ARCHIVES OF ACOUSTICS
2, 1, 35-45 (1977)

ACOUSTIC MEASUREMENT OF THE SHEAR COMPLIANCE OF SILICONE OIL

RYSZARD PŁOWIEC

Institute of Fundamental Technical Research
Polish Academy of Sciences (Warszawa)

A method of measurement is described and the results of measurement of the modulus limit shear compliance J_∞ of four samples of synthetic oil with different molecular weight compared. Oil properties have been measured acoustically by determining the characteristic shear resistance at a stress frequency of 30 MHz and 450 MHz and in the temperature range from 0°C to −100°C.

It was found that the increase of molecular weight has only little influence on the limit of the modulus of shear compliance of the liquid.

1. Introduction

It is a well known fact that viscosity characterizes a liquid medium only in the case of its distortion at comparatively low frequencies. As the liquid is subjected to distortions of increasing frequency its (dynamic) viscosity decreases while the liquid shear modulus of elasticity (G) increases. At very high frequencies the dynamic liquid viscosity decreases to zero while the shear modulus of elasticity asymptotically approaches a large value (the limiting value, G_∞). Furthermore, it was found that this limit of the liquid of the modulus of elasticity G_∞ is of the same order of magnitude as the modulus of elasticity of a solid.

The phenomenon of decreasing dynamic viscosity and increasing elasticity of a medium plays an essential role in lubrication, thus much attention has been devoted to measurements of this kind [1, 2].

The modulus of shear elasticity of a liquid G_∞ or the commonly used modulus of the shear compliance of a liquid J_∞ ($J_\infty = 1/G_\infty$) is an interesting quantity from the molecular viewpoint since it supplies information on the ability of molecules to perform the translational or rotational motions encountered in the lubrication process [3].

In these investigations an important role is played by ultrasonic and hypersonic vibrations which permit the production in the examined liquids of shearing stresses with a distortion frequency of over 10^9 Hz [4].

The reaction of a liquid to shearing stresses is determined acoustically by measuring the so-called characteristic shear impedance Z which is the ratio of the shearing stress (in dyn/cm^2) to the velocity of a molecule (in cm/s). Theoretically, the liquid reaction can be determined comparatively easily on the basis of a network model of liquid medium, which is valid for the propagation of plane shear waves [14]. For solids the characteristic impedance is a real magnitude and is given by

$$Z = \varrho C_T = \sqrt{\varrho G},$$

where ϱ is the density of the medium, C_T – the velocity of propagation of transverse waves in the medium and G – the shear modulus of elasticity.

In the case of viscoelastic liquids the shear impedance is a compound quantity ($Z_c^* = R_c + jX_c$), as also is the shear modulus ($G^* = G' + jG''$), thus

$$Z_c^* = \sqrt{\varrho G^*}.$$

With a sufficiently high frequency the imaginary component of the impedance (X_c) is considerably smaller than the real component (R_c) and in this range it can practically be neglected. Thus the limiting, high-frequency shear modulus of elasticity is

$$G_\infty = R_c^2/\varrho. \tag{1}$$

When determining the absolute value of the limiting value of the shear modulus of elasticity by the acoustic method, it is also necessary to know the density of the examined medium. It is determined using one of the known physical methods.

The frequency of the distortions which should be induced in the liquid to determine the limiting value G_∞ is dependent upon the type of sample examined. This frequency should be considerably higher than that of viscoelastic relaxation f_0, the time of this relaxation $\tau(\tau = 1/f_0)$ being given by

$$\tau = \eta/G_\infty,$$

where η is the static viscosity of the examined sample. The value of the modulus G_∞ is very similar for individual liquids (Fig. 9), so that the frequency of the distortions, for example for a liquid sample with a viscosity of about 0.01 $N \times s \times m^{-2}$ (10 cP), should be higher than 10^{10} Hz. With present techniques it is possible to test liquids at frequencies up to 10^9 Hz. Thus to determine the limiting shear elasticity of a liquid with a low viscosity, the measurements are made of necessity at reduced temperatures. For such investigations liquids are selected which can be supercooled and are thus capable of giving very high viscosities and a clearly defined range of pure elasticity.

