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On the Theory of Electrocapillarity: II.

By ALEXANDER FRUMKIN.

AS Gibbs has stated, there exists a simple relation between the adsorbed quantity of a substance and the lowering effect on the surface-tension, expressed by the equation

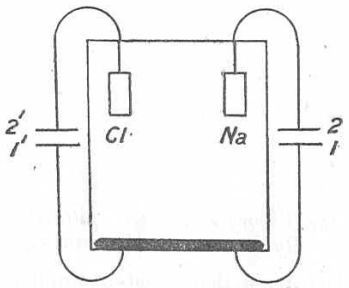
$$\Gamma = -\frac{c}{RT}\frac{\partial \gamma}{\partial c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Γ is the excess of the solute in gram-mols. per cm.^{2} of the dividing surface, c the concentration of the solute, and γ the surface-tension.

Lewis's * investigations have shown that lowering of surface-tension at a liquid/liquid interface is really accompanied by adsorption, but the observed value of T was nearly always much greater than the calculated one. Only non-electrolytes of a small molecular weight like caffeine gave satisfactory results. Lewis supposed that the observed discrepancy is due to gelatinization and to electrical effects. Unfortunately, the accuracy of Lewis's method was very limited; further experimental investigations would be of great interest.

The reasoning of Gibbs neglects the electric charge of the dividing surface. Gouy † showed that an analogous equation may be deduced for charged surfaces, if the potential difference between the two phases remains constant when the concentration of the active substance is varied. Gouy deduced therefrom that the electrocapillary curve of a solution becomes larger with increasing dilution by a constant quantity, independent of the value of γ. We will show that, using Gibbs's equation, it is possible to calculate the horizontal distance between the ascending and descending branches of electrocapillary curves at different concentrations, and that the calculated values are in fair agreement with the observed ones. We must first consider what form Gibbs's

Fig. 1.



equation will have if we take separate account of the absorption of the anion and the cation. For this purpose let us use an arrangement already employed by Chapman ‡ (fig. 1). A mercury drop and two electrodes from Na and Cl are

* Phil. Mag. (6) xv. p. 499 (1908); xvii. p. 466 (1909); *Zeit. phys. Chem.* lxxiii. p. 129 (1910).

† *Journ. de Phys.* (3) x. p. 245 (1901).

‡ Phil. Mag. (6) xxv. p. 475 (1913).

immersed in a solution of NaCl. The electrodes are connected with the mercury by means of two condensers. The potential differences between the solution and the Hg, Na, and Cl electrodes are respectively ψ, ψ_1, ψ_2. The quantity of electricity which has passed through the solution since a certain moment from 1 to 2 is E_1, and from 1′ to 2′ E_2. The concentration of the NaCl, which we shall assume to be completely dissociated, is c and the surface area of the mercury s. The state of the solution is wholly determined by the values of ψ, c, and s. If we increase s by ds, keeping ψ and c constant, and c by dc keeping ψ and s constant, the work performed will be

$$dA=\left[\gamma+(\psi-\psi_1)\frac{\partial E_1}{\partial s}+(\psi-\psi_2)\frac{\partial E_2}{\partial s}\right]ds + \left[(\psi-\psi_1)\frac{\partial E_1}{\partial c}+(\psi-\psi_2)\frac{\partial E_2}{\partial c}\right]dc,$$

whence, as ψ_1 and ψ_2 are functions of c and ψ, but not of s,

$$\frac{\partial\gamma}{\partial c}-\frac{\partial\psi_1}{\partial c}\frac{\partial E_1}{\partial s}-\frac{\partial\psi_2}{\partial c}\frac{\partial E_2}{\partial s}=0, \quad . \quad . \quad . \quad (2)$$

where

$$-\frac{\partial\psi_1}{\partial c}=\frac{\partial\psi_2}{\partial c}=\frac{RT}{cF}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When a quantity of electricity equal to $\frac{\partial E_1}{\partial s}ds$ passes from 1 to 2, $\frac{1}{F}\frac{\partial E_1}{\partial s}ds$ gram-equivalents Na enter the solution and as many gr. eq. Hg are removed from it; likewise, when a quantity of electricity equal to $\frac{\partial E_2}{\partial s}ds$ passes from 1′ to 2′, $\frac{1}{F}\frac{\partial E_2}{\partial s}ds$ gr. eq. Hg and as many gr. eq. Cl are removed from the solution. On the other hand, when the surface is increased by ds, E_1 and E_2 being constant, $\Gamma_{Na}ds$, $\Gamma_{Cl}ds$, and $\frac{\epsilon}{F}ds$ gr. eq. Na, Cl, and Hg respectively, are removed from the solution; in consequence, as ψ and c must remain constant during the increase of s,

