

Biochemistry. — *Elastic-viscous oleate systems containing KCl. IV. The flow properties as a function of the shearing stress at 15° and constant KCl concentration.* By H. G. BUNGENBERG DE JONG and H. J. VAN DEN BERG.

(Communicated at the meeting of February 26, 1949.)

1. *Introduction.*

An orientating investigation¹⁾ on the viscous behaviour of KCl containing oleate sols at 25° C, was performed with a viscometer which worked with constant hydrostatic head. The maximum shearing stress (at the wall of the capillary) was therefore nearly constant (of the order of 40 dynes/cm²)²⁾. As PHILIPPOFF³⁾ has shown that under certain conditions Na oleate sols may show "structural viscosity", it seemed safe to adopt for a further investigation of the viscous behaviour of the KCl containing oleate systems methods which allow of a wide variation of the shearing stress. In Part I, II and III of this series⁴⁾ the elastic properties of these systems have been studied at 15° C (at which temperature the damping of elastic oscillations is in general much smaller than at 25° C) and at a favourable KCl concentration (at or very near to the minimum damping at the given temperature). We chose therefore the same conditions for the present work and performed all experiments with "Na-oleicum, medicinale pur.pulv. Merck", which is present in the KCl (+ KOH) medium in a relatively low concentration.

The first impression these systems make on the observer is that they are gels. The definition of gels often includes the presence of a yield value. Our first aim will therefore be to investigate if a yield value can be detected, which involves the study of the flow phenomena at low shearing stresses.

2. *Measurements at very low shearing stresses.*

The viscometer used (see fig. 1) is in principle that of MICHAUD⁵⁾, whose characteristic feature is that slight level differences are obtained by immersion of a glass rod (in our case 0.55 cm diameter) into one of the

¹⁾ H. G. BUNGENBERG DE JONG and G. W. H. M. VAN ALPHEN, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, **50**, 849, 1011 (1947).

²⁾ Dimensions of the capillary: $R = 0.0425$ cm, $l = 24$ cm; constant hydrostatical head $h = 43.1$ cm.

³⁾ W. PHILIPPOFF, Viskosität der Kolloide, Dresden (1942). Cf. p. 116, 122, 279—280 and fig. 61 (p. 128) and fig. 162 (p. 280).

⁴⁾ H. G. BUNGENBERG DE JONG and H. J. VAN DEN BERG, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, Part. I: **51**, 1197 (1948); Part II: **52**, 15 (1949); Part III: **52**, 99 (1949).

⁵⁾ F. MICHAUD, Ann. de Phys. **19**, 63 (1923).

wide tubes (we used 3.6 cm diameter) and that the movement in the capillary of the system investigated, is observed in the microscope.

For the viscometer used a level difference of 0.0239 cm is obtained by screwing the glass rod downwards or upwards over a distance of one centimeter. With the aid of the formula $P = R.p/2.l$ we obtain from the dimensions of the capillary ($R = 0.0425$ cm; $l = 24$ cm) and from the

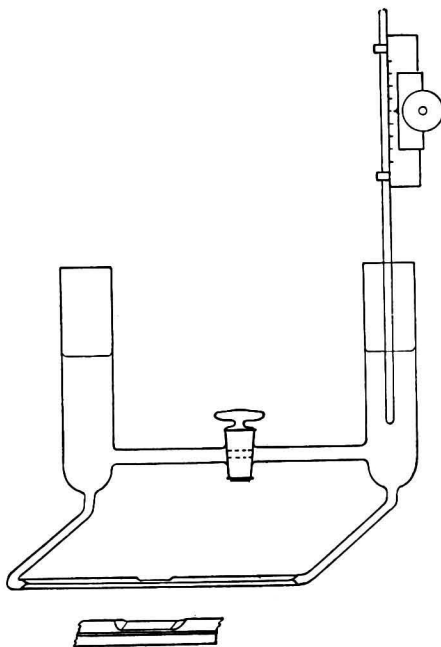


Fig. 1.

density of the soap system ($\rho = 1.066$) a value of 0.0169 dynes/cm² for P , the shearing stress at the wall of the capillary for one centimeter immersion of the rod.

