

which in turn had been standardized gravimetrically. A silver nitrate solution was standardized by Mohr's method against weighed pure sodium chloride and found to be 0.0925 *N*. This silver nitrate was then titrated against the 0.1077 *N* hydrochloric acid by the procedure just described, using 20 cc. of the buffer solution, and found to be 0.0925 *N* thus agreeing exactly with the previous standardization against pure sodium chloride by the ordinary Mohr's method. In all titrations, duplications were quite as close and end-points as clear as in the ordinary use of the Mohr method in neutral solution.

The presence of copper interferes with the end-point of this reaction, owing to the fact that the solubility of copper chromate is of the same order of magnitude as that of silver chromate and this is true generally of the heavy metals and barium. The method also fails in the presence of easily oxidized substances that react with the chromate ion.

Summary

A modification of the Mohr method for volumetric determination of silver and the halogens is described. By the use of a sodium acetate-acetic acid buffer the *P_H* value of the solution is kept between 5 and 7, thus extending the use of the Mohr method to solutions other than neutral.

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[CONTRIBUTION FROM THE LABORATORY OF COLLOID CHEMISTRY, UNIVERSITY OF WISCONSIN]

A NEW METHOD FOR THE DETERMINATION OF THE DISTRIBUTION OF SIZE OF PARTICLES IN EMULSIONS¹

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It has been pointed out by Svedberg² that the adequate characterization of a colloid solution requires a knowledge of the distribution of size of particles in the colloid system. Since the particles of a colloid system are usually not susceptible to direct microscopic measurement on account of their small size, the determination of the distribution of size of particles generally depends upon the application of the resistance-to-motion law, $f = 6\pi\eta rv$, where f is the friction developed when a sphere of radius r moves with the uniform velocity v in a liquid possessing the viscosity η .³

Very few such studies have been made upon emulsions in which the disperse phase rises under the influence of gravity. The methods which

¹ An abstract of this paper was presented before the Second National Colloid Symposium, Northwestern University, June, 1924.

² Svedberg and Estrup, *Kolloid-Z.*, **9**, 259 (1911).

³ Svedberg gives an excellent discussion of the determination of distribution of size of particles in his book (a) "Colloid Chemistry," American Chemical Society Monograph, Chemical Catalog Co., 1924.

have actually been used have involved either the direct measurement with the microscope of the sizes of a large number of drops of the disperse phase, or the application of the resistance law to observations, with the aid of the microscope, of the rate of rise of a statistically sufficient number of drops.¹ Both methods are quite laborious and in the case of small drops, the accuracy of the first method may be rather low.

For certain classes of emulsions, the distribution of size of particles may be determined very simply, however, by observing the rate of change in the apparent density of the upper portion of an emulsion into which the disperse phase is rising. The observations, when properly interpreted, give the rate of accumulation of the disperse phase into the upper portion. From the time-accumulation curve so obtained, the distribution curve may be derived in the usual fashion.⁴

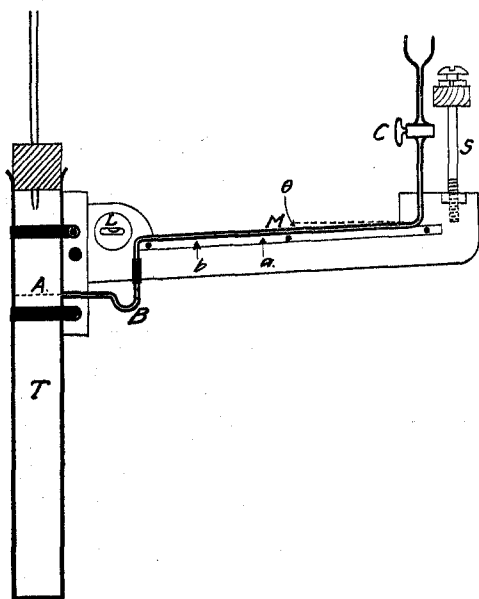


Fig. 1.

Consider a tube with a capillary side arm as illustrated in Fig. 1, and imagine that the vertical tube contains an emulsion while the capillary tube contains the pure dispersion medium. With the passage of time, the disperse phase rises, passes the plane A and causes an equal volume of the dispersion medium to move across the plane A into the lower portion. The net result, however, is a decrease in the average density of the liquid above the plane A and a corresponding and compensating decrease in the height of the liquid in the capillary tube. Therefore the rate of change of the meniscus in the capillary tube is a measure

of the rate of deposition of the disperse phase into the region above the plane A (which is thus equivalent to the balance pan in the downward sedimentation method of Odén).

