SCIENTIFIC SECTION

PHYSICS IN PHARMACY.

PART II.*

BY JOHN URI LLOYD, WOLFGANG OSTWALD AND WALTER HALLER.

INTRODUCTION.

To the thoughtful pharmacist no phenomenon observed during his work can seem unimportant or uninteresting. Even though he does not at the moment perceive its immediate, practical importance, nevertheless he questions why it occurs as well as what caused the observed variations. It is from this point of view that we have subjected the phenomena of the *form of the intermediary menisci between two liquids* to closer experimental and theoretical investigation.

The pharmacist is continuously confronted with menisci variations, *e. g.*, whenever he shakes out an aqueous extract with another solvent that is not miscible with water or only partly so. If the experiment is made in a test-tube, he is soon struck with the very varying form of the common surface (interface) between the two liquids. The senior author has already given examples of such intermediary menisci in Part I of this series on Physics in Pharmacy.[1]

Owing to the fact that now and then doubts have arisen concerning the reality of these various shapes (the indices of refraction of the glass and the liquids, of course, play their part here as will be shown further on) we[2] have reinvestigated the whole subject of these menisci by means of improved experimental methods, notably the use of photographic apparatus designed for this particular purpose. Be it stated at the outset that we have been able to confirm the previous results in all essential points. Furthermore, we shall present a survey of the chief variables which are responsible for differences in shapes of menisci. This will probably supply a theory of these phenomena in first approximation.

I.

When two immiscible liquids are put into a test-tube, the heavier one will be at the bottom, the lighter above, and between them a fine curved line of separation, the meniscus, is visible. This line may present markedly different appearances, dependent upon the nature of the fluids. It may be curved upward or downward, sometimes strongly curved in the form of a semi-circle, and again may appear flat almost like a straight line. Optically speaking the meniscus is the horizontal projection of the common surface between the two liquids; this boundary surface thus assumes very different shapes, depending upon the liquids employed. Evidently for each pair of liquids there exists a characteristic form.

However, we must not overlook the fact that the meniscus as observed does not represent the true shape of the common surface. In reality only an imperfect and distorted shape of the surface is seen. The cause of this lies in the very

* Written in German and translated by Dr. Sigmund Waldbott.

[1] John Uri Lloyd, JOUR. A. PH. A., 11 (1922), 409.

[2] Wolfgang Ostwald and Walter Haller, University of Leipzig, Germany.

strong refraction and reflection of the light rays on their passage through the glass tube and the liquid. Especially the extreme margin of the meniscus is usually not visible at all on account of total reflection. It is true one may calculate the magnitude of the optical distortions and in this manner correct the observed menisci. However, such a calculation is usually very complicated. Much time and pains would be consumed in determining by calculation the exact shape of even one single common surface.

It is possible, however, through a definite experimental arrangement, to reduce the optical distortion of the menisci to a minimum of an exactly known value, enabling us to draw a direct conclusion from the observed data as to the true form of the common surface.

The method consists, first, in surrounding the glass tube with cedar wood oil or any other liquid possessing the same refractive index as the glass, so as to avoid refraction and reflection at the outer wall of the tube. Second, only those rays of the meniscus image are utilized which issue from the glass tube parallel in a definite direction, namely, by means of distant telescope observation. This method results in particularly simplified relations which are made clear upon inspection of the path of the rays (Fig. 1).

The glass tube shown in cross-section is immersed in a basin containing the cedar wood oil. The walls of the basin are accurately plane parallel. Upon the outside of one of these walls is glued a ground glass disc which is brightly illuminated. From this disc the light incident upon the glass tube under different angles is refracted therein, and finally emanates from the basin in different directions. Only the rays issuing in a direction perpendicular to the wall of the basin, *i. e.*, parallel to each other, are being observed. In other words, the meniscus is studied by means of a telescope from as great a distance as is practicable.

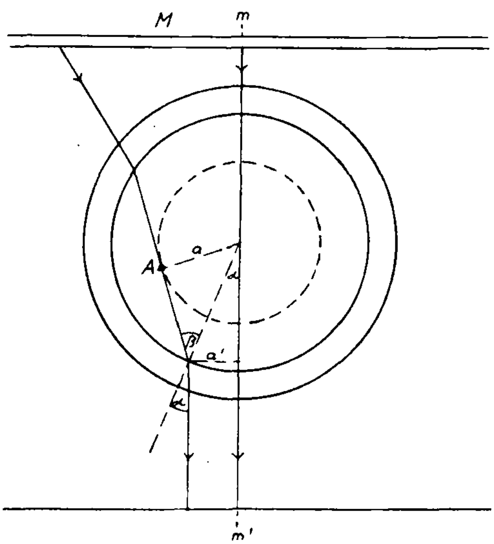

Fig. 1.

Referring to Fig. 1, if a certain ray is tangent to the meniscus at the point A, the meniscus curve is seen in the telescope within the distance a' from the perpendicular median line m, m'. However, a' is somewhat smaller than the true radius a of the meniscus. It is evident that $a' = r . \sin \alpha$; $a = r . \sin \beta$; $\frac{a}{a'} = \frac{\sin \beta}{\sin \alpha}$.

Applying furthermore the law of the index of refraction, we have $\frac{\sin \beta}{\sin \alpha} = \frac{n_1}{n_2}$, where n_1 is the refractive index of the glass, n_2 that of the liquid. Thus the ratio of the true to the apparent radius $\frac{a}{a'} = \frac{n_1}{n_2}$, *i. e.*, the width of the meniscus appears shortened in the exact ratio of the indices of refraction $n_1:n_2$. The height of the meniscus remains unaffected.