$$\left.\begin{aligned}\Gamma_{Na}&=\frac{1}{F}\frac{\partial E_1}{\partial s}, \quad \Gamma_{Cl}=-\frac{1}{F}\frac{\partial E_2}{\partial s},\\ \frac{\epsilon}{F}&=-\frac{1}{F}\left(\frac{\partial E_1}{\partial s}+\frac{\partial E_2}{\partial s}\right)=-\Gamma_{Na}+\Gamma_{Cl}\end{aligned}\right\}. \quad . \quad (4)$$

On substituting the values of $\frac{\partial E_1}{\partial s}$, $\frac{\partial E_2}{\partial s}$, $\frac{\partial \psi_1}{\partial c}$, and $\frac{\partial \psi_2}{\partial c}$ from (3) and (4) in (2) we obtain

$$\frac{c}{RT}\frac{\partial \gamma}{\partial c} = -(\Gamma_{Na} + \Gamma_{Cl}), \quad . \quad . \quad . \quad . \quad (5)$$

i. e. Gibbs's equation.

Let us now suppose that the valency of the anion is n_A and the valency of the cation n_K; instead of (3) we must put

$$\frac{\partial \psi_1}{\partial c} = \frac{RT}{n_K c F}; \quad \frac{\partial \psi_2}{\partial c} = -\frac{RT}{n_A c F}.$$

If we express the quantities Γ in gr.. eq. per cm.^{2} equation (4) will keep its form, hence

$$\frac{c}{RT}\frac{\partial \gamma}{\partial c} = -\left(\frac{\Gamma}{n}\right)_A - \left(\frac{\Gamma}{n}\right)_K. \quad . \quad . \quad . \quad (5\,a)$$

Let us compare (5 *a*) with the equation of the electrocapillary curve

$$\frac{1}{F}\frac{\partial \gamma}{\partial \psi} = \Gamma_A - \Gamma_K.$$

I. *Descending branch.*

The mercury is charged negatively. In the surface-layer there is an excess of cations and a deficiency of anions, so that Γ_A has a negative value ; the absolute value of Γ_A is at any rate less than $c\delta$, where δ is the thickness of the surface-layer and may be neglected if the solution is a dilute one *. This agrees very well with experiment, as the form of the descending branch, at a certain distance from the maximum, does not depend on the nature of the anion. In consequence we may put $\Gamma_A = 0$, whence

$$\frac{\partial \gamma}{\partial \psi} = \frac{n_K F}{RT}\frac{\partial \gamma}{\partial \log c}.$$

The integral of this equation is

$$\gamma = f\left(\psi + \frac{RT}{n_K F}\log c\right). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If $\gamma_1 = \gamma_2$,

$$\psi_1 + \frac{RT}{n_K F}\log c_1 = \psi_2 + \frac{RT}{n_K F}\log c_2,$$

whence

$$\psi_2 - \psi_1 = \frac{RT}{n_K F}\log\frac{c_1}{c_2}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

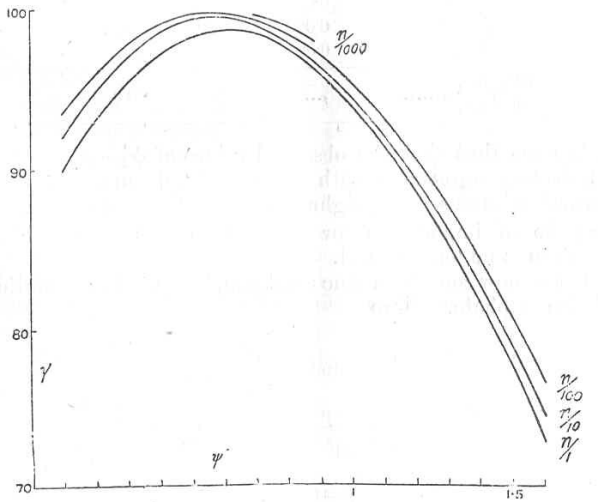
In consequence, the horizontal distance between the descending

