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XXXV. *An Experimental Investigation of Gibbs's Theory of Surface-Concentration, regarded as the basis of Adsorption.*
(Second Paper.) By WM. C. McC. LEWIS, M.A.*

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IN a previous paper † upon this subject a number of determinations were recorded, which had been carried out with a view to investigate experimentally the expression deduced by Gibbs for the surface condensation of one of the components of a two-phase system at the boundary separating the phases. Two immiscible liquids—namely a hydrocarbon oil and distilled water—were brought into contact, there being a definite interfacial tension existing at the boundary of separation. To the water there were added various substances soluble in water, but insoluble in oil, viz. sodium glycocholate, methyl-orange, and Congo-red. These substances all produced a lowering effect on the interfacial tension—such lowering effect increasing with corresponding increase in concentration of the solute.

Gibbs's expression connecting the surface-concentrating of the solute with the lowering effect on the tension and the concentration of the solute in the bulk of the (aqueous) phase is

$$\Gamma = - \frac{c}{RT} \frac{d\sigma}{dc}$$

where Γ = the mass (in grams) of the solute per square centimetre of the dividing surface in excess of what would be there supposing the concentration to remain the same as in the bulk of the solution ;

c = the bulk concentration of the solute in the aqueous phase ;

R = the gas constant ;

T = the absolute temperature ;

σ = the interfacial tension ; and

$\frac{d\sigma}{dc}$ = the rate of change of the tension with the concentration of the solute.

* Read November 27, 1908.

† Lewis, Phil. Mag. April 1908 ; also Proc. Phys. Soc. vol. xxi. p. 150 (1908).

The negative sign on the right-hand side indicates that $\frac{d\sigma}{dc}$ must be negative in order that Γ may be positive, *i. e.* those substances which lower the interfacial tension will increase in concentration at the interface.

It was shown how this expression might be applied to the phenomenon of adsorption, which is considered to be more or less a surface condensation. The determinations referred to consisted in measurements of the various quantities occurring in the above expression, and in comparing the values obtained on the two sides of the equation. The general results showed that the actually determined values for Γ far exceeded the calculated values—those found being of the order 10^{-6} grms./cm.², while the calculated ranged from 10^{-7} to 10^{-8} grms./cm.² This discrepancy was observed in the case of all the substances mentioned in the previous paper. The adsorption coefficient (Γ) was measured experimentally under two quite different conditions—namely, at an approximately *plane* surface; and secondly at a very curved surface, with concordant results in both cases.

With the view of throwing some light on the cause of this discrepancy, further determinations of a similar character were carried out and are recorded in the present paper.

It may be pointed out that the substances mentioned are electrolytes (sodium salts of organic acids) and would therefore suffer considerable dissociation in aqueous solution. To account for the discrepancy referred to one possibility suggested itself, namely, the presence of some kind of “double layer” electrical effect. Of course this may or may not be the cause, and it will be shown that for these bodies this is probably *not* the cause, but evidently the first step was to examine other electrolytes—ordinary inorganic salts of simple constitution and comparatively low molecular weight, and compare the effects obtained in these cases with that obtained for sodium glycocholate and the dye-stuffs.

Finally, to carry out adsorption determinations if possible with typical non-electrolytes and compare the results obtained in this case also.

THE INTERFACIAL TENSION BETWEEN OIL AND WATER
MEASURED BY THE DROP-PIPETTE.

The pipette was identical with that shown in fig. 1 (previous paper). An expression giving the tension directly in absolute units may be derived as follows :—

Consider the equilibrium of a drop of oil formed in water and just about to break away from the nozzle of the pipette.

Let σ = the interfacial tension ;
 a = the radius of the orifice ;
 r = the mean radius of the drop ;
 ρ_w = the density of water ;
 ρ_0 = the density of oil.

The forces tending to draw the drop off are (1) gravitational, due to the difference in densities of the oil and water

$$= \frac{4}{3} \pi r^3 (\rho_w - \rho_0),$$

and (2) the difference of pressure due to curvature,

$$= 2\pi a^2 \frac{\sigma}{r}.$$

The opposing force is due to the tension and $= 2\pi a \sigma$.

Hence

$$2\pi a \sigma - 2\pi a^2 \frac{\sigma}{r} = \frac{4}{3} \pi r^3 (\rho_w - \rho_0).$$

Applying this to the particular case of the oil in which

$$\begin{aligned} \rho_w &= 1.0, \\ \rho_0 &= 0.899, \\ a &= 0.175 \text{ cm.}, \\ r &= 0.4125 \text{ cm.}, \end{aligned}$$

we obtain $\sigma = 0.0467$ gram per cm.

or 45.8 dynes per cm.

Employing the empiric formula of Lohnstein * and Kohlrausch † the value 40 dynes per cm. is obtained.

The above expression had been already obtained when it was found that an almost identical one had been deduced by

* Lohnstein. See previous paper.

† Kohlrausch. See previous paper.

G. Guglielmo* for liquid-air surfaces. He has applied it to the case of the water-air tension with the following results:—

Radius of orifice of pipette.	Tension in milligrams/mm.
0.8 mm.	7.78
1.1 „	7.60
2.15 „	7.69
} mean 7.69 at 25° C.	

The value obtained by the capillary-tube method is 7.485 at 25° C. The results are therefore in fair agreement.

As in previous determinations, the drop-pipette was employed for the various cases of adsorption dealt with in the present paper, the only difference being that the absolute values for the tension are here calculated by means of the expression deduced above.

THE INTERFACIAL TENSION BETWEEN A HYDROCARBON OIL AND AQUEOUS SOLUTION OF ELECTROLYTE.

The oil employed was similar to that previously experimented with. About twenty electrolytes in all were examined and all showed a *lowering* effect on the oil-water tension—in general monovalent ions of small atomic weight having least effect while copper and barium salts had a marked influence. This lowering of the tension is remarkable in view of the fact that inorganic salts (with the exception of lithium) *raise* the air-water tension†. Further, it is a general property of salts to be adsorbed by charcoal; and if this is regarded as indicative of a lowering of tension at the charcoal surface, one may be perhaps justified in saying that for aqueous solutions of an electrolyte at a liquid or solid‡ interface, one may expect in all cases a lowering of tension accompanied by adsorption, while on the other hand at the solution-air surface no such generalization can be made.

