CHEMISTRY

ELASTIC VISCOUS OLEATE SYSTEMS CONTAINING KCl. XIV [1])

a) The problem of the character of the damping in the 0.6 % *oleate system.*
b) Rotational oscillations characterized by the second, third, - - - - - roots of the equation tg $\zeta = \zeta$.
c) The linear displacement in the equator plane of the sphere as a function of the distance from the centre.

BY

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(Communicated at the meeting of September 30, 1950)

1. *Introduction*

In the present investigation we will study both with the 0.6 % and the 1.2 % oleate system the elastic deviation in the equator plane of the sphere as a function of the distance from the centre.

In part III of this series we found that the damping of the elastic oscillations is of a different character in the 1.2 % oleate system (Λ proportional to R) and in the 0.6 % oleate system (Λ independent of R). As J. M. BURGERS [3]) has shown theoretically, a (small) slipping of the elastic system along the wall of the vessel might give an explanation of the fact that Λ is independent of R.

Though in part III of this series a number of quantitative consequences of this supposition could be confirmed, later on (see part VIII of this series) doubt arose as to the real existence of slipping in the 0.6 % oleate system. The lack of data which give information on the magnitude of the expected slipping along the wall is a drawback for further experimental investigations. In a letter to the authors, J. M. BURGERS was so kind to send us the following informations:

"Values of $r\Phi$, in which

$$\Phi = \frac{\sin \zeta r}{(\zeta r)^3} - \frac{\cos \zeta r}{(\zeta r)^2} \, .$$

*) Aided by grants from the "Netherlands Organisation for Basis Research (Z.W.O.)".

1) Part I has appeared in these Proceedings 51, 1197 (1948), Parts II—VI in these Proceedings 52, 15, 99, 363, 377, 465 (1949), Parts VII—XIII in these Proceedings 53, 7, 109, 233, 743, 759, 975, 1122 (1950).

2) Publication no. 10 of the Team for Fundamental Biochemical Research (under the direction of H. G. BUNGENBERG DE JONG, E. HAVINGA and H. L. BOOIJ).

3) J. M. BURGERS, these Proceedings 51, 1211 (1948) and 52, 113 (1949).

The radius R of the sphere has been taken 1, as a consequence of which $a = \zeta$.

	$\Lambda = 0$ $\zeta = 4.493$	$\Lambda = 0.523$ $\zeta = 4.561 + 0.380\,i$	$\Lambda = 0.770$ $\zeta = 4.658 + 0.570\,i$
r	$100\,r\,\Phi$	$100\,r\,\Phi$	$100\,r\,\Phi$
0	0		
0.1	3.27		
0.2	6.14		
0.3	8.30		
0.4	9.50	9.42	
0.5	9.65	9.52	9.36
0.6	8.77	8.63	
0.7	7.08		
0.8	4.81	4.77	4.68
0.9	2.34	2.67	3.01
0.95		1.97	2.67
1.00	0	1.83	2.75

Φ can not become zero for real values of r if ζ has a complex value."
Compare figure 1, which gives the above values of $r\Phi$ as a function of r.

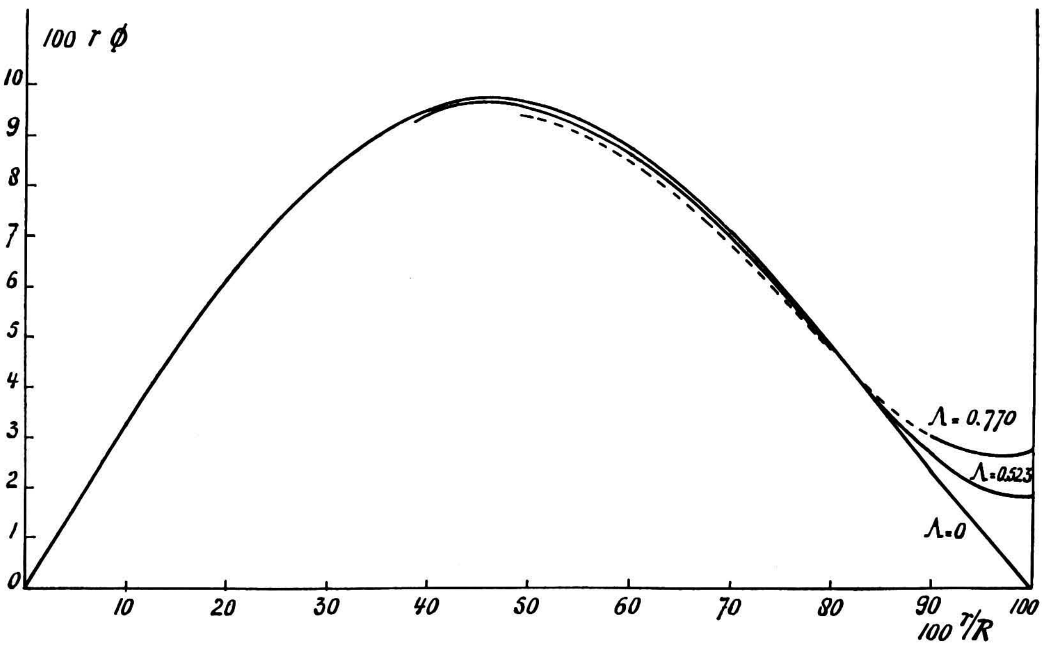

Fig. 1

2. *Methods*

As an oleate preparation we used K-oleate, prepared from chemically pure oleic acid and Na-oleate, neutral powder, from BAKER [4]) (for remarks

[4]) A generous gift of Na-oleate from the ROCKEFELLER Foundation provided the means for the experiments described in this paper.

on these preparations see part X and XIII). The experiments have been performed at room temperature (17—18°), using 0.6 % and 1.2 % oleate systems containing (besides at all times 0.05 N KOH) K_3-citrate or KCl in a concentration which corresponds to the minimum damping of the elastic oscillations (with chemically pure K-oleate: KCl = 0.98 N; with oleate from BAKER: K_3-citrate = 0.52 moles/l, KCl = 1.05 moles/l; compare part XIII of this series).

Our intention was to investigate the elastic deviations in the equator plane of a spherical vessel. Of course it would be ideal to use completely filled vessels, but than we see no way to mark the elastic system in the equator plane satisfactorily. If we use, however, exactly half filled vessels (the period of the rotational oscillation is then practically that of a completely filled spherical vessel; see part I, section 2, part VI, section 1), we have the equator plane automatically and the oleate system can in principle be marked just below this plane with the aid of the electrolytic H_2 mark described in part X. To do this, it will of course be necessary not to use the intact spherical vessels as containers for the elastic system, but to remove beforehand the upperpart of them (cut off at 3—4 mm above the equator plane).

It has appeared that when the cathode is slowly moved in a straight line through the centre we can now obtain a very satisfactory "line" of minute H_2-bubbles just beneath the surface (for further particulars see below). With appropriate illumination this track of H_2-bubbles stands out as a bright white line (of approximately 0.5—1 mm thickness) on a relative dark (citrate containing systems) or greyish (KCl containing systems) background. As the visibility of the line becomes less with time and finally vanishes altogether (gradual coalescence of the minute H_2-bubbles to bigger ones and breaking of the bubbles through the interface oleate system/ air) the photographic registration of the oscillating system must be performed soon after the marking (owing to the much higher viscosity of the 1.2 % oleate system, the line persists longer here than with the 0.6 % oleate system).

