

Biochemistry. — *Elastic-viscous oleate systems containing KCl. III*¹⁾. *The elastic properties as a function of the concentration of the oleate at 15° C and constant KCl concentration.* By H. G. BUNGENBERG DE JONG and H. J. VAN DEN BERG.

(Communicated at the meeting of January 29, 1949.)

1. Introduction.

The methods of measurement applied in the investigations described in this paper are the same as used before.

The concentration of KCl has been chosen slightly below the one used in Part II, owing to the circumstance that in the meantime we have determined more accurately the concentration necessary for obtaining the minimum damping with the oleate used in our investigations (Merck, Na-oleinicum medicinale pur. pulv.). The concentration used in Part II differs very little from this optimum concentration, so that the slight change in the composition of the electrolyte (1,43 N KCl + 0,12 N KOH at present, as compared with 1,52 N KCl + 0,08 N KOH in Part II) does not materially affect a comparison of the results. Moreover, experimenting with a system having an oleate concentration of 1,2 % we again found the proportionality between T and R , and that between Δ and R .

The extension of the investigations to systems of lower concentration, however, has shown that Δ presents a wholly different behaviour when the concentration decreases below a certain limit.

2. Period and logarithmic decrement as functions of the oleate concentration at 15° C (rotational oscillation).

As starting point we used a standard solution containing 36 gr Na-oleate per litre, with 0,36 N KOH; from this solution 8 mixtures have been prepared according to the scheme:

a cm³ of standard solution
(200 — a) cm³ KOH 0,36 N
225 cm³ KCL 3,8 N
175 cm³ H₂O,

a being 200, 175, 150, 125, 100, 80, 60 and 40 cm³ respectively. The final concentration of KCL (1,43 N) and that of KOH (0,12 N) are the same in all mixtures; the oleate concentrations amount to 1,20; 1,05; 0,90; 0,75; 0,60; 0,48; 0,36; and 0,24 % respectively.

After heavy shaking for a sufficient time the mixtures were poured out into 8 round bottom vessels of nominally 500 cm³ capacities (the actual

¹⁾ Part I has appeared in these Proceedings 51, 1197 (1948); Part II in these Proceedings 52, 15 (1949).

capacities, measured up to the beginning of the neck, have been mentioned in Table I, together with the values of the radius R derived from them). The vessels were filled well into the neck, and were kept in a thermostat of 15°C during one night, in order to obtain the desired temperature and to get rid of air. The measurements took place in the usual manner on the following day. The results together with the values of $10 \times T/2$, corrected for the decrement, have been given in Table I²⁾ 3).

TABLE I.

Elastic properties as a function of the oleate concentration at 15°C measured in completely filled spherical vessels with radius of approx. 5 cm.

Capacity in cm^3	R in cm	Oleate concentr. in gr. per 100 cm^3	n	$10 \times \frac{T}{2}$ (sec)	b_1/b_3	Δ	$(10 \times \frac{T}{2})_{\text{corr.}}$	$\lambda = \frac{T}{2\Delta}$	$G_{\text{(dynes)}}$	ν for $R=5\text{ cm}$ $(= \frac{R}{10 \times \frac{T}{2}})$	$1/\Delta$
539	5.05	1.35	53.5	5.12	1.197	0.180	5.12	2.85	51.0	0.986	5.56
500	4.92	1.20	47.7	5.81	1.252	0.225	5.81	2.58	37.6	0.845	4.44
501	4.93	1.05	40.3	6.61	1.360	0.307	6.60	2.15	29.3	0.747	3.26
500	4.92	0.90	31.2	7.84	1.590	0.464	7.82	1.69	20.8	0.629	2.16
498	4.92	0.75	24.0	9.65	1.860	0.621	9.60	1.55	13.8	0.513	1.61
534	5.03	0.60	18.8	12.82	2.151	0.766	12.73	1.66	8.2	0.395	1.31
535	5.04	0.48	13.3	16.78	2.791	1.027	16.56	1.61	4.86	0.304	0.97
528	5.01	0.36	8.0	25.70	4.764	1.561	24.94	1.60	2.12	0.201	0.64
527	5.01	0.24 ⁴⁾	2.5	49.3	(47.1)	(3.85)	42.0	(1.09)	0.75	0.119	(0.26)

²⁾ With a view to the investigation of the behaviour of $T/2\Delta$ (see below), it was considered desirable to dispose of a system with an oleate concentration still higher than those obtainable according to the recipe given in the text. This system was prepared by taking 225 cm^3 of the standard solution, 225 cm^3 KCl and 150 cm^3 H_2O ; composition: 1.35 gr oleate per 100 cm^3 , 1.43 N KCl, 0.135 N KOH. Results referring to it have been given in the first line of Table I and in the first line of Table II. It was found that the values of ν , $1/\Delta$ and G for this system are in good accordance with the lines drawn in the figures 1 and 2.

