

NO. 102.

(Published February, 1934.)

On the Relation between the Temperature
Coefficient of Viscosity and the As-
sociation of High-molecular Liquids.

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Abstract.

Careful measurements were made of the viscosities of benzene solutions of various high-molecular liquids. By means of Staudinger's equation, which expresses the relation between the viscosity and the concentration of solution, a quantity which I shall call the "viscosity association" was calculated for a number of high-molecular liquids. A simple relationship exists between the temperature coefficient of viscosity and the viscosity association of high-molecular liquids. A reasonable conclusion is deduced concerning the relation between the temperature coefficient of viscosity and the molecular structure of high-molecular liquids.

Viscosity in liquids depends not only upon the intermolecular forces described as association or cohesion, but also upon molecular structure.⁽¹⁾ Other factors such as solvation and electroviscous effects have also

(1) The fact that viscosity depends on the size and shape of the molecules is evident from the experiments carried out by Staudinger, as will be shown later.

been recognized as important in viscosity, but their effects are restricted to special cases. Viscosity may therefore generally be regarded as a function of two factors, the factor due to association (f_q) and that due to molecular structure (f_s). Our simplest assumption is that the viscosity coefficient may be expressed by the following formula, in which k is a constant :

$$\eta = k \cdot f_s \cdot f_q \quad (I).$$

The formulae for viscosity given by Gartenmeister⁽¹⁾ and by Macleod⁽²⁾ may be regarded as special forms of formula (I).

The inevitable increase in viscosity with rise of temperature may depend only on factor f_q and not on f_s , since the change in viscosity can only be ascribed to reduction of intermolecular forces as a result of the augmentation of molecular movement with increase of temperature.

As has been shown by Errera,⁽³⁾ molecular association may be caused either by permanent dipoles (polar molecular association) or by van der Waals's force (nonpolar molecular association). The sum of polar and nonpolar association, that is, the total association, can be computed from measurements of either the viscosity or the vapour pressure, whereas measurements of polarization, which give the electric moment per unit volume, enables us to estimate only polar association. After verifying the dependance of molar polarization on concentration for various solution, which consisted of a nonpolar solvent, such as benzene, and a polar solute, Errera⁽⁴⁾ extrapolated, according to a mixture rule, the limiting value of molar polarization (P_∞) that is reached by infinite dilution. From the value of P_∞ thus obtained and the value of the molar polarization of the solute in the pure state, he calculated the degree of polar association $\frac{P_\infty}{P}$. As we do not know of any ideal

(1) Zeitschr. phys. Chem. **6**, 524 (1890).

(2) Trans. Faraday Soc. **19**, 6 (1923); **21**, 145 (1925); **21**, 151 (1925).

(3) Zeitschr. phys. Chem. (A) **138**, 332 (1928).

(4) loc. cit.

rule for finding the viscosity of a binary liquid mixture that is dependent on concentration, we cannot very well apply the method that Errera used for determining polar association to that of determining total association by means of viscosity measurements. In this investigation the author attempts to compare the various degrees of total association undergone by high-molecular liquids, and to ascertain the relation between the association and the temperature coefficient of viscosity of these liquids.

We shall consider a solution; for example, a benzene solution of a highly viscous mineral oil, in which the solvent is nonpolar and the solute a nonpolar liquid such that its molecules are much larger than those of the solvent.

The viscosity of the solution is always observed to be appreciably higher than that of the solvent, even when the solution is so dilute that the individual molecules of the solute are so completely free from each other that no intermolecular forces practically act between them. This increase of viscosity must in general be ascribed to increase of f_q and f_s of formula (I). The increase of f_s is only natural, seeing that our assumption is that the molecules of the solute are larger than those of the solvent. Although we have no knowledge regarding the changes of f_q , we assume that f_q is unchanged in this case. This assumption, which may almost be equivalent to the statement that the forces acting between the molecules of the solute and of the solvent do not differ in intensity from those acting among the molecules of the solvent, themselves, may not be untenable in the light of the fact that Einstein's viscosity formula, which was deduced on the assumption that no force acts between the suspended particles and the molecules of the solvent, actually holds good for suspensoids. Staudinger⁽¹⁾ has ascertained from his experiments that the viscosity of a semi-colloidal solution always

(1) According to Staudinger [Koll. -Zeitschr. 51, 77 (1930)], the solution must be under 1.0 molar for solutes having molecular weights 300-400, and under 0.5 for semi-colloidal substances having molecular weights between 1000-10000.

increases in direct proportion to its concentration, provided the molecules of the solute do not interact. When however the concentration becomes greater and the interaction between the molecules of the solute are intensified the viscosity ceases to be proportional to the concentration, while its increase with increasing concentration is found to be very rapid, especially if the intermolecular forces between the individual molecules of the solute are much greater than those between the mole-

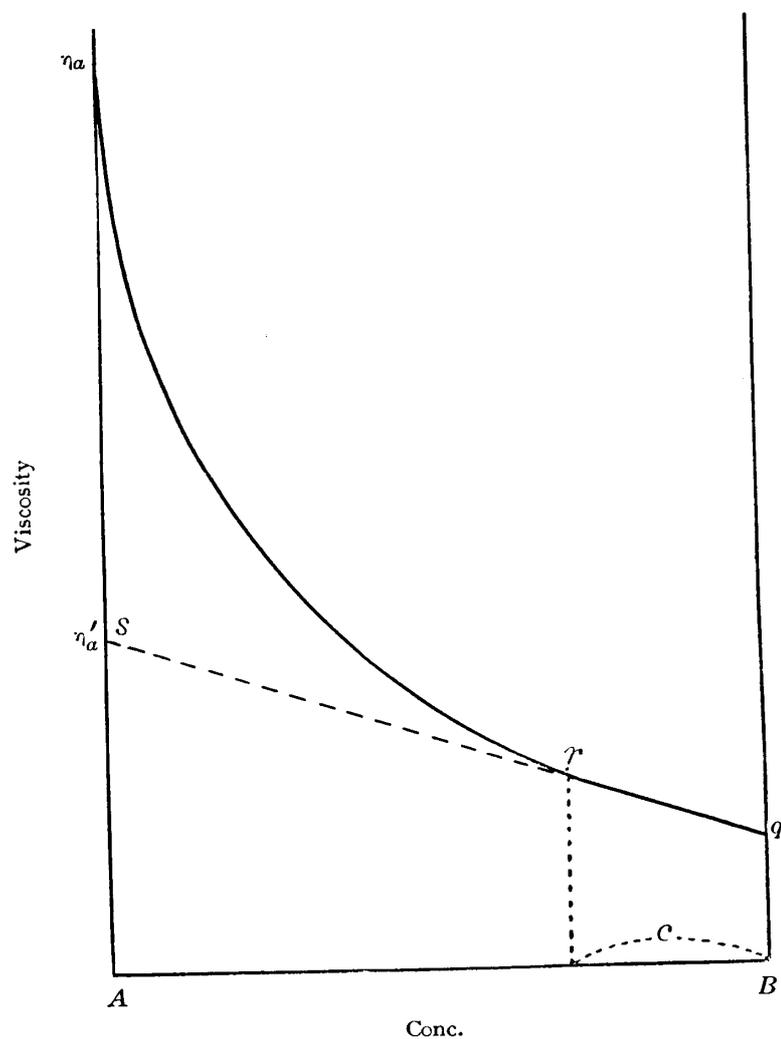


Fig. 1.