* In fact, if $c = n/100$, $c\delta$ will be of the order 10^{-12} gr. eq./cm.^{2}, whereas the quantity $\frac{c}{RT}\frac{\partial \gamma}{\partial c}$ is of the order 10^{-10} gr. eq./cm.^{2}.

branches of two solutions, whose concentrations are c_1 and c_2, s $0{\cdot}057 \log_{10}\frac{c_1}{c_2}$ ($t = 15°$) for a monovalent cation and $0{\cdot}029 \log_{10}\frac{c_1}{c_2}$ for a bivalent one. If we take account of the incomplete dissociation, we must replace c by αc, where α is the degree of dissociation. In Table I. are given the values of $\psi_2 - \psi_1$ which correspond to different values of γ (the maximum surface-tension between mercury and water is assumed to be 100). The measurements were carried out with a capillary electrometer as described by Gouy *, the large mercury electrode being always immersed in a $n/10$ solution of KCl.

Let us now denote by ψ the potential difference between the mercury in the decinormal calomel electrode and the mercury in the capillary tube, by i the value of the curren which passes through the capillary electrometer, and by w its internal resistance. Then, obviously ψ = applied E.M.F. $- iw$. The value of w was calculated, that of i deter ined

Fig. 2.



with an Edelmann string galvanometer. The term iw could be neglected at higher concentrations, but with $n/1000$ solutions it amounted to 0·01 volt and more. The electrocapillary curves of KNO_3 are plotted on fig. 2.

* *Ann. chim. phys.* (7) xxix. p. 178 (1903).

TABLE I.

KNO_3. $t=15°$ (fig. 2).

γ.	$n-1/10\,n$.	$1/10\,n-1/100\,n$.	$1/100\,n-1/1000\,n$
99·0	...	0·045	0·049
98·0	0·037	0·051	...
95·0	0·021	0·052	...
90·0	0·022	0·048	...
85·0	0·025	0·051	...
80·0	0·035	0·052	...
75·0	0·035	...	...
$\frac{RT}{F}\lg\frac{\alpha_1 c_1}{\alpha_2 c_2}$	0·051	0·054	0·056

$Ba(NO_3)_2$. $t=15°$.

γ.	$1/10\,n-1/100\,n$.	$1/100\,n-1/1000\,n$.
99·0	0·020	0·032
98·0	0·020	0·027
97·0	0·023	0·029
95·0	0·026	...
90·0	0·022	...
86·0	0·025	...
$\frac{RT}{2F}\lg\frac{\alpha_1 c_1}{\alpha_2 c_2}$	...	0·028

We see thus that the observed values of $\psi_2-\psi_1$ are in a satisfactory agreement with the calculated ones, except for normal solutions. At higher concentrations the term T_A may be of importance, or perhaps in this case Gibbs's equation is no longer valid.

Let us now consider a zinc amalgam, immersed in a solution of zinc sulphate. Here

$$\psi=\text{const.}-\frac{RT}{nF}\log c,$$

whence

$$\psi+\frac{RT}{nF}\log c=\text{const.},$$

and

$$\gamma=\text{const.},$$

i. e. the surface-tension of the amalgam does not vary with the concentration of the solution, a result which we have already obtained in a different way.

II. *Ascending branch.*

Applying to the ascending branch a reasoning similar to the above, *i. e.* assuming T_K to be zero, we obtain the equation

$$\gamma=f\left(\psi-\frac{RT}{n_A F}\log c\right),$$

whence

$$\psi_2-\psi_1=-\frac{RT}{n_A F}\log\frac{c_1}{c_2}.$$

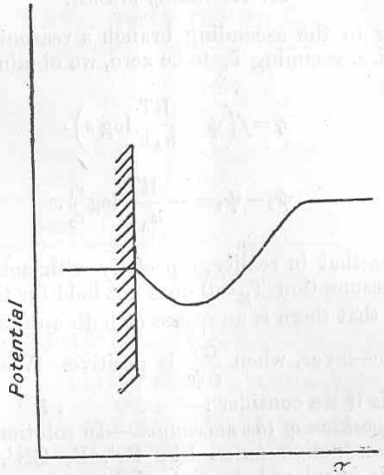
It appears that in reality, especially with active * electrolytes, the assumption $T_K=0$ does not hold for the ascending branch and that there is an excess of both anions and cations in the surface-layer, when $\frac{\partial\gamma}{\partial\psi}$ is positive. We are induced to admit this if we consider :—

