

Biochemistry. — *Elastic viscous oleate systems containing KCl.* VI¹⁾.

a) *The elastic properties as a function of the KCl concentration.*

b) *Influence of some alcohols and fatty acid anions on the elastic behaviour.* By H. G. BUNGENBERG DE JONG, H. J. VAN DEN BERG and D. VREUGDENHIL.

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1) *Introduction, and the measuring technique with half filled spheres.*

Having kept in the preceding Parts of this Series the KCl concentration constant (viz. at or very near to that concentration at which the damping of the elastic oscillation is a minimum), we will in the present communication investigate the dependence of the elastic properties on the KCl concentration (section 2).

The knowledge of this dependence is, of course, of importance for a future theory of the elastic viscous oleate systems, it is so too for studying the influence of organic substances on the elastic behaviour. A broader survey of the influence of an organic substance can indeed be obtained if its action is investigated not only at the KCl concentration of minimum damping (of the blank), but also at lower and higher KCl concentrations (section 2).

In the next sections, 3 and 4, in which the influence of a number of terms of the *n*. primary alcohols and of the fatty acid anions is studied, we were compelled (see section 3) to restrict ourselves to the KCl concentration of minimum damping. The points of view obtained in section 2 will, however, guide us in interpreting the results and will heed us from making erroneous generalizations.

For the methods (rotational oscillation in spherical vessels of known capacity at 15°) we refer to Parts I, II and III of this series, with the only exception that instead of using completely filled spherical vessels we used exactly half filled vessels. We know from the experiments in Part I (cf. *ibid.* section 2) that the period depends on the degree of filling of the vessel and that at 50 % degree of filling (by volume) the period is practically the same as in the completely filled sphere. According to not published previous work this practical equality also holds for the damping ratio b_1/b_3 , which is used for calculating Δ , the logarithmic decrement.

Half filled vessels of nominally 500 cc capacity (provided with ground in glass-stoppers) highly serve the purpose of investigating the influence of added organic substances. We first measure the elastic properties of the blank, add a small known quantity of the organic substance into the vessel (e.g. drops from a suitable micropipette, which delivers drops of known weight), shake vigorously (e.g. 5 minutes or more) and put the vessel in the thermostate (15°) till the next morning (to get rid of the

¹⁾ Part I has appeared in these Proceedings 51, 1197 (1948),

Part II—V in these Proceedings 52, 15, 99, 363, 377 (1949).

enclosed air) and measure the elastic properties anew. We continue in this way with alternately adding more substance and measuring the next morning until a sufficient number of experimental points has been obtained to characterize the action of the added substance.

This method has the advantage of economizing oleate, KCl and organic substance ²⁾, its disadvantage is that it takes many days. This disadvantage is compensated however by running a number of half filled vessels simultaneously.

The reliability of the method depends of course on the assumption that during the whole process no changes take place in the oleate system when no organic substance is added. To control this, we take a half filled sphere and treat it in the same way as the other spheres (measuring, opening the glass stopper for a short time, closing it again, vigorously shaking of the vessel, placing it in the thermostate and so on repeating this for several days). With 500 cc stoppered vessels and oleate systems containing the usual small quantity of KOH we found no changes which obviously surpassed the experimental errors.

The method described above is very convenient for added substances which exert their full influence in small concentrations already. The quantity of substance added is very small then (e.g. n. hexyl-, n. amyl-, n. butyl alcohol) and no corrections are necessary.

If the substance exerts its full influence at concentrations which correspond to additions of one to several percent, of the oleate system (e.g. methanol, ethanol), corrections are necessitated by the increase in the degree of filling and its consequences, viz. decrease of the oleate concentration and of the KCl concentration and change in the density.

The addition of one percent by volume changes the degree of filling from 50% to 50.5%. From Table I in Part I we calculate for this increase an increase of 0.35% of the period. Later, more accurate measurements gave the somewhat smaller value of 0.25%. The addition decreases also the oleate concentration by one percent, which gives an increase in the period of approximately 1% (see Part III, where we found that $\nu (= 1/T)$, is roughly speaking, proportional to the oleate concentration).

The two changes considered result therefore already in an increase of 1.25% in the period, and as the shear modulus G is proportional to ν^2 , the addition of one percent to the volume will lead, if not corrected, to a value of G which is 2.5% too low. The two other changes above mentioned will, in general, have only a slight influence when compared to the two considered here.

To come to a practical limit for the volume of an added substance, below which no corrections are needed, it is necessary to know the reproducibility of G , calculated from measurements on a number of exactly half filled vessels, using an identical oleate system.

The next survey gives the results of the measurements on the eight vessels half filled with the blank oleate system which were used for the experiments in section 3.

R (cm)	5.00	5.01	5.01	5.01	5.03	5.04	5.04	5.05
n	48.0	48.2	47.9	48.0	48.1	47.9	48.2	47.8
λ	0.222	0.222	0.222	0.223	0.219	0.224	0.219	0.222
λ (sec)	2.57	2.56	2.57	2.57	2.60	2.54	2.60	2.60
G (dynes/cm ²)	40.4	40.7	40.4	40.3	41.2	41.1	41.0	40.8

²⁾ It would of course also be economical to use spherical vessels of much smaller capacity than 500 cc, for instance 100 cc vessels, but experience taught us that it is not advisable to use them as the experimental errors are greater then. This is partly due to the more difficult measurement of the period and especially of the damping ratio (in 1.2% oleate systems T and λ are proportional to the radius, see Part II, and are therefore much smaller in 100 cc vessels than in 500 cc vessels). This may also be due to the fact that smaller vessels do not approximate the ideal spherical form so well.