Therefore with this arrangement the degree of optical distortion is accurately known and in addition is rather small, because the ratio $n_1:n_2$ is in many cases very nearly equal to 1. Nor is it necessary to know the refractive indices of glass and liquid numerically, since the reduction ratio by which the meniscus is visible, becomes directly evident from the figure itself. Figure 2 shows the mode of formation of a typical picture of the meniscus resulting from the paths of the rays described. The inner wall of the tube is represented by 2 parallel lines; the inner is the limit of the refracted rays at the diameter $2a'$, the outer is the limit of the reflected rays at the true diameter $2a$, where these rays become tangent. Both limits are very sharply defined and are separated by a dark zone. Thus the ratio $n_1:n_2$ may be very easily determined from the picture by the location of these two limits.

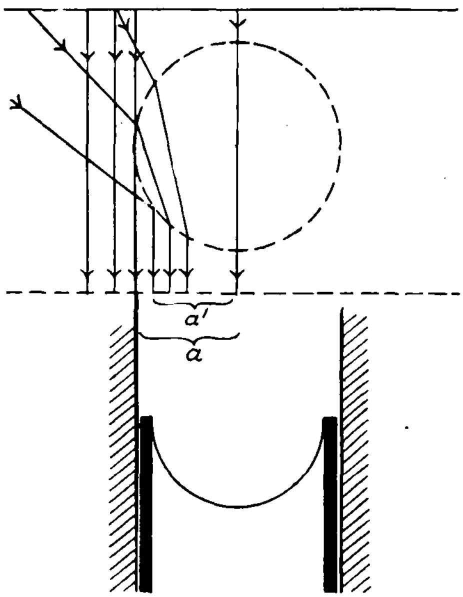

Fig. 2.

In Fig. 3, the arrangement of the experiment is given in outline. Observations are made with the telescope F to which is attached the photographic camera P. The basin upon which is glued the ground disc M is illuminated back of it by means of two bright incandescent lights. Also see photograph, Fig. 4.

II.

With regard to the shape of the meniscus between two liquids, theory allows the following prediction: The curvature of a meniscus is possible only when the

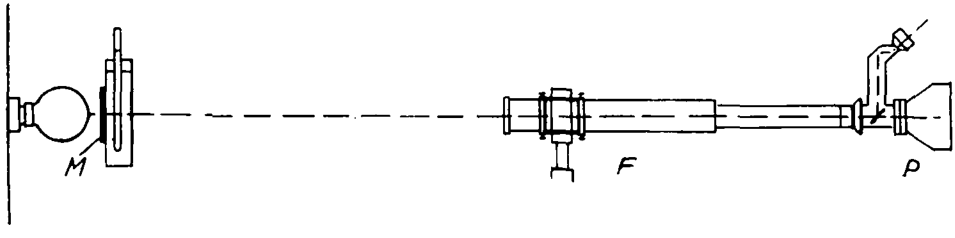

Fig. 3.

wetting powers of the liquids are of different magnitude. If both liquids wet the wall equally well, the edge angle will be 90°, the interface being a horizontal plane. But if the wetting tension of one liquid is greater than that of the other, it will try to displace the other from the glass surface by creeping along this surface. This movement in upward or downward direction opposes gravitation, resp., buoyancy resulting in differences of level between the different parts of the common surface. Thus this interface is no longer a horizontal plane but a curved surface. Now the effect of the interface tension is a tendency to equalize the curvature as much as possible and to distribute it evenly over the whole surface. The consequence is the formation of a meniscus having the shape as nearly as possible of a hemisphere.

The important bearing of the wetting power on the formation of the meniscus may be shown experimentally, *e. g.*, in the fact that in the case of hexyl-alcohol and water, either a concave or convex meniscus may be produced, according to whether the glass tube has previously been wetted with water or with hexyl alcohol. It is true in both cases that after prolonged standing a meniscus concave upward

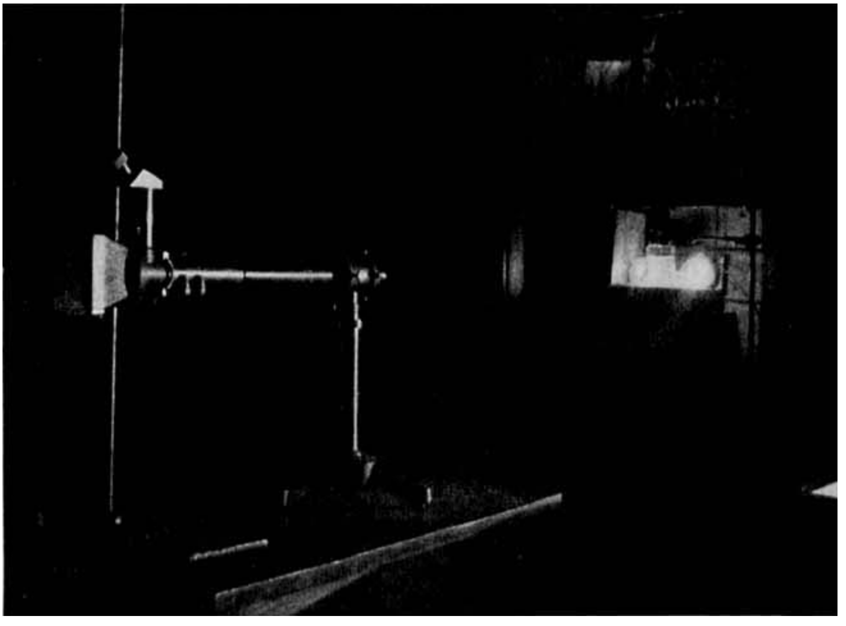

Fig. 4.

is formed because water has a greater wetting power for glass than has hexyl alcohol.

