XIII. THE VISCOSITY OF SOLUTIONS.

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1. *Theory of Einstein.* In recent years a great number of investigations, of theoretical or of experimental scope, has been carried out regarding the viscosity of solutions by different scientists, so that it seems possible to arrive at more definite ideas on this important question.

The chief theoretical investigations in this line are due to A. Einstein [1906, 1911] and von Smoluchowski [1916]. Einstein deduced in 1906 and 1911 the following formula :

$$\eta = \eta_0 (1 + 2.5 \phi) \dots\dots\dots(1)$$

in which η is the viscosity of a solution containing the volume fraction ϕ of a dissolved substance in unit volume of a solvent with the viscosity η_0 at the same temperature. This formula is only valid for very dilute solutions for which $\sqrt[3]{\phi}$ may be neglected in comparison with 1. Further it is supposed that the dissolved particles are of spherical form and of great magnitude compared with the molecules of the solvent. The formula is deduced for the case of suspensions—*e.g.* so-called colloidal solutions of sulphur or of gamboge—but as there is a continuous transition from suspensions to genuine solutions, Einstein did not hesitate to apply his formula to solutions of cane sugar in water although the sugar molecules are probably not of spherical form.

ERRATA

- page 115 line 16 from bottom, *for* Equér *read* Egnér.
- 118 last line, *for* solvent *read* solute.
- 120 line 7 from top, *for* disaggregation *read* aggregation.
- 128 line 9 from top, *for* 5·00 *read* 500.
- 130 line 9 from top, *for* great *read* greater.
- 133 line 11 from top, *for* Equér *read* Egnér.

2. *Experiments of Bancelin.* The said formula has been examined experimentally on suspensions of gamboge by Bancelin [1911, 1, 2] in the laboratory of Perrin. He found a good agreement with the theory, as the coefficient of ϕ was found equal to 2.7 (Bancelin gives 2.9, which is probably a misprint) whereas the theory demands 2.5. Still better is the agreement if we use the formula (2) below, as is seen from the following table:

% (volume)		Viscosity . 10^5		
measured	corrected	obs.	calc. 1	calc. 2
0	0	1016	1016	1016
0.09	0.09	1018	1018	1018
0.24	0.241	1023	1022	1022
0.33	0.331	1025	1025	1024
0.53	0.533	1029	1030	1029
0.66	0.665	1033	1033	1033
1.05	1.061	1044	1044	1043
2.11	2.155	1074	1074	1072

The measured percentage is given by Bancelin, the corrected one gives the volume of the gamboge granules, when the volume of the water is put equal to 100. This corrected value is, as easily seen, proportional to the molecular percentage of the gamboge. In the logarithmic formula (2) the concentration is determined in this manner (cf. § 5). The calculated values below calc. 1 are found if we suppose the constant θ in formula (2) to be 0.0111, corresponding to a value 2.56 of the constant in formula (1), whereas the figures below calc. 2 correspond to $\theta = 0.01086$ or 2.5 in Einstein's formula. 2.56 corresponds to an empirical determination of the said constant. The agreement may be regarded as perfect in both cases.

Bancelin has made experiments with granules of different diameters, namely 0.3, 1.2 or 4μ , and he always found the same value of the viscosity for the same percentage, which is also demanded by the theory of Einstein. Further this theory demands that the coefficient 2.5 shall be independent of the viscosity, η_0 , of the solvent. Bancelin determined the viscosity of suspensions of gamboge in an aqueous solution of glycerol with a viscosity fifteen times that of water. His results were wholly concordant with the theoretical predictions. Experiments with methylene blue gave consistent results.

3. *Experiments of Mifka.* Some experiments of Mifka [1911] on suspensions of silver, gold and copper, prepared in water according to the method of Bredig, indicate that these suspensions possess the same viscosity as the solvent at the same temperature. The concentrations of these solutions were only 4.25, 3.48, 2.79 resp. of the thousandth part of 1 % (volume), so

that their viscosities ought not to differ more than about 0.01 % from that of the solvent according to Einstein's theory. This difference falls wholly within the errors of observation (here about 0.05 %), so that it may be maintained that these experiments are in accordance with Einstein's theory. The conclusion, which is sometimes given, that metallic suspensions in general possess the same viscosity as the solvent, would of course not be warranted, if it were possible to prepare much stronger solutions than those investigated by Mifka.

4. *Woudstra's determinations.* Some experiments of Woudstra [1908] on suspensions of silver in water, containing *in maximo* 0.49 g. per litre, which corresponds to 0.00464 % by volume, are said to have given viscosities that *in maximo* exceeded the viscosity of water by 4.57 %, whereas the theory of Einstein demands only 0.012 %. Woudstra's experiments were carried out by means of colloidal silver prepared according to Muthmann's method and dialysed during three weeks. His values are the following. c is the concentration in mg. silver per litre, ϕ the corresponding value in volume %—the specific gravity of silver taken as 10.53— η the viscosity, $\eta_{\text{calc.}}$ found from formula (2).

c	$\phi \cdot 10^5$	η	$\eta_{\text{calc.}}$
490	464	1.0457	1.0072
385	365	1.0098	1.0056
337	319	1.0057	1.0049
289	273	1.0045	1.0041
190	180	1.0021	1.0028
93	88	1.0013	1.0014

The values are calculated on the supposition that the relative viscosity of a solution containing 0.01 vol. % is 1.0154, whereas Einstein's formula gives 1.00025, *i.e.* a sixty times smaller value of the difference from η_0 (put = 1). We shall find later, that such great deviations occur—they are probably due to a highly flocculated state of the suspended particles, similar to that of aluminium hydroxide, precipitated from a dissolved aluminium salt by means of an alkali. The most concentrated solutions give much higher viscosities than those calculated. This discrepancy vanishes with time. Thus the viscosity of the most concentrated solution was diminished after standing thirty-seven days to 1.0077, or nearly the calculated value. An addition of salts also diminishes the viscosity of the solution.