Before starting a series of measurements the stopcock in the horizontal tube connecting the wide vertical tubes is closed and a certain quantity of the oleate system is brought into the left hand wide tube. With the aid of suction the capillary and the horizontal tubes connected with it are next completely filled with the oleate system. The apparatus is then put into its definite position, the capillary plus attached horizontal tubes ⁶⁾ being immersed in a tray (standing on the stage of the microscope and provided with a glass window at the bottom) through which flows water of constant temperature ⁷⁾. Now the glass rod is moved into such a position that after

⁶⁾ Only these parts of the apparatus need be at the desired temperature, because the very high viscosity of the oleate systems practically excludes all convection currents.

⁷⁾ Running tapwater was used, which practically did not change in temperature during the measurements (constant within 0.2° C).

completely filling the apparatus it will be immersed some 5 cm into the oleate system. This original position of the glass rod will be called position "zero".

The levelling of the oleate system and the drainage of the walls of the wide tubes above the levels (which during the manipulations have become wetted by the oleate system) is then obtained by opening the stopcock (wide bore) for a sufficiently long time (we took 2—3 hours).

One is not sure, however, that after closing the stopcock exact levelling has really been accomplished (e.g. on account of very high viscosity of the system or on account of any presence of a yield value).

But the position of the glass rod which corresponds to real levelling follows from the measurements themselves⁸⁾.

The latter consist in measuring the velocity of displacement (v) of suspended particles in the axis of the capillary at various positions (p) of the glass rod. These positions are varied into both directions (reckoned from position "zero"), so that a number of values p are obtained in which the system in the capillary flows to the left and another number in which it flows to the right. Providing these p and v values with + or — signs and putting them in a graph, a symmetrical figure must result, the symmetrical point of which lies on the abscis axis (position of the glass rod) and represents that position of the rod at which real levelling exists. Various forms of such symmetrical figures can be imagined, from which a few are given under a , b , c and d in fig. 2. The vertical, dotted line represents the

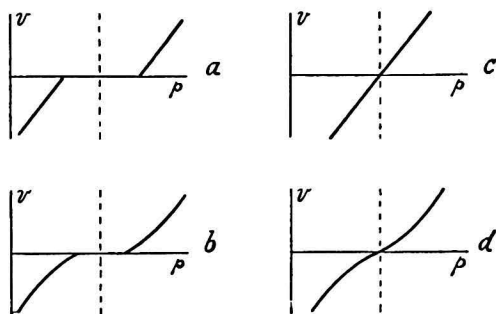


Fig. 2.

position of the rod at real levelling (which will in general differ slightly from position "zero").

In a and b a yield value is present, in c and d it is absent (or smaller than the experimental error). In c the velocity of flow is proportional to

⁸⁾ This position must remain constant during a series of measurements. This will only reasonably be the case if the stopcock after filling the apparatus has been left open for a sufficiently long time to allow the drainage of the walls. Otherwise a gradual shift of this position will occur during a series of measurements.

the shearing stress, in *a* it is a linear function of the latter and in *b* and *d* this function is more complicated.

Two oleate systems were investigated with the technique described above. They were made by mixing 50 and 125 cc respectively of a stock solution (10 gr. Na oleate + 500 cc H₂O + 50 cc KOH 2 N) with 75 cc H₂O + 75 cc KCl 3.8 N and with 75 cc KCl 3.8 N respectively. Practically the systems differ only in the final concentration of the oleate (0.45 and 1.14 gr per 100 cc). The electrolyte concentration (1.43 N KCl + 0.05 N KOH or 1.43 N KCl + 0.11 N KOH) is such that the damping of the elastic oscillations is near to its minimum value. The mixtures had now to be provided with particles, that would indicate the velocity of flow.

We will discuss this problem together with our experiments on the 0.45 % oleate system. In preparing the mixture it was thoroughly shaken and had to be left to itself for a considerable time to become approximately free from air, though some small bubbles still happened to be present. It was now tried if such entrapped air bubbles could be used as "indicators" of the velocity of flow in the axis of the capillary. An ideal indicator should have the following properties:

- a. it shall not alter the properties of the oleate system;
- b. the dimension of the particles (bubbles or drops) of the indicator shall be small in comparison with that of the capillary;
- c. its particles, etc. shall neither rise nor sink during the measurement;
- d. a sufficient number of particles should always be present in the microscopic image, so that one can select one in the axis of the capillary for each single measurement.