A certain number of these salts were selected for adsorption determinations—in the case of caustic soda the emulsion

* G. Guglielmo, *Accad. Lincei, Atti*, xv. p. 287 (1906).

† Whatmough, *Zeitschr. Phys. Chem.* vol. xxxix. p. 129 (1901).

‡ Using the word in its ordinary sense.

method* being employed; while with the rest the large-dropping apparatus was used—this being rendered necessary as the adsorption determinations were carried out for each ion of the salt separately, the concentration changes being estimated by ordinary volumetric and gravimetric means.

The Adsorption of Caustic Soda on Hydrocarbon Oil.

The values of the interfacial tension for different concentrations of the base (corrected for density) are summarized in the following table.

TABLE I.

Concentration		Interfacial Tension in dynes/cm.
per cent.	in gram-moles/litre.	
0	0	45.81
1.0	0.25	26.93
2.0	0.5	22.49
4.0	1.0	16.76
8.0	2.0	streaming from orifice of pipette — tension too small to be measured.

The values of the tension and concentration are plotted in fig. 1.

Fig. 1.

* See former paper.

Calculation of Γ by means of Gibbs's expression :—

Take as a particular case the concentration 0.3 per cent.

$$c = 0.003 \text{ grm./cc.}$$

$$R = \frac{2 \times 4.2 \times 10^7 \text{ ergs}}{\text{molecular weight}} = \frac{2 \times 4.2 \times 10^7}{20},$$

assuming complete dissociation
at this dilution.

$$T = 288^\circ \text{ abs.}$$

$\frac{d\sigma}{dc}$, i. e. the tangent to the curve (fig. 1) at the concentration
0.3 per cent.,

$$= - \frac{9 \text{ dynes/cm.}}{0.003 \text{ grm./c.c.}} = 3000.$$

Hence

$$- \frac{c}{RT} \frac{d\sigma}{dc} = \frac{7.5 \times 10^{-9} \text{ grams per cm.}^2}{\text{or } 1.9 \times 10^{-10} \text{ gram-moles per cm.}^2}$$

It has been assumed here in using the term gram-moles that the substance has been adsorbed either as undissociated base or in ionically equivalent proportions. Gibbs's expression for surface concentration does not contain any term allowing for the preferential adsorption of a single ion if any should occur. Also the measurement of concentration changes by means of changes in tension embodies the same assumption.

Experimental Determination of Γ :—

500 c.c. of caustic-soda solution (concentration 0.3 per cent.) were shaken with 1.075 c.c. of the oil until a uniform emulsion resulted. After emulsification a tension determination showed that there had been a decrease in concentration of 0.003 per cent. The diameter of the emulsion particles as measured in the microscope was on the average 3×10^{-5} cm., so that the total adsorbing surface was 107500 cm.^2

Hence

$$\Gamma = 1.5 \times 10^{-7} \text{ grm./cm.}^2 \text{ or } 3.7 \times 10^{-9} \text{ gram-moles/cm.}^2$$

$$\Gamma \text{ (calculated)} = \frac{7.5 \times 10^{-9} \text{ grm./cm.}^2}{\text{or } 1.9 \times 10^{-10} \text{ gram-moles/cm.}^2}$$

The probable error in the experimental result may amount to 25 per cent. A comparison of the observed with calculated values shows once more the considerable discrepancy which exists between them. It should be observed, however, that the absolute value of the experimental determination has fallen from the order 10^{-6} (obtained in previous cases) to 10^{-7} grm./cm.² It should also be mentioned that if any slight trace of acid were present in the oil the adsorption of a base would be considerably altered.

Re-determination of the Adsorption of Sodium Glycocholate.

Having obtained a purer specimen of the material than that used in former cases, the values for the tension between the oil and solutions of different concentrations were again determined. There were only small changes noted in the result—the calculated value for the adsorption (at a concentration 0.25 per cent.) being 7×10^{-8} grm./cm.², while in the former case the value was about 5×10^{-8} . The actual value determined by experiment was from 3.5 to 4.7×10^{-6} grm./cm.² while in the previous case it had lain between the limits 3.1 and 5.4 grm./cm.²

The Adsorption of Silver Nitrate.

In the measurements of the adsorption of this substance (and in all subsequent cases) the "large drop" * apparatus was employed. One litre of $\frac{1}{50}$ molar silver nitrate was prepared and about 750 c.c. poured into the tube through which the oil passed in the form of drops (of about 0.3 cm. diameter), and on the surface of these the solute was adsorbed. When the oil-reservoir (of 1 litre capacity) had been exhausted and the total number of drops estimated from the time taken in emptying the reservoir, the solution which had been thus treated was withdrawn and analysed. For this particular substance the silver only was estimated before and after the experiment by precipitation with hydrochloric acid, the Gooch crucible method being employed. An extremely small difference in weight was observed,

* See previous paper.

namely 1.6 milligrams of silver chloride. The total surface area of the oil was 7000 cm.²

Hence the adsorption of the silver is

$$\Gamma_{Ag} = \underline{1.7 \times 10^{-8} \text{ grm./cm.}^2}$$

A repetition of the determination gave

$$\Gamma_{Ag} = 3.4 \times 10^{-8} \text{ grm./cm.}^2$$

The mean value is therefore

$$\Gamma_{Ag} = \underline{2.5 \times 10^{-8} \text{ grm./cm.}^2}$$

It may be mentioned that the measuring vessels used in these and subsequent determinations were recalibrated for 15° C., and all solutions were cooled to this temperature in a bath before measuring out the volume.

It will be noted that the value obtained above is much smaller than for the previously mentioned substances (except caustic soda). One might therefore expect a closer approximation to the value calculated on Gibbs's expression.

Calculation of the Adsorption of Silver Nitrate.

As in previous cases the oil-solution tension curve was obtained by means of the drop-pipette. The oil employed for these measurements was not quite identical with that used with caustic soda. The values obtained (corrected for density) are given in the following table.

TABLE II.
Oil—Silver-Nitrate Solutions.

Concentration. in gram-moles per litre.	Pipette Drop-number.	Tension dynes, cm.
0	135	52
0.01	140	50
0.02	145	48.4
0.04	149	47.3

The values of the concentration are plotted against tension in fig. 2.

Fig. 2.

