Constitution and Viscosity Association of High-molecular-weight Hydrocarbons.

By Bunnosuke YAMAGUCHI.

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In his previous paper⁽¹⁾ the author determined for a number of high-molecular-weight liquids a quantity which he called the viscosity association and found the existence of a linear relationship between their viscosity association and their temperature coefficients of viscosity. In the present paper the author attempts to establish by similar studies an empirical equation expressing such a relation, and to calculate by means of the equation the viscosity association of the high-molecular-weight hydrocarbons whose chemical structure and viscosity-temperature coefficients are known, with the object of studying their viscosity association in relation to their chemical structure.

The conception of the viscosity association and the method of its measurement were fully explained in the previous paper, but it will be helpful to give their outlines, as follows:

As indicated by the tangent drawn to the curve in Fig. 1 showing the change in viscosity with concentration of a solution of high-molecular-weight liquid in benzene, viscosity changes always approximately in linear proportion with concentration for dilute solutions not exceeding the concentration C. For higher concentrations the curve bends upward, showing that viscosity increases rapidly with concentration until it finally reaches η_a, which denotes the viscosity of pure solute A when the concentration becomes 100%. If we prolong the tangent qr until it intersects the ordinate at the extreme right, the point of intersection s indicates the viscosity η'_a which the solute would have, provided no special intermolecular forces have acted between the molecules of the solute, and consequently no particular association. Since the ratio η_a/η'_a denotes, as explained in the previous paper, a quantity proportional to that part which association takes in the viscosity of the solute, we express the quantity η_a/η'_a as A_v—viscosity association:

$$A_v = \frac{\eta_a}{\eta'_a} \qquad (1) .$$

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(1) *Rept. Aeronaut. Research Inst., Tôkyô Imp. Univ.*, No. 102 (1934); *J. Chem. Soc. Japan*, **55** (1934), 353.

In determining the viscosity association, the value of η'_a may be calculated by applying Einstein's equation for the viscosity of a dilute suspensoid to solutions of such high-molecular-weight hydrocarbons as lubricating oils.

Einstein's equation of viscosity is

$$\eta = \eta_0\left(1 + k\frac{v}{V}\right) \qquad (2),$$

where V is the total volume of solution, v the volume fraction of solute in the solution, and k a constant whose value, according to Einstein, is 2.5 independent of the size of the solute particles or molecules, provided they are spherical and of uniform size. It is however known from Eisenschitz's viscosity equation⁽²⁾ and the studies of Kuhn⁽³⁾ and Staudinger⁽⁴⁾ that k depends on the molecular shape or structure of the solute.

If the solution contains g g. of solute and the density of the solute is d_a, equation (2) may be transformed into

$$\frac{\eta}{\eta_0} - 1 = \eta_r - 1 = k\frac{v}{V} = k\frac{g}{d_a V} = KC \qquad (3),$$

where $C = g\cdot 10^3/V(\text{g./l.})$, $K = k\cdot 10^{-3}/d_a$. Moreover, if the concentration is expressed in percentage C_p, the equation becomes

$$\frac{1}{d}\left(\frac{\eta}{\eta_0} - 1\right) = K_p C_p \qquad (4),$$

where d denotes the density of solution and K_p a constant characteristic of the solute, whose value, however, must be independent of the concentration of the solution. Since K_p is proportional to k/d_a, $K_p d_a$ must depend on the structural character of the solute. If we determine the value of K_p for dilute solutions of a high-molecular-weight hydrocarbon to which equation (4) is applicable, the value of η'_a of the hydrocarbon is found by putting $C_p = 100$ in equation (4), seeing that the equation in this case becomes

$$\frac{1}{d_a}\left(\frac{\eta'_a}{\eta_0} - 1\right) = K_p\cdot 100 \qquad (5),$$

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(2) *Z. physik. Chem.*, A, **158** (1932), 78.

(3) *Z. physik. Chem.*, A, **161** (1932), 1.

