

CHEMISTRY

ELASTIC VISCOUS OLEATE SYSTEMS CONTAINING KCl. X ¹⁾

- a. *A new method for marking the oleate system with small gas bubbles.*
- b. *The elastic behaviour as a function of the KCl concentration and the influence of benzene, naphthalene, hexane, heptane, glycerol and the undecylate ion hereupon.*
- c. *Remarks on differences between oleate preparations from different sources.*

BY

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1. *Introduction.*

Besides giving a description of a simplified method to perform experiments with half filled spheres (section 2) and of a method to mark the oleate system with a small quantity of minute gas bubbles (section 3), in the present communication the investigation about the action of organic substances on the elastic behaviour of the oleate system is continued.

In parts VI—IX of this series we have already investigated the influence of a number of organic substances and have classed them into three types *A*, *B*, *C*; having type *A* when the curves representing G , λ , $1/A$ and n as a function of the KCl concentration are shifted by the added substance into the direction of smaller KCl concentrations, type *C* when these curves are shifted into the opposite direction and type *B* when no shift at all occurs. Only in two cases (*n*-hexylalcohol and ethanol, both belonging to type *A*) the conclusions were based on direct experiments, viz. on the cumbersome method of investigating the above mentioned influence at a whole series of KCl concentrations. The remaining substances were classed in connection with the results obtained from an indirect method (working at only one KCl concentration, namely the one corresponding to the minimum damping of the blank), which method on account of its simplicity is a very attractive one to be used at the continuation of the investigation about the relation between the structure of an organic substance and its action on the elastic oleate system.

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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—IX in these Proceedings 53, 7, 109, 233 (1950).

²⁾ Publication no. 4 of the Team for Fundamental Biochemical Research (under the direction of H. G. BUNGENBERG DE JONG, E. HAVINGA and H. L. BOOIJ).

This indirect method is based on the assumption that type *C* really exists. Up to now we have strong indications but no direct proofs, that this assumption is true. The aim of the present communication will therefore be to control, by using the direct method that some of the substances which, on account of the indirect method were classed under type *C* (heptane and the undecylate ion), really belong to type *C*. In the same way, that benzene really belongs to type *A*. To have some more examples which are investigated by the direct method, we added to this program naphthalene, hexane and glycerol, which were not yet investigated by the indirect method neither.

As our stock of Na oleicum pur. pulv. from MERCK (used in parts I — IX) was completely exhausted and could not be replenished, the experiments were performed with Na-oleate, neutral powder, from BAKER.³⁾

As this preparation will be used in the following parts of this series too, it may not be superfluous to discuss (section 7) the points of resemblance and difference between the two preparations, so far as these are important for our purposes. A comparison with oleate, obtained from chemically pure oleic acid will be included.

2. *A simplified method for performing experiments with half filled spheres.*

For the experiments in section 4 we followed in principle the technique of the method with the half filled spheres, described in details in part VI (section 1) of this series.

The original technique of the method with the half filled spheres requires a cumbersome preparation of the series of spheres to start with. One must first prepare a large volume of the KCl containing blank system and then provide each sphere with the required quantity of weight of the blank system so that it is exactly half filled according to quantity of volume. For that purpose from the radius of each sphere the required volume of the to be added blank system must be calculated, and from the density the weight of this volume.

In this original method *G* is calculated from the formula

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

(compare part II of this series), so that for every individual sphere we have to use the radius of this sphere.

It can be shown, (see small print below) that in practice one may follow a much simpler method, provided the series of spheres to be used shows only a relatively small variation in capacity. This condition was fulfilled in our case as we had a series of Pyrex vessels with a mean

³⁾ A generous gift of Na-oleate from The Rockefeller Foundation provided the means for the experiments described in this paper.

capacity of 110 ml, the capacity varying between 109 and 115 ml. The simplified method consists of providing each sphere with exactly 55 ml of the oleate system (for particulars see below) and to use for the calculation of the G from the period only one value of R , namely the value which corresponds to a sphere of 110 ml, being twice the volume of the oleate system introduced into each sphere.

It is true that the calculated G value is not the exact value, but the error which is introduced systematically, is relatively small, because this error consists of two factors, which act in opposite directions and abolish each other for the greater part. By using for instance a 113 ml vessel and filling it with 55 ml, the G value calculated from the observed period using a value for R which corresponds to a 110 ml vessel is only 0.5 % wrong.

The two above mentioned erroneous factors which are used in the calculation are:

1. the radius of the vessel, which ought to be that of a 110 ml sphere, but in reality is smaller or larger;
2. the degree of filling, which ought to be exactly 50 %, but in reality is larger or smaller because the actual radius is smaller or larger.

For an appreciation of the influence of these two errors on the calculated G value, we must know the influence of each, apart.

As to error sub 1) we read already from the above given formula that T is proportional to R . As to error sub 2) we have already given in part I of this series, provisional data about the influence of the degree of filling on the period. By means of more experiments we came to the result (already mentioned in part VI, section 1) that a change of the degree of filling from 50 % to 50,5 % (or to 49,5 %) gives an increase (resp. decrease) in the period of 0.25 %.

Now let us take as example a vessel with a capacity of 113 ml into which we introduce 55 ml oleate system. The radius of the vessel is $\sqrt[3]{113/110} = 1.0090$ times the radius of a 110 ml vessel.

