

Biochemistry. — *Elastic viscous oleate systems containing KCl. V*¹⁾.
Viscous and elastic behaviour compared. By H. G. BUNGENBERG
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Introduction.

According to MAXWELL's well known formula $\eta = G \times \lambda$, the product of the shear modulus G (in dynes/cm²) and the relaxation time λ (in sec.) must have the meaning of a viscosity coefficient (in poises).

In this communication measurements of the elastic and of the viscous behaviour have been performed side by side at 15° to compare the product $G \times \lambda$ with the viscosity levels η_0 , η_i and η_∞ , which according to the results obtained in Part IV of this series, occur in the viscosity shearing stress diagram of markedly elastic fluids containing KCl.

2) Methods used.

Previous to measuring the flow behaviour each oleate system was investigated as to its elastic properties, for which purpose we used the rotational oscillation in completely filled spherical vessels of different radii. For particulars see Parts I, II and III of this series. The method used for obtaining a survey of the flow behaviour was in principle the same as in Part IV, in which only one capillary and a number of tubes of different diameters were used to observe the rate of displacement of a drop of petroleum.

In connection with this choice it was no longer necessary to keep the original shape of PHILIPPOFF's viscometer. The capillary and the other tubes, all of Jena glass, were therefore sealed together, and instead of the original spherical reservoirs of relatively small capacity, we used relatively wide cylindrical reservoirs (see fig. 1).

The difference in level of the oleate system (or of the calibration liquids) could be easily read off by means of a cathetometer at the beginning and the end of each separate measurement. This mean hydrostatic pressure added to or subtracted from the air pressure applied (read off on a H₂O or Hg-manometer) gave the pressure over the capillary. From this corrected pressure we calculated the value P , the (maximum) shearing stress at the wall of the capillary, for which purpose $\left(P = \frac{R \cdot p}{2L}\right)$ the length of the capillary ($L = 11,8$ cm) and its radius must be known. This

¹⁾ Part I has appeared in these Proceedings 51, 1197 (1948), Parts II, III and IV in these Proceedings 52, 15, 99, 363 (1949).

radius ($R = 0.0716$ cm) was calculated from the calibration of the viscometer with the same Newtonian liquids of known viscosity as were used in Part IV.

The other quantity necessary for the plotting of flow rate curves, V , the mean rate of flow, was calculated from the rate of displacement of the drop of petroleum by using the formula $V = 4Q/\pi R^3$.

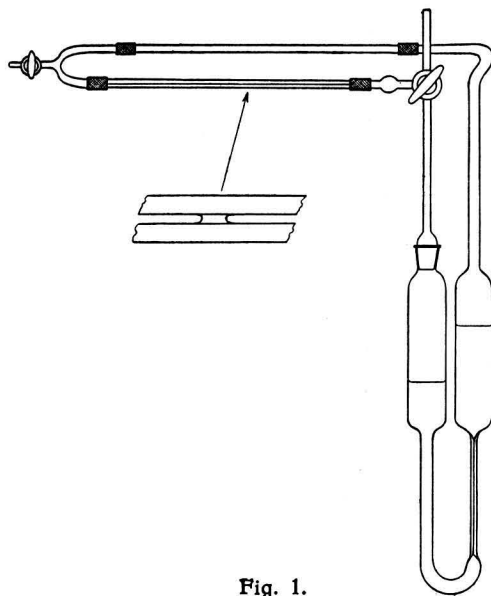


Fig. 1.

This time a wider radius of the capillary was chosen than in Part IV, as this diminishes the irregularities in the displacement of the drop of petroleum (cf. Part IV section 3, note 16), which do occur in the range of low shearing stresses with the very high viscous 1.2 and 1.8 % oleate systems. These irregularities could be further diminished by using in this range exclusively level differences between the oleate system in the cylindrical tubes and by closing the apparatus by a bent connecting tube as depicted in fig. 1. The drop of petroleum now separates two volumes of entrapped air (viz. between its own menisci and the menisci of the oleate system in the left and right reservoirs). Slight fluctuations in the temperature of the thermostat now effect slight variations in pressure on either side of the drop of petroleum which compensate one another partially. Although this device gave an improvement, nevertheless irregularities were still present, so that the measurements at low shearing stresses and very high viscosities showed a relatively bad reproducibility and the mean of a number of separate measurements may still embody a considerable error.

To check the conclusion in section 3, based on the results obtained with this viscometer, we will use in section 4 a technique by which the quantity of fluid flowing through the capillary is measured directly.

3) Comparison of the values $G \cdot \lambda$ with η_0 , η_l and η_∞ .

As in all the preceding parts of this series, we will also restrict ourselves in this section to a KCl (+ KOH) concentration, which at 15° C coincides or lies very near to the minimum damping of the elastic oscillations for the preparation of Na-oleate used (Na-oleicum med. pur. pulver. Merck).

TABLE I.