For entrapped air bubbles only *a.* is fulfilled. Very small bubbles are absent or relatively rare (contrary to *b.* and *d.*), so that one must select larger ones, which, however, are all rising upwards (contrary to *c.*). Soon after the beginning of a series of measurements no air bubbles are present any longer in the axis of the capillary and all lie now pressed at the upper part of the glasswall of the capillary.

The use of air bubbles is therefore not possible for indicating the velocity of flow in the axis of the capillary. Nevertheless it was decided to start a series of measurements on such an air bubble. There were no indications of the presence of a three-phase contact (air — soapsystem — glass), so that it was supposed that the air bubble could freely move along the glass boundary. If this assumption is correct, we would get information on the mean velocity of flow of the oleate system in a zone⁹⁾ close to the wall as function of the shearing stress and the results could be compared

⁹⁾ This zone of course depends on the relative diameter of bubble and radius of the capillary. It is further necessary that the bubble shall not alter its diameter during the whole series of experiments. In our case this requisite was nearly fulfilled.

with measurements in the axis of the capillary which were to be performed with a more appropriate indicator later on.

The results are given in fig. 3 in which v is expressed in scale-divisions of the eye piece micrometer per 100 seconds. The order in which the

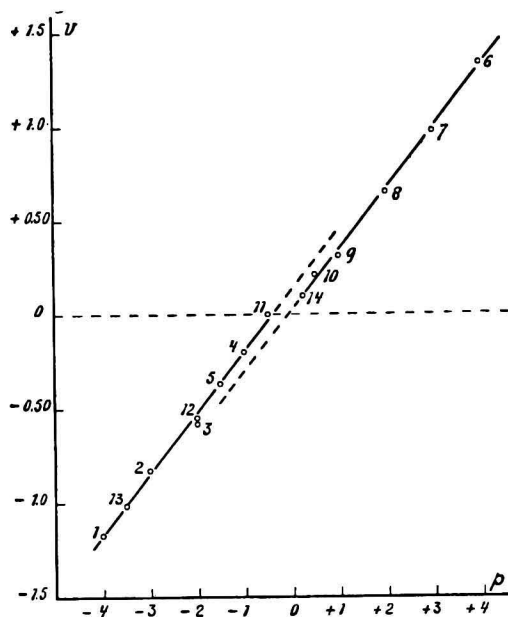


Fig. 3.

successive measurements have been taken is given by the numbers next to the experimental points. The figure obtained is of the type represented in fig. 2a, which would mean that there is a simple type of functional linear relation between rate of flow and shearing stress in the investigated range considered ($0-0.07$ dynes/cm²) as well as a yield value. The latter expressed in dynes/cm² can be calculated from half the horizontal distance of the two parallel straight lines through the experimental points, bearing in mind that every cm change in the position of the glass-rod corresponds with 0.0169 dynes/cm². The horizontal distance being approximately 0.35 cm change in position of the rod, we obtain a yield value in the order of only 0.003 dynes/cm².

But it may be seriously doubted if a yield value of the oleate system itself is really indicated by fig. 3. It is very well conceivable, that the assumption of wholly free movability of the air bubble along the glasswall (as we did) is not true and that a certain difference in pressure between the two sides of the air drop must be exceeded before the air bubble itself "yields" from its original position (pressed against the glasswall).

The measurements of the velocity of flow in the axis of the capillary were performed by using paraffine oil as an indicator. We added two drops

of paraffine oil, which slowly dripped from a 5.5 mm diameter glass rod held vertically into 200 cc of the 0.45 % oleate system. This was shaken vigorously in order to emulsify the paraffine oil. The oleate system being full of entrapped air was then left standing till the next day, to become free from air bubbles.

The system was turbid in consequence of the paraffine oil having emulsified into very small drops, which were extremely useful for indicating the rate of flow in the axis of the capillary. Indeed, paraffine oil is the nearest approach to the ideal indicator, fulfilling the requirements mentioned sub b., c. and d. on page 366.

As to exigence a. (according to preliminary experiments) the influence on the period of the rotational oscillation was found to be very slight or negligible. The velocity of flow was measured with a stopwatch by checking the time necessary for a very small drop (diameter ± 0.2 scale divisions) to move over a number of scale divisions of the micrometer, and by calculating from this the number of scale divisions per 100 sec. See table I (upper part) and fig. 4, from which it appears that:

- a. There is no indication of the presence of a yield value;
- b. the velocity of flow in the axis of the capillary is proportional to the shearing stress at the glasswall ¹⁰).