5. *The logarithmic formula.* We have seen above that Bancelin found that the viscosity of a gamboge suspension in glycerol may be written $\eta_1\eta_2$ if η_1 is the viscosity of the glycerol solution without gamboge and if η_2 is the

viscosity of a suspension of the same volume percentage of gamboge in pure water, when the viscosity of water at the same temperature is put equal to unity. This result, which is in accord with Einstein's theory, naturally suggests the idea that if two aqueous solutions of two substances possess the same relative viscosity η , then the viscosity of an aqueous solution containing both substances in the same volume ought to be η^2 . Now the two substances may be identical. If we then carry our deductions further we find that the viscosity η of an aqueous solution of the concentration c ought to be subject to the condition

$$\log \eta = \theta c \dots\dots\dots(2)$$

where θ is a constant and the viscosity of water at the same temperature is put equal to unity. This is the logarithmic formula found by myself empirically in 1887 [Arrhenius, 1887]. For dilute solutions, which I investigated at that time, it is indifferent whether the concentration is determined in per cent. of mass, per cent. of volume or molecular per cent.—in reality I used volume per cent. But when greater concentrations are examined, it is, as Kendall [1913] showed, better to express c in molecular percentage. It is remarkable that a similar assertion is true regarding other properties of solutions, *e.g.* osmotic pressure. In fact Kendall proved that the logarithmic formula is very nearly followed by mixtures in all proportions of liquids, which do not chemically react upon each other, if the concentration is expressed in molecular percentage. Equér [1917] has recently made a series of determinations on mixtures of two fluids and corroborated the conclusion of Kendall.

This statement is of great importance for controlling Einstein's formula (1). It is only valid for extremely dilute solutions and, as Smoluchowski states "it would demand an enormous work of calculation to carry the approximation further according to the method of Einstein." I have therefore used the logarithmic formula for calculating the experiments of Bancelin and in this manner I found the value 2.56 for the coefficient in formula (1) instead of the value 2.7 calculated by Bancelin, whereas Einstein's theory demands 2.5. In this case the size of the "molecules" of the gamboge is so enormous that their number in a suspension of 2.11 vol. % may be neglected in comparison with the number of the molecules of the solvent water. The molecular percentage may therefore without any sensible error be assumed to be proportional to the quantity of gamboge divided by the quantity of water in the solution examined. The same is true for all suspensions or emulsions

or solutions of albuminous substances or, in general, for what are called colloidal solutions.

6. *Suspensions of sulphur, examined by Odén* [1913]. In general it has not been possible to prepare suspensions of higher concentration, except for sulphur, and it is of great value for us that Odén has determined the viscosities of such suspensions, which contained up to 50 g. sulphur in 100 cc. I have shown [1916] that these suspensions are subject to the logarithmic formula (2) within the limits of the errors of observation.

The formula of Einstein is not applicable to the calculation of these concentrated solutions. Therefore Smoluchowski tried to construct an empirical formula with two new arbitrary constants. This formula has no greater interest; it may suffice to give, under $\eta_{\text{Smo.}}$, the tabulated values calculated by means of this formula in order to represent the observed values, $\eta_{\text{obs.}}$, for submicroscopical suspensions of sulphur (diameter of particles about 0.1μ). These observed values are the mean values for three temperatures, 5° , 20° and 40° . Below $\eta_{\text{Ein.}}$ are written figures calculated by means of formula (1) where the specific gravity of the sulphur is taken equal to 1.95; below $\eta_{\text{Arrh.}}$ figures founded on formula (2). c gives the weight (grams) of sulphur in 100 cc. of the suspension, c_1 the corresponding weight in 100 cc. of water. c_1 is proportional to the molecular percentage of the sulphur. k is the calculated constant in formula (1), which ought to be 2.5 in extreme attenuation. The viscosity of water is put equal to 1.

c	c_1	100 ϕ	k	$\eta_{\text{obs.}}$	$\eta_{\text{Ein.}}$	$\eta_{\text{Smo.}}$	$\eta_{\text{Arrh.}}$
5	5.13	2.63	3.84	1.101	1.066	1.079	1.103
12.51	13.38	6.58	4.35	1.286	1.164	1.238	1.290
25.02	28.76	13.16	5.38	1.708	1.329	1.656	1.730
50.03	67.72	26.33	10.25	3.700	1.657	4.000	3.635

The deviation of k from Einstein's value 2.5 as well as a comparison of $\eta_{\text{Ein.}}$ with $\eta_{\text{obs.}}$ indicate how far the figures of Odén differ from the formula (1). Smoluchowski's formula gives in reality the limiting value 2.5, but its agreement with the observed values is not very satisfactory, the mean deviation reaching 4.2 %. On the other hand the figures in the last column, calculated by means of formula (2) with only one arbitrary constant give an agreement within the errors of observation, the mean difference being only 0.9 %. We may conclude from this that the limiting value of k for $c = 0$ is 3.72, *i.e.* 1.5 times greater than Einstein's theory demands.

7. *Influence of hydration.* In the calculation of Odén's figures by means of formula (2) it has been supposed that no water is chemically bound to the

spherules of sulphur; in reality we have no indication at all that sulphur enters into compounds with water, all chemical evidence is against such a supposition. Therefore the good concordance between formula (2) and the experimental results is of a very high value in this case. This concordance is still better for the observations regarding amicroscopical sulphur (diameter of the particles about 0.01μ) in which case the mean difference is only 0.5 % for seven observations in the same concentration interval as above, when η changes in the proportion 1 to 5.