Measurements of the rotational oscillation with 1.8, 1.2, 0.6 and 0.3% oleate systems (containing 1.43 N KCl + 0.18 N KOH at 15° C).

| Na oleate g/100 cc | R (cm) | n | $10 \times \frac{T}{2}$ (sec.) | Λ | $10 \times \frac{T}{2}$ corr. | λ (sec.) | G (dynes/cm ²) | $G \times \lambda$ (poises) | |
|-----------------------|-----------|------|-----------------------------------|-----------|----------------------------------|---------------------|-------------------------------|--------------------------------|--|
| 1.8 | 7.46 | 50.0 | 5.41 | 0.193 | 5.41 | 2.80 | 99.8 | 263 | |
| | 4.92 | 57.8 | 3.57 | 0.137 | 3.57 | 2.61 | 99.7 | | |
| | 4.12 | 65.3 | 2.97 | 0.124 | 2.97 | 2.40 | 101.0 | | |
| | 7.46 | — | 5.40 | 0.201 | 5.40 | 2.69 | 100.2 | | |
| | | | | | | | mean | 100.2 | |
| 1.2 | 7.46 | 35.3 | 8.44 | 0.348 | 8.43 | 2.42 | 41.1 | 97 | |
| | 4.92 | 39.5 | 5.60 | 0.246 | 5.60 | 2.27 | 40.6 | | |
| | 4.12 | 41.6 | 4.55 | 0.196 | 4.55 | 2.33 | 43.0 | | |
| | | | | | | | mean | 41.6 | |
| 0.6 | 7.46 | 18.8 | 18.09 | 0.755 | 17.96 | — | 9.06 | — | |
| | 5.01 | 19.0 | 12.35 | 0.757 | 12.26 | — | 8.77 | | |
| | 4.12 | 19.1 | 10.03 | 0.763 | 9.96 | — | 8.98 | | |
| | | | | | | | mean | 8.94 | |
| 0.3 | 5.65 | 7.7 | 35.48 | 1.105 | 34.94 | — | 1.37 | — | |
| | 5.03 | 8.0 | 31.53 | 1.105 | 31.05 | — | 1.38 | | |
| | 4.12 | 8.4 | 24.48 | 1.112 | 24.11 | — | 1.53 | | |
| | 3.18 | 9.0 | 20.75 | 1.105 | 20.44 | — | 1.27 | | |
| | 1.70 | 9.4 | 10.03 | 1.109 | 9.88 | — | 1.55 | | |
| | | | | | | | mean | 1.42 | |

In a first series of measurements we investigated four oleate systems of different concentrations (1.8, 1.2, 0.6 and 0.3 g per 100 cc 1.43 N KCl + 0.18 N KOH). The results of the elastic measurements (rotational oscillation at 15° C) have been collected in Table I and represented in

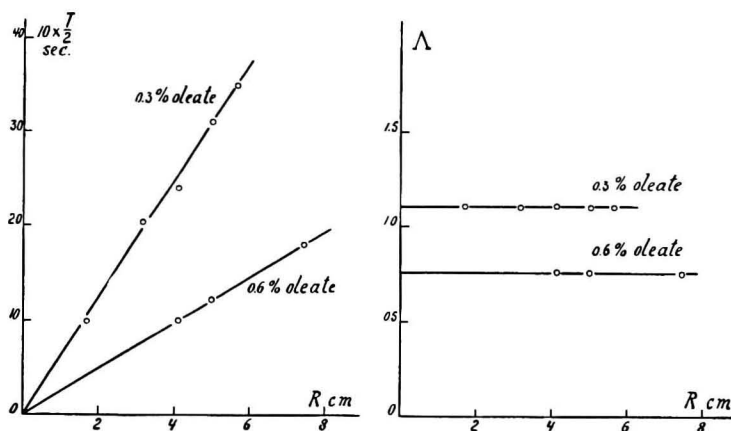


Fig. 2.

fig. 2 and 3. In accordance with the results obtained in Parts II and III of this series, we find that for oleate systems containing 0.3 and 0.6 g per 100 cc (see fig. 2 B) Δ is independent of the radius of the sphere and

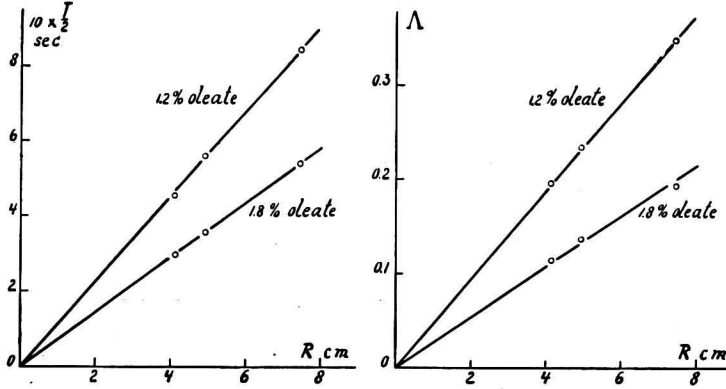


Fig. 3.