In most cases the menisci are concave upward, because the liquids of good wetting power, *e. g.*, water and glycerin (glycerol) are also heavier than most other liquids, and for this reason form the lower layer. If the well-wetting liquid is lighter than the other not well-wetting, the meniscus will be convex upward. A few examples are shown in Figs. 5–7. The enlargements of these illustrations and all other photographs of menisci presented is 2.5 times the natural size. The wetting power is very strongly affected by the degree of cleanness of the glass tube. The least amount of dirt causes the meniscus to become crooked and warped. The wetting power of a liquid for glass is also strongly diminished when the glass surface has been in contact with another liquid for a long time. If, for example, glass has lain in water for several days, amyl alcohol cannot wet the glass, but amyl alcohol will wet dry glass very well or if it has been in contact with water for only a few minutes. Other liquids behave like water. It seems that in the course of time liquid films become firmly attached to the glass. To obviate these, in our experiments, the glass tubes were all rinsed twice with concentrated sulphuric

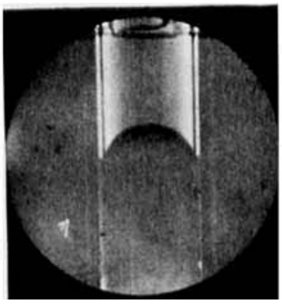

Fig. 5.

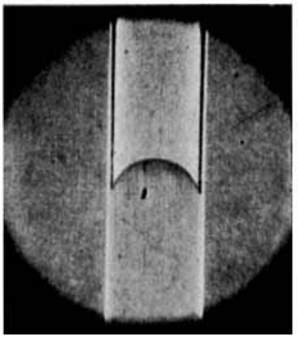

Fig. 6.

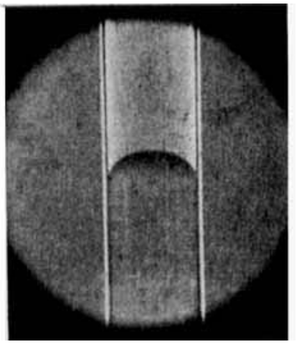

Fig. 7.

acid, washed with water and immediately filled with the pair of liquids to be investigated, shaken and allowed to stand.

In all cases we observed, first, that the better wetting liquid, *e. g.*, water, wetted the whole wall of the tube. Very gradually the water film situated between the glass and the other liquid, contracted, with the effect that now both liquids wetted the glass, one above, the other below the meniscus. A beautiful example of this kind is shown in Figs. 8 and 9. The question as to which of the liquids

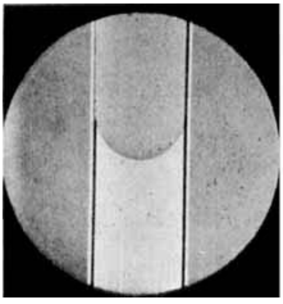

Fig. 8.

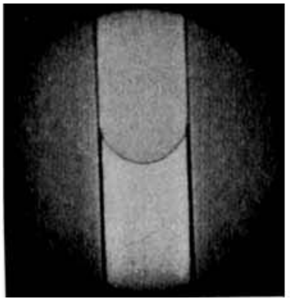

Fig. 9.

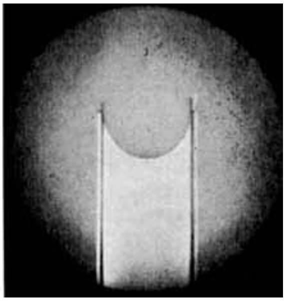

Fig. 10.

is wetting the wall of the tube, may be solved by considering the *dark zone* observed along the wall. This dark zone is caused by total reflection of the light rays at the boundary of the glass-liquid, and therefore becomes the broader, the smaller the refractive index of the liquid in contact with the glass. In Fig. 8, taken one hour after putting in the liquids, one side of the tube is still completely wetted by water; the equilibrium of wetting is completed only after 24 hours, represented in Fig. 9. In the case of benzene (benzol), the displacement of the water film requires an especially long period of time. Figure 10, representing a photograph taken after 2 days, still shows remnants of the film.

The reversed phenomenon may be noted in the case of hexyl alcohol-water.

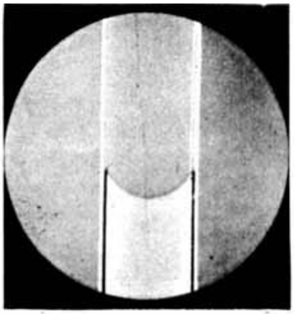

Fig. 11.

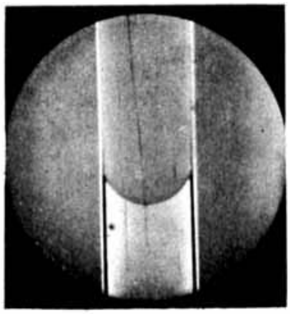

Fig. 12.

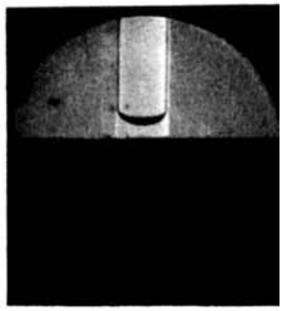

Fig. 13.

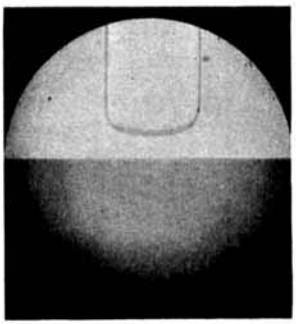

Fig. 14.

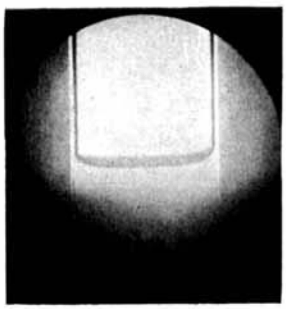

Fig. 15.

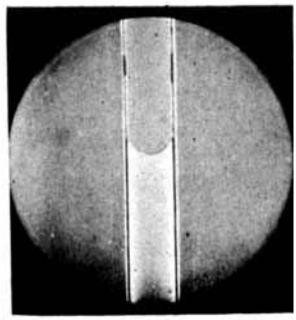

Fig. 16.

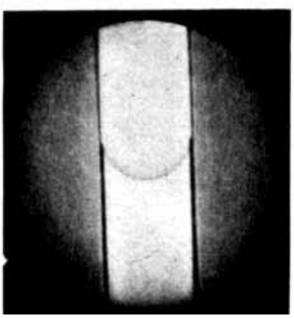

Fig. 17.