cules of the solvent. This rapid increase in viscosity is due to molecular association of the solute. Fig. 1 illustrates such a relation between viscosity and concentration, where *A* denotes a high-molecular nonpolar liquid and *B* a nonpolar solvent (benzene). For dilute solutions of concentration not exceeding *c*, viscosity is always proportional to concentration, as indicated by the tangent drawn to the curve. For higher concentration the curve bends upward, showing that viscosity increases rapidly with concentration until it finally reaches the viscosity of the pure solute (η_a), when the concentration becomes extreme. If we prolong tangent *qr* until it intersects the ordinate at the extreme left, the point of intersection *s* indicates the viscosity η'_a which solute *A* would have, provided no special intermolecular forces acted between the molecules of the solute and consequently no special association existed. In other words, η'_a represents the viscosity which the solute would have on the assumption that factor f_q , involved in the actual viscosity of the solute, had diminished to a small definite value which, according to the assumption made with regard to changes of f_q , should almost equal the value of f_q that is involved in the viscosity of benzene, thus depending entirely upon what the solvent is. If the same solvent is always used in determining η'_a , then the value of f_q involved in η'_a becomes a constant which is independent of the nature of the solute, and is peculiar to a given solvent. If we express the constant as f_q^0 , then we have according to formular (I)

$$\eta'_a = k \cdot f_q^0 \cdot f_s \quad (II).$$

As the actual viscosity of solute η_a is expressed by

$$\eta_a = k \cdot f_s \cdot f_q \quad (III),$$

we obtain the relation

$$\frac{\eta_a}{\eta'_a} = \frac{1}{f_q^0} \cdot f_q = k' f_q \quad (IV).$$

Thus quantity $\frac{\eta_a}{\eta'_a}$ is found to be proportional to the value of f_a , by which the part that association takes in viscosity is denoted. We therefore express quantity $\frac{\eta_a}{\eta'_a}$ as A_v -viscosity association. Since clearly viscosity association is intimately related to total association, it may be possible to compare the degrees of total association of high-molecular liquids, provided we know their viscosity association values. In carrying out the determination of viscosity association, the value of η'_a can be calculated by a formula, deduced as shown below.

Staudinger⁽¹⁾, who has transformed Einstein's viscosity formula into the form

$$\eta_r - 1 = K \cdot C \quad (V),$$

where η_r is the relative viscosity denoting the ratio of the viscosity of the solution (η_c) to that of the solvent (η_o), C the concentration, and the quantity $\eta_r - 1$ (which he expresses by η_{sp}) is the specific viscosity, has experimentally ascertained that the value of constant K in formula (V) depends on the structural character of the solute.

That K depends on the structure of the solute is also apparent from Eisenschitz's formula⁽²⁾ for viscosity recently established theoretically for suspensions of elongated particles. The value of K , however, must be independent of the concentration of dilute solutions. This has been confirmed by Staudinger⁽³⁾ and his collaborators for dilute solutions of a number of high-molecular substances, such as paraffin, cellulose,

(1) Staudinger and his collaborators have ascertained that, for dilute solutions of a given concentration and of a polymeric series having rod-like molecules, such as paraffin, rubber, and their derivatives, polystyrene, polyvinyl compounds, etc., the viscosity is proportional to the molecular weight and, therefore, to the length of the rod-like molecules; in other words the formula $\eta_{sp} = K_m CM$, where M denotes the molecular weight of the solute, is applicable to such solutions. [Koll. Zeitschr. 51, 71, 75 (1930); 53, 19 (1930); 54, 129 (1931); Ber. 63, 222, 721 (1930); 65, 267 (1932); Zeitschr. Phys. Chem. (A) 153, 391, (1931); 158, 135 (1932); Helv. chim. Acta 15, 213, 221 (1932), etc.].

(2) Zeitschr. Phys. Chem. 158, 78 (1932).

(3) loc. cit.

polystyrene, polyvinyl compounds, etc. In the present investigation it has been observed, as will be described later, that formula (V) is always applicable to dilute solutions in which the molecules of the solute are nonpolar and, when compared with those of the solvent, are much larger, as in the case of a benzene solution of highly viscous mineral oil.

If the concentration of the solution is expressed by percentage (C_p) the formula becomes

$$\frac{1}{d}(\eta_r - 1) = \frac{1}{d} \left(\frac{\eta_e}{\eta_o} - 1 \right) = K_p \cdot C_p \quad (\text{VI}),$$

where d denotes the density of solution and K_p , a constant peculiar to the solute. If we determine the value of K_p for a benzene solution of high-molecular liquid to which formula (VI) is applicable, the value of η'_a of the high-molecular liquid may be found by putting $C_p = 100$ in formula (VI), and since in this case the formula becomes

$$\frac{1}{d_a} \left(\frac{\eta'_a}{\eta_o} - 1 \right) = K_p \cdot 100 \quad (\text{VII}),$$

if we know the density of the high-molecular liquid d_a and the viscosity of benzene, the value of η'_a can be calculated.

The Experiment.

In the experiments, benzene was always used for the solvent. Its viscosity and density at 25°C were respectively 0.006043 poise and 0.8731. All the high-molecular liquids, whose viscosity associations were to be determined, were dissolved in benzene at various low concentrations and the viscosities of the solutions measured by a viscosimeter, which was practically similar to the viscosimeter that Ostwald and Luther⁽¹⁾ devised for volatile liquids. In order to examine the temperature

(1) E. Hatschek: Die Viskosität der Flüssigkeiten (1929) p. 46.

coefficients of the viscosities of high-molecular liquids, their viscosities were measured at various temperatures either by a Vogel-Ossag viscosimeter or by the usual Ostwald viscosimeter. The result of experiments in which solutes that were almost nonpolar were used are summarized in Tables I and II. In these tables, the fourth column gives the values of the relative viscosities of the solutions at 25°C. and the fifth column the values of K_p calculated by formula (VI). The values of η'_a and A_v , calculated by formula (VII) for high-molecular liquids used as solutes,

TABLE I.

(Measured at 25°C)

Substance	Conc. (C _p) %	Density (d)	η_r	K_p	η'_a	A_v	$\frac{\Delta\eta}{\Delta t} \times 10^3$ for 25°-45°C.	
Liquid Paraffin	1.987	0.8732	1.0310	0.0179	0.0184	0.0158	49.3	25.6
	2.805	0.8732	1.0459	0.0188				
	4.444	0.8733	1.0728	0.0188				
	5.526	0.8733	1.0871	0.0182				
	6.395	0.8735	1.1040	0.0186				
Clock Oil No. 1.	3.014	0.8742	1.0472	0.0180	0.0182	0.0161	44.5	23.6
	6.229	0.8752	1.0999	0.0184				
	7.754	0.8754	1.1228	0.0181				
Special Machine Oil	2.503	0.8739	1.0390	0.0178	0.0177	0.0159	39.6	20.8
	4.716	0.8746	1.0722	0.0175				
Refrigerator Oil	2.546	0.8739	1.0386	0.0175	0.0175	0.0158	36.0	18.5
	4.254	0.8745	1.0651	0.0174				
Zenith Clock Oil	2.290	0.8732	1.0382	0.0192	0.0192	0.0162	35.1	17.7
	4.708	0.8733	1.0788	0.0192				
Spindle Oil. A.	1.982	0.8738	1.0294	0.0170	0.0172	0.0156	25.2	12.2
	2.877	0.8739	1.0436	0.0173				
	5.580	0.8748	1.0838	0.0172				
Voltol No. 00.	2.218	0.8732	1.0315	0.0163	0.0164	0.0149	10.2	3.72
	4.617	0.8734	1.0633	0.0157				
	5.673	0.8735	1.0855	0.0173				

are also shown respectively in the sixth and the seventh columns. The last column gives the mean temperature coefficients of viscosity of the high-molecular solutes between two definite temperatures—25° and 45°C. or between 20° and 90°C. The values showing the viscosity and the density of the solutes measured at various temperatures are given in

TABLE II.

(Measured at 25°C.)

