

CHEMISTRY

ELASTIC VISCOUS OLEATE SYSTEMS CONTAINING KCl. VII¹⁾

BY

H. G. BUNGENBERG DE JONG AND H. J. VAN DEN BERG

(Communicated at the meeting of Dec. 17, 1949)

1. *Introduction.*

Besides giving a description of a contrivance for exciting rotational oscillations adapted for serial work (section 2) and some measurements of more theoretical importance with this apparatus (sections 3 and 4), this communication continues the investigation into the action of organic substances on the elastic behaviour started in Part VI of this series. The results of preliminarily investigating the action of hydrocarbons on the 1.2 % oleate system are given in section 6.

2. *Contrivance for exciting rotational oscillations adapted for serial work.*

For exciting the rotational oscillation we used an apparatus (fig. 1) which is convenient for investigations in which a number of spherical vessels of the same capacity have to be measured consecutively for a number of successive days. In performing the experiments in Part VI it was used already but so far we have not yet described it, but for the few words dedicated to it in Part III (section 4).

The principle is the same as that of the turning table described in Part I, but now the vessel is clamped round the neck in the centre of a ball bearing a, attached to a frame b by means of a brass plate c). During the measurements this frame is in a horizontal position (fig. 1 B) in such a way that the spherical part of the vessel is completely immersed into the water of the thermostate and the elastic oscillation can be observed (with the aid of the telescope of a kathetometer) through the glass window of the thermostate. After termination of the measurements the frame is turned upwards into an oblique position (dotted in fig. 1 B), so that the vessel can be replaced by the next of the series to be investigated. The thermostate is large enough for the surface left free by the frame, to hold simultaneously ten spherical vessels of nominally 500 ml immersed.

All the vessels used in such serial work have their necks wrapped up in a few layers of paper, which layers are covered with a piece of very thin rubber tubing (cylindrical fragments of cycle tubes), so as to give those necks the same external diameter.

¹⁾ Part I has appeared in these Proceedings 51, 1197 (1948), Parts II–VI in these Proceedings 52, 15, 99, 363, 377, 465 (1949).

For fastening a vessel into the frame, two brass clamps of the form depicted in fig. 1 C are placed around its neck and the cylinder they constitute is slid into the hollow brass cylinder, fastened in the central