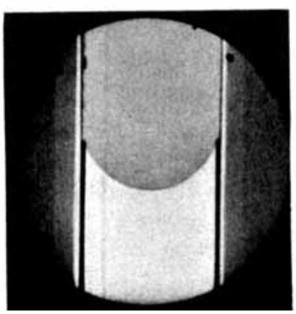

Fig. 18.

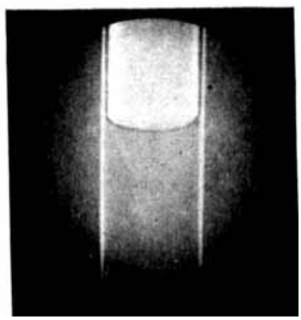

Fig. 19.

After about 1 hour, each liquid wets up to the meniscus boundary, as seen in Fig. 11. However, upon standing, darker bands move upward along the wall (see Fig. 12), indicating that the glass is wetted by the water at these places. Upon larger magnification we note that this layer is not a cohering film, but consists of a number of tiny droplets which were evidently precipitated from the wet hexyl alcohol.

In addition to the *wetting tension* and the *interface tension* between the two

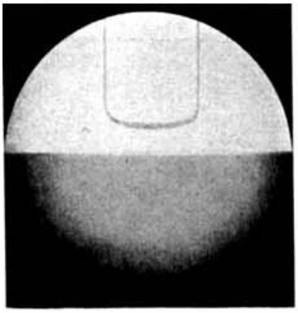

Fig. 20.

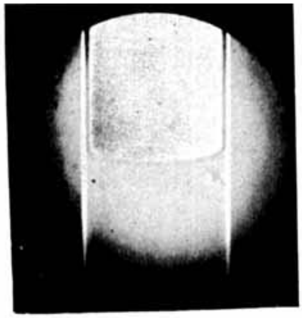

Fig. 21.

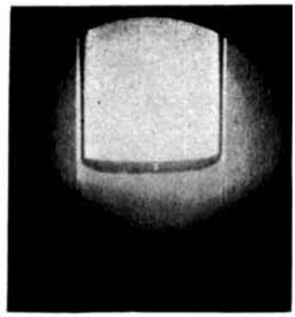

Fig. 22.

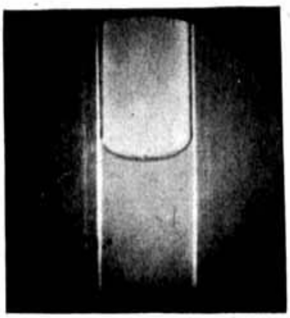

Fig. 23.

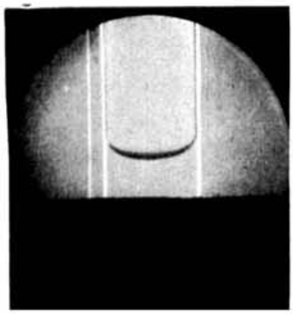

Fig. 24.

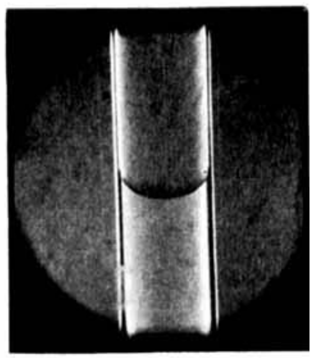

Fig. 25.

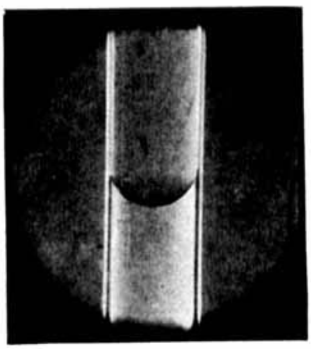

Fig. 26.

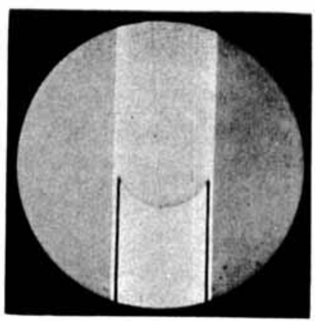

Fig. 27.

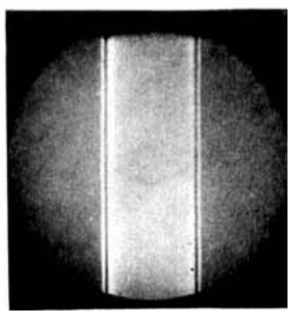

Fig. 28.

liquids, a third force, gravitation, influences the shape of the menisci. This force tends to equalize the differences of level within the meniscus, *i. e.*, to even and flatten it. The degree of flattening becomes the more pronounced, the greater the difference in density, and the smaller the interface tension between the two liquids. When the interface tension is large, the meniscus will be stretched into the form of a hemisphere as stated above. If this tension is small, able only to oppose little resistance to the deforming effect of gravitation, the meniscus will be flattened. The influence of gravitation is most notable in *wide* tubes. In wide vessels the common boundary is a plane surface up to near the margin. The increase in flattening of the menisci with increase in the width of the tube is seen in Figs. 13 to 15 for acetone-glycerol, and in Figs. 16 to 18 in hexane-water.

A phenomenon observed years ago by the senior author (J. U. L.) with acetone-glycerol and other pairs of liquids, namely, the lack of sharpness of the menisci, is

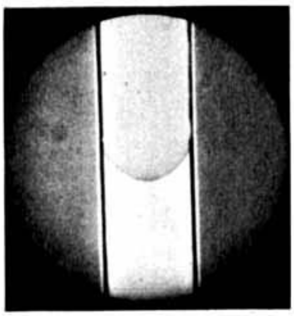

Fig. 29.