We see from this example that in practice differences up to 2% in the G value may occur. Therefore we may content ourselves not to object to the introduction of an error in the order of 1%; and corrections may be neglected, if the volume of the added substance does not exceed 0.5% of that of the oleate system.

For methanol and ethanol larger quantities must be added to characterize their influence on the oleate system and therefore corrections are necessary.

By measuring the influence of known quantities of distilled water on a vessel half filled with the blank system we determined in section 3 experimentally the correction to be applied in order to account for three of the four changes mentioned above (viz. the increase in the degree of filling, decrease in the oleate concentration and decrease in the KCl concentration. The correction for the fourth change (decrease of the density) was applied separately.

In the ethanol series in section 2, the necessity of applying corrections for the changes in the degree of filling and in the oleate concentration was made redundant by adding a volume b of ethanol and a volume $b/2$ of the oleate stocksol and, after mixing the contents of the vessel, by removing a volume of $1.5 b$ with a pipette. After the addition the oleate concentration is not changed (the stock solution having a threefold larger oleate concentration) and after the removal the original degree of filling is restored. Only a slight change in the KCl concentration remains which can be calculated. For this reason the corresponding points on the curves A , B and C of fig. 4 do not longer lie at precisely the same abscis-values (as in fig. 2).

2) *The elastic behaviour as a function of the KCl concentration and the influence of n . hexylalcohol and aethanol thereon.*

Starting from a stock solution (36 g. Na oleicum medicinale pur. pulv. Merck + 820 cc H_2O + 180 cc KOH 2 N) we made 11 mixtures according to the formula 100 cc stock solution + a cc KCl 3.8 N + (200— a) cc H_2O .

In these mixtures the oleate concentration (1.2 g. p. 100 cc) and the KOH concentration (0.12 N) are constant and the KCl concentration increases by degrees from 0.57 N to 1.90 N. The highest concentration used closely approaches the coacervation limit (slightly above 2 N KCl).

Eleven "500 cc" spherical vessels of known real capacity, the radius of which (R) had been calculated, were each exactly half filled with one of the above mixtures and put in the thermostate of 15°. The next morning the elastic behaviour was measured, and afterwards the same small quantity of n . Hexylalcohol was added to each vessel.

The mixtures were thoroughly shaken, put in the thermostate and once more measured the following morning. Two further additions of hexylalcohol were measured in the same way. Table I gives the results of these measurements³⁾.

³⁾ From experiments in Part II of this series it appeared that for the 1.2% oleate system at or near to the KCl concentration of minimum damping $A \sim R$, which enables us to calculate λ , the relaxation time. This proportionality characteristic in the 1.2% oleate system is not lost if by various causes A is increased very considerably (e.g. with increase of temperature, see Part II, or the addition of hexylalcohol, see Part V). We have therefore assumed that this proportionality is still present in the 1.2% oleate system if A is increased considerably by changing the KCl concentration to other values than that of minimum damping, or by adding the various substances used in section 3 and 4, others than hexylalcohol. As this assumption is not entirely safe of course, we give in

TABLE I.

The elastic behaviour as a function of the KCl concentration and the influence of n hexylalcohol thereon.

KCl concentration mol/l	G (dynes/cm ²)				λ (sec.)			
	Hexylalcohol concentr. mol/l				Hexylalcohol concentr. mol/l			
	blank	0.0016	0.0042	0.0094	blank	0.0016	0.0042	0.0094
0.57	—	—	13.2	28.7	—	—	0.32	0.61
0.76	17.4	21.9	30.4	44.2	0.32	0.47	0.74	0.64
0.95	30.4	32.2	38.1	80.5	0.90	1.14	1.02	0.15
1.14	35.0	37.5	46.9	— *	1.58	2.00	0.88	— *
1.235	37.7	40.9	51.0	—	2.12	1.93	0.69	—
1.33	38.9	43.1	56.7	—	2.52	1.40	0.41	—
1.425	40.2	48.7	67.8	—	2.68	0.90	0.23	—
1.52	42.2	52.5	—	—	2.47	0.76	—	—
1.615	45.5	54.9	— *	—	1.32	0.63	— *	—
1.71	51.5	62.4	—	—	0.90	0.29	—	—
1.90	63.1	— *	—	—	0.30	— *	—	—

KCl concentration mol/l	$1/\Delta$				n			
	Hexylalcohol concentr. mol/l				Hexylalcohol concentr. mol/l			
	blank	0.0016	0.0042	0.0094	blank	0.0016	0.0042	0.0094
0.57	—	—	0.33	0.93	0	0	4.0	13.1
0.76	0.38	0.63	1.17	1.21	5.1	10.7	17.8	17.0
0.95	1.40	1.84	1.78	0.37	18.6	29.3	31.4	4.0
1.14	2.65	3.45	1.70	— *	39.8	41.4	27.2	— *
1.235	3.60	3.40	1.36	—	45.1	40.5	21.0	—
1.33	4.33	2.53	0.86	—	48.1	38.5	14.9	—
1.425	4.69	1.74	0.52	—	49.4	31.8	7.0	—
1.52	4.42	1.51	—	—	48.5	24.7	1.0	—
1.615	2.46	1.29	— *	—	38.3	18.9	— *	—
1.71	1.75	0.62	—	—	29.5	9.5	—	—
1.90	0.66	— *	—	—	12.2	— *	—	—

* First mixture in each column which shows coacervation.

