CCLXXXI.—*The Ultra-filtration of Soap Solutions :
Sodium Oleate and Potassium Laurate.*

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THE method of ultra-filtration as developed in the present paper not only supplies an independent check on data observed by other means, but also results in extensive additions to our knowledge of soap solutions. It will be shown that quantitative information with regard to the following may be obtained by the proper application of this method :

1. The relative amounts of crystalloid and colloid present.
2. The osmotic pressure of the solutions.

3. The hydrolysis of soap in solution.
4. A general method of determining the hydration of colloids in solution.
5. The theory of ultra-filtration.
6. The separation of ionic micelle from neutral colloid, and determination of the composition of the ionic micelle and the diameter of the various colloidal particles.

The subject-matter will be dealt with in the foregoing order, after description of the experimental method and a brief account of the theory involved. It will be seen that the results afford striking evidence in support of the theory of colloidal electrolytes. It is necessary very carefully to examine the experimental basis of all such work in view of the remarkably discordant conclusions of such investigators as Jacques Loeb, Pauli, Bancroft, Martin Fischer, Brailsford Robertson, and ourselves. Carefully established data should be of permanent significance.

The Ultra-filter.

The design of the ultra-filter finally employed is shown in Fig. 1, which is a working drawing drawn to scale. It is a development of Hatschek's modification of that of Bechhold ("Laboratory Manual of Elementary Colloid Chemistry," Hatschek, 1920, p. 70). It was designed for use with much higher pressures than any hitherto employed; it may be surrounded by a thermostat, and the filtrate collected out of contact with the atmosphere or carbon dioxide. Finally, it lends itself to testing for absence of leakage and determination of the size of pores in the membrane without disturbing the latter, merely by removing the funnel underneath. The filter is $6\frac{1}{4}$ inches in external diameter and is designed for pressures up to 900 lb. per square inch, but it was used up to pressures of only 500 lb. per square inch (thirty-three atmospheres); a higher pressure, such as 100 atmospheres, would be distinctly advantageous. It is made of heavily nickel-plated phosphor-bronze, and has a capacity of about 250 c.c., about 70 c.c. of soap solution being actually employed. The perforations in the filter plate consist of four holes, 1 inch in diameter (not shown in Fig. 1), around the centre hole, which is half an inch in diameter. The membrane was supported on nickel gauze, and $\frac{1}{4}$ -inch rubber washers were used to render the joints air-tight. A cylinder of oxygen was used as the source of pressure. The membranes described in the present paper are useless for temperatures above 60° .

In the early part of the investigation, the analyses of the soap solutions were made by titration. In later work, a Zeiss dipping refractometer was invaluable, since only a few drops of soap

solution were required for an accurate determination of the concentration of the solution. All concentrations are expressed in terms of weight normality, referring to 1000 grams of solvent.

Fig. 1.

Diameter of the Pores of the Ultra-filter.

The methods used in preparing and testing the membranes are those of Bechhold (*Z. physikal. Chem.*, 1907, **60**, 257; 1908, **64**, 328); Schering's 10 per cent. glacial acetic acid collodion and a specially made 15 per cent. solution were employed, but it was found that a 15 per cent. solution prepared by ourselves made still denser membranes. Schleicher and Schüll filter-papers, No. 575, were used.

The most convenient method of estimating the size of pores is by determining the minimum pressure that will force air through

individual pores when the membrane is inverted under water. The diameter of the pore is inversely proportional to the minimum pressure required, being 300, 30, and $3\ \mu\mu$ for 1, 10, and 100 atmospheres, respectively. The information generally obtained from this bubble-test is the diameter of the maximum pore and the diameter and number of pores of approximately the same magnitude as the maximum pore.

Contrary to impressions derived from the literature, it was found that the pores in any one membrane vary over a very wide range of diameter, and usually only the largest of these is accessible to measurement; for instance, in one membrane there was only

The relative proportions of the various constituents of solutions of pure potassium laurate at 18°. (The asterisk * marks the field showing the proportions of acid soap, 2KL, HL, present.)

one pore as large as $300\ \mu\mu$, two being $150\ \mu\mu$, three $90\ \mu\mu$, six $75\ \mu\mu$, and eight $60\ \mu\mu$. It was more usual, however, to find about a dozen pores within 10 per cent. of the maximum pore. An indication of the diameter of the maximum pore in relation to the solution employed is given by the following data: our 15 per cent. $9\ \mu\mu$, Schering's 15 per cent. $18\ \mu\mu$, 10 per cent. $33\ \mu\mu$, 7.8 per cent. $90\ \mu\mu$, 5 per cent. $150\ \mu\mu$, and 3 per cent. $450\ \mu\mu$. (The value $9\ \mu\mu$, however, corresponds with the highest pressure available for testing, so that the pores must have been smaller, possibly much smaller.)

The Mobility of the Ionic Micelle.

