[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Ultrafiltration of Soap Solutions

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It was shown by McBain and Jenkins[1] in 1922 that ultrafiltration in the presence of a reference substance may be used as a measure of the hydration of the colloidal particles of a sol. The calculation is based upon the assumption that the reference substance dissolves only in the free solvent which is not bound to the colloidal particles and that the concentration of the ultrafiltrate represents this more concentrated intermicellar solution. If the reference substance is a non-electrolyte, the results will usually be too small and may even appear strongly negative on account of adsorption by the colloidal particles. An electrolyte is much less sorbed, but the apparent hydration will be magnified by any Donnan effect. The ideal would be to obtain the same result with non-electrolytes and electrolytes. For soap every substance hitherto examined has been found to be adsorbed by soap. It will be shown that an electrolyte may be used under conditions in which Donnan effect does not appreciably influence the result, confirming the determinations of McBain and Jenkins with potassium laurate where the hydration was found to be one molecule of water for each carbon atom and of Quick[2] who obtained a similar value from comparison of the conductivity with the dew point lowering of mixtures of potassium laurate with potassium chloride.

Supplementary experiments in the Bristol University laboratory by A. M. Bakr and G. M. Langdon with acetic acid collodion showed that this membrane interacts with soaps or dilute alkalies, liberating nitrite, nitrate and possibly acetate to an appreciable extent. All further work was therefore carried out with cellophane.

Part I of the present communication will deal with the hydration of potassium laurate in solution. Part II will comprise other experiments on ultrafiltration of soap solutions.

The ultrafiltration of a colloidal electrolyte is a complicated phenomenon even when other electrolytes have not been added. McBain and Jenkins used it as a quantitative method of discriminating between colloid and crystalloid forms simultaneously present and of determining osmotic pressure, hydrolysis-alkalinity, hydration, and even as a means of separation of the two colloidal forms of soap, the neutral and the ionic micelle, with a determination of the concentration and composition of the latter. McBain and McClatchie[3] since showed in experiments, somewhat parallel in form to those of Greenberg and Greenberg,[4] that such ultrafiltration

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[1] J. W. McBain and W. J. Jenkins, *J. Chem. Soc.*, **121**, 2325 (1922).

[2] W. C. Quick, *ibid.*, **127**, 1409 (1925).

[3] J. W. McBain and W. L. McClatchie, THIS JOURNAL, **55**, 1315 (1933).

[4] D. M. Greenberg and M. Greenberg, *J. Biol. Chem.*, **94**, 373 (1931).

is subject to influence by Donnan equilibrium. Furthermore, they discovered that the composition of an ultrafiltrate is greatly dependent upon the rate of ultrafiltration and/or the pressure employed. This they ascribed to Donnan effect. Ample confirmation of this latter influence in ultrafiltration which had hitherto escaped attention is to be found in the present work which was carried out at the University of Bristol, England, in 1922–1924 and continued at Stanford University in 1929.

Part I. The Hydration of Dissolved Potassium Laurate[5]

The type of experiment here studied may be illustrated by the striking example recorded in Table I (by H. P. L.).

TABLE I

ULTRAFILTRATION OF A SOLUTION ORIGINALLY 1.0 N_w IN RESPECT TO POTASSIUM LAURATE AND TO POTASSIUM CHLORIDE FILTERED THROUGH CELLOPHANE NO. 600 AT 120 LB./SQ. IN.

Residue		Filtrate		Hydration[a]
N_w KL	N_w KCl	N_w KL	N_w KCl	Moles H_2O/moles KL
1.000	1.000	0.01	1.194	10.3
1.088	0.9287	.014	1.182	12.8
1.062	.8544	.01	1.203	12.7
1.287	.9076	.015	1.184	9.9
1.404	.894	...	1.192	10.2
1.601	.8341	...	1.206	10.8
1.767	.8178	...	1.183	9.7
1.962	.7955	.05	1.200	9.8
2.28	.718	...	1.19	9.6
2.584	.670			

[a] Hydration in moles H_2O/mole soap $= 55.5(R_F - R)/(R_FS - RS_F)$ where all concentrations are in moles. R is the mean concentration of the reference substance above the ultrafilter and R_F in the filtrate, S is the mean concentration of soap solution above the ultrafilter and S_F that in the filtrate. The formula holds even when the soap is only imperfectly retained.