The apparatus which is used to bring the oleate system in resonance and to provide for intermittent illumination at the moments of largest elastic deviations, is given in the figs 2 and 3. Fig. 4 gives the device with which the line of H_2-bubbles is drawn.

In fig. 2 the frame, which is constituted of hook-iron, is only given by dotted lines. The cup-like half sphere *a* filled with the oleate system rests on the edge of a wide hollow cylinder *b*, which is attached to disk *c*. Connected to this disk is the axis *d*, supported by the ball-bearings *e* and *f* in the iron plates *g* and *h*. Disk *i* serves to connect the triangular rocker arm *j* (constituted of two bars *k* and *l*, joined together at one end *m*). The connecting bar *n* has ball-bearings *o* and *p* at either end. A pin in ball-bearing *o* is fixed in the hole at the end *m* of the rocker arm *j* by means of screw *q*. A pin fixed in ball-bearing *p* is connected with the middle of bar *r* (of quadratic cross-section). This bar can be moved and fixed in the desired position in the slot (also of quadratic cross-section) of bar *u* by the screws *s* and *t*. Bar *u* is fixed to the disk *v*, which latter is connected by a ball-bearing to the iron plate *x*.

An electric gramophone motor (not designed in the figure) fed by direct current and provided with an adjustable friction brake, rests with a rubber coated pulley against the edge of disk *v*. The frequency of rotation of disk *v* can be regulated by

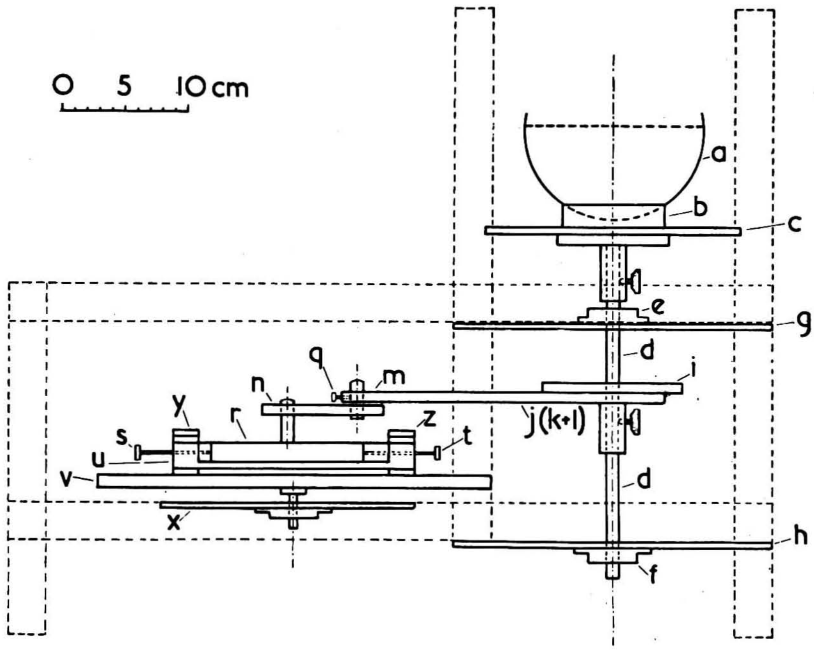

Fig. 2A

the friction brake and, for small changes of the frequency, by adjusting the e.m.f. of the direct current (taken from a stabilized rectifier). The excentricity of the pin on bar *r*, in relation to the axis of rotation of disk *v*, can be regulated by the screws *s* and *t*. As a rule we adjusted it so that cup *a*, containing the oleate system, swings to and fro over an angle of 1° or less. As the connecting rod is about

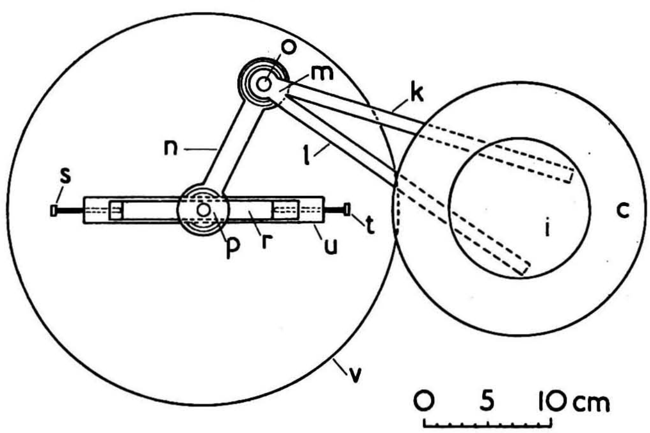

Fig. 2B

30 times (or more) as large as the exentricity which is used, the cup can be considered to swing practically sinussoidal.

The contact strips y and z are fastened to bar u, but they are isolated from it by interposed ebonite plates. They play a role with the repeated intermittent illumination which was used to take photographs of the white track of H_2-bubbles at the moments of largest deviation. Because of contact with two suitably placed contact springs the illumination current is closed at each half rotation of disk v (a 220 volt current was used and 110 volt incandescent lamps). Compare fig. 3, in which many details of fig. 2 have been left out. An iron strip, the cross-section of which is shown in the fig. 3 at a, is attached to the iron-frame above disk v. It carries the bar b, which can be turned round an axis which coincides with the rotation axis of disk v and thus be fixed in the desired position. At one end bar b carries a brass tube c, which serves to adjust the thin brass bar d in the desired

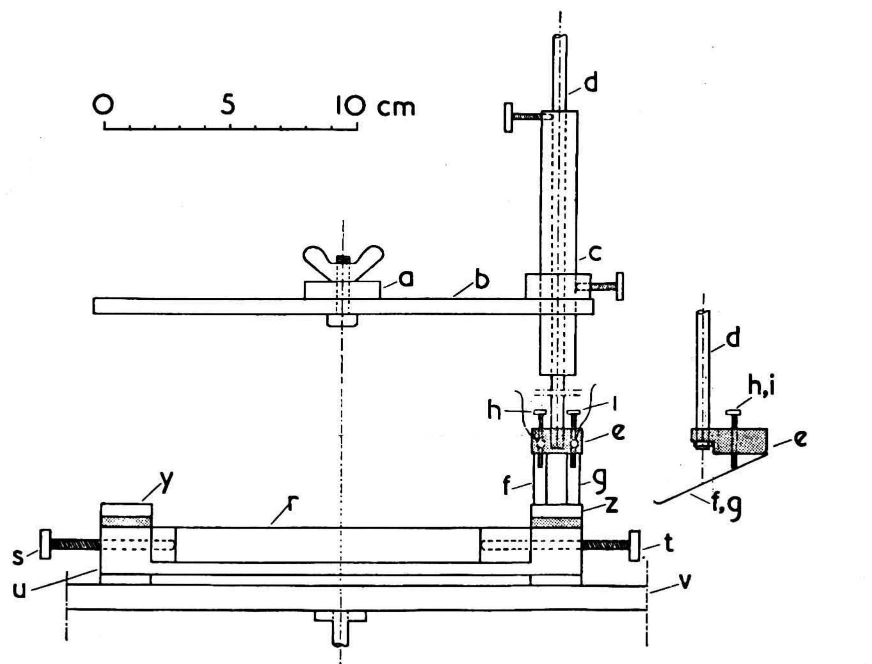

Fig. 3

position. At the lower end of d a hard rubber plate e is fixed. Two contact springs f and g, which are adjustable by the screws h and i are attached to this plate. The springs are connected to wires (not shown in the figure) which are part of the illumination circuit. Each time the contact strip y or z passes underneath the springs, the current is closed.