Oils	Conc. (C _p) %	Density (d)	η _r	K _p	η' _a	A _v	$\frac{\Delta\eta}{\Delta t} \times 10^3$	
							for 20°-90°C.	for 20°-50°C.
Mobile Oil S.R. (Nippon Oil Co.)	2.512	0.8742	1.0473	0.0216	0.0216	556	245	513
	4.125	0.8749	1.0739	0.0205				
	6.075	0.8757	1.1200	0.0226				
Aero Shell (Rising Sun Petr. Co.)	2.559	0.8737	1.0597	0.028	0.0222	126	52.6	107
	5.341	0.8744	1.1415	0.030				
	7.521	0.8750	1.1987	0.030				
Flugol (Nippon Hatu-dōkiyu Co.)	1.011	0.8736	1.0283	0.0320	0.0242	256	122	255
	1.535	0.8739	1.0407	0.0304				
	2.177	0.8742	1.0616	0.0324				
Mobile Oil A (Vacuum Oil Co.)	2.136	0.8736	1.0378	0.0195	0.0170	174	66.9	140
	3.969	0.8741	1.0671	0.0193				
	5.498	0.8744	1.0993	0.0207				
Shell C. 2A. (Rising Sun Petr. Co.)	2.148	0.8730	1.0502	0.0268	0.0206	117	45.2	90.4
	3.890	0.8732	1.0927	0.0273				
Mobile Oil W (Nippon Oil Co.)	2.010	0.8737	1.0337	0.0192	0.0170	97.8	32.1	65.9
	3.904	0.8743	1.0674	0.0198				
	6.019	0.8749	1.1045	0.0199				
Voltol (Deutsche Voltolwerke)	2.863	0.8743	1.1225	0.0264	0.0214	220	97.8	205
	5.302	0.8751	1.0690	0.0276				
Germ Oil XII (Henry Wells Oil Co.)	1.705	0.8732	1.0373	0.0251	0.0203	345	152	315
	3.704	0.8733	1.0853	0.0264				

Tables VI and VII. Since, as will be seen, all the high-molecular solutes mentioned in these tables are hydrocarbons, their molecules are regarded as being almost nonpolar. It will be seen from the tables that for these nonpolar substances, formula (VI) holds good and that the values of K_p for each solute, calculated for different concentrations of its solution, are in every case almost identical. It has been observed as indicated by points marked \circ in Fig. 2, and by Fig. 3 that the temperature coefficient of viscosity increases in direct proportion with increase in value of A_v , and that a simple straight-line relation exists between them. For the straight-line I in Fig. 3, the mean temperature coefficient of viscosity between 20°

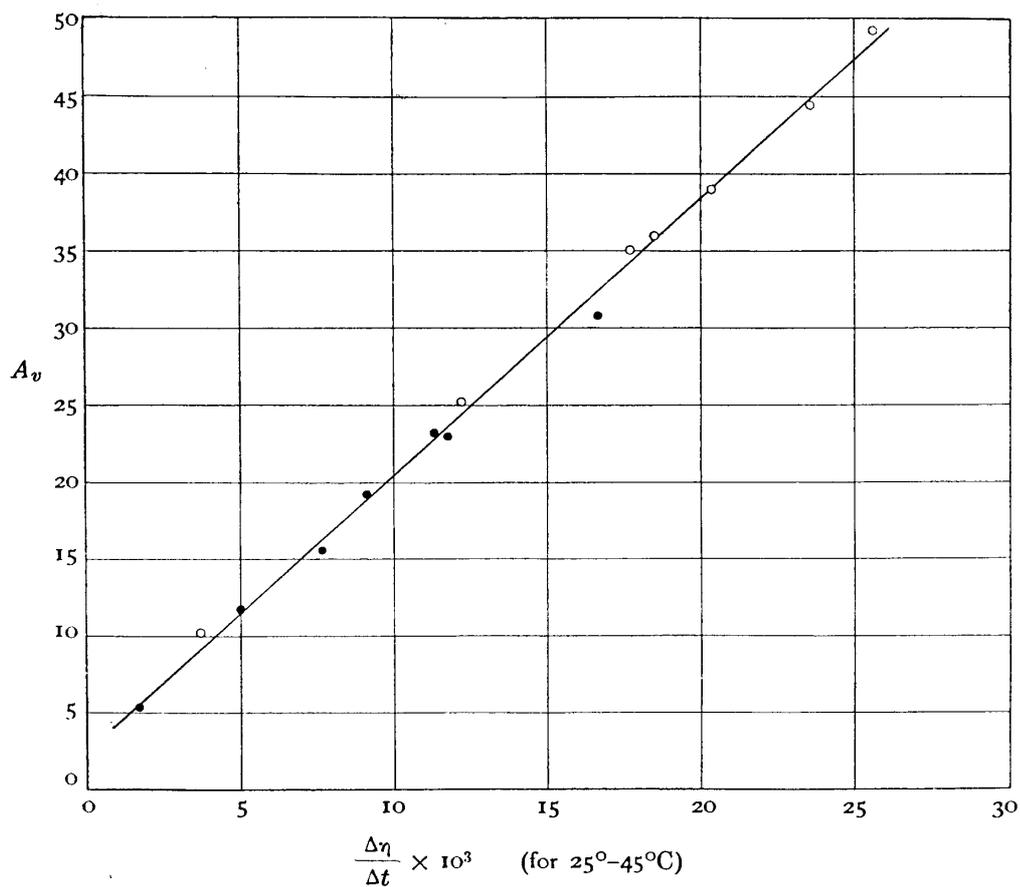


Fig. 2.

and 50°C. is taken as the abscissa, and for the straight-line II, the coefficient between 20° and 90°C. is taken. Table III gives the results of experiments for the case in which the solutes are polar high-molecular liquids, such as oleic acid and triolein. In these cases, formula (VI) is