We will first discuss the blank series (see fig. 1). The curves for λ (time of relaxation in sec.), $1/\Delta$ (the reciprocal value of the logarithmic decrement Δ), n (the number of oscillations visible through the telescope of the kathetometer) show a maximum at approximately 1.43 N KCl, and at this concentration the curve for G (shear modulus in dynes/cm²) shows an inflexion point (compare the vertical, dotted line B at 1.43 N KCl). On either side of this concentration the λ , $1/\Delta$ and n curves descend and, if extrapolated further downwards, reach the abscis axis at approximately

the following tables and figures besides the calculated values of λ the values for $1/\Delta$ as well to characterize the damping in every case. We also give n , i.e. the maximum number of observable oscillations, which, as will be discussed in section 5, gives an approximate measure of $1/\Delta$.

the two same KCl concentrations (0.63 and 2.05 N) indicated by the vertical, dotted lines A and C.

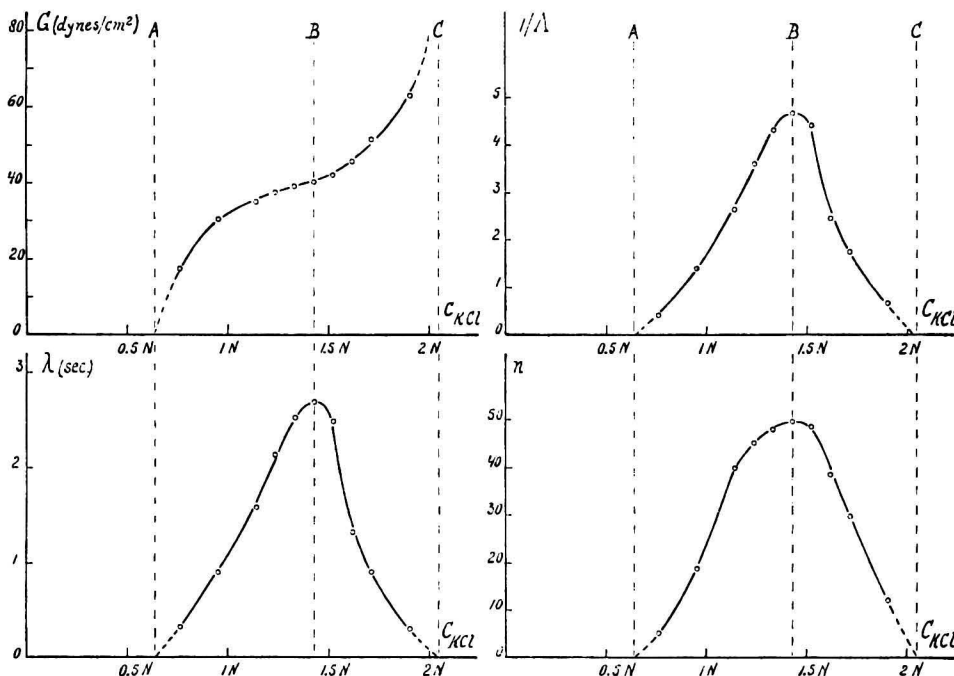


Fig. 1.

The latter of these KCl concentrations lies very near to the coacervation limit (at 2.00 N KCl not yet coacervation, at 2.09 N KCl coacervation). In the case of η we know from previous experiments that it indeed reaches the value zero just before the separation into two liquid phases (coacervate and equilibrium liquid) sets in (i.e. at slightly further increase of the KCl concentration). We may therefore say that the vertical, dotted line C indicates practically the coacervation limit.

If we now direct our attention to the G curve, we notice that it has quite another character than the λ , $1/\Delta$ or η curves. By increasing the KCl concentration G always increases, though transiently at a slower rate when nearing the KCl concentration of minimum damping (inflection point of the G curve).

It seems further probable that the G curve begins with the value zero at the KCl concentration, indicated by the dotted vertical line A and that the G curve still continues sloping upwards if the KCl concentration approaches the coacervation limit C. Any future theory of the elastic viscous oleate systems must be able to explain the characteristic shapes of the curves in fig. 1 as discussed above. For the present we do not yet wish to speculate on this matter, as we are convinced, that more facts should be known as described hitherto in this series of communications.

We now come to the influence of added hexylalcohol. Fig. 2 shows that n hexylalcohol displaces the G , λ , $1/\Delta$ and n curves. Let us consider this displacement more closely:

While retaining their character (curve with a maximum) the λ , $1/\Delta$ and n curves are displaced into the direction of smaller KCl concentrations. The height of the maximum decreases in case of displacement to the left,