The calculated adsorption, namely

$$\frac{c}{RT} \frac{d\sigma}{dc},$$

has the following value for a concentration $\frac{1}{50}$ molar :—

$$c = 0.0034 \text{ gram, per c.c.}$$

$$R = \frac{8.4 \times 10^7 \text{ ergs}}{\text{molecular weight}}.$$

The molecular weight at this dilution has been found by Smits* to be 94. $T = 289^\circ \text{ abs.}$

$\frac{d\sigma}{dc}$ is the tangent to the curve at $\frac{1}{50}$ molar concentration and is equal to

$$\frac{1.9 \text{ dyne/cm.}}{0.0034 \text{ gram./c.c.}} = 556.$$

Hence

$$\frac{c}{RT} \frac{d\sigma}{dc} = 7.3 \times 10^{-9} \text{ gram per cm.}^2$$

* Smits, *Zeitschr. Phys. Chem.* vol. xxxix. p. 418 (1902).

This refers to the salt AgNO_3 , so that on the assumption that each ion is adsorbed equivalently we obtain the calculated value for the silver ion to be

$$\Gamma_{\text{Ag}} = \underline{4.5 \times 10^{-9} \text{ gm./cm.}^2}$$

$$\Gamma_{\text{Ag}} (\text{found}) = \underline{2.5 \times 10^{-8} \text{ gm./cm.}^2}$$

The values for the experimental and calculated adsorption are thus in much closer agreement than in any previous case—the experimental being five times the calculated. The question is: Does this represent a real discrepancy even in this case, or is it to be considered as agreement within the limits of experiment? It is difficult to say, but without laying too great stress upon it, I am of opinion that there is a real (though small) discrepancy between calculated and observed values.

The Adsorption of Potassium Chloride.

Exactly similar determinations were carried out with this substance as in the case of silver nitrate, except that with this salt both the metal and acid were estimated.

The Adsorption of the Potassium of Potassium Chloride.—A very large quantity of oil was allowed to pass through the KCl solution in the large-drop apparatus. The resulting oil-surface area was 16,000 cm.^2 . The quantity of potassium present in the solution before and after adsorption was estimated as potassium sulphate. The difference in weight of the K_2SO_4 precipitate was 3.2 milligrams, whence the adsorption of the potassium is

$$\Gamma_{\text{K}} = 8 \times 10^{-8} \text{ gm./cm.}^2$$

A repetition of the experiment gave

$$\Gamma_{\text{K}} = 2 \times 10^{-8} \text{ gm./cm.}^2$$

Thus the mean value is

$$\Gamma_{\text{K}} = \underline{5 \times 10^{-8} \text{ gm./cm.}^2}$$

Calculation of Γ_{K} on Gibbs's formula:—

The values of the tension corresponding to different concentration (corrected for density) are given as follows:—

TABLE III.—Hydrocarbon Oil—Potassium Chloride.

Concentration in gram-moles per litre.	Pipette Drop-number.	Tension dynes/cm.
0	135	52
0.0125	139	50.4
0.025	140	49.9
0.05	143	48.9
0.1	147	47.8

The tension-concentration curve is given in fig. 3.

Fig. 3.

As before, the calculated adsorption for $\frac{M}{20}$ KCl is

$$c = 0.0037 \text{ gram./c.c.}$$

$$R = \frac{8.4 \times 10^7 \text{ ergs.}}{37}$$

where 37 is the osmotic molecular weight.

$$T = 289^\circ \text{ abs.}$$

$$\frac{d\sigma}{dc} = 478.$$

Hence

$$\frac{c}{RT} \frac{d\sigma}{dc} = \underline{2.3 \times 10^{-9}} \text{ gram KCl per cm.}^2 \text{ surface,}$$

which corresponds to 1.7×10^{-9} gram. of potassium,

while Γ_x (found) is 5×10^{-8} gram./cm.²

It will be noted that potassium shows a greater discrepancy than silver as regards the calculated value. The results are of about the same order as that obtained for caustic soda,

Estimation of the Adsorbed Chlorine :—

The surface area of the oil was 10,000 cm.² The change in the chlorine concentration was determined as silver chloride, the difference in weight of AgCl precipitate due to adsorbed chlorine being 0.35 milligram. Hence

$$\Gamma_{Cl} = 8 \times 10^{-9} \text{ gram./cm.}^2$$

Repetition gave $\Gamma_{Cl} = 3 \times 10^{-9}$ gram./cm.²

These quantities are, however, so small that one is only justified in stating that the adsorption of the chlorine is of the order 10^{-9} gram./cm.²

The calculated value is 1.6×10^{-9} gram./cm.², so that the agreement between calculated and observed is fairly good.

These results for potassium chloride appear to point (at least as far as the small changes in concentration observed can be trusted) to the possibility of a certain amount of separation of the ions in the process of adsorption, *i. e.* a preferential cation adsorption. If this is so, it at once suggests

some electrical effect taking place which is not taken account of in Gibbs's capillary theory.

The Adsorption of Barium Chloride.

In the case of this substance the chlorine only was estimated, this being carried out volumetrically with AgNO_3 solution. The surface area of the oil was 4000 cm.^2 . In the titration the change in concentration of chlorine due to adsorption was less than 0.1 c.c. AgNO_3 solution. From this one can only say, therefore, that the adsorption Γ_{Cl} is not of greater magnitude than $\underline{10^{-8} \text{ grm./cm.}^2}$.

Calculation of the Adsorption :—

The following table (IV.) contains the values obtained for the tension (corrected for density) at different concentrations.

The values of the tension are plotted against concentration in fig. 4. By taking the tangent to this curve the value of $\frac{d\sigma}{dc}$ is obtained for a particular concentration.

TABLE IV.

Concentration of the Barium Chloride		Density of the Solutions.	Drop-number.	Relative Tension.	Tension in dynes/cm.
Gram-moles per litre.	Per cent. anhydrous.				
0	0	1.000	153	1.000	45.81
0.062	1.29	1.009	171	0.895	40.99
0.125	2.59	1.019	188	0.829	37.98
0.2	4.14	1.038	210	0.757	34.68
0.25	5.18	1.048	222	0.722	33.07
0.33	6.90	1.066	246	0.663	30.37
0.375	7.76	1.073	255	0.644	29.50
0.5	10.35	1.099	290	0.580	26.57
1.0	20.70	1.216	419	0.444	20.34
(1.7) satd. soln.	34.00	1.289	585	0.338	15.48

Fig. 4.