In other cases there is high probability that a certain quantity of water becomes bound to the dissolved substance, *e.g.* if we investigate albuminous substances in aqueous solution. In such cases the molecular percentage has a higher value than if no water were bound, and the increase of this quantity is proportionally greater the higher the concentrations treated, if we suppose that each gram of the protein binds the same quantity of water at all concentrations. This hypothesis is true for very dilute solutions, *i.e.* solutions which contain very few gram-molecules per litre. As the proteins examined have not been more concentrated than about 30 % and their molecular weight is of the order of magnitude of about 10,000, the highest concentrations have not been more than about 0.03 normal. We may therefore suppose that their tendency to bind water is nearly constant and make our calculations on that ground.

In such cases we have to determine two arbitrary constants in the formula (2) namely not only the constant θ but also the quantity n of water bound to one gram of protein substance for the calculation of the molecular concentration. I have carried out some such calculations for some proteins, examined by Miss H. Chick [Chick 1914; Chick and Lubrzynska 1914], and furthermore determined the specific gravity of these substances from that of their aqueous solutions and calculated the value of k in formula (1). The results are given in the following table:

Substance	Sp. gravity	θ	n	k
Egg albumin	1.36	0.0184	0.7	2.95
Serum albumin	1.375	0.0207	1.5	2.14
Euglobulin	1.372	0.0625	2.2	4.91
Pseudoglobulin	1.402	0.0402	1.2	4.83
Sodium caseinogenate	1.414	0.1127	1.0	15.1

Hatschek, who [1916, 1] has tried to discredit the value of formula (2) in this journal, has still conceded that it, "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."

8. *Influence of temperature on the value of $\theta = d \log \eta / dc$ for dilute solutions.* In order to show how associated substances, which form aggregates together with the solvent, behave when the temperature changes, I have calculated some figures of Noack [1886] regarding the relative viscosity of two aqueous solutions of ethyl alcohol containing 3.38 mol. % (= 8.21 weight %) of alcohol or 27.17 mol. % (= 12.55 weight %) of water and of two solutions of acetic acid containing 4.96 mol. % (= 14.82 weight %) of CH_3COOH and 4.77 mol. % (= 1.78 weight %) of water. As units of η for the strong solutions are taken the values for the most concentrated solutions, measured by Noack, viz. solutions containing 99.28 mol. % (= 99.72 weight %) of alcohol and 99.34 mol. % (= 99.8 weight %) of acetic acid. For the weak solutions the unit viscosity is that of water at the temperature indicated in the table.

Temp. ° C.	Ethyl alcohol		Acetic acid	
	3.38 mol. %	27.17 mol. %	4.96 mol. %	99.28 mol. %
0	1.582	1.632	1.374	1.380
10	1.489	1.506	1.350	1.213
20	1.410	1.411	1.327	1.138
30	1.343	1.344	1.304	1.108
40	1.284	1.288	1.279	1.106
50	1.234	1.248	1.262	1.120
60	1.191	1.216	1.234	1.146

For the alcoholic solutions the relative viscosities decrease with increasing temperature. This decrease is more pronounced at lower temperatures than at higher ones. In the interval 0° – 60° the total decrease of θ is about in the proportion 2.5 : 1. The decrease is much less for the acetic acid solution of 4.96 mol. % so that θ sinks only in the proportion of about 1.5 : 1 and for the solution of 4.77 mol. % water in acetic acid we find a minimum of η and thereafter, between 40° and 60° an increase with temperature, which seems to indicate that here no sensible thermal dissociation takes place. The viscosity measurements show a very pronounced maximum at a concentration of 77 weight % at all temperatures between 0° and 60° . It is probable that this maximum belongs to a definite compound, namely the monohydrate of acetic acid, $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$, which corresponds to 76.93 weight %. The acetic acid of 95.23 mol. % (= 98.52 weight %) may therefore be regarded as a solution of this monohydrate in acetic acid. At lower temperatures some loose aggregates of the solvent (acetic acid) exist, which cause the diminution of θ with increasing temperature as in the other three cases treated above, but at higher temperatures these loose aggregates have nearly wholly disappeared, so that the solvent has a constant composition.

The alcoholic solutions behave in a quite different manner. The maximum viscosity belongs at 0° to a solution of 36 weight % (= 18.05 mol. %) and at 60° to a solution of 51 weight % (= 28.94 mol. %). At intermediate temperatures there is a continuous change between these two values—perhaps at higher temperatures the composition of the solution with a maximum viscosity approaches to 33.3 mol. %, corresponding to the hydrate $C_2H_5OH + 2H_2O$.

Most dilute aqueous solutions are characterised by a positive $d \log \eta / dc$ decreasing with increasing temperature. The same behaviour may be expected for dilute solutions in alcohols.

For mixtures of non-associated liquids, for instance ethyl ether (viscosity 0.00230 at 25°) and carbon disulphide (viscosity 0.00358 at 25°), $\log \eta$ is, in general, a linear function of the molecular concentration, and therefore a constant value is found for $d \log \eta / dc$ in the whole range from $c = 0$ to $c = 100$. If c represents the concentration of the more viscous component θ is positive; but if c represents that of the less viscous component θ acquires a negative value. Normally the absolute value of θ for such solutions decreases with increasing temperature.

9. *Associating substances.* Very different and much more complicated results are obtained if we investigate substances, which become dissociated through dilution, which often present maxima of viscosity at certain concentrations. A typical substance of this kind is ethyl alcohol, which consists of strongly associated molecules in a concentrated state, but, as the freezing point determinations indicate, of simple molecules, probably associated to a certain quantity of water, in very dilute aqueous solutions. I therefore give in the following table some determinations of Horiba [1910, 1912] on the viscosity of aqueous solutions of ethyl alcohol at 25° .

c	c_1	η	$\log \eta$	$\log \eta / c_1$	$\log \eta_2 / c_2$
0	0	1	0	(0.0440)	-0.000847
3.65	1.46	1.151	0.0611	0.0418	-0.000240
7.84	3.224	1.339	0.1268	0.0394	0.000435
14.88	6.403	1.708	0.2325	0.0363	0.00158
27.49	12.92	2.344	0.3696	0.0286	0.00327
40.35	20.93	2.617	0.4178	0.0200	0.00423
54.56	31.96	2.552	0.4068	0.01273	0.00473
63.95	40.92	2.375	0.3757	0.00918	0.00493
69.25	46.84	2.233	0.3489	0.00745	0.00497
79.50	60.24	1.924	0.2842	0.00472	0.00502
98.33	95.8	1.276	0.1058	0.001104	0.00502
100	100	1.2153	0.0847	0.000847	(0.00502)

c is the concentration in per cent. of weight, c_1 the molecular percentage

of alcohol, $c_2 = 100 - c_1$ that of water. For the calculation of c_1 the molecular weights 46 for alcohol and 18 for water have been used.