TABLE II.
Flow measurements at 15° C of the oleate systems of Table I.

| 1.8 g. oleate per 100 cc. | | | 1.2 g. oleate per 100 cc. | | | 0.6 g. oleate per 100 cc. | | | 0.3 g. oleate per 100 cc. | | |
|---|-------|---------|--|-------|---------|---|-------|---------|--|--------|---------|
| log V | log P | log P/V | log V | log P | log P/V | log V | log P | log P/V | log V | log P | log P/V |
| 0.14-2 | 0.15 | 2.01 | 0.56-2 | 0.29 | 1.74 | 0.97-2 | 0.15 | 1.18 | 0.99-2 | 0.50-1 | 0.52 |
| 0.53-2 | 0.50 | 1.97 | 0.75-2 | 0.56 | 1.82 | 0.10-1 | 0.36 | 1.26 | 0.33-1 | 0.81-1 | 0.49 |
| 0.70-2 | 0.76 | 2.05 | 0.59-1 | 1.18 | 1.59 | 0.25-1 | 0.51 | 1.26 | 0.55-1 | 0.00 | 0.45 |
| 0.98-2 | 1.09 | 2.11 | 1.75 | 1.73 | 0.98-1 | 0.72-1 | 0.82 | 1.10 | 0.81-1 | 0.17 | 0.35 |
| 0.41-1 | 1.37 | 1.96 | 2.03 | 1.88 | 0.86-1 | 0.99 | 1.05 | 0.06 | 0.35 | 0.38 | 0.03 |
| 0.76-1 | 1.57 | 1.81 | 2.35 | 2.26 | 0.91-1 | 1.53 | 1.21 | 0.67-1 | 0.69 | 0.47 | 0.79-1 |
| 0.38 | 1.78 | 1.40 | 2.52 | 2.53 | 0.01 | 1.86 | 1.51 | 0.66-1 | 0.83 | 0.53 | 0.70-1 |
| 1.99 | 2.05 | 0.07 | 2.71 | 2.66 | 0.95-1 | 2.14 | 1.76 | 0.62-1 | 1.24 | 0.68 | 0.45-1 |
| 2.27 | 2.29 | 0.03 | 3.05 | 2.79 | 0.74-1 | 2.40 | 1.92 | 0.52-1 | 1.60 | 0.84 | 0.24-1 |
| 2.43 | 2.51 | 0.09 | 3.76 | 3.07 | 0.31-1* | 2.53 | 2.06 | 0.53-1 | 1.88 | 1.00 | 0.12-1 |
| 2.51 | 2.65 | 0.15 | 4.24 | 3.31 | 0.07-1* | 2.89 | 2.23 | 0.33-1 | 2.17 | 1.30 | 0.14-1 |
| 2.68 | 2.86 | 0.18 | | | | 3.46 | 2.59 | 0.13-1* | 2.62 | 1.67 | 0.05-1* |
| 2.69 | 2.88 | 0.20 | | | | 4.00 | 2.89 | 0.89-2* | 3.15 | 1.96 | 0.81-2* |
| 3.61 | 3.19 | 0.58-1* | | | | 4.66 | 3.36 | 0.70-2* | 3.50 | 2.23 | 0.73-2* |
| 4.18 | 3.43 | 0.25-1* | | | | | | | 4.13 | 2.73 | 0.60-2* |
| log $\eta_0 = 2.02$ (mean of first five values of log P/V) | | | log $\eta_0 = 1.78$ (mean of first two values of log P/V) | | | log $\eta_0 = 1.23$ (mean of first three values of log P/V) | | | log $\eta_0 = 0.49$ (mean of first three values of log P/V) | | |
| log $\eta_i = 0.03 \rightarrow 0.20$ log $\eta_\infty < 0.25-1$ | | | log $\eta_i = 0.86-1 \rightarrow 0.01$ log $\eta_\infty < 0.07-1$ | | | log $\eta_i = 0.65-1$ (mean) log $\eta_\infty < 0.70-2$ | | | log $\eta_i = 0.13-1$ (mean) log $\eta_\infty < 0.60-2$ | | |
| $\eta_0 = 105$ poises $\eta_i = 1.1 \rightarrow 1.6$ poises $\eta_\infty < 0.18$ poises | | | $\eta_0 = 60$ poises $\eta_i = 0.7 \rightarrow 1.0$ poises $\eta_\infty < 0.12$ poises | | | $\eta_0 = 17$ poises $\eta_i = 0.45$ poises $\eta_\infty < 0.05$ poises | | | $\eta_0 = 3.1$ poises $\eta_i = 0.11$ poises $\eta_\infty < 0.04$ poises | | |

* After application of the correction of HAGENBACH.

that at higher oleate concentrations (1.2 and 1.8 g per 100 cc) Δ is proportional to this radius (see fig. 3 B).

In these two latter cases only the relaxation time λ and consequently a value $\eta = G \cdot \lambda$ can be calculated. Though for the purpose of comparing $G \cdot \lambda$ with η_0 , η_t and η_∞ it would suffice to measure the viscous behaviour of the 1.2 and 1.8 % oleate systems only, we have investigated the 0.3 and 0.6 % systems as well, in order to gain some insight into the flow behaviour as a function of the oleate concentration. The results have been given in Table II and represented in fig. 4 A and 7 A.

