

Significance of the Electro- capillary Curve

BY

A. FRUMKIN

АКАДЕМИЯ НАУК СССР
Институт Электрохимии
г. Москва В-71
Ленинский пр. дом № 31

REPRINTED FROM COLLOID SYMPOSIUM ANNUAL

COPYRIGHTED 1930, BY HARRY B. WEISER

SIGNIFICANCE OF THE ELECTROCAPILLARY CURVE

By A. FRUMKIN

APPLYING Gibbs'¹ theory of surface equilibria to the interface mercury-solution it is easy to show² that the following relation must hold:

$$d\sigma = Ed\phi - \sum \Gamma_i d\mu_i \quad (1)$$

In equation (1), σ is the interfacial tension, ϕ the potential difference between solution and mercury, and E the charge carried by the amount of mercury ions which must be introduced in the solution in order to keep ϕ constant when the mercury-solution interface is increased by 1 sq. cm. The quantities Γ_i and μ_i are the surface densities and thermodynamic potentials of the different independent components of the solution, with the exception of the mercury ion, as the term $Ed\phi$ is substituted in equation (1) for the term $-\Gamma_{\text{Hg}_2} d\mu_{\text{Hg}_2}$. There is no term in (1) relating to water as we fix the position of the interface assuming that the surface density of water $\Gamma_{\text{H}_2\text{O}}$ is equal to zero. If we change ϕ (*i.e.*, the concentration of mercury ions, which is supposed to be low) polarizing a mercury meniscus in a capillary tube, but keep the concentrations of the other components constant, equation (1) reduces to the well-known Lippmann-Helmholtz equation of the electrocapillary curve

$$\frac{\partial \sigma}{\partial \phi} = E \quad (2)$$

This relation could be tested by different methods³ and the experimental results have been found to be in satisfactory agreement with the theory.

The value of ϕ which makes $\frac{\partial \sigma}{\partial \phi}$ and E equal to zero presents a special interest. We shall denote this value by ϕ_{max} . The numerical values of ϕ_{max} (and in general all ϕ values) given in this paper are referred to a

¹ "The Collected Works of J. W. Gibbs," Longmans, Green and Co., 1, 230 (1928).

² Frumkin: *Ergebnisse der exakten Naturwissenschaften*, 7, 239-241 (1928).

³ Frumkin: *Z. physik. Chem.*, 103, 55 (1922); Schofield: *Phil. Mag.*, 50, 641 (1926).

normal calomel electrode. A zero value of E means that on formation of a fresh mercury surface neither do mercury ions disappear from the solution, nor are they sent into the solution; at this particular point the mercury surface carries therefore no charge. Making this statement, we really use the word "charge" as an abbreviation for "charge acquired by the metal surface through a process of exchange of ions between the metal and the solution." The relation between the change of the concentration of mercury in the solution and the charge of the mercury surface was stated for the first time by Nernst⁴. Krueger⁵ suggested that although E is equal to zero at the point $\phi = \phi_{\max}$, the mercury surface can still be negatively charged, the mercury adsorbing an amount of mercury salt, equivalent to the amount of mercury ions which have been sent into the solution by the mercury. It could be shown,⁶ however, that the concentration of mercury in the solution at the maximum point is far too small to account for such an adsorption; the assumption of a zero charge of the mercury surface at the maximum of the electrocapillary curve seems therefore to be completely justified. Determinations of electrocapillary curves have been carried out for various solutions by different investigators,⁷ and especially by Gouy.⁸ They show that the value of $\phi_{\max}$ changes strongly with the composition of the solution. This means that the potential difference between the solution and the mercury does not vanish when the mercury surface is not charged, at least not in all cases. Gouy has shown⁹ that these effects can be explained on the basis of adsorption of ions and molecules present in the solution. This theory has been developed by the present author. It is the aim of this paper to give a brief review of what we can learn about adsorption and orientation of ions and molecules from determinations of $\phi_{\max}$.

I. INORGANIC ELECTROLYTES

The position of the maximum of the electrocapillary curve in solutions of inorganic salts is determined by the nature of the anion. The

⁴ Beil: Wied. Ann., 58 (1896); Z. Elektrochem., 4, 29 (1897).

⁵ Nachr. Ges. Wiss. Göttingen, Math. physik. Kl., 33 (1904); Krüger and Krumreich: Z. Elektrochem., 19, 617 (1913).

⁶ Frumkin: loc. cit., 3, 64.

⁷ Paschen: Wied. Ann., 41, 42, 177 (1890); 43, 568 (1891); Smith: Phil. Trans. Roy. Soc., 193, 47 (1900); Rothmund: Z. physik. Chem., 15, 1 (1894); Meyer: Wied. Ann., 45, 508 (1892); 53, 845 (1894); 56, 680 (1895); 67, 733 (1899); Z. physik. Chem., 70, 315 (1910).