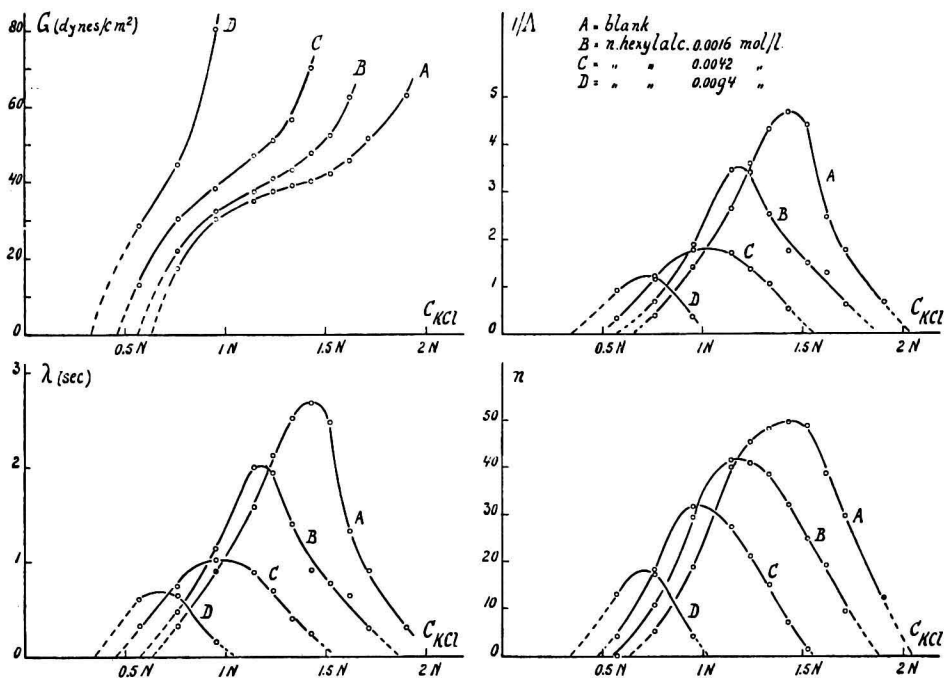


Fig. 2.

and the distance of the footpoints of these curves on the abscis axis grows smaller ⁴⁾.

When we consider the displacement of a characteristic point of these curves, viz. the maximum point, we see that it is displaced downwards to the left, which may be looked upon as to consist of a horizontal and vertical component (see fig. 3 scheme A, lower graph.)

The G curve (see fig. 2) while retaining its character of having an inflexion point is also displaced towards smaller KCl concentrations; besides it becomes steeper, in consequence of which the inflexion point becomes less marked.

When we consider the displacement of a characteristic point of this curve, viz. the inflexion point, (in practice determined by reading G at the KCl concentration of the maxima of the λ , $1/\Delta$ or n curves) we obtain

⁴⁾ The coacervation limit, which still practically coincides with the right footpoint of these curves, is therefore shifted to smaller KCl concentrations. See asterisks in Table I.

only a displacement in a horizontal direction⁵⁾ (see fig. 3 scheme A, upper graph.).

The above induces one to attribute a twofold action to the added hexylalcohol. In its presence smaller KCl concentrations are needed to set up the typical elastic viscous system (horizontal displacement of the inflexion point on the G curve and horizontal component of the displacement of the maximum point on the λ , $1/\Lambda$ and n curves), i.e. hexylalcohol facilitates the large scale associations of the soap molecules which we assume to be present in the elastic viscous system. The existence of a vertical component downwards in the displacement of the maximum point of the λ , $1/\Lambda$ and n curves, however, indicates that hexylalcohol at the same time influences these elastic structures in such a way that the damping is generally increased (without altering the shear modulus).

If for the two above actions of hexylalcohol different points of attack on the elastic structure are supposed, it may be conceived that there also exist substances, which, when added to the oleate system, share with hexylalcohol the general increasing influence on the damping, but which counteract KCl in setting up the elastic viscous system (compare fig. 3 scheme C). In between the two extreme schemes A and C of fig. 3 a

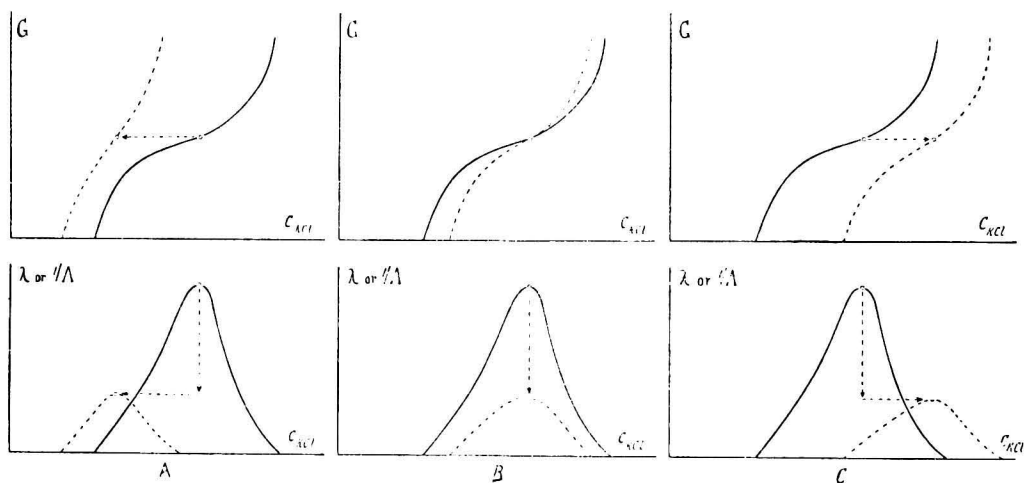


Fig. 3.

whole series of intermediate schemes may be conceived and half way it the scheme, indicated by B in fig. 3, represents a substance which neither helps nor counteracts KCl in setting up the elastic system. In the discussion of further experiments in this and following sections the schemes of fig. 3 will play a helpful rôle.

