conclusions as, for example, that the velocity of fall of mercury drops in an electrolyte solution at constant viscosity should depend on the electrical conductivity of the solution. In a sufficiently viscous medium, such as glycerine, with an increase in conductivity, the velocity of fall should increase one and a half times. As droplets fall through a column of liquid the presence of the mobile double layers on their surface gives rise to a rather considerable electric current in the liquid whose strength increases with the electrical conductivity of the medium. These conclusions were checked quantitatively by comparison with the results of measurements of currents of falling drops by N. Bach (6).

Let us now return to the consideration of the motion of a drop under the influence of an external electric field. The motion of the surface in this case (Fig. 1) evidently leads to results analogous with the case of the motion under the influence of gravity, namely to an accumulation of charges on one part of the drop (the left-hand part here) and to their depletion in another part, *i.e.*, to the appearance of a local electric field of the drop which will counteract and weaken the external field. In this manner the "self-damping" effect arises. This effect may also be described somewhat differently by introducing the concept of the convective conductivity of the mobile charged metal surface, which weakens the external field; the final result, however, is the same.[2] A quantitative analysis of these phenomena shows that equation (4) must be corrected to account for the effect of self-damping; it then takes the following form:

$$U = \frac{\epsilon E a}{2\mu + 3\mu' + \frac{\epsilon^2}{\kappa}}. \tag{5}$$

For small values of $\frac{\epsilon^2}{\kappa(2\mu + 3\mu')}$, in particular for good conducting solutions, equation (5) goes over into (4), which was discussed above. In dilute solutions as a rule $\frac{\epsilon^2}{\kappa(2\mu + 3\mu')} \gg 1$ and equation (5) goes over into

$$U = \frac{Ea\kappa}{\epsilon} \tag{6}$$

so that the mobility should fall off rapidly with dilution. It should be observed that for a given solution expression (5) has a maximum at a certain value of the charge $\epsilon = \kappa^{\frac{1}{2}}(2\mu + 3\mu')^{\frac{1}{2}}$ so that the velocity of the drop first increases with the charge and then falls off. A maximum of the mobility was actually found in the experiments of I. Bagotzkaya.

The most interesting field of application of the theory here developed is given by the so-called polarographic maxima, which, under certain conditions, appear on the current-voltage curves of the dropping mercury electrode. Due to the varying resistance of the solution along the paths of the current and to the different conditions of supply of the substances reacting on the cathode, potential differences set in between various parts of the drop, thus inducing electrocapillary motions similar to the ones here described. Upon these are superimposed the motions which are related to the process of dropping itself. On the other hand, the existence of a definite movement affects the supply of the substances reacting at the electrode and, hence, the polarization conditions and the potential differences arising between various parts of the drop. Thus, the representation of the motions on a dropping mercury electrode on the passage of a current is far more complicated than in the case of completely polarizable drop, or even in the more general case of any drop which is not an electrode, *i.e.*, for which the currents entering the drop and going from the drop to the solution are equal. It appears however, that a consistent application of the theory here developed to the case of a

---

[2] Smoluchowski (7), Bikerman (8) and others considered a similar correction for the convective conductivity of the double layer in the theory of electrokinetic movement. In this case, however, due to small mobility, this correction is considerably smaller and should be taken into consideration only in highly dilute solutions.

dropping electrode will still help us to an understanding of all the effects involved; but this is outside the scope of the present communication.

It follows from the preceding that the presence of a double layer on the surface of a liquid metal gives rise to very well-defined easily observed effects. For solid metals the electrocapillary motions disappear and, until lately, we were limited in this case to numerous, but indirect methods of observing the influence of the double layer on the properties of the metal surface. Recently P. Rehbinder and co-workers (9) discovered a phenomenon which very strikingly demonstrates the influence of the double layer on the behavior of solid metals and consists in a lowering of the hardness by the appearance of an electric field on the surface of the metal. According to the theory of the disintegration of solid bodies, as developed by Rehbinder, any factor reducing the interfacial tension of the internal surface of the microscopic cracks which arise in the process of disintegration, lowers the hardness of the body. Hardness is understood in a generalized sense as the resistance of the body to various deformations, both elastic, brittle and plastic. This theory thus presents us with an opportunity of determining the electrocapillary curves of solid metals from the variation of the hardness with polarization. In the

