LXXXIII.—*The Angles of Floating Lenses.*

By Charles George Lyons.

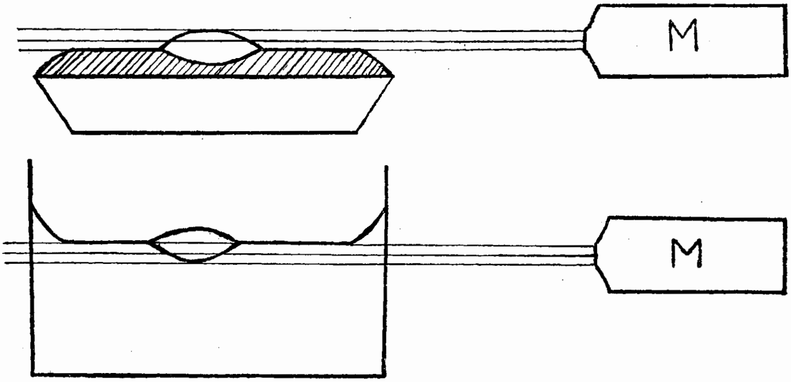
Several investigations have been made on the relationships between the statical equilibrium of an interface and the arrangement of the molecules at the boundary. Many of these studies were based on measurement of angles of contact; for example, Adam and Jessop (J., 1925, **127**, 1863) studied the variation in these angles for water against various solid substances which had been used in film experiments. Practically all of these earlier researches were concerned with the contact angles of liquids against solids, and the liquid–liquid angles have been comparatively neglected.

The exact configuration of the molecules at the surface of a solid cannot be established except in the case of a single crystal, but at a liquid boundary the molecular orientation presents much less difficulty. It seemed probable, therefore, that the measurement of liquid–liquid angles of contact would yield definite information about the molecular basis of the interfacial equilibrium. These angles are most conveniently obtained as the angles of a lens of one liquid which is floating on another liquid, both being mutually insoluble. Such angles were studied qualitatively by Quincke (*Phil. Mag.*, 1871, **41**, 454) and by Hardy (*Proc. Roy. Soc.*, 1912, *A*, **86**, 61), and quantitatively by Coghill and Anderson (*Bureau of Mines Tech. Papers*, 1924, 262); the last two authors, however, used an indirect method, calculating the angle from the dimensions of the lens on the assumption that its shape was governed solely by the surface-tension forces acting at its edges. As this assumption need not necessarily be true, it was decided to investigate these angles by direct measurement.

EXPERIMENTAL.

A drop of a liquid was placed on the surface of another in which it was insoluble, and the floating lens formed was held loosely in position by a wire just touching its surface.

FIG. 1.



The surface of the liquid was illuminated with a horizontal beam of light, and the lens was then viewed with a microscope whose axis was horizontal. Its image was projected on a camera, and a photograph of the magnified image was taken. The angles of contact and all other data were then easily and accurately measurable on the photographic plate.

As the lens was illuminated parallel to the surface of the liquid on which it was floating, there was a possibility of distortion of the image by the meniscus at the walls of the containing vessel. This distortion was avoided (see Fig. 1) by photographing the upper surface of the lens in a trough filled nearly to overflowing so that the meniscus curved downwards, and the lower surface in a glass cell in which the meniscus was attracted upwards.

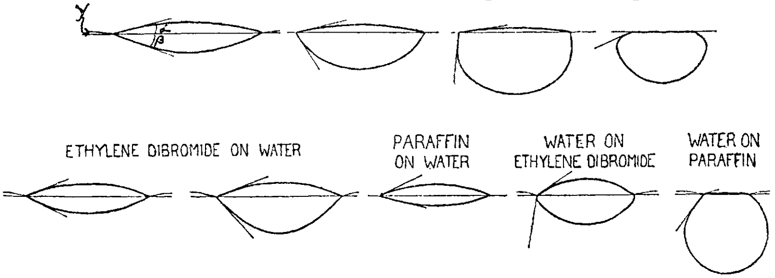
The apparatus, when finally adjusted, was tested for distortion by three methods: (1) a circular object held vertically in the surface of the liquid and perpendicular to the direction of vision was found to give a circular image; (2) by means of a graduated scale it was shown that the magnification ratio was the same vertically and horizontally; (3) pieces of wire bent into known angles gave images bearing these angles. The experimental arrangement therefore gave images of the lenses which represented their true shape.

