LIX.—On Interfacial Tension.   Part II.   The Relation between Interfacial and Surface Tension in Sundry Organic Solvents in Contact with Aqueous Solutions.

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IN Part I of this communication the author has described an apparatus in which interfacial tension can be measured in absolute units.   It is now proved that there is a very intimate connexion between the interfacial tension at the surface separating immiscible liquids and the surface tensions of the liquids.

From a consideration of the conception that surface tension is due to the attraction of molecules lying in the surface by those immediately surrounding and beneath them, it appeared probable that if the internal forces giving rise to this phenomenon were, like gravitational or electrostatic force, independent of the chemical nature of the molecules concerned, interfacial tension would be the difference between the two surface tensions.

This hypothesis, when tested, was found to be only very approximately true in some cases, whilst in others the discrepancy was considerable.   Further investigation revealed the cause.

When two liquids are in contact, each is saturated with the other at the surface of contact, consequently it is necessary to substitute for the surface tensions of the two liquids those of their mutually saturated solutions.   When the latter were determined, with the precautions detailed below, it was found that the following law was accurately true in the case of pure solvents :—The interfacial tension between two liquids A and B is the difference between the surface tension of A saturated with B and the surface tension of B saturated with A.

When the interfacial tension is measured by the capillary method described in Part I, due consideration must be given to the phenomena of wetting.   All the liquids described in this paper wet glass ; here, the capillary rise is the difference.   In Part III, where mercury, which does not wet glass, is dealt with, the capillary forces act in the same direction in glass tubes ; hence the capillary depression is the sum.   A convention as to the sign of the forces has thus to be adopted, since the true interfacial tension is always the difference between the forces.

The following appear to form exceptions to the law :

(1) Immiscible liquids that react chemically.

(2) Mercury and liquid amalgams in contact with certain electrolytes.

(3) **The** old interface separating certain solutions where surface concentration has occurred.

The Measurement of the Surface Tension of Saturated Liquids.

When the surface tensions of mutually saturated liquids were being measured, the liquids were shaken in a separator and run into cylindrical bottles, about $4\frac{1}{2}$ cm. in diameter, with straight sides about $12\frac{1}{2}$ cm. in height. Selected capillary tubes were employed (see Part I), the same tubes being used for all the measurements recorded. The capillary tube was allowed to rest in a vertical position against the walls of the bottle (see Fig. 1). The bottle and the capillary tube were cleaned (see Part I) and dried in an air-oven before each measurement. When observations were being made, the bottle was inclined to allow the liquid to fill the tube completely, and the position of equilibrium of the column on falling was noted. The bottle stood in a water-bath at a known temperature, except at the moment when measurements were being taken, and was closed by a cork to prevent evaporation of volatile, saturating liquid. It was found, however, that there was a considerable error in such determinations due to volatilisation of the saturating liquid into the space above the liquid, whereby the surface layer became weaker, and in the case of aqueous solutions the observed tensions were too high. This source of error was eliminated by a simple expedient (Fig. 1). This consisted of a

FIG. 1.

cylinder of wire gauze (A) supported by two wires fixed into the cork and filled with cotton wool moistened with a few drops of the saturating liquid (chloroform, ether, etc.), the vapour of which maintained saturation of the air space. Readings taken every few minutes proved that the capillary rise, which fell at first, became constant after a short interval, usually thirty to forty minutes, complete saturation having been effected. If the temperature fell slightly subsequently, condensation occurred on the walls of the bottle and an oily layer appeared, but the position of equilibrium remained constant.

It was subsequently found that in the case of pure liquids the shaking in a separator was unnecessary, since only the surfaces
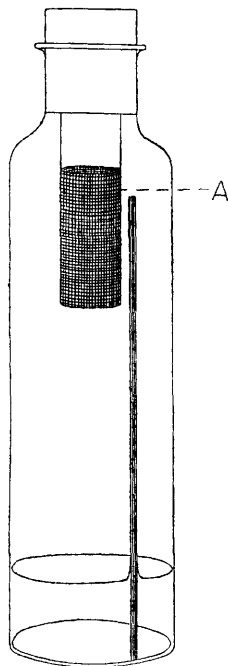
were active.   Exactly the same effect was obtained when a pure solvent was placed in the bottle and the air space was saturated with the vapour of the immiscible liquid, as when the two liquids had been previously shaken together.   This circumstance made it possible to take measurements when dealing with certain colloidal sols such as gelatin, where almost permanent emulsification occurred on shaking the sol with an immiscible liquid.