In previous communications from this laboratory, the conductivity and osmotic activity of soap solutions have been studied

and a theory of colloidal electrolytes has been advanced. According to this, soap when in true solution behaves entirely as a crystalloid, but the undissociated soap may be aggregated to form particles of neutral colloid, whereas if the fatty ions are aggregated (without loss of electrical charge) they form colloidal particles known as the ionic micelle, which are supposed to contain some neutral colloid. On account of its well-known small molecular weight and the clear distinction between its behaviour in crystalloidal and colloidal form, soap is one of the best representatives for the study of the theory of this comprehensive group, lacking the ambiguity of the corresponding study of protein or of gelatin with their unknown molecular weight and basic and acidic functions (for reference see this vol., p. 621; also, "Third Colloid Report of the British Association for the Advancement of Science"; Salmon, this vol., p. 711). Figs. 2 and 3 embody the results which have been deduced by Miss M. H. Norris solely from conductivity and freezing-point data in the case of the two soaps studied in the present paper.*

The concentrations ascribed to the ionic micelle depend directly on the mobility postulated for it. The total osmotic activity of a moderately concentrated solution of sodium oleate as measured by the freezing point is so small that even if the whole osmotic effect is ascribed to the sodium ion less than half the observed conductivity is accounted for, and it is necessary to postulate for the ionic micelle an equivalent conductivity at least equal to that of the potassium ion and therefore several-fold greater than that of the fatty ions from which it is derived.

It is now seen from Fig. 3 that the concentrations deduced from this assumption leave, as the only constituents present in appreciable amount, neutral colloid, ionic micelle, and the equivalent amount of the sodium ion. This equilibrium is almost fully established in $0.2N_w$ -oleate and it is almost unchanged on proceeding to $1.4N_w$ and beyond. Potassium oleate, for which the data are fuller, presents very similar results. A method immediately arises for calculating the hydration of the total soap and checking the assumed value for the mobility of the ionic micelle. Accepting the type of equilibrium shown and assuming that the mobility of the ionic micelle and the number of molecules of hydrate water combined with or sorbed by one molecule of total soap is the same in $0.4N_w$ and $1.6N_w$ solutions, the following equations may be set up

* The following values were involved in Miss Norris's calculations:—mobilities of the simple fatty ions = 20.7; ionic micelle = $K' = 64.7$; $Na' = 43.6$; $OH' = 174$; $k_{KL} = 0.22$; $k_{NaOl} = 0.04$. Five per cent. of the total oleate in the $0.05 N_w$ -solution was assumed to be present as ionic micelle.

to represent the conductivity and the lowering of freezing point, respectively. From the freezing point, the weight normality of the potassium ion referred to the true solvent water only is equal to $t^\circ/1.858$.

From the conductivity this true weight normality of the potassium ion is equal to

$$\frac{\mu_v}{u+v} \times \text{apparent } N_w \times \frac{h+s}{s},$$

The relative proportions of the various constituents of aqueous solutions of pure sodium oleate at 18°. (The asterisk * marks the field showing the proportion of acid soap, $2\text{NaOl}.\text{HOl}$, present.)

where h is the hydrate water and $h + s$ is the total water associated with one gram-atom of potassium and u is the mobility of the potassium ion, equal to 64.7. It is evident, by combining these two equations, that h and v are determined, since for $0.4N_w$ and $0.6N_w$, $h + s_1 = 1667$ and $h + s_2 = 2500$ grams of water.

Inserting numerical data, the mobility deduced for the oleate micelle is 77.9 mhos, and the hydration, 289 grams, equals 16 mols.

of water. The mobility thus appears to be even higher than that of the potassium ion, and the hydration is of the magnitude expected from the new data in the present paper (p. 2336) and from previous studies.

It is interesting to notice that we have now two lines of evidence which would indicate that at least eight or ten ions must be contained in one ionic micelle, since otherwise the osmotic pressure of the ionic micelle would be so appreciable as to affect the calculation in the direction of requiring a still higher mobility. Again, if the ionic micelle has a mobility only four times that of the laurate or oleate ion, the principle of Stokes's law would require an agglomeration of at least eight ions to account for this, even neglecting hydration; further, this becomes a minimum of ten ions if it is assumed that the osmotic pressure of one colloidal particle is the same as that of one ion or molecule. On the other hand, the general conclusion to be drawn from the present work on ultra-filtration is that ten is about the maximum number of ions contained in any one particle of ionic micelle.

The Equilibrium Crystalloid $\rightleftharpoons$ Colloid.

The crystalloidal constituents of a soap solution are simple undissociated soap such as potassium laurate, simple fatty ion (L'), hydroxyl ion, and sodium ion. It will be shown that for our present purpose the hydroxyl ion is negligible, and only that portion of the sodium ion which corresponds to the simple laurate ion can be mechanically separated from colloidal ionic micelle. Hence, on filtration through a very dense membrane, only crystalloidal soap and its simple ions will pass into the filtrate, whilst both forms of colloids, namely, ionic micelle $(L')_x$ and neutral colloid $(KL)_n$, will be held back. It is thus possible to obtain a direct experimental check on the conclusions arrived at in previous papers that there is a true, reversible equilibrium between all these constituents, and also to prove the numerical values thus assigned in Figs. 2 and 3.

According to Salmon (*loc. cit.*), a solution which is normal with regard to both potassium chloride and potassium laurate contains practically the whole of the soap in colloidal solution, chiefly as neutral colloid, although partly as ionic micelle. Using the densest membrane, it was found that no potassium laurate passed through. This result was supported by other experiments on $0.6N_w$ - and $0.5N_w$ -potassium chloride with $1.1N_w$ - and $1.5N_w$ -potassium laurate, respectively, where likewise the soap was all in colloidal form.