³⁾ Professor BURGERS has pointed out that the formulae used for the derivation of the corrected value of the period (compare Part II, these Proceedings, p. 17) is valid only in those cases where the damping is due either to viscous resistance or to relaxation of the elastic stresses. It cannot be applied when the damping is a consequence of slipping. As relaxation certainly is operative with the more concentrated systems and some influence may persist also with systems of smaller concentration, we have provisionally applied the formula in all cases. The influence of the correction usually is small.

A calculation based upon the formula derived for the case where damping is due exclusively to slipping, will be given by BURGERS in the article following this communication, for the system having an oleate concentration of 0.6%. For systems with still smaller concentrations, which show very large values of Δ , there appears to remain an unsolved problem.

⁴⁾ With this system the decrement appeared to be very large, so that it had to be determined from the ratio b_1/b_2 . The value of b_1/b_3 given in the Table, has been calculated from that of b_1/b_2 ; the results, and also the values of Δ , $T/2\Delta$ and $1/\Delta$ have been put between brackets, as their reliability will be less than that of the other results.

When the reciprocal value of $(10 \times T/2)_{\text{corr}}$ is represented as a function of the oleate concentration, a practically straight line is obtained. As the radii of the 8 vessels are slightly unequal, it is necessary to correct for the differences; making use of the proportionality between T and R found before (and checked also with the systems used now), we reduced all values to the same radius $R = 5,00$ cm with the aid of the formula:

$$T = \frac{5}{R} \times T_{\text{corr}} = \left(10 \times \frac{T}{2}\right)_{\text{corr}} \cdot \frac{1}{R}, \text{ or } \nu = \frac{1}{T} = \frac{R}{\left(10 \times \frac{T}{2}\right)_{\text{corr}}}.$$

The reduced frequencies ν have been mentioned in the 11th column of Table I and are represented in fig. 1a as a function of the oleate concentration. It will be seen that *the frequency of the rotational oscillation for constant radius is a linear function of the oleate concentration.*

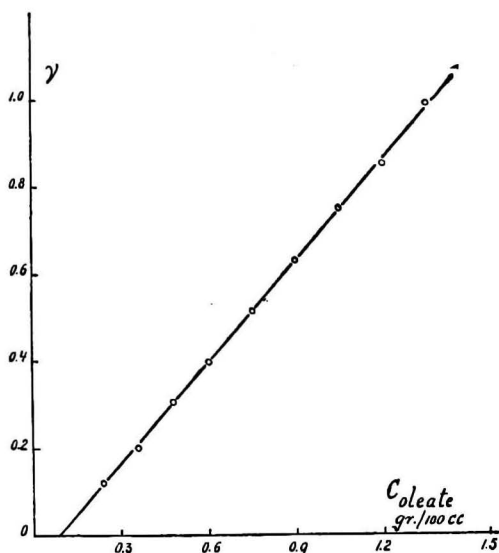


Fig. 1a.

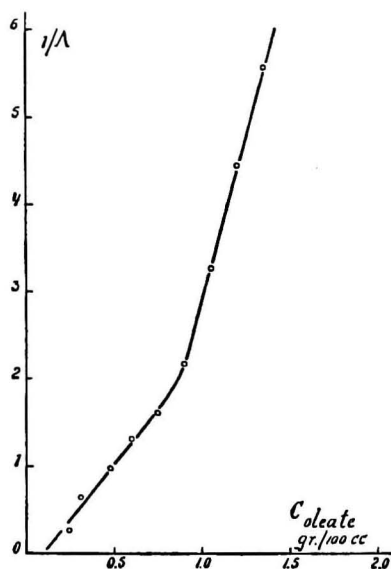


Fig. 1b.

If we may assume — what looks very probable — that the straight line can be extrapolated downward until it meets the horizontal axis, a point of intersection is obtained at an oleate concentration of 0,09 gr per 100 cm³ (approx. 3 millimol oleate per litre). Hence we can distinguish between two regions of oleate concentration: no elastic phenomena are found with a concentration in the region from zero to 3 millimol per litre; whereas elastic phenomena present themselves with concentrations exceeding 3 millimol per litre. — It will afterwards be seen that the second domain must still be subdivided.