In Table I, the interfacial tension of the liquid mentioned in column 1 in contact with water is given in column 6.   The liquids were purified and redistilled.   The difference between the values in columns 2 and 4 is given in column 5.   The close agreement between the calculated values in column 5 and the observed values in column 6 will be noted.   Column 7 gives the temperature at which the observations were made.

TABLE I.

Oil.	Surface tension of water saturated with the oil.	Surface tension of the dry oil.	Surface tension of the oil saturated with water.	Interfacial tension calculated.	Interfacial tension observed.	Temperature.
Benzene	63·2	28·4	28·8	34·4	34·4	19°
Ethyl ether	28·1	17·7	17·5	10·6	10·6	18
Aniline	46·4	41·9	42·2	4·2	4·8	26
Chloroform	59·8	27·2	26·4	33·4	33·3	18
Carbon tetrachloride...	70·2	26·7	26·7	43·5	43·8	17
Nitrobenzene	67·9	43·4	43·2	24·7	24·7	18

The interfacial tension of pure liquids is invariable at constant temperature; surfaces had the same tension after five minutes and after twenty-four hours in each of the above cases.   When, however, one of the liquids is complex, that is, an aqueous solution, colloidal sol, or mixture of two or more organic solvents, the interfacial tension frequently depends on the age of the contact surface, because concentration of one or more of the constituents of the solutions often occurs.   It seems probable that the law stated above holds true in nearly all phases of these cases also, but where the value of the tension is rapidly changing it is only practicable to make comparable observations of the interfacial and surface tensions in particular circumstances, and at times dynamical methods must be employed where statical ones are unsuitable.   The author has endeavoured to find in each case the interfacial tension of freshly formed surfaces, and of old surfaces when final equilibrium had been reached.   In all these complex contact surfaces so far examined, the underlying cause of surface concentration appears to be this : at any given temperature the interfacial tension tends towards a minimum ; it never increases spontaneously with age.   If, therefore, one of the constituents of a mixture has a lower interfacial tension

than the others, it is attracted towards the contact surface, the movement in the case of organic solvents and of many colloidal sols proceeding for many hours.   The three classes are considered separately below.

Mixed Organic Solvents.

The figures in Table II prove that the law holds good in the case of mixtures of organic solvents when the interfaces are freshly formed or old surfaces are disturbed.   In some cases mixtures of nearly allied solvents behave like pure solvents, and the interfacial tension retains the same value in the case of old surfaces.   Where, however, one of the ingredients has a much lower interfacial tension than the other constituents, this is found to be slowly drawn towards the surface of separation, concentration proceeding here for many hours, during which the interfacial tension falls slowly.   Thus, when water is brought into contact with benzene to which a small proportion of a liquid (such as oleic acid) which has a lower interfacial tension than itself has been added, the interfacial tension falls slowly for several hours.   The question arises, Does the interfacial law still hold in the cases of the older surfaces when equilibrium has been reached and the interfacial tension has become constant ? It appears that the apparent equilibrium applies only to the contact surface.   The oleic acid in twenty-four hours reaches a new concentration and the water a new degree of saturation at the interface, but the changes do not extend to the body of the two liquids, which retain the same surface tensions as they had when the contact surfaces were fresh.   This class therefore does not obey the law in regard to old surfaces, though this may in reality be due to our inability to measure the surface tensions at the actual interface.

All the various commercial products from petroleum, even after they had been distilled with steam in the presence of sodium hydroxide to remove traces of saponifiable oils, showed more or less adsorption with time, due to the presence of constituents of low interfacial tension.

In Table II, the values of the tensions for the mixed solvents shown in column 1 are given.   Where two figures are bracketed, the larger refers to surfaces five minutes old, and the smaller to those twenty-four hours old.   Where only one figure is given, this applies to both.

In several instances surface concentration had already occurred to a measurable extent at surfaces five minutes old, and the interfacial tension, even at this early stage, was already somewhat below the calculated value.   In the case of liquid paraffin, B.P., the adsorption was so rapid that no accurate measurement of the

TABLE II.