The filtrate from a solution which was $0.233N_w$ and $0.103N_w$ with respect to sodium oleate and chloride, respectively, contained

soap corresponding to not more than $0.001N_w$ -crystalloidal sodium oleate.

When filtering $0.493N_w$ -solutions of pure potassium laurate, it was found that the concentration of the filtrate was $0.046N_w$ -potassium laurate, independent of the pressure (between six and twelve atmospheres). The fact that the concentration of the filtrate is independent of the pressure, even although there is a large range in the size of pores in the membrane, shows that the particles of ionic micelle and neutral colloid were distinctly larger than the largest pore in the membrane, demonstrating the sharp break in dimensions between colloid and crystalloid. Similarly, the concentration of the filtrate from sodium oleate was independent of the pressure.

Tables I and II present the results of filtration of the laurate and oleate through this dense membrane, which thus measures the total amount of soap present in crystalloidal form. In each case, the solution was first concentrated by filtration to the desired extent, thereupon the filtration was continued for many hours, returning to the solution from time to time the whole of the filtrate coming through in the hope that the final sample taken should nearly correspond with the equilibrium. The filtrate was analysed by the usual titration methods for laurate and potassium. Repetition of these experiments should give more accurate results, particularly if the refractometric method of analysis is employed. A careful study of the pressures should also be made so as to ensure that no crystalloidal soap is being held back, in accordance with the theory of ultra-filtration developed in a later section. The results deduced by other methods, described in previous communications, which are known to be inaccurate in the second decimal place, are given for comparison. It will be seen that the nature of the equilibrium is undoubtedly confirmed, and it becomes extremely difficult to question the main hypothesis of our theory of colloidal electrolytes. In both cases, all the soap is present in crystalloidal form in $0.01N_w$ -soap solutions. With increasing concentration, the proportion of soap in crystalloidal form diminishes very rapidly. The $0.01N_w$ -sodium oleate and potassium laurate were filtered immediately after being prepared. It is possible that the colloidal acid soap formed by hydrolysis had not agglomerated sufficiently to be held back.

The Osmotic Pressure of Soap Solutions.

Ultra-filtration permits of a determination of osmotic pressure, since, for any membrane that holds back any definite set of constituents, the osmotic pressure is the minimum pressure under

which filtration can occur. A strictly semi-permeable membrane is one which separates water from all the other constituents of the solution, and the minimum pressure required corresponds with results obtained by such methods as lowering of freezing point.

TABLE I.

Filtration of potassium laurate at 12–18° through a membrane with pores certainly less than 9 $\mu\mu$ in diameter, giving the concentration of total crystalloidal laurate soap.

Solution filtered.	Crystalloid.			Colloid.		
	A.	B.	C.	A.	B.	C.
0.01 <i>N_w</i>	0.01 <i>N_w</i>	—	—	0.00 <i>N_w</i>	—	—
0.174	0.028	0.06 <i>N_w</i>	—	0.146	0.11 <i>N_w</i>	—
0.210	0.042	0.06	0.06 <i>N_w</i>	0.15	0.15	0.15 <i>N_w</i>
0.277	0.043	0.05	—	0.234	0.23	—
0.313	0.044	0.05	—	0.269	0.26	—
0.370	0.045	0.04	—	0.335	0.33	—
0.493	0.046	0.02	0.04	0.447	0.47	0.46
0.547	0.048	0.02	—	0.499	0.53	—
0.679	0.052	0.04	—	0.627	0.64	—
0.750	0.052	0.06	—	0.698	0.69	—
0.808	0.052	0.07	—	0.756	0.74	—
0.998	0.054	0.12	—	0.944	0.87	—
1.000	0.054	0.12	0.07	0.946	0.88	0.93

A = by filtration; B = from conductivity and freezing-point data; C = from *E.M.F.* and freezing-point data.

TABLE II.

Filtration of sodium oleate at 12–18° through a membrane with pores certainly less than 9 $\mu\mu$ in diameter, separating colloid from crystalloid.*

Solution filtered.	Concentration of filtrate.	Colloid retained.	Conductivity and freezing point.	
			Crystalloid.	Colloid.
0.01 <i>N_w</i>	0.01 <i>N_w</i>	0.00 <i>N_w</i>	—	—
0.144	0.001	0.143	0.02 <i>N_w</i>	0.12 <i>N_w</i>
0.188	0.001	0.187	0.01	0.18
0.227	0.001	0.226	0.01	0.21
0.349	0.0015	0.347	0.00	0.35
0.450	0.002	0.448	0.00	0.45
0.558	0.002	0.556	—	—

* Although freezing-point data are lacking, *E.M.F.* measurements have given a value for the sodium ion in 0.6*N_w*-solution equal to 0.11*N_w*, in agreement with the 0.12*N_w* indicated in Fig. 3.