The viscosity decreases when the dissolved molecules form greater aggregates. Therefore the quotient $\log \eta/c_1$ also decreases with increasing concentration c_1 . The binding of water to the alcohol molecules would have an opposite effect, *i.e.* increase the viscosity on *dilution*, but the influence of the disaggregation predominates. If we regard the series from the other side, the water behaves in the same manner. The water molecules associate with each other when the concentration of water, c_2 , increases. For this case we have to choose the viscosity of pure alcohol as unit, *i.e.* to put $\eta_2 = \eta/1.2153$. The figure 1.2153 for pure alcohol is not given by Horiba but is calculated from the data of Thorpe and Rodger [1894]. We also see that $\log \eta_2/c_2$ decreases with increasing c_2 . But this decrease is very small till we reach concentrations $c_2 = 100 - c_1$ of about 60 % (mol.). The two named effects here nearly compensate each other.

In similar cases, when chemical changes occur on dilution we are not entitled to expect $\log \eta/c$ to remain constant, when the concentration changes. Only for solutions so dilute that further dilution does not change their composition may such constancy be expected. For this case we have then to look for the value,

$$(d \log \eta/dc)_0 = \theta \dots\dots\dots(2 a)$$

where the index 0 indicates infinite dilution or concentration zero, as the characteristic constant θ . For alcohol dissolved in water θ is about 0.044 and for water dissolved in alcohol θ is about equal to 0.00502 if we calculate with molecular concentrations.

10. *Solutions of nitrocellulose.* This is precisely the manner in which Baker [1913] treated his data regarding the viscosity of solutions of nitrocellulose in different solvents. He expresses the concentration (c) in grams per 100 cc. of solution. As instance I give below Baker's Table II of solutions in acetone at 25°. I have supposed that the molecular weight of nitrocellulose is so great, that the number of its molecules may be neglected in comparison with that of the acetone molecules, and by means of the specific gravity I have calculated the number of grams of nitrocellulose in 100 g. of acetone. This number is written under c_1 and is very nearly proportional to the molecular percentage of the nitrocellulose. The viscosity of acetone at 25° is given as $\eta = 3.15 \cdot 10^{-3}$ c.g.s. units. This number is taken as unit for η in the table.

c	c_1	η	$\log \eta$	$\log \eta/c_1$
0	0	1	0	(2.2)
0.2212	0.2809	3.88	0.589	2.096
0.5261	0.6778	18.7	1.273	1.878
0.7922	1.008	56	1.748	1.734
1.058	1.349	143	2.160	1.602
1.640	2.094	711	2.852	1.358
2.348	3.008	5050	3.703	1.230
3.865	4.782	53300	4.727	0.949

Just as for alcohol the quotient $\log \eta/c_1$ sinks with increasing concentration and viscosity. But the quotient diminishes only in the proportion 2.2 : 1, when η increases in the proportion 1 : 50,000, whereas for the alcohol solution in water the same decrease of the quotient is followed by an increase in η only in the proportion 1 : 2.6.

Just as with the alcohol, it is generally supposed that nitrocellulose in a concentrated state consists of molecular aggregates, which are in this case very large. On solution in acetone or some other solvent these aggregates are partially broken down and in higher degree the greater the dilution. This explains why $\log \eta/c_1$ decreases with increasing concentration. It is evidently not possible to explain this behaviour by supposing that the nitrocellulose binds a part of the solvent, for in this case, and if the dissolved molecules do not alter their composition with concentration, the quotient $\log \eta/c_1$ would diminish with increasing concentration. Now Hatschek has tried [1916, 1] to calculate the quantity n of the solvent bound to 1 g. of nitrocellulose and found a negative value of about - 30 cc. We quite agree with him that this result "is devoid of any physical meaning." But therefrom to conclude that formula (2) has no physical meaning, as Hatschek does, seems the less cautious as Baker himself in calculating his experiments has on purely empirical grounds been led to the formula (2 *a*), derived from formula (2), which Baker seems not to have known. Baker's investigation may therefore be regarded as giving a very strong confirmation of formula (2), in direct opposition to Hatschek's opinion. Baker has found that the constant θ in formula (2 *a*) decreases with increasing temperature, which is characteristic of solutions of substances which form molecular complexes with the solvent. It is therefore probable that this very general feature also prevails for solutions of nitrocellulose, a conclusion to which Baker was also led from other considerations. This is also indicated through the contraction on dissolving "blasting soluble nitrocellulose" in acetone, when the total volume diminishes by about one-third of the volume of the dissolved substance.

The specific gravity of nitrocellulose is 1.634 according to Escales. If we recalculate the figures given by Baker for $d \log \eta/dc$, where c is expressed in grams per cc. and natural logarithms are used, so that we obtain the corresponding values for volume per cent. and in common logarithms, we get the value of θ in formula (2). In the case tabulated above Baker has the figure 6.22, which reduced in the said manner gives $\theta = 4.42$, *i.e.* 406 times as great as the value demanded by Einstein's theory. The values given by Baker for different solutions fall between 3.22 and 10.45 corresponding to values of θ between 2.29 and 7.43 which are 210 and 684 times as great as the theoretical value calculated by Einstein.