Oil.	Surface tension of water saturated with the oil.	Surface tension of the oil.	Surface tension of the oil saturated with water.	Interfacial tension, calculated.	Interfacial tension, observed.	Temperature.
Amyl alcohol	26·3	24·4	21·5	4·8	4·8	18°
Cresylic acid	37·8	37·1	34·3	3·5	3·9	18
Petrol	69·6	22·0	22·0	47·6	$\left\{\begin{matrix}46·4\\37·1\end{matrix}\right\}$	18
White spirit	69·5	25·2	25·1	44·4	$\left\{\begin{matrix}42·3\\39·4\end{matrix}\right\}$	18
Paraffin oil	73·0	24·8	24·7	48·3	$\left\{\begin{matrix}48·7\\43·1\end{matrix}\right\}$	18
Liquid Paraffin, B.P.......	73·0	31·6	31·5	41·5	$\left\{\begin{matrix}(41)\\15·1\end{matrix}\right\}$	17
Turpentine	63·0	27·2	27·2	35·8	$\left\{\begin{matrix}34·2\\28·8\end{matrix}\right\}$	18
Amyl alcohol, 5 % + $\}$... Benzene, 95 %	41·4	28·0	26·0	15·4	$\left\{\begin{matrix}16·7\\16·1\end{matrix}\right\}$	17
Aniline, 5 % + $\}$ .... Benzene, 95 %	57·1	29·4	29·6	27·5	27·1	17
Cresylic acid, 1 % + $\}$... Benzene, 99 %	56·5	29·1	28·7	27·8	27·5	17
Oleic acid, 1 % + $\}$...... Benzene, 99 %	63·0	29·3	29·2	34·8	$\left\{\begin{matrix}30·8\\24·2\end{matrix}\right\}$	17

fresh surface was possible by the author's statical method. By the dynamical method the value 41 was obtained when drops were allowed to form rapidly from a special pipette of wide bore. When the drops formed slowly the value fell to about one-half.

Aqueous Solutions.

In Table III the interfacial tensions between benzene and aqueous solutions of the compounds in column 1 are recorded. The differences between the values in columns 5 and 6 are given in column 7; they are in close agreement with the observed values in column 8.

TABLE III.

Solute.	Density of the aqueous solution.	Gram-mols. of solute per litre.	Surface tension of solution.	Surface tension of solution saturated with benzene.	Surface tension of benzene saturated with the solution.	Interfacial tension, calculated.	Interfacial tension, observed.	Temperature.
Sodium chloride ...	1·0012	0·1	72·2	64·0	28·9	35·1	34·9	18°
„ „ ...	1·041	1·0	74·4	65·5	28·7	36·8	37·3	19·5
„ „ ...	1·187	5·0	83·5	72·0	29·1	42·9	42·5	17
Sodium hydroxide ...	1·046	1·0	74·8	65·3	28·9	36·4	37·7	18
„ „ ...	1·191	5·0	84·5	72·7	29·0	43·7	44·7	17
Sulphuric acid	1·0275	0·5	73·0	62·5	28·0	34·5	35·0	25
„ „	1·151	2·5	75·6	65·7	28·9	36·8	36·6	18
„ „	1·291	5·0	77·45	66·2	28·9	37·3	37·1	18
Sodium thiosulphate	1·041	0·1	73·5	63·4	28·7	34·7	34·6	20
Glycerol	1·114	5·0	70·9	57·7	28·7	29·0	28·6	20
Sucrose	1·014	0·1	73·7	62·7	28·7	34·0	34·4	20
„	1·135	1·0	75·3	63·0	28·9	34·1	34·1	18

The law holds true in all these cases, the interfacial tension after five minutes remaining constant for twenty-four hours. This does not mean that surface concentration does not take place but it does prove that if it occurs it is complete, within measurable limits, in the case of surfaces five minutes old.

Colloidal Sols.

The sols were prepared as follows and kept under sterile conditions.

Gelatin.—Coignets Extra (Gold Label) was filtered. The viscosity of this sol varies considerably with its age, but the interfacial tension was found to be independent of the viscosity.

Gum Acacia.—Filtered aqueous sol.

