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Biochemistry. — *Oleate systems containing potassium chloride in which the KCl concentration is still too low for coacervation. III. Influence of KCl and alcohols on the elastic behaviour.* By H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN.

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

1. Introduction.

The high viscous sols originated by KCl addition in a definite concentration trajectory preceding coacervation, show elastic phenomena. Shaking such a high viscous system in a test tube, fixes shorter or longer the air bubbles in the gelatinous mass. By rotating the testtube with a pull round the axis, — say nearly 45° — one may observe a pendulation of the air bubbles several times to and fro.

Leaving now the testtube alone, all the air bubbles, even the very small ones, ascend and after a shorter or longer time (e.g. some hours) they have left the high viscous system.

We therefore get the impression that the system acquires elastic properties in a mechanical way (the pull), becoming thus in this way a gel, but losing these elastic properties when left alone. This peculiar behaviour thus may be called in a way the contrast of thixotropic behaviour (where a system is fluid when shaken, but becomes solid when left alone).

Though we aim to study this elastic behaviour more in detail by more accurate methods later on, we here give the results obtained by a very primitive technic. These results concern the same variables, which have been investigated in the two previous communications ¹⁾ with regard to the viscosity of oleate systems containing KCl, viz. KCl concentration and influence of alcohols.

2. Measurement of the elastic properties.

In the time of oscillation will be implied in the next the time between two turningpoints of an airbubble. The oscillation time appears to depend on the nature of the oleate system and on the dimensions of the cylindrical tube containing the system.

This was investigated at a system obtained by mixing in a stoppered bottle: 25 cc oleate sol + 28 cc KCl 3.8 N + 47 cc dest. water. (The oleate sol was prepared as in communication II from 40 gr. Na oleate + 2000 cc dest. water + 200 cc KOH 2N).

The mixture is shaken vigorously until a homogenous system is obtained.

It is of a high viscosity and represents nearly the viscosity maximum in fig. 2 of communication I.

¹⁾ H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, 50, 849 (1947) (I) and 50, 1011 (1947) (II).

This system is now put to different heights in a measuring glass of 24 mm internal diameter, waited for the ascension of the very large airbubbles and measured (roomtemp.). The technic of measuring is as follows. The cylindrical tube is turned with a pull over a limited — not too large — angle.

When an airbubble, situated near the wall of the tube, takes its first turning point, a stopwatch is set on. The number of the next turning points, just visible with the naked eye, is counted and when the oscillations are practically finished, the stopwatch is stopped.

In this way a number n for the number of observed turning points and a time t (sec) for the total duration of the oscillation phenomenon is obtained. This measurement is repeated ten times and from the average values for n and t the oscillation time t/n may be computed. After some experience one gets satisfactory reproducible data.

At the first place the oscillation time of a bubble appeared to be dependent on the column height of the oleate system: if the column height amounts to less than $2 \times$ the diameter of the cylindrical tube, too small values for t/n will be obtained.

But if the column height exceeds $2 \times$ the diameter of the tube, t/n appears to be practically independent from the height. We therefore take column heights of the oleate system, being at least $2.5 \times$ the diameter of the tube and perform the measurements on air bubbles situated in the upper zone.

Still further was investigated the influence of the width of the bottle, always taking care that the column height amounted to at least $2\frac{1}{2} \times$ the width of the cylindrical tube.

Next table presents the complete data, in order to demonstrate one instance of the measurements.

TABLE I.

Diameter of the cylindrical tube in mm														
60		47		43		35.5		28		18		8.7		
t	n	t	n	t	n	t	n	t	n	t	n	t	n	
9.0	5	9.4	7	8.4	7	7.6	7	5.4	7	3.6	7	1.0	5	
8.2	5	9.6	7	8.2	7	8.2	8	5.0	7	3.4	7	1.2	5	
8.8	5	9.0	7	7.0	6	8.0	8	6.8	8	3.4	7	1.2	6	
10.0	6	9.2	7	7.8	7	8.4	8	4.8	7	3.8	7	1.2	5	
10.0	6	9.6	7	7.8	7	8.0	8	5.6	8	3.2	7	1.2	5	
10.0	6	9.2	7	8.0	7	8.4	8	5.0	7	3.4	7	1.2	5	
10.6	6	10.6	8	8.6	7	8.4	8	5.4	7	3.6	7	0.8	4	
10.8	6	10.8	8	8.4	7	8.2	8	5.2	7	3.6	7	0.8	4	
12.4	7	10.0	8	8.6	7	8.0	8	4.8	7	3.8	7	1.0	4	
12.4	7	12.4	9	9.2	7	8.2	8	6.0	8	3.4	7	1.0	4	
mean	10.2	5.9	10.0	7.5	8.2	6.9	8.14	7.9	5.4	7.3	3.44	7	1.06	4.7
t/n	1.73		1.33		1.19		1.03		0.74		0.49		0.23	

If the oscillation time t/n is plotted against the diameter of the cylindrical tube, the result is a straight line through the zero of the diagram i.e. the oscillation time is proportional to the diameter of the tube.