Comparing fig. 4 with fig. 3 (in which the same arbitrary units for the velocity of flow have been used) we perceive from the far smaller inclination of the straight lines in the latter figure, that the mean velocity in a zone next to the wall (in which zone the air bubble moved) is much smaller than in the axis of the capillary. Unfortunately we did not measure the dimension of the air bubble and of the capillary (the diameter of the bubble may have been in the order of $\frac{1}{5}$ of the capillary diameter), so that no quantitative calculations can be made to examine whether this difference in rate of flow is compatible with laminar flow. Except for any future indications to the contrary it seems probable that in the range of small maximum shearing stresses (0 — approximately 0.07 dynes/cm²) the oleate system, although it shows marked elastic properties, behaves as a Newtonian liquid.

We therefore conclude that our oleate systems, although they make the impression of being gels, can be described better by the term: "elastic fluids".

¹⁰) Fig. 4 deviates slightly from the simple scheme of fig. 1c, in as much the experimental points do not lie exactly on one straight line. Instead of it the points lie on two straight lines, with a slightly different inclination, meeting each another at the same point of the horizontal level at $v = 0$. In connection with the order of the measurements (alternatingly a point with a positive v and a point with a negative v , and further choosing these points in such a way that their absolute values become increasingly smaller) the shape of fig. 3 can be explained by a slight gradual shifting to the left as has been discussed in note 8. The conclusions a. and b. in the text are of course not endangered by this circumstance.

TABLE I.

Velocity of flow (v , in scale divisions per 100 sec) in the axis of the capillary.

System investigated	Immersion depth (p) of the glassrod in cm, relative to the original position									
	+4	+3	+2	1+	+0.5	-0.5	-1	-2	-3	-4
0.45% oleate system at 15.4° (see fig. 4) mean:	6.85	5.36	3.69	1.94	1.04	-0.65	-1.55	-3.32	-5.22	-6.96
	7.06	5.45	3.61	1.90	1.09	-0.69	-1.52	-3.27	-5.18	-6.96
			3.55	1.86	1.03	-0.61	-1.50	-3.27		
				1.88						
1.14% oleate system at 14.4° (see fig. 5) mean:	0.357	0.248	0.164					-0.202	-0.276	-0.351
	0.350	0.241	0.158					-0.204	-0.259	-0.348
	0.351	0.242	0.161					-0.195	-0.277	-0.349
	0.351	0.244	0.161					-0.200	-0.271	-0.349

The results obtained with the 1.14 % oleate system on the whole are the same. Because of the much higher viscosity of this more concentrated oleate system the drainage factor becomes of great importance now. (We waited 3 hours for levelling with open stopcock). The influence of this factor becomes plainly visible during the measurements, for after each displacement of the glassrod it will now take a long time until the new position of the levels is exactly reached in consequence of the slow drainage of the walls of the tubes and of the glassrod after the latter has been moved up, and of slowly renewed positions of the menisci against these

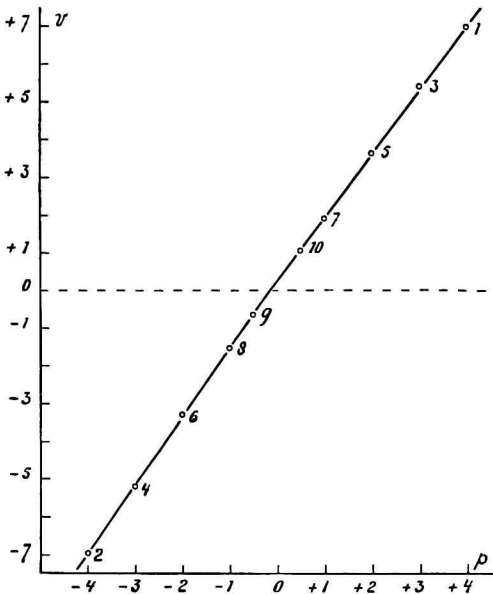


Fig. 4.