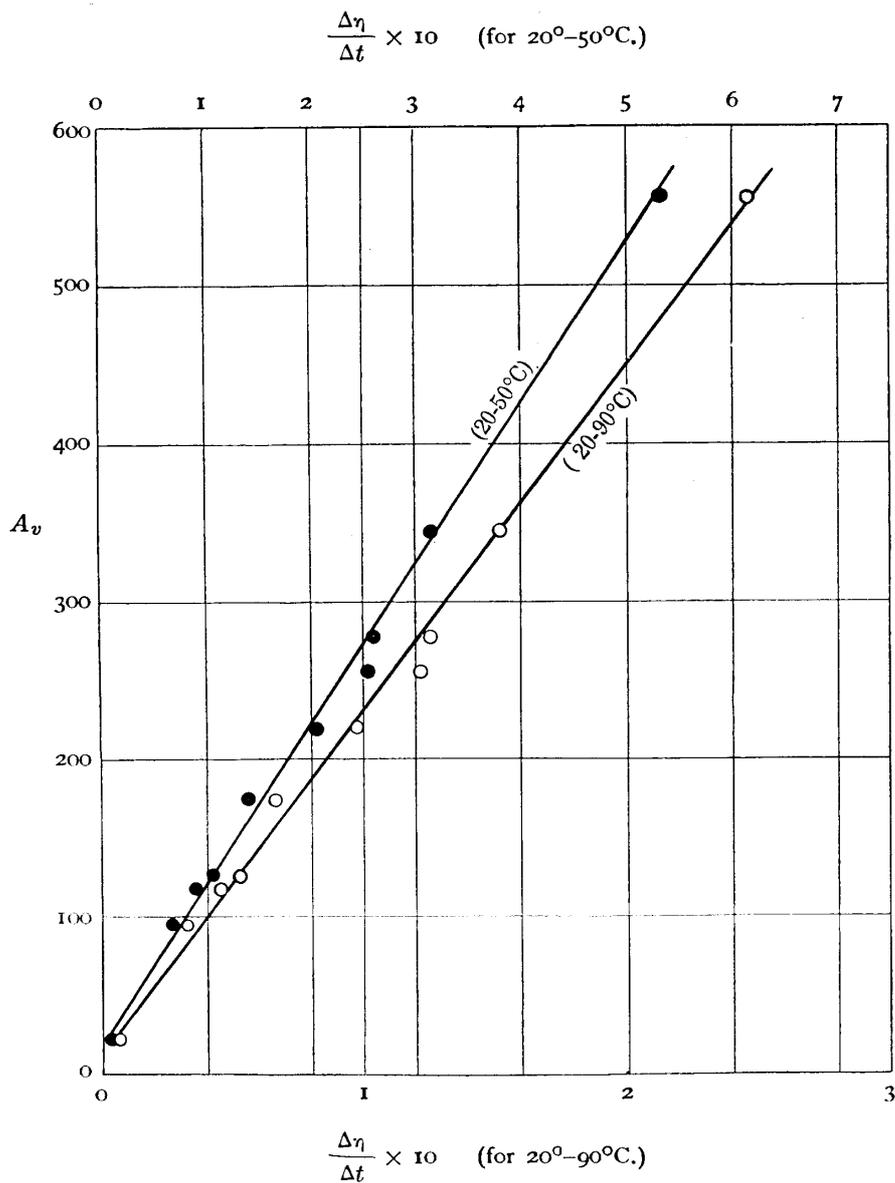


Fig 3.

TABLE III.

(Measured at 25°C.)

Substance	Conc. (C_p) %	Density (d)	Efflux time in viscosimeter (sec.)			η_r	K_p	K_∞	η'_a	A_v	$\frac{\Delta\eta}{\Delta t} \times 10^3$	
			Visc. No. 1	Visc. No. 2	Visc. No. 3						for 25°-45°C.	for 20°-90°C.
Soybean Oil	0 (pure benzene)	0.8731	63.1	61.0	55.1	1	—	—	—	—	—	—
	1.381	0.8736	65.5			1.0386	0.0320					
	2.859	0.8742	68.6			1.0885	0.0354					
	4.129	0.8748	71.4			1.1337	0.0371					
	5.343	0.8753	74.0			1.1757	0.0376					
	1.362	0.8736		63.3		1.0383	0.0322					
	2.700	0.8742		66.0		1.0833	0.0354					
	4.143	0.8748		68.9		1.1317	0.0364	0.0260	0.0206	23.0	11.8	7.18
	5.405	0.8753		71.5		1.1751	0.0371					
	6.138	0.8756		73.25		1.2043	0.0380					
	1.308	0.8736			57.1	1.0369	0.0323					
	2.811	0.8742			59.9	1.0885	0.0361					
	3.747	0.8746			61.6	1.1999	0.0366					
	5.232	0.8752			64.4	1.1716	0.0375					
	Oleic Acid	1.431	0.8732	65.45			1.0374	0.0299				
1.489		0.8732		63.35		1.0386	0.0297					
2.702		0.8733	67.7			1.0731	0.0310	0.0252	0.0196	15.6	7.7	
4.617		0.8734			62.4	1.1329	0.0330					
5.960		0.8735			64.7	1.1748	0.0336					
Triolein	1.310	0.8737		63.2		1.0368	0.0322					
	3.124	0.8747			60.3	1.0964	0.0353	0.0260	0.0206	30.8	16.7	
	5.030	0.8756			64.0	1.1648	0.0374					
Sipalin MOM	1.996	0.8752	64.9			1.0310	0.0177					
	4.037	0.8775		64.7		1.0660	0.0186	0.0170	0.0162	23.3	11.3	
	6.026	0.8794			60.4	1.1041	0.0194					
Sipalin AOM	2.018	0.8754	65.0			1.0328	0.0186					
	3.664	0.8772	66.8			1.0636	0.0198					
	4.033	0.8776		64.9		1.0694	0.0196	0.0180	0.0168	19.2	9.1	
	6.306	0.8802			60.9	1.1142	0.0206					
Triacetin	2.357	0.8782	64.45			1.0274	0.0132					
	4.522	0.8829		63.8		1.0576	0.0144	0.0122	0.0145	11.7	5.0	
	6.256				58.8	1.0836	0.0151					
Butylstearate	1.956	0.8725	65.2			1.0326	0.0191					
	4.025	0.8719			59.2	1.0710	0.0203	0.0182	0.0154	5.4	1.7	
	5.700	0.8714			61.0	1.1049	0.0211					
Castor Oil	1.205	0.8740		63.2		1.0371	0.0353					
	1.413	0.8741	65.9			1.0456	0.0370					
	2.189	0.8747		65.4		1.0741	0.0387	0.0305	0.0238	277	247	126
	3.717	0.8757			62.0	1.1286	0.0395					
	4.770	0.8765			64.5	1.1751	0.0418					

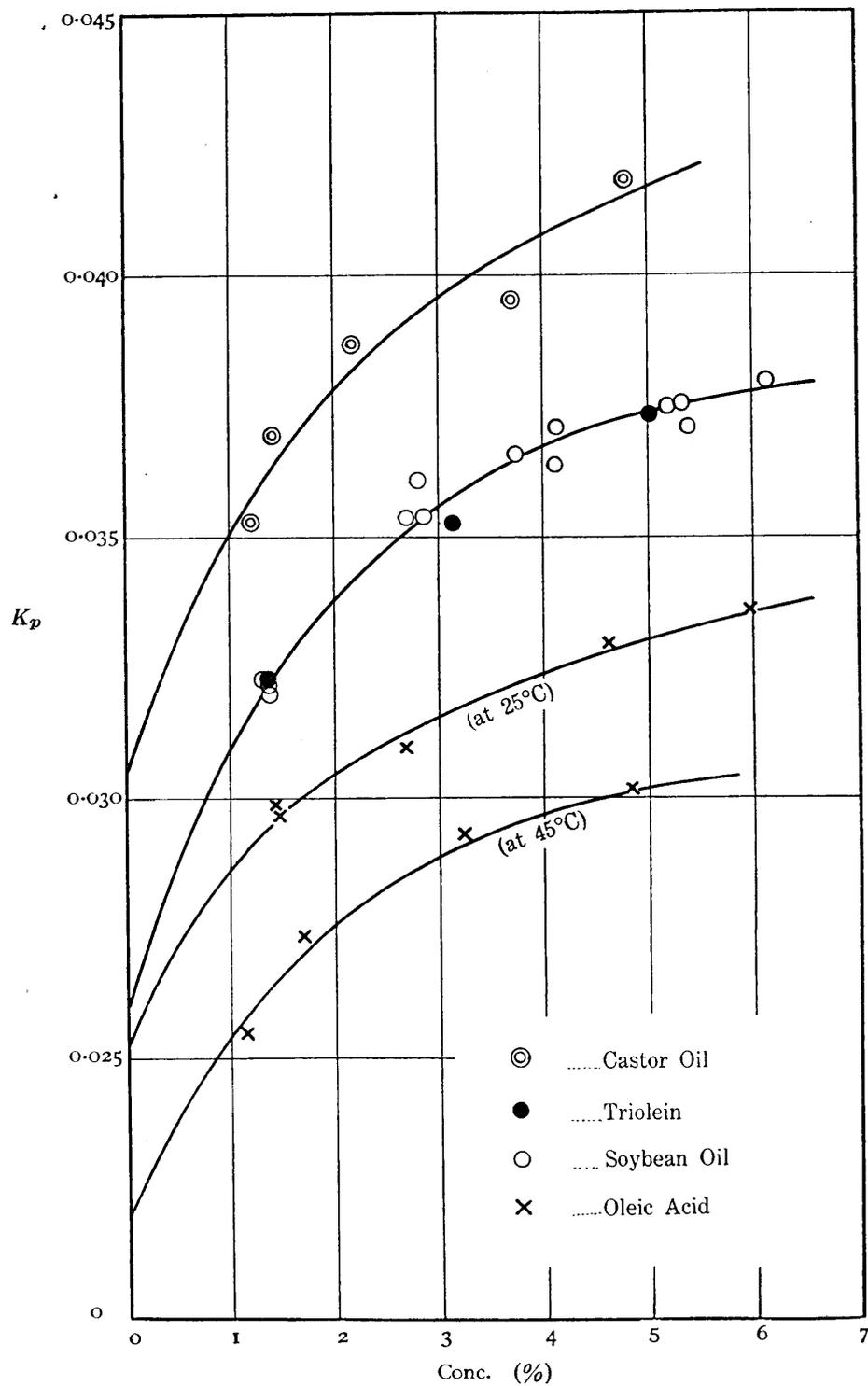


Fig. 4 (a).