Gum Tragacanth.—The powdered gum, moistened with a little alcohol, was treated with water, concentrated on the water-bath to remove the alcohol, diluted to volume and filtered under sterile conditions in an incubator at 37°. The insoluble matter adsorbed much of the gum, the original 0·5 per cent. sol only containing 0·32 per cent. after filtration.

Starch.—Two per cent. unfiltered sols of various starches differ greatly in viscosity, that of potato starch being 53·2 (water = 1), and that of rice starch only 3·7.

The sterile sols were allowed to stand in tall, covered cylinders for some days while the insoluble matter slowly settled at an average rate of about 2 cm. per day. The insoluble matter adsorbed a large proportion of the starch, the decanted clear arrowroot sol only leaving 0·488 per cent. on evaporation instead of 2 per cent.; the viscosity meanwhile had fallen from 7·6 (unfiltered) to 1·52 (clear, decanted).

Lord Rayleigh's classical experiments (*Proc. Roy. Soc.*, 1890, **47**, 281) have proved that the surface tension of soap solutions, when the surface is not more than one-hundredth of a second old, is the same as that of water, although when the surface is only a few seconds old the value may fall to approximately one-half, owing to the extremely rapid concentration of the soap at the surface. If colloidal sols behave like soap solutions and have the same surface tension as water in freshly formed surfaces, it might be anticipated that the sols in contact with benzene would, at the moment of contact, have the same interfacial tension as benzene and water. The application of ripple and jet methods of measurement to the sols mentioned below does not appear to have been undertaken. By Donnan's drop-pipette method it is possible to make a comparison of the interfacial tension between benzene and colloidal sols with that between benzene and water, and if the drops are forming

very rapidly (about ninety per minute) the surfaces are still fairly fresh.

In Table IV the number of drops of benzene formed in the sols is compared with the corresponding number formed in water at the same rate at 18°. From these numbers it appears that surface concentration in these cases does not take place so rapidly as in soap solutions, where very much larger drop numbers are obtained under the same conditions, and that the sols in question have nearly the same interfacial tension at this stage as water.

TABLE IV.

Sol.	Number of drops of benzene formed.	Interfacial tension observed after 15 minutes.
[Water	84	34·4]
0·5 per cent. Gelatin...............	96	21·0
0·1 ,, ,, ,, ...	85	26·1
10 ,, ,, Acacia	87	32·9
5 ,, ,, ,, ...	86	34·6
1 ,, ,, ,, ...	85	36·3
0·5 ,, ,, Tragacanth, 0·32 *	92	25·9
2 ,, ,, Arrowroot, 0·488*	85	36·3
2 ,, ,, Patent Starch	85	36·3

* Percentage concentration after clarification.

The interfacial tension of these sols in contact with benzene, measured by the statical method when the surfaces were fifteen minutes old, is recorded in column 3. From a comparison with the drop numbers in column 2 it will be seen that considerable concentration had occurred in the case of gelatin and tragacanth. As the interface grew older equilibrium generally supervened very slowly, owing to the lowering of the surface tension as surface concentration of the colloid proceeded. It was therefore necessary to make observations at intervals over twenty-four hours; even then it was doubtful in a few cases whether adsorption had reached measurable limits, but it was difficult to keep the apparatus at a constant temperature for longer periods by means of the water-jacket, and the error due to the variation in temperature effected minute changes in the interfacial tension. Starch sols formed an exception, for here equilibrium was reached almost immediately. But it was not only the interfacial tension of the sols in contact with benzene that changed with time. The surface tensions of the sols, alone and also when saturated with benzene, also altered, and it was found that the values of these tensions, observed at surfaces of the same age, were in agreement with the interfacial law.

The general behaviour will be made evident by considering one example in detail. A 10 per cent. sol of gum acacia had a surface

tension of 72·8 dynes per cm. when the surface was freshly disturbed, but the value diminished gradually for several hours as surface concentration occurred, and after twenty-four hours it was 69·0. The surface tension of this sol saturated with benzene changed similarly, and was found to be 53·0 after twenty-four hours. The interfacial tension in contact with benzene was 32·9 dynes per cm· when the contact surfaces were fifteen minutes old, but fell to 27·6 after three hours, and to 25·9 after twenty-four hours.