We have further calculated the shear modulus G with the aid of BURGERS' formula ⁵⁾:

$$T_0 = \frac{2\pi}{4,99} R \sqrt{\frac{\rho}{G}},$$

taking $\rho = 1,072$. The results obtained have been given in column 10 of Table I. Making use of the result obtained for the frequency ν , we may at once write down the formula:

$$G \sim (\text{oleate concentration} - 0,09)^2.$$

This relation is illustrated in fig. 2, which gives the values of G as a

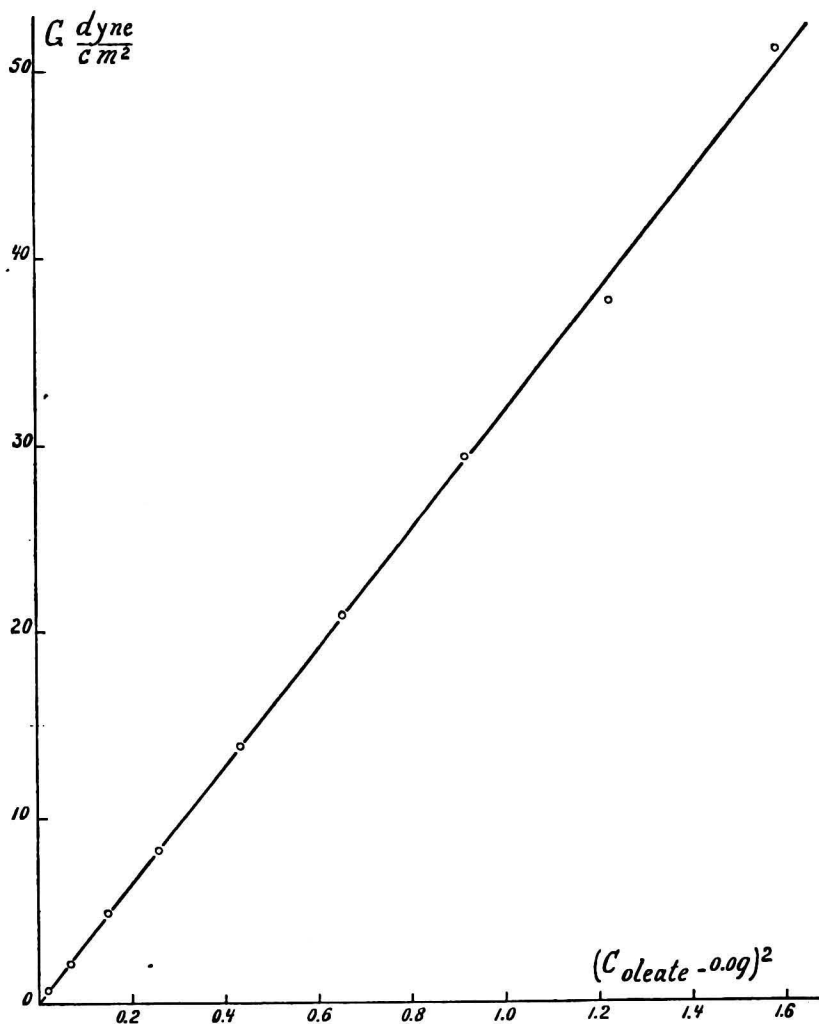


Fig. 2.

⁵⁾ J. M. BURGERS, Damped oscillations of a spherical mass of an elastic fluid, these Proceedings 51, 1211 (1948), eq. (17). — It should be noted that the quantity ν introduced by BURGERS has a different meaning from the one used here.

function of the square of (oleate concentration decreased by 0,09). The result undoubtedly will be of great importance for a future theory of the elastic oleate systems; however, at the present moment we will not bind ourselves to any assumptions concerning their internal structure.

The next point to be considered is the damping. When the value of $1/\Delta$ (column 12 of Table I) is represented as a function of the oleate concentration (fig. 1b), a curve is obtained with two branches, the lower branch presenting a similar character as the curve for ν given in fig. 1a. The experimental points are situated closely to a straight line, cutting the horizontal axis at the oleate concentration 0,09, so that the following relation appears to be valid for this branch:

$$1/\Delta \sim (\text{oleate concentration} - 0,09).$$

Provisionally assuming that the damping is caused by relaxation of the elastic tension — as had been proved in the case of the 1,2% system considered in Part II — we have calculated a nominal relaxation time $\lambda = T/2\Delta$ from our data. This quantity has been given in column 9 of Table I and is represented as a function of the oleate concentration in fig. 3 (full drawn curve, marked $R = 5$). At low concentrations (above 0,09) the curve exhibits a horizontal branch, as must be expected from what has been observed concerning the curves for ν ($= 1/T$) and $1/\Delta$. This horizontal part is followed by a markedly ascending branch.

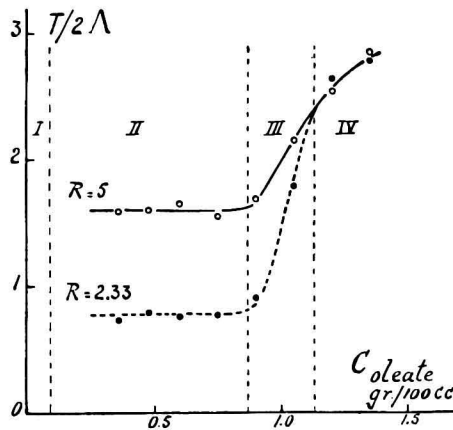


Fig. 3.