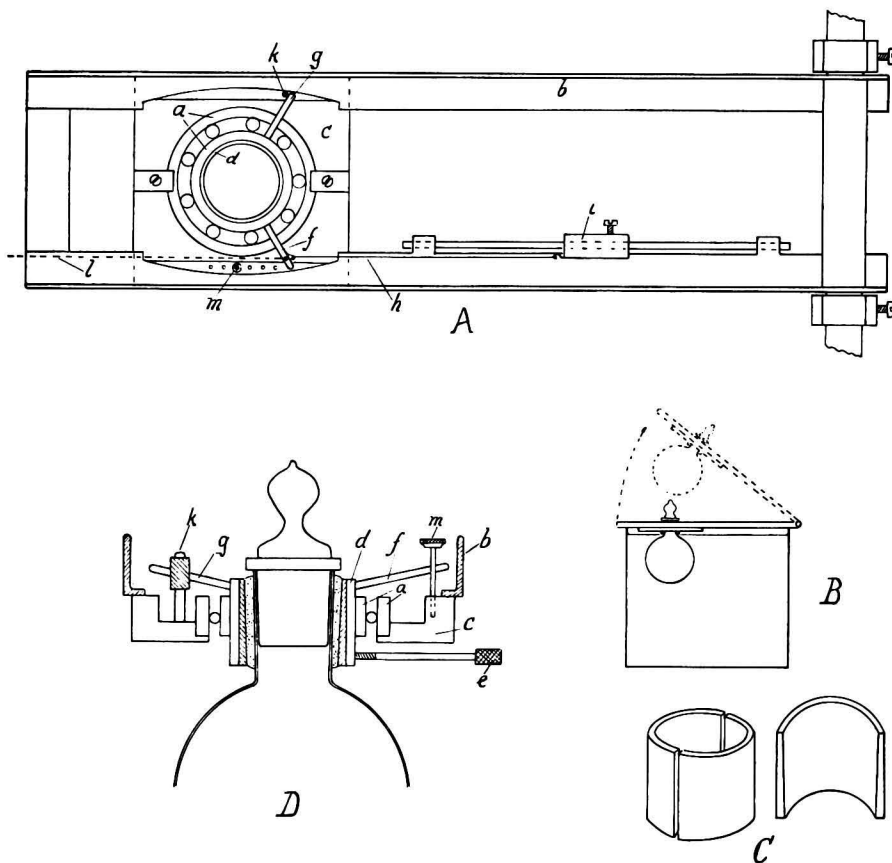


Fig. 1

hole of the ball bearing (d in fig. 1 A and 1 D), and is fixed by turning on screw e. The hollow brass cylinder carries two spikes f and g which limit the possibility of rotation of the ball bearing and consequently that of the vessel too (see below). A rubber string h stretched between the hooks on spike f and brass piece i always tends to make the vessel rotate anticlockwise, but this is prevented by the spike g pressing against the rod k attached to the ground plate. See fig. 1 A and 1 D.

For starting the rotational oscillation we pull very gently at string l (dotted), till spike f touches pin m (which may be placed at will into one of a series of holes), then we let the string l go. String h now sets the vessel rotating anticlockwise till spike g hits against rod k. In order to render the impact between g and k non-elastic, k is covered with a piece of rubber tubing. The vessel comes to a sudden standstill and the elastic oscillations of the oleate system in the vessel set in.

The impulse given may be regulated in two ways: *a*) by shifting brass piece *i*, which will modify the tension in string *h*, when this is in the position of rest, *b*) by placing pin *m* into one of the other holes, which will impart more or less extra extension to the string *h* when we pull at *l*.

3. *Influence of the intensity of the impulse used for exciting the damped rotational oscillation on the events during the first and following periods.*

The following survey gives a number of effects in consequence of increasing the impulse (imparted by the string) on a 1.2 % oleate system (15°; 1.43 N KCl + 0.05 N KOH, i.e. nearly the salt concentration of minimum damping) contained in a half filled spherical vessel of nominally 500 ml capacity.

pin in hole	work done g-cm	10 × T/2 between turning points 5-15 sec.	10 × T/2 between turning points 20-30 sec.	b_1/b_3 (5, 6, 7, 8)	b_1/b_3 (15, 16, 17, 18)	<i>n</i>	amplitude between turning points 0-1 at 0.5 R (scale divisions ocular micrometer)	depth of dimple top beneath surface (scale divisions ocular micrometer)
I	33	5.44 ± 0.02	5.39 ± 0.02	1.250 ± 0.004	—	34.3 ± 0.3	between 5 and 15	12
II	68	5.54 ± 0.02	5.41 ± 0.02	1.249 ± 0.006	—	39.5 ± 0.2	between 25 and 30	20
III	114	5.66 ± 0.02	5.39 ± 0.02	1.249 ± 0.006	—	43.9 ± 0.2	± 50	29
IV	162	5.71 ± 0.02	5.40 ± 0.02	1.251 ± 0.006	—	44.7 ± 0.1	± 60	38
V	213	5.71 ± 0.02	5.41 ± 0.02	—	—	44.8 ± 0.1	± 60	45
VI	321	—	—	—	1.247 ± 0.006	—	± 60	52
turning table	—	5.60 ± 0.02	5.39 ± 0.02	1.252 ± 0.006	—	44.7 ± 0.2	—	—

Some of the effects were already known qualitatively and are now illustrated by numbers, some conform suppositions already made, others again furnish entirely new data.