For a solution of strength $\frac{M}{50}$ we have

$$c = 0.0041 \text{ gram./cc.}$$

$$R = \frac{8.4 \times 10^7}{75},$$

where 75 = osmotic molar weight,

$$T = 289^\circ \text{ abs.}$$

$$\frac{d\sigma}{dc} = 427.$$

Hence

$$\frac{c}{RT} \frac{d\sigma}{dc} = \underline{5.4 \times 10^{-9} \text{ gram BaCl}_2 \text{ per cm.}^2},$$

$$\text{or } \underline{1.6 \times 10^{-9} \text{ gram. chlorine,}}$$

$$\Gamma_{\text{Cl}} (\text{found}) \approx 10^{-8} \text{ gram./cm.}^2$$

The result obtained here is of too qualitative a nature to show whether there is agreement or not.

Adsorption of Copper Chloride.

With this substance both copper and chlorine were separately estimated.

The Adsorption of the Copper :—

The oil-surface area was 8000 cm.² The copper in the solution was estimated electrolytically, both before and after the adsorption. The change in weight of the electrode was only 0.2 milligram.

Hence

$$\Gamma_{\text{Cu}} = 2.5 \times 10^{-8} \text{ grm./cm.}^2$$

A repetition of the determination gave

$$\Gamma_{\text{Cu}} = 4.5 \times 10^{-8},$$

or mean value

$$\Gamma_{\text{Cu}} = \underline{3.5 \times 10^{-8} \text{ gram per cm.}^2}$$

Estimation of the Chlorine :—

As in previous cases, this was estimated as silver chloride. The difference in weight of the AgCl precipitate was 6 milligrams. The surface-area = 8000 cm.², and hence

$$\Gamma_{\text{Cl}} = 1.8 \times 10^{-8} \text{ grm./cm.}^2$$

A repetition of the determination gave

$$\Gamma_{\text{Cl}} = 2.3 \times 10^{-8};$$

so that the mean value is

$$\Gamma_{\text{Cl}} = \underline{2 \times 10^{-8} \text{ grm./cm.}^2}$$

Hence

$$\Gamma_{\text{Cu}} + \Gamma_{\text{Cl}} = \underline{5.5 \times 10^{-8} \text{ grm./cm.}^2}$$

Calculation of the Adsorption of CuCl₂ :—

The following table gives the value of the tension (corrected for density of the solution) at different concentrations :—

Hydrocarbon-Oil and CuCl₂.

Concentration in gram-moles per litre.	Pipette Drop-number.	Tension in dynes/cm.
0	135	52
0.0125	140	49.9
0.025	143	48.9
0.05	147	47.8
0.1	154	45.8

These values are plotted in fig. 3.

For a solution of concentration M/50

$$c = 0.0027 \text{ grm./cm.}^3,$$

$$\frac{d\sigma}{dc} = 518,$$

$$R = \frac{8.4 \times 10^7}{51}.$$

Where 51 is the molecular weight at this concentration as determined by Biltz*.

$$T = 289 \text{ abs.}$$

Hence

$$\frac{c}{RT} \frac{d\sigma}{dc} = 4.0 \times 10^{-9} \text{ gram CuCl}_2 \text{ per cm.}^2,$$

$$\Gamma_{\text{Cu}} + \Gamma_{\text{Cl}} (\text{found}) = 5.5 \times 10^{-8} \text{ grm./cm.}^2$$

We have here once more inequality between observed and calculated values. It should be noted that it is the experimental value of Γ which is always the greater, and there are indications that the cation is adsorbed in somewhat greater quantity than the chemical equivalent of the anion.

Further determinations with other electrolytes must be undertaken before one could definitely state whether this important fact—the separation of the ions—takes place or not.

Before going on to discuss in more detail, however, the data already given, the experiments carried out with non-electrolytes will first be briefly recorded.

THE ADSORPTION OF NON-ELECTROLYTES.

The chief difficulty at the outset with regard to almost all non-electrolytes is their small solubility in water. It is not easy, therefore, to draw a comparison between the tension effects produced by these bodies and the effects produced by electrolytes. Altogether seventeen non-electrolytes were examined as regards their influence on the interfacial tension. Two of these—aniline and p-nitrosodimethylaniline—were

* Biltz, *Zeit. Phys. Chem.* vol. xl. p. 199 (1901).

found to be soluble in the oil, and to this is probably due their comparatively marked effects on the tension *.

The following table (p. 532) contains the values obtained from the various substances examined.

The value obtained for cane-sugar is worthy of note. The lowering effect is small, although a more concentrated solution was employed than in the case of any other substance. The result is in agreement with that observed at the air-surface, in which case the presence of cane-sugar has no appreciable effect.

In the case of all these substances (except iodine which was practically without effect) there is a lowering of tension at the interface which on Gibbs's theory must be accompanied by adsorption. The same general rule, therefore, as regards the effect at the oil-surface seems to hold for non-electrolytes as for electrolytes.

The Anomalous Behaviour of Saponin.

Saponin is a non-electrolyte whose aqueous solutions are characterized by foaming, thus pointing to considerable

* *The Tension between two partially miscible phases.*

The Laplace theory of capillarity shows that the work required to form unit area of interface between two liquids A and B is given by the expression

$$\frac{1}{2}(\rho_A - \rho_B)^2 \int_0^\infty z\psi(z)dz = \sigma_{AB},$$

where ρ_A and ρ_B = the densities of the liquids A and B respectively and the integral is supposed constant for all substances. This expression leads to the following relationship:—

$$\sqrt{\sigma_{AB}} = \sqrt{\sigma_{BC}} + \sqrt{\sigma_{CA}},$$

which has not been verified by experiment, but shows in a general way what takes place at the surface. Lord Rayleigh has on this hypothesis calculated the effect of making the transition gradual between A and B by the interposition of n liquids whose densities are in arithmetical series, in which case it is shown that the energy due to surface-tension is reduced to $(n+1)$ of its original value. Hence any diminution in the abruptness will diminish the energy due to surface-tension. The solubility of the aniline in the oil causes the diminution in abruptness, and consequently we find very marked lowering of tension.

TABLE IV.
Interfacial Tension : oil-solution.

