XXVIII. THE VISCOSITY AND HYDRATATION OF COLLOIDAL SOLUTIONS.

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In a paper published in this *Journal* Miss Chick [1914] has calculated the hydration factors for a number of proteins from the author's formula for the viscosity of emulsoid sols. By means of this formula the volume of the disperse phase, i.e. the hydrated protein, is obtained from the relative viscosity, and the hydration or association factor is then found by comparing this volume with the weight of dissolved substance. Miss Chick's results are: (1) that for each protein the association factor is constant over a considerable range of concentration, and (2) that its value lies between 1.57 for crystallised egg albumin and 8.63 for sodium caseinogenate, these figures being the numbers of grams of water associated with each gram of protein in solution.

In a recent paper under the above title Arrhenius [1916] criticises these results and considers them open to grave doubt, chiefly on the ground that the factors are very much larger than those determined (by other methods) in the case of the most highly hydrated salts in solution, such as $\text{MgCl}_2 + 12\text{H}_2\text{O}$ (equivalent to about 2.3 g. of water per g. of salt), which hydrate is known only at -16.8° , while the viscosity figures for proteins were obtained at a temperature of 25° .

Arrhenius then applies to the viscosity figures treated by Miss Chick his well-known formula:

$$\log \eta = \theta C, \dots\dots\dots(1)$$

in which C however now means the molecular concentration, while θ is a constant and η the relative viscosity. For substances like proteins, whose molecules are extremely large compared with those of water, he considers that C is expressed with sufficient accuracy by the equation

$$C = \frac{100p}{100 - (n + 1)p}, \dots\dots\dots(2)$$

in which p is the number of g. of solute in 100 g. of solution, and n the hydration factor, i.e. the number of g. of solvent associated with each g. of solute, and therefore withdrawn from the free solvent.

The complete expression for the logarithm of the viscosity of a solution, in which the molecular weight of the solute is high compared with that of the solvent, is accordingly:

$$\log \eta = \theta \frac{100p}{100 - (n+1)p}, \quad \dots\dots\dots(3)$$

and as this expression contains only two constants, θ and n , it is obvious that these can be calculated from two sets of experimental data. Solving equation (3) for $(n+1)$ we obtain:

$$n+1 = \frac{100}{p} - \frac{100\theta}{\log \eta}, \quad \dots\dots\dots(4)$$

and if we introduce two pairs of coordinated values p_1, η_1 , and p_2, η_2 :

$$n+1 = \frac{100}{p_1} - \frac{100\theta}{\log \eta_1} = \frac{100}{p_2} - \frac{100\theta}{\log \eta_2}. \quad \dots\dots\dots(5)$$

By elimination we find the value of θ :

$$\theta = \left(\frac{1}{p_1} - \frac{1}{p_2} \right) : \left(\frac{1}{\log \eta_1} - \frac{1}{\log \eta_2} \right), \quad \dots\dots\dots(6)$$

and by introducing the value thus found into either of the equations (5) the value of n . It is not very clear why Arrhenius suggests that n should be found by trial, as the strict procedure is certainly more expeditious as well as more elegant.

The formula (3), when applied to Miss Chick's viscosity figures, fits with remarkable accuracy, and the values of θ and n are constants over the whole range with slight exceptions. The agreement is least satisfactory for sodium caseinogenate, which shows the highest viscosity for a given weight of protein, and Arrhenius ascribes the latter to dissociation.

In order to get away from the analogy with hydrated salts—the cogency of which the author must confess himself unable to admit—and from dissociation, it seems highly desirable to test Arrhenius's formula by applying it to sols in organic solvents, such as india rubber and nitrocellulose sols. Although dissociation is certainly absent in both cases, these colloids produce, for the same weight of substance, rises in viscosity which are enormous compared even with sodium caseinogenate. They may also be expected to be highly solvated or associated, as the criterion from which Arrhenius anticipates a high degree of hydration in the protein sols applies even more emphatically: viz. they swell enormously in their respective solvents.

The data to be used below are taken, in the case of rubber, from a paper by Schidrowitz and Goldsbrough [1909], and in that of nitrocellulose from a very complete investigation by Frank Baker [1913]. The first column shows the concentration as stated by the authors, viz. g. per 100 cc. of solution. As Arrhenius's formula contains the concentration by weight, the second column shows p , the *weight* of substance in 100 g. of solution. These values are exact for the nitrocellulose sols, as the densities of the sols are given by the author; for the rubber sols the densities are not available and the value of p is therefore approximate only, but in view of the low concentrations the possible error is certainly slight.

From these values of p and the observed viscosities (stated in all cases as relative viscosities, that of the solvent being taken as unity) the constants θ and n have been calculated by solving the equations (5) and (6). This involves the assumption that the method used for calculating the molecular concentration of proteins in water is equally applicable to rubber in benzene, and nitrocellulose in acetone or ether-alcohol—an assumption which is no doubt sufficiently correct, although the molecules of solute are smaller and those of solvent larger, than the molecules of protein and water respectively.

As a first example we may take a typical rubber sol (hard Para in benzene):

	g. in 100 cc.	p	η	$\log \eta$
(1)	0.25	0.281	2.5	0.39794
(2)	0.50	0.562	6.8	0.83251
(3)	1.00	1.124	32.3	1.50920

From these three sets of values we can form three pairs of equations and can thus calculate θ and n in three different ways. We thus obtain the following values:

From (1) and (2)	$\theta = 1.354$	$n = 14.4,$
From (1) and (3)	$\theta = 1.441$	$n = -7.5,$
From (2) and (3)	$\theta = 1.652$	$n = -21.5.$

These values are so divergent that the formula cannot be said to apply at all. More striking even is the negative sign of n when the higher viscosities are taken into account. The mere attempt to define a *negative solvation factor* is sufficient to demonstrate the physical impossibility of these results.