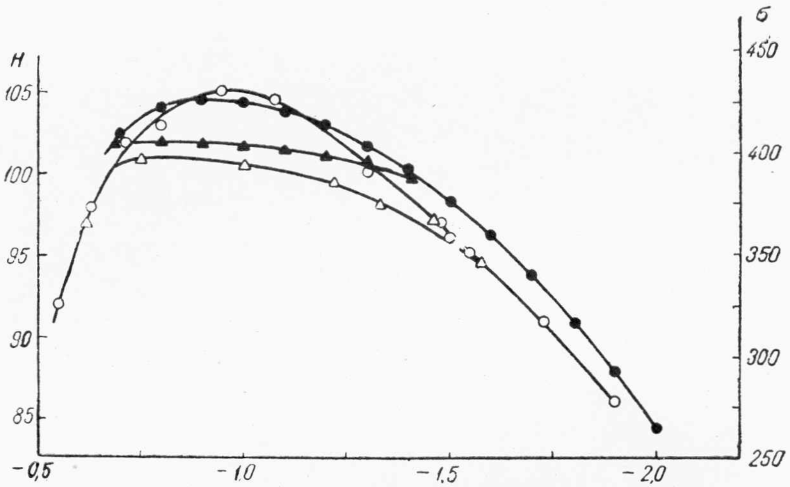

FIG. 5

Hardness, H, of Thallium and Interfacial Tension, σ, of Thallium Amalgams in Electrolyte Solutions as Functions of the Potential, φ, Referred to the Normal Calomel Electrode.

○—Hardness of thallium in 1 N Na_2SO_4,
△—The same in 1 N Na_2SO_4 + i-$C_5H_{11}OH$, 0.185 mols/liter
●—Interfacial tension of thallium amalgam (41.5% Tl) in 1 N Na_2SO_4,
▲—The same in 1 N Na_2SO_4 + i-$C_5H_{11}OH$, 0.175 mols/liter

experiments of Rehbinder and Wenstrem the hardness was measured by the decrease in the amplitude of a pendulum pressing upon the body under investigation by means of a glass ball of small radius. A drop of a conducting solution was placed on the part of the surface which came in contact with the pendulum, so that the metal could be polarized with the aid of an external electromotive force. The greater the disintegration of the metal, the greater the amount of the energy of the pendulum absorbed, and the more rapid the decrement of the oscillations. The hardness H was determined quantitatively as the reciprocal logarithmic decrement of the oscillation amplitude. The curves in Fig. 5 give the hardness as a function of the potential for metallic thallium in various solutions, according to Rehbinder and Wenstrem; for comparison are shown the electrocapillary curves of a thallium amalgam containing 41.5% of thallium, which were obtained from direct measurements of the metal-solution interfacial tension by Frumkin and Gorodetzkaya (10). The potentials are referred to the normal calomel electrode. The striking similarity between the curves of hardness and the true electrocapillary curves, which holds even for the curves of complex form observed in the presence of adsorbed organic substances, leaves no doubt that we are dealing in both cases with the same phenomenon and confirms the correctness of the views developed by Rehbinder. We should observe also that according to the data of Karpachev and Stromberg (11) obtained from measurements with molten electrolytes, the electrocapillary curves of concentrated thallium amalgams and of pure molten thallium differ comparatively little. The curves of hardness were obtained for a number of metals, as well as for graphite and tellurium (9). Table I gives the values determined up to now for the potentials at the maxima of these curves in N Na_2SO_4 solution, referred to the potential at the maximum of the electrocapillary curve of mercury in the same electrolyte. The second column gives the potentials at the maxima of the electrocapillary curves for molten metals in KCl + LiCl measured by Karpachev and Stromberg at 420–450° C. (550° C. in the case of tellurium) and referred to the maximum of the electrocapillary curve of mercury at 420° C. in the same medium.

TABLE I

	Maximum of the curve of hardness	Maximum of electrocapillary curve
Tellurium	+0.79	+0.70
Graphite (in NaCl)	+0.13	—
Mercury	—	(0.0)
Lead	−0.37	−0.37
Zinc	−0.42	−0.45
Thallium	−0.49	−0.57

The electrocapillary curve of molten carbon could not, of course, be measured but, from the dependence of the wettability on the potential, the maximum of the electrocapillary curve for graphite according to the measurements of Bruns and Chugunov (12) should be at 0.28 on our scale. As is evident from Table I, there is a satisfactory agreement between the results of measurements of the hardness and the interfacial tension of various substances. We are thus forced to the conclusion that measurements of the hardness as a function of the polarization represent an effective method of determining the point of zero charge, *i.e.*, the potential at which the charge of the double layer becomes zero and the accompanying decrease in the metal-solution interfacial tension vanishes.