⁸ Ann. chim. phys., (7) 29, 145 (1903); (8) 8, 291 (1906); (8) 9, 75 (1906).

⁹ Ann. phys., (9) 7, 129 (1917).

cation does not exert a marked influence except in the case of small differences which are observed between the curves of some acids and their salts. The character of the influence of the anion can be illustrated in a convenient way by Fig. 1, which is taken from Gouy. There is a large group of salts which raise the maximum value of the interfacial tension $\sigma_{\max}$ above the value observed in pure water, or at least do not cause a marked lowering of $\sigma_{\max}$. Carbonates, phosphates, arsenates, sulphates and hydroxides belong to this group. The values of $\phi_{\max}$ which are observed in normal solutions of these salts lie between the limits 0.47 and 0.52 volt. Salts of other anions lower $\sigma_{\max}$ more or less and cause a shift of the maximum toward increasing values of ϕ , as is shown in Fig. 1. The following values of $\phi_{\max}$ are observed in normal solutions of some salts: NaClO₄ 0.55, KCl 0.56, KNO₃ 0.56, KBr 0.65, KCNS 0.72, KI 0.82, K₂S 0.92. The depression of the maximum shows that in these solutions there is a positive adsorption of the salt on an uncharged surface of mercury. The fact that as a result of this adsorption the maximum is shifted toward increasing values of ϕ can be explained if we assume that the adsorbed salt forms a double layer at the mercury-water interface, its anions being turned toward the mercury phase. This theory which was proposed by Gouy accounts also for the difference in the rôle of the

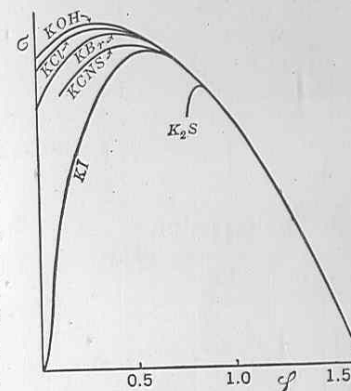


FIG. 1.—Electrocapillary curves of solutions of different inorganic electrolytes.

cation and the anion, as the anions are held in this double layer by specific adsorptive forces, whereas the cations are electrostatically attracted by the negative charges of the anions. It is interesting to compare the order of adsorbability of anions at the mercury-water interface which can be determined in this way from electrocapillary measurements with the order of adsorbability at the water-air interface. The author, using an electrostatic method showed¹⁰ that the surface of many salt solutions are negatively charged at higher concentrations compared to pure water, indicating the presence of an excess of anions in the outer part of the surface layer. The results of these electrostatic measurements were corroborated by measurements of surface tension. The

¹⁰ Z. physik. Chem., 109, 34 (1924); Frumkin, Reichstein and Kulvarskaja: Kolloid-Z., 40, 9 (1926).

following order of increasing adsorbability of anions at the air-water interface was established:



It is probable that this is also the order of decreasing energies of hydration of the ions, at least for ions of a similar structure. If we compare the behavior of anions at the two interfaces water-air and water-mercury we see that for many ions the order of increasing adsorbability is the same in both cases. With other ions, however, there is a pronounced specific influence of the mercury surface. The most striking example is given by the S'' anion which is at the beginning of the series in the case of the air-water interface and at the end of the series in the case of the mercury-water interface. The adsorbabilities of the halogen ions compared to the NO_3' and ClO_4' ions are also much greater in contact with mercury.

II. ORGANIC COMPOUNDS

Solutions of organic non-electrolytes have been extensively investigated by Gouy¹¹ and some additional measurements have been carried

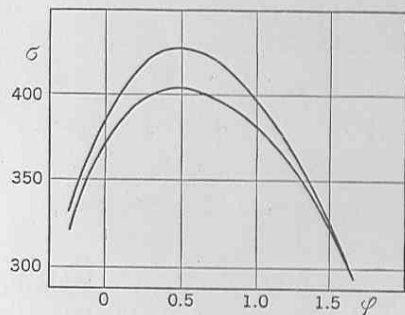


FIG. 2.— $n\text{Na}_2\text{SO}_4$ and $n\text{Na}_2\text{SO}_4 + \text{Saccharose}$.

out by the author in collaboration with Donde and Kulvarskaja. It is convenient to compare the electrocapillary curve, which is observed after the addition of the organic substance, with the original curve of the solution which contains the inorganic electrolyte only. This is shown in Figs. 2, 3, and 4. So far as the position of the maximum is involved, the organic substances can be divided into three classes: (1) those which do not materially change the value of ϕ_{max} (Fig. 2); (2) those which shift the maximum to smaller values of ϕ (Fig. 3); (3) those which shift it to larger values of ϕ (Fig. 4). The shape of the curves which is observed in solutions of organic substances is sometimes quite characteristic, as is shown by Fig. 3. This indicates that the adsorption of the organic molecule varies strongly with the surface charge of the mercury. A mathematical treatment of this problem has been given by the author,¹²

¹¹ Ann. chim. phys., (7) **29**, 145 (1903); (8) **8**, 291 (1906); (8) **9**, 75 (1906).