In Table I it is seen that the composition of the filtrate is 1.2 N_w potassium chloride while that of the residue changes from 1.0 N_w potassium laurate and 1.0 N_w potassium chloride, to 2.6 N_w potassium laurate and 0.67 N_w potassium chloride. If the filtrate is regarded as a true sample of the free liquid in the soap solution, the bound water of a colloidal soap is 10 or 11 moles of water per mole of dissolved colloidal soap. The last value for hydration given in the table refers to a heterogeneous mixture of middle soap with isotropic soap solution because it is during the formation of the last two residues that the transformation begins from isotropic solution to anisotropic liquid middle soap.

Very similar data were obtained in the Bristol laboratory by M. C. Field (1926) who, however, continued the experiment into the homogeneous region, anisotropic liquid middle soap, the residue then changing from

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(5) Where not otherwise noted all experiments are by Y. K.

2.856 KL + 0.654 KCl to 3.372 KL + 1.217 KCl, the hydration being 8.6.

It may be noted in passing that the change in apparent hydration as the residue becomes concentrated and the reference substance more dilute is very different from that predicted for Donnan effect and is indeed of opposite sign, hydration itself being the chief factor.

We hope to show that the results given in Table I are correctly interpreted. The values found by Jenkins were 11.8 and 11.6 at the beginning of the ultrafiltration. Those by Kawakami are 11.7, 11.8 and 11.7.

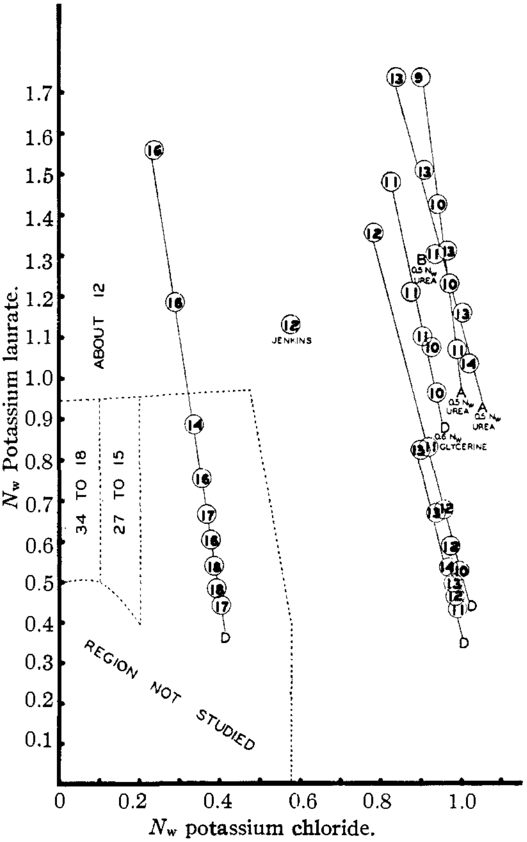

Fig. 1.—Apparent hydration of potassium laurate in solution.

Similar values were found with potassium chloride in the presence of 0.5 N_w urea, but the urea itself was sufficiently sorbed by the soap even in the presence of the potassium chloride to give the apparently negative value for hydration, −0.69. In the absence of salt mixtures, originally 1.0 N_w potassium laurate and 0.5 N_w urea gave the still more negative values, −2.02, −2.30, −2.66 and −2.01. In the presence of decinormal potassium chloride values averaging −2.1 were obtained, independent of the procedure used in making up the solution.

Glycerin, likewise, is sorbed, and solutions originally 1.0 N_w potassium laurate, 1.0 N_w potassium chloride and 0.6 N_w glycerin gave the successive negative values −8.3, 8.4, 9.4, 8.9, 7.2, but the corresponding positive values from the potassium chloride were +10.4, 9.9, 10.5, 10.9 and 10.9.

To save space, nearly 100 measurements are recorded graphically in Figs. 1 and 1a, the abscissas being mean concentrations of potassium chloride above the ultrafilter and the ordinates, the mean concentrations of potassium laurate, likewise above the ultrafilter, the numbers giving the hydrations found, and the lines connecting successive filtrations in each series of experiments. Figure 1a is merely a five-fold enlargement of the portion of Fig. 1 dealing with solutions of potassium chloride of less than 0.2 N_w in order to show the actual numerical results which are replaced for lack of space on Fig. 1 by the statement as to the general results here obtained. Since four procedures were followed and the differences are of significance, each series is labeled with a capital letter to indicate the procedure.[6] These were as follows:

Procedure	Cellophane	Treatment of cellophane	Press., atm.	Stirring
A	600	Used dry	50	None
B	600	Used dry	50	Stirred
C	1200	Used dry	50	Stirred
D	1200	Soaked	25	Stirred

Discussion

A fair description of the results portrayed in Figs. 1 and 1a is that in the regions lying outside the dotted zones, procedures A, B and C give a hydration value for potassium laurate in solution equal to 12 moles of water per equivalent of soap.[7] On the right hand side of Fig. 1 all procedures give this result.