To obtain the angles of a given lens, the microscope was focused on a medial section, and the angles were measured on the photographic plate with a protractor. The values obtained were probably accurate to ± 2°, the value of γ, the angle formed by the meniscus of the supporting liquid (see Fig. 2), being the most difficult to obtain, as it was usually small.

FIG. 2.

Oleic acid on

p_H 1·8 p_H 5·9 p_H 6·9 p_H 9·7



With this apparatus, lenses of oleic acid on aqueous solutions of various p_H were studied; also lenses of ethylene dibromide, carbon tetrachloride, and nujol (medicinal paraffin) on water, and of water on the last three liquids. The angles made by the liquid boundaries at the edge of the lens with the horizontal are given in Table I, in which surface tensions are given in dynes/cm., and Fig. 2 contains

TABLE I.

Liquid.	Lens.	α.	β.	γ.	σ_{12}.	σ_{23}.	σ_{13}.
Water	Oleic acid	10°	20°	0°	32·5	15·7	42·5
HCl, p_H 1·8	,,	13	28	2	32·5	16·0	44·5
*p_H 5·9	,,	13	57	0	32·5	11·7	41·0
*p_H 6·9	,,	7	96	0	32·5	9·7	35·0
*p_H 9·7	,,	Small	157	—	32·5	Small	34·0
$C_2H_4Br_2$	Water	34	99	4	73·0	36·5	38·7
CCl_4	,,	28	99	−11	73·0	45·0	26·7
Paraffin	,,	17	127	8	73·0	51·0	22·0
Water	$C_2H_4Br_2$	21	25—48	6—9	38·7	36·5	73·0
,,	CCl_4	12	Variable		26·7	45·0	73·0
,,	Paraffin	25	14	2	22·0	51·0	73·0

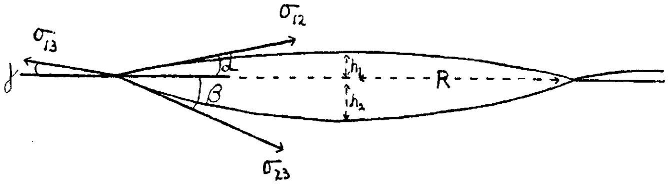
* These solutions were obtained by the use of phosphate buffers.

diagrams of the shapes assumed by the lenses under different conditions. From these, it is seen that the shape can be varied within wide limits, the lower submerged surface being particularly sensitive to changes in the conditions. Alteration in the size of the lens within the diameter range 0·4—2·5 mm. caused no appreciable alteration in the angles.

Discussion.

These results show that not only the shape but also the submergence of the lens changed when the surface tensions at the boundaries were varied. The fraction of the lens below the level of the surface of the bulk liquid ranged from 0·4 almost to unity for different pairs of liquids. The oleic acid series was especially interesting, for, as the underlying solution increased in alkalinity, the lens sank steadily into it, the lower surface becoming more and more curved and the value of β steadily rising.

Fig. 3.



The shape of the lens was shown in this way to be controlled chiefly by the interfacial tension between the two liquids. This tension gradually decreased from 16·0 dynes/cm. to a very small value as the alkalinity rose, while the individual surface tensions of the two liquids (against air) remained practically constant.

These results are qualitatively explicable on the simple theory of the lens equilibrium. This demands that the angles should be controlled solely by the surface-tension forces, in such a way that at the edge of the drop the three surface tensions are in statical equilibrium as shown by the triangle of forces (Neumann's triangle). These conditions may be written in the form of the two equations

$$\sigma_{12}\sin\alpha - \sigma_{23}\sin\beta + \sigma_{13}\sin\gamma = 0 \quad . \quad . \quad . \quad (1)$$

$$\sigma_{12}\cos\alpha + \sigma_{23}\cos\beta - \sigma_{13}\cos\gamma = 0 \quad . \quad . \quad . \quad (2)$$

where σ_{12} and σ_{13} are the surface tensions of the liquids (in air), and σ_{23} is their interfacial tension, the angles being as shown in Fig. 3. From these equations it will be seen that if the interfacial tension is decreased while the surface tensions remain nearly constant, the lower angle of contact, β, will gradually increase so that $\sigma_{23}\sin\beta$ may still balance the vertical component of σ_{12}. This angle must become re-entrant if the horizontal component of the surface tension of the lens liquid becomes greater than that of the supporting liquid. The observed changes in the oleic acid lenses as the interfacial tension is progressively decreased are in agreement with these predictions.