In Table V are given the results obtained with surfaces twenty-four hours old. Where two values are bracketed the higher refers to the fresh surface, and the lower to the twenty-four hour-old surface; otherwise, the value does not alter with age. The difference between the values in columns 3 and 4 is given in column 5, and agrees fairly well with the figure in column 6, although the agreement is not so good as that in Table III.

TABLE V.

Sol.	Surface tension of the sol.	Surface tension, after 24 hours, of the sol saturated with benzene.	Surface tension of benzene saturated with sol.	Interfacial tension after 24 hours, calculated.	Interfacial tension observed after 24 hours.	Temperature.
0·5 per cent. Gelatin	71·1 / 65·5	48·2	28·9	19·3	19·9	18°
0·1 ,, ,, ,, ...	69·4 / 66·4	50·2	29·0	21·2	23·4	17
10 ,, ,, Gum Acacia	72·8 / 69·0	53·0	28·9	24·1	25·9	18
5 ,, ,, ,, ,, ...	73·0 / 70·3	56·0	28·7	27·3	29·9	19
1 ,, ,, ,, ,, ...	73·5	62·9	28·9	34·0	34·5	18
0·5 ,, ,, Gum Tragacanth, 0·32*	70·0 / 57·8	45·3	28·9	16·4	19·2	18
2 ,, ,, Arrowroot, 0·488* 73		64·0	28·8	35·2	35·7	19
2 ,, ,, Patent Starch .... 73·8		63·5	28·9	34·6	36·3	18

* Percentage concentration after clarification.

The meniscus of a twenty-four hour-old sol in a capillary tube standing in a closed bottle exhibits in some cases a distinctly gel-like character. When the contents of the tube are allowed to exude slowly on to a watch glass, this gel-like surface, retaining the form of the meniscus, and having a depth equal to its diameter, may be seen floating in the body of the sol for some minutes before it is absorbed.

Soap Sols.

The surface and interfacial tensions of nine dilutions of soap sols, belonging to three typical classes, in contact with benzene were investigated. The behaviour of these sols resembled in general

that of the colloid sols mentioned above, the chief difference being the more rapid surface concentration in the case of the soap sols.

From Lord Rayleigh's observations on surface tension (*loc. cit.*) it may be anticipated that the interfacial tension between the soap sols and benzene, at the moment of contact, would be the same as that between water and benzene. The freshest contacts that the author observed were those formed in the manner described in the case of the colloid sols.

In column 8 of Table VI the number of drops of benzene, formed in the soap sols as quickly as they could be accurately counted is compared with the number of drops formed in water in the same circumstances. The results prove that the interfacial tensions at these contact surfaces, which must be considerably under one second old, are 75—21 per cent. of that of benzene–water contacts (34·4 dynes per cm.).

The interfacial tension determined by the preceding statical method became constant after five minutes in seven out of the nine dilutions, whilst, in the surface tension measurements of the sols themselves, in contact with air, equilibrium was only established after 10—120 minutes. Surface concentration therefore appears to be more rapid at benzene- than at air-contacts.

It is probable that very fresh contacts, one-hundredth of a second old, would obey the interfacial law stated above. Old contacts, when surface concentration was complete, did not do so, the observed interfacial tension being higher than that calculated from the surface tensions of the immiscible liquids. This may be due to a smaller surface concentration at benzene contacts than at saturated soap sol-air surfaces, but the measurements may be appreciably affected by hydrolysis of the soap, the free fatty acid being dissolved by the benzene and a more alkaline, aqueous sol remaining.

The soap sols were prepared as follows. Ten grams of the oil mentioned in column 1 (Table VI) were saponified by that volume of a solution of sodium hydroxide (D 1·30) which experience had shown yielded a neutral soap, the soap was dissolved and the solution made up to 100 c.c. The other dilutions were prepared from the 10 per cent. sol. A 10 per cent. cocoa-nut sol crystallised after some days, and a 1 per cent. sol gelled, but on warming and cooling both remained clear mobile fluids for more than twenty-four hours, and the measurements were made on the recently cooled sols. All observations were made at 17—18°. The observed interfacial tensions for contacts after twenty-four hours and after five minutes are given in columns 6 and 7 respectively; the calculated tensions, that is the difference of the values in columns 3 and 4, are given in column 5.

TABLE VI.