The measurements described below are made at reduced temperatures, from 0 to −100°C, with samples from four types of a synthetic oil at two measuring frequencies 30 MHz and 450 MHz, to investigate the effect of the molecular weight on the limiting value of the shear compliance.

2. Acoustic determination of shear resistance

The characteristic value of the impedance of a liquid can be best evaluated by measuring the coefficient of reflection of ultrasonic waves at the boundary of two media of which one is a known medium and the other the liquid to be examined. Crystalline or fused quartz, for which the shear impedance Z_q and its dependence temperature are known, is used for the former medium.

To measure the coefficient of reflection k by means of a quartz transducer a pulse of vibrations is set up on the cylindrical surface of a fused quartz delay line. A suitable cut of the transducer provides a pulse of transverse vibrations with a polarisation perpendicular to the direction of wave propagation. This pulse, which propagates along the delay line, will be reflected from the surface opposite the transducer. Should this surface be in air, the reflection of the pulse ($k = 1$) will be virtually complete, but if the surface is located in a liquid, the coefficient of reflexion will be [5]

$$k = \frac{Z_c - Z_q}{Z_c + Z_q}. \tag{2}$$

The very high damping of transverse waves in liquids means that formula (2) is valid even for a comparatively thin layer of liquid on the surface of the delay line.

Within the elastic range of a liquid where $X_c = 0$, and also when $X_c \ll R_c$, formula (2) can be written as

$$R_c = Z_q \frac{1-k}{1+k}, \tag{3}$$

where k is the ratio of the voltages of the signals that correspond to the reflected and incident pulses.

3. The characteristics of the examined liquids

The liquid used for the investigations was a synthetic oil, trifluoropropyl methylsiloxane (FS 1265), produced by the British firm Midland Silicone Limited. This liquid is a linear polymer, free of main chain branches. Four samples of this liquid with different lengths of the chain were examined. The static viscosity of the different types at room temperature (20°C) and their mean molecular weights ($\bar{M}_n$) are stated below:

Sample	η	$\bar{M}_n$
A	1,72 P (0.172 N.s.m.$^{-2}$)	1720
B	30,0 P (3.0 N.s.m.$^{-2}$)	9050
C	179,0 P (17.9 N.s.m.$^{-2}$)	20000
D	8120,0 P (812.0 N.s.m.$^{-2}$)	72600

4. Measuring system

The diagram of the measuring system is shown in Fig. 1. The operation of the system is controlled by square impulse generator (*1*) which modulates the oscillator at a frequency of 200 Hz to obtain vibrations at this frequency from the impulse transmitter. These impulses then induce transverse vibra-

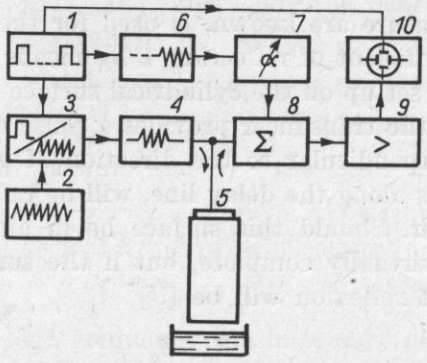

Fig. 1. Diagram of measurement system

1 – square pulse generator, *2* – continuous wave generator (oscillator), 3 – modulator, *4* – h.f. pulse transmitter, *5* – transducer, *6* – comparative pulse generator, *7* – regulating attenuator, *8* – totalizing system, *9* – amplifier, *10* – oscilloscope

tions on the quartz transducer (*5*) with BT cut. The induced vibrations are propagated along the cylindrical delay line made of fused quartz. The impulses, after being reflected from the opposite end of the line, are received by the same transducer which acts as a receiving transducer at times between the transmitted impulses. The received impulses are then amplified (*9*) and, after detection, visualized on an oscilloscope screen (*10*).