(4) Staudinger, "Die Hochmolekularen Organischen Verbindungen," p. 56 and seq., Berlin.

rendering calculation of η'_a possible, so long as we know the density of the hydrocarbon d_a and the viscosity of the solvent η_0. For certain solutes, such as those having strong polarity and those of highly polymerized molecules, equation (4) is invalid, because it is found that for such compounds, K_p increases with increasing concentration, even though the solutions may be very dilute. As, however, it is possible, even in this case, to determine by the same equation the values of K_p for any solute at different concentrations, the value of K_∞ that K_p assumes at infinite dilution, in which the molecular association of the solute completely disappears, can be approximately determined by graphical extrapolation as described in the previous paper. We can therefore calculate the value of η'_a by inserting the value of K_∞ thus determined, instead of K_p, in equation (5), and accordingly determine the value of A_v.

The Experiment. (1) *Equation expressing the relation between the viscosity association and the viscosity-temperature coefficient of hydrocarbons.* In order to obtain an empirical equation representing the relation between their viscosity association and viscosity-temperature coefficients, careful measurements of viscosities at different temperatures as well as the determination of viscosity association were made of four samples of oils having different chemical compositions and viscosity characteristics. The method of experiment was similar to that used in the previous investigation. The determination of viscosity association was carried out at 25°C., with benzene as the solvent. Its viscosity and density at 25°C. were respectively 0.006043 poise and 0.8731. The results of the experiments are summarized in Table 1, in which the third column shows the relative viscosities of dilute solutions of oils at 25°C. and the fourth column the values of K_p calculated by equation (4). The values of η'_a and A_v, calculated by equations (5) and (1) for the oils, are also shown respectively in the fifth and sixth columns. The last column gives their mean temperature coefficients between 25 and 45°C. of both absolute and kinematic viscosities—$(\Delta\eta/\Delta t)_{25-45^\circ\mathrm{C.}}$ and $(\Delta\nu/\Delta t)_{25-45^\circ\mathrm{C.}}$. The values of their viscosities measured at various temperatures and their densities at 25°C. are given in Table 2. The result shows that the values of K_p for each oil, calculated for different concentrations of solution, are in every case almost identical, indicating that equation (4) holds good. The relation between the viscosity-temperature coefficient and the viscosity association of the oils is shown in Fig. 2 by circles. Since, in agreement with the results of the previous study, the viscosity-temperature coefficient increases in linear proportion with increase in the value of A_v, a linear relationship exists between them. In Fig. 2, dots, showing the results for the oils used in the previous study (see Table 3), are found to fall almost on the same straight-line as do the small circles obtained in the present investigation. This straight-line may be expressed by

$$A_v = 4.5 + 1230\left(\frac{\Delta\eta}{\Delta t}\right)_{25-45^\circ\mathrm{C.}} \qquad (6) .$$

The seventh column in Table 1 shows the ratio of viscosity association to density at 25°C. for each oil, and since

$$\frac{A_v}{d_a} = \frac{\eta_a}{d_a \eta'_a} = \frac{\nu_a}{\eta'_a} \qquad (1') ,$$

the value of the ratio can be obtained by the values of kinematic viscosity ν_a and η'_a at 25°C. As illustrated in Fig. 3, a linear relationship also exists between the ratio of A_v/d_a and the mean temperature coefficient of kinematic viscosity, the relation being expressed by

$$\frac{A_v}{d_a} = 4.5 + 1230\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45^\circ\mathrm{C.}} \qquad (7) ,$$

which is found to have the same numerical constants as equation (6).

Although in the foregoing cases, we have taken as the temperature coefficient of viscosity for oils its mean value between 25 and 45°C., it seems more reasonable to study their viscosity-temperature coefficients at 25°C. (if these are calculable) in relation to their viscosity association. As found by S. Erk and H. Eck,(5) the change in viscosity with temperature of mineral oils may be precisely expressed by Walther's equation(6)

$$(\nu + 0.8)^{(T^m)} = k_1 \qquad (8) ,$$

where ν is the kinematic viscosity in centistokes and T the absolute temperature. As it has been confirmed that equation (8) holds fairly good for the oils used in the present investigation, the writer has used in calculating their viscosity-temperature coefficients at 25°C. the equation

$$\frac{d\nu}{dt} = -m\,(\log k_1)\frac{\nu + 0.8}{T^{m+1}} \qquad (9) ,$$

which is derived by differentiating equation (8). In the calculation, the numerical values of the constants m and k_1 for each oil were obtained

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(5) *Physik. Z.*, **37** (1936), 113.