The most interesting case is obtained with the membranes described in the previous section, where all the crystalloidal constituents pass through while all the colloidal constituents together with the sodium ions equivalent to the ionic micelle, are retained. Here, the minimum pressure for ultra-filtration will be almost entirely due to the sodium ions and will afford a measure of the

ionic micelle as distinct from simple laurate or oleate ions. Finally, it is seen that with a coarse membrane which retains only neutral colloid, a few cm. pressure suffice to effect ultra-filtration. There are thus as many kinds and values of osmotic pressure as there are constituents in a solution, provided that the separation takes place at consecutive stages.

In practice there are two difficulties, one being the excessive slowness of ultra-filtration in the neighbourhood of the corresponding osmotic pressure, so that with the present apparatus the observed values would tend to be too great, even when the membrane is carefully watched for the first drops of filtrate. The other complication arises from the alterations and readjustments of equilibrium that take place in the filtrate, which of course directly affect the osmotic pressure. Hence, the only measurements adduced here are those referring to soap solutions in which the soap is entirely in the form of colloidal electrolyte.

In an experiment with 1.0*N*_w-potassium laurate at 12–18°, no filtrate appeared in eleven hours with a pressure of 6.0 atmospheres, whereas two and a half hours later, with a pressure of 7.1 atmospheres, drops were collecting.

Table III gives the values thus obtained together with the concentration of sodium ions (equivalent to the ionic micelle) deduced therefrom, and for comparison, the concentration of ionic micelle deduced from conductivity and freezing point, and from *E.M.F.*, respectively. The agreement between the three methods is within the experimental error.

TABLE III.

Comparison of concentration of ionic micelle corresponding to minimum pressures required for ultra-filtration with values deduced by previous methods.

Solution filtered (<i>N</i> _w).	Atmospheres required.	Ionic micelle.	From conductivity and freezing point.	From <i>E.M.F.</i>
0.4-K Laurate.	2.9	0.13	0.13	0.14
0.6-K Laurate.	4.7	0.21	0.21	0.20
1.0-K Laurate.	7.1	0.32	0.36	0.33
0.2-Na Oleate.	1.0	0.045	0.036	—
0.4-Na Oleate.	2.7	0.12	0.08	(0.07)

Bancroft, in propounding research problems in colloid chemistry (*J. Ind. Eng. Chem.*, 1921, **13**, 261), states that concentrated soap solutions show practically no rise in boiling point, and that this must be due to adsorption. His statement requires substantiation, since it directly calls in question all the data published from this laboratory on the osmotic activity of soap solutions by the four methods of vapour pressure, dew point, freezing point, and now

ultra-filtration, all of which show that soap solutions exhibit an osmotic activity about half that of sucrose or carbamide.

The Hydrolysis of Soap in Solution.

The only previous determinations are those from this laboratory by *E.M.F.* and catalysis and conductivity measurements, all of which show that the concentration of hydroxyl ion is about 0.001*N* and that the other product of hydrolysis, in the case of sodium palmitate at 90°, is 2NaP,HP; further, investigations of a free acid incapable of hydrolysis, namely, hexadecanesulphonic acid, show that its behaviour in other respects is closely similar to that of the higher soaps (Norris, this vol., p. 2161). Bancroft, however (*loc. cit.*; also "Applied Colloid Chemistry," 1921, p. 225), considers that it should be possible, by analysing the filtrate in ultra-filtration, to prove a high degree of hydrolysis combined with adsorption of the sodium hydroxide in concentrated solutions. We confess inability to interpret the experimental data for soap solutions according to such an idea.

The hydrolysis-alkalinity as measured by ultra-filtration through the densest membranes, holding back all colloidal constituents, is shown in Tables IV and V. The alkalinity of the filtrate is determined by titration after adding four volumes of boiled-out alcohol.

TABLE IV.

Hydrolysis-alkalinity of potassium laurate solutions at 12—18° as measured by ultra-filtration.

Conc. of solution (N_w).	Conc. of OH' (N_v).	Per cent. hydrolysis.	Conc. of solution (N_w).	Conc. of OH' (N_v).	Per cent. hydrolysis.
0.277-K Laurate	0.0016	0.58	0.679-K Laurate	0.0012	0.18
0.370-K Laurate	0.0020	0.54	0.808-K Laurate	0.0010	0.12
0.493-K Laurate	0.0013	0.26	1.000-K Laurate	0.0009	0.09

TABLE V.

Hydrolysis-alkalinity of sodium oleate solutions at 12—18° as measured by ultra-filtration.

Conc. of solution (N_w).	Conc. of OH' (N_v).	Per cent. hydrolysis.	Conc. of solution (N_w).	Conc. of OH' (N_v).	Per cent. hydrolysis.
0.144-Na Oleate	0.0012	0.80	0.558-Na Oleate	0.0019	0.34
0.188-Na Oleate	0.0012	0.64	0.252-Na Oleate	0.0008	0.32
0.32-Na Oleate	0.0018	0.57	0.106-NaCl		
0.450-Na Oleate	0.0024	0.53			

The hydrolysis-alkalinity as determined by ultra-filtration is nearly the same as given by previous measurements at 90°. It was expected to be somewhat less, but the discrepancy, if real, is readily accounted for as the result of membrane hydrolysis (Donnan, *Z. Elektrochem.*, 1911, **17**, 578), which would tend to exaggerate

the alkalinity found. The quantitative evaluation of the effective membrane hydrolysis is impossible without definite knowledge of the degree of solubility of the acid soap formed. Another circumstance which diminishes the accuracy of the results is that the laurate solutions were made by taking theoretical amounts of lauric acid. For this reason no stress can be laid on the results obtained and on the very similar results obtained with N_w -potassium laurate containing N -potassium chloride. Addition of 0.1*N*-sodium chloride to 0.25*N_w*-sodium oleate diminished the hydrolysis-alkalinity to 0.0008*N_w*-hydroxyl ions.