The increased submergence of the lens as the interfacial tension decreases follows directly from considerations of the free energy of the system. As the interfacial tension decreases, the surface energy at the liquid–liquid boundary decreases, and the area of this interface must increase at the expense of the other surfaces. This effect is analogous to the spreading of a liquid over a solid surface if the interfacial tension is low; and is only complicated because the surface of the supporting liquid is not an immobile plane as in the case of a solid.

Failure of the Simple Theory.—The fact that Coghill and Anderson's values of the angles did not agree with the simple theory, despite the fact that they were calculated on equations which should have secured agreement, indicated the need for a closer analysis of the lens equilibrium.

It is well known that the determination of surface tensions by Quincke's method (*loc. cit.*), based on the measurement of drops of liquid resting on a solid, gives values which are at least 10% too high. It was shown by Worthington (*Phil. Mag.*, 1885, **20**, 51) that this is due to the neglect of the internal pressures caused by the curvature of the drop surfaces. Coghill and Anderson's equations must therefore involve errors of a similar magnitude.

The lenses used in this investigation were considerably smaller than those used by the earlier workers, and therefore this effect should be present in even greater intensity. An analysis of the results obtained confirmed this deduction, for, when the vertical and horizontal components of the surface tensions * were evaluated in accordance with equations (1) and (2), it was found that their sum often differed considerably from zero. This is shown in Table II, in which cols. 4 and 8 should be zero if the equations were valid.

This effect of the internal pressure may be compared with the difference in the angle of contact between advancing, stationary, and retreating boundaries of a liquid on the surface of a solid. Nevertheless, there can be no direct comparison of the angles of a floating lens with the solid–liquid angles of contact, because the surface of the supporting liquid does not remain a plane.

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* The values of the surface tensions and interfacial tensions were chiefly taken from the International Critical Tables, Vol. 4. Those for the interfacial tensions between oleic acid and aqueous solutions of various p_H were Hartridge and Peters's values (*Proc. Roy. Soc.*, 1922, *A*, **101**, 348), confirmed by the capillary-rise method with the actual solutions used in this investigation.

TABLE II.

Liquid.	Lens.	1. σ_{12} $\sin\alpha$.	2. $-\sigma_{23}$ $\sin\beta$.	3. σ_{13} $\sin\gamma$.	4. $\Sigma\sigma$ $\sin\theta$.	5. σ_{12} $\cos\alpha$.	6. σ_{23} $\cos\beta$.	7. $-\sigma_{13}$ $\cos\gamma$.	8. $\Sigma\sigma$ $\cos\theta$.
Water	Oleic acid	5·6	− 5·3	0·0	0·3	32·0	14·7	−42·5	4·2
HCl, p_H 1·8	,,	7·3	− 7·5	1·5	1·4	31·7	14·1	−44·4	1·4
*p_H 5·9	,,	7·3	− 9·8	0·0	− 2·5	31·7	6·4	−41·0	− 2·9
*p_H 6·9	,,	4·0	− 9·6	0·0	− 5·6	32·2	− 1·0	−35·0	− 3·8
$C_2H_4Br_2$	Water	40·8	−35·9	2·7	7·6	60·5	− 5·7	−37·8	17·0
CCl_4	,,	34·3	−44·4	−5·0	−15·1	64·4	− 7·0	−26·2	31·2
Paraffin	,,	21·5	−40·7	3·1	−16·4	69·8	−30·7	−21·8	17·3
Water	$C_2H_4Br_2$	13·9	−27·1 to −15·4	11·4 to 7·6	− 1·8 to 6·1	36·1	33·1 to 24·4	−72·5 to −72·1	− 3·3 to −11·6
,,	Paraffin	9·3	−12·3	1·5	− 0·5	19·9	49·5	−72·9	− 3·5

* These solutions were obtained by the use of phosphate buffers.

Neither of these series of angles can as yet be correlated with the known orientation of the molecules at the interface, nor can the molecular mechanism which decides the values of the angles of contact be determined. But the significance of the angle γ is quite clear, for it depends solely on the depth to which the lens is submerged. The vertical component of the surface tension of the lower liquid must support the lens if its weight and buoyancy do not exactly balance, and this component can only be zero (*i.e.*, $\gamma = 0$) when these two forces are equal and opposite.