For solutions whose viscosities, for the same amount of solute, are still higher than in the preceding example, the factor n becomes negative for the whole range, while at the same time the general agreement is much improved.

As example we may take nitrocellulose in acetone (the first three sets of values in F. Baker's Table II):

	g. per 100 cc.	p	η	$\log \eta$
(1)	0.2212	0.2802	3.87	0.58912
(2)	0.5261	0.6647	18.73	1.27254
(3)	0.7922	0.9977	55.87	1.74720

If we again calculate the three constants from all three pairs of equations we find:

From (1) and (2)	$\theta = 2.266$	$n = -28.7,$
From (1) and (3)	$\theta = 2.282$	$n = -31.4,$
From (2) and (3)	$\theta = 2.350$	$n = -35.2.$

Here the constancy of θ and n , although far from perfect, is not unreasonably bad, especially if we consider that the assumption of a constant solvation factor is not based on any known facts and is not inherently probable. The factor, however, is always negative and is thus devoid of any physical meaning. Nevertheless the values calculated from (2) and (3) may be used for calculating the next higher viscosity with reasonable accuracy.

If we take a further example showing still higher viscosity the results become much more erratic. The data are those for nitrocellulose in ether-alcohol (the first three values in Baker's Table XX).

	g. per 100 cc.	p	η	$\log \eta$
(1)	0.3284	0.4342	8.49	0.92880
(2)	0.5977	0.7882	26.33	1.42049
(3)	0.9230	1.214	114.50	2.05866

The constants obtained are:

From (1) and (2)	$\theta = 2.75$	$n = -66.6,$
From (1) and (3)	$\theta = 2.50$	$n = -39.1,$
From (2) and (3)	$\theta = 2.08$	$n = -19.7.$

Any discussion of these results is of course impossible, but the negative solvation factors are striking.

A fourth example, in which the rise in viscosity is much more moderate, although still higher than with any protein, may be of interest. The data again refer to india rubber in benzene:

	g. in 100 cc.	p	η	$\log \eta$
(1)	0.25	0.281	1.6	0.20412
(2)	0.50	0.562	2.9	0.46240
(3)	1.00	1.124	16.6	1.22011

The two constants are:

From (1) and (2)	$\theta = 0.644$	$n = 37.6,$
From (1) and (3)	$\theta = 0.654$	$n = 34.4,$
From (2) and (3)	$\theta = 0.666$	$n = 33.6.$

In this case the constancy of both factors is fairly satisfactory and the value of n is positive throughout. Even if it were possible, which of course it is not, to disregard the negative factors found in the previous examples, the question would still have to be answered why a solvation factor of 34 should be possible with one colloid, whereas a factor of 8.6 should be entirely incredible in another case.

Since the formula given by Arrhenius is apparently purely empirical and is not, as far as the author is aware, deduced from any physical considerations, a discussion is possible (and called for) only on purely mathematical grounds. The logarithm of the viscosity is in the formula equated with a product, one factor of which is a constant, θ , while the other, considered simply analytically, is a function of p and of a variable parameter, n . As the $\log \eta$ curves are very simple curves of a type strongly resembling in general habitus the curves of the family

$$y = \frac{100p}{100 - (n + 1)p}$$

where n , as already explained, is a variable parameter, there is at least a strong probability that by a suitable choice of n a curve can be found which will coincide with a given $\log \eta$ curve over a considerable length, within the limits of experimental error, provided both are drawn to suitable scales. The latter condition of course finds its analytical expression in the proportionality factor θ . Although the factor n is introduced with a physical meaning, we have seen that negative factors, which have no possible physical meaning, result from the application of the formula to many cases, and such negative factors occasionally achieve the desired result, i.e. more or less close interpolation or approximation to experimental results.

The formula therefore seems to be a purely analytical device for representing a viscosity, or rather $\log \eta$, curve, the approximation being achieved by a factor n which in some cases is devoid of any physical interpretation. It is therefore certainly an unwarranted assumption that values of n , which are physically possible and happen to agree with a priori assumptions such as the very dubious parallel between hydrated salts and colloids which "swell strongly in water," necessarily have the physical

meaning ascribed to them, and that the higher values calculated with the aid of the author's formula are therefore necessarily incorrect.

It is only fair to add, in conclusion, that a difficulty also arises when an attempt is made to apply the author's viscosity formula to the examples treated above, or to highly emulsoid sols generally, a difficulty however which does not amount to a physical impossibility or even improbability. If the association factor is calculated say for the 0.5 % concentration of the first example ($\eta = 6.8$) we find that about 62 % of the total volume of solvent is already associated with the solute. A 1 % sol would therefore be impossible, if the association factor were constant. There is certainly nothing inherently improbable about decreasing association with increasing concentration, and it is not difficult—as the author has found—to construct empirical functions connecting concentration and solvation. As this is again a purely mathematical exercise affording no insight into the mechanism of association, the matter is more profitably left open until a rational solution of the whole problem, which is by no means hopeless, can be accomplished.

SUMMARY.

By applying his logarithmic formula to the viscosities of protein sols as determined by Miss Chick, Arrhenius obtains hydration factors ranging from 0.7 to 2.2. Since these figures are of the same order of magnitude as those found for hydrates of salts in solution, Arrhenius considers that they represent the actual conditions and that for the same reason the much higher factors calculated by applying Hatschek's formula are impossible. In the present paper Arrhenius's formula is applied to sols in organic solvents and it is shown that in several instances negative association factors result, which of course have no physical meaning. The conclusion is therefore drawn that Arrhenius's formula is a purely analytical interpolation formula and that the association factors calculated from it need not, even when they happen to be positive and therefore physically possible, have the physical meaning which he ascribes to them.

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