A few days afterwards measurements have been performed with the same series of oleate solutions in a vessel of radius $R = 2,33$ cm (the same vessel being used in all cases). The results have been collected in Table II. In the last column of this Table the frequencies have been reduced to a radius $R = 5,00$ cm. When represented as a function of the oleate concentration they give rise to a similar curve as that obtained from the data of Table I, although the values appear to be a few percent higher.

The corresponding differences in the values of G are somewhat larger, as is to be expected in view of the proportionality of G with ν^2 . This fact must be ascribed to a slight change within the system. What is much more interesting, however, are the values of $T/2\Delta$, which have been represented by the broken curve (marked $R = 2,33$) in fig. 3.

TABLE II.

Elastic properties as function of the oleate concentration at 15° C measured in a completely filled spherical vessel of 2.33 cm radius.

Oleate concentr. in gr per 100 cm ³	n	$10 \times \frac{T}{2}$ (sec)	b_1/b_3	Δ	$(10 \times \frac{T}{2})_{\text{corr.}}$	$\lambda = \frac{T}{2\Delta}$	$G_{\text{(dynes)}}$	ν for $R=5$ cm $(= \frac{R}{10 \times \frac{T}{2}})$	$1/\Delta$
1.35	59.3	2.28	1.085	0.082	2.28	2.78	54.8	1.022	12.2
1.20	50.7	2.57	1.102	0.097	2.57	2.64	43.1	0.907	10.3
1.05	43.4	3.00	1.182	0.167	3.00	1.79	31.7	0.767	5.98
0.90	34.2	3.64	1.488	0.398	3.63	0.91	21.6	0.642	2.52
0.75	24.8	4.49	1.790	0.582	4.47	0.77	14.3	0.521	1.72
0.60	20.8	5.86	2.182	0.781	5.82	0.76	8.4	0.400	1.28
0.48	14.2	7.68	2.608	0.959	7.59	0.79	5.0	0.307	1.04
0.36	9.0	11.48	4.581	1.522	11.16	0.73	2.29	0.209	0.66
0.30	7.0	15.52	6.751	1.910	14.88	0.78	1.29	0.157	0.52
0.24 ⁶⁾	5.0	20.32	(8.010)	(2.081)	19.30	(0.93)	0.77	0.121	(0.48)

It will be seen that the two curves, deduced from the data of Tables I and II respectively, nearly coincide at the higher concentrations. Going downward they separate, and in the domain of the lower concentrations two distinct, approximately horizontal lines are found, giving the average values: 1,60 (derived from the experiments with $R = 5$ cm) and 0,76 (derived from the experiments with $R = 2,33$ cm). The ratio of these numbers is $1,60/0,76 = 2,11$, which is almost the same as the ratio of the two radii, *viz.* $5,00/2,33 = 2,15$.

This result is very remarkable and stands in sharp contrast with that of the experiments described in Part II, which showed a relaxation time independent of the radius. We must conclude that with the lower concentrations the damping is due to a phenomenon of a different nature. It is of importance to consider this matter in more detail.

3. Period and logarithmic decrement of the 0,6 % oleate system as functions of the radius for the rotational oscillation.

In order to have at our disposal a sufficient quantity of oleate solution, we mixed a number of the mixtures already used in the preceding experiments, in such a way that the final mixture obtained (2,35 litres in all) had an oleate concentration of 0,6 %.

⁶⁾ Compare footnote 4).

In a single day we investigated the elastic behaviour as a function of the radius, in the way as has been described in Part II. The vessels used were of smaller dimensions (the largest having a capacity of 1,5 litre); the radii, calculated from the measured capacities, varied from 7,46 till 2,33 cm. This made it possible to perform all experiments with the aid of the turning table, all vessels being completely immersed in thermostate water of 15° C.

TABLE III.

Period and logarithmic decrement as function of the radius at 15° C (0,6% Oleate in 1,43 N KCl + 0,12 N KOH; rotational oscillation).

R (cm)	n	$10 \times \frac{T}{2}$ (sec)	b_1/b_3	Λ	$(10 \times \frac{T}{2})_{\text{corr.}}$	$G(\text{dynes})$	α
7.46	19.7 ± 0.2	19.12 ± 0.03	2.156 ± 0.019	0.768 ± 0.009	18.98 15.86 12.62 10.22 7.51 5.76	8.11 8.44 8.27 8.65 8.37 8.58	5.37 5.53 5.44 5.41 5.40 5.51
9.36	20.0 ± 0.3	15.98 ± 0.02	2.140 ± 0.024	0.761 ± 0.011			
5.01	19.8 ± 0.1	12.71 ± 0.02	2.141 ± 0.009	0.761 ± 0.004			
4.15	20.5 ± 0.3	10.30 ± 0.02	2.196 ± 0.023	0.787 ± 0.010			
3.00	20.4 ± 0.3	7.57 ± 0.02	2.173 ± 0.024	0.776 ± 0.011			
2.33	21.5 ± 0.2	5.81 ± 0.01	2.160 ± 0.028	0.770 ± 0.013			
} mean 0.770					} mean 8.40		} mean 5.44

The results of the measurements, together with the values of Λ and those of $(10 \times T/2)_{\text{corr.}}$ have been given in Table III. In fig. 4 these values have been represented as functions of the radius R . The same as with the system of 1,2 % oleate concentration, it is found that the period is directly proportional with R also for the 0,6 % system. The logarithmic decrement for the 0,6 % system on the contrary proves to be independent of the radius.

