

Citation:

H.R. Kruyt, The influence of surface active substances on the stability of suspensoids, in:
KNAW, Proceedings, 15 II, 1912-1913, Amsterdam, 1913, pp. 1344-1349

precipitate. In a solution of one part of methylene-blue in 500,000 parts of distilled water the phenomenon was not so clear as in a solution of the same strength made with ditch-water or KNOPP'S fluid. A number of experiments in test tubes with methylene-blue, salts, gall-nut- and Spirogyra-tannin led to the conclusion that the appearance of a precipitate is not only affected by the presence of salts but that also atmospheric oxygen comes into play and finally, that methylene-blue itself has no precipitating action, but that in one way or another a tannin precipitate is formed which gradually takes up more and more of the dye. How the precipitate is produced I cannot definitely say, but its formation does certainly not depend on a simple precipitation of tannin by methylene-blue, as PFEFFER assumes.

Chemistry. — *“The influence of surface-active substances on the stability of suspensoids”*. By Dr. H. R. KRUYT. (Communicated by Prof. P. VAN ROMBURGH.)

In the chemical literature of the colloids it is generally stated that electrolytes exert a great, and non-electrolytes no action on the stability of suspensoids, at least when those non-electrolytes are not colloids themselves. BODLÄNDER¹⁾ found that the formation of sediment in a suspension of colloids was much accelerated by electrolytes, “dagegen sind die Nichtleiter wirkungslos”. And FREUNDLICH²⁾ states of a series of organic substances that they “in grossen Ueberschuss selbst bei tagelanger Einwirkung, keinen Einfluss auf die Beständigkeit des Arsensulphidsols ausübten.” This, however, merely shows that these substances themselves do not cause a coagulation in a direct manner.

If, however, we take the standpoint of the ingenious theory developed by FREUNDLICH³⁾, the complete absence of any influence on the stability is absurd. For when the stability is determined by the electric charge of the particle (HARDY⁴⁾, BURTON⁵⁾) and when this charge is formed by the selective ion-adsorption (FREUNDLICH l.c.) a cause which exerts an influence on the adsorption cannot be inert towards the stability.

¹⁾ Nachr. Göttingen 1893, 267.

²⁾ Diss. Leipzig, 1903, p 13, Zeitschr. f. physik. Chem. 44, 129 (1903).

³⁾ Consult his Kapillarchemie, Leipzig 1909.

⁴⁾ Zeitschr. f. physik. Chem. 33, 385 (1900).

⁵⁾ Phil. Mag. [6] 12, 472 (1906).

Now an adsorbed substance is displaced by another adsorbed substance; this is dependent on the degree to which that second substance is itself adsorbed¹⁾; if to a suspensoid system is added a substance which itself becomes strongly adsorbed it would be astonishing indeed if it left the stability of the system unmodified.

As a rule, we possess a measure for the stability of a system in the limitation value.²⁾ Meanwhile it is as well to consider in how far we must attach value to this relation. A complete coagulation in a short time occurs when of an added electrolyte so much gets dissolved that the colloid has become isoelectric. But this adsorption will also be modified by an added substance.

If, for instance, we have a As_2S_3 sol this consists of particles of arsenious sulphide dispersed in water, these particles at their preparation have adsorbed hydrogen sulphide in such a manner that an electric double layer has formed in such a way that the layer of S'' -ions lies at the side of the solid particle and the H-ion layer at that of the liquid. If now we add a substance A which is adsorbed positively, the condition of that double layer will be modified because A displaces H_2S , S'' as well as H. When effectuating coagulation by means of an electrolyte such as $BaCl_2$, adsorption also takes place of $BaCl_2$, Ba^+ and Cl^- and the limitation value will be attained when the quantities of Ba^+ and S^- are equivalent.³⁾ But this adsorption process also experiences a similar influence from the substance A. The change in the limitation value under the influence of A is therefore the resultant of those two actions. Perhaps these might just neutralise each other? This seems to have always been an assumption not mentioned. Although we know as yet but little about the displacement in the capillary layer, such a symmetry did not seem to me probable and therefore the subjoined investigation was carried out, provisionally for the purpose of orientation.

The substance to be admixed should give rise to a strongly positive adsorption and hence, according to GIBBS's principle it must strongly reduce the surface tension. In this relation account must, of course, be taken of the surface tension solid-liquid; the measurement thereof is, as yet, almost impracticable, but experience has taught us up to the present (and theoretically this may be expected) that the surface tension must as a rule proceed similarly to that for liquid gas. Hence, as strongly adsorbable components were chosen those which strongly lessen the surface tension of water.

¹⁾ Cf. FREUNDLICH and MASIUS, Gedenkbuch VAN BEMMELN (Helder 1910), 88.

²⁾ A version of the German word "Schwellenwert".

³⁾ Cf. WHITNEY and OBER, Zeitschr. f. physik. Chem. 39, 630 (1902).