Substance.	Per cent. Concentration.	Molar Concentration.	Relative Tension.
Water			1·00
Iodine	0·035	$\frac{1}{360}$	slightly > 1·00
Hydroquinone	1·0	$\frac{1}{11}$	„ < 1·00
Boric acid	0·1	$\frac{1}{62}$	0·97
Urea	0·8	$\frac{1}{7}$	0·97
Diphenylthiourea.....	< 0·1	...	0·96
Milk sugar	1·0	$\frac{1}{36}$	0·96
Succinimide ..	0·2	$\frac{1}{48}$	0·94
Phenol	0·1	$\frac{1}{94}$	0·94
Mercuric cyanide	1·0	$\frac{1}{25}$	0·91
p-nitrosodimethylaniline...	< 0·1	$< \frac{1}{150}$	0·89
Cane-sugar	6·0	$\frac{1}{6}$	0·88
Amygdalin	1·0	$\frac{1}{51}$	0·82
Ethyl acetate	3·6	$\frac{2}{5}$	0·70
Caffeine	1·0	$\frac{1}{21}$	0·71
Aniline	3·0	$\frac{1}{31}$	0·68

lowering of tension *. It has also been noticed that bubbles blown with saponin solution appear to gelatinize, so that when once formed they show a crinkled appearance on contraction. Solutions of this substance showed the following effects at the oil-water interface. On increasing the concentration, there was first of all a rise of tension reaching a maximum at about 0·005 per cent. This was followed by a rapid fall and at 0·025 per cent. a slower fall to 0·05 per cent., beyond which the tension remained constant. Measurements were taken up to 0·4 per cent., at which point streaming

* See a paper bearing upon this subject by S. A. Shorter, Phil. Mag. vol. xi. p. 317 (1906).

effects began to be observable, so that no further readings could be taken. These peculiarities are shown in fig. 5.

Fig. 5.

It seems probable that the gelatinizing effects which have been observed at the air-surface are also effective at the oil-interface. Experiments were carried out to test whether the substance was soluble in the oil. It was found to be insoluble.

Of the substances enumerated in Table III., it will be seen that caffeine shows the most marked effects in proportion to its concentration. It was therefore selected as a suitable substance wherewith to carry out adsorption determinations.

Determination of $\frac{d\sigma}{dc}$ for Caffeine.

The material was obtained from Kahlbaum. Its molecular weight was determined by lowering of the freezing-point of water, and was found to be in agreement with the formula (weight 194). The substance employed is the monohydrate and crystallizes from water in long needles. That caffeine is a good example of a non-electrolyte follows from the value for its dissociation constant determined by Wood *, namely, 4×10^{-14} , which is of the same order as the constant for water.

* Wood, Journ. Chem. Soc. vol. lxxxix. p. 1844 (1906).

The sample of caffeine was first tested, as in previous cases, for any solubility in the oil. The same drop-number was obtained with the oil filtered from caffeine as for the oil fresh from the stock. Caffeine is therefore insoluble in hydrocarbon oil.

The following table (Table V.) contains the determinations of the interfacial tension for caffeine solutions of different

TABLE V.

Per cent. Concentration of Anhydrous Caffeine.	Drop- number.	Relative Tension.	Tension in dynes/cm.
0	146	1.000	48
0.046	153	0.954	45.8
0.092	158	0.924	44.4
0.114	161	0.907	43.5
0.229	171	0.853	40.9
0.457	184	0.793	38.1
0.915	201	0.726	34.8

Fig. 6.

concentrations, the tension being measured by the drop-pipette. It will be noted that this oil is not quite identical with that previously employed.

The interfacial tension is plotted against concentration, giving the curve on fig. 6. The tangent to the curve gives the value of $\frac{d\sigma}{dc}$ at the desired concentration.

Calculation of the Absorption Coefficient:—

As before, the expression for the adsorption is

$$\Gamma = -\frac{c}{RT} \frac{d\sigma}{dc}.$$

For a solution of concentration 0.114 per cent. (anhydrous) caffeine the right-hand side of this expression has the following numerical value:—

$$c = 0.114 \text{ per cent.} = 0.00114 \text{ grm./c.c.,}$$

$$R = \frac{2 \times 4.2 \times 10^7}{194} \text{ ergs,}$$

$$T = 288^\circ \text{ abs.,}$$

$$\frac{d\sigma}{dc} = \frac{3 \text{ dynes/cm.}}{0.00114 \text{ grm./c.c.}}$$

$$\therefore \frac{c}{RT} \frac{d\sigma}{dc} = \underline{2.4 \times 10^{-8} \text{ grm./cm.}^2}$$

It will be noted that this value is approximately of the same order as the similarly calculated values for previous substances. The substitution of a non-electrolyte for a simple inorganic salt does not seem therefore to have any marked effect on the theoretical value for the adsorption coefficient. It would seem, therefore, that in both cases we are dealing with a factor of the same magnitude as regards its effect on the tension and the consequent value of $\frac{d\sigma}{dc}$. It will be remembered, however, that the results obtained in previous cases pointed to the existence of certain discrepancies between observed and calculated values of Γ . It is of particular interest, therefore, to attempt to measure Γ directly for caffeine, since in this case there is no possibility of separation of ions.

Determination of Γ for Caffeine in Aqueous Solution.

The emulsion method* was employed in this determination.

Solutions of caffeine approximately 0.125 per cent. were prepared, and 500 c.c. shaken in steamed-out glass vessels for three days with about 1-2 c.c. of oil. The resulting emulsions were very uniform under the microscope, the average diameter of the particles being 6×10^{-5} cm. It is worthy of note that this is of the same order as the average diameter of the particles in the previous cases.

The results of two emulsion experiments are given below :—

Caffeine solution (approx. 0.125 per cent.).

Experiment no.	Drop-number before emulsification.	Drop-number after emulsification.	Area of oil-surface.
1	160	160, 160 $\frac{1}{4}$	87,130 cm. ²
2	160, 160 $\frac{1}{4}$	160 $\frac{1}{2}$, 160 $\frac{1}{4}$	127,310 cm. ²

The results show that there was *no readable difference in the concentration of the solution before and after emulsification—the difference being a small fraction of a drop*. Special experiments were undertaken to determine the accuracy of the readings made with the pipette, and it was found that for a small drop-number such as 160 the readings were reproducible to within about $\frac{1}{4}$ th of a drop.