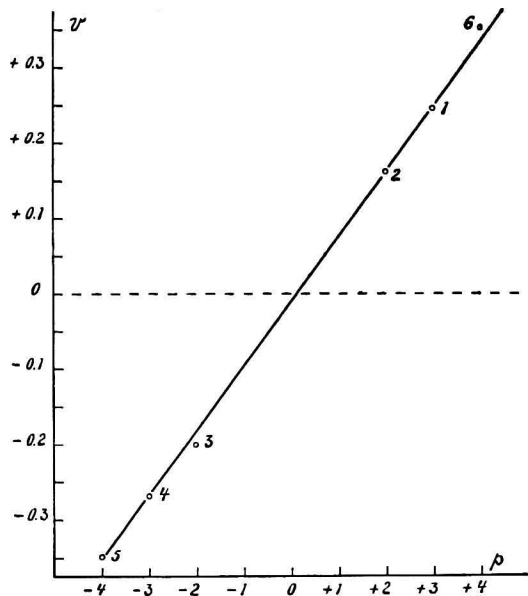


Fig. 5.

glass-surfaces after the glassrod has been lowered). The experimental results show this influence of the drainage factor (see table II and fig. 5). The apparently irregular positions of the experimental points around the straight line drawn can be accounted for from the above if we take the order of the separate measurements into consideration (indicated by the figure next to each experimental point).

We perceive, for instance, that the greatest deviation of a point from the straight line occurs if the glassrod has been displaced over a great distance just before the measurement. See point 3 and point 6, which both show too high a velocity (as can be expected from the above). Taking these disturbing influences of slow drainage and of slowly renewed wetting into consideration, we feel justified in concluding that also in the case of the 1.14 % oleate system no yield value is present and that the velocity of flow is proportional to the maximum shearing stress at the wall. In the domain of very low shearing stresses (0—0.07 dynes/cm²) this oleate system, since it shows very marked elastic properties and at the same time behaves as a Newtonian liquid, should not be described as a gel but as an elastic fluid.

3. *Measurements at higher shearing stresses.*

An investigation of the flow behaviour in a large range of much higher shearing stresses (order of 1—1000 dynes/cm²) showed that the simple flow behaviour we met at very low shearing stresses (section 2) is lost.

In principle we followed the method described by PHILIPPOFF¹¹⁾ and calculated from the experimental data the quantities V ($= 4Q/\pi R^3$), the mean velocity of flow expressed in cc/sec., and P ($= R.p/2L$), the shearing stress at the wall of the capillary expressed in dyne/cm².

A survey of the flow behaviour is then obtained by drawing a curve — the flow rate curve — through the experimental points in a diagram in which $\log V$ is represented as a function of $\log P$.

But for the differences mentioned below, the same device was adopted for observing the velocity of displacement of a drop of petroleum in a calibrated tube placed horizontally. Differences: a. only one capillary was used, and as a consequence a number of tubes of different diameters for the drops of petroleum; b. the viscometer was calibrated with a Newtonian liquid of known viscosity, from which measurement the radius R of the capillary (its length being known = 11.8 cm) was calculated (which value $R = 0.0542$ cm was needed for the calculation of the quantities V and P mentioned above).

The use of only one capillary, though not in every respect a happy choice¹²⁾, made it possible to exclude, that the peculiar shape of the flow

¹¹⁾ W. PHILIPPOFF, *Kolloid Z.*, **75**, 155 (1936).

¹²⁾ It is of course not to be expected that with one capillary it will be possible to measure the rate of flow accurately in the large tract of P -values used.

At very high P -values and low viscosity the rate of flow of the oleate system is so great

rate curve, obtained with oleate systems containing KCl, was somehow connected with the successive use of capillaries of different diameters. The curves obtained in b. made it further possible to control that in our viscosimeter the Newtonian calibrating liquids showed, indeed, a quite normal behaviour.

Fig. 6 gives in a $\log V$ vs $\log P$ diagram the flow rate curves of the two calibration liquids used (60 % sucrose at 15° and a mineral oil purchased