1. We were aware already (cf Part I, section 6) that the quadrantal oscillation, which is excited simultaneously with the rotational oscillation gains relatively in importance by increasing the impulse. This is elucidated when one compares the columns 8 and 9, which show that the vertical dimension of the dimple — to be regarded as a measure of the initial amplitude of the quadrantal oscillation (cf Part I, section 12) is ever increasing, whereas the amplitude of the rotational oscillation soon reaches its maximum value.

2. It was also known that the number of observable oscillations *n* is independent of the intensity of the impulse, except in the case of very weak impulses, where *n* becomes smaller (cf Part I, section 9). This phenomenon is illustrated in column 7.

3. Fresh information is given in the columns 5 and 6, which show

that b_1/b_3 , hence Λ (because $\Lambda = 2.303 \log. b_1/b_3$) has the same value if measured from four consecutive turning points shortly after exciting the oscillation (no 5—8) or much later (no 15—18), when the oscillation has veritably grown synchronous. It was already known that Λ is independent of the intensity of the impulse in the latter case (Part I). Column 5 shows this to be true too shortly after starting the oscillations.

4. The findings in columns 5, 6, 7 and 8 combined, confirm the explanation we gave provisionally (Part I, section 9) of the constancy of n (provided very weak impulses are not used). We do see indeed that in column 7 n grows constant at the same impulse, as where in column 8 the amplitude between the turning points 0—1 becomes constant. Then it is comprehensible that if Λ is always constant (columns 5 and 6) n too must be constant (the number of oscillations required to reduce the same initial amplitude to the same very small amplitude, which has just grown imperceptible physiologically).

The usefulness in emergency cases of the change in n as an approximate measure of the change in $1/\Lambda$ in a certain types of comparative investigations (with vessels of the same radius) becomes then understandable too (compare Part I, section 10; Part VI, section 5 and in the present communication section 7) as $n \times \Lambda$ should be constant.

5. Finally, the well known fact that the first oscillations have too large a period and may not be used for the calculation of G (compare Part I, section 6a) is illustrated by comparing the columns 3 and 4. We notice, that the difference between the values of column 3 and 4 increases, but finally becomes constant. This seems to occur at the same intensity of the impulse where n (column 7) and the amplitude (column 8) grow constant, for which phenomenon we have no explanation. When the turning points 20—30 are used, the period proves to be independent of the intensity of the initial impulse, and, as further experiments showed, the period has the same value as when we use the turning points 15—25, 25—35 or 30—40. The disturbances which were present initially have died out and the damped oscillation is now truly synchronous.

4. *The half-periods between consecutive turning points before the damped oscillation has become synchronous.*

Using an analogous soap system, though in a 1.5 l vessel and with an unknown, but constant, impulse (turning table, see Part I) we have made measurements of the term between the turning points 0—20, 1—20, 2—20, etc. which when subtracted, gave the time between the turning points 0—1, 1—2, 2—3, etc. They are given in figure 2, in which the horizontal dotted line represents the value of $T/2$ (0.801 ± 0.002) from measurements of the term between the turning points 25—35. Though the values for $T/2$ between two consecutive turning points

have a relatively great mean error (0.03—0.04; every time indicated in the figure) as a consequence of the subtraction (e.g. $0-20 = 17.02 \pm 0.02$ sec.; $1-20 = 16.11 \pm 0.02$ sec.; therefore $0-1 = 0.91 \pm 0.04$ sec.), one gets the impression, that the wavy nature of the curve before the level, characteristic of damped isochronous oscillations, has been reached, is nevertheless real. An explanation cannot be given, but we think that it stands in relation with the phenomena we observed in Part I, section 12, where the spherical wave travelled towards the centre and back, and went a few times to and fro.