No very reliable quantitative relations can therefore be obtained from these determinations, as we are evidently dealing with a very small change in concentration, *i. e.*, a very small adsorption. The important feature is this—that *the calculated value of Γ (viz. 10^{-8} grm./cm.²) would also correspond to a small fraction of a drop as indicating concentration change*; while a value for Γ of the order obtained in the case of sod. glycocholate and the dyes (viz. 10^{-6} grm./cm.²) would have been indicated by a change of 4-5 drops, which would of course have been

* See previous paper.

perfectly readable. These experiments therefore show that *caffeine is very much less adsorbed than sodium glycocholate, Congo red, or methyl orange.*

It is perhaps going beyond the limits of accuracy warranted by the drop-pipette method to make an approximate calculation of the Γ from the data given above. Taking the second experiment, the change in concentration corresponds to about $\frac{1}{8}$ th of a drop. This is only approximate, and in all probability would give a *maximum* value for Γ . From a curve* obtained by plotting the drop-numbers against concentrations given in Table IV. it is found that $\frac{1}{8}$ th of a drop corresponds to a change in concentration of 0.00094 per cent., and hence the total amount of caffeine removed from the 500 c.c. emulsified is 0.0047 gram. The total adsorbing surface is 127310 cm.², hence

$$\Gamma = 3.7 \times 10^{-8} \text{ grm./cm.}^2,$$

$$\Gamma \text{ calculated} = 2.4 \times 10^{-8} \text{ grm./cm.}^2$$

An attempt was at once made to increase the adsorbing area in order to get more trustworthy data. It was found, however, that the limit had almost been reached in the case of the second emulsion—only a little more than 2 c.c. of oil can be emulsified by 500 c.c. of caffeine solution of 0.1 per cent. concentration. The method is therefore limited in this direction. A further attempt at more accurate measurement was made by employing a pipette of much larger oil-capacity (about 500 c.c.). The drop-number against water was 2042, in place of 146 in the case of the smaller pipette. The drop-number against a solution of 0.1 per cent. concentration was 2383. One result was obtained in which the change of concentration before and after emulsification amounted to 5 drops, which corresponded to 3.5×10^{-8} grm./cm., but on attempting to reproduce these values quite variable results were obtained, owing to the change in wetting of the pipette during the long course (over two hours) of a single determination.

It appears probable from the foregoing attempts to measure

* The curve is a straight line between drop-numbers 155-200. A fraction of a drop can therefore be read fairly accurately.

If in the case of caffeine, that we are dealing with a quantity too small to be determined with accuracy by the method hitherto pursued. It may be possible by employing, for example, colloidal mercury instead of the oil to determine the caffeine adsorption at a mercury surface with accuracy.

Behaviour of Sodium Glycocholate and Caffeine in contact with Charcoal.

In view of the considerable difference between the values for the adsorption of these two substances at the oil-surface, it was of interest to compare the results obtained with charcoal. The material was the same as that employed by Freundlich—namely, Merck's blood-charcoal purified by acid. Freundlich has observed that the further washing of this material does not affect the result of the adsorption determinations, and this was confirmed in the present instance by the fact that there was not the slightest change in the oil-water tension in the case of distilled water which had been shaken up with a quantity of charcoal.

Adsorption of Sodium Glycocholate :—

500 c.c. of a solution 0.3 per cent. concentration were treated with one gram of charcoal, and the decrease in bulk-concentration of the solute amounted to 0.125 per cent. The change in concentration was measured by means of the change in value of the oil-solution tension as given by the drop-pipette. The drop-difference (before and after) was 47.

Hence 1 gram charcoal adsorbs from a 0.3 per cent. solution 0.625 gram sodium glycocholate.

Adsorption of Caffeine :—

500 c.c. of solution 0.218 per cent. concentration (*i. e.*, approximately equimolar with the sodium glycocholate solution) brought into contact with one gram of charcoal gives a drop-difference of 10, which corresponds on the caffeine curve to a change in concentration of 0.108 per cent.

Hence 1 gram charcoal adsorbs from a 0.218 per cent. solution 0.324 gram of caffeine.

It will be noted that the behaviour of caffeine and sodium glycocholate towards charcoal and oil is very different. In contact with charcoal there appears to be no very marked difference as regards the magnitude of the adsorption for both substances. Possibly this may be due to oxidation of the caffeine by means of the oxygen adsorbed on the charcoal surface.

Calculation of the Range of the Concentration Effects at the Oil-surface.

Consider the case of an infinite mass of solution (of a non-electrolyte in water) whose bulk-concentration is c_1 and

surface-concentration c_2 . Suppose one gram-mole of solute transferred from the bulk into the surface-layer. The osmotic work done is

$$RT \log \frac{c_2}{c_1}.$$

There is a corresponding decrease in the surface energy due to adsorption of the solute given by

$$- \frac{d\sigma}{d\Gamma};$$

and equating these two expressions,

$$RT \log \frac{c_2}{c_1} = - \frac{d\sigma}{d\Gamma}.$$

Experimental case:—

If we assume that the solution of caffeine obeys in all probability Gibbs's expression for surface-condensation, from the data previously given we may construct the following table:—

Aqueous solution of Caffeine at 15° C.

Per cent. Bulk-concentration (anhydrous).	Tension in dynes/cm.	Γ calculated from Gibbs's equation in gram./cm.^2
0.0	48	0.0
0.046	45.8	1.2×10^{-8}
0.092	44.4	1.8 "
0.114	43.5	2.0 "
0.229	40.9	2.3 "
0.457	38.1	2.8 "
0.915	34.8	3.0 "

The tension was plotted against Γ , and the tangent to the curve taken at the point corresponding to a bulk-concentration 0.114 per cent. The tangent gives

$$\frac{d\sigma}{d\Gamma} = \frac{7.25 \text{ ergs/cm.}^2}{1 \times 10^{-10} \text{ gram-moles/cm.}^2} = 7.25 \times 10^{10}.$$

At this point

$$\Gamma = 2 \times 10^{-8} \text{ gram./cm.}^2 = 1 \times 10^{-10} \text{ gram-moles/cm.}^2$$

The equation therefore becomes

$$\log_e c_2 = \log_e c_1 + \frac{7 \cdot 25 \times 10^{10}}{RT}.$$

$$\therefore \log_{10} c_2 = \log_{10} 0 \cdot 0064 + 0 \cdot 044 \\ = -2 \cdot 1498.$$

$$\therefore c_2 = 0 \cdot 0071 \text{ gram-moles per litre} \\ = 0 \cdot 00138 \text{ grm./c.c.}$$

Now if D is the range through which the surface-concentration effects are practically complete, it follows that the average concentration in the surface-layer is given by the expression.

$$c_2 = \frac{\Gamma}{D},$$

$$\text{or} \quad D = \frac{\Gamma}{c_2};$$

and on substituting the values obtained above it is found that

$$D = 14 \times 10^{-6} \text{ cm.}$$

It is evident that we have here obtained a value for the "range of molecular action," as may be seen by comparing it with other estimates of the same quantity.