To calculate G we ought to use this radius, but at the same time we ought to perform the measurement of the period with 56.5 ml oleate in the vessel. If the latter was the case the period would be 1,0090 times the one measured with an exactly half filled vessel of 110 ml.

In reality, however, the 113 ml vessel contains only 55 ml oleate system instead of 56.5 ml, that is to say, its degree of filling is not exactly 50 %, but only 48.7 %, in other words 1.3 % to low. Therefore the period measured with the 113 ml vessel will be 0.65 % lower than the one that would have been found if the vessel had been exactly half filled.

Therefore the period which we measure with the 113 ml vessel at a degree of filling of 48,7 % will be $0.9 \% - 0.65 \% = 0.25 \%$ higher than the period measured with an exactly half filled 110 ml vessel.

Using the radius of the 110 ml vessel the actual period measured with the 113 ml vessel will (because G is proportional to $1/T^2$) therefore introduce systematically an error of only 0.5 % in the calculated value of G .

The great practical advantage of the above, simplified, method is not so much that the calculation of G from the experimentally determined periods, becomes easier but above all that the preparation of a series of vessels, with which an experiment is performed becomes much more convenient.

As each vessel must be provided with a constant volume of the highly viscous elastic oleate system, the latter can be simply produced in each vessel apart by adding successively (by pipettes or burettes) adequate volumes of two low viscous solutions (the KCl solution and the stock oleate solution) and mixing thoroughly afterwards.

As to the other quantity, which we always measure, viz. n , this one is only slightly dependent on the radius of the vessel. Besides, in the neighbourhood of a degree of filling of 50 %, this n is very slightly dependent on small variations of the degree of filling. We found for instance a decrease in n of 0.09 % at a decrease of 1 % in the degree of filling. Therefore no error in n is to be feared for by using the above simplified method.

3. *Electrolytic H₂ mark.*

Up to now we used small air bubbles, shaken carefully into the oleate system, to be used in the measurements as indicators of the elastic movements. This method has two drawbacks: 1) the danger that a too large volume of bubbles is introduced, which effects the n - and T -values (see part I, section 3), 2) the visibility through the telescope of the kathetometer of very small amplitudes depends on the size of the air bubbles, if the oleate system is not perfectly clear. Formerly this second drawback was not felt, as we worked with oleate from MERCK, but it was strongly felt by working with the new oleate preparation from BAKER, the KCl systems of which were somewhat turbid at 15°.

So we looked for another method to mark the oleate system, which had to fulfil the conditions: 1) that we could introduce a small, limited number of bubbles, 2) that these bubbles are of uniform size. Both conditions were fulfilled by introducing electrolytically obtained H₂ bubbles into the oleate system.

The electrodes consist of a platinum wire as anode and a thin enamelled copper wire of which only the end is freed from enamel as cathode. By closing the current (4 Volt, from an accumulator) very small H₂ bubbles of uniform size are detached from the bare end of the enamelled copper thread ⁴⁾.

By special experiments it has been proved that bubbles introduced in this way have no influence upon the n - and T -values of the elastic oleate systems, even if we let them be formed during several minutes. In practice it is already sufficient to close the current during about 5 seconds.

Fig. 1 gives the apparatus we used. The two electrodes (*Cu*, *Pt*) are attached to the thin copper bars *a* and *b*, which can be raised or lowered through holes in the ebonite plates *c* and *d*, and can be fastened in the desired position by the screws *e* and *f*.

⁴⁾ One must take care to make the copper thread the cathode, otherwise green streaks (copper hydroxide or oleate) are formed around it when the current is closed.

These ebonite plates are attached to either ends of a brass tube *g*. This tube can be lowered or raised through a hole in the brass piece *h* (and can be fastened at the desired position by means of screw *i*).

For experiments in which a number of half filled or completely filled vessels of the same capacity are used, both tube *g* and the relative position of the electrodes can be adjusted once and for all, so that, placing the apparatus upon the edge of a vessel, the electrodes are automatically in the right position (fig. 1*B*). If the apparatus is not in use it is placed on the edge of a sufficiently wide glas tube near the thermostate.

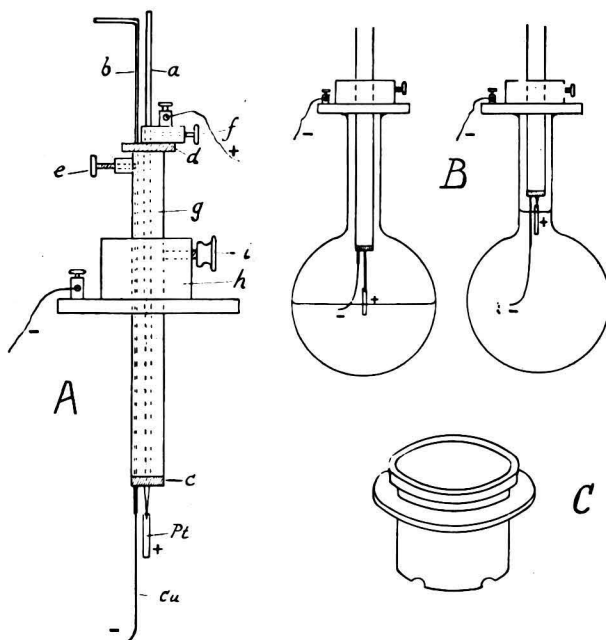


Fig. 1

It has appeared that in the special case of the half filled 110 ml vessels, which have been left overnight in the thermostate (to become free of air) and which are marked electrolytically, those vessels give a too large value of n and a slightly erroneous value of T . These errors do not occur if the vessels are vigorously wheeled round their axis beforehand, wheeling five times to and fro.