⁵⁾ At the KCl concentrations corresponding with the maxima of the λ , $1/\Lambda$ and n curves A, B, C and D, we read of the following values of G on the corresponding G curves A, B, C and D: 40.5, 39, 40 and 38 dynes/cm², which cannot with certainty be considered as really different.

We also investigated the influence of ethanol on G , λ , $1/\Delta$ and n in an analogous way as described above for the influence of n hexylalcohol.

We shall not give elaborate tables of the results but represent them graphically in fig. 4. When we compare this figure with fig. 3 we see that

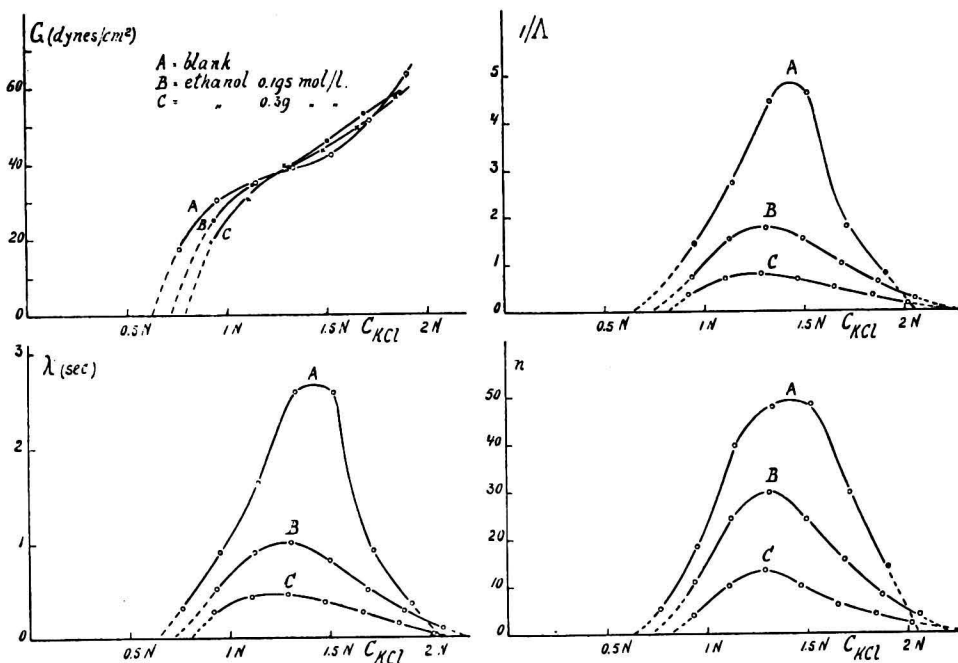


Fig. 4.

it greatly resembles scheme B. The following points show however, that it is not identical with it. In the first place the maximum points on the λ , $1/\Delta$ and n curves are not displaced downwards in the vertical direction only, but there is still a slight horizontal component of the displacement to the left.

Secondly, the G curves do not intersect at the KCl concentration corresponding to the minimum damping of the blank (1.43 N) but at lower concentrations (± 1.25 N).

Ethanol therefore corresponds to a case intermediate between the schemes A and B, which stands much closer to B than to A on account of the slight horizontal displacement to the left relative to the vertical displacement downwards.

We must further remark that ethanol shows another complication, which cannot be predicted from the simple schemes of fig. 3. If we direct our attention to the course of the λ , $1/\Delta$ and n curves at KCl concentrations above approximately 1.7 N, we perceive that those in the presence of ethanol cut the blank curve. Here the coacervation limit is shifted not to smaller KCl concentrations but to higher. A similar phenomenon is present in the course of the G curves above 1.7 N KCl. Those corresponding to systems to which ethanol has been added, tend now to cut the G curve of the blank. Both facts seem to

indicate that the action of ethanol still depends on the absolute value of the KCl concentrations. With concentrations up to ± 1.7 N ethanol is a substance which slightly helps KCl in building up the elastic system, with concentrations higher than ± 1.7 N it counteracts KCl slightly.

3) *Influence of the first six terms of the n . primary alcohols on the elastic behaviour of the 1.2 % oleate system at the KCl concentration of minimum damping.*

As our stock of Na oleicum medicinale pur. pulv. Merck was nearly exhausted and could not possibly be replenished, we decided to use for the experiments in this and the following section the large volume of oleate system, which had already served in previous experiments (on the dependence of T and Δ on R , see Part II of this series). It had the composition 1.2 g. oleate per 100 cc 1.52 N KCl + 0.08 N KOH, which electrolyte composition lies near to the minimum damping of the elastic oscillations. Eight spherical vessels of nominally 500 cc capacity (with radii varying from 5.01—5.04 cm) were exactly half filled with this system, put in the thermostate (15°) and measured the next morning.

Six of these vessels were used to determine the influence of the six alcohols, the seventh to control that the blank does not alter its properties with time and the eighth to ascertain part of the corrections to be applied to the experiments with methanol, ethanol and the highest concentrations of n propanol (cf. small print in section 1). We shall not give elaborate tables of the results, but represent them graphically in fig. 5. In this figure G , λ , $1/\Delta$ and n are given as functions of the logarithm of the alcohol concentration (the latter in moles/l).

