

hydrate of thiosulphuric acid, trihydrate of sulphur up to tetrahydrate of hydrogen sulphide. The hydrogenation runs from H_2SO_4 over sulphur monohydrate, pentahydrate of thiosulphuric acid, tetrahydrate of sulphur to tetrahydrate of hydrogen sulphide.

All compounds play a role in the microbiological sulphur cycle (BUNKER 1938).

14. The above considerations merely want to call attention to possibilities of a graphic representation of chemical reactions which is primarily of didactic interest, as much that is left to memory may be reproduced now at will.

The diagrams make us realize the significance of hydrogenations, hydrations and oxidations. It enables us, moreover, in case of carbon compounds, to realize, in first approximation, energy-exchange in various reactions.

Leiden-Buitenzorg 1945—1946.

LITERATURE.

- BAAS BECKING, L. G. M. and E. A. HANSON, Proc. Roy. Ac. Sc. Amsterdam 40, 1 (1937).
 BEYERINCK, M. W. and D. C. J. MINKMAN, Centrbl. Bakt. II, 25, 30 (1910).
 KLUYVER, A. J. and H. J. L. DONKER, Chem. d. Zelle u. Gewebe 13, 134 (1925).
 SCHLOESING, TH. and A. MUNTZ, C.R. 84, 301 (1877).
 STOKES, G. G., Proc. Roy. Soc. 49, 174 (1891).
 VIRTANEN, A. L. and T. LAINE, Nature 141, 748 (1938).

Biochemistry. — *Oleate systems containing potassium chloride in which the KCl concentration is still too low for coacervation. II. Influence of polar organic non-electrolytes.* By H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN.

(Communicated at the meeting of March 29, 1947.)

1. Influence of polar organic non-electrolytes on the shape of the KCl curve.

In the first communication ¹⁾ we have investigated the influence of KCl on the viscosity of diluted oleate sols and in this communication now follows the influence of non-electrolytes, particularly of normal primary alcohols on this KCl curve.

40 gr. Na-oleate (MERCK) is dissolved in 2000 cc dest. water by rolling it in a large glass stoppered bottle. Afterwards is added 200 cc KOH 2 N. This oleate stocksolution may be preserved in the frigidair.

The mixtures contain: 5 cc oleatestocksol. + a cc KCl 3.8 N + b cc alcoholsolution + [15 — (a + b)] cc dest. water.

For organic compounds which dissolve difficultly in water another method was used according to which a known quantity of organic compound was dissolved in a definite quantity of stocksol., while by diluting this latter sol. with the stocksol. a series of sols was prepared with various concentrations of organic compound.

It appears now that we may divide the organic compounds into two groups, concerning their influence on the KCl curve.

In the first group — e.g. methylhexyl keton or n. octanol ²⁾, see lower parts of fig. 1 and 2, the KCl curve moves as a whole to smaller concentrations, while the maximum of the curve becomes lower and the inflexion point in the ascending curve branch becomes less pronounced or even disappears.

In the second group — e.g. acetone or ethanol, see upperparts of fig. 1 and 2 — the KCl curve just moves to higher concentrations, while here too the maximum becomes lower and the inflexion in the ascending curve branch becomes less clear or disappears. In contrast to the first group, the maximum flattens more and more when the curve moves on.

¹⁾ H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, 8, 849—858 (1947).

²⁾ In the experimental series with methyl-hexyl-keton is not used the usual Na-oleate serving for the investigation of the three other compounds, but a Na-oleate prepared from oleic acid and recrystallised from alcohol. Though the blank curve has the same character as the other blank curves (compare Communication No. I, 4), there still are some differences: the KCl concentrations where a) the system is pulling threads, b) the viscosity maximum is reached and c) coacervation occurs, are obviously smaller.

As to the KCl concentration at which the system is pulling threads for the first time (indicated by arrows \downarrow) this is lowered by methylhexyl-keton and n. octanol and raised by acetone and ethanol.