¹² Z. Physik., **35**, 792 (1926); Frumkin and Obrutschewa: Biochem. Z., **182**, 220 (1927); Obrutschewa: *Ibid.*, **207**, 25 (1929).

but it will not be discussed in this paper. The observed shift of the maximum shows that the existence of an adsorbed layer of molecules of substances belonging to groups

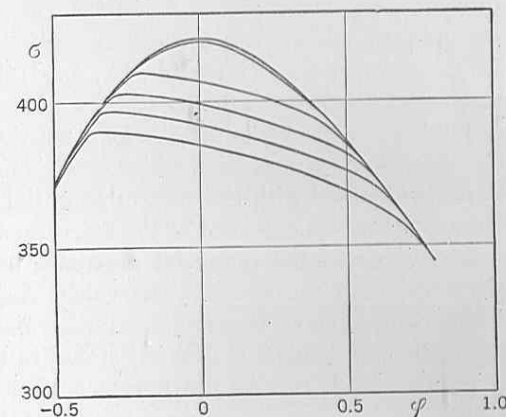


FIG. 3.— $n\text{NaCl} + x\text{C}_6\text{H}_{11}\text{OH}$ $x = 0, \frac{1}{10}, \frac{1}{5}, \frac{1}{2}, 1, 2, 4$ mols per liter.

2 and 3 produces a potential difference between the mercury and the solution. This was pointed out for the first time by Gouy. If we disregard the effect caused by the water molecules themselves, this potential difference is positive for group 2 (positive end of the molecule turned toward the mercury), and

negative for group 3 (negative end of the molecule turned toward the mercury). It was shown by the experiments of Kenrick,¹³ Guyot,¹⁴

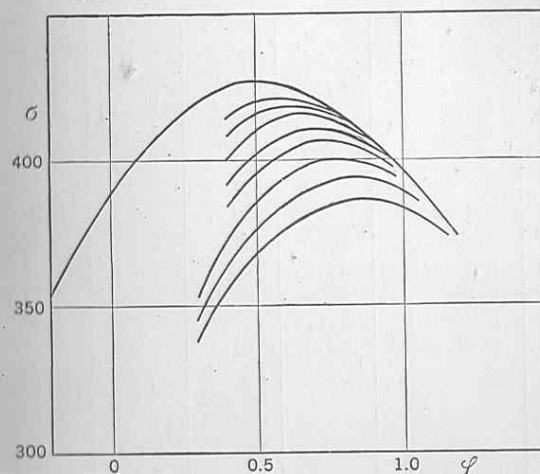


FIG. 4.— $n\text{H}_2\text{SO}_4 + x\text{CS}(\text{NH}_2)_2$ $x = 0, \frac{1}{8}, \frac{1}{4}, \frac{1}{2}, 1, 2$ mols per liter.

and by those of the author¹⁵ that the adsorption of organic compounds at the air-water interface gives rise to similar electric effects and it seemed worth while to compare the results obtained in both cases. A computation of the available data carried out by the author¹⁶ some time ago is reproduced in Table I. Δ is the lowering of the surface tension of water by the dis-

¹³ Z. physik. Chem., **19**, 625 (1896).

¹⁴ Ann. phys., (10) **2**, 501 (1927).

¹⁵ Z. physik. Chem., **111**, 190 (1924); **116**, 485 (1925); **123**, 321 (1926); Cf. also, Frumkin and Williams: Proc. Nat. Acad. Sci., **15**, 400 (1929).

¹⁶ *Loc. cit.*, **2**, 258-264; a few misprints which occur in this paper have been corrected here. Cf. also, Harkins and Ewing: J. Am. Chem. Soc., **42**, 2539 (1920).

solved substances and ϵ is the potential difference at the air-solution interface, assuming a zero value for the potential difference between air and pure water. Δ_{Hg} and ϵ_{Hg} represent the corresponding quantities for the mercury-water interface, *i.e.*, Δ_{Hg} is the lowering of the maximum interfacial tension, caused by the organic substance and ϵ_{Hg} the difference between the value of ϕ_{max} in a solution of an inactive electrolyte (Na_2SO_4) and in a solution which contains the organic substance. The latter is identical with the drop of potential connected with the layer of organic molecules adsorbed at the mercury-water interface, if we ascribe a zero value to the potential difference mercury—pure water at the electrocapillary maximum. The values Δ_{Hg} and ϵ_{Hg} refer to solutions which contain some electrolyte, as otherwise the determination of ϕ_{max} would be impossible. If it is not stated to the contrary this electrolyte is normal Na_2SO_4 . As the presence of the electrolyte influences the activity of the dissolved organic substance, the comparison between the values of Δ and ϵ and the values of Δ_{Hg} and ϵ_{Hg} can be only semi-quantitative. The numerical values given in Table 1 have been taken from different sources. A list of references is given below.¹⁶