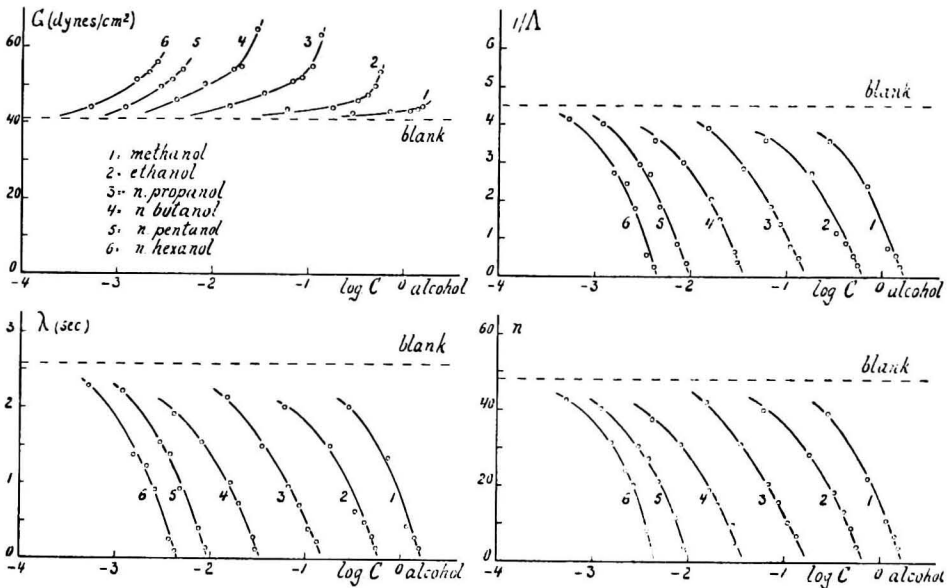


Fig. 5.

We see that all alcohols decrease λ , $1/\Delta$ and n , and increase G . In the case of methanol the increase of G is so slight however, that one may doubt if it surpasses the experimental errors (taking into account that here the greatest correction had to be applied, which of course diminishes the reliability of the actual augmentation of the G curve above the blank level).

In connection with what was said in section 2, we come to the conclusion that the shift to the left in horizontal direction of the inflection point on the G curve in fig. 1 diminishes in the order $6 > 5 > 4 > 3 > 2 > 1$, by which it is perhaps not excluded that 1 = methanol shows already a very slight shift to the right.

As we have investigated here (fig. 5) the action of the alcohols at the KCl concentration of minimum damping, λ , $1/\Delta$ and n can only decrease of course. Here too we have the same order of the curves as we had for G .

For a future theory of the action of n primary alcohols it is important that their action increases very considerably every time the alcohol is lengthened with one carbon atom. Below we give for instance the logarithms of the alcohol concentration corresponding to a decrease of λ , $1/\Delta$ and n to 50 % of its original value.

	n hexyl alcohol	n amyl alcohol	n butyl alcohol	n propyl alcohol	ethanol	methanol
λ	0.27-3	0.58-3	0.06-2	0.67-2	0.32-1	0.84-1
$1/\Delta$	0.32-3	0.63-3	0.15-2	0.74-2	0.34-1	0.85-1
n	0.35-3	0.64-3	0.12-2	0.73-2	0.37-1	0.84-1
mean logarithmic difference	0.31		0.49	0.60	0.63	0.50

The differences in the logarithms correspond (at least when going from methanol to amylalcohol) to ratios of approximately 3 or 4 (the logarithmic differences of two succeeding G curves is of the same order or even greater). This reminds us of the ratios occurring in TRAUBE's rule and suggests that the alcohol molecules exert their influence in the adsorbed state, and that in the latter state the carbon chain of the alcohol lies flat against certain either external or internal surfaces of the elastic soap structures.

4) *Influence of the fatty acid anions C_8-C_{14} on the elastic behaviour of the 1.2 % oleate system at the KCl concentration of minimum damping.*

Preliminary experiments showed that the viscous and elastic properties of the oleate systems containing KCl are not only sensitive to alcohols, but to a great many classes of organic non electrolytes as well, hydrocarbons included.

This sensitivity to organic non electrolytes of all kinds is also found in

the two phase (coacervate/equilibrium liquid) oleate systems, which are formed from the one phase elastic viscous oleate systems at a somewhat higher KCl concentration. The characteristic influence of organic non electrolytes manifests itself here in the change of the partial solubility of the two phases (at constant KCl concentration) and can be conveniently studied by measuring the shift of the coacervation limit (i.e. the KCl concentration which is just needed for the separation into two phases) ⁶⁾.

So far as our experience reaches and speaking very generally it appears that as regards the connection between constitution and action of organic non electrolytes analogous rules hold for both the one phase elastic viscous oleate systems and the two phase (coacervate/equilibrium liquid) oleate systems.

It was recently shown in our laboratory by H. L. BOOIJ that oleate coacervates are also sensitive to organic anions and that in the case of the fatty acid anions, the action of the same bound quantity depended in an unexpected way on the number of carbon atoms of the fatty acid anion ⁷⁾. From C_7 onward the coacervation limit is shifted to higher KCl concentrations, but this shift reaches a maximum value for undecylic acid (C_{11}) and diminishes thereafter very considerably (at C_{14} — C_{16}), to increase one more to approximately the level as reached with C_{11} if the hydrocarbon chain of the fatty acid anion is sufficiently lengthened (C_{20} — C_{22}).