invalid⁽¹⁾, and as will be seen from Table III and Figs. 4 (a) and 4 (b), the value of K_p increases with increasing concentration, even though

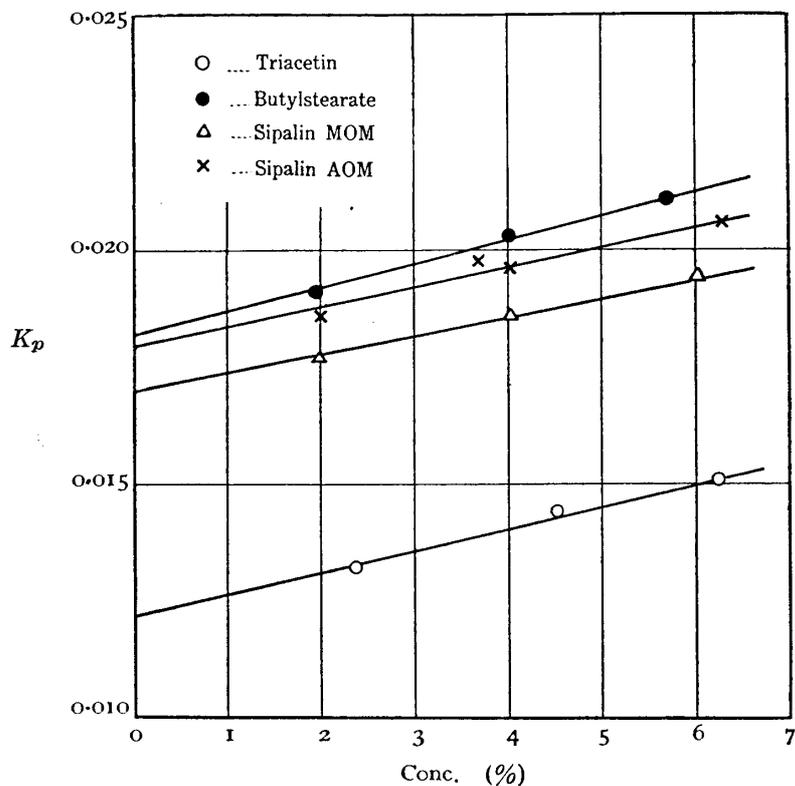


Fig. 4 (b).

(1) Recently Kramer and Van Natta [Journ. phys. Chem. 36, 3176 (1932)] have made careful measurements on the viscosities of solutions of polymeric hydroxydecanoic acids. By calculating the values of K_p for the solutions from their data, we can also see that K_p increases with increasing concentration, as shown by the following table in which the result for a polymer of molecular weight 1710 is given as an example.

Conc. (C_p)	Density at 25°C. (d)	η_r at 25°C	$K_p = \frac{\eta_r - 1}{d \cdot C_p}$
0.1028	1.5826	1.0245	0.150
0.2532	1.5814	1.0663	0.166
1.311	1.5715	1.3950	0.192
2.718	1.5588	1.9053	0.214
4.591	1.5419	2.7949	0.254

A similar tendency of the K_p -values is observable in Staudinger's data for polyvinylacetate and cetylester of capric acid. [Ber. 63, 3132 (1930); Zeitschr. phys. Chem. (A) 158, 43 (1932)].

the solutions be very dilute. This must be ascribed to the existence of polar association amongst the polar molecules of the solute, since it may be considered that although the degree of polar association approaches zero value with increasing dilution, the association does not vanish even in dilutions so high that nonpolar association disappears, doing so only at infinite dilution. The reasonableness of this consideration is obvious from investigations made by Lunge⁽¹⁾ and by Williams and Kramer⁽²⁾, for the purpose of studying the dependance of polar association on concentration.

As it is possible, however, to know the value of K_p for each polar solute at different concentrations, the value of K_∞ which K_p assumes at infinite dilution, in which the polar association completely disappears, may be approximately determined by graphical interpolation as shown in Figs. 4 (a) and 4 (b) we can therefore calculate the value of η'_a by inserting the value of K_∞ instead of K_p in formula (VII), and thus determine the value of A_v for the solute. The values of K_∞ , η'_a and A_v that were determined in the above manner are shown in columns 9, 10, and 11 of Table III. The relation between the viscosity association and the temperature coefficient of viscosity for the high-molecular liquids that are given in the table is shown in Fig. 2 by points marked • which are found to fall almost on the same straight-line as do the points for the nonpolar liquids. We therefore conclude that a definite straight-line relation always exists between the temperature coefficient of viscosity and the viscosity association of high-molecular liquids, whether they are polar or nonpolar.

Table IV shows the results of experiments carried out at 45°C. As will be seen from Fig. 5, the values of A_v that were determined at this temperature have also a straight-line relation to the temperature coefficients of viscosity.

(1) *Zeitschr. Physik* 33, 169 (1925).

(2) *Journ. Amer. Chem. Soc.* 48, 1888 (1926).

TABLE IV.

(Measured at 45°C.)

Oils	Conc. (C _p) %	Density (d)	η _r	K _p	η' _a	A _v	$\frac{\Delta\eta}{\Delta t} \times 10^3$		
							for 25°-45°C.	for 20°-90°C.	
Mobile Oil A	0 (pure benzene)	0.8523	1	—	—	—			
	2.155	0.8530	1.0357	0.0194	} 0.0196	0.0131	62.2	107	66.9
	4.327	0.8538	1.0733	0.0198					
Shell C. 2A.	1.968	0.8524	1.0456	0.0272					
	4.348	0.8526	1.1004	0.0271					
Mobile Oil W.	2.764	0.8535	1.0446	0.0189	} 0.0190	0.0129	35.0	59.8	32.1
	4.301	0.8542	1.0703	0.0192					
Clock Oil No. 1	3.451	0.8538	1.0511	0.0174	} 0.0173	0.0121	20.3	23.6	
	5.529	0.8545	1.0812	0.0172					
Sipalin AOM	2.420	0.8551	1.0354	0.0172	} K _∞ 0.0160	0.0121	11.5	9.1	
	3.914	0.8569	1.0593	0.0177					
	5.353	0.8585	1.0853	0.0186					
Oleic Acid	1.149	0.8525	1.0250	0.0255	} K _∞ 0.0220	0.0138	11.0	7.7	
	1.639	0.8526	1.0396	0.0274					
	3.229	0.8528	1.0806	0.0293					
	4.826	0.8531	1.1246	0.0302					

We cannot always say that the higher the viscosity of a liquid, the greater will be its temperature coefficient of viscosity. As shown in Fig. 6, oleic acid has a smaller temperature coefficient than Sipalin AOM, although at temperature 45°C, the former has greater viscosity than the latter. Fig. 7 shows also that the temperature coefficient of viscosity of Mobile Oil A is higher than that of Shell Oil 2A, although both oils have nearly the same viscosity at 50°C. We cannot therefore predict the temperature coefficient of viscosity of a liquid from its viscosity value, although we can do so from its A_v value, since A_v is definitely related to the temperature coefficient of viscosity. For liquids having the same viscosity at a certain temperature, namely the same value of η_a, the