To measure the amplitude of a received signal an auxiliary transmitter (*6*) of the same frequency is impulse-modulated with a short delay in relation to the main transmitter. The output signal from the auxiliary transmitter is passed through an attenuator (*7*) with precise and continuous attenuation control to meet in the totalizing system with the received signal. Both signals are then amplified and, after detection, visualized on the oscilloscope screen. The delay of the auxiliary impulse is controlled in such a manner that both impulses, received and auxiliary, are very near to each other. The latter can then be easily reduced to the same amplitude as the former by means of the attenuator (*7*). To increase the measurement accuracy advantage is taken of signals reflected repeatedly from the delay line. The coefficient of reflection k is determined from the difference in the attenuation of consecutive echoes for air (q_p) and for the examined liquid (q_c),

$$k = q_p/q_c,$$

where $q = A_n/A_{n+1}$, A_n and A_{n+1} denote the amplitudes of consecutive impulse reflections.

A measuring system operating on a similar principle has been used at a frequency of 450 MHz with only a quartz crystal being used in direct contact with the liquid. This crystal has been iduced to emit transverse vibrations in a special resonance cavity by the method described in a previous publication [6].

5. Measurement results

The measurements of the density of liquid samples as a function of temperature were made by means of a pycnometer. The measurement error of the liquid density by this method is estimated to be $\pm 0.1\,\%$. The density of each sample for about 10 different temperatures within the range from $-70°C$ to $50°C$ has been determined.

For all measured temperatures linear dependence of density on temperature was found to exist within the investigated temperature range, in agreement with the equation

$$\varrho_{(T)} = \varrho_0[1-\alpha_0(T-T_0)] \ [\mathrm{g/cm^3}]. \tag{4}$$

Table 1. Values of the parameters of the density, eq. (4)

Specimen	ϱ_0	$\alpha_0(\times 10^4)$	T_0[K]
A	1.3515	7.4	151.6
B	1.3707	5.83	156.0
C	1.3945	6.02	163.0
D	1.4315	6.99	166.6

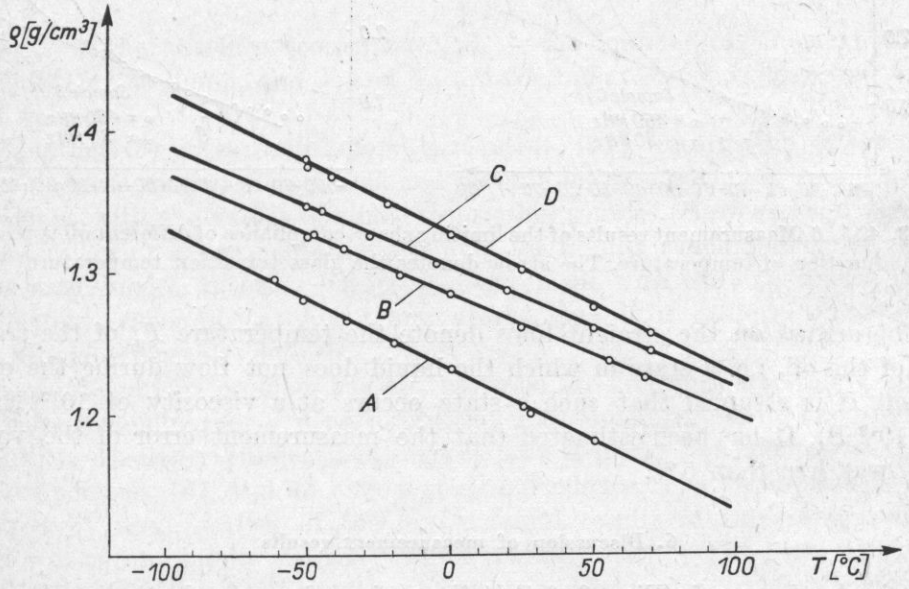

Fig. 2. Variations of the density of the liquids tested as a function of temperature

The values ϱ_0, α_0 and T_0 for individual liquid types are given in Table 1.