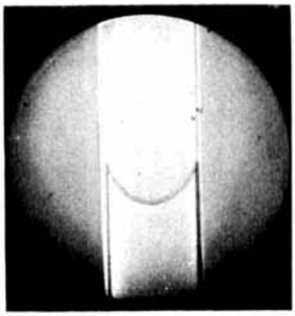

Fig. 30.

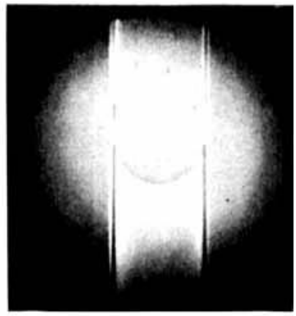

Fig. 31.

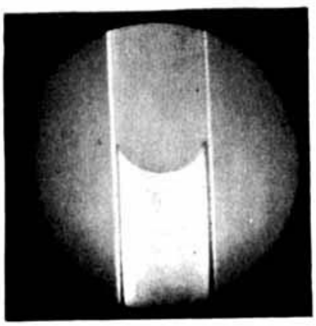

Fig. 32.

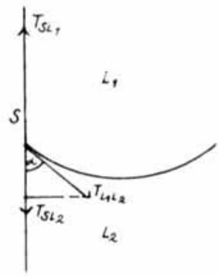

Fig. 33.

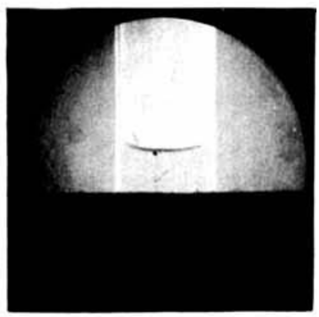

Fig. 34.

very remarkable. With acetone-glycerol the meniscus does not appear as a sharply defined shadow as is the case normally, but is seen only as an indistinct grey line, which cannot be made to appear more distinct even through attempted adjustment of the telescope. Apparently this phenomenon is due to diffuse, muddy reflection of the light rays incident upon the surface of the meniscus from below. Thus, if these rays are intercepted (*e. g.*, by partly covering the ground glass disc M) a perfectly sharp lower meniscus line is obtained, as shown in Figs. 19–22 for acetone-glycerol and 23–24 for methyl ethylketone-glycerol. We will leave open the question whether this phenomenon is caused by the spontaneous formation of droplets at the common surface described by I. Traube and R. Klein[1] for similar pairs of liquids.

[1] Traube and P. Klein, *Kolloid-Z.*, 29 (1921), 236.

III.

In order to investigate a possible connection between the form of the menisci and the *nature of the liquids*, experiments were made with various groups of substances and homologous series.

1. *Alcohol-Water*, Figs. 25–27. The menisci are somewhat flattened, mostly so with butyl alcohol, least with hexyl alcohol. Thus, the flattening is the more pronounced the shorter the carbon chain. Flattening also runs parallel with solubility. Butyl alcohol (butanol) is more easily soluble and the lower homologs, propanol, ethanol and methanol are miscible with water in all proportions.

Fig. 35.

Fig. 36.

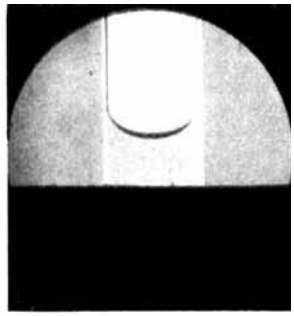

Fig. 37.

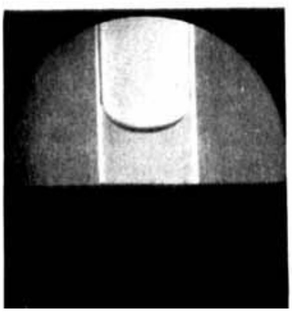

Fig. 38.

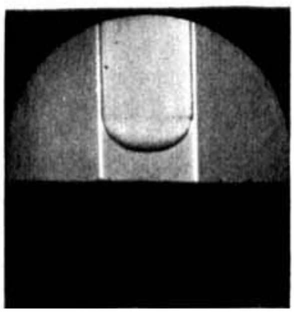

Fig. 39.

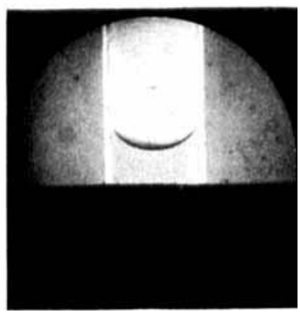

Fig. 40.

2. *Ester-Water*, Figs. 28–32. The interface tension between these esters and water is materially greater than with alcohols, therefore, the menisci are hardly flattened at all. With increasing length of the carbon chain, the interface tension becomes greater, being so strong with heptyl acetate (Fig. 32) as to bring down the wetting limit, which enables the meniscus to relax to a more even surface. Then the meniscus is no longer tangential to the wall but meets the glass surface under a certain angle. In this case there is an equilibrium of forces between the surface tensions, as represented in Fig. 33. The downward interface tension $T_{L_1L_2}$ acts oppositely to the upward wetting tension $T_{SL_1} - T_{SL_2}$, and the relation must exist: $T_{SL_1} - T_{SL_2} = T_{L_1L_2} \cos . \alpha$. It appears that with heptyl acetate, the interface tension $T_{L_1L_2}$ begins to exceed the wetting tension $T_{SL_1} - T_{SL_2}$ in the homologous series, resulting in the edge-angle α becoming greater than $0°$.

3. *Alcohol-Glycerol*, Figs. 34–35. The menisci obtained with glycerol in the place of water are as a rule flatter. Evidently the interface tension is smaller.

4. *Ester-Glycerol*, Figs. 36–41. All menisci are somewhat flattened, and all

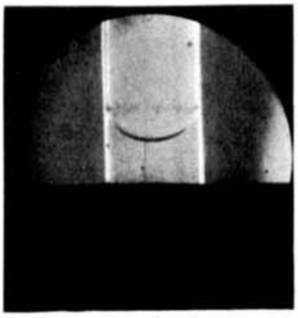

Fig. 41.