(1) *The position of the maximum.*—In solutions of electrolytes with an active anion like Br′, I′, CN′, SCN′, the maximum is displaced to the right, as compared with solutions of electrolytes with an inactive anion, like NO_3', SO_4'', OH′. Thus the maximum surface-tension in $n/10$ KNO_3 corresponds to $\psi=0·57$ volt, in $n/1$ KNO_2 to $\psi=0·61$, and in $n/1$ KI to $\psi=0·87$. Let us consider the portion of the electrocapillary curve of $n/1$ KI between 0·57 and 0·87 volt, supposing that the first value of ψ really corresponds to the zero potential difference between mercury and solution. If $0·57<\psi<0·87$, $\epsilon>0$, and, in consequence, the potential of the mercury must be higher than the potential of the nearest layer of the solution; as the whole potential difference between solution and mercury is positive, the potential in the surface-layer must vary with the distance from the mercury surface in a way shown by fig. 3. The rise of potential can be caused only by free positive charges, and in consequence we must assume an excess of anions immediately at the mercury surface and at some distance from it an excess of cations, a circumstance which has already been pointed out by Gouy †.

* We call an electrolyte active if it gives an electrocapillary curve with a depressed maximum. The activity of anorganic electrolytes depends on the anion.

† *C. R.* cxxxi. p. 939 (1900).

Fig. 3.



(2) *Salts with active cations.*—Gouy * has shown that similar to the active anions Br′, I′, CN′, there exist active cations like $N(C_2H_5)_4$, $S(CH_3)_3$. The electrocapillary curves of salts of these anions have a normal ascending branch and an altered descending one. For instance, the ascending branch of a solution of $[N(C_2H_5)_4]_2SO_4$ coincides with the ascending branch of a solution of Na_2SO_4, whilst the descending branch of $[N(C_2H_5)_4]_2SO_4$ is considerably depressed. But if the anion is active, the activity of the cation manifests itself in the ascending branch as well as in the descending one. Thus, comparing the electrocapillary curve of two salts with an active anion like $N(C_2H_5)_4Br$ and KBr, we see that their ascending branches are different. We must, therefore, admit that in presence of an active anion, the cation is adsorbed even in the ascending branch.

(3) *The value of the horizontal displacement of the ascending branch.*—If $T_K > 0$,

$$\frac{n_A F}{RT}\frac{\partial\gamma}{\partial \log c} > \frac{\partial\gamma}{\partial\psi},$$

and the horizontal distance between the ascending branches of two solutions whose concentrations are c_1 and c_2 must be greater than $\frac{RT}{n_A F}\log\frac{c_2}{c_1}$.

* *Ann. chim. phys.* (8) ix. p. 87 (1906).

The experimental determination of $\psi_2-\psi_1$ presents some difficulties caused by the lack of mobility of the capillary meniscus, especially at low concentrations. The results obtained do not pretend therefore to a high degree of accuracy. Nevertheless, we may see from Table II. that the value of the displacement with SO_4'' and Cl′ is approximately equal to $\frac{RT}{n_A F}\log\frac{c_2}{c_1}$ at low concentrations, whereas with an active anion like I′ much greater displacements are observed. The same phenomenon is shown to a less degree with the Cl′ ion in a concentrated solution.

The data for H_2SO_4 were obtained in the same way as the data for KNO_3 and $Ba(NO_3)_2$ in Table I., a correction for the potential difference between H_2SO_4 and the $n/10$ KCl of the calomel electrode being made; the approximate data for NaCl and KI were calculated from the measurements of Gouy *.

TABLE II.

H_2SO_4. $t=20°$.

γ.	n–1/10 n.	1/10 n–1/100 n.
95·0	0·042	0·031
90·0	0·038	0·028
85·0	0·032	0·022
80·0	0·027	0·023
75·0	0·027	0·023
70·0	0·027	...

NaCl. $t=18°$.

90·0	0·09	0·05

KI. $t=18°$.

90·0	0·15	0·11
75·0	0·09	...