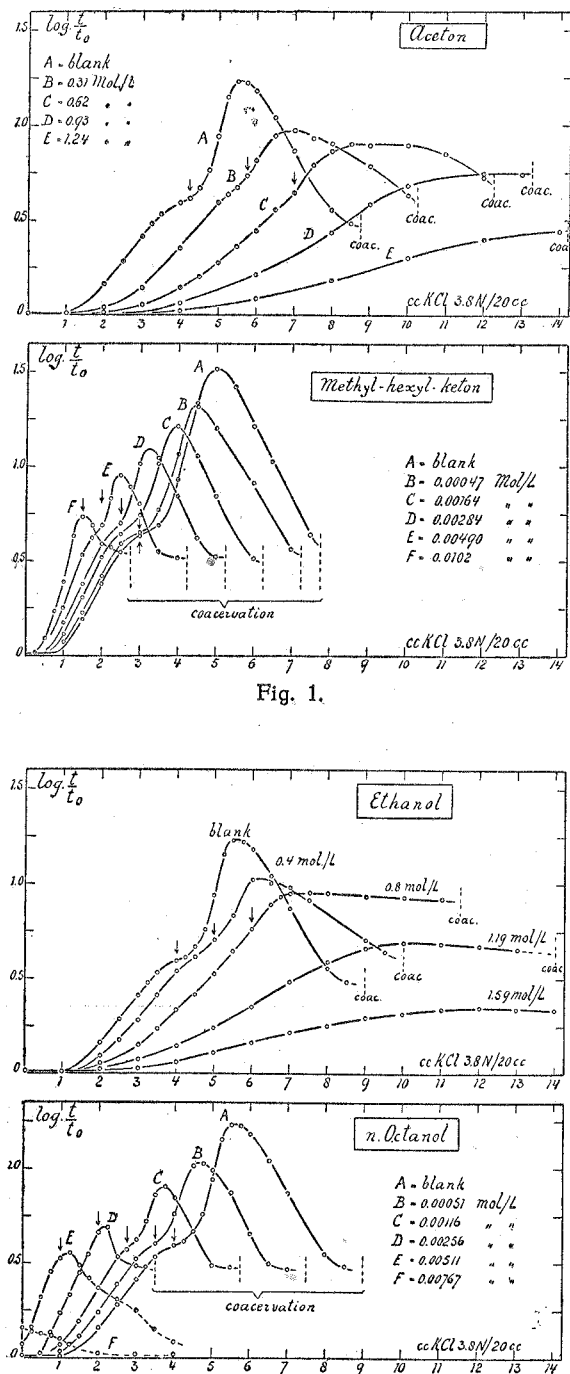


Fig. 1.

Fig. 2.

Further all curves agree in principle with that which holds for the blank curve: at the arrow the property of pulling threads appears for the first time, it is becoming more distinct with increasing KCl concentrations, to decrease again at approaching the coacervation limit. These properties gradually grow weaker however.

This is particular clear for acetone and ethanol at which the system even fails to pull threads at the two largest constant concentrations.

With n. octanol the systems of curve F are not pulling threads at all, but this is probably based on another cause: these systems are not clear, but blue opalescent.

Along the curve E a similar opalescence appears already along the right descending curve branch and though no coacervation occurs anymore (the same along curve F), the property of pulling threads stops at $KCl = 3$.

Finally we want to discuss the coacervation limit. We notice that compounds of the first group move on these limit to smaller KCl concentrations, compounds of the second group to higher concentrations.

Compare fig. 3 in which the coacervate volumes (in % of the total volume) are plotted as functions of the KCl concentrations (the

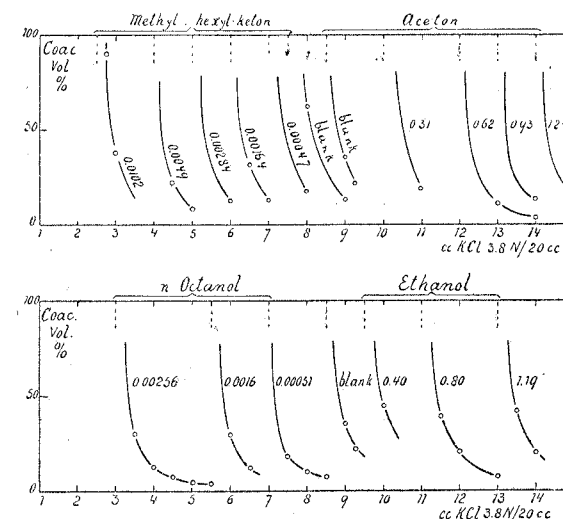


Fig. 3.

coacervation limit being the KCl concentration at which the coacervate volume = 100 %).

Thus we meet in several properties a similarity with previous experiences concerning the influence of organic non-electrolytes on oleate coacervates; (at constant KCl concentrations)³). There we could also discern two groups of non-electrolytes.

³ H. G. BUNGENBERG DE JONG, G. G. P. SAUBERT and H. L. BOOY, *Protoplasma* 30, 1 (1938).

The higher terms of a homologous series (e.g. methylhexylketon, octanol) act "condensing" while the first terms of a homologous series act "opening" (e.g. acetone, ethyl alcohol).