The Hydration of Soap in Solution; a General Method.

The hydration of soap may be defined as the total number of gram-molecules of water chemically combined with or sorbed by one gram-equivalent of the soap. This can readily be measured by ultra-filtration (McBain, "Third Colloid Report of the British Association for the Advancement of Science," 1920, p. 19) provided that a suitable indifferent reference substance is available. The extent of the increase of concentration of the reference substance found in the filtrate above that in the original solution is a measure of the water abstracted by the colloid from the solution. If membranes are used which allow one colloidal constituent to pass through whilst another is retained (see a later section), it should be possible to measure the hydration of each. In experiments cited in Tables VI and VII, in which the corresponding chlorides were used as reference substances, it is highly probable that these are slightly sorbed by the soap; if so, the true values for the hydration are correspondingly greater (compare T., 1921, 119, 1372, 1380, 1381, 1674). Further, the hydration in the absence of these salts should be distinctly greater.

These experiments constitute very direct proof that the soap in these solutions is colloidal and that it has the high degree of hydration predicted from earlier work.

TABLE VI.

Minimum values for the hydration per equivalent of potassium laurate in solutions at 12–18° in the presence of potassium chloride.

	N_w of K Laurate.	N_w of KCl.	Hydration found.
Earlier filtrate	0.000	0.762	11.8 H ₂ O
Solution above	1.129	0.581	
Later filtrate	0.000	0.768	
First solution above	1.000	1.000	11.6 H ₂ O
Filtrate	0.000	1.276	
Final solution above	1.056	0.991	

TABLE VII.

Minimum values for the hydration per equivalent of sodium oleate in solutions at 12—18°.

	N_w of Na Oleate	N_w of NaCl.	Hydration found.
First solution above	0.2517	0.1029	
Filtrate	0.0013	0.1077	9.2 H ₂ O
Final solution above	0.2770	0.1028	

Theory of the Ultra-filter.

Excess of pressure inhibits ultra-filtration by stopping up the pores; with insufficient pressure, ultra-filtration becomes extremely slow or ceases altogether. It is only with suitably chosen intermediate pressures that deliberately planned ultra-filtration can be carried out and trustworthy information obtained regarding the diameters of the pores or filtered particles. Both the pressure used in the ultra-filtration and the osmotic pressure of the solution are decisive factors.

According to Bechhold (*Z. physikal. Chem.*, 1908, **60**, 328), collodion membranes only allow the passage of particles with diameters of not more than one-tenth that of the pores, but the evidence for his conclusion is speculative. It is difficult to ascertain the maximum ratio between diameter of particles passing through an ultra-filter and the diameters of pores as determined by the bubble-test. Bechhold's factor, one-tenth, is obviously a rough empirical correction for a number of factors operating under his experimental conditions.

Hatschek in collaboration with Bechhold has studied the effect of pressure on the diameter of deformable oil globules, which could be forced through pores measured by the air-bubble method (*Kolloid Z.*, 1910, **7**, 86). He found that with high pressures oil drops could be forced through pores of diameter many times smaller than that of the drops themselves; he also concluded that the pores were not more than half the size indicated by the air-bubble test, but the precaution does not seem to have been taken of applying the air-bubble test after the ultra-filtration. Bechhold (*Kolloid Z.*, 1921, **29**, 81), in filtering lecithin sols, obtained a similar increase in the amount of substance in the filtrate with increasing pressure.

The evidence goes to show that under suitably chosen conditions the diameter of the particles approximately corresponds with the diameter of the pores which just let them pass through. There is no indication in any of our observations that soap particles are deformable; indeed, we know of no reason for supposing that the

colloidal particles in soap solutions are of a liquid or emulsoid nature. Instead of more and more soap being forced through under high pressures, the filter becomes clogged to almost any desired extent. Bechhold mentions that Burian (*Arch. Fisiol.*, 7) has obtained a similar result with egg-albumin containing salt.

Of course, the relation between diameter of particles and of pores is much more complicated if the particles are not spherical. The length of a molecule of soap must be about 2 or 3 $\mu\mu$, and this must be many times its breadth, and we have no information as to the form of either the ionic micelle or the neutral colloid. It will be shown that for practical purposes it is possible to express the size of each kind of colloid in terms of diameter of pores, and that the neutral colloid in the oleate is very many times coarser than the ionic micelle.