In more exact language, let A and s be the cross-sectional areas of the plane A and the capillary tube, respectively; d_m and d_p the densities of the dispersion medium and the disperse phase, respectively. As P grams of the disperse phase, rising, passes the plane A, it displaces an

⁴ Odén, *Bull. Geol. Inst. Univ. Upsala*, 16 (1916). Ref. 3 a, pp. 144 ff. Fischer and Odén, *Proc. Roy. Soc. Edinburgh*, 44, 98 (1924).

equal volume of the dispersion medium, or Pd_m/d_p grams. Therefore the decrease in pressure per square centimeter on the plane A is $\frac{1}{A} \left(P \frac{d_m}{d_p} - P \right) = \frac{P}{A} \left(\frac{d_m - d_p}{d_p} \right)$. To compensate this change, the meniscus falls in the capillary tube from a to b , changing the pressure by the quantity $d_m(a - b) \sin \theta$. But the fall in level in the capillary tube introduces into the wider tube a quantity of liquid given by $d_m(a - b)s$, which raises the level and increases the pressure upon A by the quantity $d_m(a - b) \frac{s}{A}$. Equating the total changes in pressure in the vertical and capillary tubes gives $-\frac{P}{A} \left(\frac{d_m - d_p}{d_p} \right) + d_m(a - b) \frac{s}{A} = -d_m(a - b) \sin \theta$; and solving for P finally yields, $P = \frac{d_p \cdot d_m}{d_m - d_p} [A \sin \theta + s] [a - b]$. The value of P obtained when a and b are the original and final positions of the capillary liquid should agree with the quantity of disperse phase in the volume below the plane A as determined by analytical means, if no "creaming" has taken place before the original observation a , and if the separation of the disperse phase from the region below A is finally complete. An accumulation curve may then be constructed to show the relationship between P and time.⁵

Apparatus

The apparatus (Fig. 1) was mounted on a wooden frame and clamped securely to a vertical rod in a thermostat.

A spirit level L was fastened to the wooden frame so as to be level when a plumb line hung parallel to the side of the tube T . A leveling screw S fastened to a crossbar in the thermostat served to adjust the level of the apparatus. The bend B in the capillary tube prevented the disperse phase from passing up through the capillary. A glass scale was mounted under the capillary tube and readings were made with a microscope. Tube T was provided with a stopper through which a glass tube drawn out to a short orifice extended in order to cut down the evaporation of the volatile disperse phase.

The angle of the capillary was determined by two different methods. The first of these was to measure the length of two projected sides of the right triangle formed between the tube T and plumb line when the apparatus was clamped with M horizontal. This gave 0.0765 as the average value of $\sin \theta$. In the other method, the tube was clamped in place in the thermostat with T vertical. The apparatus was filled with water so that the meniscus in M stood near the lower end. A vertical micrometer screw was mounted above the tube T with a glass thread fastened to its lower end. This was brought just into contact with the water surface and readings were taken on the micrometer screw and the capillary scale. The micrometer screw could be read to 0.001 cm. and check readings made to 0.002 cm. The capillary scale was read to 0.005 cm. with

⁵ The principle of the method is similar to the sedimentation method of Wiegner [*Landw. Vers. Sta.*, **91**, 41 (1919)] and of Wo. Ostwald and F. v. Hahn [*Kolloid-Z.*, **30**, 62 (1922)], but so modified and improved that emulsions with a rising disperse phase may be studied.

a maximum variation of 0.01 cm. From the change in height of the liquid in the tube T upon addition of successive portions of water and the corresponding capillary readings, the angles for different portions of the capillary were determined. These differed by a maximum of 3% for different positions along the scale and gave an average value for $\sin \theta$ of 0.0767. The appropriate value was used for the $\sin \theta$ at different positions along the capillary.

The cross section of the tube T was determined just above and below the manometer tube junction by means of the change in the vertical micrometer screw readings upon the addition of 5 cc. of water. The cross section was found to be 4.400 sq. cm. The height to the junction was 29.2 cm., and the liquid height used was 39.2–39.6 cm.

The rate of evaporation was determined with a layer of benzene on the surface of the water in the tube T, and the drift down the manometer tube with time measured. This was done over a period of 36 hours and an average movement of 0.009–0.01 cm. per hour noted. This correction which was practically constant from hour to hour was applied to the following observations. By modifying the top of the vertical tube so that it communicates with the air through a supplementary bulb containing benzene and immersed in the thermostat, the rate of evaporation has been decreased further.