Thus we may suppose, that in the oleate systems, which we are studying here (at KCl concentrations smaller than the coacervation limit) similar rules concerning the relation between effect and constitution will exist.

2. Influence of increasing concentrations of *n*. primary alcohol at three different but constant KCl concentrations.

The first six terms of the *n*. primary alcohols have been further investigated.

They will be indicated in the following by a figure representing the number of C-atoms: methyl- (1); ethyl- (2); *n*. propyl- (3); *n*. butyl- (4); *n*. amyl- (5) and *n*. hexyl- (6) alcohol.

In this investigation a Na-oleate preparation was used, of which the viscosity-KCl curve is already given in communication I (fig. 2) showing the following characteristic KCl concentrations:

just pulling threads 4,5 cc KCl 3,8 N/20 cc;
viscosity maximum 5,75 cc KCl 3,8 N/20 cc;
coacervation limit 9,25 cc KCl 3,8 N/20 cc.

We now made measurements at three KCl concentrations which were kept constant, viz. at

3,5 cc KCl 3,8 N/20 cc, at which the oleate system thus still pulls no threads (fig. 4 A);

at 5,75 cc KCl 3,8 N/20 cc, at the viscosity maximum (fig. 4 B) and

at 8,0 cc KCl 3,8 N/20 cc, just before the coacervation limit (fig. 4 C).

The final oleate concentration was always 0,455% and the KOH concentration was also kept constant viz. 0,0455 N. (The latter to exclude auto-sensibilisation, see communication I).

In fig. 4 the values of $\log. t/t_0$ are plotted as functions of the logarithms of the alcohol concentrations (in mols per L.).

The values t_0 are here equal to the times of flow of similarly composed mixtures (KCl, KOH and alcohol) without oleate.

In the figures A, B and C the dotted horizontal line presents the value of $\log. t/t_0$ at an alcohol concentration = 0. The figure added to a curve indicates the concerning alcohol (e.g. 5 = amyl-alcohol). The curves are drawn continuously when the oleate system is homogeneous, dotted when they are heterogenous (coacervated) or blue opalescent.

A first view on fig. 4 shows already that the influence of an alcohol is the stronger the longer its carbon chain.

At the viscosity-maximum of the KCl curve (fig. 4 B), all six alcohols appear to act in the same direction. They very strongly decrease the viscosity.

The opposition between compounds which move the KCl curve to smaller or higher KCl concentrations resp., already discussed in 1) is not indicated here.

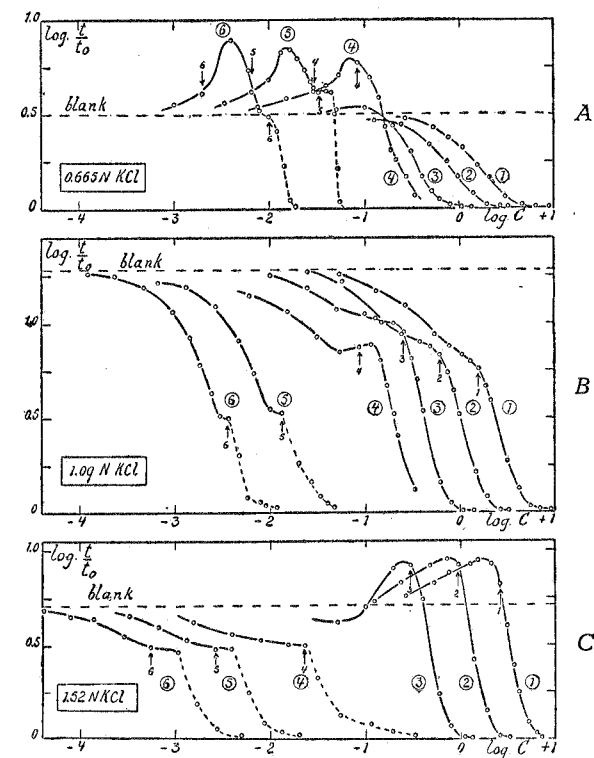


Fig. 4.

Compare fig. 1 and 2, from which we may predict this already: notice the intersection of the different curves with a vertical line drawn through the maximum of the blank curves.

At the other chosen KCl concentrations however, an entirely different behaviour occurs as the six alcohols do not alter the viscosity in one direction only.

In fig. 4 A, 5 and 6 first increase the viscosity to a maximum, but after that the viscosity decreases. 3, 2 and 1 on the contrary just decrease the viscosity.