III. *The maximum.*

In the neighbourhood of the maximum T_A and T_K are quantities of the same order of magnitude, and no definite inference can be drawn from (5 *a*). A very interesting attempt to find out the equation of that portion of the electrocapillary curve was made by Chapman †. Assuming that the ions in the surface-layer are in equilibrium under the

* *Ann. chim. phys.* (7) xxix. p. 145 (1903).
† *Loc. cit.*

influence of osmotic and electrostatic forces, he calculated the distribution of potential in the surface-layer and the value of ϵ for a given potential difference between mercury and solution. The resulting equation of the electrocapillary curve is

$$\gamma_{\text{Max.}}-\gamma=\frac{2RT}{F}\sqrt{\frac{Kp}{2\pi}}\left(e^{\frac{FV}{4RT}}-e^{-\frac{FV}{4RT}}\right)^2, \quad . \quad . \quad (8)$$

where K is the specific inductive capacity of water, p the osmotic pressure of the ions in the bulk of the solution, and $V=\psi-\psi_{\text{Max.}}$ As Chapman's reasoning involves the assumption that the ions in the double layer behave like perfect gases, equation (8) especially at higher concentrations can be used only for small absolute values of V. It seemed to me therefore of interest to test eq. (8) in the neighbourhood of the maximum. Table III. contains the experimental values of $\gamma_{\text{Max.}}-\gamma$ in c.g.s. units for KCl, KNO_3, and Na_2SO_4, and the values calculated by means of equation (8), assuming $K=81$, $t=18°$, and $p=\alpha cRT$, where α is the degree of dissociation of KNO_3. Moreover, Table III. contains values of $\gamma_{\text{Max.}}-\gamma$ calculated by means of the classical formula

$$\gamma_{\text{Max.}}-\gamma=aV^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

a being determined from the value of $\gamma_{\text{Max.}}-\gamma$ which correspond to $V=1$ volt.

Table III. shows a very great discrepancy between the calculated and the observed values: the influence of concentration is much less pronounced, as it ought to be according to (8); moreover, $\gamma_{\text{Max.}}-\gamma$ is approximately proportional to V^2. Thus, the results of experiment are unfavourable to Chapman's assumption concerning the conditions of the equilibrium in the double layer. As Chapman's reasoning is thermodynamically correct, equation (8) must be in agreement with (6). In fact, for great values of V, we have

$$\gamma_{\text{Max.}}-\gamma=\frac{2RT}{F}\sqrt{\frac{Kp}{2\pi}}e^{\frac{FV}{2RT}}=\text{const.}\sqrt{c}\,e^{\frac{FV}{2RT}}=\text{const.}\,e^{\frac{F}{2RT}\left(V+\frac{RT}{F}\lg c\right)}.$$

With the help of equation ($5a$) we may calculate the value of absorption of any ions, except those of mercury, as we cannot vary their concentration without varying ψ. It is easy to give to the equation of the electrocapillary curve

$$\frac{\partial\gamma}{\partial\psi}=\epsilon+\Gamma_{Hg}F$$

TABLE III.

Calcul. by means of (8). KNO_3.

V \ c	0·05 v.	0·1 v.	0·15 v.
n.	2·67	13·8	...
n/10.	0·96	4·96	...
n/100.	0·32	1·67	5·57
n/1000.	0·10	0·54	1·79

Calcul. by means of (9). KNO_3.

V \ c	0·05 v.	0·1 v.	0·15 v.
n.	0·28	1·14	...
n/10.	0·26	1·03	...
n/100.	0·22	0·90	2·02

Observed KNO_3.

V \ c	0·05 v.	0·1 v.	0·15 v.
n.	0·34	1·36	...
n/10.	0·29	1·20	...
n/100.	0·25	0·98	2·3

Observed KCl.

V \ c	0·05 v.	0·1 v.	0·15 v.
n/10.	0·43	1·38	...
n/100.	...	0·85	2·2
n/1000.	0·37	...	...

Observed Na_2SO_4.

V \ c	0·05 v.	0·1 v.	0·15 v.
n/10.	0·34	1·35	...
n/100.	0·34	1·0	2·35

the form of an equation of adsorption of mercury ions. In fact, let us put

$$d\psi=-\frac{RT}{nF}\frac{dc}{c},$$

then

$$\frac{c}{RT}\frac{\partial\gamma}{\partial c}=-\frac{1}{n}\left(\frac{\epsilon}{F}+\Gamma_{Hg}\right),$$

a formula quite analogous to ($5a$).

Laboratory of Physical Chemistry,
The University, Odessa.

P.S.—After this paper was already forwarded to the editors we received here Gouy's article (*Ann. Phys.* (9) viii. p. 129, 1917), where similar considerations are developed.