To this end the contrivance for exciting the rotational oscillation described in part VII was complemented with a short wide brass-cylinder (fig. 1*C*) which fits exactly over the inner ring of the ball bearing (*d* in fig. 1 of part VII). This cylinder is provided with two flanges, so that it may serve as a pulley for a string slung around the cylinder. With this string the vessel can thus be wheeled round whereby one wheels to and fro.

The values of n and T found after first wheeling round the half filled 110 ml vessel and thereafter marking the oleate system electrolytically are exactly the same as those found with the former method whereby the system was marked with wheeled in air bubbles. In state of rest (after standing overnight) the too high value of n develops again.

These phenomena are absent in completely filled 110 ml vessels. This induces one to attribute them to a (reversible) consolidation at the interface oleate system/air, which persists when the system is marked electrolytically, but is removed by mechanical agitation of this interface.

Still this explanation does not seem sufficient, as curiously enough the above complications were not (or only in a very slight degree) met with half filled 500 ml vessels. The question, whether this abnormal behaviour is only present with the new oleate preparation of BAKER (the solutions of which become turbid at 15°) and is absent with the oleate preparation of MERCK (the solutions of which remain clear at 15°), could not be answered, because we had no more left of the latter preparation.

4. *G and n as functions of the KCl concentration and the influence of benzene, naphthalene, hexane, heptane, glycerol and the undecylate ion thereupon.*

When not stated otherwise, the experiments in this section have been performed with 1.2 % oleate systems at 15°, using the simplified technique of the method with the half filled spheres (section 2).

The oleate systems are marked electrolytically and the rotational oscillation is excited with the contrivance described in part VII of this series.

This simplified technique is extremely convenient for the filling of the vessels with oleate systems in which the KCl concentration must be varied.

We used a series of "110 ml" vessels (varying from 109 – 115 ml) so that each vessel had to be provided with 55 ml of the oleate system. Starting from a stock (2.4 %) oleate solution containing 0.1 N KOH, the vessels were filled according to the receipt: x ml KCl 3.75 N + $(27.5 - x)$ ml H₂O + 27.5 ml stock oleate solution.

Afterwards they were closed with the glass stoppers and vigorously shaken. After standing overnight in a thermostate of 15°, the vessels were wheeled round and next the oleate systems were marked electrolytically (section 3). The so obtained measurements give information on the elastic behaviour of the blank 1.2 % oleate system as a function of the KCl concentration. Further we proceeded quite according to the original method of half filled spheres, a description of which is given in part VI of this series. For the addition of known quantities of hexane, heptane or benzene the dripping pipette described in a previous communication⁵⁾ was used. The dripping pipette could not be used in the case of glycerol, as the great quantities which had to be added in order

⁵⁾ H. G. BUNGENBERG DE JONG and L. J. DE HEER, these Proceedings 52, 733 (1949).

to obtain measurable effects, no longer allowed the total volume of the oleate system to remain practically constant. We followed therefore another way. We first measured a blank series (receipt see above) using the usual 2.4 % stock oleate solution (24 g Na oleate per liter, containing 0.1 N KOH). Thereafter we repeated the measurements with a number of analogous 2.4 % stock oleate solutions, in which we used: y ml glycerol + (950 $-y$) ml H₂O instead of the 950 ml H₂O. Thus we could prepare stock oleate solutions with various concentrations of glycerol.

With the experiments with the two solid substances: naphtalene and undecylic acid we still had to follow another way. In the usual 2.4 % stock oleate solution we introduced a weighed amount of naphtalene which was dissolved by warming up carefully till 80° (melting point of naphtalene) under continual shaking. After cooling the naphtalene remained dissolved. Another portion of the 2.4 % stock oleate solution (without naphtalene) was also warmed up and cooled in precisely the same way.

Two more stock solutions, both containing naphtalene, were obtained by mixing the above stock solutions in various proportions. Each of the four stock solutions apart were used for the preparation of a series of KCl containing oleate systems following the usual receipt. The measure-