(6) *Maschinenbau*, **10** (1931), 671; *Oel Kohle Erdoel Teer*, **12** (1936), 221.

by introducing into equation (8) its viscosities at 25 and 90°C. The results of calculation are given in Table 2. Fig. 4 gives the relation between the viscosity-temperature coefficients thus calculated and the viscosity association of the oils, showing that the relation is also a linear one. In this figure, dots show the results of similar calculations for two of the oils used in the previous study, namely, Aero Shell and Voltol.

(2) *Viscosity characteristics of viscous solutions of polystyrenes.* In order to ascertain on the one hand whether equation (7) holds similarly for viscous solutions of high-molecular-weight hydrocarbons as for liquid hydrocarbons or not, and on the other hand in order to observe the effect of molecular length of high-molecular-weight solutes upon both the viscosity association and the viscosity-temperature coefficient of the solutions, determination of the latter two quantities was carried out for viscous solutions of three polystyrenes that differ markedly in polymerization. In the experiments, the value of K_∞ of each polystyrene was determined by measuring the viscosities of its dilute solutions both in benzene and in ethyl acetate, the results being shown in Table 4, from which it will be seen that the value of K_∞ of each polystyrene differs according as whether benzene or ethyl acetate is used for the solvent in the determination, the value for benzene always greatly exceeding that for ethyl acetate. A similar fact was also found previously by Staudinger and Heuer(7) as well as by the present author,(8) the difference in K_∞ according to solvent being ascribed to difference in degree of solvation, with the conclusion that the molecules of polystyrene are practically not solvated in ethyl acetate, whereas they are greatly solvated in benzene. Therefore in calculating the η'_a of a polystyrene, instead of using its value of K_∞ determined in benzene, we should use that determined in ethyl acetate. As it is known that oils show no appreciable solvation either in benzene or in ethyl acetate, in the foregoing experiments, the values of K_p for oils determined in benzene were used in calculating η'_a, their values of K_p, as the example given in Table 5 shows, not virtually differing whether the solvent used is benzene or ethyl acetate.

In calculating η'_a for viscous polystyrene solutions in benzene, concerning which the relation between viscosity-temperature coefficient and viscosity association is to be studied, the following equation

$$\frac{1}{d_a}\left(\frac{\eta'_a}{\eta_0}-1\right) = K_\infty C_a \tag{5'}$$

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(7) *Z. physik. Chem.*, A, **171** (1934), 129.

(8) *Kolloid-Z.*, **72** (1935), 51.

must be used instead of equation (5), where C_a and d_a respectively denote the concentration (%) and the density of the viscous solution whose η_a is to be obtained. Table 6 shows the values of η'_a and A_v/d_a thus calculated by equations (5′) and (1′) for six different solutions of polystyrenes in benzene, giving also their kinematic viscosities at 25 and 45°C. and their mean viscosity-temperature coefficients between 25 and 45°C. For these solutions, as will be seen from Fig. 5, a linear relationship exists between $(\Delta\nu/\Delta t)_{25-45^\circ\mathrm{C.}}$ and A_v/d_a, the straight-line being expressed by equation (7) as for oils. The degree of polymerization of the three polystyrenes used, which differs greatly, is believed to be nearly proportional to their values of K_∞. As will be seen from Table 6, solution No. 1 has a smaller value of A_v/d_a, and consequently a lower viscosity-temperature coefficient than solution No. 5, although the two have nearly the same viscosity at 25°C., the reason for which must be that the molecules of polystyrene I have a much longer structure than those of polystyrene III. Since the difference in viscosity-temperature coefficients between solutions 2 and 6, which have almost the same viscosity at 25°C., can also be explained similarly, it is concluded that for viscous solutions of high-molecular-weight hydrocarbons having the same viscosity at a certain temperature, the longer the molecule of solute, the lower is the temperature coefficient of viscosity. It is of interest, in this connection, to note that the solutions of polystyrene I have an extremely high viscosity index; for example, solution No. 3 shows a viscosity index of 180.