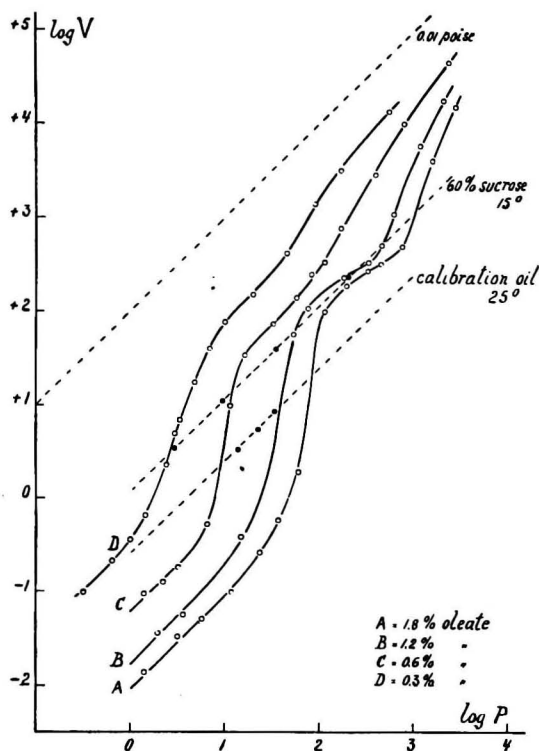


Fig. 4 A.

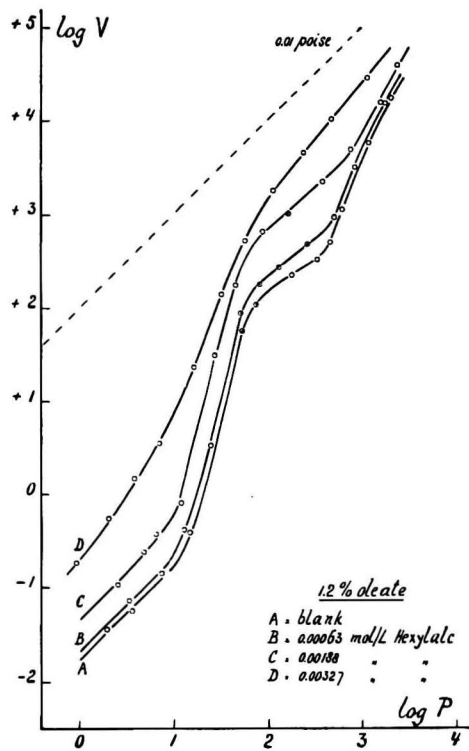


Fig. 4 B.

A second series of measurements was started from the 1.2 % oleate system (which served as a blank) to which small amounts of n.hexylalcohol were added. The results of the elastic measurements (rotational oscillation at 15° C) have been collected in Table III and represented in fig. 5 and 6.

It was found that the addition of hexylalcohol in the two concentrations which still permitted elastic measurements, does not change the proportionality between Δ and the radius of the spherical vessel. Therefore λ values and consequently $\eta = G \cdot \lambda$ values could be calculated. For the third concentration of hexylalcohol elastic measurements were no longer possible. It was nevertheless interesting to include also this latter oleate

TABLE III.

Measurements of the rotational oscillation with 1.2% oleate systems (1.43 N KCl + 0.18 N KOH) containing n. Hexylalcohol at 15° C. (For blank see Table I.)

| n. Hexylalcohol mol/L | R (cm) | n | $10 \times \frac{T}{2}$ (sec.) | Λ | $10 \times \frac{T}{2}$ corr. | λ (sec.) | G (dynes/cm ²) | G x λ (poises) |
|--------------------------|-----------|------|-----------------------------------|-----------|----------------------------------|---------------------|---------------------------------|---------------------------|
| 0.00063 | 7.46 | 33.6 | 8.12 | 0.459 | 8.09 | 1.76 | 44.6 45.1 45.2 38.9(?) | 71.2 |
| | 5.04 | 34.7 | 5.45 | 0.337 | 5.44 | 1.61 | | |
| | 4.12 | 38.1 | 4.44 | 0.288 | 4.44 | 1.54 | | |
| | 3.18 | 39.4 | 3.70 | 0.224 | 3.70 | 1.65 | | |
| | | | | | | mean 1.64 | mean 43.5 | |
| 0.00188 | 7.46 | 10.2 | 7.68 | 1.528 | 7.46 | 0.49 | 52.5 53.1 50.7 | 25.9 |
| | 4.92 | 13.7 | 4.95 | 1.026 | 4.89 | 0.48 | | |
| | 4.12 | 17.2 | 4.22 | 0.804 | 4.19 | 0.52 | | |
| | | | | | | mean 0.50 | | |

system in our investigations of the viscous behaviour. The results of these measurements have been collected in Table IV and represented in fig. 4 B and 7 B.