If W_1 is the weight of the lens, W_2 that of the lower liquid displaced, and r the radius of the lens, then

$$2\pi r\sigma_{13}\sin\gamma = W_1 - W_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

if the small correction for the lowering of the meniscus of the lower liquid at the edge of the lens be neglected.

From Table III it is seen that this equation holds for all the lenses studied in this investigation: cols. 4 and 5 should be identical if the equation is valid, and the differences actually obtained are within the limits of experimental error. The weights were calculated from the cross sections of the lenses measured on the photographic plates, their areas and centres of gravity being determined directly. Weights are given in dynes and r in mm.

TABLE III

Liquid.	Lens.	1. r.	2. W_1.	3. W_2.	4. $W_1 - W_2$.	5. $2\pi r\sigma_{13}\sin\gamma$.
Water	Oleic acid	1·6	1·36	0·96	0·4	0·0
p_H 1·8	,,	2·3	7·6	6·1	1·5	2·1
p_H 5·9	,,	1·95	9·2	8·8	0·4	0·0
p_H 6·9	,,	1·4	5·3	5·7	−0·4	0·0
p_H 6·9	,,	1·7	12·0	12·9	−0·9	0·0
$C_2H_4Br_2$	Water	1·46	5·25	4·1	1·15	2·4
CCl_4	,,	1·65	12·8	17·2	−4·4	−5·2
Paraffin	,,	0·73	8·7	6·4	2·3	1·4
Water	Paraffin	1·77	2·5	1·4	1·1	2·4
,,	$C_2H_4Br_2$	1·89	17·8	5·5	12·3	13·3
,,	,,	1·89	11·1	2·5	8·6	9·0

In order to obtain a more definite analysis of the conditions of lens equilibrium, it is necessary to make assumptions which simplify the problem. The lenses which have been studied were not very large, and as their surfaces did not depart very much from segments of spheres, it is justifiable to assume that they actually had this shape. Under these conditions, the principle of virtual work may be used to make a more definite examination of the statical equilibrium of the lens.

Consider a lens of radius R, formed of two spherical segments of radii r_1 and r_2, and heights h_1 and h_2 (Fig. 3). Then

$$R^2 = r_1{}^2 - (r_1 - h_1)^2 = 2r_1h_1 - h_1{}^2 = 2r_2h_2 - h_2{}^2 \quad . \quad (4)$$

Let the lens be given a small displacement increasing its radius to $R + dR$ without transference of liquid from one segment to the other, *i.e.*, without altering the volume of either segment. Then $R \,.\, \Delta R = r \,.\, \Delta h + h \,.\, \Delta r - h \,.\, \Delta h$. The volume V of a segment of height h of a sphere of radius r is equal to $\pi h^2(r - \frac{1}{3}h)$, and therefore

$$\Delta V = \pi(2hr \,.\, \Delta h + h^2 \,.\, \Delta r - h^2 \,.\, \Delta h)$$

By the conditions of the displacement, $\Delta V = 0$, hence $\Delta r = -(2r - h)\Delta h/h$, and by substitution in the above equation it follows that

$$R \,.\, \Delta R = -r \,.\, \Delta h = r \,.\, \Delta A/2\pi(r - h) \quad . \quad . \quad . \quad (5)$$

where A is the superficial area of the segment and is equal to $2\pi rh$. During this displacement work is done (1) by the surface tension forces, owing to change in superficial area of each surface of the lens and of the underlying liquid, (2) by the internal-pressure forces caused by the curvature of the lens surfaces, and (3) by gravity and the upward thrust of the displaced liquid, owing to the change in position of the centre of gravity of each segment of the lens. The magnitude and sign of these effects are now evaluated in turn, and the conditions of equilibrium are then obtained by equating their algebraic sum to zero.

(1) The total work done by the surface-tension forces is given by the algebraic sum of the products of the surface tensions and the change in area, *i.e.*, by

$$\sigma_{12}\Delta A_1 + \sigma_{23}\Delta A_2 - \sigma_{13}\Delta(\pi R^2) \cos \gamma$$

By substituting from (5), it is found that this work is equal to

$$2\pi R \,.\, \Delta R[\sigma_{12}(1 - h_1/r_1) + \sigma_{23}(1 - h_2/r_2) - \sigma_{13} \cos \gamma] =$$
$$2\pi R \,.\, \Delta R[\sigma_{12} \cos \alpha + \sigma_{23} \cos \beta - \sigma_{13} \cos \gamma] \quad . \quad . \quad (6)$$

Neumann's triangle [equation (2)] demands that the expression between the brackets should be zero for equilibrium. This follows necessarily where only the surface tensions are considered.