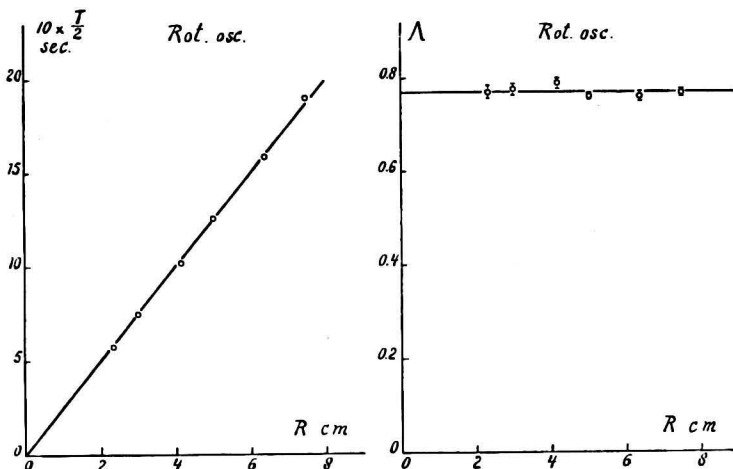


Fig. 4.

4. Comparison of periods and logarithmic decrements of the 0,6 % system as found for the three forms of oscillation.

In connection with the result just found BURGERS informed us that it would be of interest to have values of T and Λ for the three forms of oscillation, measured in one and the same vessel, so that R would be the same for all.

As the stock of Na-oleate (Merck Na-oleicum medicinale) had been used up, we had to use a preparation from a different source (Na-oleate, neutral powder, made by BAKER ⁷⁾). As we knew that there may always be found differences in the properties of various samples of Na-oleate (even when they are taken from two unopened bottles delivered by the same factory at the same time), and as we had no experience with the Baker preparation, it was considered desirable to perform measurements with two spheres, of radii $R = 5,62$ and $R = 2,99$ cm respectively. This would give an opportunity of checking whether the new material (having the same concentration of 0,6 % Na-oleate in 1,43 N KCl + 0,12 N KOH) likewise would show the proportionality between T and R , with Λ independent of R .

The method applied was the same as used before, but a slightly different way of exciting the rotational and the quadrantal oscillations was chosen. The principle is the same as with the turning table, but the vessels are clamped about the neck in the centre of a ball bearing, in such a way that they are hanging well until the neck in the thermostate water of 15° C. The measurements have been executed in one consecutive series in a single day. The results are given in Table IV.

The first point to be considered is whether the new preparation exhibited a similar behaviour as the old one. This does not primarily refer to the absolute values of T and Λ for the same radius, which indeed appear to

TABLE IV

Comparison of period and logarithmic decrement of the 0.6% oleate system for the three forms of oscillation.

R (cm)	Type of oscillation	n	$10 \times \frac{T}{2}$ (sec)	b_1/b_3	Λ	$(10 \times \frac{T}{2})_{\text{corr.}}$	$\frac{T}{2\Lambda}$	G	α
5.62	Rotational	24.9 ± 0.2	10.70 ± 0.01	1.696 ± 0.016	0.528 ± 0.009	10.66 ± 0.01	2.02	14.6	10.5
	Meridional	24.7 ± 0.1	8.21 ± 0.02	1.498 ± 0.009	0.404 ± 0.006	8.19 ± 0.02	2.03	15.0	10.8
	Quadrantal	24.4 ± 0.3	6.81 ± 0.02	1.407 ± 0.012	0.342 ± 0.009	6.80 ± 0.02	1.99	14.8	10.5
							mean 2.01	mean 14.85	mean 10.8
2.99	Rotational	28.2 ± 0.1	5.63 ± 0.02	1.677 ± 0.017	0.517 ± 0.010	5.61 ± 0.02	1.09	14.9	10.8
	Meridional	25.8 ± 0.1	4.39 ± 0.02	1.494 ± 0.022	0.402 ± 0.015	4.38 ± 0.02	1.09	14.9	10.8
	Quadrantal	27.4 ± 0.1	3.61 ± 0.02	1.382 ± 0.008	0.324 ± 0.006	3.60 ± 0.02	1.11	14.9	11.1
							mean 1.10	mean 14.85	mean 10.8

⁷⁾ As it was impossible to buy Na-oleate from MERCK, we have directed ourselves to the Rockefeller Foundation, which kindly put at our disposal a large quantity of the preparation mentioned in the text in order to make possible the continuation of our researches on oleate systems. We are glad to express our great thanks for this help.

be different ⁸⁾, but rather to the functional relations between T and R , and between Λ and R . For this purpose we have represented the values of $T_0, T_1, T_2; \Lambda_0, \Lambda_1, \Lambda_2$ as functions of R in fig. 5. The diagram proves that indeed a state of the oleate system is present, fully comparable to that which was found in our former measurements.