		<i>Method.</i>
Quincke	5×10^{-6} cm.	"Wedge method."
Reinold & Rücker.	$1 \cdot 2 \times 10^{-6}$	Limiting thickness of soap film.
Wiener	$1 \cdot 2 \times 10^{-6}$	Effect on phase of reflected light.
Plateau	$11 \cdot 4 \times 10^{-6}$	Limiting thickness of glycerine film.
Drude	$1 \cdot 7 \times 10^{-6}$	" " soap film.
Parks	$13 \cdot 4 \times 10^{-6}$	Wetting of powders.
Johannot	from 10^{-6} to 10^{-8}	soap film.

DISCUSSION OF RESULTS.

The conclusions to which the foregoing experiments point are :—

- (1) Caffeine in aqueous solution, in all probability obeys Gibbs's law quantitatively.
- (2) Ordinary inorganic salts—Potassium chloride, Silver nitrate, Barium chloride, and Copper chloride—are

adsorbed in quantities which are of the same order as the Gibbs's calculated effect, though the experimentally found values are in all cases *greater* than the calculated. Caustic soda shows a more marked discrepancy between calculated and observed values.

- (3) Complex organic salts—Sodium glycocholate, Sodium oleate *, Congo red, and Methyl orange—show a very large discrepancy between observed and calculated values. The first thing is therefore to consider the various possibilities of accounting for this large discrepancy.

The Adsorption of Sodium glycocholate, &c.

First can the excess exhibited by these substances be explained by an extension of the capillary theory ?

The expression

$$\Gamma = - \frac{c}{RT} \frac{d\sigma}{dc}$$

is deduced on the assumption that we are dealing with *one* component only which suffers surface-concentration, *i. e.*, the solute. Since the above-mentioned substances are salts, they will be associated, and almost entirely so, at the dilution worked with. Milner †, in deducing the Gibbs's expression, has allowed for dissociation by the introduction of van't Hoff's factor (*i*) thus :

$$\Gamma = \frac{c}{iRT} \frac{d\sigma}{dc}$$

This is, however, really the expression employed in the foregoing experiments, since in all cases for the evaluation of *R* (the gas constant) the molecular weight of the solute in *solution* has been employed. By simply making this allowance for dissociation, therefore, the discrepancy between observed and calculated values for adsorption is still very marked—as a matter of fact, such a correction acts in the opposite direction.

The next possible explanation may lie in incorrectness in

* Reference will be made later to this substance.

† Milner, Phil. Mag., Jan. 1907.

the assumption (which has been made throughout) that the water suffers no surface density-change.

It is very probable that water has not quite the same density in the surface-film as in the bulk of the liquid. Evidence for this is to be found in the phenomenon of heat evolution observed by Parks and others, when water is poured upon finely-divided powders of silica, quartz, glass, &c., where chemical action is of course excluded. Also one must not overlook the fact that in the adsorption of sodium glycocholate and the dyes we are dealing with surface-concentrations far exceeding the ordinarily accepted values for their solubility. Of course in using the term "solubility" we assume that the surface-layer water possesses the same properties as water in bulk. For a solution of sodium glycocholate of 0.25 per cent. bulk concentration, Γ was found to be 5×10^{-6} gm./cm.² The value of the range through which the surface-concentration is sensibly different from the bulk has been shown to be approximately 14×10^{-6} cm. Hence the *average* surface-concentration is 0.37 gram per c.c. or 37 per cent., while the ordinarily accepted value for the solubility of sodium glycocholate is 3.9 per cent. There was, however, no visible colour change on the oil surface due to any precipitation.

Again, methyl orange* showed an adsorption for which $\Gamma = 5.5 \times 10^{-6}$, whence the average concentration is 39 per cent. The actual solubility is only 0.078 per cent.

The substances therefore which have shown very great discrepancies as regards Gibbs's theory are *those whose surface concentration greatly exceeds their solubility in the solvent*. For the other substances examined, viz. caffeine and the inorganic salts, *in no case is the ordinary solubility exceeded*, and the adsorption of these substances is in much closer agreement with theory. Thus the surface-concentration of caffeine was found to be 0.26 per cent., while its solubility at ordinary temperature is 1.35 per cent. For silver nitrate the surface-concentration was approximately 0.28 per cent., while its solubility is 122 per cent. at 0° C. Similarly for potassium chloride, barium chloride, and copper chloride.

* See previous paper, *l. c.*

Another possibility however presents itself—namely, the existence of some electrical effect, such as an electrostatic attraction, causing the discrepancy, since sodium glycocholate and the dyes are electrolytes. If this were so, one would also expect somewhat of the same order of discrepancy manifesting itself in the case of the ordinary inorganic salts. Such does not take place. Caustic soda alone has marked effects, and shows an adsorption 20 times greater than the calculated. The other substances generally show a discrepancy of about 5 to 8 times. To whatever cause this smaller discrepancy is due, it is unlikely that the same reason is to be assigned to the very much larger discrepancies observed for sodium glycocholate.

The only other possible means, apparently, of explaining the want of agreement is on the assumption that we are dealing with some irreversible phenomenon of the nature of gelatinization upon the oil surface. The fact of the surface-concentration being much greater than the ordinarily accepted value for the solubility, is in agreement with this view. It should be pointed out, however, that the overstepping of the solubility limit does not seem to be essential to gelatinization, as will be seen by referring to the determinations carried out with saponin. The solubility of this substance is great; according to Beilstein it is completely miscible with water, and although this cannot actually be the case, the constancy of the tension at comparatively dilute solutions cannot be explained by the solubility having been reached. This is a very striking case showing the sensitiveness of the tension to gelatinizing effects. The hypothesis of gelatinization has been put forward by Milner* to explain the behaviour of sodium oleate, although in this case the tension curve was continuous and quite similar to the sodium-glycocholate curve. From some unpublished experiments by Mr. H. E. Potts in this Laboratory, it was found that sodium oleate showed an adsorption at the oil surface, the magnitude of which was of the order 10^{-6} gram./cm.², while the calculated was of the order 10^{-8} gram./cm.², that is to say a discrepancy very similar to sodium glycocholate.