(2) Under the conditions governing the displacement given to the lens (*i.e.*, no volume change of either segment), the total work done by the internal pressures is found to be zero if the lens surfaces are accurately spherical segments, thus : The displacement of a ring of the surface subtending an angle ω at the centre of curvature is $\Delta r \,.\, (1 - \cos \omega) + \Delta h \,.\, \cos \omega$; the total work done by the internal pressure is therefore

$$\int \frac{2\sigma}{r} \,.\, 2\pi r^2 \Delta(\cos \theta)[\Delta r \,.\, (1 - \cos \omega) + \Delta h \,.\, \cos \omega] \quad . \quad (7)$$

and on integration and substitution this integral is found to vanish.

(3) The height of the centre of gravity of a spherical segment above its basal plane is

$$\bar{h}_1 = R^4/4h^2(r - \tfrac{1}{3}h) - (r - h) \quad . \quad . \quad . \quad . \quad (8)$$

The work done by gravity on the lens is $- gV_1\rho_1 \,.\, \Delta h_1$, and the work done by the upward thrust is therefore $- gV_2(\rho_2 - \rho_1) \,.\, \Delta h_2$, where V_1 and V_2 are the volumes of the upper and lower segments of the lens, and ρ_1 and ρ_2 are the densities of the lens liquid and the supporting liquid, respectively.

By differentiating equation (8) and substituting from equations (4) and (5), it follows that the total work from both these causes is equal to

$$- 2\pi R \,.\, \Delta R \,.\, g \,.\, [\tfrac{1}{2}R^2\rho_2 - h_1\rho_1(r_1 - \tfrac{1}{3}h_1) - h_2(\rho_2 - \rho_1)(r_2 - \tfrac{1}{3}h_2)] \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now, from the principle of virtual work, the sum of expressions (6) and (9) must be zero; the conditions for equilibrium are therefore given by

$$[\sigma_{12} \cos \alpha + \sigma_{23} \cos \beta - \sigma_{13} \cos \gamma] - g[\tfrac{1}{2}R^2\rho_2 - h_1\rho_1(r_1 - \tfrac{1}{3}h_1) - h_2(\rho_2 - \rho_1)(r_2 - \tfrac{1}{3}h_2)] = 0 \quad . \quad . \quad . \quad . \quad (10)$$

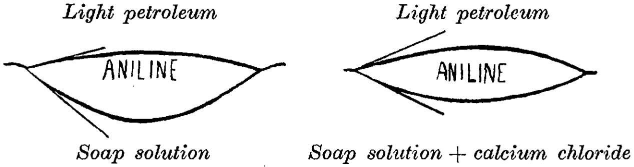
This equation may be tested experimentally. All the relevant data are obtained from the photographic plates, and collected in Table IV (linear measurements being in mm., and tensions in dynes/cm.). Col. 6 reproduces the values of the first term in equation (10) as given in Table II (col. 8) for the examination of equation (2); col. 7 contains the (negative) values of the second term in equation (10) which is applied as a correction to equation (2). The smallness of the algebraic sum of cols. 6 and 7, as given in col. 8, shows that the agreement between equation (10) and experiment is good, and that this equation is a definite improvement on the simpler equation (2) derived from Neumann's triangle. Lenses of carbon tetrachloride, ethylene dibromide, and paraffin on water still show a serious discrepancy. In these cases, the photographic records indicated that the segments were markedly divergent from spheres

TABLE IV.