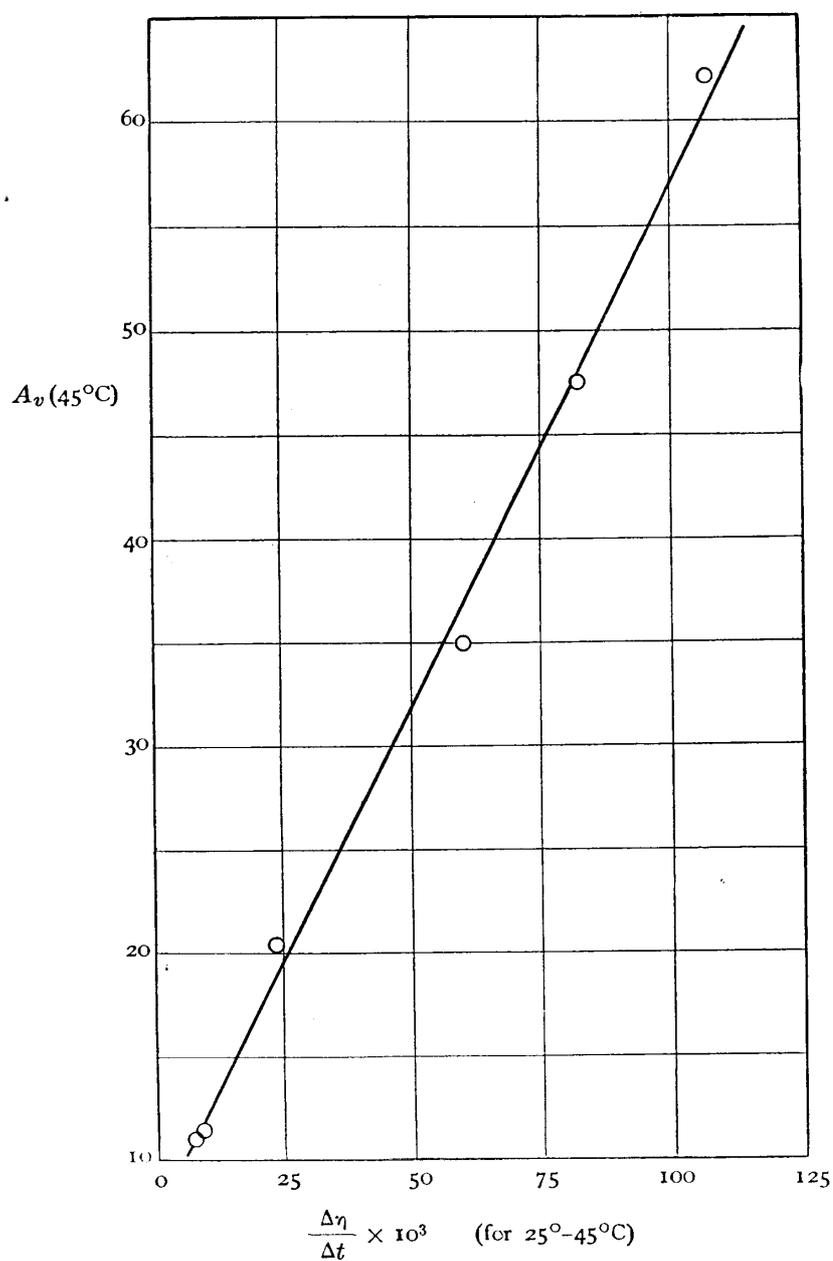


Fig. 5.

temperature coefficient of viscosity must be inversely proportional to the value of η'_a determined at that temperature, and since η'_a is related by formula (VII) to K_p , the coefficient must decrease with increasing values

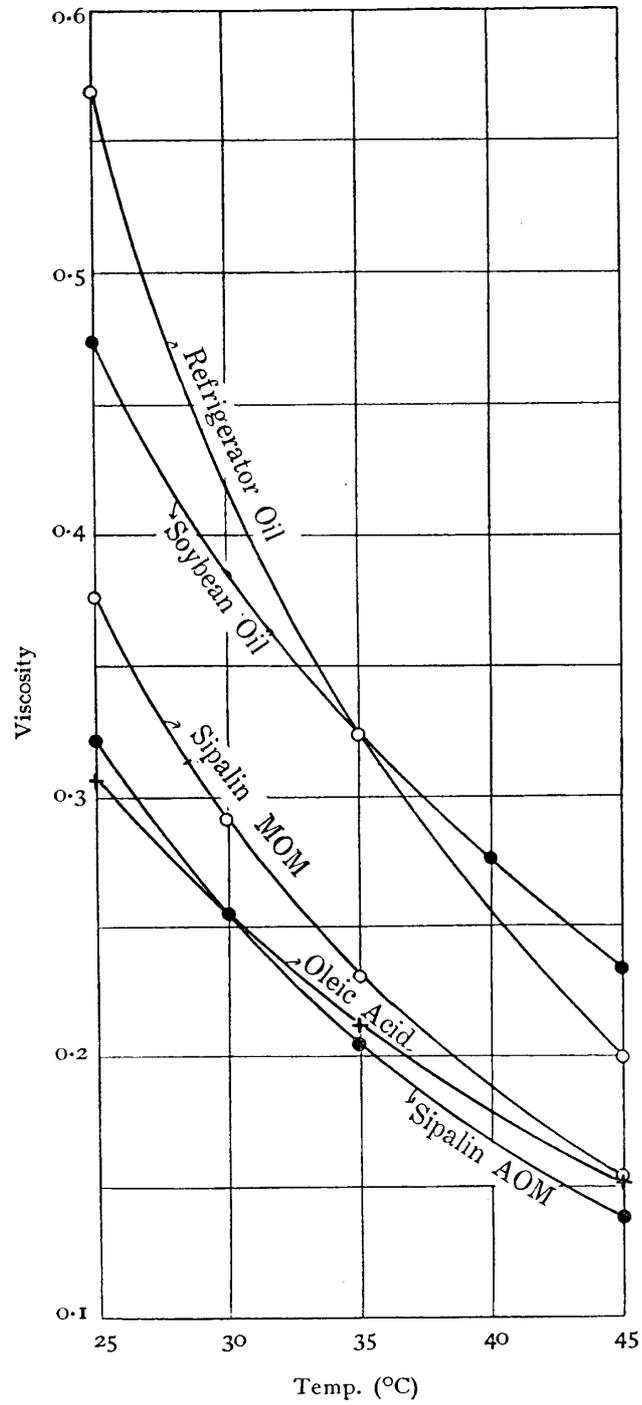


Fig. 6.