Because, at resonance of the excited rotational oscillations there will be a phase difference of approximately 90°, bar b is turned and fixed in such a position, that contact is made just at the zero deviation of the exciting oscillation. The photographs will then show the maximum deviations of the oleate system in both directions, whereas the swinging glass vessel is then always at the same position of zero deviation.

For direct observation of the elastic deviations through the telescope of a kathetometer, but also for taking photographs with intermittent illumination, a mirror, under an angle of about 45°, can be placed above vessel a in fig. 2. To support this mirror two of the four vertical hook-iron bars which belong to the frame and are placed around the axis *d*, are longer, namely the left one at the foreside and the right one at the backside. Clamps, the details of which are not given in the figure, allow to fasten the axis to which the mirror is fixed and to adjust its inclination.

The mirror can easily be removed and this must be done for the electrolytic marking of the oleate system. Its place must then be taken by a contrivance which

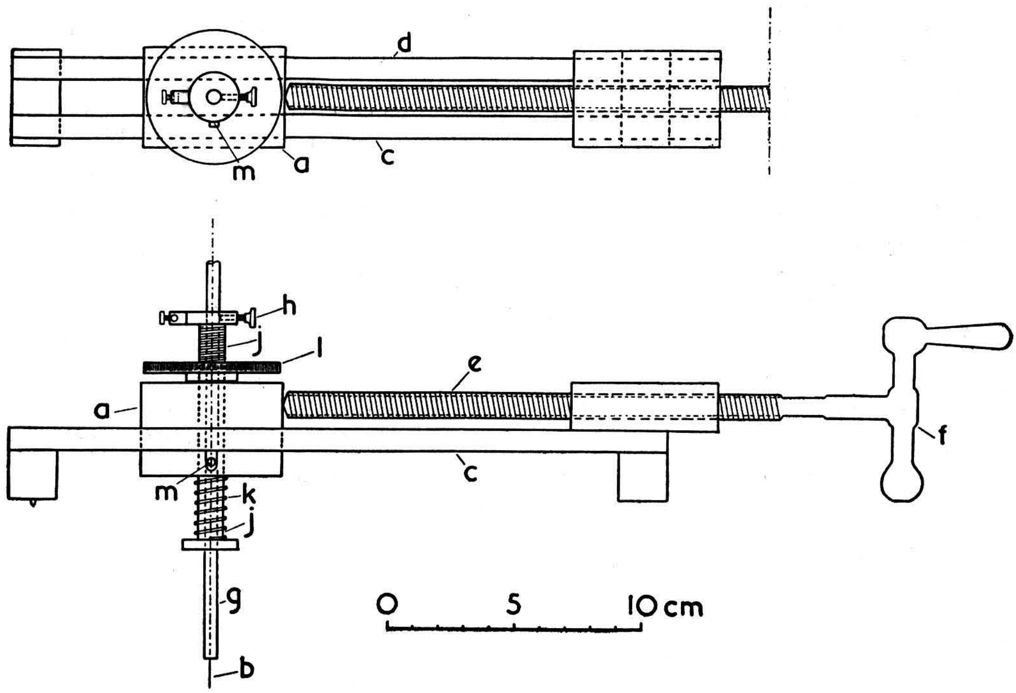

Fig. 4

allows to draw the "white line" through the centre of the equator plane of vessel *a*. This contrivance (see fig. 4) consists in principle of a suitable shaped massive brassblock *a* carrying the adjustable Pt-electrode *b*, two guiding brass bars (of quadratic cross-section) *c* and *d* and a long screw *e*, with handle *f*.

By turning this handle block *a* can be slowly pushed from the right to the left, as a result of which the Pt-electrode *b* moves in a straight line from the glass wall via the centre to the opposite glass wall of the vessel *a* in fig. 2. The Pt-electrode *b* is fastened to a thin brass bar *g*, which by loosening and fastening screw *h*, can be adjusted to such a position that the Pt-electrode just dips into the surface of the oleate system. This adjusting must be not done close to the glass wall as here the oleate system is curved upwards by capillary forces.

The electrode *b*, which must be the cathode, receives its current through a wire connected to a clamp opposite to *h*. As anode we also use a Pt-wire which dips somewhere in the oleate system, but in any case far from the place where the white line must be drawn. It appeared to be of advantage to use a potentiometric device which allows to use the most favourable e.m.f. (e.g. 2.7 Volt). This is that one which just develops sufficient H_2-bubbles during the relatively long time which the drawing of the line (a few minutes) takes.

A too fast movement of the electrode may lead to breaks and the white line than turns into a number of isolated tracks.

The speed of movement must therefore be such that the relaxation of the elastic tensions can occur sufficiently. Just before reaching the opposite glass wall the circuit is opened. There are then still enough minute H_2-bubbles around it to finish the last part of the white line.

Having arrived here, we must wait some 20 seconds to allow for the relaxation of the elastic tensions. If one lifted the electrode out of the surface at once, disturbance of the white line would occur.

But also after these 20 seconds the electrode must be removed out of the surface of the oleate system with care, as at a fast movement new elastic tensions are set up. Disk *l*, tube *j*, spring *k* and pin *m* (attached to *j*) in a vertical slot in block *a*, serve this end. By turning disk *l* the tube *j* can only move vertically, upwards or downwards, but cannot turn around its axis. So by turning disk *l* the electrode *b* can slowly be removed out of the surface of the oleate system.

3. *Preliminary experiments. The existence of a series of rotational oscillations of the elastic oleate system and the ratios of their periods.*

Starting from the experimental disposition described in section 2 and gradually increasing the frequency of the exciting oscillation of the glass vessel, one obtains at first resonance of the simple type of rotational oscillation (the type studied hitherto in the preceding parts of this series) [5]. At the moments of largest deviation the white line of H_2-bubbles has the form as is depicted in fig. 5, case I. At further increase of the frequency

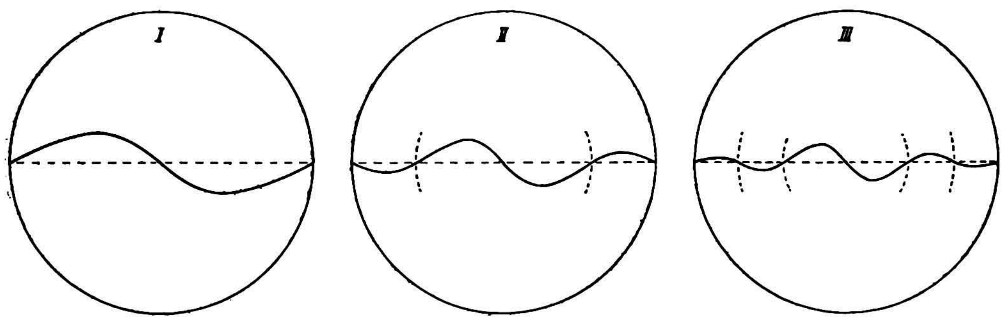

Fig. 5

one obtains resonance of more complicated rotational oscillations, compare in fig. 5 the cases II, III. The oleate system still oscillates in concentric shells, but interposed between glass wall and centre there are now one or two nodal spherical surfaces. The experimental equipment did not allow to increase the frequency further. The aim of this would have been to observe still more members of this series of rotational oscillations.