When we now turn to the practical side of determining the period, which we need for the calculation of G and which consists in measuring the time for ten consecutive turning points, it will be clear that we must not use the first ten for this aim. In fig. 2 we have also inserted

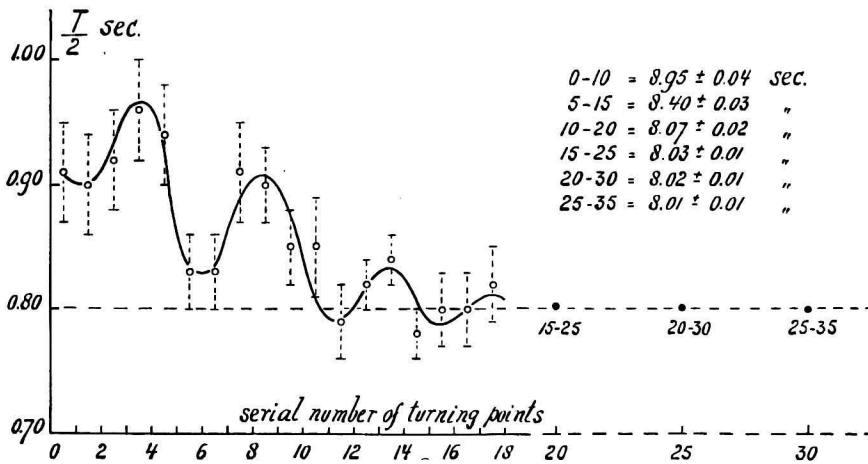


Fig. 2

$10 \times T/2$ each time starting from a later turning point. The values for 0—10 and 5—15 follow directly by subtraction from the above determinations. The others have been determined separately. We see that $10 \times T/2$ is within the experimental error equal for the determinations in which we use 20—30, and 25—35. This applies even for 15—25, though we may assume from fig. 2 that at the beginning of this tract there are still small undulations of the individual half periods. As these undulations occur practically around the isochronous level, now they cancel out each other.

A systematic error exceeding the experimental error is introduced when the turning points 10—20 are used, the mean value of T being already 0.6 % too high, that is the calculated value of G would be 1.2 % too low. The systematic error is much greater if we use the turning points 5—15 (T is 4.7 % too high). If we use 0—10 the systematic error is very great (T is 11.6 % too high).

In the given example, where we worked with an oleate system of relatively small decrement, we must therefore allow some 15 turning points to pass, so about one third of the total number of observable oscillations, before beginning with the measurement of the period.

In studying the influence of various factors (such as of temperature, KCl concentration, oleate concentration, of an added organic substance) we often had to measure oscillations which were far more damped. It is our general impression that the number of turning points we had to leave unused is proportionally smaller then. If for instance n is only 12, we may safely use the turning points 5–10 for measuring T .

5. *A simplified method of investigating the actions of organic substances on the elastic behaviour giving a maximum of information.*

In part VI of this series the actions of n hexylalcohol and of ethanol have been studied on the positions of the curves which represent G (the elastic shear modulus), $1/\Lambda$ (Λ = logarithmic decrement), λ (relaxation time) and n (the maximum number of observable oscillations) as functions of the KCl concentration. The results, combined with those obtained concerning the actions of other n . primary alcohols and of the n . fatty acid anions C_8 – C_{12} at only one particular KCl concentration (minimum damping of the blank oleate system) lead to a scheme, which may play a useful rôle in the study of the actions of organic substances on the elastic behaviour of the oleate system. In this scheme, which we reproduce here once more as fig. 3, the fully drawn curves relate to the