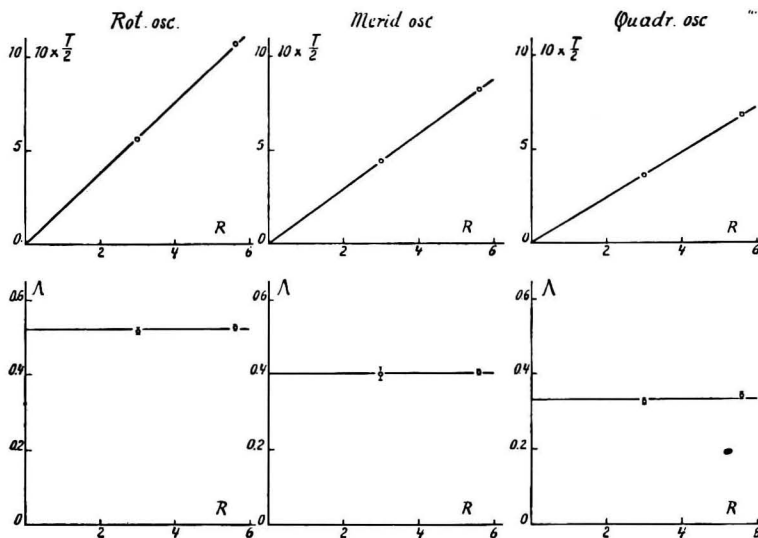


Fig. 5.

The quantity $T/2 \Lambda$ consequently cannot be interpreted as a relaxation time, as it appears to be different for the two radii. The ratio of the values obtained (average value for the three forms of oscillation) differs from the quotient of the radii by not more than 2% ($2,01/1,10 = 1,84$; $5,62/2,99 = 1,88$). As T proved to be proportional to R , this means that for a given form of oscillation Λ is independent of R . Inspection of the data given in column 6 of Table IV shows that for the rotational oscillation, considered separately, the ratio differs from that of the radii by 2%; for the meridional oscillation the difference is 1%; while for the quadrantal oscillation it is slightly larger, viz. 5%. But we know from our former work (see Parts I and II) that with the latter type of oscillations the accurate measurement of the damping is very difficult. When now again we calculate the ratios of the periods and of the logarithmic decrements, obtained for the various types of oscillation, the

⁸⁾ When the data referring to the rotational oscillation, given in Table IV, are compared with those given in Table III for the same radius, it appears that the new preparation obtained from BAKER has both a smaller period and a smaller logarithmic decrement. The new preparation consequently has a larger shear modulus and a smaller damping. In conformity with the experience related in Parts I and II that n increases when the damping becomes smaller, it was found that the new preparation showed larger values for n .

following numbers are found:

$$\begin{array}{l}
 R = 2,99 \text{ cm} \\
 R = 5,62 \text{ cm}
 \end{array}
 \left.
 \begin{array}{l}
 T_0/T_1 = 1,281 \\
 A_0/A_1 = 1,286 \\
 T_0/T_1 = 1,302 \\
 A_0/A_1 = 1,307
 \end{array}
 \right\}
 \begin{array}{l}
 \text{mean} \\
 1,294
 \end{array}
 \quad
 \begin{array}{l}
 T_0/T_2 = 1,558 \\
 A_0/A_2 = 1,596 \\
 T_0/T_2 = 1,568 \\
 A_0/A_2 = 1,544
 \end{array}
 \left.
 \right\}
 \begin{array}{l}
 \text{mean} \\
 1,567
 \end{array}$$

If the fluctuations of the ratios are left out of account (having regard to the mean errors of the individual determinations these fluctuations on the whole are within the possible errors), we may conclude that there are to be found only two distinct ratios, one referring to T_0/T_1 and A_0/A_1 , the other one referring to T_0/T_2 and A_0/A_2 . The averages obtained for these two ratios are 1,294 and 1,567 respectively, which values differ by not more than 1 % from the values 1,283 and 1,557 predicted theoretically for the periods on the basis of BURGERS' formulae.