By direct visual observation we could further observe that in case II of fig. 5, the nodal point does not lie half way centre and glass wall, but somewhat closer to the centre. We observed further that in the cases II

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[5]) For the experiments in this section we used a vessel with $R = 5.0$ cm, the vessel swinging over a total angle of $42'$.

and III the linear elastic deviations are always largest between centre and the nearest nodal point.

By visual observation it is not possible to measure the positions of the nodal points, but we have tried to determine the ratios of the periods of the cases I, II and III. To this end we measured, through the telescope, the deviations as a function of the frequency of the exciting oscillation of the glass vessel and thus obtained resonance curves. From the positions of the resonance frequencies we thus obtained the ratios enlisted in the next survey (in which the suffixes I, II and III written near T indicate, that the period is meant to belong to the types of oscillation I, II and III of fig. 5).

oleate concentr.	salt concentr.	T_{II}/T_{I}	T_{III}/T_{I}
0,6 %	0.52 mol/l K_3-citrate . . .	0.574	0.426
	1.05 „ KCl	0.564	—
	1.05 „ KCl	0.572	—
1.2 %	1.05 „ KCl	0.570	0.440
		mean = 0.570	*mean* = 0.433

The above figures are certainly not very accurate because of the not sufficient constancy of the electromotor driving the swinging device [6]).

Still the few measurements which could be performed clearly showed that the rotational oscillations II and III are not harmonics (in the ordinary sense) of I, for the ratios of their resonance frequencies are no integers.

4. *Characteristics of the first, second and third rotational oscillation of an elastic fluid enclosed in a spherical vessel, for the case that slipping along the wall is absent.*

The possibility of an infinite series of rotational oscillations has already been mentioned by BURGERS [7]), in a passage which runs as follows: "The rotational oscillation considered in that paper which is determined by the first root $\zeta = 4{,}493$ of the equation tg $\zeta = \zeta$, is the first one of an infinite series of possible rotational oscillations; it is characterized by the absence of a nodal point in the function Φr, whereas the other solutions have 1, 2, - - - nodal points respectively."

It seems indicated to consider if the rotational oscillations of higher order observed in section 3 may correspond to those mentioned by BURGERS.

The formula for the first rotational oscillation (case I in fig. 5)

$$T = \frac{2\pi R}{4.493}\sqrt{\frac{\varrho}{G}},$$

[6]) As this error increased more and more the study of resonance curves had to be abandoned for the time present.

[7]) J. M. BURGERS, these Proceedings 52, 113 (1949); see footnote 3 on page 113.

will retain its general form for the rotational oscillations of higher order, but for the numerical factor 4.493, which must be replaced by one of the further roots of the equation tg $\zeta = \zeta$. We found the following values for a few further roots: second root = 7.725; third root = 10.904; fourth root = 14.066. With the same elastic system in the same vessel the ratio of the periods of any two rotational oscillations will then be inversely proportional to the ratio of the roots determining these rotational oscillations. Thus:

$$T_{\mathrm{II}}/T_{\mathrm{I}} = 4.493/7.725 = 0.582$$
$$T_{\mathrm{III}}/T_{\mathrm{I}} = 4.493/10.904 = 0.412$$

Comparing the calculated ratios with those found experimentally ($T_{\mathrm{II}}/T_{\mathrm{I}} = 0.570$; $T_{\mathrm{III}}/T_{\mathrm{I}} = 0.433$; see survey in section 3) we get the strong impression, that the series of rotational oscillations observed in the oleate systems is the series determined by the successive roots ζ of the equation tg $\zeta = \zeta$.

Two further properties of the rotational oscillations of the oleate system which were observed visually in section 3, (the node in case II of fig. 5 lies not exactly at 0.5 R, but somewhat closer to the centre; the linear amplitude is largest between centre and adjacent node) also follow from the mathematical equations. Compare table I and fig. 6, in which for the first, second and third rotational oscillations the linear amplitude ($r\Phi$) has been given as a function of the distance r from the centre. The amplitudes have been expressed in percents of that at the maximum (first rotat. oscill.) or at the maximum closest to the centre (second and third rotat. oscill.).

For calculating this table we start from the expression

$$\frac{\sin \zeta r - \zeta r \cos \zeta r}{\zeta\,(\zeta r)^2},$$

which gives — apart from a coefficient — the linear displacement $r\,\Phi$ in the equator plane, if R is taken 1. [8]) As we wish to express the linear displacements in percents of the displacement at the maximum (first rotat. oscill.) or at the maximum closest to the centre (second and third rotat. oscill.), it suffices to calculate the expression

$$\frac{\sin \zeta r - \zeta r \cos \zeta r}{(\zeta r)^2}$$

for a number of values of r (0.1; 0.2; —) and taking for the first rotational oscillation $\zeta = 4.493$, for the second $\zeta = 7.725$ and for the third $\zeta = 10.904$. We must, however, know the value of this expression at the above-mentioned maximum, which involves the knowledge of those values of r where the maxima or minima are situated. By differentiation we obtain the equation $\operatorname{tg} z - \dfrac{2z}{2-z^2} = 0$, in which $z = \zeta\, r$. This equation has been solved graphically and we obtained for the positions of the maxima or minima: first rotat. oscill. $r = 0.463$ (max.); second

[8]) J. M. BURGERS, these Proceedings **51**, 1211 (1948).

TABLE I

The linear amplitude of the first, second and third rotational oscillation as a function of the distance (r) from the centre. The linear amplitude is expressed in percents of that at the maximum (first rotat. oscill.) or at the maximum closest to the centre (second and third rotat. oscill.)

first rotational oscillation $\zeta = 4.493$			second rotational oscillation $\zeta = 7.725$			third rotational oscillation $\zeta = 10.904$		
	$100\, r/R$	linear amplitude		$100\, r/R$	linear amplitude		$100\, r/R$	linear amplitude
centre	0	0	centre	0	0	centre	0	0
	10	33.7		5	29.1		5	40.4
	20	63.2		10	55.6		10	73.8
	30	85.5		15	77.2		15	94.6
	40	97.7		20	92.2	max.	19.1	100
	45	99.9	max.	26.9	100		25	89.4
max.	46.3	100		30	98.5		30	66.7
	48	99.8		35	90.1		35	37.1
	50	99.3		40	75.3		40	6.7
	60	90.3		45	56.1	node	41.2	0
	70	72.8		50	34.4		45	— 18.4
	80	49.5		55	12.8		50	— 34.0
	90	24.1	node	58.2	0	min.	54.5	— 38.5
	95	11.3		60	— 6.8		60	— 32.5
wall	100	0		65	— 22.5		65	— 19.1
				70	— 33.2		70	— 2.8
			min.	76.9	— 38.5	node	70.8	0
				85	— 32.0		75	12.2
				90	— 22.9		80	22.0
				95	— 11.7	max.	84.4	24.9
			wall	100	0		90	20.7
							95	11.4
						wall	100	0

rotat. oscill. $r = 0.269$ (max.) and $r = 0.769$ (min.); third rotat. oscill. $r = 0.191$ (max.), $r = 0.545$ (min.) and $r = 0.844$ (max.).