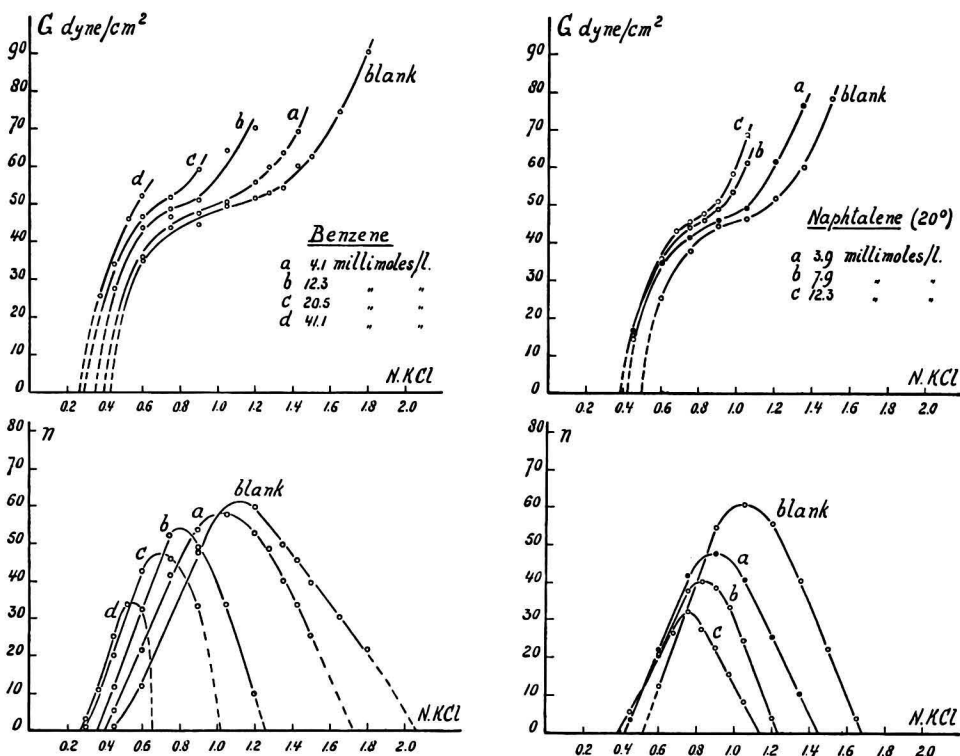


Fig. 2-3

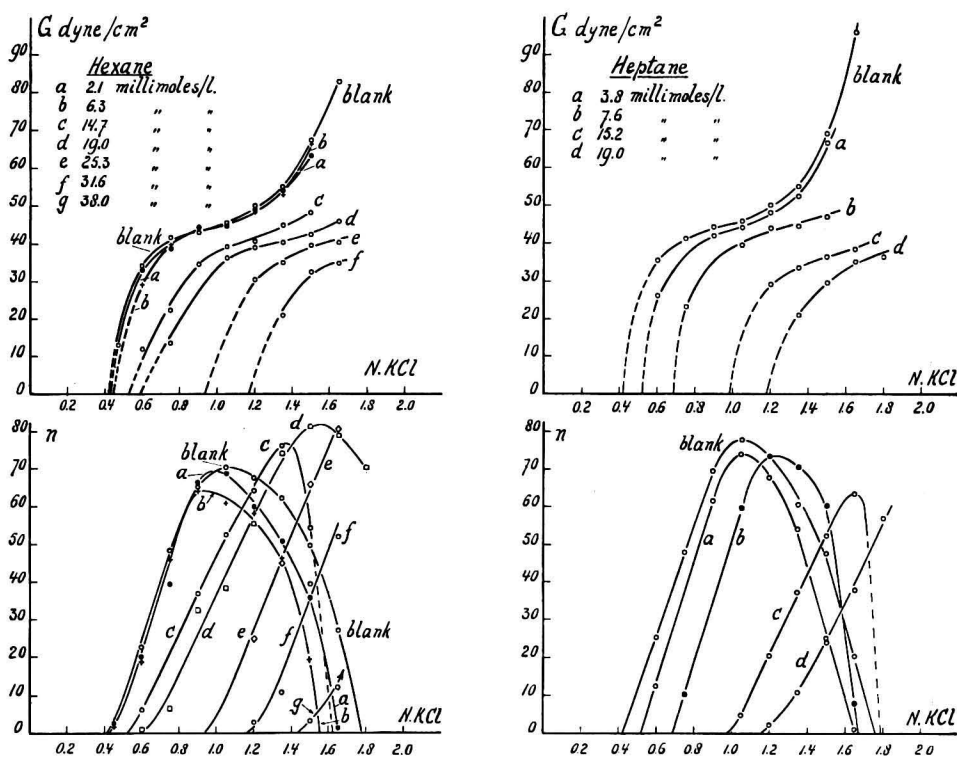


Fig. 4-5

ments had to be performed at 20° , because in consequence of the advanced season no sufficiently cold tap water for cooling was available any longer to keep the thermostat at 15° .

In the series with the highest naphtalene concentration a small fraction of the naphtalene had crystallized in the form of very thin leaflets which were embedded in the elastic system, so that the actual naphtalene concentration was somewhat smaller than 12.3 milli moles/l.

In the case of undecylic acid (which, as there is an excess of KOH in the stock oleate solution, forms undecylate) we followed the same procedure as stated above for naphtalene. The requisite temperature for dissolving the undecylic acid was only 50° here. The experiments were performed at the usual temperature of 15° .

We had to content ourselves with the measurement of the period T and of the maximum number of observable oscillations n , as none of us was able to perform the very difficult measurement of the decrement.

In the preceding parts VI — IX we have given many examples from which the narrow correlation between n and $1/\lambda$ is evident (in varying the KCl concentration or the concentration of an added organic substance, always providing that we keep the oleate concentration and the radius of the vessels constant). Therefore in the present and in following

parts of this series, we feel justified to use n as a relative measure for $1/\lambda$ for those experiments which fulfil the above conditions.

We shall not give elaborate tables of the results, but we shall represent them graphically in the figures 2 – 7.