5. *The nature of the damping in the 0,6 % oleate system.*

After the measurements described in sections 3 and 4 had been finished, professor BURGERS informed us that all results obtained with the 0,6 % oleate system could be explained if it be assumed that the damping is a consequence of slipping of the elastic system along the wall of the vessel. In this case we have the following formulae ⁹⁾:

$$T = \frac{2\pi R}{\beta} \sqrt{\frac{\rho}{G}}; \quad \Delta = \frac{2\pi}{\beta} \frac{\sqrt{G\rho}}{\kappa}.$$

where κ is a coefficient characterising the friction experienced in slipping, while the factor β is a numerical quantity, having the well known values 4,49 for the rotational oscillation, 5,76 for the meridional oscillation and 6,99 for the quadrantal oscillation respectively. The formulae show that for every type of oscillation the period is proportional to the radius, whereas the logarithmic decrement is independent of it; moreover, when we pass from one type of oscillation to another type, both period and decrement change in the same ratio, so that there is full conformity with the experimental results for the 0,6 % oleate system. — The values of G and κ calculated with these formulae have been given in the final two columns of Tables III and IV. It is found that the preparation obtained from Baker gives higher values both for G and for κ , than the preparation obtained from Merck ¹⁰⁾ ¹¹⁾.

⁹⁾ See J. M. BURGERS, paper quoted in footnote ⁵⁾ above, eq. (18).

¹⁰⁾ When G has already been calculated, it is possible to obtain κ from the relation $\kappa = TG/\Delta R$, which is an immediate consequence of the formulae for T and Δ given in the text.

¹¹⁾ As mentioned already in footnote ³⁾ above, BURGERS has recalculated the values for the 0.6% systems with the equations given in the article following this communication (Note on the damping of the rotational oscillations of a spherical mass of an elastic fluid in consequence of slipping along the boundary, these Proceedings p. 113).

6. *The frictional coefficient operative in slipping as a function of the oleate concentration.*

According to fig. 3 the nature of the damping appears to present the same character as that found with the 0,6 % oleate system, for a series of concentrations which extend upward to approximately 0,9 %. If we apply the formulae mentioned in the preceding section to all systems of Tables I and II with concentrations not exceeding 0,9 %, a series of values of the coefficient κ is obtained, which shows a marked decrease of κ with decreasing concentration, as will be evident from Table V¹²⁾.

TABLE V.

Frictional coefficient operative in slipping as function of the oleate concentration.

Oleate concentration in gr. per 100 cm ³	From the data of Table II		From the data of Table II	
	κ	$\kappa/(C_{\text{oleate}} - 0.09)^2$	κ	$\kappa/(C_{\text{oleate}} - 0.09)^2$
0.90	14.25	21.7	16.91	25.8
0.75	8.67	19.9	9.43	21.6
0.60	5.42	20.8	5.37	20.6
0.48	3.11	20.5	3.39	22.3
0.36	(1.35)	(18.5)	(1.44)	(19.8)
0.30	—	—	(0.86)	(19.5)
0.24	(0.33)	(14.5)	(0.61)	(27.1)

It is found that the quotient of κ by the square of (oleate concentration — 0,09) presents values which may be considered as approximately constant (having regard to all errors inherent to the measurements). The numbers referring to the lower concentrations and put in brackets are not

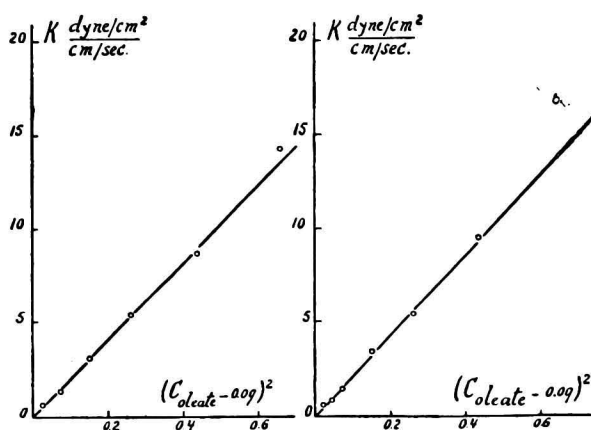


Fig. 6.

¹²⁾ The calculations on which are based the values of κ given in Table V, are all made with the aid of the first order formulae mentioned in the preceding section, as obtained by BURGERS in his first article.

reliable, owing on one hand, to difficulties in the measurement of Δ and on the other hand, to the fact that the theory given by BURGERS cannot explain values of Δ exceeding approx. 1,06. — The fact that the value obtained with the concentration of 0,9 % seems to be somewhat in excess, may be an indication that we ought to limit our domain at a slightly lower value, approx. 0,87 %, as is proved also by the position of the bend in the curve for $1/\Delta$, given in fig. 1 B.

For the rest of the domain one gets the impression that the relation:

$$\kappa \sim (\text{oleate concentration} - 0,09)^2$$

is rather satisfactory (compare fig. 6). The relation between κ and concentration would then be the same as that between G and concentration, given in section 2.