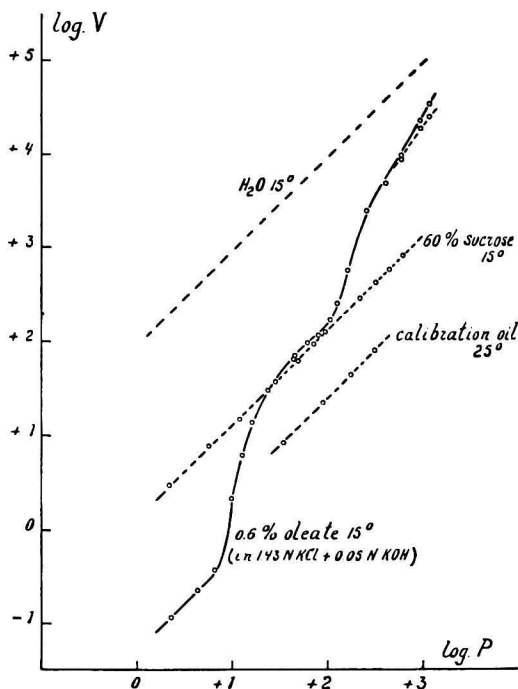


Fig. 6.

from and calibrated by the laboratory of the "Bataafsche Petroleum Maatschappij", Amsterdam¹³) and the flow rate curve of an approximately 0.6 % oleate system (containing 1.43 N KCl + 0.05 N KOH) at 15° C.

that the correction for the kinetic energy (HAGENBACH) had to be made (see note 14). At very low P -values the rate of flow of the oleate system is extremely small and a capillary tube had to be used for the drop of petroleum. The displacement of this latter drop (read off on the scale divisions of an eye piece micrometer) was observed in the telescope of a cathetometer. Certain difficulties, which seriously interfered with the accurate measurements of the rate of flow of very high viscous oleate systems, will be discussed in note 16.

¹³) The mineral oil had a kinematic viscosity of 4,424 Stokes at 25°. According to F. J. BATES and associates, Polarimetry, Saccharimetry and the Sugars, circular of the National Bureau of Standards, C 440, Washington 1942, see table p. 671, the 60 % sucrose solution must have a viscosity of 80,1 centipoises at 15°. The sucrose used was recrystallized and from the flow data obtained with the two calibration liquids, followed a viscosity of $79,6 \pm 0.7$ centipoises of the 60 % sucrose solution which agrees well with the value given above.

The curves (dotted ones) of the two calibration liquids, as is to be expected, are straight lines with a slope of practically 45° .

The curve for the oleate system, although presenting a similar course at low values of $\log P$, considerably deviates with further increase of $\log P$ ¹⁴). The shape of this curve, as we will see in the next communication of this series, is characteristic for the oleate systems containing KCl, which show marked elastic phenomena, although its position in the $\log V$ vs $\log P$ diagram still depends on a number of variables.

The typical flow behaviour is perhaps more conveniently represented by fig. 7, in which the abscissae are once more $\log P$ values, the ordinates, however, giving the values of $\log P - \log V$. The latter quantity has the meaning of the logarithm of a viscosity η (expressed in poises) at the given value of $\log P$. These curves will therefore be called viscosity-shear stress curves.

We see from fig. 7 curve A that our 0.6 % oleate system behaves as a Newtonian liquid ($\log P - \log V$ independent of $\log P$) at low values of

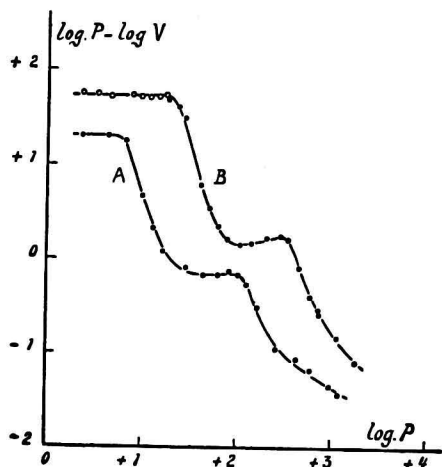


Fig. 7.

the shearing stress only. Obviously we have here the continuation of the simple flow behaviour we met in section 2, at much lower $\log P$ values.

The viscosity of the 0.6 % oleate system in fig. 7 in this range is of the order of 20 poises ($\log P - \log V = \pm 1.30$). However, with increasing $\log P$ values the viscosity decreases extremely strongly. At the highest P values investigated, its viscosity (of the order of 4 centipoises only) is still on its way downward.

It seems probable that at still higher $\log P$ values the viscosity-shear

¹⁴) Application of the correction of HAGENBACH had a visible influence on the course of the flow rate curve in fig. 6 at the three highest P -values used. These corrected values lie on the drawn curve, those that have not been corrected on the dotted curve.

stress curve will reach asymptotically an end value, which, according to PHILIPPOFF, may be denoted by η_{∞} . If we denote the highest horizontal level by η_0 , the peculiarity of our oleate systems containing KCl consists in the occurrence of an additional level¹⁵⁾ situated between η_0 and η_{∞} . This level may be denoted by η_i (i = intermediate).