Preparation of Emulsions

The studies reported in this paper were made with emulsions of benzene and water.

The benzene was purified according to the usual method for removing thiophene. The fraction used distilled at 78.55–78.60° (739.6 mm.). The density at 25° compared with that of water at the same temperature was 0.8754. The soaps were prepared from pure fatty acids according to the method of White and Marden.⁶

The emulsions were prepared under the following arbitrary conditions.

One cc. of the emulsifying agent dissolved in either benzene or water was placed in each of two 120cc. oil-sample bottles. The required amount of benzene was then added and enough water to make the volume up to 100 cc. The water was added in 20cc. portions and the mixture was shaken for 15 seconds between additions. The samples were then shaken by hand for five minutes at an approximate rate of 100 shakes per minute. When desired, the emulsions were further emulsified by means of a Briggs' homogenizer.⁷ The homogenizer was used with a constant pressure difference of 60 cm. of mercury. The pressure over the emulsion in the receiver was either approximately 14 or 74 cm. of mercury.

Determination of Size-Distributions

In accordance with the theoretical considerations already given, accumulation curves were constructed with P as ordinate and the corresponding time in hours as abscissa. Fig. 2 is a typical accumulation curve. All of the accumulation curves were found to be quite smooth and very similar in general appearance.

The distribution curves were determined from the accumulation curves according to the previously cited method given by Svedberg^{3a} by taking dS as the distance between the ordinate intercepts of two successive tangents to the accumulation curve. The radius of the particles in μ (10^{-4}

⁶ White and Marden, *J. Phys. Chem.*, **24**, 618 (1920).

⁷ Briggs, *ibid.*, **19**, 223 (1915).

cm.) is plotted against the ratio of the change in weight dS to the change of radius dr . Hence the area under any portion of the curve represents the actual weight of benzene dispersed in particles whose sizes vary be-

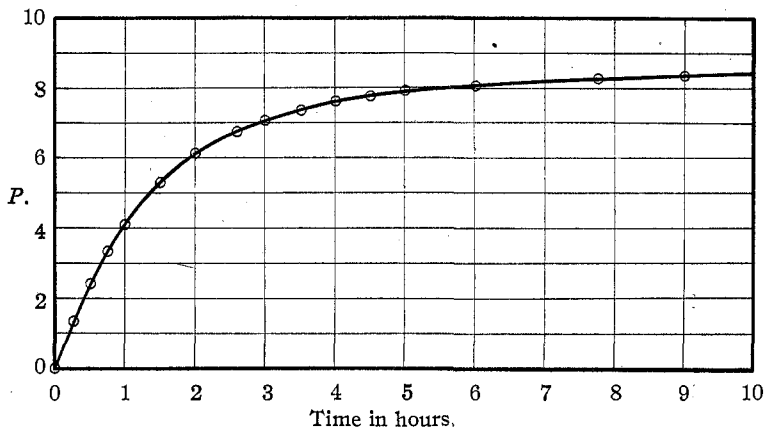


Fig. 2.—Accumulation curve, 10% benzene-in-water emulsion.
0.0005 *N* Potassium palmitate solution.

tween those values represented by the bounding abscissa. Curve 2 of Fig. 3 is the distribution curve derived from the accumulation curve given in Fig. 2. The greatest weight of benzene in this emulsion was dis-