We might be inclined to derive from these measurements another characteristic for the elastic behaviour of oleate systems viz. the damping, being the reciprocal value of the total number of observed turning points. It may be seen from the table, that this number n has a value of approximately 7 at tubes of 47—18 mm diameter, while it is lower at smaller or larger tubes.

These lower values are probably erroneous and may be caused by difficulties in observing the oscillations. The difficulty with too narrow tubes consists in the small amplitude and the small oscillation time. In very wide tubes on the other hand, too much airbubbles are visible on different depths at the same time. As all these bubbles differ in amplitude during the oscillation, a too large uncertainty of observation exists.

Taking the above into consideration, we believe to conclude that the damping, for which we take the reciprocal value of n , is independent from the diameter of the tube.

But it will be clear that the reproducibility of n and also of t will be much less satisfactory than of t/n .

The observer gets experienced in the just visible observation of a turning point.

(Compare the increase of n in the columns of the table for 60 and 47 mm).

Using a magnifying glass, increases the observation of the number of turning points.

Hence, n has to be observed in the same way, which was done always with the naked eye.

By means of a small microscope however, it was investigated if during the whole oscillation phenomenon, the oscillation time remains really constant, i.e. if we have to do with a damped harmonic oscillation.

Therefore were measured — at an oleate system showing by microscopic observation 10 turning points —, the total time for 10, 9, 8, etc. until 2 turning points, and these times plotted against the number of turning points. A straight line through the zero of the diagram results, but only if the amplitude at the beginning is sufficient small.

When the amplitude is larger, the oscillation times of the first oscillations are relatively too large, reaching a normal value again at the next oscillations.

As this detail was not yet known to us at the performance of the now following measurements, no account could be yet kept with it.

We established however, that the systematic error, which is caused by the latter in the determination of t/n was of small importance compared by the very large alterations of the oscillation time when varying the KCl concentration or adding alcohols. When however by a variable, t/n is only but little decreasing while n is very strongly decreasing at the same time, this systematic error may accomplish, that t/n remains apparently constant.

3. *Changes of the elastic behaviour of the oleate systems by increasing the KCl concentration.*

For these and the next measurements always was used a cylindrical tube of 28 mm diameter. Mixtures were being prepared of constant oleate concentration and increasing KCl conc. as amply described in communication I. (See fig. 2.)

In the table, the added quantities KCl 3.8 N, concern in the same way 20 cc mixtures (though for the filling of the measuring tube 40 cc of this mixture had to be prepared).

Thus the results (table II) may be compared at once. Moreover the roomtemp. (25°) was the same as in the measurements of the viscosity in communication I.

TABLE II.

cc KCl 3.8 N in 20 cc mixture	t sec. (mean)	n sec. (mean)	t/n	Remarks
4	—	0	~ (?)	pulls no threads.
4.5	3.36	2	1.68	threads very thin.
4.75	3.54	3	1.18	threads very thin.
5	4.10	3.8	1.08	threads thin.
5.25	4.72	4.8	0.98	} gradual transition to short and thick threads.
5.5	4.80	5.5	0.87	
5.75	5.30	7	0.76	
6	5.09	6.9	0.74	
6.5	5.46	8.1	0.67	} gradual transition to long and thin threads.
7	5.72	9.17	0.62	
7.5	5.86	9.9	0.59	
8	5.35	9.55	0.56	
8.5	3.84	7.4	0.52	} not yet coacervated. coacervated.
8.75	2.92	5.5	0.53	
9	2.10	4	0.53	
9.25	—	—	—	

The values t, n and t/n are plotted in the upper part of fig. 1 against the KCl concentration. At KCl values until 4 cc no elastic phenomena appear.

Where they occur for the first time (4.5 cc KCl) the oscillation time t/n has its greatest value and decreases continuously when increasing the KCl concentration, to attain a horizontal level just before the coacervation limit (between 9 and 9.25 cc KCl).

The time, in which one may observe oscillations, and the total number of turning points, increases to a maximum and decreases afterwards again.

From choosing either t or n as a measure of the reciprocal value of the damping of the oscillation follows that the damping with increasing KCl concentration passes a minimum.

If we compare, the curves of t/n and t or n resp. with the viscosity curves (fig. 1 lower part), we notice only one correlation between elastic and viscous behaviour.

The elastic phenomena do appear for the first time at the inflexion point in the left ascending branch of the viscosity curve.