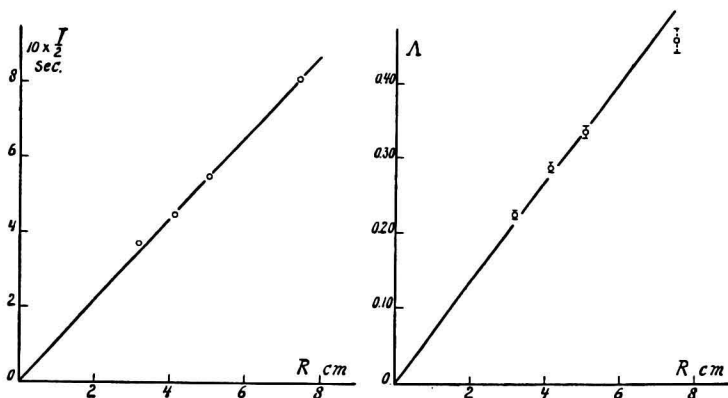


Fig. 5.

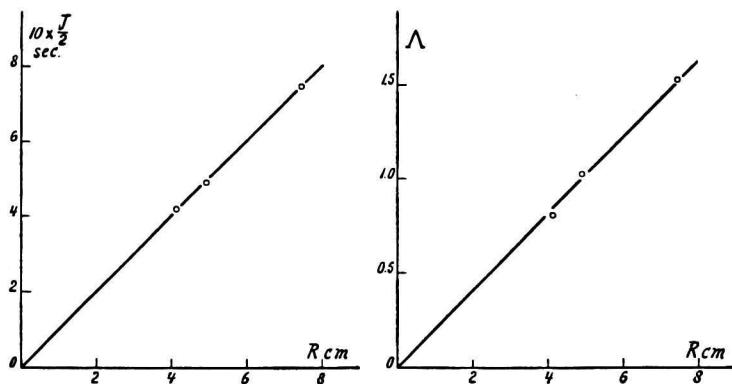


Fig. 6.

In discussing the results of the above two series of measurements we will first say a few words on the viscous behaviour. The flow rate curves of fig. 4 A and 4 B (log V as a function of log P) and the viscosity-

TABLE IV.

Flow measurements at 15° C of 1.2% oleate systems containing various concentrations of n Hexylalcohol..

| 0.00063 mol/L hexylalcohol | | | 0.00188 mol/L hexylalcohol | | | 0.00327 mol/L hexylalcohol | | |
|--|---------|-----------|--|---------|-----------|-------------------------------|---------|-----------|
| log V | log P | log P/V | log V | log P | log P/V | log V | log P | log P/V |
| 0.86-2 | 0.53 | 1.67 | 0.03-1 | 0.41 | 1.38 | 0.26-1 | 0.97-1 | 0.71 |
| 0.15-1 | 0.87 | 1.72 | 0.38-1 | 0.68 | 1.31 | 0.74-1 | 0.32 | 0.58 |
| 0.62-1 | 1.11 | 1.50 | 0.57-1 | 0.81 | 1.24 | 0.17 | 0.59 | 0.42 |
| 0.52 | 1.40 | 0.88 | 0.91-1 | 1.09 | 1.19 | 0.55 | 0.86 | 0.31 |
| 1.94 | 1.72 | 0.78-1 | 1.47 | 1.44 | 0.97-1 | 1.36 | 1.22 | 0.86-1 |
| 2.25 | 1.92 | 0.67-1 | 2.24 | 1.66 | 0.42-1 | 2.14 | 1.51 | 0.37-1 |
| 2.43 | 2.12 | 0.69-1 | 2.82 | 1.95 | 0.14-1 | 2.72 | 1.76 | 0.03-1 |
| 2.68 | 2.42 | 0.74-1 | 3.01 | 2.22 | 0.21-1 | 3.25 | 2.07 | 0.82-2* |
| 2.97 | 2.71 | 0.75-1 | 3.35 | 2.58 | 0.22-1 | 3.65 | 2.39 | 0.74-2* |
| 3.49 | 2.93 | 0.45-1* | 3.69 | 2.89 | 0.20-1* | 4.01 | 2.68 | 0.67-2* |
| 4.19 | 3.26 | 0.07-1* | 4.19 | 3.21 | 0.01-1* | 4.46 | 3.06 | 0.61-2* |
| | | | 4.60 | 3.38 | 0.78-2* | | | |
| log $\eta_0 = 1.70$ (mean of first two values of log P/V) | | | log $\eta_0 = 1.35$ (mean of first two values of log P/V) | | | log $\eta_0 > 0.71$ | | |
| log $\eta_i = 0.66-1 \rightarrow 0.75-1$ | | | log $\eta_i = 0.14-1 \rightarrow 0.22-1$ | | | η_i level degenerated | | |
| log $\eta_\infty < 0.07-1$ | | | log $\eta_\infty < 0.78-2$ | | | log $\eta_\infty < 0.61-2$ | | |
| $\eta_0 = 50$ poises | | | $\eta_0 = 22$ poises | | | $\eta_0 > 5$ poises | | |
| $\eta_i = 0.46 \rightarrow 0.56$ poises | | | $\eta_i = 0.14 \rightarrow 0.17$ poises | | | $\eta_i =$ level degenerated | | |
| $\eta_\infty < 0.12$ poises | | | $\eta_\infty < 0.06$ poises | | | $\eta_\infty < 0.04$ poises | | |

* After application of the correction of HAGENBACH.

shear stress curves of fig. 7A and 7B (log V —log P as a function of log P) show with one exception (the lowest curve in fig. 7B) the same characteristics viz. η_0 level, a tendency to reach an η_∞ level and the presence of an intermediate "level", η_i , the experimental points on it lying either on a practically horizontal line or on lines that are sloping upwards to the right: shear rate thickening (as the corresponding curves in Part IV of this series, cf. fig. 7 in that publication). These characteristics were already discussed in Part IV, so that we need not discuss them again.