For calculating the positions of the nodes, the expression

$$\frac{\sin \zeta r - \zeta r \cos \zeta r}{\zeta\, (\zeta r)^2}$$

must be zero, therefore $\sin \zeta r - \zeta r \cos \zeta r = 0$ or $\operatorname{tg} \zeta r = \zeta r$, which equations have the roots $\zeta r = 0$, $\zeta r = 4.493$, $\zeta r = 7.725$, $\zeta r = 10.904$, --------.

For the *first rotational oscillation* $\zeta = 4.493$, consequently $\zeta r = 0$ and $\zeta r = 4.493$ are the roots of the equation $\operatorname{tg} \zeta r = \zeta r$, in which r is smaller than or equal to 1. Thus here the linear displacement is only zero at the centre ($r = 0$) and at the wall of the vessel ($r = 1$). There is no node between centre and wall.

For the *second rotational oscillation* $\zeta = 7.725$. Therefore here the first three roots of $\operatorname{tg} \zeta r = \zeta r$ must be considered.

The linear displacement is here zero at $r = 0$ (centre), $r = 4.493/7.725 = 0.582$ (node) and $r = 1$ (wall).

For the *third rotational oscillation*, characterized by $\zeta = 10.904$, we find similarly that the linear displacement is zero at $r = 0$ (centre), $r = 4.493/10.904 = 0.412$ (node), $r = 7.725/10.904 = 0.708$ (node) and $r = 1$ (wall).

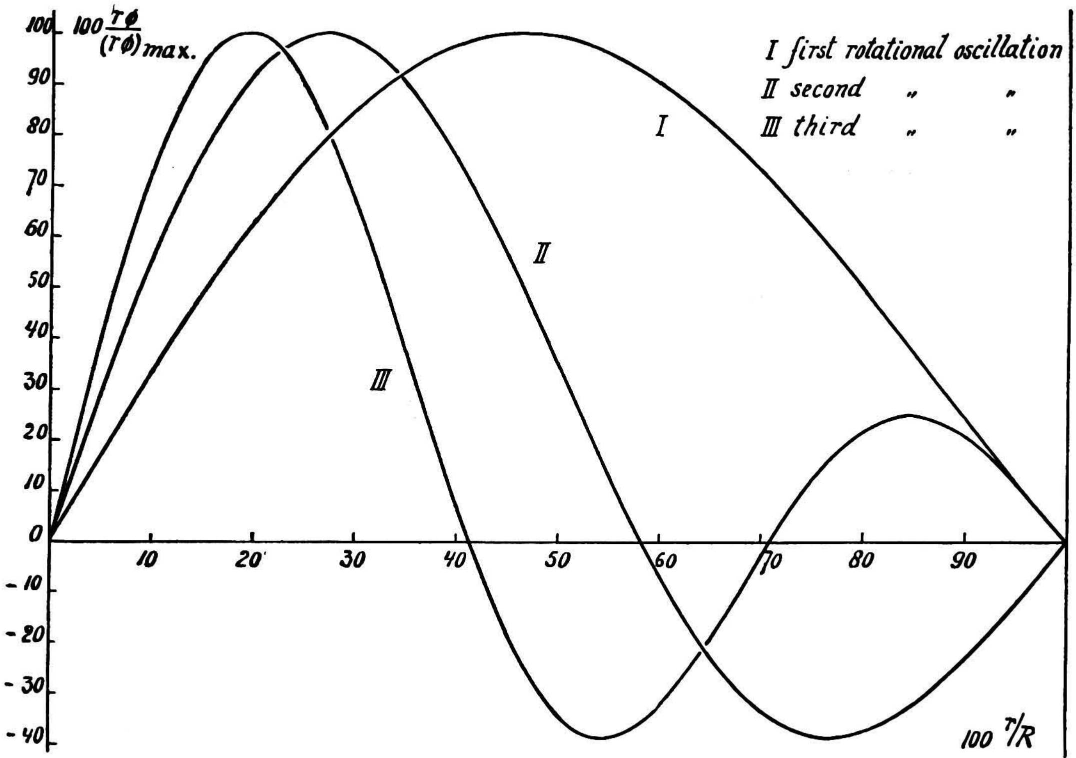

Fig. 6

5. ***Measurements of the linear displacement as a function of the distance from the centre, on oscillating*** 1.2 % ***and*** 0.6 % ***oleate systems***

As is discussed in section 2) the photographs of the white track of minute H_2-bubbles were made by repeated intermittent illumination at the moments of largest elastic deviations (alternatively in opposite directions). As the frequency of the exciting oscillation was brought as near as possible to the resonance frequency of the rotational oscillation of the oleate system (at which a phase difference of approximately 90° exists between exciting and excited oscillations) the glass vessel is always practically in the same position (approx. zero deviation).

If there is no slip of the oleate system along the glass wall — as in the 1.2 % oleate system, because of $\Lambda \infty R$ — we must therefore expect photographs of the type I in fig. 7. In these photographs the two intersecting (at the centre) S-shaped curves meet at either side in a single point at the glass wall.

If there is a slip of the oleate system (as was supposed by J. M. BURGERS in order to give an explanation of Λ being independent of R which was observed in the 0.6 % oleate system; compare fig. 1) we would expect photographs of the type II in fig. 7, in which the two curves do not meet in a single point at the glass wall.

All photographs of the first rotational oscillation actually obtained, as well with 1.2 % as with 0.6 % oleate systems, showed, however, type III of fig. 7, in which the two curves meet in points situated at a short distance before the glass wall (exaggerated in fig. 7; the gap amounting to $\pm$ 2 %

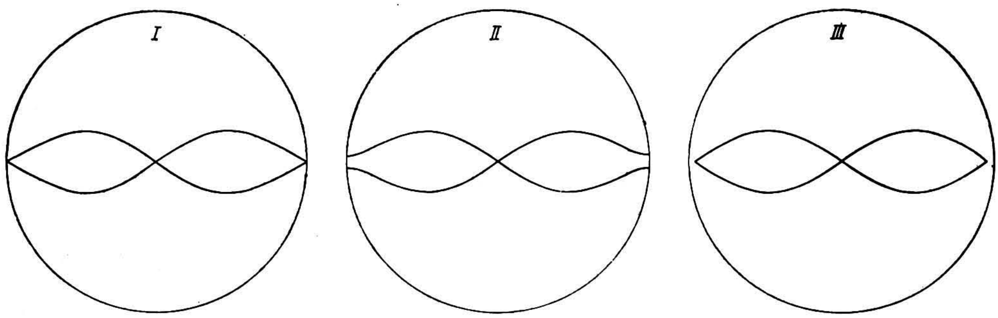

Fig. 7

of R). The same we found for the second rotational oscillation. At first sight one may think that a nodal point lies close to the glass wall, but we never observed the continuation of the apparently intersecting curves between "point of intersection" and glass wall.