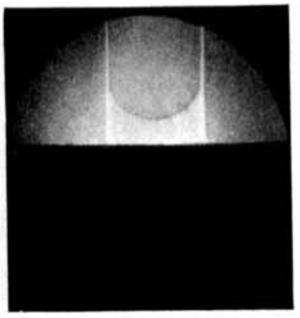

Fig. 42.

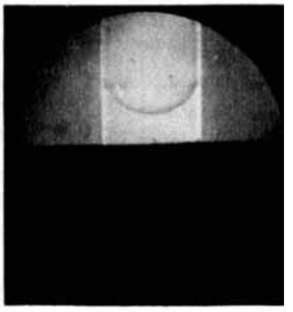

Fig. 43.

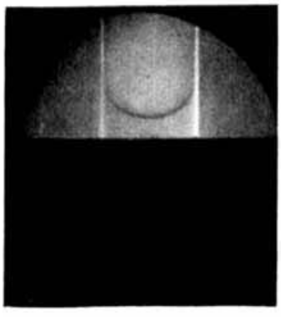

Fig. 44.

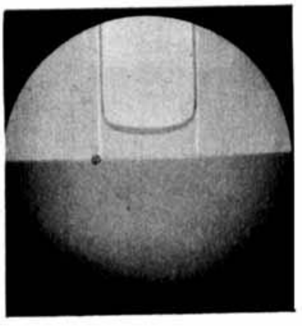

Fig. 45.

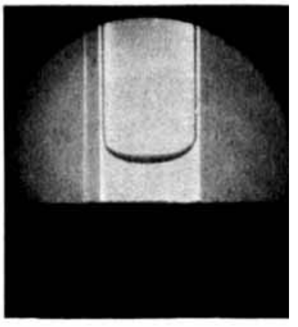

Fig. 46.

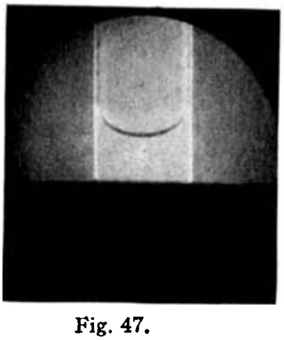

Fig. 47.

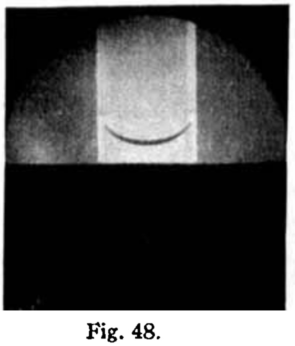

Fig. 48.

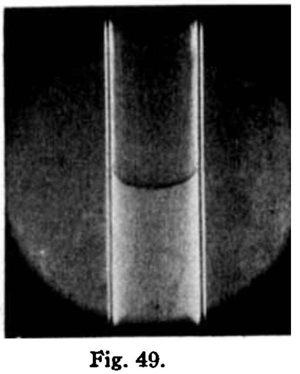

Fig. 49.

about to an equal degree. No alteration could be observed with increasing length of the carbon chain.

5. *Benzene-Glycerol*, Figs. 42–44. A faint but uniform flattening is also noticeable here in all cases.

6. *Ketone-Glycerol,* Figs. 45–48. In this example we again see very plainly the increased rounding of the menisci upon the lengthening of the carbon chain. Here again there is parallelism between flattening and solubility. Acetone is quite soluble in glycerol.

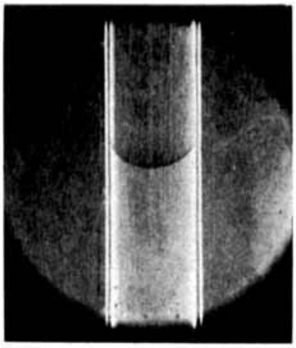

Fig. 50.

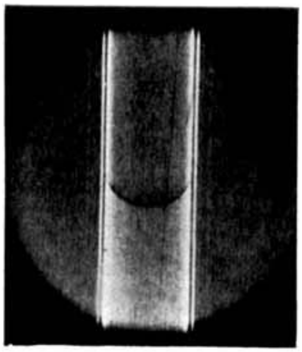

Fig. 51.

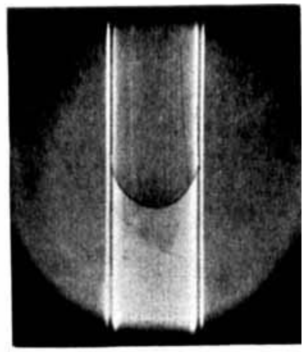

Fig 52.

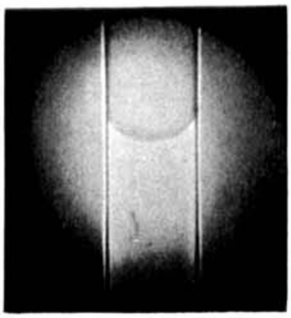

Fig. 53.

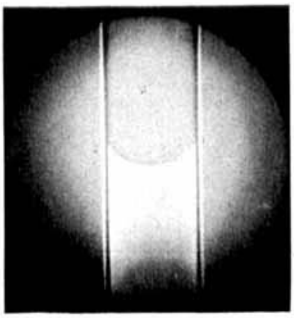

Fig. 54.

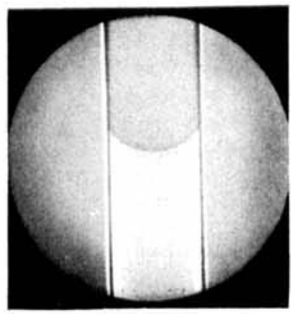

Fig. 55.

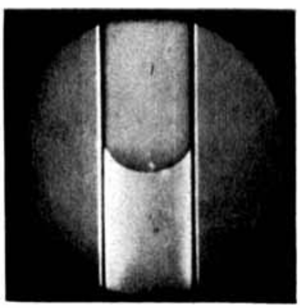

Fig. 56.