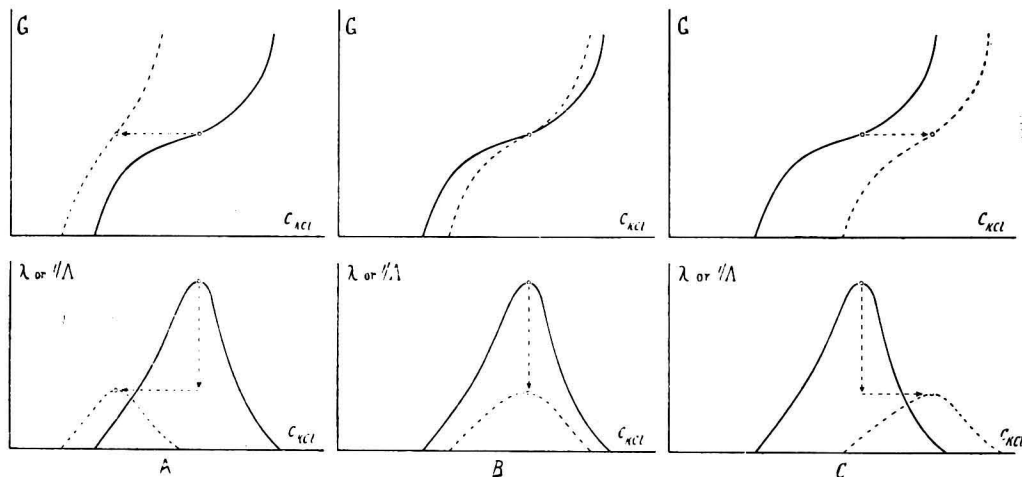


Fig. 3

blank oleate system, the dotted ones to oleate systems containing a certain amount of an organic substance. We see now that the added substance may shift the G , $1/\Lambda$ (or λ or n) curves either in the direction

of smaller KCl concentrations (Type *A*, e.g. n. hexylalcohol) or in the opposite direction (type *C*, e.g. the undecylate anion). In between these alternatives a type *B* may be conceived showing not any shift in horizontal direction. In Part VI we found that ethanol approached this type closely already, as the horizontal shift, though still of type *A*, is relatively small here. Further particulars about these shifts, which we found experimentally for hexylalcohol, we have provisionally assumed to be valid not only for other substances belonging to case *A*, but for those belonging to case *C* as well. These particulars are the following:

- a.* Both in the absence and presence of an organic substance the inflexion point of the *G* curve always lies at the same KCl concentration as the maximum of the $1/A$, λ or n curves.
- b.* The ordinate value of the inflexion point of the *G* curve does not alter when the *G* curve shifts towards either lower or higher KCl concentrations.
- c.* The displacement of the maximum on the $1/A$, λ or n curves consists of two components: I) a horizontal component towards either lower or higher KCl concentrations, and II) a vertical component which has always a downward direction.

The above induces one to attribute a twofold action (possibly at two different points of attack on the elastic structure) to an added organic substance:

1. The shifts in horizontal direction (viz. those of the inflexion point of the *G* curve, horizontal component of the shift of the maximum on the $1/A$, λ or n curves), indicate that an organic substance may aid KCl in building up the typical elastic viscous system (case *A*; a smaller KCl concentration is needed than for the blank) or it may counteract KCl (case *C*; a greater KCl concentration being needed now) or it may be indifferent in this respect (case *B*).

2. For all three types *A*, *B* and *C* the shift in vertical direction however is downwards (the maximum of the shifted $1/A$, λ or n curves always being lower than that of the blank). This strongly suggests that the organic substance has a second point of attack on the elastic structure, which in general leads to more damping. For a further study of the actions of organic substances it would be ideal if for each substance we had got time and enough material to investigate it so thoroughly as we did it in Part VI on hexylalcohol and ethanol. In actual practice it is hardly possible to follow this way, and it has besides the great disadvantage that it is not possible then to compare a number of substances in the same series (so with the same oleate sol).

A simpler form of experimentation, but in which such comparison (of e.g. some 8 substances) is possible consists in working at one constant KCl concentration. But then we have to consider how to choose this

KCl concentration that the results should give a maximum of information. In principle we can choose KCl concentrations which are lower than, equal to, or higher than the KCl concentration of minimum damping (of the blank).