The added arrow indicates the KCl concentration (4.5 cc), at which the liquid flowing out of the viscosimeter starts to pull threads. There is no

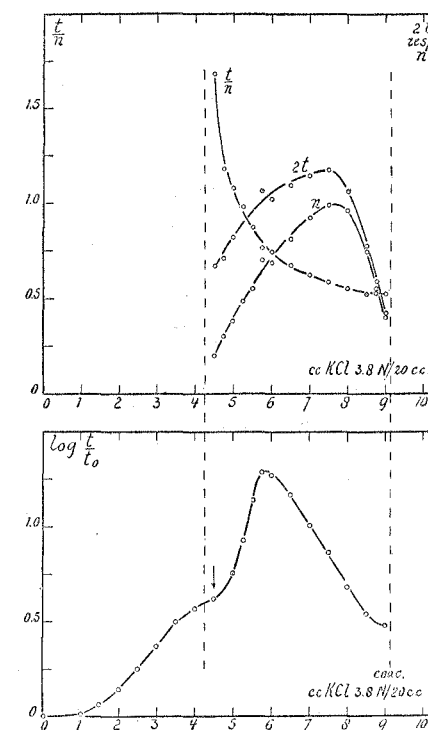


Fig. 1.

threadpulling at KCl = 4 cc. The left dotted vertical thus indicates nearly the "Thread limit" (KCl = 4.25 cc).

The right dotted vertical indicates in the same way the coacervation limit (at 9.13 cc KCl).

There is no reflection of the viscosity maximum in the t/n, t or n curves (no inflexion points or extreme values).

In the same way there are no peculiarities in the viscosity curves at KCl concentration (7.5 cc KCl) at which t- or n-curves resp. show a maximum.

These facts will be important from the viewpoint of alterations in the structure of the "soap micells", occurring with increasing KCl concentration and finally resulting in coacervation. We will still withhold however from further speculations.

4. *Influence of normal alcohols on the elastic behaviour of oleate systems at the maximum of the viscosity KCl curve.*

Mixtures were being prepared corresponding to the maximum of the viscosity KCl curve all in the same way as in communication II, (5.75 cc

KCl 3.8 N per 20 cc final volume) to which had been added increasing concentrations of alcohols. Again measurements occurred in a measuring tube of 28 mm diameter. Roomtemp. amounted to 24—25°, fig. 2 shows the results as function of the logarithm of final alcohol concentrations (in mols per L). Arrows indicate the alcohol concentrations at which the thread-pulling propertie is lost (compare communication II).

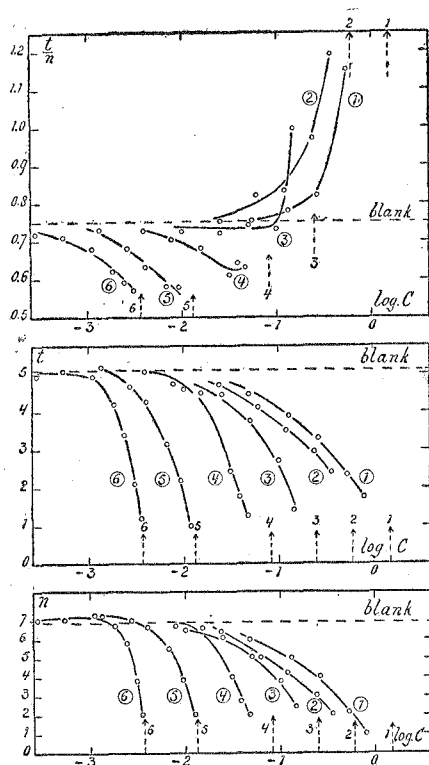


Fig. 2.

Summarizing the influence of alcohols on the elastic behaviour of oleate systems, we conclude:

1. A normal primary alcohol acts on the oscillation time t/n as well as on the damping (reciprocal value of t or n resp.) at the lower concentrations, the longer its carbon chain.

Compare e.g. in fig. 2 b the logarithmic distance of the curves 6 and 1 when t decreases on its half-value. This distance amounts to 2.18, i.e. hexylalcohol acts already in a $150 \times$ smaller concentration as methylalcohol.

2. In the homologous series a change of action occurs concerning the influence on the oscillation time: methyl- and aethylalcohol increase t/n , n. butyl-, n. amyl- and n. hexylalcohol decrease t/n .

n. Propylalcohol acts as typical transition term, has small influence at first, but in higher concentrations the t/n curve ascends rapidly and is even situated then at the left side of the ethylalcohol curve.

Perhaps the n. butylalcohol curve tends also to ascend after a strong descending in the beginning.

3. No change of action occurs in the homologous series concerning the influence of alcohols on the damping. All t and n curves descend i.e. all alcohols increase the damping.