To see if now again a parallel could be drawn between elastic oleate systems and oleate coacervates, we decided also to include in the present investigation the influence of a number of fatty acid anions (from C_8 — C_{14}) on the elastic properties of the 1.2 % oleate system at the KCl concentration of minimum damping. The method we followed was the same as in section 3 (half filled vessels of nominally 500 cc capacity 15°) and because a sufficient amount of KOH is present in the oleate system, we added known amounts of the fatty acids themselves (the terms with m.p. below room temperature as drops of known weight, the solid terms weighed amounts of the crystals). To accelerate the dissolution of the added acids, the vessels were agitated for 5 min. while immersed in a waterbath of 52°, the contents were thoroughly shaken then and the vessels replaced in the thermostate of 15° and the measurements made the next morning.

In order to check if this warming up of the oleate system has in itself no influence on the elastic behaviour after cooling down to 15° (though at the temperature of $\pm 45^\circ$ as was reached during the heat treatment the oleate system is no longer elastic) a spherical vessel half filled with a blank system was subjected to the same treatment for three consecutive

⁶⁾ H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN, these Proceedings 50, 1011 (1947).

⁷⁾ H. L. BOOIJ and H. G. BUNGENBERG DE JONG, *Biochimica Acta*, in press.

days. It was found that an influence exceeding the experimental errors could not be detected⁸⁾.

The results of these measurements are represented in fig. 6. In connection with the discussion in section 2 (c.f. fig. 3) it is easy to see that the results are compatible with the assumption that the lower fatty acid anions (C_8 — C_{11}) shift the G , the λ , the $1/\Delta$ and n curves of the blank in the reverse directions as hexylalcohol did in fig. 2. This assumption⁹⁾ explains why in fig. 6 the G curves for C_8 , C_9 , C_{10} and C_{11} bend downwards (in contrast to the G curves for the higher terms of the alcohols in fig. 5, which bend upwards). With the alcohols (fig. 5) any contrast in the course of the λ , $1/\Delta$ and n curves, which here (fig. 6) too only¹⁰⁾ bend downwards, is, however, not to be expected, since here too we started with a blank oleate system at the KCl concentration of minimum damping (see scheme C of fig. 3).

In the four diagrams of fig. 6 we notice that the action of the fatty acid anions increases in the order $C_8 < C_9 < C_{10}$.

We see, however, that C_{11} is slightly less or very slightly more active than C_{10} (c.f. 100 G/G_0 diagram and the remaining ones, respectively). The next term C_{12} is decidedly less active than C_{11} .

All this means, that for a same concentration of the fatty acid anions, the above mentioned shifts of various curves (G , λ etc. in fig. 3, scheme C) towards higher KCl concentrations do not increase indefinitely with the length of the carbon chain of the fatty acid anion, but that these shifts reach a maximum value at about C_{10} or C_{11} . A further lengthening diminishes this shift rapidly (C_{12}) and the characteristic property of the lower fatty acid anions is already lost at C_{14} . Obviously this anion (myristate-) resembles the oleate anion that much already, that it no longer counteracts the elastic structures built up by the KCl in the oleate system, but even positively contributes to the elastic properties of the oleate system. This positive contribution reveals from the strong increase of G , λ , $1/\Delta$ and n above the blank values, just as a further increase of the oleate concentration of the blank will also bring about.

⁸⁾ In the survey below four numbers are placed each time behind the symbols $10 \times \frac{T}{2}$, b_1/b_3 and n . They give the values found before the heat treatment, and after the first, the second and third heat treatment:

$$\begin{array}{l} 10 \times \frac{T}{2} : 5.60; 5.59; 5.59 \text{ and } 5.59 \text{ sec.} \\ b_1/b_3 : 1.248; 1.250; 1.247 \text{ and } 1.250 \\ n : 46.5; 46.6; 46.6 \text{ and } 46.8 \end{array}$$

⁹⁾ For the undecylate ion subsequent work has confirmed this assumption.

¹⁰⁾ We neglect here that the curves mentioned, first run in fig. 6 in the opposite direction and after reaching a maximum located some 6—10 percent above the blank value take the course discussed in the text. This curve form is to be expected if the KCl concentration in the blank oleate system (here 1.52 N) does not exactly correspond with the KCl concentration of the minimum damping (according to table I = 1.43 N) but is slightly higher.

When we summarize the result of the above measurements it appears that there is really a parallel with the action of the fatty acid anions on