In these figures G (the elastic shear modulus) and n , are given as functions of the KCl concentration for the blank series and for a few series with constant concentrations of the added organic substance.

For several reasons (see small print below) the results obtained with the six organic substances can not be compared quantitatively with one another. In the next section we therefore confine ourselves to the discussion of the characteristics occurring in each of the figures 2 – 7 apart.

The reasons hinted at in the above are the following:

1. the experimental conditions at the measurements are not always the same (the naphthalene series was performed at 20°, the other series at 15°),
2. in some series the stock oleate solutions have been warmed up during a short time (naphthalene 80°, undecylate 50°, see above) in the remaining series not,
3. the electrolytic marking was not yet used in the series with benzene. The series with hexane was the first which was marked in this way. Perhaps we had not yet enough experience how to wheel round the vessels before marking

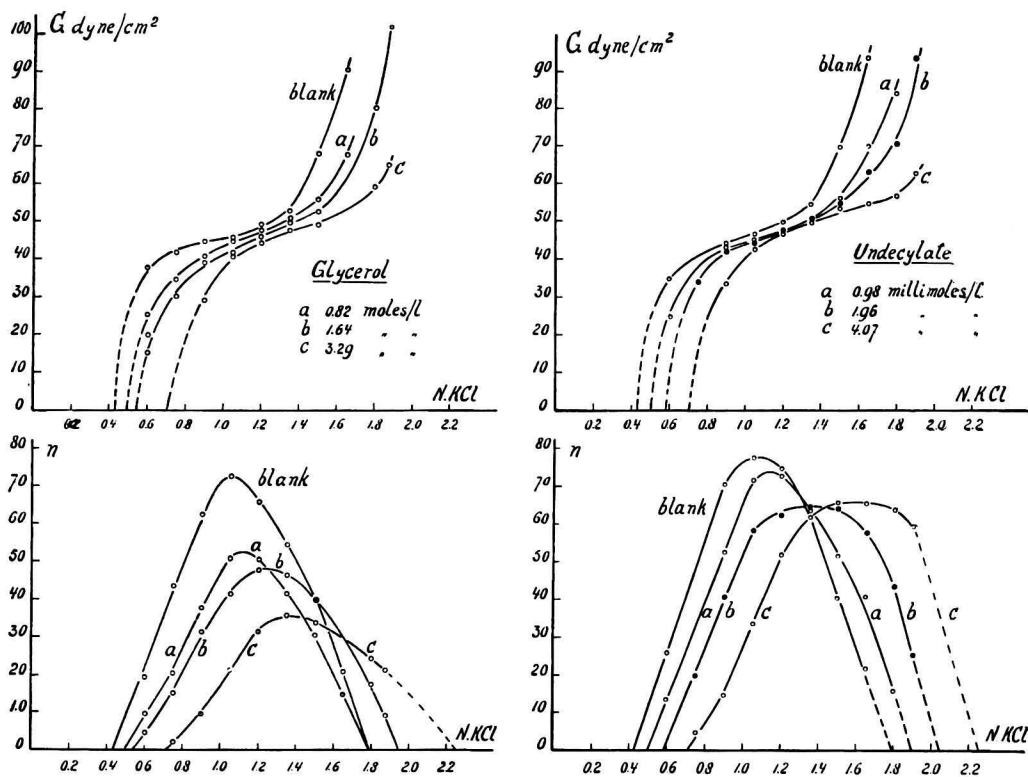


Fig. 6—7

them. The situation of the experimentally determined points was more irregular here than usual. The maximum of the n curve becomes higher here in its shifting to the right. Such an increase has never been found with other substances and must therefore be considered with suspicion,

4. the oleate used in the experiments is not strictly the same, though we always used oleate of BAKER bearing the same lot number. It has appeared that the contents of flasks with the same lot number may show quantitative differences. To make the experiments more comparable we soon used mixtures of the contents of five flasks. This was not yet done in the series with benzene, which series shows a higher value of G at the inflexion point of the blank G -curve than the other series (50 instead of ± 46). It also shows a higher value of that KCl concentration where the right footpoint of the n -curve is situated ($\pm 2.05 N$ instead of $\pm 1.78 N$),
5. the six series of experiments are extended over a period of some six months. If we assume that the contents of all flasks bearing the same lot number were originally identical, than the quantitative differences, mentioned in 4 between the samples of oleate in different flasks, must be the result of changes of the oleate with time which may proceed with different rates in the individual flasks. Therefore one must fear that samples of oleate taken regularly from one and the same mixture at different times will no longer be strictly comparable.

5. Discussion of the results.

A. Referring to the Introduction for the aims of the experiments in section 4, the results confirm: 1) that type C (a shift of the G and n curves in the direction of higher KCl concentrations) really exists, 2) that conclusions drawn from the indirect method are confirmed by the direct method. Heptane (fig. 5) and the undecylate ion (fig. 7) indeed follow type C and benzene (fig. 2) indeed follows type A .

B. Glycerol (fig. 6) belongs to type C and very great concentrations are needed to obtain measurable effects. We had expected this from the results obtained with the n -primary alcohols (parts VI and VIII of this series). n -Hexanol is a very pronounced representant of type A and acts already at very small concentrations. From n -pentanol over n -butanol, n -propanol and ethanol to methanol there is a gradual transition. The latter stands already very near to type B and acts only at relatively great concentrations. Introduction of more hydroxyl groups in the molecule, leaving the number of carbon atoms as small as possible might therefore result in a substance of type C . As these three hydroxyl groups will make the uptake of the glycerol molecule in the oleate micelles more difficult, glycerol was expected to act only at large concentrations.