The distance between the "point of intersection" of the curves and the glass wall has been shown to be only an optical delusion. Close to the glass wall the oleate system is curved upwards by capillary forces. We made photographs of the glass vessel with a thermometer scale rounded off at both ends resting with its ends on the glass wall (practically in the equatorplane). In the case of the not filled glass vessel (thermometer scale in air) we obtained photographs, in which the image of the ends practically coincides with the image of the inner wall of the glass vessel. If, however, water or the oleate system was poured into the vessel, so that the scale is just beneath the surface, photographs were obtained which show an empty space between the ends of the scale and the wall of the vessel.

Further measurements of the photographs and comparison with the thermometer scale itself resulted in: *a*) that the used photographic camera gave practically no distortion of the scale if it was photographed in air, *b*) the same result, except for the regions close to the glass wall, was obtained if it was covered with water or 1.2 % Na-oleate solution. Before evaluating the function $r\Phi = f(r)$ from the photographs of the oscillating systems, the values of r were corrected with the aid of a table based on the above photographs of the scale, when it was covered with the oleate system.

Enlarged images (of approx. 30 cm diameter of the negatives) were projected on millimeter paper with the aid of a projector lantern and with a pencil the curves and the wall of the vessel were drawn over. [9]) On these drawings on large scale

[9]) We are much indebted to H. L. Booij for making these drawings. Because of the inconstancy of the electromotor during the repeated intermittent exposition the images were often not sharp and therefore difficultly visible.

we measured the distance between the two inner sides of the vessel and the intersection point in the centre. This ought to give two equal values of R, but in some cases gave slightly different values. Now we measured, at both sides of the centre, the vertical distance of the curves at $r/R = 0.1$, 0.2 etc., which gave two sets of the twofold values of the vertical distance at 10 %, 20 % etc. of the radius. From these we obtained the meanvalue l of the single deviation (still as a vertical distance) as a function of r/R [10]), or — if we take $R = 1$ — as a function of r (the latter still as the distance from the centre to the footpoint of the perpendicular). For a comparison with the mathematical theory we must, however, calculate

TABLE II

Measurements on the 1.2 % oleate system of the linear amplitude ($r\,\Phi$) of the first rotational oscillation as a function of the distance (r) from the centre. The linear amplitude is expressed in percents of that at the maximum

no. 1		no. 2		no. 3		no. 4	
$100\,r/R$	$r\,\Phi$	$100\,r/R$	$r\,\Phi$	$100\,r/R$	$r\,\Phi$	$100\,r/R$	$r\,\Phi$
5.9	18.5	5.8	17.1	6.4	19.1	5.3	18.4
11.7	36.3	11.8	35.7	12.8	38.7	10.6	36.6
22.7	64.3	22.9	63.2	25.0	71.7	21.0	66.6
33.4	86.9	33.6	85.9	35.6	90.2	31.2	88.3
43.4	97.6	43.7	96.9	45.4	99.3	41.2	98.4
46.3	100.0	46.6	100.0	48.2	100.0	44.2	100.3
52.8	97.6	53.2	99.0	54.4	97.3	51.0	98.9
62.8	88.6	62.3	89.3	63.2	87.1	60.9	91.5
71.4	71.9	71.5	72.2	71.8	65.6	70.7	75.3
80.8	48.5	80.9	46.7	80.9	40.4	80.6	51.5
90.7	21.0	90.7	20.5	90.7	15.2	90.7	23.6
95.9	6.6	95.9	7.5	95.9	4.4	95.9	9.4
99.4	0	99.4	0	99.0	0	100.5	0

no. 5		no. 6			
$100\,r/R$	$r\,\Phi$	$100\,r/R$	$r\,\Phi$	$100\,r/R$ mean	$r\,\Phi$ mean
5.4	16.9	5.7	18.1	5.8	18.0
10.8	35.7	11.4	35.4	11.5	36.4
21.4	65.4	22.4	63.9	22.6	65.9
31.7	86.6	33.0	87.3	33.1	87.5
41.7	98.5	43.1	98.8	43.1	98.3
44.7	99.3	46.0	100.0	46.0	99.9
51.5	99.6	52.6	97.8	52.6	98.4
61.2	91.3	62.0	89.8	62.1	89.6
70.9	74.3	71.3	70.9	71.3	71.7
80.6	51.8	80.8	46.8	80.8	47.6
90.6	24.5	90.7	19.4	90.7	20.7
95.9	10.5	96.2	6.4	96.0	7.5
99.9	0	99.4	0	99.5	0

[10]) A correction for the actual value of r/R because of the above discussed distortion, was only necessary for $r/R = 0.90$ and 0.95.

from this the length of the arc ($= r\,\Phi$) as a function of the corresponding value of r, which we will denote with $r_{corr.}$. From l and r we know tg Φ and therefore Φ in radians. Arc Φ is obtained by multiplication with $r_{corr.}$, which latter is obtained by multiplication of r with sec Φ.

Table II gives the results of six measurements on the first rotational oscillation (no 1—6) with the 1.2 % oleate systems, in which different oleate preparations have been used (no 1, 2, 3, chemically pure K-oleate; no 4, 5, 6 Na-oleate from BAKER), also vessels of different diameters (no 1—5 with $R = 5.07$ cm, no 6 with $R = 4.34$ cm) and different salt media (no 1—3 with 0.98 N KCl: no 4—5 with 1.05 N KCl and no 6 with 0.52 moles/l potassium citrate).

Table III (first rotational oscillation) and IV (second rotational oscil-

TABLE III

Measurements on the 0.6 % oleate system of the linear amplitude ($r\,\Phi$) of the first rotational oscillation as a function of the distance (r) from the centre. The linear amplitude is expressed in percents of that at the maximum

no. 7		no. 8			
$100\,r/R$	$r\,\Phi$	$100\,r/R$	$r\,\Phi$	$100\,r/R$ mean	$r\,\Phi$ mean
5.2	19.8	5.1	18.5	5.2	19.2
10.3	33.3	10.2	35.4	10.3	34.4
20.6	66.9	20.3	67.7	20.5	67.3
30.7	89.4	30.3	87.6	30.5	88.5
40.7	99.0	40.4	99.0	40.6	99.0
43.8	100.3	43.4	99.7	43.6	100.0
46.7	100.0	46.4	100.0	46.6	100.0
50.7	100.2	50.3	97.6	50.5	98.9
60.6	91.0	60.4	89.4	60.5	90.2
70.6	73.1	70.4	71.2	70.5	72.2
80.5	46.5	80.4	48.7	80.5	47.6
90.7	16.6	90.6	22.4	90.7	19.5
96.2	3.8	95.9	9.0	96.1	6.4
98.5	0	100.4	0	99.5	0

lation) give the measurements with the 0.6 % oleate systems (at all times Na-oleate from BAKER and a salt medium of 0.52 moles/l potassium citrate) with different vessels (no 7, 9 and 10, with $R = 4.34$ cm; no 8 with $R = 5.07$ cm).