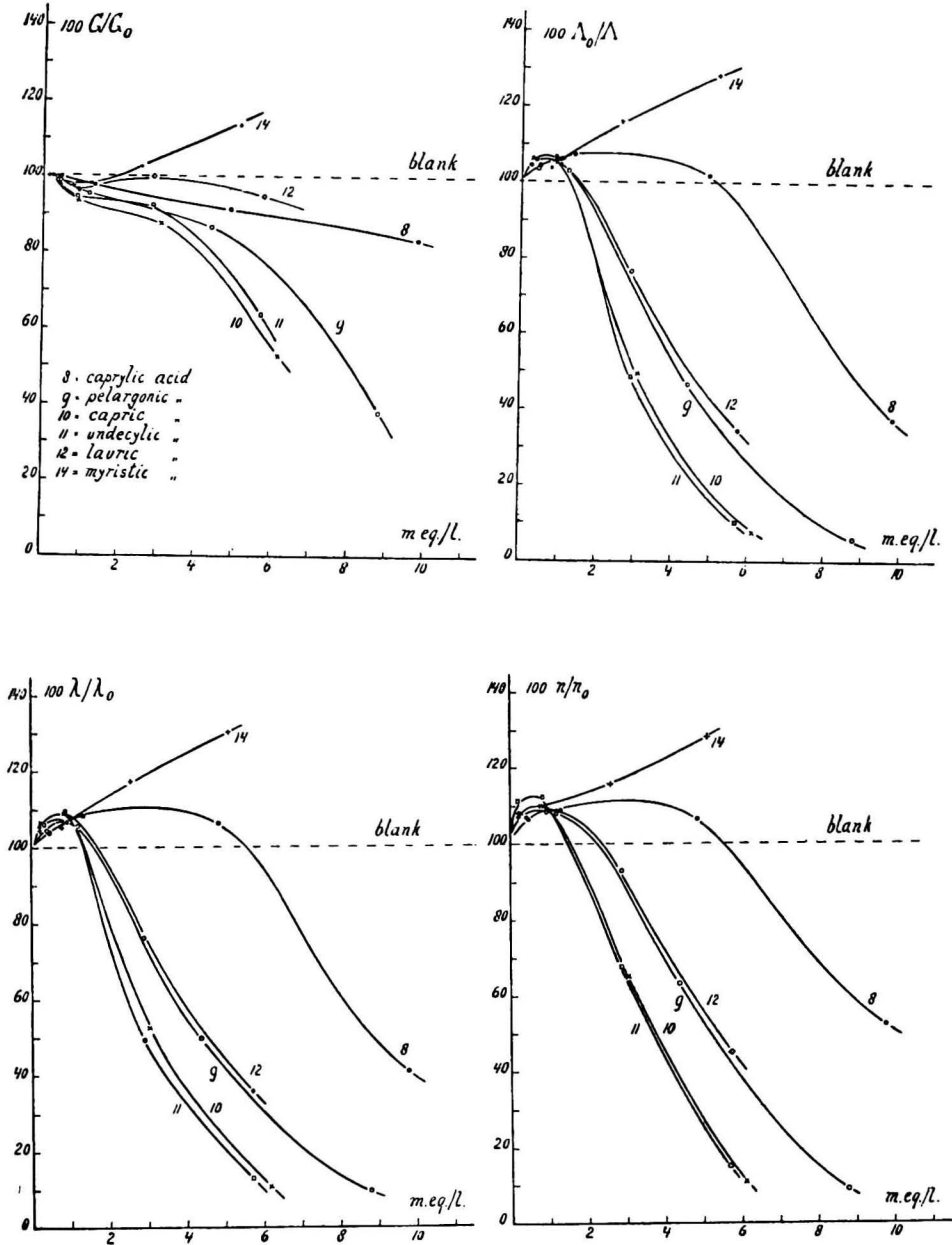


Fig. 6.

oleate coacervates, where the undecylate ion also takes an extreme position.

5) Correlation between n and Δ .

In the preceding Parts of this series, we have also inserted in many Tables referring to elastic measurements the values for n , i.e. the maximum number of observable oscillations (cf. already Part I, section 7, 9 and 10). An inspection of the above mentioned Tables will reveal that n decreases whenever Δ increases and reversely, but in none is the correlation between n and Δ a very simple one. In these Tables we considered the influence of the type of oscillation, the radius of the vessel, the temperature and the concentration of the oleate.

In the present communication, these four data are held constant while the KCl concentration is varied or when held constant small amounts of organic substances are added. Now the correlation between n and Δ is far much simpler and can be expressed very roughly speaking by $n \cdot \Delta = \text{constant}$.

To show this, we have inserted in the figures of this communication graphs in which the ordinates are n and $1/\Delta$ or $100 n/n_0$ and $100 \Delta_0/\Delta$.

It is true $n \cdot \Delta$ is not really constant so that the graphs for n/n_0 give a deformed picture of the graphs for Δ_0/Δ (see eg. fig. 1 and 2, and 4). Nevertheless the former give qualitatively the same details as the latter. Compare fig. 5 and especially fig. 6.

The above may be of practical importance, as it is not always easy to find an observer who is able to perform the difficult measurement of the decrement. In such a case the determination of the period and of the maximum number of observable oscillations can help to continue investigations of the type given in section 3 and 4, viz. those on the connection between the action of an organic substance and its structure.

Summary.

1) If the KCl concentration is increased the values of G , λ , $1/\Delta$ and n are very low (presumably zero) at the first appearance of elastic phenomena. The last three increase to a maximum and then decrease to zero just before the coacervation limit is reached. G increases in this whole tract of KCl concentrations. The G curve shows an inflexion point at the KCl concentration corresponding to the maxima of the λ , $1/\Delta$ and n curves.

2) The influence on the elastic behaviour of a number of n primary alcohols and of fatty acid anions has been studied and it appeared that the former (C_1-C_6) help the KCl in setting up the typical elastic viscous systems, the latter (C_8-C_{11}) counteract KCl in doing so.

3) The action of the alcohols increases considerably with increasing length of the carbon chain, each following term of the homologous series requiring for the same effect a 3—4 fold lower concentration than the preceding one.

4) The action of the fatty acid anions increases with the length of the carbon chain but this holds only up to C_{11} (undecylate), the action diminishes rapidly by further lengthening the carbon chain (C_{12}) and it has wholly disappeared in C_{14} .

5) For a certain type of work and under conditions described, the maximum number n of observable oscillations, may in emergency cases be used as an approximate measure of $1/\Delta$.

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