11. *Solutions of rubber.* Hatschek has also used some determinations by Schidrowitz and Goldsbrough [1909, 1, 2] on rubber solutions for calculations by means of which he tries to attack formula (2). Hatschek uses the following figures regarding hard Para rubber in benzene. η is the relative viscosity, that of the solvent being taken as unit. The concentration c is given in grams per 100 cc. and these cannot be recalculated to cc. in 100 cc. benzene, because "for the rubber solutions the densities are not available." The value of $\log \eta/c$ is therefore "approximate only but in view of the low concentrations the possible error is certainly slight."

c	η	$\log \eta$	$\log \eta/c$	$\log \eta_{\text{calc.}}$	$\eta_{\text{calc.}}$
0.25	2.5	0.40	1.60	0.39	2.5
0.50	6.8	0.83	1.66	0.78	6.0
1.00	32.3	1.51	1.51	1.56	36.3

As $\log \eta/c$ is greater in the second case than in the first one, a calculation of n , *i.e.* the quantity of benzene bound to 1 g. of rubber, gives a positive value $n = 14.4$. The inverse is true if we compare the second and the third measurement, they give $n = -21.5$, which is evidently physically impossible. Against this it must be said that the whole calculation is illusory, as the magnitude of the experimental errors is not considered. From the measurements of Kirchhof [1914] quoted below it is very probable that these errors may reach 10 or 12 % and, as the figures given above show, it is possible to reconcile these data of Schidrowitz and Goldsbrough with the demands of formula (2) within the said limit of errors. Hatschek in his calculations uses logarithms with five decimals, which correspond to an accuracy of 0.003 %. It is therefore not to be wondered at that his results become highly "erratic."

Kirchhof has given a great number of measurements on the viscosity at 20° of solutions of indiarubber in different solvents. The concentration ranges between 0.5 and 3 % (g. in 100 cc.) and the viscosities are expressed

in that of the corresponding solvent as unit. His results are given in the following table, corresponding to Kirchhof's Table IV. The data in the table are relative viscosities, observed and calculated by means of formula (2). Kirchhof also gives no specific gravities of his solutions, the calculation is therefore only approximate as in the preceding case.

Solvent	0.5 %	1 %	2 %	3 %
Gasolene, obs. ...	1.9	4.3	—	94.0
calc. ...	2.1	4.47	—	89.1
Benzene, obs. ...	2.1	4.7	23.5	97.3
calc. ...	2.16	4.7	21.9	102.2
Carbon tetrachloride, obs.	2.6	7.5	—	211.3
calc.	2.45	6.03	—	219
Tetrachloroethane, obs. ...	2.5	6.9	—	168
calc....	2.40	5.76	—	191
Pentachloroethane, obs. ...	3.0	8.7	46.0	284.5
calc....	2.6	6.76	45.7	309

The last figure for pentachloroethane is given by Kirchhof as 213.5 but a recalculation of the original observations in Table I and Table IV gives 284.5.

Kirchhof has made experiments with different pressures from 10 to 60 cm. of water. For distilled water he has found the times of flow to be 50.6 seconds if the pressure was 10 cm. and 10.0 seconds if it was 60 cm. As the times of flow are supposed to be strictly proportional to the viscosity they ought to be in inverse proportion to the pressures and the first figure should be 60 sec. if the second figure is right. Still worse is the agreement for gasolene where the time of flow is 32.2 sec., instead of 45.6 sec., and for benzene 28.6 instead of 40.8. The last figures, 45.6 and 40.8 respectively, are six times the time of flow at a pressure of 60 cm. water. This great disagreement, reaching in the three cases 18.6, 38.5 and 44.2 %, depends upon the very short time of flow at the higher pressure (10.0, 7.6 and 6.8 seconds). It is very much to be regretted that Kirchhof has preferred just these high pressures (60 cm. water) for the determinations given in his Table IV, reproduced above. It must therefore be said that the calculated figures agree with the observed ones within the errors of observation, although the difference in one case is nearly 25 % (this may of course be due to an accidental error). The figures of Schidrowitz and Goldsbrough do not contain any data from which the errors of observation might be estimated, but they very much resemble those of Kirchhof. Therefore I find it possible or even probable that, as said above, their figures agree satisfactorily with the demands of the logarithmic formula, especially as they characterise their experiments as "preliminary."

If we now calculate the values of θ in formula (2) for these substances we find:

	θ	A
Hard Para rubber in benzene ...	1.435	132
Indiarubber in gasolene ...	0.618	57
„ „ benzene ...	0.637	59
„ „ carbon tetrachloride ...	0.74	68
„ „ tetrachloroethane ...	0.722	67
„ „ pentachloroethane ...	0.788	73
„ „ trichloroethylene ...	0.584	54

The specific gravity of the rubbers is not given, it is supposed to have been 0.95. Below A is written how many times the θ values exceed the theoretical value deduced from formula (1). This ratio is not as great as for the solutions of nitrocellulose, but still they are amongst the largest observed.

12. *Hatschek's formula for solvation (hydration).* Hatschek [1911, 1912, 1, 2] has given a formula for calculating the quantity of solvent, which is bound to 1 g. of the dissolved substance. The unbound quantity of the solvent is supposed not to exceed 70 % of the total volume. The formula is very simple, it has the form:

$$\eta_0/\eta = 1 - \sqrt[3]{\phi} \dots\dots\dots(3)$$

where η , as usual, is the viscosity of the solution, η_0 that of the solvent and 100ϕ is the volume per cent. of the dissolved substance with its associated solvent. Regarding this formula Smoluchowski says: "It may be an interpolation formula of a certain use in many cases, but it is probably of no general signification, as it is impossible to give it a rational foundation." Till now its practical application has been very scant. Hatschek gives himself [1916, 1] an example when he says: "If the association factor is calculated, say for the 0.5 % concentration of the first example (0.5 % Para rubber in benzene $\eta = 6.8$; cf. § 11) we find that about 62 % of the total volume of solvent is already associated with the solute. A 1 % solution would therefore be impossible if the association factor were constant. Therefore the association factor must be lower for the 1 % solution. There is certainly nothing inherently improbable about decreasing association with increasing concentration." Now we must confess that the formula has a very reduced interest if it does not give a constant association factor. Hatschek has himself emphasised the high value of Miss Chick's calculations, because his formula gives nearly constant results for the association factor (cf. below).