It is remarkable that the curve deviating from this typical curve form, (at its lowest in fig. 7B) belongs to an oleate system, the elastic properties of which could not be measured on account of the exceedingly great damping of the oscillations (at most only two turning points were present). The viscosity-shear stress curve characteristic of the markedly elastic oleate systems (marked on account of smaller damping) has now degenerated to one in which an η_i level is no longer present and it already strongly resembles the curve form found in many cases of non Newtonian viscosity, in which there are only two levels (η_0 and η_∞).

We might further draw attention to a similarity on the one hand and a difference on the other between the influences of lowering the oleate concentration and of adding n. hexylalcohol at a constant oleate concentration. Comparing fig. 7 A with fig. 7 B we see in both cases that the viscosity-shear stress curve as a whole is displaced downwards. In lowering

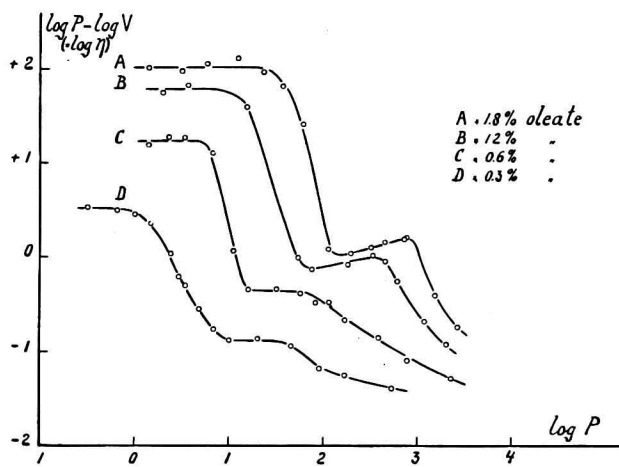


Fig. 7 A.

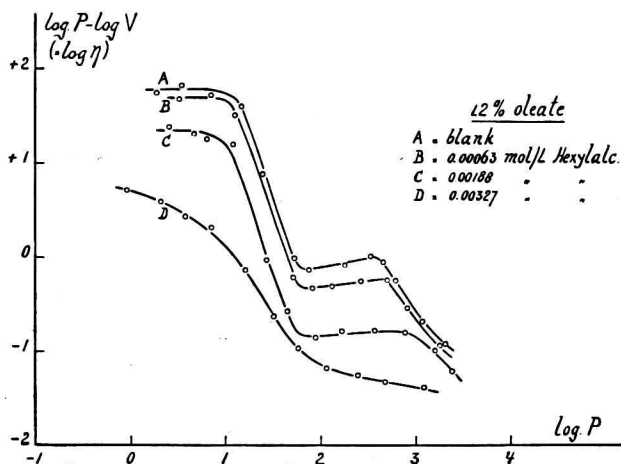


Fig. 7 B.

the oleate concentration, see fig. 7 A, the viscosity-shear stress curve is at the same time displaced to the left in a highly marked way. When adding hexylalcohol at a constant oleate concentration this displacement is absent, however.

We have now come to the comparison of the values $G \cdot \lambda$ with η_0 , η_i and η_∞ , and refer to Table V, in which we have collected the numerical values of these quantities for the four oleate systems in which this comparison is possible.

We perceive from this Table that the product $G \cdot \lambda$ does not coincide with any of the three η levels observed. The product is extremely different from η_∞ , still very different from η_i , but it is of the same order of magnitude as η_0 .

TABLE V.
Comparison of $G \times \lambda$ with η_0 , η_i and η_∞

| Composition | | $G \times \lambda$ (poises) | η_0 (poises) | η_i (poises) | η_∞ (poises) |
|--------------------------|-------------------------|--------------------------------|----------------------|----------------------|---------------------------|
| Oleate (g. per 100cc) | Hexylalcohol (mol/L) | | | | |
| 1.8 | — | 263 | 105 | 1.1 → 1.6 | < 0.18 |
| 1.2 | — | 97 | 60 | 0.7 → 1.0 | < 0.12 |
| 1.2 | 0.00063 | 71 | 50 | 0.46 → 0.56 | < 0.12 |
| 1.2 | 0.00188 | 26 | 22 | 0.14 → 0.17 | < 0.06 |

4) *The discrepancy between the values found for η_0 and for $G \cdot \lambda$.*

The same order of magnitude of the values found for η_0 and $G \cdot \lambda$ gives rise to the question if these values are really equal and if only experimental errors cause the discrepancy formed.

The difficulties we met with in measuring high η_0 values at low shearing stresses, and the discussion of these difficulties²⁾ made us much more suspicious regarding the reliability of the average η_0 values than regarding that of the average G or λ values.