The subjoined investigations were, therefore, carried out to demonstrate in the first instance the existence of the influence of surface-active substances on the limitation value. Hence, they were carried out by means of an arbitrary colloid As_2S_3 sol with an arbitrary electrolyte $BaCl_2$ with addition of substances, which in diverse degrees lower the surface tension of water, namely first of all, isoamyl alcohol, isobutyl alcohol, propyl and ethyl alcohol the σ - c lines of which (σ surface tension, c molecular concentration) had been determined by TRAUBE¹⁾.

T A B L E I. *Isoamyl alcohol.*

Conc. of the alcohol	Limitation value		Limitation value relat.
	water	alc. mixture	
0	1.08	—	1.00
66	1.08	1.16	1.07
78	1.07	1.32	1.23
92	1.07	1.38	1.29

T A B L E II. *Isobutyl alcohol.*

0	0.87	—	1.00
101	0.87	0.96	1.10
201	0.87	1.02	1.17
302	0.87	1.13	1.30

T A B L E III. *Propyl alcohol.*

0	0.92	—	1.00
197	0.92	1.06	1.15
393	0.92	1.14	1.24
787	0.92	1.30	1.41

T A B L E IV. *Ethyl alcohol.*

0	0.87	—	1.00
1560	0.87	0.97	1.12

¹⁾ Lieb Ann. d. Chem. 265, 27 (1891).

TABLE III. *MAGNESIUM.*

Nutrient liquid: In a Jena glass apparatus 50 cm³ distilled water, in which dissolved 2% glucose, 0,15% ammonium nitrate, 0,1% kaliumsulfate, 0,05% kaliumchlorid, 0,05% crystallised fosforic acid, 0,01% manganesechlorid. Cultivated at 34° C. in ERLLENMEYER flasks of 200 cm³ capacity of Jena glass.

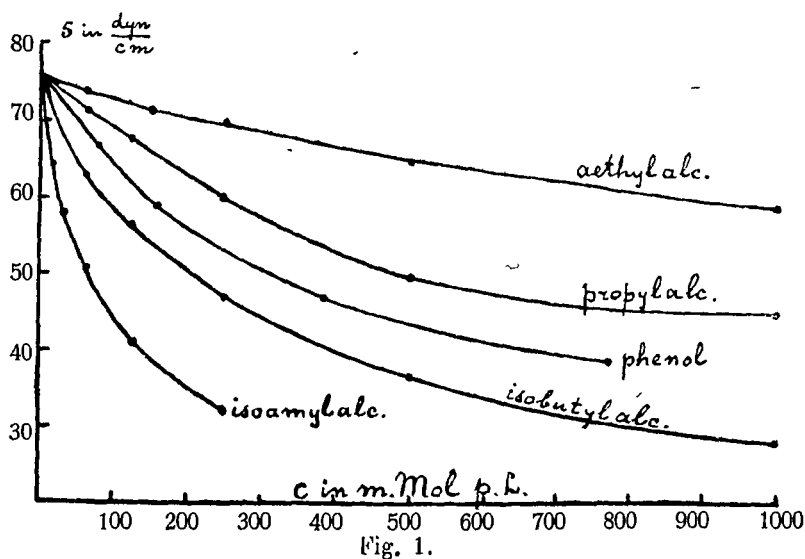
No.	Added	Growth and spore formation after				
		1	2	3	4	8 days
1	—	—	—	—	—	—
2	—	—	—	—	—	—
3	0,001 mgr. MgSO ₄ ·7Aq ($\frac{2}{24700000}$ gr. mol. p. L.)	—	—	—	—	?
4	0,005 " " ($\frac{1}{2470000}$ " ")	—	—	—	—	—
5	0,01 " " ($\frac{2}{2470000}$ " ")	—	—	—	—	+ (slight)
6	0,05 " " ($\frac{1}{247000}$ " ")	—	germination	+	+	+++ , no spores
7	0,1 " " ($\frac{2}{247000}$ " ")	—	+	+	++	++++ , " "
8	0,3 " " ($\frac{6}{247000}$ " ")	germination	+++ , no spores	+++ , beginning spore formation	+++ - +++++ , rather many spores	++++ , hardly any spores
9	0,5 " " ($\frac{1}{24700}$ " ")	+	++++ , beginning spore formation	++++ , already rather many spores	++++ , id.	++++ , beginning spore formation
10	0,8 " " ($\frac{1,6}{24700}$ " ")	+	++++ , no spores	++++ , few spores	++++ , beg. spore formation	++++ , rather many spores
11	1 " " ($\frac{2}{24700}$ " ")	+				++++ , id.
12	2,2 " " ($\frac{4,4}{24700}$ " ")	+				
13	5 " " ($\frac{1}{2470}$ " ")	+				
14	11 " " ($\frac{2,2}{2470}$ " ")	+	+++ no spores	++++ , few spores	++++ , few spores	++++ , many spores
15	25 " " ($\frac{5}{2470}$ " ")	+				
16	100 " " ($\frac{2}{247}$ " ")	+				
17	10 mgr. berylliumsulfate	—	—	—	—	—
18	10 " "	—	—	—	—	—
19	5 " lithiumnitrate	—	—	—	—	—
20	10 " calciumnitrate (free from water)	—	—	—	—	—

To 10 cc. of the sol were added with constant shaking 5 cc. of a solution of the organic substance (or water for the blank experiments which were repeated each time) and about 15 minutes later 1 cc. of a BaCl_2 solution. The whole was then again shaken and then once more two hours afterwards, the BaCl_2 concentration, which was just incapable to cause a *complete* coagulation, represented the limitation value. Those values may be taken as being accurate within two units in the second decimal.