Kirchhof has used formula (3) for calculating his figures and has not observed the difficulties which occur in nearly all the results. A glance at the figures in his Table V gives no good prognosis for the use of formula (3).

The results of Miss Chick, which are regarded by Hatschek as the best proof of his formula, are considered by herself to be very encouraging. I give below a typical example, the calculations regarding the viscosity of pseudoglobulin. c is the concentration in per cent. of weight, η the relative viscosity in regard to the solvent water, B is the volume occupied by 1 g. dissolved substance as hydrate calculated according to formula (3) and said to be nearly constant, when the volume, p , of the hydrated molecules exceeds 50 % of the total volume— p is given in per cent. of the total volume.

c	η	p	B	
3.61	1.40	2.3	0.64	
5.95	1.85	9.7	1.603	
8.32	2.59	23.2	2.716	
10.04	3.43	35.6	3.441	
11.82	4.70	48.8	3.990	
14.06	8.05	68.8	4.585	Mean value 4.50 (4.496)
16.43	13.74	79.7	4.627	
18.45	23.31	87.6	4.499	
20.37	38.79	92.4	4.272	

The formula should be valid if p exceeded about 50 %. Instead of that we find that B , which ought to be constant, increases strongly until p reaches about 80 %. This increase is also very pronounced from $p = 50$ % on, which corresponds to the interpolated value $B = 4.06$, although Miss Chick says that "the value $v/c (= B)$ remained constant when the disperse phase occupied more than one-half the total volume." At $p = 74.06$ is a peculiar point, for if the hydrated molecules are spherical, they are tightly packed there, so that the spheres touch each other on all sides. Above this point formula (3) cannot be valid. We find that at higher values of p this deficiency of the formula is manifested by a decrease of B with increasing concentration. At higher concentrations than $c = 20$ % B would decrease still more rapidly. Through this circumstance the function B passes through a maximum, in the neighbourhood of which its value is approximately constant, and this is then said to be a proof that the formula is correct. I think it would be more justifiable to say that the formula gives unreliable results in the neighbourhood of the said point. According to this it seems clear that Smoluchowski has overestimated the practical value of formula (3). The hyperbolic form of equation (3) makes it unfit to represent the regularly continuous course of η with concentration.

13. *Viscosity of rice-starch suspensions.* From Odén's investigations on colloidal sulphur it is evident that the viscosity of its solutions

increases more rapidly with concentration than according to a linear formula:

$$\eta = \eta_0 (1 + k\phi) \dots\dots\dots (1 a)$$

where k is a constant, which according to Einstein ought to be 2.5. Hatschek [1910, 1911, 1913, 1916, 2] has also deduced a similar formula, in which k has the value 4.5. Regarding this deduction, Smoluchowski makes the remark, that "it is erroneous (unrichtig) and consequently the formula, with $k = 4.5$, lacks any general signification." Hatschek believed that the discrepancy between his formula and Odén's experiments depended upon disturbances due to the use of capillary viscosimeters in the determinations. He therefore made some experiments in collaboration with Miss Edith Humphrey [1916] with a modification of the viscosimeter of Couette. The substance examined was rice-starch in granules of 0.003 mm. diameter, suspended in a mixture of toluene and carbon tetrachloride. The calculated viscosities showed a very great dependence on the velocity of rotation of the instrument. The calculated viscosity of the solvent increased by about 10 %, when this velocity increased in the proportion 1 to 5. With the suspensions the inverse was true, a 6 % suspension diminished its apparent viscosity by about a third for the said increase of velocity. Further a kind of hysteresis took place, so that the viscosity of the solvent seemed to be about 5 % greater if the velocity decreased, than if it increased. Evidently this cannot be right for mixtures of such liquids as toluene and carbon tetrachloride—for coagulating solutions a kind of hysteresis in the opposite direction is often observed; cf. § 14. It must be said that the apparatus used was far inferior to the capillary viscosimeter. Hatschek is of the opinion that the measurements with the highest velocity used, 125° per second, are the most reliable. He has given the results in curves and I have taken the following figures from measurements on the curve signed 125 of his fig. 3.

Volume %		Relative viscosity			Difference %
given	corrected	H.	measured	calculated	
0	0	1	1	1	—
2	2.041	1.3	1.288	1.275	-1.0
4	4.167	1.6	1.647	1.642	-0.3
6	6.384	2.1	2.109	2.137	+1.3

The corrected value of the volume per cent. is expressed in the volume of the solvent taken as 100, in order that it should be proportional to the molecular concentration. Below H. are written the figures estimated by Hatschek. From these figures he concludes that the linear formula (1 a) is valid up to

4 % of volume, but not to 6. It is clear that, if more than one decimal had been used, this assertion would have proved to be false unless errors of observation as great as 3 % are admitted. But under such circumstances the accuracy is quite insufficient for examining the validity of formula (1 a). On the other hand we learn from the last two columns that the logarithmic formula (2) represents the observations with a much higher accuracy, and well within the limits of the errors of observation. It must therefore be said that these experiments confirm the observations of Odén, which also obey the logarithmic formula, instead of showing them to be incorrect. The same cannot of course be said regarding the linear formula (1 a).

θ in formula (2) is in this case 0.0517, *i.e.* 4.76 times greater than the value demanded by Einstein and 2.7 times greater than that expected by Hatschek.