		1.	2.	3.	4.	5.	6.	7.	8.
Liquid.	Lens.	R.	h_1.	r_1.	h_2.	r_2.	$\Sigma\sigma\cos\theta$.		
Water	Oleic acid	1·6	0·16	7·7	0·20	4·15	4·2	−1·3	2·9
p_H 1·8	,,	2·3	0·32	8·1	0·60	5·36	1·4	−0·8	0·6
p_H 5·9	,,	1·95	0·24	8·7	1·07	2·50	−2·9	2·4	−0·5
p_H 6·9	,,	1·40	0·10	14·1	1·37	1·54	−3·8	3·9	0·1
p_H 6·9	,,	1·7	0·10	12·1	1·83	2·1	−3·8	3·5	−0·3
p_H 9·7	,,	1·7	0·0	—	1·6	1·6	−0·5 (app.)	−1·5	−2·0 (app.)
Water	Paraffin	1·77	0·40	4·75	0·28	8·3	−3·5	3·7	0·2
,,	$C_2H_4Br_2$	1·89	0·41	6·8	0·49	4·76	−3·3	2·0	−1·3
,,	,,	1·89	0·41	6·8	1·11	1·7	−11·6	8·0	−3·6
$C_2H_4Br_2$	Water	1·46	0·47	2·60	0·85	1·9	17·0	−1·8	15·2
CCl_4	,,	1·65	0·46	2·80	1·71	1·6	31·2	1·0	32·2
Paraffin	,,	0·73	0·09	25·0	2·44	1·3	17·3	−2·2	15·1

(the lenses of oleic acid on very alkaline solutions were also not spherical), and the discrepancy between theory and experiment must be attributed to this fact. When the lens surfaces approach segments of spheres satisfactory agreement is obtained. It is seen that Neumann's triangle is obeyed only for very large drops, in which forces other than the surface tensions are negligible.

FIG. 4.



Floating Lenses at the Liquid–Liquid Interface.—When water was placed at a light petroleum–aniline interface, it spread completely over it, but when the surface tension of the water was lowered by the dissolution of a small quantity of soap (0·01% of sodium palmitate) a floating lens was obtained of which the angles were $\alpha = 30°$, $\beta = 76°$, $\gamma = 0°$. Lenses of aniline were similarly formed at the light petroleum–soap solution interface, the angles being $\alpha = 14°$, $\beta = 52°$, $\gamma = 14°$.

It was thought the addition of calcium chloride to the soap solution might prove interesting from the point of view of the theory of emulsions. Actually, such addition did alter the angles of the lens, and when sufficient calcium chloride was added to carry the solution over the inversion point, the angles became $\alpha = 25°$, $\beta = 24°$, $\gamma = 0°$, for a lens of aniline between light petroleum and the aqueous solution, and $\alpha = 25°$, $\beta = 95°$, $\gamma = 35°$, when the aqueous solution was floating between the other liquids. The former case is the more interesting, for here it was clearly seen that the alteration of the lens shape was illustrative of the phenomenon of emulsion inversion (compare Fig. 4), the curvature of the lower surface being greatly diminished owing to the tendency to curve in the opposite direction.

When these observations were compared with those on oleic acid, where a large curvature was associated with a low interfacial tension, it was seen that this tendency towards inversion could be explained by the raising of the interfacial tension σ_{23}.

Bancroft and Tucker (*J. Physical Chem.*, 1927, **31**, 1681) have deduced that the character of an emulsion is determined by the sign of the difference $\sigma_{23} - \sigma_{12}$. If $\sigma_{23} > \sigma_{12}$ the water will tend to be emulsified in the oil, but if $\sigma_{23} < \sigma_{12}$ the oil will tend to be emulsified in the water. The present observations support these conclusions by direct experiment, since it is concluded that the raising of the interfacial tension σ_{23} is favourable to inversion from oil in water to water in oil.

The changes occurring when the soap solution lies between the aniline and the light petroleum were neither as large nor as definite as in the case just considered. This may now be attributed to the fact that σ_{23} and σ_{12} were affected in roughly the same proportion.

The Mechanism of Emulsification by Soap.—Practically all the theories advanced to explain emulsification have received much adverse criticism, and Bancroft and Tucker believe that the surface-tension relationship mentioned above affords the only criterion by which the character of the emulsion can be decided. An objection to this view is that it gives no clue to the molecular mechanism of emulsification.

An attempt has been made to elucidate the mechanism in the case of emulsification by soap. The explanation tentatively suggested is based on the results of experiments on film dissolution (Lyons and Rideal, *Proc. Roy. Soc.*, 1929, *A*, **124**, 343), and on a modification of the wedge theory of emulsions. This theory in its original form broke down when it was shown that the molecules in the interfacial film were by no means close-packed, for Griffin (*J. Amer. Chem. Soc.*, 1923, **45**, 1648) found that the area occupied by a soap molecule at the oil–water interface was 44 Å.U., whereas Harkins and Beeman (*ibid.*, 1929, **51**, 1674) showed that an emulsion could be formed with an interfacial area of 190 Å.U.