The results have been represented in three figures only (fig. 8 A, 8 B and 9) using as "experimental points" the means of the values r and $r\Phi$ on each horizontal row of the tables II, III and IV. These points, the endpoints to the right with $r\Phi = 0$ included, lie close to the theoretical curve in particular in the figs 8 A and 8 B [11]). These curves have been drawn

[11]) The endpoints to the right, which represent $r\,\Phi = 0$, lie at a value of the abscissa which is somewhat lower (0.5 % in fig. 8; 2 % in fig. 9) than $100\,r/R = 100$. This is possibly caused by the fact that we used the correction here following from

TABLE IV

Measurements on the 0.6 % oleate system of the linear amplitude ($r\,\Phi$) of the second rotational oscillation as a function of the distance (r) from the centre. The linear amplitude is expressed in percents of that at the maximum closest to the centre

no. 9		no. 10			
100 r/R	$r\,\Phi$	100 r/R	$r\,\Phi$	100 r/R mean	$r\,\Phi$ mean
6.1	32.9	5.5	30.4	5.8	31.7
11.8	59.6	10.8	56.0	11.3	57.8
17.3	83.5	16.0	77.4	16.7	80.5
22.5	96.6	21.2	93.9	21.9	95.3
27.2	100.0	26.1	99.3	26.7	99.7
31.8	95.8	30.9	97.6	31.4	96.7
36.4	86.7	35.7	88.0	36.1	87.4
40.9	71.9	40.4	71.2	40.7	71.6
45.6	52.6	45.3	48.1	45.5	50.8
50.3	29.9	50.2	23.9	50.3	26.9
55.2	7.7	55.2	3.2	55.2	5.5
60.3	10.9	60.3	13.0	60.3	−12.0
65.4	27.1	65.3	31.5	65.4	−29.3
70.5	35.8	70.4	40.8	70.5	−38.3
75.5	38.7	75.4	41.4	75.5	−40.1
80.6	37.3	80.6	38.5	80.6	−37.9
85.5	29.7	85.5	29.1	85.5	−29.4
90.7	18.6	90.7	15.8	90.7	−17.2
96.2	4.5	96.2	3.1	96.2	− 3.8
98.8	0	97.2	0	98.0	0

according to the data given in table I, which table represents $r\Phi$ as a function of r in the case that there is no slipping along the wall of the vessel.

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photographs of the thermometer scale (covered with oleate system), which were taken while the vessel was at rest (see above). In the rocking vessel the distortion close to the wall in the direction of the abscissa will presumably be larger because of centrifugal effects.

The latter may even change the plane interface into a slightly hollow one, which will cause an extra optical distortion over the whole diameter of the vessel. This might explain why in fig. 9 the part of the curve from the first maximum up to higher values of r/R is displaced slightly to the left of the theoretical curve.

If one draws the curves for each of the no. 1—6 of table II one observes that at $r/R = 0.96$ the correspondence with the theoretical value of $r\,\Phi = 9$ % (following from table I) is sometimes better, sometimes worse than that of the mean value of $r\,\Phi$ given in table II (= 7.5 %). The same applies for the correspondence of the single abscissa values and the mean abscissa value with the theoretical value $r/R = 1.00$ for the endpoints to the right with $r\Phi = 0$. It appears that both kinds of deviations from the theoretical values are slight (in order of the experimental errors) for those experiments in which the values of the angular displacement Φ at the maximum (at $r/R = 0.463$) were the smallest. These were the series no. 4 and 5 with $\Phi = 0.213$ and 0.256. The differences are larger for the no. 1, 2 and 6, in which Φ at the maximum was respectively 0.375, 0.392 and 0.353. The difference is the largest for no. 3, where Φ was the largest of all ($\Phi = 0.465$).

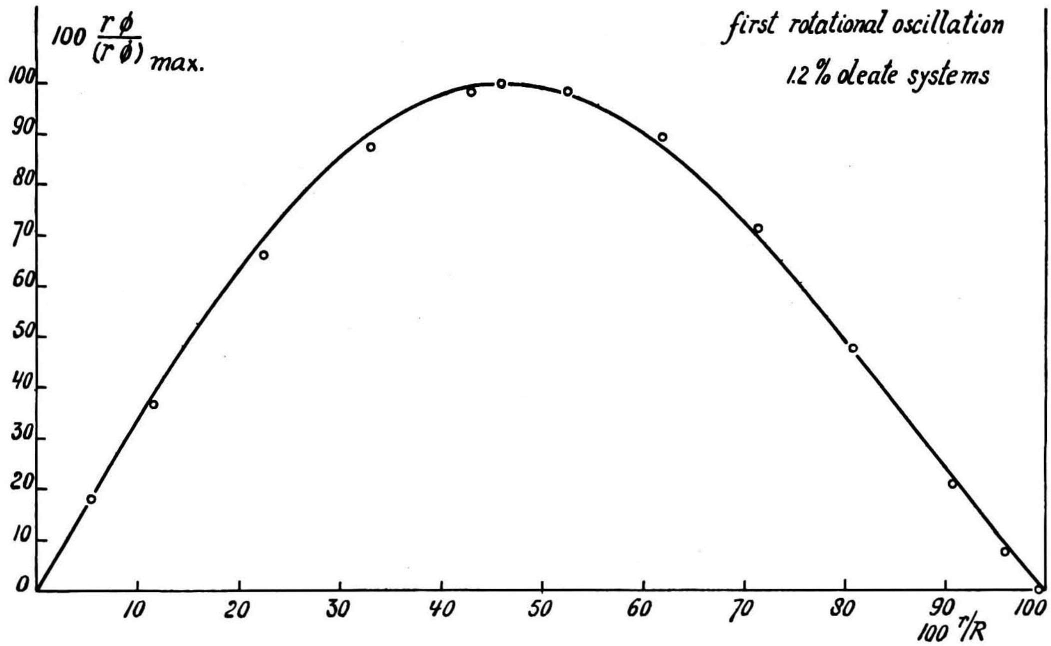
$100\,\frac{r\phi}{(r\phi)_{max.}}$
first rotational oscillation
1.2 % oleate systems
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
100 r/R

Fig. 8A

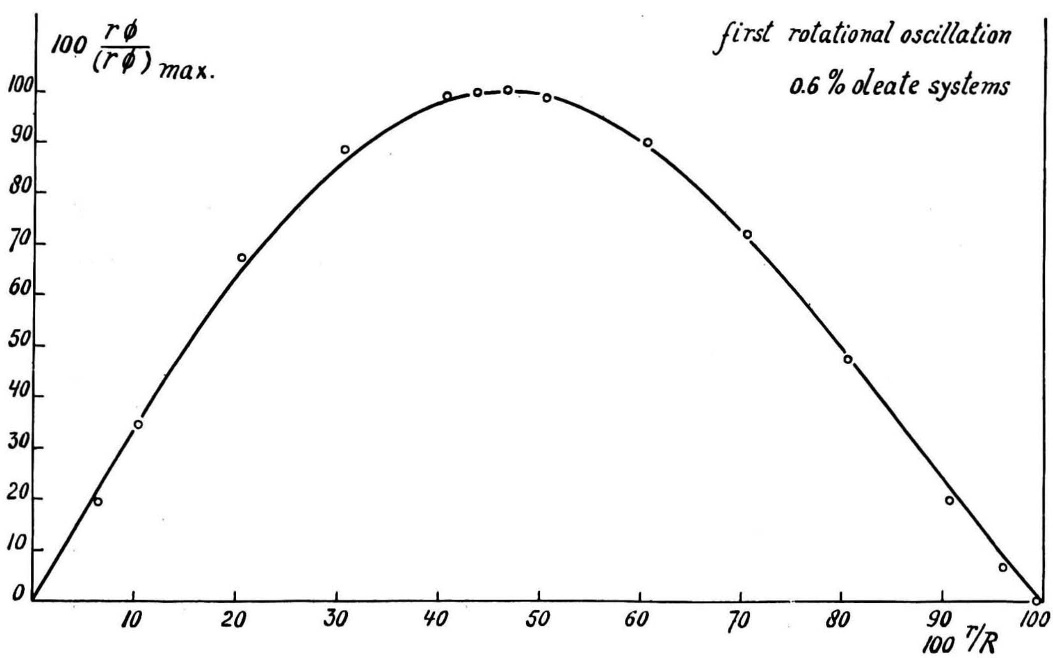
$100\,\frac{r\phi}{(r\phi)_{max.}}$
first rotational oscillation
0.6 % oleate systems
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
100 r/R