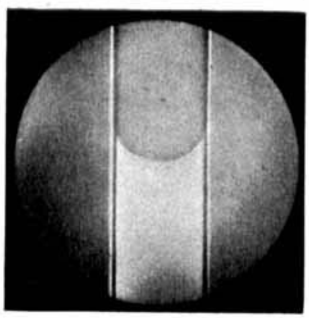

Fig. 57.

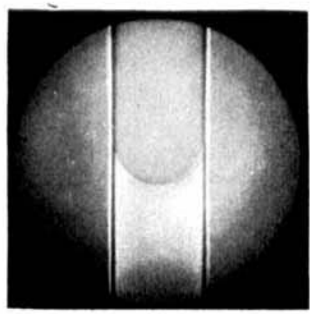

Fig. 58.

7. If *Solutions* or any mixtures of liquids are used in the place of water or glycerol, a relation may be noted between *concentration* of the solutions and the shape of the menisci. An example is hexane with alcohol-water mixtures, as shown in Figs. 49–52. Hexane is soluble in completely anhydrous alcohol, hence yields

no meniscus with it. However, if the alcohol contains but a small quantity of water, the meniscus will be flat, but becomes more and more round the more water the lower liquid contains. Again, solubility and flattening of the menisci run parallel in this case.

While with alcohol-water mixtures only relatively large differences in concentration have a notable effect on the shape of the menisci, there are a few substances of which even very small quantities are sufficient to reduce the interface tension to almost zero. To these "capillary active" substances belong, among others, soap, *i. e.*, sodium oleate. In Figs. 53–58 are shown menisci between

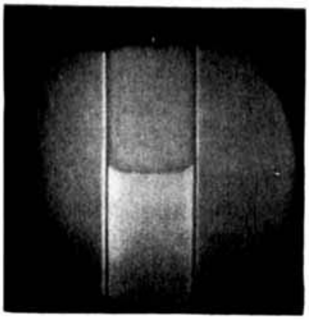

Fig. 59.

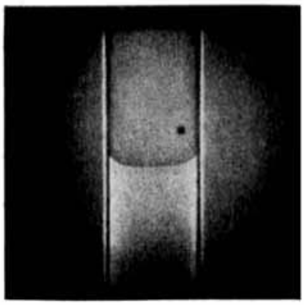

Fig. 60.

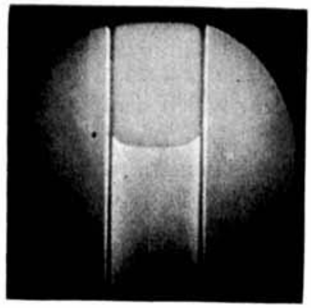

Fig. 61.

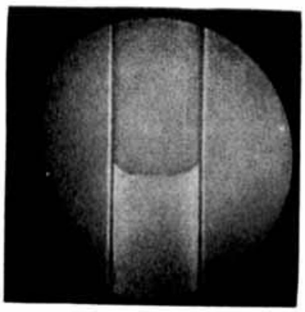

Fig. 62.

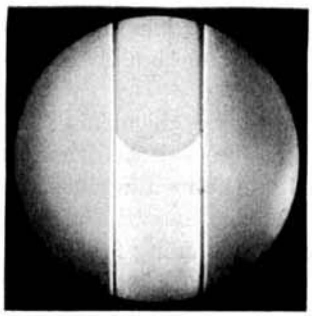

Fig. 63.

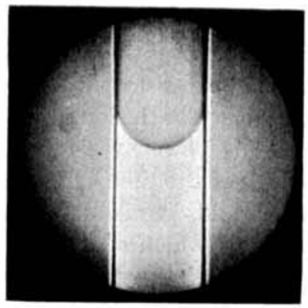

Fig. 64.

aqueous sodium oleate solutions and pure paraffin oil. In Figs. 59–64 are menisci between the same sodium oleate solutions and pure sesame oil in place of paraffin oil. Evidently in both cases a very small concentration of soap (0.25%) is sufficient to reduce the interface ten-

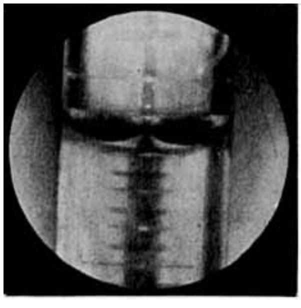

Fig. 65.

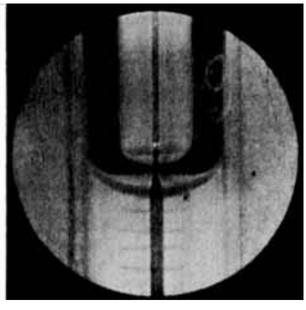

Fig. 66.

sion considerably. A distinct difference is observable between the two oils: The menisci obtained with sesame oil are essentially flatter at higher concentrations than with paraffin oil. Probably this may be explained by the existence of polar groups in sesame oil while, in paraffin, the molecules are saturated.

The last illustrations, Figs. 65 and 66, are photographs of a *Schellbach strip* back of a meniscus. One may distinctly note that the lower edge of the meniscus lies below the point of the Schellbach strip.

SUMMARY.

The menisci between two liquids in glass tubes have greatly varying but typical forms depending upon the nature of the liquids, a fact years ago pointed out by the senior author (John Uri Lloyd).

The present study gives sixty-one photographs of menisci of the most varied origin, which completely confirm and supplement the former subjective observations. The photographs were obtained by the aid of a specially adapted optical arrangement in which the distortions of the image of the meniscus through refraction of light have been minimized and in addition are quantitatively defined. The optical arrangement is based on the following main principles: The glass tube containing the meniscus is suspended in a basin containing oil of cedar wood, and is observed at some distance by means of a telescope. The oil, having the same refractive index as glass, prevents refraction and reflection of light on the outer wall of the glass tube. The refraction at the inner wall of the tube involves but a small distortion of the image of the meniscus. When the latter is observed from a distance (*i. e.*, by means of parallel rays) the meniscus is narrowed simply in the ratio of the indices of refraction of liquid and glass, *i. e.*, $n_2 : n_1$, while its height remains undistorted.