C. Naphtalene (fig. 3) and benzene (fig. 2) belong to type A , heptane (fig. 5) and hexane (fig. 4) however belong to type C (with a certain restriction see below under E). This suggests a marked difference in action between aromatic and aliphatic hydrocarbons (see already part VII of this series). Systematic work on the action of hydrocarbons will be published later in this series.

D. In part VI we have seen that the inflexion point on the G -curve (in practice determined by the reading of the value of G corresponding

with the maximum of the n -curve) is shifted by n -hexanol and by ethanol in a horizontal direction only, i.e. the G value practically retains its original value. The following survey gives the G values (in dyne/cm²) corresponding to the maxima of the n curves for the experiments in section 4, viz. on every horizontal row first the G value of the blank, then the one of the first, second, third and fourth addition.

| Substance added | blank | 1e add. | 2e add. | 3e add. | 4e add. |
|----------------------|-------|---------|---------|---------|---------|
| benzene | 50 | 50.5 | 50 | 50.5 | 49 |
| naphtalene | 46 | 45.5 | 46 | 46 | — |
| hexane | 46 | 45 | 44 | 45.5 | 43.5 |
| heptane | 46 | 45 | 44.5 | 38.5 ? | — |
| glycerol | 46 | 46 | 47 | 47.5 | — |
| undecylate | 47 | 47 | 51 | 54 | — |

Taking into consideration the experimental errors and the error made by estimating the position of the maxima of the n -curves, it may be concluded that here too, when the G curve is displaced by the added substance, the G value at the inflexion point of the G curve practically retains the same value for the first five substances of the survey.

With the undecylate ion, however, the G value distinctly increases. This may eventually be ascribed to its resemblance with the oleate ion, its uptake in the oleate micelles contributing to G at the inflexion point of the shifted G curve. An increase of G at the inflexion point indeed occurs if extra oleate is added to the oleate system, but in this case (as later experiments have shown) no marked shift of the inflexion point occurs towards lower or higher KCl concentrations.

E. Fig. 8 gives the KCl concentration as function of the concentration of the added substance for three characteristic points of the n curves in the figures 2 — 7 and in the analogous figures 2 and 4 in part VI of this series, viz. the KCl concentration corresponding to the left footpoint (l. fp.), to the maximum (max.) and to the right footpoint (r. fp.) of the n curves. If it is assumed that a given organic substance, when acting on the elastic oleate system can under all circumstances be classed under one of the types *A*, *B* and *C*, then the graphs for hexanol, benzene, naphtalene, glycerol and undecylate give no indications against this assumption. Hexanol, benzene and naphtalene belong to type *A*, the three curves for l. fp., max. and r. fp. showing a descent in each graph. Glycerol and undecylate belong to type *C*, these curves showing a rise.

The remaining graphs in fig. 8, those for ethanol, hexane and heptane bear a more complicated character. This indicates that a rigid division of organic substances into three classes (showing the types *A*, *B* and *C*) is based on too simple an assumption (see already part VI section 2). Ethanol behaves as a weak representant of type *A* at the KCl concentration of minimum damping of the blank (maximum of the n -curve). At the KCl concentration of the right footpoint of the n -curve, however,

ethanol behaves as a representant of type *C*. With increase of the KCl concentration ethanol therefore shows the following transition in type:



An analogous transition consequent on the increase of the KCl concentration is also present with the investigated alkanes, providing that we only consider the action of small additions. From the direction the curves denoted l. fp., max. and r. fp. take initially, there follows for increasing KCl concentration the transitions in type:

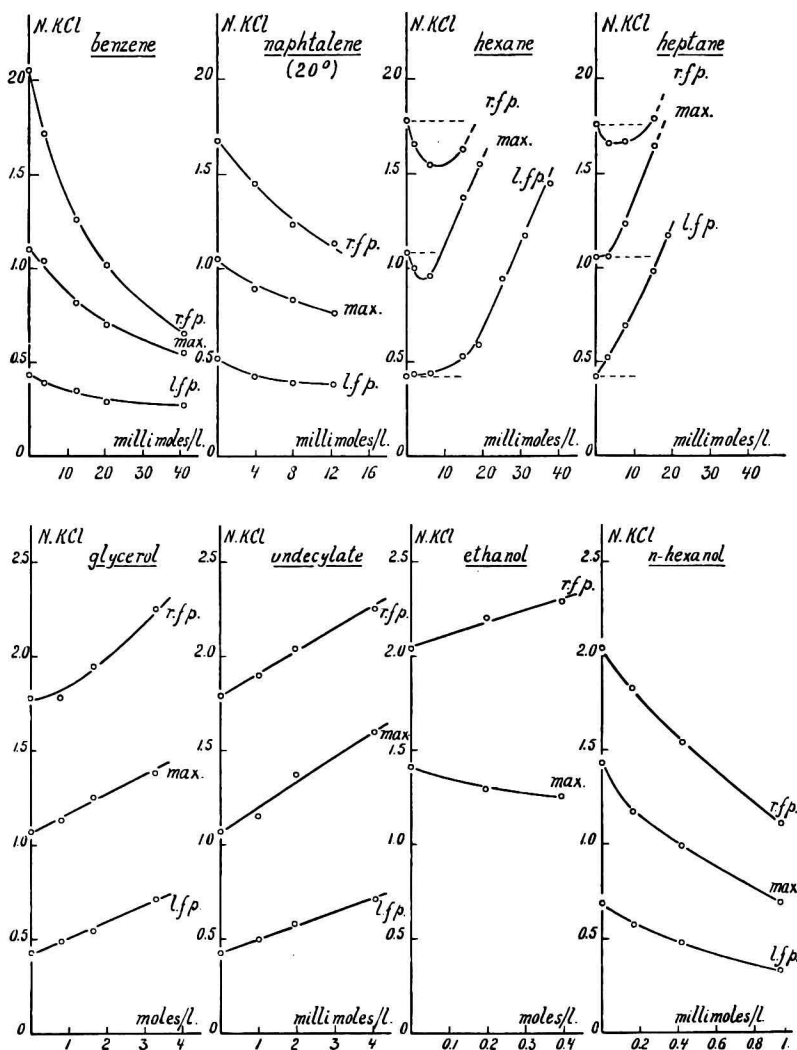


Fig. 8

Considering now the whole course of each of the curves denoted l. fp., max. and r. fp. we perceive that most of them show a transition in type consequent on the concentration of the added substance:

| Substance added | Left footpoint | Maximum | Right footpoint |
|-------------------|-------------------|---------------------------------|---------------------------------|
| hexane | $B \rightarrow C$ | $A \rightarrow B \rightarrow C$ | $A \rightarrow B \rightarrow C$ |
| heptane | C | $B \rightarrow C$ | $A \rightarrow B \rightarrow C$ |

In section 6 we will return to the above transitions in type.

F. By plotting the results obtained with benzene or naphthalene (substances typically following type *A*) $G-n$ diagrams are obtained (only sketched schematically in fig. 9 *A*), which bear quite the same character as the $G-n$ diagram for *n*-hexanol (fig. 2 *B* in part IX of this series). If we do the same with the results obtained with undecylate (represented schematically in fig. 9 *B*) a diagram is obtained

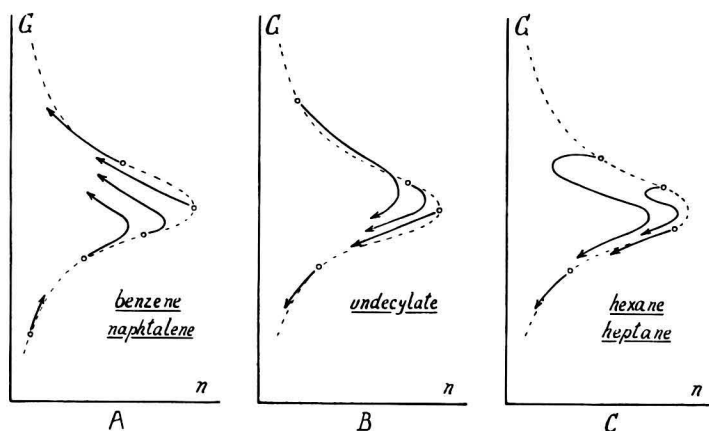


Fig. 9

which corresponds to what we might expect on account of the discussions in part IX (section 1, fig. 1) for a substance typically following type *C*. The results obtained with hexane and heptane give $G-n$ diagrams (see scheme fig. 9 *C*) in which at KCl concentrations higher than (or in the case of hexane corresponding to) the KCl concentration of minimum damping, the $G-n$ curves show a quite new type. The *S* shape of these curves, however, becomes understandable if we look at the transition in type, $A \rightarrow B \rightarrow C$, which occurs at higher KCl concentrations consequent on the increase in concentration of hexane or heptane. The *S* shape can be considered as a succession of initial courses of the $G-n$ curves represented in the diagrams 3, 6 and 9 of fig. 1 in part IX of this series.

6. *The action type (A, B or C) as a resultant of two components which act in opposite directions.*

The transitions of type ($A \rightarrow B \rightarrow C$ and $C \rightarrow B \rightarrow A$) met with in section 5 sub *E* call for a serious reflection on the question whether it

is correct to divide organic substances once and for all into three types *A*, *B* and *C*, according to their action on the elastic oleate system. It is evident that ethanol, hexane and heptane cannot be classed in either of these groups, their type of action depending on the circumstances (their own concentration and the concentration of the KCl on hand).

It seems appropriate to consider the type of action, shown by an organic substance, to be principally of compound nature, viz. as the resultant of two component actions exerted simultaneously by the added substance on essentially different places in the elastic structures, being present in the oleate system. Each of those component actions — if present alone — would shift the G and the λ (or $1/\lambda$ or n) curve into opposite directions (into the directions of higher or lower KCl concentrations). If one of these component actions preponderates within the tract of given concentrations of the organic substance itself, (at a given oleate concentration) and of the KCl being present, there result a “typically type *A*” (e.g. *n*-hexanol) or a “typical type *C*” (e.g. undecylate).