TABLE 1

Substance	Concentration	Δ	Δ_{Hg}	ϵ	ϵ_{Hg}
Methyl alcohol.....	molar	7.2	3.3	0.10	0.02
Ethyl alcohol.....	molar	15.9	9.5	0.23	0.08
Propyl alcohol.....	molar	29.1	31.0	0.32	0.24
Iso-amyl alcohol.....	0.1 molar	30.0	31.0	0.25	*~0.25
Tertiary amyl alcohol.....	0.1 molar	20.4	22.6	0.29	0.35
Allyl alcohol.....	molar	21.5	24.2	0.26	0.15
Acetic acid.....	2 molar	17.3	12.2	0.22	0.00
Propionic acid.....	molar	25.0	23.3	0.27	0.11
Normal butyric acid.....	saturated			~0.35	0.14
Normal caproic acid.....	0.07 molar	39.0	36.8	0.34	0.21
			(+0.3 normal KNO_3)		
Ether.....	saturated	~43	29.3	~0.52	≥ 0.38
Ethyl acetate.....	saturated			~0.58	≥ 0.43
Acetone.....	molar	17.4	15.2	0.38	0.25
Paraldehyde.....	saturated			0.36	~0.45
Ammonia.....	molar	2.4	2.4	0.08	0.02
Triethyl amine.....	0.1 molar	22.2	32.3	0.53	~0.35
			(without Na_2SO_4 addition)		
Glycol.....	molar	3.1	7.1	0.10	0.03

* This symbol ($\sim$) means approximate value.

TABLE 1.—Continued

Substance	Concentration	Δ	Δ_{Hg}	ϵ	ϵ_{Hg}
Glycerine.....	molar	0.4	9.3	0.02	0.005
Saccharose.....	molar	-2.0	23.8	0.002	0.00
Oxalic acid.....	0.1 molar	0.3	1.6	-0.004	-0.04
Malonic acid.....	molar	4.2	11.8	-0.006	-0.055
Benzene.....	saturated	~13.	23.1	0.01	0.11
Phenol.....	0.1 molar	11.6	36.6	0.03	-0.15
<i>p</i> -Cresol.....	0.1 molar	20.8	50.0	0.01	-0.20
<i>o</i> -Cresol.....	0.1 molar	28.6	51.5	0.26	-0.29
Anisol.....				0.17	-0.05
				(0.02 molar)	(satu- rated)
Pyrocatechol.....	0.1 molar	3.0	29.7	-0.01	-0.18
Hydroquinone.....	0.1 molar	1.1	28.0	-0.03	-0.20
Resorcinol.....	0.1 molar	2.1	29.7	-0.04	-0.22
Pyrogallol.....	molar	12.7	40.8	-0.05	-0.25
Aniline.....	0.01 molar	0.3	17.4	0.01	-0.03
Aniline.....	0.1 molar	8.0	46.8	0.12	0.02
<i>o</i> -Toluidine.....	saturated		40.8	0.30	0.05
Nitrobenzene.....	0.007 molar			0.03	-0.25
Benzoic acid.....	0.01 molar	2.0	22.9	0.08	-0.05
<i>o</i> -Phthalic acid.....	0.01 molar			0.02	-0.15
Benzyl alcohol.....	saturated	*~30.0	54.9	0.33	0.11
Benzylamine.....	saturated		61.3	~0.50	~0.35
Chloroform.....	saturated	~19.0	20.8	~-0.05	-0.2
Chloral hydrate.....	molar			-0.37	~-0.35
Chloroacetic acid.....	molar	12.2	24.6	-0.10	-0.09
Trichloroacetic acid.....	molar	22.6	33.6	-0.42	~-0.25
Bromoacetic acid.....	molar	12.6	38.9	-0.09	~-0.2
β -Chloropropionic acid.....	0.1 molar		14.1	0.02	-0.02
β -Iodopropionic acid.....	0.2 molar		73.1		-0.32
Ethyl iodide.....	saturated		39.7	~0.0	-0.35
β -Chlorobutyric acid.....	0.25 molar		44.6		0.02
Urea.....	molar	-0.3	7.5	0.001	-0.05
Thiourea.....	molar	-0.1	39.7	-0.03	-0.36
			(+ normal H_2SO_4)		
Thioacetic acid.....	0.35 molar		35.0		-0.32
α -Thiolactic acid.....	0.15 molar		40.5		-0.07
Tetra propylammonium chloride	0.1 molar	3.4	16.4	0.24	0.24
			(without Na_2SO_4 addition)		

* This symbol ($\sim$) means approximate value.