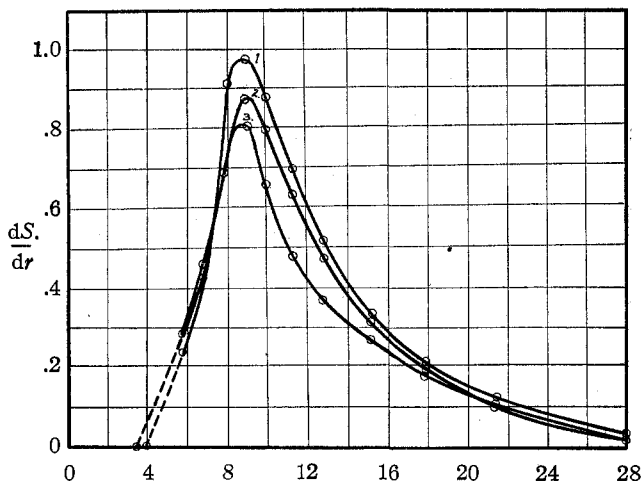
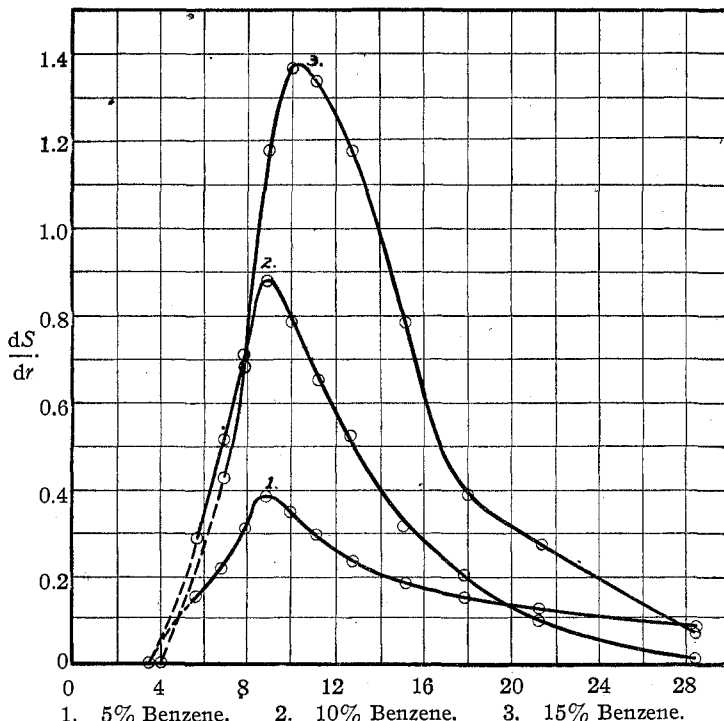


Fig. 3.—Distribution curves, 10% benzene-in-water emulsions.
0.0005 *N* Potassium palmitate solution.

persed into particles the size of which is given by the maximum in the distribution curve.

The degree of reproducibility of the distribution curves is shown by

Fig. 3. The three curves are for three different emulsions prepared under as nearly identical conditions as possible, being homogenized twice with the pressure in the receiver approximating 14 cm. of mercury. The three curves are similar in type and the maxima appear at very nearly the same radius for all three curves. The values for the maxima are as follows: Curve 1, maximum 8.8 μ ; Curve 2, maximum 9.0 μ ; Curve 3, maximum 8.6 μ . The actual values of the masses do not check so well, due to the experimental difficulties in emulsifying all of the material. A



1. 5% Benzene. 2. 10% Benzene. 3. 15% Benzene.
Fig. 4.—Effect of change of benzene concentration on distribution of sizes.
0.0005 *N* Potassium palmitate.

little of the benzene invariably sedimented before the initial reading could be taken. This usually varied from 0.4–1.0 g. as estimated by the depth of the surface layer of benzene in the vertical tube. This estimate was of course a minimum value, as a considerable portion of the emulsion particles that had risen above *A* still remained dispersed. For example, in the case of Curve 1, 174 cc. of 10% benzene emulsion was used, that is, 17.4 cc. of benzene. Just after the first reading, 1.75 cc. of benzene had settled out. Subtracting this, 15.65 cc. remained dispersed and $15.65 \times \frac{29.2}{39.3} = 11.6$ cc. (or 10.15 g.) had yet to cross

the boundary *A*. The experimentally determined amount that settled up to the time when the motion of the capillary liquid became that of the evaporation drift (17 hours) was 9.15 g. This shows that some very finely dispersed benzene had not settled or, more probably, that the initial estimate of the amount settled just up to the time of the first reading was low.

The final point giving the minimum size was not determined in the same way as the other points. It was obtained by considering that the sedimentation was completed at the time when the movement of the capillary liquid became that apparently due to evaporation. Of course such was not really the case, and the last section of the curve is merely dotted. In reality, the curve probably should become tangent to the