It is necessary to develop a theory of ultra-filtration, for non-deformable particles, as follows. Suppose we have a membrane with constant pores of every conceivable diameter up to and including a value a and, further, that there is in the solution a series of crystalloidal and colloidal constituents the diameters of which, from the coarsest to the finest, are equal to a, b, c, d , and e , e being the water molecule itself, and that the partial osmotic pressures of the first four constituents are P_a, P_b, P_c , and P_d . It is obvious that only an infinitesimal pressure will be necessary to cause solution to flow through any pore the diameter of which is at least equal to a , so that a pore in diameter from a upwards would merely act as a leak. There are two principles involved in the action of all the other pores :

1. Only those constituents may pass through any given pore the diameter of which is less than the pore.
2. Nothing will pass through any given pore unless the pressure in use exceeds the osmotic pressure of every other constituent that is coarse enough to be held back.

There are thus two ways in which a given constituent may be prevented from passing through a given pore ; namely, through the pore being smaller than the particle in question, or through the pressure in use not exceeding the osmotic pressure of some constituent of greater diameter than the pore in question.

The interplay of these two principles produces an unexpectedly complicated picture, but it will become apparent that there is a series of definite filtrates, each of approximately fixed concentration, obtainable with any given membrane, and each corresponding with a definite range of pressure. The whole range of conceivable pressures is therefore divided up by certain critical osmotic pressures, at which sharp breaks occur in the composition of the filtrate.

This definite composition follows, since, according to our hypothesis, only a definite set of pores will be functioning for all pressures lying between a pair of these critical osmotic values; for then, according to Poisseuille's law, the proportion of all the liquid flowing through, which is allotted to any one pore, remains independent of the total pressure. Between such a pair of pressures, altering the pressure merely alters the speed, so that the proportion passing through any one pore is only varied when, in consequence of a critical pressure being exceeded, additional pores are brought into play.

Turning now to the more detailed consideration of the membrane and the series of constituents postulated above, for all very low pressures filtrate I will be coming through pores of diameter a and will be merely unchanged solution; all pores of diameter less than a are out of action. As soon as the pressure exceeds the osmotic pressure P_a , pores lying between a and b will come into play; and the portion of the solution flowing through these pores will be deprived of constituent a , so that the gross composition of the filtrate can now be called filtrate II. The question as to whether pores lying between b and c are out of action or not depends entirely on whether P_a is greater than P_b ; if it is, then the pressure used has brought them also into action and they are contributing towards filtrate II, a solution deprived of both constituents A and B. Similarly, if P_c is greater than P_a , all pores smaller than c are out of action.

Filtrate III will then be reached when P_c is exceeded, and now we have pores of diameter a discharging unchanged solution, those between a and b holding back A only, those between b and c holding back both A and B, and those between c and d holding back A, B, and C, whilst if P_d is smaller than the critical value P_c , all pores, without exception, down to those of the diameter, e , of the water molecule itself, will be in action, those between d and e producing pure water. It does not matter even if P_d is the lowest osmotic pressure of all, pores smaller than d do not come into use until P_a , P_b , and P_c are all exceeded.

For the membrane assumed, we have deduced three possible filtrates of fixed composition, I, II, and III. If none of the pores is quite as big as a , filtrate I is eliminated and no filtration will take place until the pressure in use exceed either P_a or P_b , whichever is the greater. Filtrates II and III are correspondingly altered in composition, since now they are not admixed with filtrate I. Similar reasoning applies if a denser membrane is used in which the diameter of the largest pores lies between b and c .

An illustration of these effects was given in a previous section,

where nothing passed through a dense membrane until the osmotic pressure of the ionic micelle and its accompanying sodium ions had been exceeded. Not even the crystalloidal soap or the simple laurate and potassium ions could come through, although their osmotic pressures were greatly exceeded; that is, until the osmotic pressure corresponding with the ionic micelle was reached. It is further evident that the filtrate must be at least slightly more dilute than corresponds to the crystalloidal matter in solution, since every pore, down to those of diameter e , must have come into action simultaneously, producing filtrate III.

In a soap solution, the coarsest constituent is the neutral colloid $(\text{NaOl})_x$ or $(\text{KL})_x$ with an osmotic pressure presumably equal to a few cm. only of water, so that filtrate II should be obtainable in any membrane the largest pores of which lie between neutral colloid and ionic micelle and only these pores can act. As a general rule, it should be stated that the only way to ensure that any constituent capable of passing through the filter is not separated from the corresponding solvent is to utilise pressures below the partial pressure of the constituent in question.

Theoretically, there should be a difference in composition between solution and filtrate when any solution whatsoever is being filtered under pressures which exceed the osmotic pressure of any constituent. Practically, the difference in the case of a crystalloidal solution would be slight unless the relative number of pores of diameter greater than d is severely limited.

Finally, apart from the possibility of deformable particles, there is one further complication which must be reckoned with in all work on ultra-filtration, and that is clogging of the pores, either mechanically or by adsorption. This, however, can be tested for by interrupting the experiment from time to time to carry out a bubble test. Tables VIII, IX, and X illustrate such clogging action, and the last also shows that high pressures may free the pores again temporarily. The data for filtrate III show the expected dependence of the composition on the individual membrane, but they also show a further deviation with pressure which indicates a real variation from Poisseuille's law.

Separation of Ionic Micelle from Neutral Colloid.