In other words, for high concentrations of ions, whether derived from soap or from potassium chloride, a hydration value of 12 moles is indicated. Figure 2 portrays this result, using dew point lowering as an indication of total ionic concentration, and it is seen that where the ionic concentration is high the results converge to a value between 11 and 12, independent of the concentration of the soap. At low ionic concentrations other much larger values result.

The principle, now commonly known as the Donnan equilibrium, was given its present quantitative formulation by Gouy and Chapman for the diffuse double layer, was later derived by Donnan for membrane equilibria, and very much later reobtained by Debye and Hückel in their formulation of the ionic atmosphere in ordinary electrolytes. In the well-known work of Gouy it was shown numerically that the diffuse double layer extends outward from a charged body to a very appreciable depth in excessively dilute solutions of ions but that with the presence of increasing concentration it rapidly shrinks to almost negligible dimensions. This supports the interpretation suggested above that the hydration value of 11 or 12 is not appreciably in error due to Donnan effect. On the other hand, the Donnan

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(6) The apparatus used was that developed at Göttingen, with electromagnetic stirring. However, all the parts, including the stirrer, coming into contact with the solution were replaced by pure silver. The temperature was between 22 and 26°.

(7) Only two results altogether do not agree, and one of those is an initial result with procedure C which must be somewhat too large on account of the effect of the dry membrane. The other is the uppermost result in Fig. 1a and must be ascribed to experimental error.

effect is evident and becomes preponderant in the lower ionic concentrations and accounts for the apparent hydration becoming several fold greater.

McBain and McClatchie have shown how the rate of ultrafiltration or pressure used in ultrafiltration becomes a test of the extent to which the Donnan effect is present. The Donnan effect in ultrafiltration, which is not to be confused with a non-existent equilibrium across the membrane used in ultrafiltration but relates to the atmosphere surrounding every charged ion or particle in every solution, evidences itself by dependence of the concentration of the filtrate upon rate or pressure. The higher the pressure, the more dilute the ultrafiltrate because in rapid ultrafiltration the ionic atmospheres which are impoverished as regards electrolytes with a common ion (K^+) are increasingly encroached upon and yield a solution more nearly like the average cross-sectional value of the composition of the liquid. At slow rates and low pressures the ultrafiltrate is a truer sample of intermicellar liquid and hence is more concentrated and would if so accepted give exaggerated values for hydration.

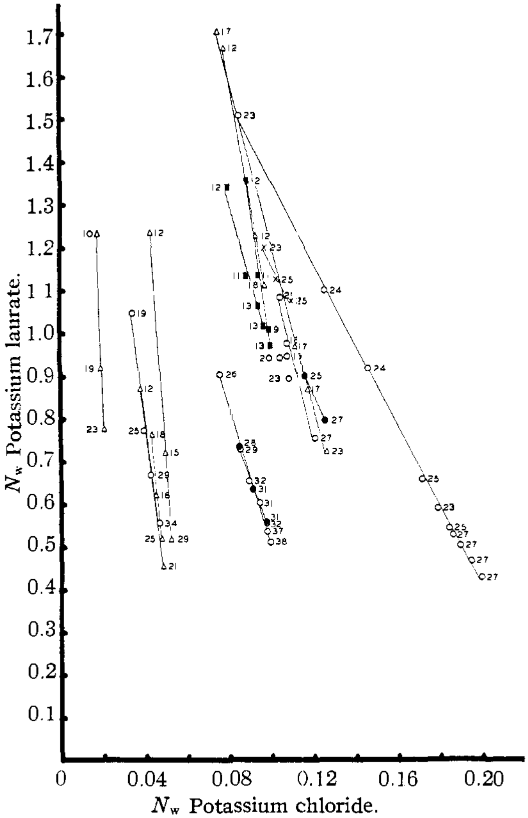

Fig. 1a.—Enlargement of portion of field in Fig. 1 for dilute potassium chloride: ■, procedure B + 0.5 N_w urea; △, procedure C; ○, procedure D; ●, procedure D + 0.5 N_w urea; ×, data of M. C. Field.