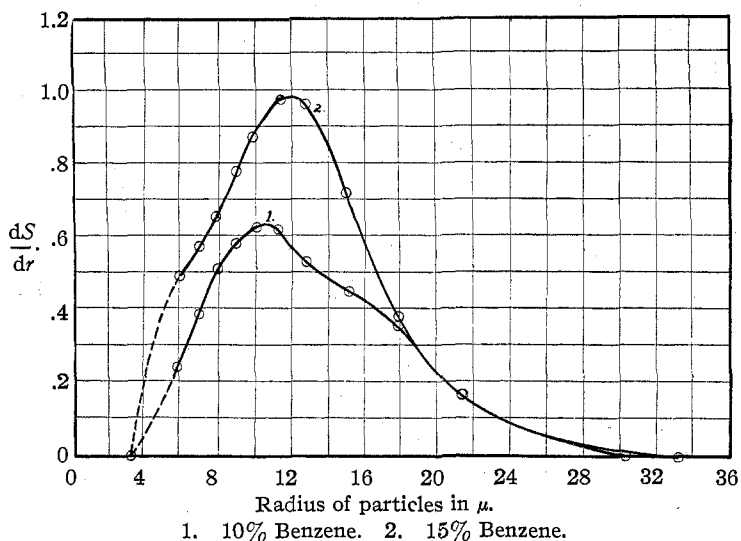


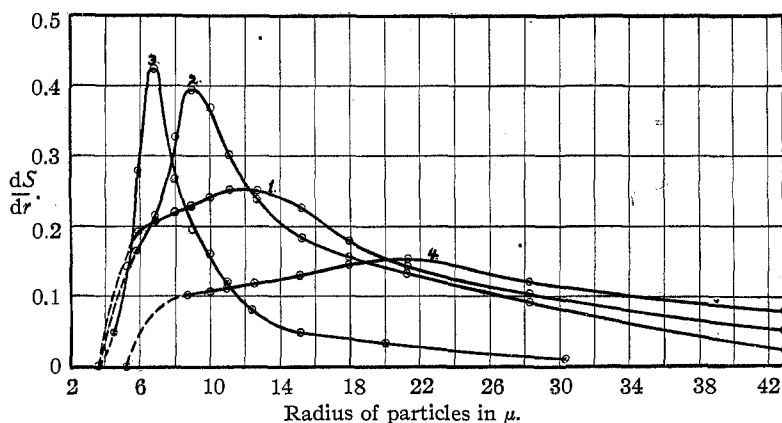
Fig. 5.—Effects of change of benzene concentration on distribution of sizes.
0.0005 *N* Potassium oleate solution.

radius axis more gradually than the dotted line indicates. Superficially, the curve would resemble a Maxwellian distribution curve.

In Figs. 4 and 5 are given curves showing that the position of the maximum is not changed greatly by considerable changes in the concentration of the emulsion. The maxima occur for the following radii: Curve 1, maximum at 8.9 μ ; Curve 2, maximum at 9.0 μ ; Curve 3, maximum at 10.2 μ . The three emulsions were prepared using the same procedure, and each was homogenized twice under low pressure (14 cm.). A comparison of the curves shows that the efficiency of emulsification is but slightly changed by changes in the concentration of the emulsion, even when the total quantity of emulsifying agent remains constant. Furthermore, the rate of settling is not greatly changed due to the mutual interference of the

settling particles. The apparent increase in the average size of particle with concentration may be real and due to the fact that the concentrated emulsions contained relatively less emulsifying agent, or the drops may actually have been of the same sizes, but settled faster in accordance with the theoretical calculations of Cunningham⁸ upon the rate of fall of a cloud of uniform particles.

Fig. 5 gives results for emulsions of benzene in water stabilized with potassium oleate. The method of preparation was that used in obtaining the results just discussed: Curve 1, maximum at 10.4 μ ; Curve 2, maximum at 11.8 μ . Comparing Curves 1 and 2 with the corresponding curves of Fig. 4 (Curves 2 and 3) one may note that the oleate



1. No homogenization. 2. Homogenized twice (at low pressure). 3. Homogenized four times (at low pressure). 4. Homogenized twice (at high pressure).

Fig. 6.—Effect of homogenization of 5% benzene-in-water emulsions. 0.0005 *N* Potassium palmitate.

gives a maximum corresponding to a larger size of dispersed particles. According to the theory of Langmuir⁹ and Harkins,¹⁰ and as partially verified experimentally by Finkle, Draper and Hildebrand,¹¹ the oleate should give the larger particles, as the cross-sectional area of a hydrocarbon group containing a double bond is greater than that of a saturated hydrocarbon group.¹² Presumably this tends to give less curvature to the monomolecular layer of oriented molecules.

The influence of homogenization is shown by the curves of Fig. 6. The results may be summarized as follows: Curve 1, maximum at 12.0 μ

⁸ Cunningham, *Proc. Roy. Soc. (London)* **83**, 357 (1919).

⁹ Langmuir, *Chem. Met. Eng.*, **15**, 468 (1916).

¹⁰ Harkins, *THIS JOURNAL*, **39**, 541 (1917).