There are no colloidal particles of diameter larger than $15\ \mu\mu$ in solutions of potassium laurate. In sodium oleate, on the other hand, the particles of neutral colloid all lie between $75\ \mu\mu$ and $450\ \mu\mu$, whilst those of ionic micelle are definitely smaller than $15\ \mu\mu$. More accurate measurements in the separation of micelle from the neutral colloid in laurate solutions were not attained

owing to our not having foreseen the necessity of providing apparatus that would withstand the extreme pressures required for the bubble tests; and also because we had not developed in time the theory of the preceding section which is necessary to clear up the otherwise confusing data. All we can assert is that the ionic micelle both of laurate and of oleate is too large to pass through a membrane which showed no pores at all under a pressure of 33 atmospheres, which would have revealed any pores down to $9\ \mu\mu$. The diameter of the ionic micelle is therefore not very many times the length of the laurate or oleate molecule.

The particles of neutral colloid correspond with diameter a , and those of ionic micelle with b . All pressures less than those found in the fifth section for the ionic micelle P_b should therefore yield filtrate II with membranes the largest pores of which measure between 15 and $75\ \mu\mu$. It is proposed to show that this was the case with $0.2N_w$ -sodium oleate, which consistently yielded a filtrate of $0.04N_w$ with pressures less than P_b , and a more dilute filtrate when P_b was exceeded (filtrate III). For a given pressure, filtrate III is found to become more dilute as the pores get clogged. Since the osmotic pressure of the ionic micelle and its accompanying sodium ions so greatly exceeds that of the small amount of crystalloid present, filtrate III comes from three sets of pores producing pure water, solution of crystalloid, and solution of crystalloid plus ionic micelle, respectively. Typical data with membranes of different density are given in Tables VIII and IX. Of course, time is required to wash out the membrane and obtain a correct filtrate. The pore diameters given are those found by actual test during the course of the experiment. The diameters found with membranes that were contaminated with soap solution were calculated on the assumption that the surface tension was that of pure water. Such pores were therefore really smaller than here indicated.

TABLE VIII.

Filtration of $0.2N_w$ -sodium oleate showing a constant filtrate of $0.04N_w$ with pressures less than the osmotic pressure of the ionic micelle (one atmosphere), and a more dilute one when that is exceeded.

Series I.

Largest pore	$75\ \mu\mu$							
Atmospheres	0.05	0.03	0.05	0.07	0.08	3	5	7
Filtrate N_w	0.040	0.040	0.040	0.040	0.040	0.035	0.027	0.020

Series II.

Largest pore	$75\ \mu\mu$				$60\ \mu\mu$		$45\ \mu\mu$
Atmospheres	0.8	0.8	0.8	0.7	0.7	0.3	0.05
Filtrate N_w	0.015	0.040	0.040	0.040	0.040	0.040	0.040

Series II (continued).

Largest pore	45 $\mu\mu$							45 $\mu\mu$
Atmospheres	3	3	3	5	5	0.7	0.7	0.7
Filtrate N_w	0.040	0.035	0.035	0.027	0.027	0.027	0.040	0.040

Series III.

Largest pore	18 $\mu\mu$							15 $\mu\mu$
Atmospheres	5		0.8	0.7	0.5	0.3		0.05
Filtrate N_w	0.025		0.040	0.040	0.040	0.040		0.040

Series IV.

Largest pore	75 $\mu\mu$			60 $\mu\mu$	45 $\mu\mu$	18 $\mu\mu$		15 $\mu\mu$
Atmospheres	5	3	0.8	0.05	5	5	0.08	0.05
Filtrate N_w	0.027	0.035	0.040	0.040	0.025	0.023	0.040	0.040

TABLE IX.

Filtration of 0.296 N_w - and 0.435 N_w -sodium oleate showing a constant filtrate of 0.055 N_w and 0.092 N_w , respectively, with pressures less than the osmotic pressure of the ionic micelle (1.5 and 2 atmospheres).

Series I, with 0.296 N_w -oleate.

Largest pore	75 $\mu\mu$	75 $\mu\mu$	75 $\mu\mu$	60 $\mu\mu$	45 $\mu\mu$	45 $\mu\mu$
Atmospheres	5	1.2	0.3	0.3	0.3	0.05
Filtrate N_w	0.033	0.055	0.055	0.055	0.055	0.055

Series II, with 0.296 N_w -oleate.

Largest pore	300 $\mu\mu$	75 $\mu\mu$	75 $\mu\mu$	75 $\mu\mu$	75 $\mu\mu$	75 $\mu\mu$
Atmospheres		0.7	5	6.7	8.3	
Filtrate N_w		0.055	0.033	0.029	0.020	

Series III, with 0.296 N_w -oleate.

Largest pore	300 $\mu\mu$							
Atmospheres	6.7	6.7	6.7	5	5	0.7	0.7	0.3
Filtrate N_w	0.05	0.085	0.020	0.08	0.033	0.055	0.055	0.055

Series IV, with 0.296 N_w -oleate.

Largest pore	300 $\mu\mu$							
Atmospheres	5	5	5	6.7	6.7	6.7	1.2	0.3
Filtrate N_w	0.07	0.085	0.033	0.033	0.09	0.06	0.055	0.055

Series V, with 0.435 N_w -oleate.