This is also to predict from the fig. 1 and 2, if we notice the intersection of the different curves with a vertical line at a KCl concentration smaller than that at which the blank system gets pulling threads.

Considering in the same way the intersection points with a vertical line at KCl = 8 c.c. 3,8 N/20 cc, it becomes clear that the action in fig. 4 C will be the reverse of fig. 4 A 6, 5 and 4 are decreasing already immediately, while 3, 2 and 1 first increase to a maximum, only to decrease later on.

We thus conclude from fig. 4, that in the series of the primary alcohols

a reversal occurs in the way on which its individual terms influence the KCl curve.

Methyl-, ethyl- and n. propyl alcohol move the KCl curve to higher KCl concentrations, while n. butyl-, n. amyl- and n. hexylalcohol (and still higher terms also e.g. n. octylalcohol, see fig. 2) to lower concentrations.

A more close inspection of fig. 4 A and C shows propylalcohol as a transition term.

In small concentrations its action corresponds just for a while to butyl-, amyl- and hexylalcohol, in higher concentrations however it corresponds entirely to ethyl- and methylalcohol.

This means an obvious similarity with the previous investigated influence of alcohols on oleate coacervates, in which the same characteristic points have been found: a) an alcohol is acting in a lower concentration the longer the carbonchain, b) there occurs a change of action in the homologous series concerning the direction in which an alcohol is acting c) n. propyl alcohol comes out as transition term.

One would expect now that butyl-, amyl-, and hexylalcohol in a sufficient concentration always will produce coacervation.

This is the case at the highest KCl concentration anyway (fig. 4 C); at lower KCl concentrations there is a removal to higher terms in the homologous series with respect to the coacervation.

In this manner butylalcohol does not perform coacervation at 5.75 cc KCl (fig. 4 B), while amylalcohol and hexylalcohol still do.

At 3.5 cc KCl (fig. 4 A) the systems with n. amylalcohol do not even typically coacervate anymore (blue opalescent systems appear), though n. hexylalcohol still does.

Finally we have to discuss the influence of the alcohols on the elastic properties (thread-pulling capacity).

The capacity of pulling threads is strongly pronounced at the maximum of the KCl curve.

It appears now that all alcohols act on this phenomenon in one direction, namely annullating (see arrows \uparrow in fig. 4 B).

The same holds for the blank at $KCl = 8 \text{ cc } 3.8 \text{ N}/20 \text{ cc}$, where the capacity of pulling threads is weaker (see arrows \uparrow in fig. 4 C).

Concerning alcohols producing coacervation the thread-pulling stops just before the coacervation limit, as for the alcohols producing no coacervation (4, 3, 2, 1 in fig. 4 B and 3, 2, 1, in fig. 4 C) the thread-pulling stops near to a distinctive change of course in the viscosity curve.

In fig. 5 the concentration trajectories in which threads are pulled are indicated by continuous lines.

The alcohol concentration for annullating these properties appears to be the lower, the longer carbon-chain it contains.

In the cases B and C nothing indicates a division of the alcohols into two groups, as they all annullate the thread-pulling.

In case A, the KCl concentration (3.5 cc) is chosen in such manner that the blank system is still not pulling threads.

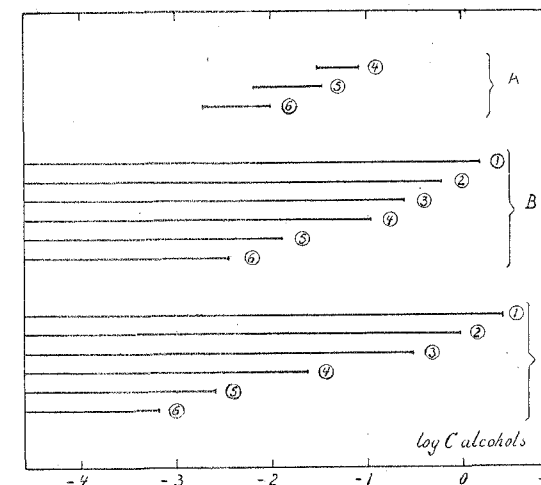


Fig. 5.

The alcohols 6, 5 and 4 may here originate the threadpulling (arrows \downarrow in fig. 4 A).

The alcohols 3, 2 and 1 on the contrary do not proceed any thread-pulling.

The alcohols 6, 5 and 4 apparently annullate the thread-pulling in higher concentrations, which they originated in lower concentrations (arrows \uparrow in fig. 4 A).

See A in fig. 5, with indicated trajectories in which threads are pulled.