Fig. 8B

The results with the 1.2 % oleate systems are quite as were to be expected (cf part III: $\Lambda \infty R$), but those with the 0.6 % oleate systems enforce our doubt as to the real existence of slipping along the wall of the vessel. Compare in the introduction the different character of the damping in the 1.2 % and in the 0.6 % oleate system.

To be certain that for the 0.6 % oleate systems under the conditions of saltconcentration and temperature as were used in photographing the elastic deviation Λ is still independent of R, Mr H. J. VAN DEN BERG was so kind to determine Λ at 0.48 moles/l potassium citrate [12]) and at 17° in quite the same way as is given in details in the parts II and III of this series. The results (see survey below) leave no doubt as to the reality of Λ being independent of R.

R (cm)	b_1/b_3	Λ	
3.01	1.440 ± 0.008	0.365 ± 0.006	
5.64	1.446 ± 0.010	0.369 ± 0.007	*mean*
6.77	1.436 ± 0.009	0.362 ± 0.006	$\Lambda = 0.366$
9.24	1.444 ± 0.008	0.368 ± 0.006	

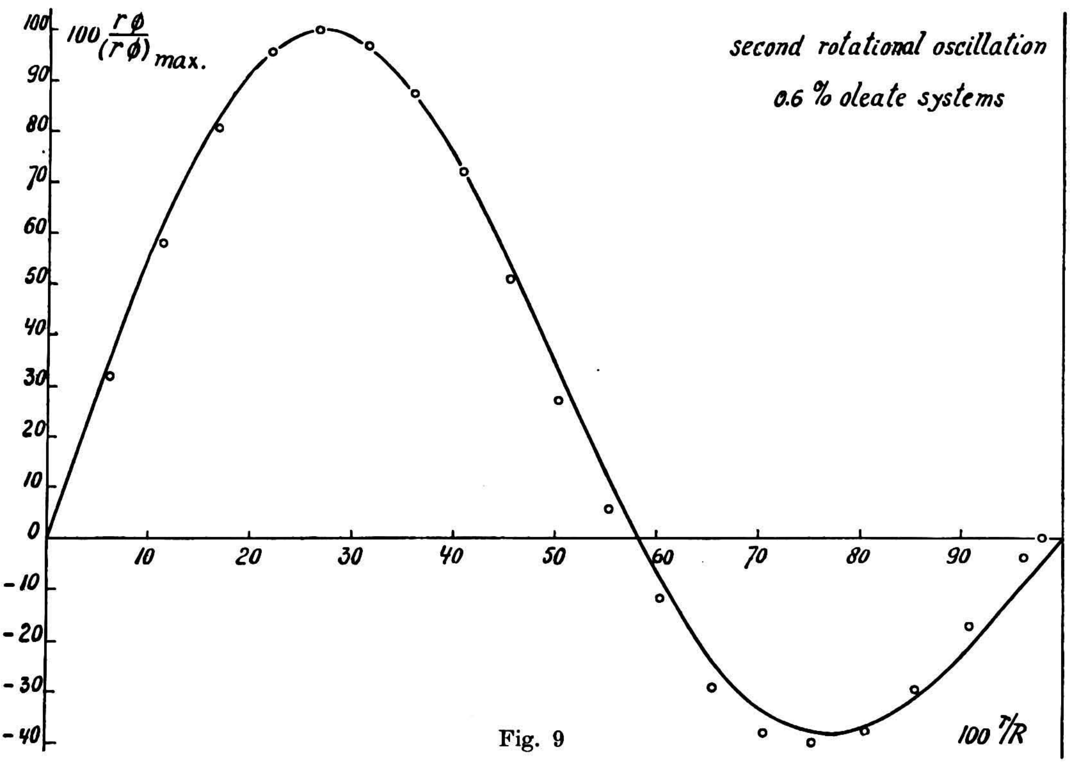

Fig. 9

[12]) The oleate preparation of BAKER, used in these control experiments showed a slightly different position of the citrate concentration corresponding to minimum damping (0.48 instead of 0.52 moles/l). This explains the choice of the citrate concentration.

Still we have to consider another point before we may safely draw a conclusion. In fig. 1 we perceive that the value of $r\Phi$ at the wall decreases with decreasing Λ. As in our case Λ is lower than in the two examples of fig. 1 with finite values of Λ, one could imagine that $r\Phi$ at the wall might be so small as to disappear in the experimental errors.

We must therefore know which value for $r\Phi$ one might expect in the case of slipping along the wall at $\Lambda = 0.366$. On our request J. M. BURGERS was so kind to provide us with the means to calculate approximately this $r\Phi$ in percents of $r\Phi$ at the maximum and it appeared that we have to expect here a value of 13 %.

Such a great value of $r\Phi$ would easily have been found in our experiments if it had really been present. We therefore come to the conclusion that the problem of the nature of the damping in the 0.6 % oleate systems (Λ independent of R) is still unsolved.

6. *Summary*

1. The linear displacement in the equator plane of the sphere as a function of the distance from the centre has been determined on oscillating 1.2 % and 0.6 % elastic oleate systems. For technical reasons exactly half filled spheres had to be used instead of completely filled ones.

2. The results obtained with the 1.2 % oleate systems (in which Λ is proportional to R) are corresponding reasonably well with the theoretical expectations for an oscillating spherical mass of an elastic fluid, which does not slip along the wall of the vessel.

3. The results obtained with the 0.6 % oleate systems (in which Λ is independent of R) are exactly like the results obtained with the 1.2 % oleate systems, that is a slipping of the elastic system along the wall of the vessel could not be detected.

4. As a consequence we must take back the conclusion made in part III of this series that the damping in the 0.6 % oleate system is described satisfactory by the case treated theoretically by J. M. BURGERS, in which the damping is a consequence of slipping of the elastic fluid along the wall of the vessel (in spite of the fact that this theory gives a Λ which is independent of R and a number of quantitative relationships which were confirmed in part III).

5. By increasing the frequency of the exciting oscillation a number of further rotational oscillations has been observed with the oleate system. They correspond to oscillations characterized by the second, third, - - - roots of the equation tg $\zeta = \zeta$.

6. The linear displacements as a function of the distance to the centre has been determined for the second rotational oscillation and here too a reasonable correspondence was found with theoretical expectations.

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