The following conclusions can be drawn from Table 1: Aliphatic oxygen compounds with one polar group (alcohols, acids, ethers, esters, ketones) being adsorbed give rise at both interfaces to positive potential differences between the outer phase and the solution. The adsorption and the electric effect are larger at the air-water interface. The difference is greater for acids than for alcohols and decreases with increasing length of the chain. The compounds which contain a sufficient number of carbon atoms exert a very similar action on the mechanical and electrical properties of both interfaces. This shows that the structure of the surface layer must be the same in the two cases. This conclusion is supported by the calculation of the amount adsorbed in the more concentrated solutions.¹⁵ We must assume therefore that at the mercury-water interface there exists the same orientation which is known to exist at the air-water interface, *i.e.*, the polar group must be turned toward the water and the hydrocarbon chain toward the mercury. The introduction of a higher number of polar groups in the molecule of an organic compound lowers, as it is well known, its adsorbability at the air-water surface. This decrease of the adsorbability is much less pronounced at the mercury-water interface. The difference is especially noticeable in the case of saccharose, which is negatively adsorbed at the air-water interface, and positively adsorbed (strongly) at the mercury-water one. The adsorption of saccharose does not give rise to a positive potential difference between mercury and water. We must conclude, therefore, that the orientation of the molecule, which is to be considered as the cause of the electric effect has, disappeared in that case. It is probable that the saccharose molecules lie flat at the mercury-water interface, the polar group of the molecule having the possibility to approach the mercury surface. The interaction between the polar groups and the metal causes an increase of the work of adsorption which partly counterbalances the influence of the increased affinity toward the solvent, which made the adsorption negative in the case of the air-water interface. The adsorption of dibasic acids at the air-water interface causes a slightly negative potential difference between the air and the water. This negative effect is much more pronounced in the presence of mercury. We shall see that this is a general phenomenon: the presence of mercury favors in many cases that kind of orientation of the adsorbed molecule which gives a negative value of ϵ_{Hg} . Thus, different phenols which behave in a rather different way at the air-water interface, the univalent phenols giving positive and the polyvalent negative effects, all give very large negative effects and a much greater lowering of interfacial tension at the mercury-water interface. It can also be shown that the adsorbed molecules are much more closely packed in the latter case. Also, the

presence of mercury strongly reduces the differences in the behavior of isomers which are observed at the air-water interface (*cf.* the data for the two cresols and the three dioxybenzols). It would appear that the occurrence of the negative potential difference is connected with the presence of a polar group in the molecule, as benzene itself gives a positive value of ϵ_{Hg} . Although it is difficult at the present moment to give an adequate picture of the structure of these surface layers, it seems hardly possible to account for the high adsorbability of the polyvalent phenols at the mercury-water interface in any other manner than to assume that the polar groups of the phenol molecule are attached to the mercury surface. A similar behavior is indicated in the case of the adsorption of phenols by charcoal.¹⁷ With aniline the value of ϵ_{Hg} changes from negative to positive when the concentration is increased. The shape of the electrocapillary curve which is observed with aniline solutions also indicates that two different orientations of the aniline molecule at the mercury-water interface are possible, one of them giving a positive, and the other a negative effect.

Benzoic acid, benzyl alcohol and benzylamine are all more strongly adsorbed at the mercury-water interface than at the air-water interface; with benzoic acid as with the phenols, the electric effect is negative in the first case and positive in the second case. The specific influence of the mercury surface manifests itself also when halogenated compounds are adsorbed. Many of these give negative values of ϵ , which shows that in the surface layer of their solutions the negatively charged halogen atom is turned outward. The ϵ_{Hg} values of substances belonging to this group are negative too, but the lower of the interfacial tension is very much larger when the adsorption occurs at the water-mercury interface. In the case of iodine compounds an enormous lowering of the interfacial tension is observed. This behavior is in complete agreement with the behavior of the iodine ion. If the length of the hydrocarbon chain is increased, the ϵ_{Hg} (and ϵ) values become positive, showing that the hydrocarbon chain occupies the space available in the surface layer and pushes the halogen atom out.

Sulphur compounds, like iodine compounds, are very strongly adsorbed at the mercury-water interface (compare the behavior of the S^{2-} ion).¹⁸ The case of thiourea which raises the surface tension of water, but causes a great lowering of the interfacial tension and a large negative electric effect at the mercury-water interface, is especially interesting. The adsorption of thiourea at the surface of mercury appears to be in many respects a process quite similar to the formation

¹⁷ Frumkin: *Rec. trav. chim.*, **48**, 288 (1929).