From the scheme fig. 3 we can now read for these three KCl concentrations the sign of the change of G and of $1/\Lambda$, λ or n , if an organic substance of the types A , B or C is added.

The nine cases constructed in this way have been given schematically in fig. 4. We perceive from this scheme that maximum information is

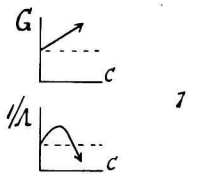
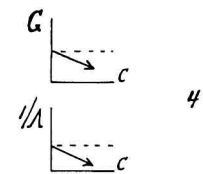
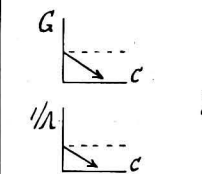
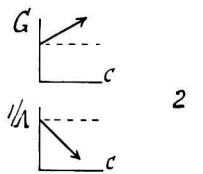
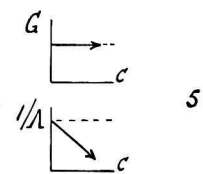
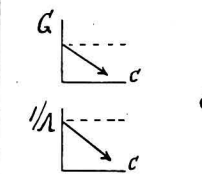
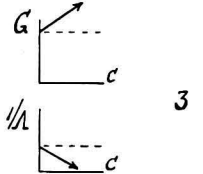
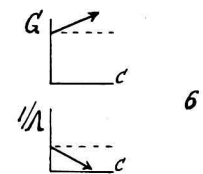
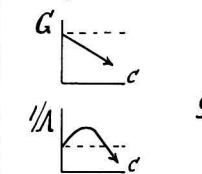
	Type A of fig. 3	Type B of fig. 3	Type C of fig. 3
$KCl < KCl_{min.damping}$	 1	 4	 7
$KCl = KCl_{min.damping}$	 2	 5	 8
$KCl > KCl_{min.damping}$	 3	 6	 9

Fig. 4

obtained only, if we choose the KCl concentration of minimum damping for our experiments, as it is possible then to distinguish between the types A , B and C (cf. fig. 4 cases 2, 5 and 8). At other KCl concentrations we get less information, while any discrimination between each two types is no longer possible. At a lower concentration than that of minimum damping the types B and C cannot be distinguished (In fig. 4 case 4 = case 7), and at a higher concentration than that of minimum damping the same applies to the types A and B (In fig. 4 case 3 = case 6).

We have already availed ourselves of the above considerations in Part VI, though we had not yet given them explicitly there. For the fatty acid anions C_8-C_{12} we obtained results as those in case 9 of fig. 4, and as we know that the constant KCl concentration used in this

experiment (1.52 N) was slightly greater than that of minimum damping (1.43 N), it was concluded that these fatty acid anions belong to type C .

6. *Influence of some hydrocarbons 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 exhausted and could not possibly be replenished, we had (just as with the alcohols C_1-C_6 and the fatty acid anions C_8-C_{14} in Part VI of this series), to make use of the large volume of oleate system, which had already served in previous experiments (viz. those on the dependence of T and A on R ; cf. Part II of this series). It had the composition 1.2 g oleate per 100 ml 1.52 N KCl + 0.08 N KOH, which electrolyte composition lies near to the minimum damping of the elastic oscillations. This system was used as such for the following experiments.

TABLE I

Influence of some hydrocarbons on the elastic behaviour of the 1.2 % oleate system at approximately the KCl concentration of minimum damping (15°)