The measurement points and equation (4) for $\varrho_{(T)}$ have been plotted in Fig. 2 for the different samples of liquid. Measurements of shear resistance R_c at different temperatures within the range from 0 to $-100°C$ and at frequencies of 30 MHz and 450 MHz were made by the method described above. During the measurement the temperature was controlled by means of a platinum resistance thermometer with an accuracy of $\pm 0.1°C$.

The measurement results in the form of quotient ϱ/R_c^2, being the liquid shear compliance, J_∞, are shown for the different samples in Figs. 3-6.

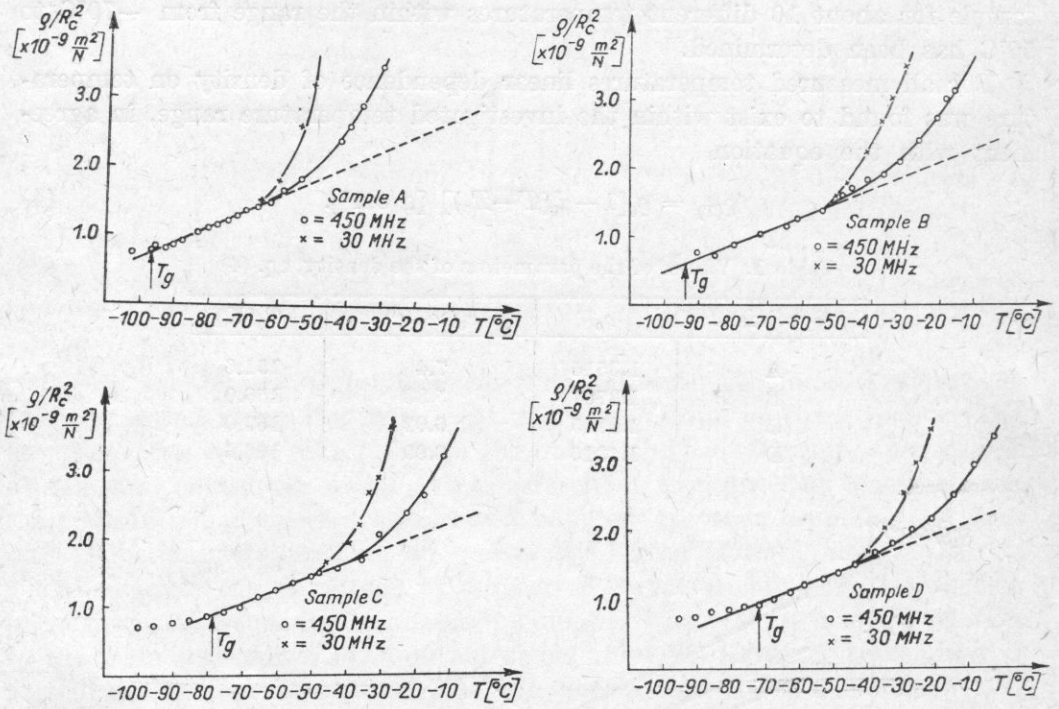

Fig. 3, 4, 5, 6. Measurement results of the limiting shear compliance of different oil types as a function of temperature. The arrow denotes the glass transition temperature

The arrows on the straight lines denote the temperature T_g of the transition of the oil, i.e. a state in which the liquid does not flow during the experiment. It is assumed that such a state occurs at a viscosity of 10^{12} Ns/m^2 (i.e. 10^{13} P). It has been estimated that the measurement error of the values of R_c was less than 5%.