¹⁸ *Cf.* Frumkin: *Kolloid-Z.*, **47**, 229 (1929).

of a complex compound between the mercury ion and the thiourea in a homogeneous solution.

To summarize, we can say that whereas in some cases the structure of the layer adsorbed at both interfaces is practically the same, in other cases large differences are observed, caused by a specific interaction between the mercury surface and definite constituents of the molecule. A negative charge of the part of the molecule which is turned toward mercury seems to favor the possibility of such an interaction.

III. NON-AQUEOUS SOLUTIONS

As various dissolved substances affect the value of $\phi_{\max}$ it is natural to assume that the molecules of the solvent can act in a similar way. It appeared therefore worth while to determine the value of $\phi_{\max}$ in non-aqueous solutions and to compare the results obtained with those which are observed in aqueous solutions of the same electrolytes.¹⁹ The ϵ_{Hg} values in Table 2 indicate the shift of the maximum caused by the substitution of the non-aqueous solvent for water under those conditions when there is no adsorption of the electrolyte. The calculation of these values involves some assumptions which may make them uncertain by a few centivolts; nevertheless there can be no doubt that the position of the maximum depends on the nature of the solvent. The E values have been obtained by comparing the potential difference air-organic solvent with the potential difference air-water.²⁰ The substitution of the alcohols and of acetone for water exerts a similar influence in both cases, just as we should expect from the data given in Table 1.

TABLE 2

	ϵ	ϵ_{Hg}
Methyl alcohol.....	0.38	0.13
Ethyl alcohol.....	0.38	0.20
Acetone.....	0.57	0.33

Table 2 shows also that in absence of any dissolved capillary active substance the molecules of the solvent itself can give rise to a difference of potential between the solution and the mercury which makes the determination of the so-called absolute zero of potential with the help of electrocapillary methods impossible.

¹⁹ Frumkin: Z. physik. Chem., **103**, 43 (1922); *Loc. cit.*, **2**, 267.

²⁰ Z. physik. Chem., **111**, 190 (1924); **116**, 485 (1925); **123**, 321 (1926); *Cf. also*, Frumkin and Williams: Proc. Nat. Acad. Sci., **15**, 400 (1929).

IV. ELECTROCAPILLARY CURVES OF AMALGAMS AND OTHER METALS

Electrocapillary curves of dilute amalgams of different metals have been investigated by Rothmund,²¹ Gouy,²² and Christiansen.²³ They found that these curves do not differ markedly from the curve of pure mercury, and on this basis it was often assumed that the position of the point of zero charge is independent of the nature of the metallic phase. But with a more concentrated amalgam of a Bi + Pb + Sn alloy Gouy observed a marked shift of $\phi_{\max}$ and a similar shift was found by

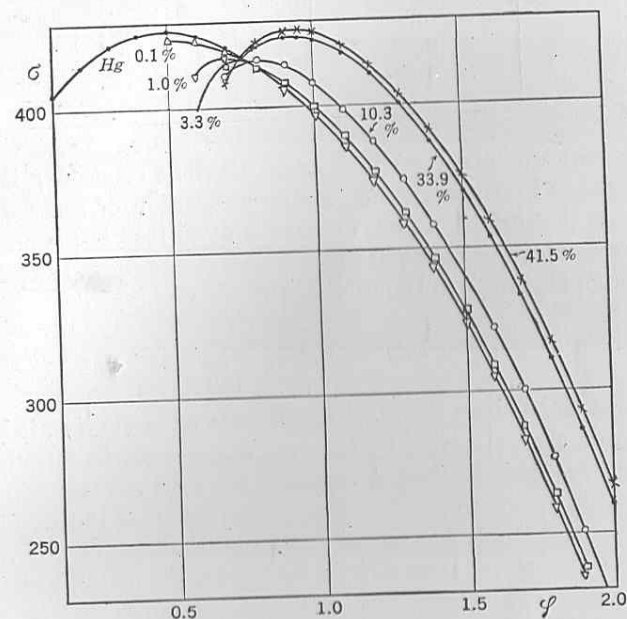


FIG. 5.—Hg and Tl amalgams with 0.1%, 1.0%, 3.3%, 10.3%, 33.9%, and 41.5% Tl in $n\text{Na}_2\text{SO}_4$.

Rothmund in the case of a thallium amalgam. Rothmund ascribed it, to be sure, to secondary effects. Frumkin and Gorodetskaya²⁴ made an extensive study of the behavior of Tl-amalgams in different solutions and found that an addition of thallium causes a large increase of $\phi_{\max}$ as is shown by Fig. 5 and by the first and second columns of Table 3,

²¹ *Loc. cit.*, **7**.

²² Ann. Phys., (9) **6**, 5 (1916).

²³ Drud. Ann., **16**, 382 (1905).