Largest pore	75 $\mu\mu$	75 $\mu\mu$	75 $\mu\mu$	60 $\mu\mu$	45 $\mu\mu$	45 $\mu\mu$	45 $\mu\mu$	45 $\mu\mu$
Atmospheres	2.7	1.8	0.3	1.3	5	1.3	0.3	0.05
Filtrate N_w	0.06	0.092	0.092	0.092	0.04	0.092	0.092	0.092

In Table X and XI are given data which throw light on the maximum diameter of the particles of neutral colloidal sodium oleate; these are certainly all smaller, and probably several times smaller, than 450 $\mu\mu$, and certainly all larger than 75 $\mu\mu$. Much lower pressures should have been employed. As in Table IX, Series III and IV, the filtrates increased in concentration to a maximum and then fell off as the pores were clogged.

TABLE X.

Maximum concentration of filtrates from 0.296 N_w -sodium oleate, and ascertained diameter of largest pore at that time.

Pressure (atms.).	Largest pore.		Filtrate N_w .	Pressure (atms.).	Largest pore.		Filtrate N_w .
	Initial.	Final.			Initial.	Final.	
0.7	300 $\mu\mu$	75 $\mu\mu$	0.055	0.7	75 $\mu\mu$	70 $\mu\mu$	0.055
5	75 $\mu\mu$	150 $\mu\mu$	0.085	5	300 $\mu\mu$	150 $\mu\mu$	0.085
7	75 $\mu\mu$	150 $\mu\mu$	0.09	7	300 $\mu\mu$	150 $\mu\mu$	0.09
8	75 $\mu\mu$	300 $\mu\mu$	0.20	9	300 $\mu\mu$	300 $\mu\mu$	0.20

TABLE XI.

Filtrates from sodium oleate solutions through coarse membranes.

Solution. N_w .	Filtrate. N_w .	Largest initial pore.	Pressure (atms.).
0.21	0.21	450 $\mu\mu$	—
0.40	0.40	450 $\mu\mu$	—
0.30	0.20	300 $\mu\mu$	8
0.30	0.09	150 $\mu\mu$	7

Concentration and Composition of the Ionic Micelle.

In the preceding section there has been conclusively shown a definite separation of the colloidal constituents of sodium oleate solutions. At least 95—98 per cent. of the ionic micelle must have appeared in the filtrates, since they came through unaltered with pressures as low as 0.05 atmosphere. Again, the filtrate is the same when there are no pores larger than 15 $\mu\mu$ as when some equal 75 $\mu\mu$, which shows that unless some of the particles of ionic micelle are very many times larger than all the others, they must all be of nearly equal dimensions. Similar reasoning shows that all the particles of neutral colloid existing independently of the particles of ionic micelle must be greater than 75 $\mu\mu$ in diameter.

We have, then, from 0.214, 0.296, and 0.435 N_w -sodium oleate, constant filtrates of 0.040, 0.055, and 0.092 N_w , respectively, which must contain ionic micelle and crystalloidal matter only. The crystalloidal matter is mostly sodium hydroxide and it is less than 0.001 N_w (the corresponding particles of acid soap are probably coarse and cannot exceed a few thousandths normal).

Since the gross composition of the ionic micelle is given by these filtrates, and since we already know its concentration in electrochemical equivalents (see Table III), we can at once inquire as to how far the ionic micelle consists merely of aggregated oleate ions and in how far these are contaminated with neutral colloidal oleate. The data are given in Table XII, and it is at once seen that the ionic micelle is mainly composed of aggregated (and hydrated) oleate ions and that most of the neutral colloid exists in quite separate particles.

TABLE XII.

Concentration of ionic micelle and of neutral colloid, respectively, in sodium oleate solutions as found by ultra-filtration, compared with aggregated oleate ion and neutral colloid as deduced from conductivity and freezing-point methods; showing that they are present as two distinct sets of particles.

Solution. $N_{\text{g.}}$	Ultra-filtrate.		Conductivity and freezing point.	
	Ionic micelle.	Neutral colloid.	$(\text{Ol}')_{\text{n.}}$	$(\text{NaOl})_{\text{z.}}$
0.214	0.040	0.174	0.038	0.176
0.296	0.055	0.241	0.055	0.241
0.435	0.092	0.343	0.087	0.348

A conclusion from much of our recent work is that perhaps the most important difference between the various soaps arises from the widely differing amounts and properties of neutral colloid, that is, un-ionised colloidal electrolyte, which we have now shown to be separate from the ionic micelle.

Summary.

1. A theory of ultra-filtration through permeable and semi-permeable membranes has been developed.

2. Ultra-filtration of potassium laurate and sodium oleate has confirmed the values, deduced by other methods described in previous communications, for hydrolysis, osmotic pressure, and amounts of crystalloidal and colloidal matter.

3. A general method for determining the solvation of the colloid by ultra-filtration has been described, and it has been shown that soap in solution contains at least 10 molecules of hydrate water per equivalent of soap.

4. The ionic micelle has been separated from neutral colloid by ultra-filtration; the diameter of the particles of ionic micelle is only a few times the length of the molecule, and its approximate formula is $(\text{Ol}')_{10} \cdot m\text{H}_2\text{O}$. Whereas the particles of neutral colloid of potassium laurate are less than $15 \mu\mu$ in diameter, those of sodium oleate are about ten times larger.

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