6. Discussion of measurement results

It is clearly seen in Figs. 3-6 that the region of purely elastic liquid occurs in a comparatively narrow temperature range, between the temperature (T_g) of the glass transition of the liquid and the temperature at which the

viscoelastic relaxation predominates. Within this range the quotient ϱ/R_c^2 has the same value both for frequencies 30 MHz and 450 MHz. The constant value of the quotient ϱ/R_c^2 for various frequencies confirms the occurrence in the liquid of the elastic range. For this reason, in order to separate the elastic range from the relaxation range and to evaluate the temperature dependence of the limiting compliance J_∞, it is necessary to use at least two frequencies for the measurement.

The literature contains many papers dedicated to calculating G_∞ or J_∞ or describe their dependence on the temperature. For instance, for hydrogen-bonded liquids the dependence

$$J_\infty = J_\infty^0 + \frac{BV}{n_H N}\left[\exp\left(-\frac{\Delta H}{RT}+\frac{\Delta S}{R}\right)+\frac{V_f}{V}\right] \tag{5}$$

has been derived [12], where J_∞^0 is the magnitude of the limiting elasticity which is characteristic for glassy liquids, B is a constant for a given liquid, V – the molar liquid volume, n_H – the number of hydroxide groups per molecule, N – Avogadro's number, R – the ideal gas constant, and ΔH and ΔS – quantities required for the description of the temperature and pressure dependencies. On the other hand, REE, REE and EYRING [15] have derived for the limiting liquid shear elasticity the formula

$$G_\infty = \frac{6RT}{2Z_n(V-V_0)}, \tag{6}$$

where T is the absolute temperature, Z_n – the number of the next closest molecules in the liquid, and V and V_0 are the molar liquid volume and molar solid volume.

Equation (5) gives satisfactory agreement [13] within the supercooled range and the magnitudes of ΔH and ΔS for many associated liquids are in agreement with the values obtained from other sources. However equation (6) agrees well with experimental results only for liquids which satisfy Maxwell's viscoelastic model. In other liquids the agreement with the experiment is not satisfactory, especially at low temperatures, and it is at low temperatures that G_∞ is preferably defined.

A quite complex problem has proved to be the description of the nature of the variations in G_∞ (or J_∞) as a function of temperature from experimental results [7, 8]. Other publications suggest both a linear dependence of G_∞ on the temperature [8], and an exponential dependence. The description is complicated by some scatter of the experimental results in this comparatively narrow range of liquid elasticity which permits both possibilities of dependence. The reason for the considerable scatter of the measurement points are the technical limitations of making an accurate measurement of the resistance of a liquid and its temperature.

Latterly in the literature the notion of a linear dependence of J_∞ on the temperatures has prevaited, as described by the formula [10]

$$J_\infty = \frac{1}{G_\infty} = \frac{1}{G_\infty^0}[1+B(T-T_0)]. \tag{7}$$

This dependence is entirely empirical, but it proves its practicability exceptionally well when compared with the results of measurements at various temperatures and frequencies [11]. It may be assumed that the above form for J_∞ as a function of temperature is connected with the variation of a free liquid volume $V_f = V - V_0$, where V is the characteristic volume equal to $1/\varrho$, $V_0(1/\varrho_0)$ is the packing volume of molecules encountered in the vitreous state at the temperature T_0.

The linear dependence of J_∞ on the temperature may be expected to occur when the density of the tested liquid has a linear temperature dependence as described by equation (4). The free liquid volume is in this case

$$V_f = \frac{\varrho_0 - \varrho}{\varrho_0 \varrho} = \alpha_0 V(T-T_0),$$

where α_0 is the coefficient of expansion at the temperature T_0 and is defined in Table 1. Substituting this into equation (7), the approximate formula for the limiting liquid shear compliance can be written [8]

$$\frac{1}{G_\infty} \cong \frac{1}{G_\infty^0} + \frac{\alpha_0}{G_1}(T-T_0). \tag{8}$$

The approximation covers the range $G_\infty^0 \gg G_1$, where $1/G_1$ is the compliance connected with the relaxation of the structure and the appearance of a free volume.