14. *Irregularities.* In working with emulsions with a tendency to coagulate we meet with many difficulties. Such a case has been investigated by Freundlich and Ishizaka [1913]. They prepared a solution of $\text{Al}(\text{OH})_3$ according to the method of Crum and coagulated it by means of $\text{K}_4\text{C}_6\text{N}_6\text{Fe}$. m designates the quantity of $\text{Al}(\text{OH})_3$, expressed in grams of Al_2O_3 per litre, η the relative viscosity at 25°.

m	η	$\log \eta$	$\log \eta/m$	$\eta_{\text{calc.}}$	A
0.187	1.154	0.0622	0.333	1.135	543
0.28	1.231	0.0902	0.322	1.210	526
0.48	1.408	0.1485	0.310	1.386	507
1.12	2.069	0.3158	0.282	2.140	461

As seen from these figures $\log \eta$ is nearly proportional to the concentration m and the calculated values of η agree tolerably well with the observed values. But there is a pronounced tendency of $\log \eta/m$ to decrease with increasing concentration. The coagulating solution looks, to begin with, just like the uncoagulated, but its viscosity increases slowly, and at first after several hours, if the solution is not too concentrated, the flocculation becomes visible. It is supposed that the maximal viscosity is reached before this point, but that is not at all proved and in all cases it is probably rather difficult to determine this maximal viscosity, which is tabulated above under η . Further this viscosity is, for more concentrated solutions, dependent on the mechanical treatment. Thus the maximal viscosity 2.069 of the last solution changes to 1.62 after shaking. Under such circumstances it is clear that deviations between the observed and the calculated values may occur. The maximal viscosity depends also in a high degree on the coagulating power of the salt added as is seen from the following table for different salts of potassium or ammonium. The solution used was always the same with $m = 0.88$.

Coagulating salt	η	Potassium salicylate	1.929
Potassium nitrate	1.423	„ sulphate	1.998
„ thiocyanate	1.423	„ ferrocyanide	2.000
Ammonium chloride	1.481		

From the specific gravity, 3.85, of Al_2O_3 I have calculated the specific gravity of $\text{Al}(\text{OH})_3$ under the assumption that no change of volume takes place on hydration. With the figure 2.21, found in this way, I have calculated how many times, A , the θ -value for 1 vol. % $\text{Al}(\text{OH})_3$, exceeds the theoretical figure 0.01086. As seen, A reaches the value of about 5.00. Probably the floccules correspond to a much higher degree of hydration than that expressed by the formula $\text{Al}(\text{OH})_3$, so that A should be considerably diminished.

Similar remarks may be made regarding some determinations of Bingham and Durham [1911], in which small additions of potassium chloride increased the viscosity of suspensions of infusorial earth, in one case by 60 %, or diminished that of a suspension of clay by about 37 %, whereas one drop of acetic acid increased the viscosity of a graphite suspension by 81 %. The influence increases with the concentration of the suspension. Evidently we have here to do with a change in the state of flocculation. These suspensions do not at all follow the formula (2) for higher concentrations. Probably the flocculation makes the suspended particles cling to the walls of the viscosimeter tube, thereby narrowing it. We must therefore use formula (2 *a*). In this case it is sufficient to calculate A from the values of not too concentrated suspensions. For infusorial earth (3.2 vol. %) A increases with temperature, as is seen from the following table:

Aqueous suspensions		Alcoholic suspensions	
Temp. ° C.	A	Temp. ° C.	A
25	3.03	30	2.59
45	3.37	45	2.83
65	3.74	65	3.97
75	3.82		

For china clay (in 2.48 % suspension) the corresponding figures are:

Temp. ° C.	A
35	6.33
45	6.28
65	6.70

For graphite (Acheson's "aquadag," 0.4 vol. %) the figures are rather irregular and give a decrease of A , from $A = 7.12$ at 30° to $A = 6.55$ at 65° .

For solutions of indiarubber the irregularities are perhaps still greater than in the last named cases as Fol [1913] has shown. The viscosity of a solution diminishes, when it is allowed to flow repeatedly through the tube of the viscosimeter. This corresponds to the behaviour of the suspensions of $\text{Al}(\text{OH})_3$ on shaking. But if we make a solution of a given quantity of rubber in a given quantity of benzene and shake this solution, its filtrate, taken after 24 hours, has a greater viscosity than if it had not been shaken. This depends upon a disintegration of small solid particles on shaking, so that they pass through the filter. But the increase of the viscosity is greater than corresponds to the increased concentration. This peculiarity is probably connected with the circumstance that the parts of the rubber which enter at first into solution give a lower viscosity than the parts dissolved later on. The viscosity of a rubber solution diminishes on standing.

From what has been said it seems evident that it is necessary to use the greatest precaution if we wish to draw theoretical conclusions from measurements on the viscosity of substances which exhibit such irregularities, specially when the measurements were made at a time when these irregularities were much more imperfectly known than they are to-day.

15. *The values of k in formula (1 a).* We have seen above that Bancelin's experiments gave a brilliant confirmation of Einstein's theory, demanding $k = 2.5$. Further the experiments of Mifka are well in concordance with this theory. But all other experiments on colloidal solutions, quoted above, give too high values of k .

To begin with, the experiments of Odén for colloidal sulphur give the following values:

For submicroscopical solutions (diam. of granules $100\mu\mu$) at 5° , $k = 3.60$.

” ” ” ” ” ” 20° , 3.67.

” ” ” ” ” ” 40° , 3.88.

For amicroscopical solutions (diameter $10\mu\mu$) at 25° , 4.73.