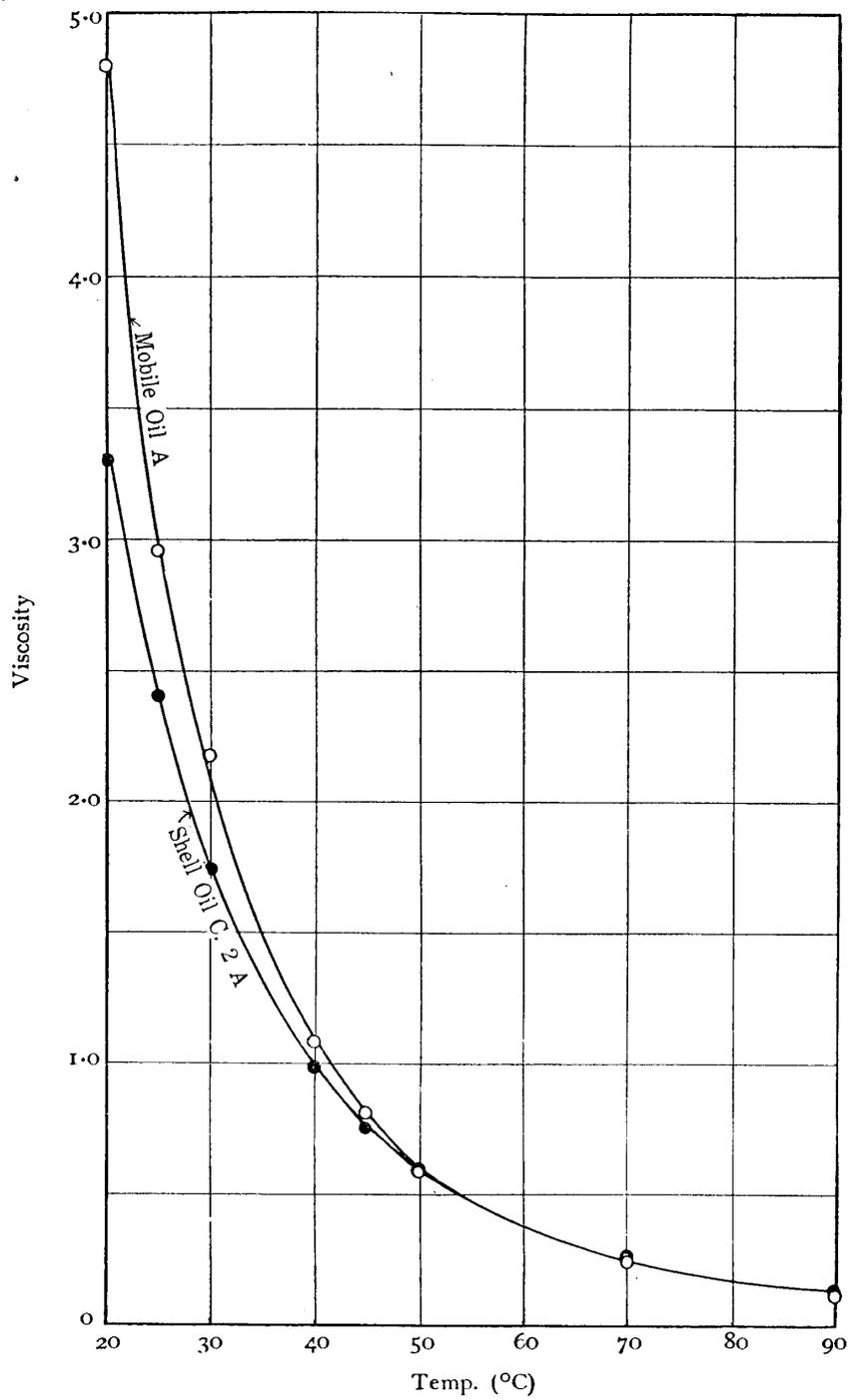


Fig. 7.

of K_p . As already mentioned, K_p depends on the molecular structure of the solute, and it is known from Staudinger's investigations that the more elongated the structure, the greater is the value of K_p , even if the solutes have the same molecular weight.⁽¹⁾

We can therefore conclude that, for liquids of like viscosities at a certain temperature, the longer the molecule the higher is the temperature coefficient of viscosity. It will be seen from Fig. 6 that oleic acid, whose viscosity is almost equal to that of Sipalin MOM at 45°C. and to that of Sipalin AOM at 30°C, has the lowest temperature coefficient of viscosity of the three substances. This can only be due to the fact that the molecules of oleic acid have a longer structure than those of the others.⁽²⁾ Rubber, as is well known, has a very large and strikingly elongated molecular structure in its solution, whence the mean molecular weight of the solution must be considerably larger than the molecular weight of the solvent, even in very dilute solutions. If therefore we compare the temperature coefficient of viscosity of a dilute solution of rubber with that of a liquid, whose molecular length differs but little from the solvent but is equal in viscosity to the solution at a certain temperature, the value of the former must be smaller than the latter, Table V and Fig. 8 show to what extent the temperature

TABLE V.

Liquids	Viscosity (poise)			$\frac{\Delta\eta}{\Delta t}$ (for 25°-45°C.)
	25°C.	35°C.	45°C.	
<i>m</i> -Xylene solution of pale crepe (0.44%)	0.05559	0.04760	0.04355	1.38×10^{-3}
Benzylbenzoate	0.07632	0.05607	0.04294	1.67×10^{-3}
Pelargonic Acid	0.06867	0.05234	0.04108	1.38×10^{-3}

(1) This is also evident from Eisenschitz's formula and Kuhn's formula for viscosity. [Zeitschr. phys. Chem. (A) 161, 7 (1932)].

(2) The value of K_∞ calculated for oleic acid as shown in Table III, is greater than the values of K_∞ for Sipalin MOM and Sipalin AOM.

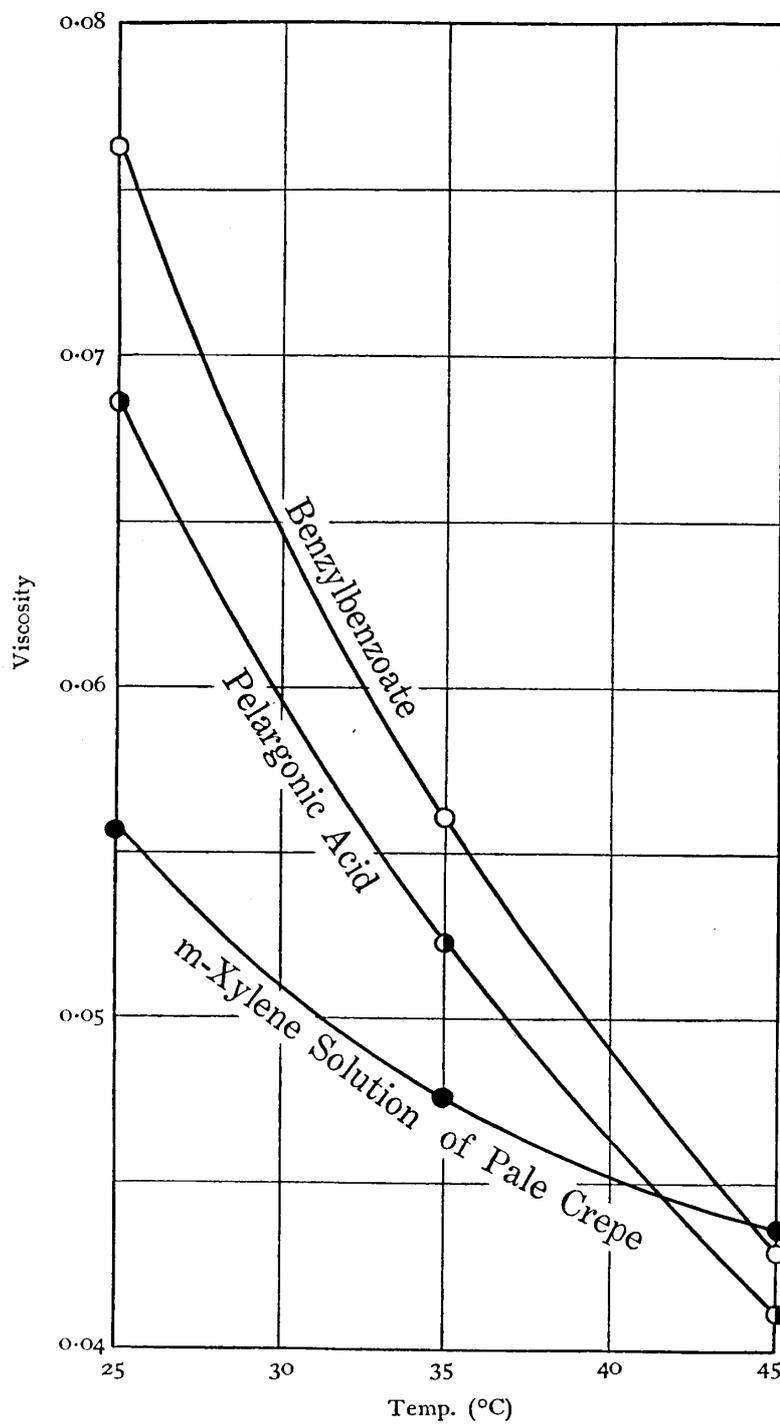


Fig. 8.