The dependence of G_∞ and J_∞ on the free liquid volume also occurs in equations (5) and (6). In the absence of hydrogen bonds in the liquid equation (5) can be reduced to equation (7).

The comparison of the results of measurement on different oil samples at various temperatures and frequencies has assisted in finding a linear dependence for the variation of J_∞ with temperature. This variation is represented in Figs. 4-6.

Table 2 states the magnitudes of J_∞^0, B and T_0 evaluated from equation (7) for the different oil types.

Table 2. Values of the parameters of the rigidity modulus, eq. (7)

Specimen	$\frac{1}{G_\infty^0}$ [$10^9 m^2/N$]	β	T_0[K]
A	0.2	0.112	151.6
B	0.154	0.125	156.0
C	0.297	0.0627	163.0
D	0.331	0.057	166.6

In this manner the range of variations of the limiting shear compliance as described by formula (7) and shown in Figs. 3-6 can be divided into two regions:

a) the region over which J_∞ is measured directly where the experimental results obtained confirm the validity of equation (7) (continuous line in Figs. 3-6),

b) the region over which J_∞ cannot be measured directly because of the predominant effect of the viscoelastic relaxation. In this region an extrapolation is used – which agrees with formula (7) – to determine the value of J_∞ within the relaxation range (broken line in Figs. 3-6).

A comparison of the measurement results of the limiting shear compliance and its temperature dependence for the liquid samples tested is shown in Fig. 7. It can be seen that differences in the limiting value of the shear compliance for types B, C and D are insignificant in spite of a considerable difference in the static viscosity of these samples.

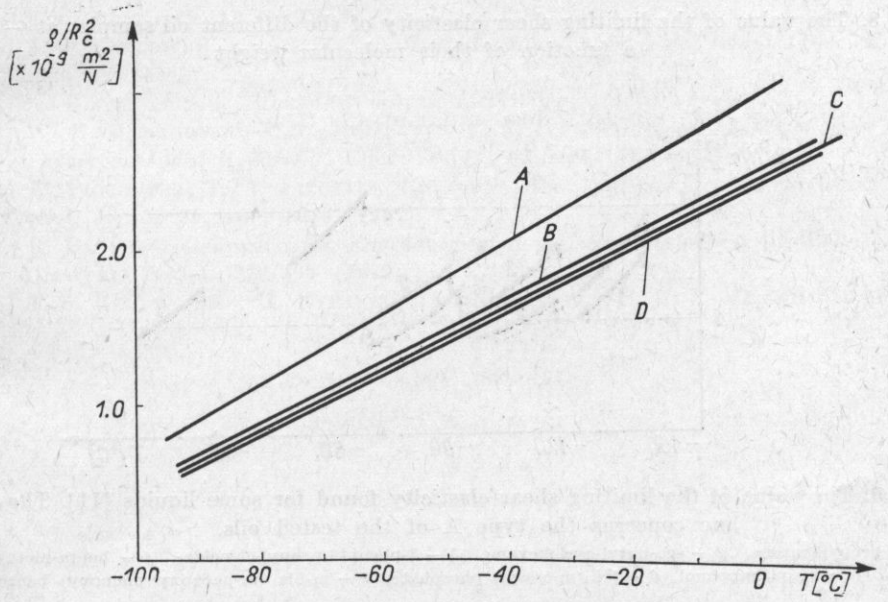

Fig. 7. Comparison of the variation of the limiting shear compliance with temperature for the different oil samples

The value of the limiting shear elasticity exhibited by the samples at a temperature of −80°C as a function of their mean molecular weight $\bar{M}_n$ is shown in Fig. 8. It can be seen that the molecular weight has an insignificant effect on the limiting modulus G_∞. Despite large differences in the molecular weight between the samples the values of G_∞ vary within comparatively narrow limits $(0.9\text{-}1.25)\times 10^9$ N/m².