7. Distinction of a number of domains of oleate concentration.

We return to the consideration of the dependence of the elastic properties on the oleate concentration.

In the first place it is of importance to delimit the domain in which the behaviour corresponds to that found with the 0,6 % system (T proportional with R and Δ independent of R). In fig. 3 this domain is characterized by the two distinct horizontal curves for $T/2\Delta$. It has been found that this domain extends upwards to an oleate concentration of approx. 0,87 % (ca. 29 millimol per litre). Downward it extends at least to 0,3 % (ca. 10 millimol per litre). The values derived with a concentration of 0,24 % must be considered as unreliable, and we cannot check whether $T/2\Delta$

Domain	Concentration in gr oleate per 100 cm ³	Dependence of T and Δ on the radius for constant oleate conc.	Ratios for T and Δ at constant radius and constant oleate concentration	Dependence of G , κ and λ on oleate concentration
I	0 — 0.09	$\nu = 1/T = 0$		$G = 0$
II	0.09 — 0.87	$T \sim R$ Δ independent of R $T/2\Delta \sim R$ $T/\Delta R = \kappa/G$ independent of R	$\frac{T_0}{T_1} = \frac{A_0}{A_1} = 1.28$ $\frac{T_0}{T_2} = \frac{A_0}{A_2} = 1.56$	$G \sim (C_{ol} - 0.09)^2$ $\kappa \sim (C_{ol} - 0.09)^2$
III	0.87 — 1.1	$T \sim R$		$G \sim (C_{ol} - 0.09)^2$ with same factor as in II
IV	1.1 — 1.35 (possibly extending further)	$T \sim R$ $\Delta \sim R$ $T/2\Delta = \lambda$ independent of R	$\frac{T_0}{T_1} = \frac{A_0}{A_1} = 1.28$ $\frac{T_0}{T_2} = \frac{A_0}{A_2} = 1.56$	$G \sim (C_{ol} - 0.09)^2$ with same factor as in II λ increasing with oleate concentration.

remains the same until the limiting concentration of 0,09 % (ca. 3 millimol per litre). Nevertheless as a provisional assumption we may suppose this to be the case.

At the highest concentrations investigated (1,2 % and 1,35 %) the quantity $T/2 \Delta$ has the meaning of a relaxation time. This domain appears to extend downward until a concentration of approx. 1,1 %. Between 0,87 % and 1,1 % there is a transition region.

In this way we arrive at the four domains given in the survey.

It should be kept in mind that the limits between these domains, determined at a temperature of 15° C with a given concentration of KCl etc., may be functions of various parameters, including the purity of the oleate used.

Summary of Part III:

1) An investigation of the elastic properties as a function of the oleate concentration (with constant concentration of KCl and at a temperature of 15° C) has shown that:

- a) the frequency of the rotational oscillation in completely filled spherical vessels of constant radius is a linear function of the oleate concentration, becoming zero at a concentration of 0,09 % (3 millimol oleate per litre);
- b) the elastic shear modulus is proportional to (oleate concentration — 0,09)²;
- c) the quantity $T/2 \Delta$, which has the meaning of a relaxation time in the case of the 1,2 % oleate system, loses this meaning when the concentration decreases below 0,9 %.

2) In order to arrive at a more complete characterization of the elastic behaviour of oleate systems in the domain mentioned sub 1 c), the following problems have been investigated with the 0,6 % oleate system:

- a) Period and logarithmic decrement as functions of the radius of the spherical vessel; it appeared that the period is proportional to R , while the logarithmic decrement was independent of it;
- b) period and logarithmic decrement as functions of the type of oscillation (rotational, meridional, quadrantal); it appeared that the quotients T_0/T_1 and Δ_0/Δ_1 had the value 1,28, the quotients T_0/T_2 and Δ_0/Δ_2 the value 1,56, the same as was the case with the oscillations damped in consequence of relaxation.

The results mentioned sub a) and b) are in conformity with a theoretical case, treated by J. M. BURGERS, referring to the oscillations of an elastic medium slipping along the walls of the spherical vessel.

- 3) It is possible to distinguish four domains of the oleate concentration:
 - (I) from 0 to 0,09 %, in which elastic phenomena are absent;
 - (II) from 0,09 % until 0,87 %, where Δ is independent of R ;

(III) from 0,87 % until 1,1 %, in which the relation between A and R changes in character;

(IV) above 1,1 % where $A \sim R$.

4) The quantities G and either λ or κ are functions of the oleate concentration:

a) in the domains II, III and IV a single formula

$$G \sim (c_{o1} - 0,09)^2$$

is obtained;

b) the relaxation time λ , characteristic for the damping in domain IV, increases with the oleate concentration;

c) the frictional coefficient κ , operative in slipping in domain II, presents the same dependence on the concentration as G : $\kappa \sim (c_{o1} - 0,09)^2$.