Soap sol.	Surface tension of the sol after 4 hours.	Surface tension of the sol saturated with benzene, after 24 hours.	Surface tension of benzene saturated with the sol.	Interfacial tension calculated.	Interfacial tension observed after 24 hours.	Interfacial tension observed after 5 minutes.	Number of drops of benzene.
[Water	73·4	63·2	28·6	34·6	34·4	34·4	84]
10 % Castor Oil	35·1	30·9	28·6	2·3	3·0	3·0	398
1 % ,, ,, ...	35·8	32·0	28·6	3·4	5·6	5·7	249
0·1 % ,, ,, ...	43·5	46·2	28·6	17·6	23·2	23·2	124
10 % Olein (commercial) ...	26·6	26·3	28·6	−2·3	1·6	1·6	237
1 % ,, ,, ...	25·7	26·8	28·6	−1·8	3·3	3·5	214
0·1 % ,, ,, ...	25·4	38·1	28·6	9·5	17·2	21·3	113
10 % Cocoanut Oil (pressed)	26·5	26·7	28·6	−1·9	2·7	2·7	306
1 % ,, ,, ,,	23·3	27·7	28·6	−0·9	5·2	5·2	249
0·1 % ,, ,, ,,	29·4	50·7	28·6	22·1	27·6	27·6	114

The author's results indicate that surface concentration is much more widely prevalent than is generally supposed, and that it affects solutions of every description. It seems not improbable that this phenomenon affects certain physical measurements such as viscosity and lubrication tests.

The study of interfacial tension may throw light upon many chemical and biological problems. Whenever investigation proves that the interfacial tension of two immiscible liquids is not constant at a given temperature, or that the liquids do not obey the interfacial tension law, surface concentration, or electrical or chemical action, is indicated.

In Part III it will be shown that interesting electro-chemical relationships can be explained by means of the interfacial tension law.

Two minor instances of its use in directing attention to chemical changes were noted during the investigation, and are perhaps worth recording.

Carbon disulphide in contact with water and air does not obey the interfacial tension law. The surface tension of water saturated with carbon disulphide is 72·2, and that of carbon disulphide saturated with water is 32·1; the interfacial tension should therefore be the difference, 40·1. The observed figure was 49·3.

The discrepancy was found to be due to the chemical interaction of air, water, and carbon disulphide. When the two liquids are shaken together in a separator for a few seconds, an almost invisible film of a substance insoluble in either liquid separates at the interface. This is made more apparent by draining off the carbon disulphide, when the film is compressed into the restricted area just above the tap and is thus more easily seen. When the two

liquids are allowed to remain in contact for several hours in a wide, stoppered bottle, decomposition proceeds, and a yellowish-brown precipitate forms at the interface.   Purification of the carbon disulphide in various ways failed to yield a product which did not show these changes, and samples obtained from three firms behaved alike.   The nature of the oxidation product was not investigated.

Turpentine in contact with air undergoes oxidation so rapidly that the accurate measurement of its interfacial tension in contact with water is made very difficult.   The slightest contact with air during distillation makes a great difference in the product.   Samples of the same specimen of turpentine were distilled as described in column 1 below.   The interfacial tension of the distillate in contact with water is noted in column 2.

Distilled in a vacuum with an air-inlet tube passing to the bottom of the flask	10·3
Distilled at the ordinary pressure from a half-filled flask	25·8
Steam distilled from a half-filled flask	27·8
Distilled and cooled in a vacuum	34·2

All these distillates had the same surface tension in contact with air, namely, 27·2.   They changed slowly in character when stored in partly filled, stoppered bottles.   Thus the sample with an interfacial tension 25·8 gave the value 20·9 after a few hours, and after it had been stored for sixteen days in a half-filled bottle the interfacial tension had fallen to 12·9.   The specimen which originally showed 34·2, after having been kept for 111 days in a nearly full bottle, gave the value 20·1, and another portion of the same specimen, after 111 days' storage in a bottle, the neck of which was plugged with cotton wool, had an interfacial tension of 1·06 only.   The changed products, after having been shaken with a dilute solution of sodium hydroxide to remove acid matter which had been formed, and redistilled in a vacuum, regained their original properties; it was thus shown that the oxidation only affected a moderate proportion of the whole liquid.

The change of interfacial tension with temperature will be the subject of a further communication.

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