* *Loc. cit.*

Mention may also be made that Freundlich and Losev* have found that certain dyestuffs produced amorphous precipitates on the charcoal surface during adsorption determinations. This was an irreversible process (the precipitates being insoluble in water), and as such might be considered as analogous to gelatinization.

It is possible, therefore, that some irreversible effect of the nature of gelatinization is the real cause of the discrepancy between observed and calculated values in the adsorption of sodium glycocholate, Congo red, and methyl-orange.

The Adsorption of Inorganic Salts from Aqueous Solution.

It has already been pointed out that for certain purely inorganic salts, discrepancies are found between observed and calculated values of the adsorption, but that the existence of these discrepancies might be considered as not quite proved owing to possibility of great experimental error. On the whole, however, it is believed that there really does exist a small discrepancy which requires explanation. Attention might be drawn to the fact that in the cases measured the metal, *i. e.* the cation, shows an excess, while in the case of potassium chloride, and possibly also in barium chloride, the chlorine (the anion) is much nearer to the calculated value. This at once suggests some separation of ions, that is partial selective adsorption due to some electrical effect. The value, however, for the adsorption of the chlorine in copper chloride is scarcely in accord with the preceding statement. Granting that there is a tendency for selective ionic adsorption, it is evident that the phenomenon cannot be completely covered by Gibbs's capillary expression, in the deduction of which no allowance is made for any such ionic separation. Of course for non-electrolytes, where no ionic separation is possible, Gibbs's expression ought to hold quite readily, and experiment confirms this, although the determinations are unfortunately of a more qualitative character than one could wish. In electrolytes, the separation of cation from anion may possibly be regarded as

* Freundlich and Losev, *Zeit. Phys. Chem.* vol. lix. p. 284 (1907).

local electrolysis at the surface of the oil—that in fact we are dealing with a cell of small dimensions the poles of which are the two homogeneous masses, and the heterogeneous layer separating the masses functions as the “electrolytic medium.” If this is so, we must treat the question as one of electrolytic conduction, but first of all it must be shown that there exists an electrical potential-difference between the electrodes, *i. e.* between the oil and the water. Owing to the non-conducting nature of the oil one cannot employ the usual methods, but by emulsifying the oil (*i. e.* converting it into small particles suspended in water) and placing the emulsion in an electrostatic field, it can be observed whether any motion of the particles takes place or not. This was done experimentally as follows:—

A simple Nernst form of U-tube, identical with that employed by Burton*, having a vertical capillary tube affixed at the bend through which water slowly runs so as to form a definite surface of separation (in both limbs) between the water and the oil-water emulsion, is fitted with platinum electrodes dipping into the emulsion. A potential-difference of 230 volts was maintained between the electrodes, and the movement of the emulsion-water boundary down in one limb and up in the other was read off on a scale attached to the vessel. It was found that the particles moved towards the anode, being therefore negatively charged. The velocity of the particles was 4.3×10^{-4} cm./sec. under a gradient of 1 volt/cm.

Burton† has deduced an expression for the potential existing between the particles of colloidal metals and the water in which they are suspended, viz.:

$$V = \frac{4\pi}{K} \frac{\eta v}{X},$$

where V is the p.d. required (in electrostatic units);
 K is the specific inductive capacity of the medium;

* Burton, Phil. Mag. ii. p. 434 (1906).

† Burton, *loc. cit.*

η is the viscosity of the medium ;

$\frac{v}{X}$ is the velocity of the particles under (electrostatic) unit potential gradient,
 X being the p.d. maintained between the poles.

Applying this to the present case of oil suspended in water, we obtain

$$V = 0.00048 \text{ electrostatic unit,}$$

or 0.15 volt.

There is thus quite a measurable potential existing between the oil and water ; and in considering the adsorption of electrolytes we must not overlook this fact. It may be mentioned, in passing, that the above value for the potential is quite of the same order as that obtained by Burton for various colloidal metals.

Since the oil has been shown to be negatively charged, one would not be surprised, speaking generally, that the cation should be selectively adsorbed.

SUMMARY.

- (1) The adsorption of various substances on a hydrocarbon-oil surface has been measured. The results are collected in the following table :—

Substance.	Adsorption per cm. ² of the substance assumed to be in the form of <i>undissociated salt</i> or in chemically equivalent ionic proportions.	
	Found value.	Calculated value.
Sodium glycocholate ..	5×10^{-6} gm./cm. ²	7×10^{-8} gm./cm. ²
Congo-red	3.7×10^{-6}	1.1×10^{-7}
Methyl-orange	5.5×10^{-6}	1.2×10^{-7}
Sodium oleate	10^{-6}	10^{-8}
Caustic soda	1.5×10^{-7}	7.5×10^{-9}
Caffeine	3.7×10^{-8}	2.4×10^{-8}

Substance.	Adsorption of cation per cm. ²		Adsorption of anion per cm. ²	
	Found value.	Calculated value.	Found value.	Calculated value.
Silver nitrate	gm./cm. ² 2.5×10^{-8}	gm./cm. ² 4.5×10^{-9}	gm./cm. ²	2.3×10^{-9}
Potassium chloride .	5×10^{-8}	1.7×10^{-9}	10^{-9}	1.6×10^{-9}
Barium chloride ...		3×10^{-9}	not $\geq 10^{-8}$	1.6×10^{-9}
Copper chloride ...	3.5×10^{-8}	2×10^{-9}	2×10^{-8}	2×10^{-9}

- (2) The large discrepancy between observed and calculated values for the first four substances is possibly due to gelatinization upon the oil-surface.
- (3) Caffeine obeys Gibbs's law within the limits of experimental error.
- (4) There is evidence of slight *selective* adsorption, the cation more than the anion, probably due to electrical effects, since the oil is shown to be negatively charged, the potential-difference between the oil and water being approximately 0.15 volt.

In conclusion, I gladly take this opportunity of expressing my gratitude to Professor F. G. Donnan for his advice and assistance in this work.