Substance	concentration milli- moles/l	G corr.	A	λ sec.	n	100 A_0/A	100 λ/λ_0	100 n/n_0
tetrahydro- naphthalene	blank	41.8	0.219	2.52	47.5	100	100	100
	0.6	43.8	0.264	2.04	42.7	83.0	81.0	89.9
	1.8	50.9	0.395	1.27	26.0	55.4	50.4	54.7
	3.5	—	—	—	0—1	—	—	0—2
toluene	blank	41.9	0.221	2.49	47.8	100	100	100
	2.1	49.9	0.425	1.19	32.9	52.0	47.8	68.8
	4.2	56.7	1.398	0.34	14.1	15.8	13.7	29.5
benzene	blank	42.0	0.222	2.48	47.7	100	100	100
	2.1	46.8	0.292	1.79	39.5	76.0	72.2	82.8
	7.7	58.3	1.586	0.29	10.8	14.0	11.7	22.6
cyclohexane	blank	41.1	0.225	2.53	47.4	100	100	100
	3.2	47.1	0.291	1.83	39.5	77.3	72.3	83.3
	6.4	49.3	0.375	1.39	25.9	60.0	54.9	54.6
	9.7	47.1	0.759	0.70	13.0	29.6	27.7	27.4
heptane	blank	41.8	0.220	2.51	47.6	100	100	100
	2.0	42.3	0.226	2.43	45.3	97.3	96.8	95.2
	4.0	42.6	0.229	2.39	44.9	96.1	95.2	94.3
	8.1	38.2	0.230	2.51?	44.1	95.7	100.0?	92.6
	13.1	31.9	0.278	2.27	43.0	79.1	90.4	90.3
	18.1	22.5	1.193	0.63	12.8	18.4	25.1	26.9
20.6	16.6	2.286	0.38	6.0	9.6	15.1	12.6	
decahydro- naphthalene	blank	42.0	0.221	2.49	47.7	100	100	100
	1.5	41.8	0.230	2.39	45.8	96.1	96.0	96.0
	7.4	37.3	0.287	2.04	40.6	77.0	81.9	95.1
	12.3	26.2	0.593	1.18	20.0	37.2	47.4	41.9
	16.3	12.8	2.381	0.42	5.0	9.3	16.9	10.5

Mean value of the blanks: $G = 41.8$; $A = 0.221$; $\lambda = 2.50$; $n = 47.6$

For the methods (rotational oscillation in spherical vessels of known capacity, 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 (as already described in details in Part VI of this series; cf. there sections 1 and 3).

The results are given in Table I and fig. 5.

In this figure the values of G (the shear modulus in dyne/cm²) are given as such. For the purpose of comparing the influence of the hydrocarbons on $1/\Lambda$ (Λ = the logarithmic decrement), λ (relaxation time in seconds) and n (the maximum number of oscillations observable through the telescope of the kathetometer), the corresponding graphs have been drawn on the same scale. This is reached by using as ordinates the values $100 \Lambda_0/\Lambda$, $100 \lambda/\lambda_0$ and $100 n/n_0$, in which the index zero indicates the value of Λ , λ and n for the blanks.