If the component actions would happen to compensate one another exactly, in the considered tract of the above mentioned concentrations, there would result a “typically type *B*”. One understands easily how unlikely it will be that the latter case will ever be realized, the two component actions being themselves functions of the concentrations of the added organic substance and of the KCl being present. As the points of attack in the elastic structure are essentially different these functions cannot be of exactly the same nature. A complete compensation of the two component actions may be possible of course, but at a given KCl concentration this will only be the case at one concentration of the added substance. A compensation within a whole range of KCl concentrations and of concentrations of the organic substance seems highly improbable.

This corresponds exactly to our experience. We have not yet met a substance which follows “typically type *B*”. Instead of it we have met substances “standing near to type *B*”, being “weak representants of type *A* or type *C*”, which, however, alter their type of action in the opposite type when the concentrations of the substance itself or the KCl concentration are changed.

The graphs for hexane and heptane in fig. 8 may illustrate this. In the transitions of type *A* \rightarrow type *C*, there is at a given KCl concentration only one concentration of the added substance, where one might speak of type *B*, viz. at the minima of the curves denoted max. (hexane) and r. fp. (hexane and heptane).

7. *Quantitative differences between oleates from different sources.*

Qualitatively the oleate preparations from MERCK and from BAKER show the same behaviour of the elastic systems prepared from them.

Already in part III of this series we observed that equally concentrated oleate systems prepared from these preparations showed different values for G and λ (λ and n) at the same KCl concentration. If on comparing the blank curves, which represent

G and n as a function of the KCl concentration, in fig. 2 and 4 of part VI (MERCK's oleate), with those in the fig. 2-7 in the present communication (BAKER's oleate), once more quantitative differences appear to be present. MERCK's oleate showed a higher value for the KCl concentration corresponding to the minimum damping, a lower value of n at the maximum of the n -curve (i.e. a higher value of Δ) and a higher coacervation limit (the KCl concentration at the right foot point of the n -curve).

There also was a difference in the outward appearance of the 1.2 % oleate systems at 15°, those of MERCK's oleate being practically clear, those of BAKER's oleate being markedly turbid. An analysis kindly made by Prof. HAVINGA showed that BAKER's oleate contained an appreciable amount of palmitate (in the order of 20 %). However one must also take into account that the preparation of MERCK was rather old (± 7 years), though it had been stored in the original unopened paraffinized bottles. The BAKER preparation on the other hand was investigated within half a year after receiving it. Thus it was uncertain which factor was mainly responsible for the different positions of the G - and n -curves. Mr. C. DE BOCK has kindly prepared for us a sample of chemically pure oleic acid free from saturated fatty acids and from linoleic acid; mp 13° with which we determined the position of the G and the n curve. The results showed that the KCl concentration of minimum damping, the value of n and the KCl concentration of the right footpoint of the n -curve do not differ much from the analogous values obtained with BAKER's preparation.

We have therefore the strong impression that the quantitative difference between BAKER's and MERCK's oleate preparations were mainly due to the age of the latter preparation. The relative position of the G and n curves suggest that as a result of the advanced deterioration of the oleate, substances have been produced which act according to type C (a shift of the G and n curves in the direction of higher KCl concentrations, accompanied by a lowering of the maximum of the n curve).

8. *Remarks on the use of half filled and completely filled spherical vessels of 110 and 500 ml capacity.*

Formerly we used as a rule, vessels of approximately 500 ml. The experiments in section 4 were performed with 110 ml vessels, which save 4/5 of the necessary chemicals. The aim of the above was to find out if still reliable experiments are possible with such small vessels. For the purposes of the present investigation the results were still good enough, but for future work on the relation between the structure of organic substances and their influence on the elastic properties of the oleate system, we will return to the use of 500 ml vessels if we want to use the method of the half filled spheres. In general we have the impression that the strive for an economic use of the chemicals goes at the cost of an increase in the experimental errors.

In order to investigate quantitative relationship completely filled vessels should be used instead of half filled ones (decidedly no "surface consolidation", see section 3) and here too we prefer 500 ml vessels above 110 ml vessels.

9. *Summary.*

1. Two new methods have been described: 1) the marking of the elastic oleate system with small H_2 bubbles obtained electrolytically, 2) a simplified way for the performing of experiments with the technique of the half filled vessels.

2. The influence of added benzene, naphthalene, hexane, heptane and undecylate was studied on the position of the curves which represent G (shear modulus) and n (maximum number of observable oscillations,

an approximate reciprocal measure for the logarithmic decrement) as functions of the KCl concentrations.

3. In the range of studied concentrations (both of the added substance and of KCl) benzene and naphthalene act typically according to type *A*, glycerol and undecylate act typically according to type *C*.

4. With hexane and heptane depending on each of the above mentioned concentrations, either type *A* or type *B* or type *C* may occur. A change in one of the concentrations keeping the other constant may lead to a transition in action type (e.g. $C \rightarrow B \rightarrow A$ at increase of the KCl concentration and $A \rightarrow B \rightarrow C$ at increase of the hexane concentration).

5. The hypothesis is drafted that each action type is the resultant of two components acting in opposite directions (type *A* and *C* if one preponderates over the other, type *B* when they compensate each other exactly).

6. The hypothesis sub 5 explains the occurrence of transitions in the type of action (mentioned in sub 4) and the unlikeliness of finding an organic substance which "follows typically type *B*", i.e. which within a whole range of concentrations of itself and of the KCl shows the action type *B*.

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