For all the other suspensions or emulsions examined (with exception of serum albumin, an exception perhaps due to errors of observation) the values of k have been found to exceed 2.5, in many cases a hundredfold and more. The question arises: what is the cause of this discrepancy? Smoluchowski has pointed to the probable cause. He says: "For the sphere this value (k) has evidently a minimum value, as it by virtue of its rolling movement has influence upon the smallest possible volume of the liquid in its state of shearing." Therefore the coefficient 2.5 in Einstein's formula applied to

colloidal solutions must be regarded as a minimum value. But there is evidently no sufficient ground to replace it by a higher value as Hatschek proposes.

There is another peculiarity, which Smoluchowski has not observed, namely that k in formula (1 *a*) decreases with increasing diameter of the spherical particles, as is seen from Odén's measurements. Now we know that the Brownian movement of the suspended particles increases, when their dimensions are diminished. Therefore the same quantity of smaller particles will come in contact with a great number of molecules of the solvent through their speedier movement, than the same quantity of bigger particles. This circumstance will also increase the value of A when the dimensions of the particles decrease.

On the same ground, as the Brownian movement increases with temperature, the value of A or of k will increase with temperature. This effect is very pronounced in Odén's figures. It is due not only to the movement of the suspended particles, but also to that of the molecules of the solvent. This must be true for particles of any form and it is seen from the experiments on suspensions of clay and ground infusoria that this statement is true. When molecular aggregates of the solvent are formed their disaggregation with increasing temperature has the inverse effect.

For substances which are hydratated θ decreases with rising temperature. This depends upon the partial dissociation of the hydratated molecules with increasing temperature, whereby the volume concentration of the dissolved or suspended "molecules" diminishes. This seems to be the case with most aqueous solutions and Miss Chick has observed it for the solutions of protein substances. The low value of $k = 2.14$ for serum albumin is probably due to errors of observation, which have caused a too high value of the hydration factor, n . The decrease of A with increasing temperature for graphite suspensions is perhaps due to a diminished agglutination of the particles, for it is not probable that graphite forms hydrates.

The hydration has a great effect on the viscosity at higher concentrations and causes positive deviations from formula (2), if we calculate the values as if no hydration took place. We have not found any instance of such positive deviations for solvents which are non-associated in contradistinction to the highly associated water. Therefore it is not probable that these non-associated solvents in the cases examined hitherto, especially with solutions of india-rubber or nitrocellulose, enter into molecular aggregates with the dissolved molecules, as is maintained by Hatschek on the ground of calculations by

means of his formula (3). But probably many alcoholic solutions behave as aqueous ones. On the other hand suspensions of infusorial earth in alcohol, as well as similar suspensions of infusorial earth, clay or graphite in water show a θ -value, that increases with temperature. In this case we have no hydration nor alcoholation of the suspended particles. The very high viscosity of these suspensions in greater concentrations, which is followed by a very pronounced deviation from formula (2) depends on a formation of large aggregates between the suspended particles themselves, which form a kind of felt which obstructs the capillary tube. Similar cases will probably be very common in agglutinating or coagulating suspensions in higher concentrations.

The very large values of θ or A found in most cases have a similar explanation. Every chemist knows fairly well the voluminous flocculi of hydrated alumina which on desiccation crumble to nearly insensible granules. It is quite natural to suppose that the high value of A , about 500, in this case depends on this voluminous nature. The hydrated particles may further, as Smoluchowski says, possess a spongy structure or be formed as spherulites consisting of very fine needles radiating from a centre. The high values of A found for solutions of indiarubber or nitrocellulose suggest a similar form for the corresponding aggregates, which may also cling to the walls of the viscosimeter tube and cause similar deviations from formula (2) as for suspensions of clay or infusorial earth or graphite. Many examples of such a behaviour in more concentrated solutions are found in the memoirs of Schidrowitz and Goldsbrough. This behaviour seems very probable for indiarubber in the dissolved state, the solutions being extremely sticky. Regarding the similar property of moist clay, on which its high plasticity depends, Le Chatelier [1914, p. 481] has drawn attention to the circumstance that it is a consequence of the fine laminated structure of kaolin. The same may be true for graphite which crystallises in thin hexagonal scales. Probably its high lubricating power is connected with this property. Evidently we have here to do with capillary forces which attain a predominant influence for laminated substances in the form of very fine dust.

Hatschek has also made the objection against formula (2) that it has no theoretical foundation. Lees [1900, 1901] has given such a one (cf. also § 5). But it is also to be remembered that the most "rational" laws have originally been built up from purely empirical foundations.

16. *Summary.* The formula of Einstein, as applied to colloidal solutions, represents a limiting law. It has been confirmed by the experiments of

Bancelin. But in most cases the viscosity is much higher than this law demands. The anomalies depend on the Brownian movement, on the non-spherical form of the suspended particles, on formation of aggregates with the solvent especially on hydration or on sticking together of suspended particles, circumstances which all increase the viscosity. The logarithmic formula (2) is found to be valid for true solutions as well as for pseudosolutions (emulsions and suspensions). Deviations from this formula are caused through chemical changes occurring on dilution.

The chemical changes occurring on mixing solvent and solute are the following:

(1) The solvent may be associated and its complex molecules may be dissociated by the addition of the solute. This process is followed by a diminution of the viscosity. A rise of temperature exerts also such a dissociating influence, whereby a diminution of θ in formula (2) results.

(2) A dissociation of the molecules of the solute has an opposite influence, so that the viscosity increases thereby. This corresponds to a higher viscosity of suspensions with small spherical granules, compared with that of a similar suspension with larger granules. If the suspended particles possess a laminated structure, they form felty aggregates, which in higher concentrations raise the viscosity.

(3) Association between molecules of the solute and of the solvent increases the viscosity. In this case the dissociating influence of rising temperature diminishes θ in formula (2).

Objections made against the validity of the logarithmic formula, raised in this journal by Hatschek, do not bear a close analysis. Experimental attempts by Hatschek and Miss Humphrey to disprove this formula have wholly failed. Hatschek's formula for calculating the degree of binding between solvent and solute not only lacks theoretical foundation but is also incompatible with experimental facts.

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