If it is permitted to interpret the viscosity-shear stress curve of the 0.6 % oleate system from the point of view of its structure, we obtain the following picture: At very low shearing stresses (0—0.07 dynes/cm², see section 2) there is a structure in the oleate fluid which allows a steady flow proportional to the shearing stress. This is still possible at slightly higher shearing stresses (the η_0 level in fig. 7) but above a certain value (in fig. 7 in the order of 8 dynes/cm²) this structure breaks down in two steps. In the first step the "viscosity" decreases from approximately 20 poises to approximately 0.7 poises, in the second step, beginning in fig. 7 at approximately 100 dynes/cm², it decreases to values which are only a few times larger than that of the corresponding KCl solution (order of 0.01 poise) without the oleate. It is further important to remark, that the two steep curve branches and the intermediate level of the viscosity curve are well defined. One may switch over to other P values situated far apart and into both directions without influencing the position of the flow rate curve. This means that if we spoke above of a structure in the oleate fluid, this structure is not one which breaks down irreversibly. On the contrary, the structure postulated is one which in accordance with the prevailing shearing stresses, practically immediately breaks down to or rebuilds itself to certain equilibrium states.

In this connection it seems of importance, that soaps belong to "Association Colloids" and it suggests that the very high viscosity at the η_0 level of rather diluted oleate systems is connected with large scale associations of the oleate molecules. Such associations in principle represent equilibria.

It might be supposed that these equilibria are influenced by sufficiently large shearing stresses and that the above mentioned "breaking down or rebuilding the structure" is connected with it.

Fig. 7, curve *B*, gives the results of measurements with an approximately 1.2 % oleate system at 15° C. The black dots represent measurements with the same viscometer used for the 0.6 % oleate system. At the low log P values the rate of flow of this far more viscous system becomes so small, that as a result of disturbances connected with the small radius of the capillary¹⁶⁾, it became impossible to obtain reliable measurements.

¹⁵⁾ A similar type of flow rate curve was found by PHILIPPOFF in 13.84 % Na-oleate solutions, containing NaOH and 1.62—7 % *m*-Kresol at 20°. See his book (quoted in note 2) on p. 279—280, fig. 162.

¹⁶⁾ The entrapped air between the meniscus of the oleate system and the drop of petroleum in the capillary makes a sensitive air thermometer. Slight fluctuations in the temperature of the thermostat reflect themselves in an irregular displacement of the

That here too a η_0 level (analogous to that of the 0.6 % oleate system) is actually present¹⁷⁾, follows from measurements (white dots) with a viscometer provided with a capillary of wider bore ($R = 0.1062$ cm).

Curve *B* shows the same general characteristics as curve *A* so that we need not discuss its form again. Increase of the oleate concentration has obviously two consequences, a. the values of the η levels become higher (for curve *B* $\eta_0 = \pm 52$ poises, $\eta_i = \pm 1.5$ poises, η_∞ , not reached, lies below 0.08 poises), b. the values of the (max.) shearing stress at which "the structure breaks down" are greater (first step: order of 20 dynes/cm²; second step: order of 300 dynes/cm²)¹⁸⁾.

Comparing the curves *A* and *B* more closely we perceive, however, a difference in the position of the intermediate η "level". In *B* the experimental points do not lie on a horizontal line, but on one that is slightly sloping upwards to the right.

We are here dealing with "shear rate thickening", the viscosity increasing ($\pm 1.3 \rightarrow 1.7$ poises) with increasing shearing stress. This might indicate, that the "residual structure" left after the first step downwards (from the η_0 niveau) is modified at further increase of the shearing stress in such a way that it offers more resistance to flow, before definitely breaking up (fall of the curve towards the η_∞ level).

This shear rate thickening at the intermediate "level" is obviously facilitated by an adequate concentration of the oleate, which point will be of importance for a theory on the internal state of our oleate systems.