The film experiments proved that a residual bimolecular film of acid soap was the stable surface configuration on alkaline solutions. It was thought that such a bimolecular leaflet might also be present at the oil–water interface, in which case it would have a profound influence on the emulsifying power of the soap solution.

There was little evidence by which the probability of this assumption could be judged,* but Briggs and Schmidt (*J. Physical Chem.*,

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* Miss Laing (*Proc. Roy. Soc.*, 1925, *A*, **109**, 28) had concluded that the existence of the bimolecular leaflet was proved by Griffin's results, but her conclusions were based on a misunderstanding.

1925, **19**, 479) had noticed that the stability of an emulsion of benzene in soap solution was increased by the addition of 0·1% of free alkali, although further alkali decreased the stability. It seemed possible that this variation in the stability of the emulsions might be connected with the alteration in composition of the residual bimolecular film with change in the alkalinity of the solutions, and experiments were therefore devised to test this possibility. A series of soap solutions of known p_H was made by the addition of caustic soda to a 0·01% sodium palmitate solution. A preliminary electrometric titration had been carried out to ensure that the solutions were made of standard alkalinity. These solutions were shaken with benzene under standardised conditions, and the stabilities of the emulsions thus formed were compared. Although the experiments were only semi-quantitative, the results obtained were quite definite.

On solutions more acid than p_H 8·0, both the benzene-in-water and the water-in-benzene emulsion had but little stability, but that of the former phase steadily increased from p_H 8·0 to p_H 10·0 at which it reached a maximum. The latter emulsion only attained an appreciable stability on solutions more alkaline than p_H 10·0, and stability increased with alkalinity until salting-out of the soap occurred. Both phases were almost equally stable in the p_H range 10—12. It was also observed that the frothing power of a soap solution ran strictly parallel to the stability of the benzene-in-water phase, and also reached a maximum at p_H 10·0.

The existence of the bimolecular leaflet at the surface of soap solutions seems well-established, and the similarity between frothing power and emulsifying power seemed to confirm the presence of this bimolecular leaflet at the benzene–water interface. A comparison was therefore made between the p_H values obtained in these emulsion experiments and in the film experiments, and it was found that they were identical.

On solutions where a benzene-in-water emulsion is the more stable, the film experiments showed that the lower layer of the equilibrium bimolecular leaflet was not completely packed. On very alkaline solutions, where a water-in-benzene emulsion is the more stable, the equilibrium bimolecular film had considerably less than half the area of the original unimolecular film. On solutions where the two layers were equally packed, the emulsions were of almost equal stability. These observations, therefore, support the view that emulsification depends on the presence of a bimolecular leaflet, while a unimolecular film shows little tendency to cause emulsion formation.

The mechanism of emulsification may now be pictured as follows.

When a soap molecule is first adsorbed at the interface it will be in the form NaP,HP, and will thus give a double film equally packed on either side. On solutions less alkaline than p_H 10 the equilibrium lower (aqueous) layer will be less densely packed than the upper layer, and this equilibrium state must be reached by one of two processes, *viz.*, either a transference of molecules across the interface, or a curving of the boundary. In emulsion formation the latter effect predominates. In order to increase the packing of the upper layer and decrease that of the lower layer of the initially symmetrical film, the boundary curves with the upper layer inside, squeezing it and giving an oil-in-water emulsion. A similar analysis accounts for the stability of water-in-oil emulsions on very alkaline solutions where the lower layer is probably more closely packed than the upper. Over the range at which a symmetrical leaflet is stable, the boundary will not curve preferentially in either direction, and neither form of emulsion will be more stable than the other.

These experiments have shown that this tentative suggestion of the bimolecular leaflet at the oil–water interface is consistent with the known data on emulsification by soaps. There is not yet sufficient evidence to show whether a similar explanation can be applied to other cases.

Summary.

The shapes and angles of liquid lenses floating on the surface of a different liquid have been studied by a photomicrographic method. The angles are subject to wide variations, and are especially sensitive to alterations in the interfacial tension between the two liquids. It has been shown, further, that these angles differ from those calculated on the basis of Neumann's triangle, and the causes of the difference have been investigated.

The contact angles at a junction of three liquids have been investigated with reference to the theory of emulsification. It has been suggested that emulsification by soap may be determined by the existence of a bimolecular soap leaflet at the oil–water interface.

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