On the right of Fig. 1 the results are independent of whether the pressure is 25 or 50 atmospheres. In Fig. 1a, where the total ionic concentrations are much less, the effect of pressure is very great, as may be seen by comparing the results of procedure D with those of B and C.

We must conclude that soap in solution is much more heavily hydrated than ordinary grained out soap.

It is quite clear from the results obtained in Figs. 1a or 2 that in more dilute solutions the Donnan equilibrium or ionic atmosphere occupies most of the volume of the solution and the ionic atmospheres may even be mutually compressed.[8] McBain and McClatchie have pointed out that for ordinary colloids where the ionic concentrations are so much less, this necessitates a revision of existing P_H and C_H values as well as all other ionic concentrations in ordinary colloidal sols.

Part II. Other Ultrafiltration Experiments

Urea is but little sorbed by curd fibers of sodium palmitate in the presence of saturated solution of sodium chloride. This is shown by two experiments with 0.5 N_w urea and sodium palmitate which was originally 1.0 N_w sodium palmitate but through filtration increased to 2.9 and 2.6 N_w, respectively. Hydrations obtained (by Y. K.) were 1.78 and 2.05, mean 1.91, as compared with the value 2.0 to 2.1 already established by several different methods.[9]

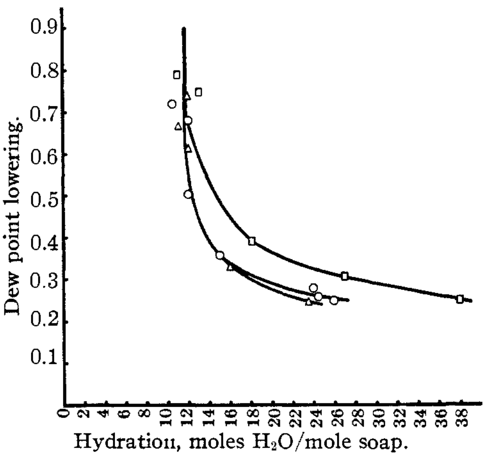

Fig. 2.—Apparent hydration values for potassium laurate at the different total ionic concentrations corresponding to definite dew point lowerings*: □, 0.5 N_w potassium laurate; ○, 1.0 N_w; △, 1.4 N_w.

* Dew point lowering at 18° taken as 0.22° for 1.0 N_w potassium laurate; and for additions of 0.5, 0.6, 0.7, and 1.0 N_w potassium chloride, 0.44°, 0.50°, 0.57°, and 0.77°, respectively; others by interpolation.

Evidently saturated salt largely displaces urea from the surface of the curd fibers.

McBain and Jenkins showed that the apparent hydration of sodium oleate was less than that of potassium laurate, namely, 9 H_2O, using 0.1 N_w sodium chloride with 0.25 N_w sodium oleate. Similarly, here potassium oleate gave lower results than potassium laurate. In both cases we believe that this improbable conclusion is merely caused by greater sorption of the salt by oleate than by laurate. It has been shown in previous communications that curd fibers of soap sorb all electrolytes to a measurable extent except when prevented by the competition of another substance in large excess. The percentage effect is, of course, least in concentrated solutions of electrolyte.

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(8) It is useful to carry in mind that decinormal solutions of electrolytes contain so many ions per cubic centimeter that their average distance apart cannot exceed 20 Å.

(9) J. W. McBain and M. Taylor, *J. Chem. Soc.*, **115**, 1300 (1919); J. W. McBain and H. E. Martin, *ibid.*, **119**, 1369 (1921); J. W. McBain and C. S. Salmon, *ibid.*, **119**, 1374 (1921); M. E. Laing, *ibid.* **119**, 1669 (1921).

In the experiment (by Y. K.) in which the original concentrations 0.461 N_w potassium oleate and 1.027 N_w potassium chloride gradually changed to 0.921 and 0.924, respectively, apparent hydrations were found equal to 4.8, 5.9, 6.9 and 7.7 moles of water per equivalent of potassium oleate. In another series with 0.5 N_w potassium oleate and 0.1 N_w potassium chloride changing to 2.1 N_w potassium oleate and 0.05 N_w potassium chloride the apparent hydrations, including Donnan effect, were 17, 25, 12 and 15. Similar irregular results (11, 18, 23, 20) had been obtained (by H. P. L.), using an original solution of 1.1 N_w potassium oleate and 0.05 N_w potassium chloride. However, it must be remembered that all the latter solutions are anisotropic plastic liquids in which stirring and true sampling are both impossible.