In the next communication, in which another viscometer will be used, we will meet with more examples of this shear rate thickening and once

petroleum drop (standstills with time and occasional temporary changes in the direction of displacement occurred). This irregular movement of the drop does not reflect a property of the oleate system; indeed in section 2, where we used still lower shearing stresses, but observed the flow of the oleate system itself in the capillary, we always found completely steady flow. It is still possible to investigate highly viscous oleate systems with the petroleum drop method, but one must for that end follow the displacement of the drop for a long time. Yet such a determination may be wrong, if apart from the relatively fast fluctuations in temperature, there happens to occur a slow and slight displacement (e.g. a few 0.01°) of the mean temperature of the thermosatte during the single measurement. Therefore one ought to repeat such measurements many times, which would take many hours for the location of a single point on the η_0 level. It is easier to use a viscometer having a capillary of wider bore, which reduces the influence of the said disturbances on the measurements considerably (the quantity of fluid flowing through the capillary per second being proportional to the fourth power of the radius). The viscometer used to measure the η_0 level of the 1.2% system is, however, not suited to measure the whole flow curve with it.

¹⁷⁾ From the results of section 2 the occurrence of an η_0 level at low values of the shearing stresses was already certain (proportionality between rate of flow and shearing stress).

¹⁸⁾ The approximately 0,6 and 1,2% oleate systems used for these experiments are not wholly comparable in age and composition. It is therefore not allowed to compare them quantitatively, e.g. as regards the functional relation between η_0 and oleate concentration.

more we will find it clearly present at higher oleate concentrations (1.2 and 1.8 %) and absent at lower ones (0.6 and 0.3 %). This absence might of course be only apparent, as the method used is not accurate enough to detect a very slight shear rate thickening.

4. *Certain particularities of the oleate systems containing KCl explained by the shape of their flow curves.*

If we have a relatively large vessel (e.g. 1L) partially filled with an 1.2 % oleate system and try to pour out its contents, we have not the least difficulty in doing so. Certainly the fluid does not impress us as being extremely viscous. This is caused by sufficient shearing stresses being set up, so that the system does no longer behave as a fluid of ± 50 poises viscosity, but as one of materially lower viscosity. When the fluid is poured out, our working point is no longer on the η_0 level, but much lower.

In Part I (see section 12) we described the appearance of a dimple in the surface of the oleate system soon after excitation of the rotational oscillation. It is followed by a slight elevation of the surface, which may last some seconds (see fig. 6g and h in Part I). Now we can understand why this elevation may last several seconds. During the vigorous motion attending the formation of the dimple and its disappearance, the oleate fluid does not behave as a very high viscous system (too large shearing stresses).

A certain quantity of the oleate system is then brought above the horizontal level. As the large shearing stresses have meanwhile disappeared, a certain quantity of oleate system with the viscosity corresponding to the η_0 level, lies a fraction of a millimeter higher than the surrounding surface. So the shearing stresses which try to level out this elevation are very small, and therefore even its edge may remain visible for a couple of seconds, before it rounds off.

5. *Summary.*

1. The viscous behaviour of a few oleate systems containing KCl which showed marked elastic properties, has been investigated at 15° , with the techniques given by MICHAUD in the range of very small shearing stresses and by PHILIPPOFF in the range of larger shearing stresses.

2. In the domain of very small shearing stresses (shearing stresses at the wall of the capillary varying from 0—0.07 dynes/cm²) the oleate system showed a steady rate of flow proportional to the shearing stress.

3. A yield value could not be demonstrated. Our elastic oleate systems, which at first sight may make the impression of gels, can for this reason be better characterised as elastic fluids.

4. In the domain of larger shearing stresses (order 1—1000 dynes/cm²) flow rate curves were obtained, which show a very strong decrease in the viscosity (more than 500 times) in a two step process.

5. After the first step downwards (from the η_0 level) the viscosity retains over a certain range of shearing stresses, nearly the same value (the 0.6 % oleate system) or it increases slightly ("shear rate thickening; 1.2 % oleate system) before the second step downwards (towards the η_∞ level) sets in.

6. The sequence in which the shearing stress is varied does not change the position of the flow rate curve. If a structure is postulated in the original oleate system, which is broken down in a two step process, it must be one which, in accordance with the prevailing shearing stresses, allows a rapid and completely reversible rebuilding. In this connection some suggestions are made regarding the role of large scale associations of the oleate molecules.

7. A few particularities of the elastic oleate systems containing KCl described previously find an explanation from the shape of the flow rate curves.

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