We decided therefore to compare a new $G \cdot \lambda$ with η_0 , the η_0 value no longer being obtained with the aid of the petroleum drop method, but by directly measuring the quantity of the oleate fluid flown through the capillary of the viscometer. The latter was of the type as depicted in fig. 1 and the measurements consisted in reading at stated intervals the position of the levels of the oleate fluid in the equally wide reservoirs, (which were in direct communication with the air) with the aid of a cathetometer. A larger radius of the capillary³⁾ ($R = 0.1062$ cm, $L = 12.1$ cm) was taken and a smaller diameter of the cylindrical reservoirs ($= 1.773$ cm) to reduce the time which the measurements still required (the series of seven given in the table below took two whole days).

From the effective hydrostatic height⁴⁾ $\left(\Delta h / \ln \frac{h_1}{h_2} \right)$, the density of the oleate fluid, the change in position of the levels during the time elapsed, the dimensions of the capillary and the diameter of the reservoirs the viscosity was calculated with the aid of POISEUILLE's formula.

This method gave satisfactory results only if, after filling the apparatus and bringing about an initial level difference one does not start with the

²⁾ See section 2 and in Part IV section 3, note 16.

³⁾ The radius of the capillary was calculated from flow measurements with the same calibration liquids as were used in Part IV.

⁴⁾ See E. HATSCHEK, Die Viskosität der Flüssigkeiten, Dresden 1929.

measurements immediately, but checks the flow of the oleate fluid for several hours by means of a counter air pressure (to give the walls of the cylindrical reservoirs time to drain)⁵⁾. The counter pressure is then removed and some hours later one begins with the measurements.

The apparatus functions well if after the intermission between two level readings, the level has risen in one reservoir quite as much as it has fallen in the other.

As we had no more Na oleinicum "Merck" in stock and it could not be purchased either, we used Na oleate, neutral powder, "Baker"⁶⁾ for the renewed comparison of $G \cdot \lambda$ and η_0 at 15° C. The composition of the system investigated was 1.2 g oleate per 100 cc (1.25 N KCl + 0.05 N KOH)⁷⁾. Table VI contains the η_0 values obtained by the above method

TABLE VI.

Measurements of the viscosity of 1.2% oleate system (oleate "Baker" in 1.25 N KCl + 0.05 N KOH) at 15° C.

| Mean P (dynes/cm ²) | 32.10 | 27.97 | 23.98 | 23.26 | 17.82 | 14.56 |
|-----------------------------------|-------|-------|-------|-------|-------|-------|
| η (poises) | 68.2 | 76.0 | 74.9 | 77.9 | 76.6 | 74.7 |
| η_0 mean = 76.0 poises | | | | | | |

at a number of (mean) shearing stresses at the wall of the capillary⁸⁾. One perceives that compared with the large fluctuations of the log η_0 values in the Tables I and II the fluctuation of η_0 is small now, so that we may trust its mean value much better. Table VII gives the results

TABLE VII.

Measurements of the rotational oscillation of 1.2% oleate system (Oleate "Baker" in 1.25 N KCl + 0.05 N KOH) at 15° C.

| R (cm) | n | $10 \times \frac{T}{2}$ (sec) | b_1/b_3 | λ | λ (sec) | G (dynes/cm ²) | $G \times \lambda$ (poises) |
|-------------|------------|----------------------------------|----------------|---------------|--|--|--------------------------------|
| 2.98 | 60.3 | 3.13 | 1.118 | 0.112 | 2.79 } 2.88 } mean 2.90 } 2.87 2.91 } | 46.6 } 47.1 } mean 48.1 } 46.6 44.7 } | 134 |
| 4.99 | 63.5 | 5.21 | 1.198 | 0.181 | | | |
| 7.16 | 68.0 | 7.40 | 1.291 | 0.255 | | | |
| 4.99* | 61.2 ± 0.2 | 5.35 ± 0.03 | 1.202 ± 0.0034 | 0.184 ± 0.003 | | | |

* Measurement several days later during the flow experiments. From this single measurement would follow $G \cdot \lambda = 130$ poises. One is however not sure to conclude from a single measurement to a real decrease of $G \cdot \lambda$ with time.

⁵⁾ Cf. in Part IV section 2, notes 8 and 10 from which follows the necessity of taking a long time for this drainage.

⁶⁾ We are glad to express our profound gratitude to the Rockefeller Foundation, which kindly put at our disposal a large quantity of KCl and of the preparation mentioned in the text in order to enable us to continue our researches on oleate systems.

⁷⁾ The KCl (+ KOH) concentration at which the damping of the elastic oscillations is a minimum lies lower than for the oleate preparation of MERCK. It was recently ascertained that it lay even a little lower than the concentration mentioned in the text, which lies still close to this minimum.

⁸⁾ In the execution of these measurements we were assisted by W. W. H. WEIJZEN and W. A. LOEVEN, to whom we also wish to express our thanks here.

obtained in the investigation on the rotation oscillation (see also fig. 8). When we compare now the mean η_0 value ($= 76$ poises) with the mean $G \cdot \lambda$ value ($= 134$ poises) we still come to the same result as in the preceding section: η_0 is not equal to, but smaller than $G \cdot \lambda$, though both are of the same order of magnitude.