TABLE VI.

Liquids	Viscosity (poise)				$\frac{\Delta\eta}{\Delta t}$ (at 25°-45°C.)	Density				
	25°C.	30°C.	35°C.	40°C.		45°C.	25°C.	30°C.	35°C.	40°C.
Liquid Paraffine	0.7785		0.4399		0.2675	0.8797		0.8730		0.8672
Clock Oil No. 1	0.7172		0.4048		0.2458	0.9161		0.9094		0.9029
Spec. Machine Oil	0.6311		0.3506		0.2142	0.9196		0.9130		0.9070
Refrigerator Oil	0.5683		0.3234		0.1980	0.9195		0.9134		0.9071
Zenith Clock Oil	0.5682		0.3378		0.2146	0.8751		0.8695		0.8640
Spindle Oil A	0.3936		0.2336		0.1492	0.9172		0.9106		0.9044
Voltol No. 00.	0.1526		0.1068		0.07823	0.8951		0.8885		0.8824
Triolein	0.6345	0.5150	0.4262	0.3555	0.3005	0.9264	0.9231	0.9199	0.9165	0.9131
Soybean Oil	0.4730	0.3837		0.2755	0.2336	0.9275	0.9245		0.9183	0.9154
Sipalin MOM	0.3764	0.2920	0.2308		0.1535	0.9934	0.9897	0.9860		0.9807
Sipalin AOM	0.3215	0.2547	0.2051		0.1393	0.9952	0.9916	0.9879		0.9788
Oleic Acid	0.3062		0.2118		0.1523	0.8909		0.8843		0.8775
Triacetin	0.1702		0.1054		0.07036	1.1570		1.1467		1.1363
Butyristearate	0.08334		0.06296	0.05564	0.04928	0.8566	0.8532	0.8495	0.8460	0.8425

TABLE VII.

Oils	Temp. (°C)	Density	Viscosity (poise)	Oils	Temp. (°C)	Density	Viscosity (poise)
Mobile Oil S.R. (Nippon Oil Co.)	20	0.9419	17.37	Shell C. 2A (Rising Sun Petr. Co.)	20	0.8897	3.303
	25	0.9390	10.33		25	0.8867	2.404
	30	0.9360	6.880		30	0.8836	1.739
	40	0.9300	2.997		40	0.8780	0.9895
	45	0.9271	2.061		45	0.8750	0.7580
	50	0.9249	1.441		50	0.8725	0.5924
	70	0.9124	0.4817		70	0.8605	0.2633
Mobile Oil W. (Nippon Oil Co.)	90	0.9010	0.2027	90	0.8489	0.1358	
	20	0.9327	2.323	Aero Shell (Rising Sun Petr. Co.)	20	0.9146	3.8214
	25	0.9294	1.645		25	0.9110	2.673
	30	0.9265	1.113		40	0.9010	1.042
	40	0.9205	0.6029		50	0.8944	0.6250
	45	0.9176	0.4500		90	0.8675	0.1405
	50	0.9144	0.3474				
70	0.9028	0.1489					
Mobile Oil A. (Vacuum Oil Co.)	90	0.8907	0.0774	Castor Oil	20	0.9685	9.048
	20	0.9246	4.801		25	0.9650	6.592
	25	0.9215	2.960		30	0.9619	4.424
	30	0.9187	2.182		40	0.9552	2.319
	40	0.9130	1.082		45	0.9521	1.660
	45	0.9100	0.8140		50	0.9490	1.229
	50	0.9075	0.5917		70	0.9359	0.4633
Germ Oil (Henry Wells Oil Co.)	70	0.8956	0.2400	90	0.9230	0.2197	
	90	0.8843	0.1176	Soybean Oil	20	0.9310	0.5754
	20	0.9069	10.82		25	0.9275	0.4730
	25	0.9039	7.010		30	0.9245	0.3837
	30	0.9010	4.932		40	0.9183	0.2755
	40	0.8954	2.468		45	0.9154	0.2336
	50	0.8903	1.364		50	0.9122	0.1986
70	0.8783	0.5199	70		0.9000	0.1152	
Voltol	90	0.8670	0.2462	90	0.8878	0.07288	
	20	0.9384	7.019	Flugol (Nippon Hatu-dōkiyu Co.)	20	0.9439	8.765
	25	0.9359	4.692		25	0.9405	6.202
	30	0.9330	3.153		30	0.9375	4.027
	40	0.9273	1.598		40	0.9314	2.016
	50	0.9214	0.8744		50	0.9256	1.108
	70	0.9103	0.3477		70	0.9131	0.4456
90	0.8990	0.1708	90		0.9011	0.2163	

coefficient of viscosity of *m*-xylene solution of pale crepe⁽¹⁾ (0.44%) is lower than that of benzylbenzoate and of pelargonic acid, whose respective viscosities are almost equal to that of the solution at 44° and 42°C. Voltol oil⁽²⁾ is known to have a lower temperature coefficient of viscosity, compared with other mineral oils whose viscosities differ but little from that of Voltol oil. This must be regarded as being due to the highly polymerized molecules that are contained in Voltol oil, the existence of which has been verified. It is also easily explained that fatty oil is generally much lower in temperature coefficient of viscosity than mineral oil; for the former has a greater molecular structure than the latter, at least when the viscosity of the two oils do not greatly differ. The conclusion of Sullivan and his collaborators⁽³⁾, who investigated the viscosity of lubricating oils made by polymerizing olefins, is that the temperature coefficient of viscosity of the polymers decreases with increasing molecular weight of normal olefins and increases with increasing branching of the chains for isomers—a conclusion well in accord with the foregoing theory of the author.

Tokyo, November, 1933.

(1) According to Staudinger, the molecular weight of rubber in its solution is about 18000 [Zeitschr. phys. Chem. (A) 153, 411 (1931)]. If we adopt this molecular weight, the mean molecular weight of 0.44% *m*-xylene solution of rubber becomes about 896, which is much greater than the molecular weights of either benzylbenzoate ($M = 212$) or pelargonic acid ($M = 158$).

(2) Vogel: Zeitschr. angew. Chem. 35, 56 (1922).

(3) Journ. Ind. Eng. Chem. 23, 610 (1931).

第 百 二 號

(昭和九年二月發行)

抄 錄

高分子量液體の粘度の温度係數と 分子會合度との關係に就いて

所 員 理學博士 山 口 文 之 助

減摩油に於ても又種々の航空機用計器に使用される制動液に於ても重要な性質の一つとして粘度の温度係數の小なることが望まれるが、さて如何なる分子よりなる液體が粘度の温度係數小にして如何なる分子構造を有つ液體に於て其が大であるかといふに我々は今日未だ液體の粘度の温度係數と分子構造との間の明確な一般量的關係を知らざる爲め其に對する明答をなすことが出來ないのである。若し吾人の研究により液體の粘度の温度係數と他の性質特に分子構造との間の關係が明確に闡明せらるならば其は單に學術上興味あるばかりでなく工業上減摩油、制動液等の製出に對する有益なる指針となること疑を容れない。本研究に於ては著者は各種の高分子量液體のベンゼン溶液の粘度の精密なる測定を行ひ、溶液の濃度と粘度との關係を表はす「シュタウチンガー」の粘度式により著者が粘度會合度と命名せる量を各種高分子量液體について計算し、之によつて高分子量液の粘度の温度係數と粘度會合度との間に簡單なる關係の存在するを確め、尙高分子量液の分子構造と粘度の温度係數との間の關係に就いて論じた。

昭和九年十一月