Fig. 9 shows the values of G_∞ in the neighbourhood of the glass transition temperature of the various liquids and their variation with temperature as

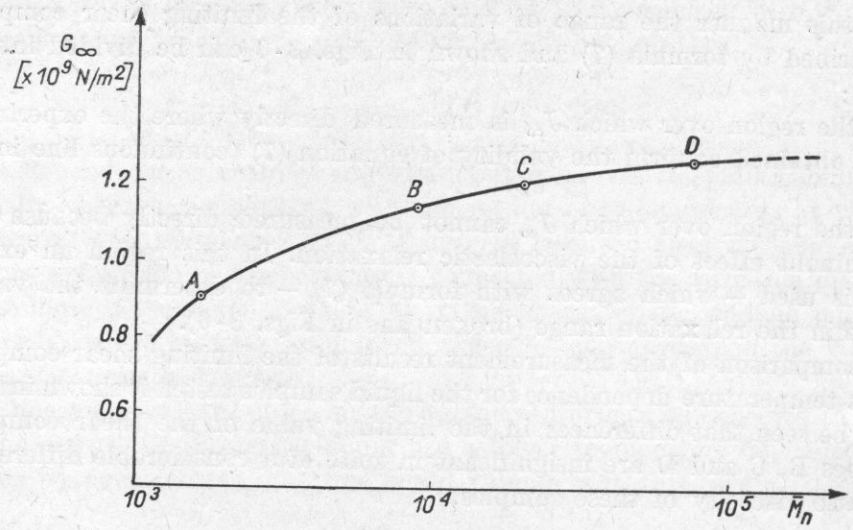

Fig. 8. The value of the limiting shear elasticity of the different oil samples at −80°C as a function of their molecular weight

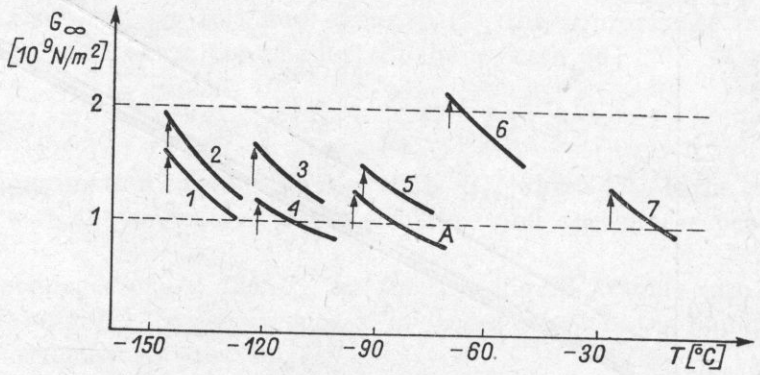

Fig. 9. The value of the limiting shear elasticity found for some liquids [11]. The broken line concerns the type A of the tested oils

1 — n-propylbenzene, *2* — sec-butyl-cyclohexane, *3* — 3-phenyl propyl-chloride, *4* — hepta-methylnonane *5* — 3-phenyl propanol, *6* — tri (m-cresyl) phosphate, *7* — m-bis (m-phenoxy phenoxy) benzene

quoted by other authors [11]. It is worth noting also that in spite of a large differentiation of the liquids compared in Fig. 9 (simple and polymer liquids) the absolute values of the limiting shear elasticity G_∞ in the vicinity of the vitrification temperature are approximatly the same, being within the limits $(1\text{-}2)\times 10^9$ N/m^2.

Acknowledgment. The measurements described were performed during the author's post-graduation scientific practice at the University of Glasgow (G. Britain). The author is anxious to express his gratitude to Prof. J. LAMB for his contribution in enabling these measurements to be performed.

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Received on 8th May 1975

Revised 15 Juni 1976