¹¹ Finkle, Draper and Hildebrand, First National Colloid Symposium Monograph, June, 1923; *THIS JOURNAL*, **45**, 2780 (1923).

¹² See Langmuir, *ibid.*, **39**, 1868 (1917). Adam, *Proc. Roy. Soc. (London)* **99**, 336 (1921); **101**, 452 (1922).

(no homogenization); Curve 2, maximum at 8.9μ (homogenized twice at low pressure); Curve 3, maximum at 7.0μ (homogenized 4 times at low pressure); Curve 4, maximum at 21.3μ (homogenized twice at high pressure). Homogenization with a low pressure over the emulsion in the receiver (14 cm. of mercury) obviously increases the degree of dispersion of the benzene-in-water emulsion stabilized with soap. However, with gelatin as stabilizer, a benzene-in-water emulsion is broken completely by a single such homogenization. Emulsions stabilized with free fatty acids such as palmitic acid or capric acid were found to be partially broken by such treatment. With atmospheric pressure in the receiver, homogenization tended to break all the emulsions studied. The surprising difference in the effects of the two methods of homogenization may be due to the difference in the rate of evaporation of the benzene in the two cases. Thus, homogenization with low pressure allowed a rapid evaporation of the benzene and caused thereby a pronounced foaming. The formation and breaking of bubbles and laminae is probably quite effective in increasing the dispersity of the emulsion.

This work is being continued. For emulsions, such as water-in-benzene, in which the disperse phase sinks under the influence of gravity, the capillary side-arm meets the vertical tube near its bottom. A detailed discussion of the bearing of the investigation upon theories of emulsification is reserved for a future paper.

Since this paper was submitted for publication, weight-distribution curves for benzene-in-water emulsions with potassium palmitate as stabilizer have been determined by the microscopic measurement of 1500 particles for each determination; these curves checked satisfactorily with those obtained by the sedimentation method herein described.

We wish to acknowledge our indebtedness to Professor J. Howard Mathews for his interest and cooperation in this research.

Summary

1. A new and simple method for determining the distribution of size of particles in emulsions with a rising disperse phase has been described.
2. It has been shown that distribution curves can be checked with a fair degree of accuracy for two emulsions prepared under the same conditions.
3. The position of the maxima in the distribution curves was found to be but slightly changed by changes in the concentration of the emulsions.
4. As a stabilizing agent, potassium oleate tends to give an emulsion with larger drops than does potassium palmitate, in accordance with the wedge theory of emulsification.
5. Homogenization under low pressure in the receiver was found to increase the degree of dispersion of benzene-in-water emulsions stabilized

with potassium soaps, but tended to break emulsions containing gelatin or free fatty acids as stabilizers. Homogenization with atmospheric pressure in the receiver caused a breaking of the emulsion in the cases investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY OF BRISTOL]

THE SORPTION OF TOLUENE AND ACETIC ACID AND THEIR MIXTURES BY CARBON

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In a previous paper² a general method was described for determining the true sorption of both solvent and solute in place of the merely relative values obtained in the usual way for solutions. This is done by reaching equilibrium through the vapor phase, the carbon being kept at a temperature higher than that of the liquid to prevent capillary condensation of liquid in the pores. From the increase in the weight of the carbon and analysis of the residual liquid, the absolute amount of each component sorbed is directly determined. The amount of solvent sorbed from a solution is much less than that which is sorbed when the pure solvent alone is taken.

In the present paper it will be seen that a maximum value for sorption is obtained with pure toluene and with pure acetic acid which is independent of the absolute temperature; that the ratio between the saturation values is that of the molecular weights (acetic acid being present as double molecules); and that when solutions are employed, the total amount sorbed still corresponds to a complete film in which a certain number of double molecules of acetic acid have replaced a corresponding number of molecules of toluene.

Experimental Method

The apparatus used is illustrated in the paper referred to, except that here two electrically heated thermostats were employed for the upper and lower bulbs, respectively, so that they could be kept at any pair of temperatures desired. The upper bulb was of 40 cc. and the lower bulb of 20 cc. capacity. The charcoal was weighed into the upper bulb and after the addition of the liquid, the whole was immersed in a mixture of liquid carbon dioxide and ether, evacuated and sealed. In a "direct" experiment, the liquid is placed initially in the lower bulb so that the carbon has

¹ Experimental work by A. M. Bakr. Presented at the New York meeting of the American Chemical Society, Sept., 1921.

² *J. Chem. Soc.*, 119, 454 (1921).