It may be useful to mention some points of correspondence and of difference, to get in the future a deeper insight into the nature of the elastic oleate systems and the structure of oleate coacervates.

ad. 1: The same influence of the length of the carbon chain holds for the influence of alcohols a) on the volume of the oleate coacervate²⁾ b) on the viscosity of oleate systems at KCl concentrations still too low for coacervation³⁾.

ad. 2: A change of action occurs in the same way with the influence of alcohols on the volume of oleate coacervates²⁾.

Methyl- and aethylalcohol increase the volume, they act "opening". n. Butyl- and n. amylalcohol decrease the volume, they act "condensing". n. Propylalcohol behaves as transition term.

We also met with a change of action in high viscous oleate systems at the maximum of the viscosity KCl curve: methyl-, aethyl-, n. propyl-, and n. butylalcohol do *not* accomplish coacervation in contrast to n. amyl- and n. hexylalcohol³⁾.

The transition term is shifted one term higher up in the homologous series, probably caused by the here smaller final KCl concentration.

ad. 3: All six alcohols considerably decrease the high viscosity of the oleate system mentioned under ad 2) (followed by coacervation or not)³⁾.

Summary.

1. A provisional method to characterise the elastic behaviour of high viscous oleate systems, containing KCl was indicated.

An orientating investigation was accomplished about the influence of KCl and of the first six terms of the homologous series of normal primary alcohols.

2. The elastic behaviour occurs only, when a definite KCl concentration is exceeded, nearly corresponding with the appearance of the phenomenon of thread-pulling and with the inflexion point on the ascending branch of the viscosity-KCl curve.

3. The oscillation time decreases with increasing KCl concentration. The damping firstly decreases, passes a minimum and increases afterwards.

²⁾ H. G. BUNGENBERG DE JONG, G. G. P. SAUBERT and H. L. BOOY, *Protoplasma* **30**, 1 (1938).

³⁾ H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN, *Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam*, **50**, 1011 (1947).

4. The elastic behaviour of maximum viscous KCl oleate systems is altered by alcohols. An alcohol acts in lower concentrations, the longer its carbon chain.

5. In the homologous series of the alcohol a change of action occurs with respect to the oscillation time. The first two terms increase, the 4th, 5th and 6th decrease the oscillation time.

n. Propylalcohol acts as transition term.

6. All six terms increase the damping.

7. Analogies to the influence of KCl and of alcohols on the viscosity of high viscous oleate systems and on the volume of oleate coacervates is briefly mentioned.

Botany. — *Uptake and transport of chlorine by parenchymatic tissue of leaves of Vallisneria spiralis. II. Analysis of the transport of chlorine.*
By W. H. ARISZ.

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

§ 1. *Introduction.*

After it had appeared that leaves of *Vallisneria* when exposed to the light are apt to take up chlorine from highly diluted concentrations of balanced salt solutions, the transport of the absorbed chlorine ions in the leaf was examined. With the simple phenomenon that a leaf brought into a KCl solution absorbs chlorine, it is an obvious assumption that this is done by the epidermal cells, which subsequently transport the absorbed chlorine to the deeper lying cells. Though it is imaginable that the ions diffuse inwardly along the cell walls and consequently the more inward cells can also obtain salt from the external solution, such a diffusion in the cell walls will, if it is possible, proceed extremely slowly, because the concentration of ions in the medium is low, and with these submersed leaves no suction of water from the outside to the inside takes place, in consequence of which salts might be transported together with the absorbed water. It is quite certain that the subepidermal cells absorb chlorine as well, because they increase their osmotic concentration to the same degree as epidermal cells, as appears from plasmolysis experiments. How this transport takes place is still unknown and it is no simple thing to investigate this by means of a suitable experiment. This problem is much easier to be solved, when we bring a part of the leaf in touch with a salt solution and next try to find out whether transport is possible to other parts of the leaf which are not in direct touch with the salt solution. Such leaflengths must have obtained their increase in salt through transport in the leaf tissue from the part that is in direct touch with the salt solution. Such a research has been made in my laboratory by Miss KOK for Li-salts and caffeine while ARISZ and OUDMAN examined the transport of asparagine and caffeine by bringing a small part of the leaf in touch with an agar gel to which the substances had been added. In this way we get a purely local absorption of the substances by a certain part of the leaf and the transport to the rest of the leaf can be examined. As the agar used contained some chlorine the rest of the leaf was not put between agar, but between moist filter paper. This prevents transpiration in the free part of the leaf so that no suction of liquid from the part lying in agar can occur. This method of administering the salt solution locally in an agar gel is (for experimental reasons) much to be preferred to the method of bringing a part of the leaf into a separate box filled with a liquid, because the proper closing