²⁴ Z. physik. Chem., **136**, 451 (1928).

which gives the values of $\phi_{\max}$ observed with different amalgams in normal Na_2SO_4 solution.

TABLE 3

Per Cent Tl	$\phi_{\max}$	Point of Zero Charge from Dropping Electrode Measurements
0	0.48	
1.0	0.67	0.668
3.35	0.73	
10.35	0.80	0.792
33.9	0.92	0.898
41.5	0.93	

A similar shift was observed with quite different solutions; it cannot therefore depend on a difference in the adsorption of some dissolved substance at the surface of pure mercury and on that of the amalgams. The application of the Gibbs' theory of surface equilibria to the case of a thallium amalgam gives the relation:²⁵

$$d\sigma = E dy - \Gamma_{\text{Tl}} d\mu_{\text{Tl}} - \Sigma \Gamma_i d\mu_i \quad (3)$$

The quantity E has here the same significance as in (1), *i.e.*, it is equal to the electric charge carried by the ions which must be introduced in the solution in order to keep ϕ constant for unit increase of surface. In this equation μ_{Tl} is the thermodynamic potential of the thallium in the amalgam and Γ_{Tl} is the surface density of thallium or the amount of thallium adsorbed per unit surface, both from the metallic phase and from the solution. The theoretical development shows that an adsorption of the thallium ion cannot be distinguished from the adsorption of thallium dissolved in mercury by experiment. The position of the interface is defined by the condition $\Gamma_{\text{Hg}} = 0$. Making certain assumptions it is possible to give by means of equation (3) a complete mathematical treatment of the electrocapillary curves observed with amalgams of different thallium content, but we shall consider here only the simplest case. If the constitution of the amalgam and the solution do not vary, equation (3) reduces as in the case of a pure metal to the Lippman-Helmholtz equation:

$$\frac{\partial \sigma}{\partial \phi} = E$$

²⁵ Z. physik. Chem., **136**, 451 (1928).

The validity of this equation in the case of amalgams has been tested by F. J. Cirves at the University of Wisconsin.²⁶ The method used was that of "null solutions," which has been worked out by Palmaer²⁷ and Smith and Moss.²⁸ Adding increasing quantities of a thallium salt to a Tl free solution it is possible to find a concentration of Tl ions for which the potential difference between a dropping amalgam electrode and still amalgam is zero. An increase in the amalgam surface at this point causes no change of the concentration of Tl ions in the solution, *i.e.*, the quantity E is equal to zero. This is the so-called null solution. By determining the e.m.f. of the cell, normal calomel electrode/null solution amalgam, and comparing it with the value of $\phi_{\max}$ we can test the validity of equation (2). Some of the results obtained by Cirves are summarized in the third column of Table 3. The measurements have been carried out in an hydrogen atmosphere. The agreement between the numbers of the second and third columns must be considered as satisfactory, as the uncertainty in the determination of $\phi_{\max}$ may amount to 0.01 or even 0.02 volt.

The method of null solutions has been applied by Cirves to Cd-amalgams as well. The position of the point of zero charge of different Cd-amalgams in normal KCl solution and normal KBr_2 solution is given in Table 4. The values for pure mercury have been determined from the corresponding electrocapillary curves.

TABLE 4

Per Cent Cd	Point of Zero Charge	
	Normal KCl	Normal KBr
0	0.56	0.65
0.0003		0.703
0.001		0.711
0.004	0.625	0.724
0.01	0.640	0.736
0.1	0.680	0.760
1.0	0.714	
4.8	0.746	0.818

As is shown by Table 4 even a small addition of cadmium to mercury causes a marked shift of $\phi_{\max}$.

²⁶ Unpublished data.

²⁷ Z. physik. Chem., **59**, 129 (1907).

²⁸ Phil. Mag., (6) **15**, 478 (1909).