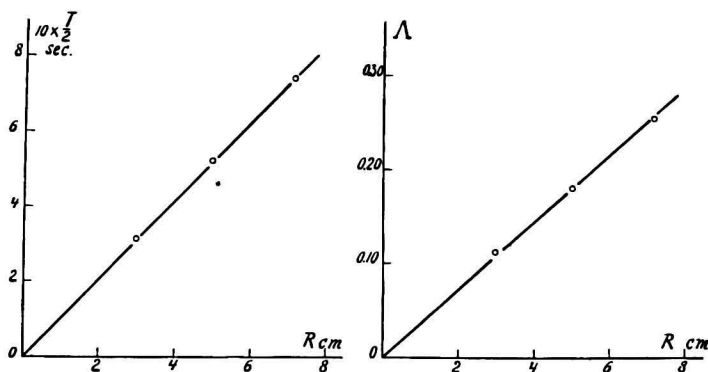


Fig. 8.

We could leave it at this general conclusion, but it is interesting that there appears to be a system in the disagreement between the two values. See the following survey. (Table VIII), giving the five cases in which η_0 and $G \cdot \lambda$ could be compared, arranged in the order of decreasing η_0 .

TABLE VIII.

| Concentration Oleate | n. Hexylalc. Mol/L | η_0 (mean) (poises) | $G \cdot \lambda$ (mean) (poises) | $\eta_0/G \cdot \lambda$ |
|----------------------|--------------------|-----------------------------|--------------------------------------|--------------------------|
| 1.8 % (MERCK) | — | 105 | 263 | 0.40 |
| 1.2 % (BAKER) | — | 76 | 134 | 0.57 |
| 1.2 % (MERCK) | — | 60 | 97 | 0.62 |
| 1.2 % (MERCK) | 0.0006 | 50 | 71 | 0.70 |
| 1.2 % (MERCK) | 0.0018 | 22 | 25.9 | 0.85 |

We see from column 5 that the disagreement between η_0 and $G \cdot \lambda$ decreases with a decreasing value of η_0 . Cf. fig. 9, which gives $\eta_0/G \cdot \lambda$ as a function of η_0 and which shows that the experimental points fairly coincide with a curve drawn through $\eta_0/G \cdot \lambda = 1$ at $\eta_0 = \text{zero}$. This might mean that MAXWELL'S relation $L = G \cdot \lambda$ in principle holds good, but that certain unknown systematic errors⁹⁾ in the experimental methods we used for determining G or λ or η , distort this equality and the more so as the absolute values of these quantities are higher. But it might also mean that the equation representing the connection between η , G and λ for our

⁹⁾ The fear of any occurrence of a systematic error in the mean η_0 values obtained in section 3 has been considerably diminished by the fact that the experimental point obtained in this section with a quite different viscosimetric technique lies on the same curve as the other experimental points (see fig. 9).

systems is really of a more complicated nature and approximates to $\eta = G \cdot \lambda$ at low values of these quantities.

Be that as it may, the same order of magnitude found for $G \cdot \lambda$ and for η_0 seems to indicate that the mechanism of viscous flow in the range of small shearing stresses is mainly due to relaxation of elastic stresses.

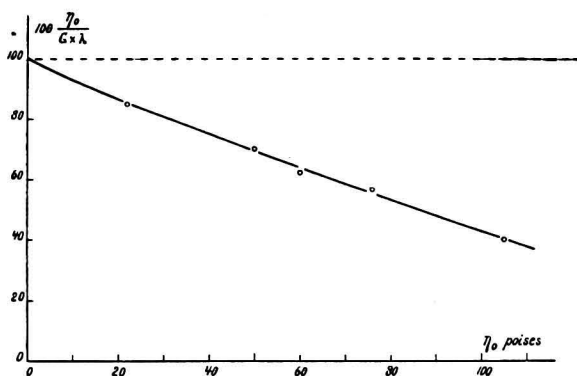


Fig. 9.

Summary.

1) The viscous and the elastic behaviour of a number of oleate systems containing KCl have been investigated at 15° C side by side to compare the viscosity coefficient calculated from elastic measurements ($\eta = G \cdot \lambda$, MAXWELL) with the viscosity coefficients η_0 , η_i and η_∞ manifesting themselves as levels in the viscosity-shearing stress diagram of the oleate systems.

2) It has been found, that both η_∞ and η_i are far smaller and of a quite different order than $G \cdot \lambda$, that η_0 , however, the viscosity coefficient at low shearing stresses, is of the same order of magnitude as $G \cdot \lambda$.

3) The percentual difference between η_0 and $G \cdot \lambda$ (η_0 has always turned out to be smaller than $G \cdot \lambda$) decreases in a marked way with decreasing absolute value of these quantities.

4) This suggests that either still unknown systematic errors, which increase percentually with increasing values of G , λ or η_0 , bring about this difference; or that a more complicated relation between G , λ and η is operative for the oleate fluid, which at small values of these quantities may practically be simplified to $\eta = G \cdot \lambda$.

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