The potential difference which remains between metals in electrolyte solutions when the charges of the double layers become zero should be regarded as analogous to the Volta potential between metals *in vacuo* (except for a correction related mainly to the possibility of a different orientation of the water molecules at the surface of various metals (13)). Thus, measurements of the hardness as a function of the potential allow us in a number of cases to solve the problem which has occupied electrochemists from the time of Volta's experiments and which was formulated with such remarkable lucidity by Langmuir (14), namely the determination of the extent to which the electromotive force of galvanic circuits depends on the contact potential difference between the metals.

SUMMARY

In the present communication the mechanism of certain phenomena connected with the presence of a double layer at a metal-solution interface is discussed. The forces acting on a completely polarizable metal particle placed in an electric field in electrolyte solutions are considered. It is shown that the same action of an external field on the charges of the double layer which in the case of a dielectric gives rise to the usual electrokinetic movement, induces electrocapillary movement in a liquid metal drop. The theory of these movements has been developed by B. Levich and the author. Quantitative expressions are given for the velocity of the electrocapillary movement. In highly conducting solutions or at low values of the charge this velocity approaches the velocity of a particle bearing a free charge equal to that of the inner sheet of the double layer. The nature of the damping effect exercised by the charges of the double layer on the movement of the liquid metal surface is considered. This effect brings a decrease in the mobility with increasing dilution, and the appearance of a maximum on the curve representing the velocity of movement as a function of the surface charge.

The values of the potentials corresponding to zero surface charge, as determined by Rehbinder and Wenstrem, from the relation between the

hardness of metals and polarization are compared with the values of the potentials at the maxima of the electrocapillary curves of molten metals according to Karpachev. It is shown that there is a satisfactory agreement between the results of the measurements by the two methods.

REFERENCES

1. Christiansen, *Ann. Phys.* [4] **12**, 1072 (1903).
2. Craxford, *Phil. Mag.* **16**, 268 (1933); Craxford, Gatty and McKay, *ibid.* **23**, 1079 (1937).[3]
3. Antweiler, *Z. Elektrochem.* **44**, 719, 831, 888 (1938); Stackelberg, *ibid.* **45**, 490 (1939).[4]
4. Frumkin and Levich, *Acta Physicochim. U.R.S.S.* (in print).
5. Krjukova and Kabanov, *J. Phys. Chem. (U.S.S.R.)* **15**, 475 (1941).
6. Bach, N., *Acta Physicochim. U.R.S.S.* **1**, 27 (1934).
7. Smoluchovski in Graetz, Handb. der Elektrizität u. des Magnetismus, **9**, 296 (1914).
8. Bikerman, *Z. physik. Chem.* **163**, 378 (1933); **171**, 209 (1934); *Trans. Faraday Soc.* **36**, 154 (1940).
9. Rehbinder and Wenstrem, *J. Phys. Chem. (U.S.S.R.)* **19**, 1 (1945); *Acta Physicochim. U.R.S.S.* **19**, 36 (1944) and unpublished data.
10. Frumkin and Gorodetzkaya, *Z. physik. Chem.* **136**, 451 (1928).
11. Karpachev and Stromberg, *Acta Physicochim. U.R.S.S.* **12**, 523 (1940); **16**, 331 (1942).
12. Bruns and Chugunov, *Acta Physicohim. U.R.S.S.* **18**, 351 (1943).
13. Frumkin, *J. Chem. Phys.* **7**, 552 (1939).
14. Langmuir, *Trans. Faraday Soc.* **29**, 15 (1916).

[3] The authors arrive at the conclusion that a metal particle in a field E is subject to a net force $E\theta$, where θ is the total surface charge of the metal (corresponding in our notations to $4\pi a^2\epsilon$). In reality the net electric force acting on the particle as a whole is equal to zero.

[4] Antweiler and Stackelberg came nearer than any other authors to a qualitatively correct comparison of the mechanisms of electrokinetic and electrocapillary motions. However, their assumption that the process of electrolysis on the metal-solution interface is indispensable for the appearance of electrocapillary motions is incorrect and has affected a number of their conclusions. Contrary to their assumption the best conditions for the development of electrocapillary motions are realized in the case of a completely polarizable surface.