In the tables are given the concentrations relating to the final total volume in millimols. per Litre. In the last column the limitation values have been recalculated so as to make the value for pure water = 1.00.

From these tables it is indeed evident that the alcohol concentration has an influence on the limitation value; this influence appeared to vary for the different alcohols and therefore it was thought desirable to make a comparison of their influence on the capillarity of water, with their adsorbing properties, and consequently with their power of displacement.

This comparison may be readily effected with the aid of the subjoined figure constructed from data obtained by TRAUBE l.c. (The line for phenol will be discussed presently). $\sigma_{\text{H}_2\text{O}}$ is taken therein as 76.0.



From the tables I—IV we now notice that the order of the admixed substances in which they effectuate an increase of the limitation value is: isoamyl, isobutyl, propyl, and amyl alcohol,

while, according to the figure the order for the power of lowering the surface tension is the same.

This result is, therefore, undoubtedly in harmony with the adsorption theory. The only question still to be answered is why the added substances *increase* the limitation value. This however, was to be expected on account of the manner in which displacement takes place as shown from the research of FREUNDLICH and MASIUS (l.c.). What they found is as follows: Let substance A be adsorbed according to the equation:

$$\frac{x}{m} = a c^n$$

or expressed in logarithms

$$\log \frac{x}{m} = \log a + \frac{1}{n} \log c$$

(x the quantity adsorbed, m the amount of adsorbent, c the concentration of the liquid in equilibrium, a and n constants).

If now a substance B is added in definite concentration, the adsorption of A takes place according to the equation:

$$\log \frac{x'}{m} = \log a' + \frac{1}{n'} \log c$$

The investigation always showed that $\frac{1}{n'}$ is smaller than $\frac{1}{n}$. As

the dependency of $\log \frac{x}{m}$ on $\log c$ is represented by a straight line, we readily perceive that the reduced coefficient causes a stronger displacement of A by B in the higher concentrations of A than in the lower ones.

If now in the experiments described above the alcohol is added to the sol the concentration of the liquid in stability-promoting ions will be exceedingly small in comparison with the concentration of BaCl_2 when the limitation value is attained. If now we assume that the adsorption of each of these substances by itself is about the same, it will be readily perceived that the displacing influence will hinder the *charge* of the particle in a much lesser degree than the *discharge*. Hence an *increase* in the limitation value.

Meanwhile it will be as well to dispense with further theories until the matter cited above has been extended by the investigation of more colloids and other organic substances as well as of other (particularly uni- and trivalent) coagulating ions. With this investigation I have already made a start.

The following fact has already been disclosed: aromatic substances

are always adsorbed much more strongly than might be surmised from their influence on the surface tension ¹⁾. I determined stalagmometrically the σ -c figure for phenol (also given in the figure); although it appeared to lie between that of isobutyl and propyl alcohol, the influence exerted by addition of phenol is greater than that caused by isobutyl alcohol, exactly as was to be expected. This investigation is being continued, also in connection with a direct investigation as to the adsorption of the substances added.

A more extended investigation in various directions appears to me desirable all the more because the results may elucidate several other problems in the chemistry of the colloids. I will again refer to this matter in due course.

Meanwhile the results obtained are interesting when taken in connection with the researches of H. LACHS and L. MICHAËLIS ²⁾, who found that surface-active non-electrolytes exert no influence on the adsorption of electrolytes: the above described investigation, however, makes us surmise that although these two kinds of substances should not be put on a par with each other without further evidence, a displacement takes place nevertheless. The effect of the displacement, however, seems to elude the direct measurement, but it may be demonstrated by measurements of the limitation values. Hence, the said investigators could find a displacement effect for isoamylalcohol only, just the very alcohol which according to our research exerts the strongest power of displacement.

Utrecht, March 1913.

VAN 'T HOFF-Laboratory.

Microbiology. — "*Potassium sulfur, and magnesium in the metabolism of Aspergillus niger.*" By Dr. H. J. WATERMAN. (Communicated by Prof. M. W. BEIJERINCK).

In earlier investigations I have shown that the elements carbon, nitrogen, and fosfor occur in large quantities in young mould material, but that, when it grows older, a considerable portion is again excreted as carbonic acid, ammonia, and fosforic acid ³⁾. During the development the plastic aequivalent of the carbon lowers to the half; as to the nitrogen, there is a threefold accumulation, whereas the quantity of fosfor in a young mould layer is ten times as large as that

¹⁾ Compare for instance I. TRAUBE, Verh. d. deutschen physik Ges **10**, 880 (1908). In the Table on p. 901, Aniline the only aromatic compound, occupies a quite special position.

²⁾ Zeit-chr. f. Elektrochemie **17**, 1 (1911)

³⁾ Folia microbiologica Bd. 1 p. 422, 1912. These Proceedings 1912.