A glance at fig. 5 reveals that the hydrocarbons investigated exert

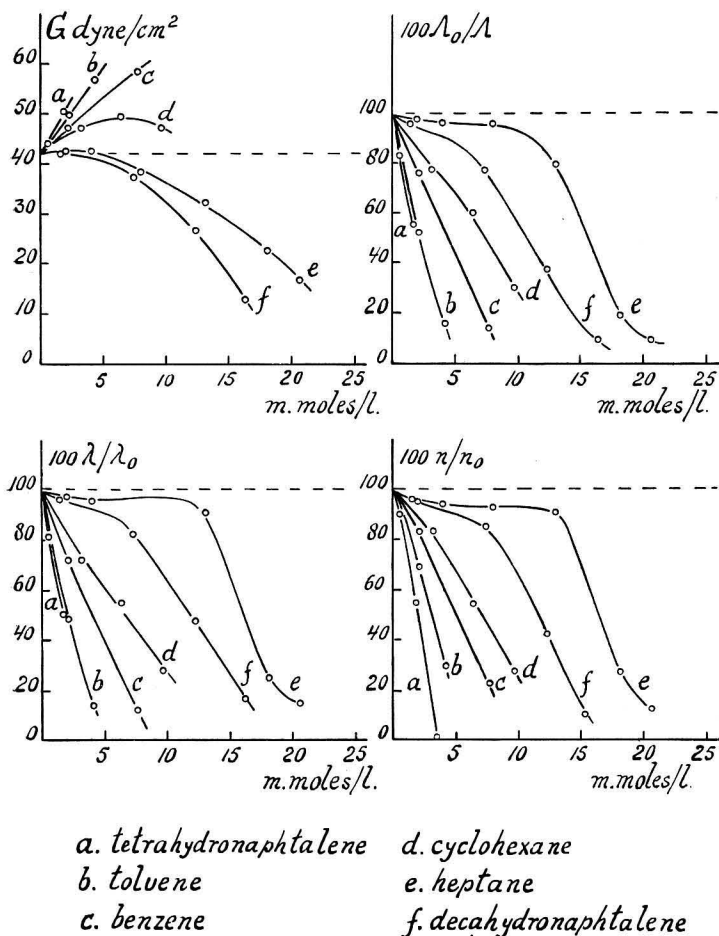


Fig. 5

their influence at very different concentrations, and what is above all interesting, we can distinguish two groups. The hydrocarbons of the first group, comprising tetrahydronaphtalene, toluene, benzene and cyclohexane increase G , the hydrocarbons of the second group comprising heptane and decahydronaphtalene decrease G . Both groups, however, do not differ as regards the direction in which the remaining quantities $1/A$, λ and n are changed. All hydrocarbons diminish these quantities.

Since we are actually working in the above experiments with hydrocarbons very near to the KCl concentration of minimum damping, we must conclude from the discussion in section 5 that tetrahydronaphtalene, toluene, benzene and cyclohexane shift the G , $1/A$, λ and n curves in the direction of smaller KCl concentrations (in a certain sense they aid the KCl in building up the elastic system), that heptane and decahydronaphtalene on the other hand shift these curves in the reverse direction (they counteract KCl in setting up the elastic system).

It is noteworthy that in the first group we find hydrocarbons (tetrahydronaphtalene, toluene, benzene) which contain one aromatic ring, and that in the second group we find saturated hydrocarbons (heptane, decahydronaphtalene). Yet this criterion is not sufficient, since we perceive that cyclohexane, though saturated belongs to the first group nevertheless. It will be clear that much more research on the action of hydrocarbons will be necessary in order to come to a better understanding of the connection between structure and action. Systematic work in this direction is now going on, the results of which will be published in this series later on.

7. Correlation between n and A .

On comparing in fig. 5 the $100 n/n_0$ graph with the $100 A_0/A$ graph we find a striking similarity. Other examples of this correlation were already given in Part VI, section 5, where the experimental conditions for its occurrence and also its significance and practical importance have already been discussed.

Summary.

1. A contrivance for exciting rotational oscillations adapted for serial work has been described. It makes it possible to impart impulses of known, different intensities.

2. The influence of the intensity of the impulse on the events during the first and following periods has been investigated. The results confirm inter alia a supposition made in Part I of this series how to explain the constancy of n (the maximum number of observable oscillations).

3. Particulars have been given concerning the half periods between consecutive turning points before the damped oscillation has become isochronous.

4. A simpler form of experimentation (in which the KCl concentration is kept constant) has been discussed for the study of the action of organic substances on the elastic behaviour of oleate systems. It has been shown by diagrams that maximum information can be obtained only if the KCl concentration corresponds to that of the minimum damping of the blank oleate system.

5. A preliminary investigation has been made on the influence of hydrocarbons on the elastic behaviour of the 1.2 % oleate system at the KCl concentration of minimum damping. From its results it was concluded that tetrahydronaphtalene, toluene, benzene and cyclohexane aid KCl in building up the elastic system, and that heptane and decahydronaphtalene counteract KCl in setting up the elastic system.

Department of Medical Chemistry
University of Leiden.