Our information regarding the value of $\phi_{\max}$ for other metals is rather limited. Hevesy and Lorenz²⁹ have determined the electrocapillary curves of molten Pb and Sn, but owing to the uncertainty of the reference electrode and differences of temperature it is difficult to compare the position of the maxima. It would appear that the maximum of the Sn and Pb curves are shifted as compared with Hg in the same direction as it is in the case of Tl- and Cd-amalgams. The maximum point of liquid gallium has been determined by Frumkin and Gorodetzkaya.³⁰ The behavior of gallium in alkaline and neutral solutions is complicated by the formation of an oxide film, but in acid solution (normal KCl + 0.1 normal HCl) the value of $\phi_{\max}$ could be measured with sufficient accuracy and was found to be equal to 0.9 volt. This is practically all we know from direct measurements about the influence of the nature of the metallic phase on the value of $\phi_{\max}$. Various methods have been proposed with the purpose of finding the point of zero charge of metallic surfaces, based on other principles. The whole question has been discussed by the present author³¹ in another place. It appears to him that the only method whose results can be directly compared with those based on the determination of $\phi_{\max}$ and on the use of dropping electrodes is the adsorption method which was proposed for the first time by Billitzer.³² The method is based on the fact that the formation of the double layer at the solid-liquid interface causes definite measurable changes in the composition of the solution if the surface area of the solid substance is large enough. This makes it possible to determine at least the sign of the surface charge. Billitzer tried to apply this method to colloidal platinum and found the point of zero charge at a value of ϕ equal to about -0.12 , but it appears that Billitzer did not take into account one source of error (adsorption of alkali by the products of oxidation of platinum)³³ which makes this value too low. An extensive study of the adsorption of electrolytes by activated charcoal carried out by Bruns and Frumkin³⁴ led them to the conclusion that activated charcoal acts in this case as a gas electrode and that the zero point for charcoal must lie between the limit $\phi = 0.2$ and $\phi = 0.3$. The zero point for Pt may come into the same interval or even correspond to a still lower value of ϕ , although the value given by Billitzer, as will be shown elsewhere, is certainly too low.

²⁹ Z. physik. Chem., **74**, 443 (1910).

³⁰ Z. physik. Chem., **136**, 215 (1928).

³¹ Loc. cit., **2**, 271-273.

³² Z. physik. Chem., **45**, 327 (1903).

³³ Cf. Pennycook: J. Chem. Soc., **135**, 623 (1929).

³⁴ Z. physik. Chem. (A) **141**, 141 (1929).

The data which have been obtained for platinum, charcoal, mercury, and the amalgams indicate that the position of the point of zero charge is strongly influenced by the nature of the metallic phase. That means we can build up a cell in which there will be no ionic double layers at the surface of both electrodes and which still will have a definite e.m.f. Thus between mercury and a 41.5 per cent Tl-amalgam, both being polarized in a Na_2SO_4 solution so as to make the values of E equal to zero, there will be a potential difference of 0.45 volt. As there has been no exchange of ions between the metals and the solution in our cell, and no adsorption of ions at the surface of the metals, the potential difference exhibited by the cell may be readily compared to a contact potential difference between metals in a vacuum. It follows therefore from the study of electrocapillary phenomena that contact potentials must constitute an important part of the e.m.f. of ordinary galvanic cells, a result which is certainly contrary to the assumption of the majority of electrochemists. It was found by numerous investigators³⁵ that the sign of the charge of a metal determined by cataphoretic methods (ξ -potential) usually does not agree with the sign which was expected from the position of the metal in the electrochemical series. In many cases this discrepancy must certainly be explained by adsorption phenomena, which complicate the structure of the double layer, as it was shown by Freundlich³⁶ and Stern,³⁷ but the theory outlined in this paper indicates still another possibility. As the position of the point of the zero charge changes with the nature of the metallic phase, it appears altogether impossible to find the sign of the charge of a metal from its electrode potential. A metal which would carry a positive charge in a definite solution, if its zero point would coincide with the zero point of mercury, can be in reality negatively charged and vice versa. So long as there are no accurate determinations of the position of the point of zero charge of different metals, we cannot say to what extent the observed discrepancies have to be ascribed to the influence of some adsorption effects on the structure of the double layer. Let us take as an example metallic cadmium. Cataphoretic experiments indicate in some cases a positive charge of the cadmium surface (Coehn and Shafmeister)³⁵ but it follows from the value of the potential of a cad-

³⁵ Billitzer: Z. Elektrochem., **8**, 638 (1902); **14**, 624 (1908); **15**, 439 (1909); Garrison: J. Am. Chem. Soc., **45**, 37 (1923); Coehn and Shafmeister: Z. physik. Chem., **125**, 401 (1927).

³⁶ Freundlich and Rona: Sitzgsber. preuss. Akad. Wiss. Physik. Math. Kl., **20**, 397 (1920); Freundlich and Ettisch: Z. physik. Chem., **116**, 401 (1925); Freundlich: "New Conceptions in Colloidal Chemistry," Dutton and Company, New York.

³⁷ Stern: Z. Elektrochem., **30**, 508 (1924).

mium electrode that the charge of the cadmium surface must be negative for all possible concentrations of Cd-ions if the cadmium zero point coincides with the mercury zero point. But if we suppose that the cadmium zero point is shifted in the direction indicated by the experiments with Cd-amalgams quoted above by some 0.27 volt (the shift observed with a 4.8 per cent amalgam being 0.19 volt), the cadmium surface in a normal KCl solution would be positively charged even if the concentration of Cd-ions is as low as $3 \cdot 10^{-5}$ normal.

LABORATORY OF COLLOID CHEMISTRY,
UNIVERSITY OF WISCONSIN,
MADISON.