Our conclusion is that the form of the menisci is generally dependent upon the wetting power, the interface tension and the density of the liquids as well as the width of the tube. As a result of the wetting tension the common surface between the liquids is pulled up or down along the wall. This tends to increase the common surface, which seeks to contract, assuming first a hemispherical shape. Gravitation then flattens the meniscus, the more so the greater the difference in density of the two liquids and the wider the tube.

Menisci between acetone and glycerol exhibit a diffuse reflection of light at the common surface. This phenomenon may perhaps be ascribed to the spontaneous formation of turbid emulsions at the common surface, which Traube and Klein have observed in similar pairs of liquids.

A study was made of the possible influence of the nature of the liquids upon the shape of the menisci, and the following pairs of liquids were examined: *n*-alcohol-water; *n*-alkylacetate-water; *n*-alcohols, glycerol; *n*-alkylacetate, glycerol; *n*-ketone, glycerol; homologous benzenes, glycerol. In the homologous series, the flattening of the menisci becomes sometimes more pronounced with the shortening of the chain of carbon atoms. Apparently there is also a relation between flattening and solubility.

If one of the liquids is a solution, the form of the meniscus will depend upon concentration. Examples demonstrated are: alcohol-water mixtures toward hexane, and sodium oleate solutions toward paraffin oil and sesame oil.

EXPLANATION OF ILLUSTRATIONS.

Figs. 1-4.—See text.
Fig. 5.—Water on ethylene bromide.
Fig. 6.—Water on chloroform.
Fig. 7.—Alcohol (50% by vol.) on carbondisulphide.
Fig. 8.—Hexane on water after 1 hour.
Fig. 9.—Hexane on water after 24 hours.
Fig. 10.—Benzene on water, remnants of film.
Fig. 11.—Hexylalcohol on water after 1 hour.
Fig. 12.—Hexylalcohol on water after 24 hours.
Fig. 13.—Acetone on glycerol.
Fig. 14.—Acetone on glycerol.
Fig. 15.—Acetone on glycerol.
Fig. 16.—Hexane on water.
Fig. 17.—Hexane on water.
Fig. 18.—Hexane on water.
Fig. 19.—Acetone on glycerol, without screen.
Fig. 20.—Acetone on glycerol, with screen.
Fig. 21.—Acetone on glycerol, without screen.
Fig. 22.—Acetone on glycerol, with screen.
Fig. 23.—Methylethylketone on glycerol, without screen.
Fig. 24.—Methylethylketone on glycerol, with screen.
Fig. 25.—Butylalcohol on water.
Fig. 26.—Amylalcohol on water.
Fig. 27.—Hexylalcohol on water.
Fig. 28.—Methylacetate on water.
Fig. 29.—Propylacetate on water.
Fig. 30.—Butylacetate on water.
Fig. 31.—Amylacetate on water.
Fig. 32.—Heptylacetate on water.
Fig. 33.—See text.
Fig. 34.—Amylalcohol on glycerol.
Fig. 35.—Hexylalcohol on glycerol.
Fig. 36.—Methylacetate on glycerol.
Fig. 37.—Ethylacetate on glycerol.
Fig. 38.—Propylacetate on glycerol.
Fig. 39.—Butylacetate on glycerol.
Fig. 40.—Amylacetate on glycerol.
Fig. 41.—Heptylacetate on glycerol.
Fig. 42.—Benzene on glycerol.
Fig. 43.—Ethylbenzene on glycerol.
Fig. 44.—Propylbenzene on glycerol.
Fig. 45.—Acetone on glycerol.
Fig. 46.—Methylethylketone on glycerol.
Fig. 47.—Methylbutylketone on glycerol.
Fig. 48.—Methylhexylketone on glycerol.
Fig. 49.—Hexane on alcohol (90% by vol.).
Fig. 50.—Hexane on alcohol (75%).
Fig. 51.—Hexane on alcohol (50%).
Fig. 52.—Hexane on water.
Fig. 53.—Paraffin oil on Na oleate soln. (5%).
Fig. 54.—Paraffin oil on Na oleate soln. (3%).
Fig. 55.—Paraffin oil on Na oleate soln. (1%).
Fig. 56.—Paraffin oil on Na oleate soln. (0.5%).
Fig. 57.—Paraffin oil on Na oleate soln. (0.25%).
Fig. 58.—Paraffin oil on water.
Fig. 59.—Sesame oil on Na oleate soln. (5%).
Fig. 60.—Sesame oil on Na oleate soln. (3%).
Fig. 61.—Sesame oil on Na oleate soln. (1%).
Fig. 62.—Sesame oil on Na oleate soln. (0.5%).
Fig. 63.—Sesame oil on Na oleate soln. (0.25%).
Fig. 64.—Sesame oil on water.
Fig. 65.—See text.
Fig. 66.—See text.

DETERMINATION OF QUININE.

A rapid method for actual quinine determination is reported on by Gustave A. Sticht in *Chemist Analyst*, 18, 6 (1929), No. 3.

Quinine may be separated from cinchonidine and the other cinchona alkaloids by precipitating as the acid quinine tartrate. Quinine may be assayed from cinchona bark as follows: The bark is powdered and placed in a bottle containing the solvent (105 cc. chloroform and 420 cc. toluol) to which is added a solution of 20% ammonia water. The bottle is agitated mechanically or by hand. Three or four extractions are made and the total extract is evaporated to 50 cc. and made alkaline. Quinine sulphate may settle out. To this, citric acid and sodium citrate mixture are added. The insoluble acid quinine citrate settles out. This salt is anhydrous and contains 62.79% quinine alkaloid.—B. S.—*Squibb Abstract Bulletin* (August 14, 1929).