Nevertheless we will still see in communication III that at the maximum of the viscosity KCl curve (5.75 cc KCl) a division may be shown into two groups, with n. propylalcohol as transition term, from measurements of these elastic systems.

If we review the data from this and the first communication the question arises, if the high viscous and elastic oleate systems appearing at KCl concentrations still too low for coacervation may be considered as stadia preparing the coacervation or as systems sui generis.

We are inclined to the latter.

Indeed it was established already over and over again that factors, strongly attacking the typical high viscosity or the thread-pulling, do not prevent the coacervation anyway (even sometimes stimulate the coacervation, e.g. influence of temperature in Communication I).

Then it may be mentioned that the change of action in the homologous series of the alcohols concerning the influence on the viscous and elastic behaviour is independent of the KCl concentration; as for the influence on the coacervation however, the change of action shifts to higher terms when the KCl concentration decreases.

Summary.

1. A constant concentration of a polar non-electrolyte (e.g. an alcohol or keton) moves the viscosity KCl curve either to higher concentrations (the first terms of a homologous series) or to lower concentrations (the higher terms of a homologous series).

A middle term may show a transition character: in smaller concentrations it corresponds with the higher terms of a homologous series, in larger concentrations with the lower terms.

2. While the viscosity curve is moving as mentioned in 1), the maximum of viscosity decreases, the inflexion point in the left ascending curve branch gets less pronounced or disappears, while the phenomenon of thread-pulling declines or stops altogether.

3. The influence at 3 different, but constant KCl concentrations of methyl- (1), ethyl- (2), n. propyl- (3), n. butyl- (4), n. amyl- (5) and n. hexyl-alcohol (6) on the viscosity and the thread-pulling was investigated more in detail.

4. The influence on the viscosity still depends on the selection of the KCl concentration, being evident from 1) and 2).

At a KCl concentration before the inflection point. 6, 5 and 4 do increase the viscosity until a maximum is reached and decrease afterwards. 2 and 1 only decrease the viscosity, while 3 acts as transition term.

At the maximum of the KCl viscosity curve all terms of the homologous series just decrease the viscosity.

At still higher KCl concentrations now 2 and 1 increase the viscosity to a maximum and 6, 5 and 4 decrease, while 3 acts as transition term again.

5. The concentrations at which an alcohol acts on the viscosity (either increasing or decreasing) or on the phenomenon of threadpulling resp. (either stimulating or suppressing) is the smaller the more carbon atoms the alcohol contains.

Botany. — *Uptake and transport of chlorine by parenchymatic tissue of leaves of Vallisneria spiralis. I. The active uptake of chlorine.* By W. H. ARISZ.

(Communicated at the meeting of October 25, 1947.)

§ 1. Introduction.

The phenomenon of the active uptake of substances in plant cells has been extensively investigated on various objects. Many investigators have done this on disks of storage organs. Besides various advantages these objects have this disadvantage that the uptake is not a normal phenomenon in their case, but takes place as a result of wounding and regeneration. Therefore the uptake which is found here and which is inherent with the formation of new protoplasm and the protein metabolism departs in some respects from the normal uptake. STEWARD's generalization that only very active cells having the capacity for further growth show an active uptake seems premature.

Others have investigated the process of uptake in unicellular seaweeds which are much less apt to take up substances actively, such as *Valonia* and various *Characeae* as *Nitella*.

The greater number of researches, however, has been made with the roots of higher plants, in which an uptake occurs which in some respects resembles the active uptake in storage tissues and unicellular sea weeds. It has appeared, however, that this uptake is of a complicated nature because in their case we have not only to deal with the uptake by the root cells, but also with the transport of salts to the xylem. Therefore it is important that there is a fourth group of objects, the leaves of water plants, in which the problems are in some respects a little simpler.

Especially *Elodea* has served as an object for investigations.

In our own researches *Elodea* gave no distinct result, while with *Vallisneria* the results on uptake of salts proved to be much more suitable for analytical purposes. Besides this object has the advantage that not as in the case of *Elodea*, leaves and stalk were examined at the same time, but only the very homogeneous leaf tissue. For these long leaves it is moreover possible to trace the transport of the absorbed substances in the leaf. As far as I know, these leaves have not been used in absorption- and transport experiments, since BIERBERG worked with them in 1909 in a research on the influence of protoplasmic streaming on the transport.

The last ten years a series of researches have been made in Groningen on *Vallisneria*, in which the details of these processes have been extensively examined. As early as 1932 Miss A. KOK of Groningen had repeated BIERBERG's investigation on the uptake of Lithium salts and she had also examined the transport of caffeine. Next followed extensive quantitative