Turning to pure soap solutions, two experiments (by H. P. L.) were attempted at 90°. In the first an unusually dense old specimen of No. 600 cellophane yielded filtrates approximately 0.04 N_w from a solution of 0.5 N_w sodium palmitate, showing that the membrane was approaching a condition of semi-permeability even for soap molecules. Fresh No. 400 cellophane at 90° allowed a filtrate of 0.24 N_w sodium palmitate to come through from 0.6 N_w sodium palmitate. This is just the concentration of simple crystalloidal soap which is given in the constitution diagram of McBain, Taylor and Laing[10] as deduced from conductivity and dew point lowering and likewise supported by McBain and Salmon's measurements for the sodium amalgam electrode at 90°.

Steeping in water at 90° appeared to make the membranes denser. For example, a 1.0 N_w potassium laurate, filtered through No. 2400 (laminated) cellophane at room temperature, allowed about 0.09 N_w to come through (this being somewhat more crystalloid than is shown in the constitution diagram); this upon heating to 90° soon dropped to a value of 0.03 N_w potassium laurate, the filtrate finally being almost free from soap. Again, M. C. Field (1926) found that No. 1200 cellophane membrane at 90° began to hold back even some potassium chloride in a mixture of the latter with potassium laurate, concentrations of both increasing above the ultrafilter.

Summary

It is shown that hydration in colloidal sols may be measured by the method of ultrafiltration, yielding a concentration of indifferent reference substance which is greater in the filtrate than in the original or residue.

If the reference substance is a dilute electrolyte, Donnan effect is superimposed in the same direction and the concentration likewise depends upon the pressure used in ultrafiltration through a given membrane.

However, in sufficiently high ionic concentrations these other effects disappear. For potassium laurate the hydration is found to be 12 moles of water per equivalent of soap in the solution.

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(10) J. W. McBain, M. Taylor and M. E. Laing, *J. Chem. Soc.*, **121**, 629 (1922).

The hydration of curd fibers of sodium palmitate, salted out by saturated sodium chloride, was again confirmed, using urea, as two moles of water to one equivalent of soap.

Thick cellophane membranes kept at 90° tend to become impermeable even toward ordinary ions.

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The Surface Tension of Mercury and of Water in Contact with Saturated Vapors of Organic Liquids[1]

BY F. E. BARTELL, LEE O. CASE AND HENRY BROWN

Introduction

It was predicted by Gibbs[1a] that if the surface tension of mercury were measured in contact with a saturated vapor of another liquid, as with water vapor, the value of this surface tension would be equal to the interfacial tension of mercury against liquid water (σ_{12}) plus the surface tension of liquid water in contact with its own vapor (σ_{23}). If σ_{13} be taken to represent the value of the surface tension of mercury against the saturated vapor of the other liquid, then

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \tag{1}$$

This relation obtains because a film of liquid is adsorbed or is condensed on the mercury from the saturated vapor. Gibbs believed that at saturation vapor pressures the condensed film would be of such thickness that its interior would have the properties of a phase in mass.

The thermodynamic condition that governs the application of equation (1) is that the surface tension of the mercury in the presence of its own vapor, σ_1,[2] must be greater than the sum of σ_{12} and σ_{23}.

Previous Results for Films on Mercury.—The experimental data previously used by Iredale[3] to test equation (1) for mercury surfaces indicate that this equation holds for saturated water vapor in contact with mercury but not for other saturated vapors against mercury. The measured surface tension value of mercury in the presence of the saturated vapor was in every case (except for water) greater than the sum of the interfacial

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[1] The material presented in this paper is from a portion of a dissertation submitted by H. Brown to the Graduate School of the University of Michigan, in partial fulfilment for the Degree of Doctor of Philosophy, 1932.

[1a] Gibbs, "Collected Works of J. Willard Gibbs," Longmans, Green and Co., New York, 1928 Vol. I, p. 235, *cf.* p. 258.

[2] In the designation of surface and interfacial tensions, the use of the symbol σ with two numbers for a subscript represents the surface or interfacial tension between two phases mutually saturated with each other and in equilibrium in contact with each other. In case only one number appears as a subscript, the symbol then stands for the surface tension of a pure liquid in contact with its own vapor and air.

[3] Iredale, *Phil. Mag.*, [6] **49**, 603 (1925).