(3) *Constitution and viscosity association of high-molecular-weight hydrocarbons.* As already mentioned, the viscosity-temperature coefficient of a high-molecular-weight hydrocarbon or its solution is definitely related to its A_v value, and since the latter denotes the ratio η_a/η'_a, the former must be a function of η_a and η'_a. For this reason, in order to elucidate the relation between the chemical constitution and the viscosity-temperature coefficient of high-molecular-weight hydrocarbons, it behooves us to study the separate effects of chemical constitution on both η_a and η'_a. As to the effect of chemical structure on viscosity, i.e. η_a, various interesting conclusions have recently been obtained by Mikeska's elaborate investigation(9) on the viscosity characteristics of fifty-two synthetized hydrocarbons and also by Wiggins's study(10) on the constitution and viscosity characteristics of hydrocarbons. Since, as previously stated, $K_p d_a$ is dependent on molecular structure, it is evident from equation (5) that η'_a is likewise affected by chemical constitution. In order

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(9) *Ind. Eng. Chem.*, **28** (1936), 970.

(10) *J. Inst. Petroleum Tech.*, **22** (1936), 305.

to study the effect of chemical constitution on $K_p d_a$ and η'_a, we selected twenty-three representative hydrocarbons out of the number which Mikeska synthetized in his investigation, and determined⁽¹¹⁾ their mean viscosity-temperature coefficients between 25 and 45°C. from his viscosity data, and calculated from the coefficients thus determined their values of $K_p d_a$ and η'_a with the aid of equations (7), (1′), and (5). A similar calculation was made also for 1,1-dicyclohexylhexadecane and 1-cyclohexyl-2-hexahydrobenzylheptadecane from the data of Landa and Čech.⁽¹²⁾ The results are given in Table 7(a) and 7(b), from which the following interesting conclusions on the effect of chemical constitution on $K_p d_a$ and η'_a were drawn.

1. *Effect of length of side chain.* (a) A comparison of the results for compounds Nos. 26, 15, and 16 as well as of those for Nos. 1 and 2 leads to the conclusion that, for a given cyclic nucleus with a straight paraffinic side chain, the value of η'_a increases with length of side chain. (Compare also No. 11 with No. 13, No. 37 with No. 38, and No. 12 with No. 14.)

(b) The value of η'_a, as is evident from the results for compounds Nos. 15 and 28, is not appreciably affected by the number of side chains, provided the number of paraffinic carbon atoms attached to a given nucleus remains unchanged.

2. *Effect of straight chains as compared with branched chains.* A comparison of the results for compounds Nos. 2 and 3 as well as of those for Nos. 16 and 17 shows that, for a given number of carbon atoms, straight chains are more effective in increasing the value of η'_a than branched chains. (Compare also No. 12 with No. 13, and No. 38 with No. 39.)

3. *Effect of ring structure.* (a) A comparison of the results for compounds Nos. 1, 15, 40, and 48 indicates that, for a given paraffinic chain, the greater the complexity or the number of the cyclic rings attached to it—in other words, the more effective the cyclic groups in increasing the total length of the molecule, the higher is the value of η'_a. (Compare also No. 11 with No. 37, and No. 13 with No. 38.)

(b) Reduction of the aromatic to the corresponding hydro-aromatic rings slightly increases the value of η'_a. (Compare No. 15 with No. 37, No. 2 with No. 13, No. 3 with No. 12, No. 17 with No. 39, and No. 16 with No. 32 or No. 38.)

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(11) For the determination, the extra- and inter-polation of their viscosities at 25 and 45°C. were made with the aid of the viscosity-temperature chart of Ubbelohde.

(12) *Collection Czechoslov. Chem. Commun.*, **6** (1934), 423.

4. *Effect of olefinic linkages in the side chain.* As will be seen from the results for compounds Nos. 3 and 5, and also from those for Nos. 17 and 18, an olefinic linkage in the side chain does not appreciably affect the value of η'_a.

5. *Effect of allocation of cyclic nucleus within the molecule.* According to a comparison made of the results for compounds Nos. 48 and 51, the effect of allocation of the cyclic nucleus within the molecule has no appreciable effect on the value of η'_a.

As already mentioned, the viscosity-temperature coefficient of a high-molecular-weight hydrocarbon depends not only on its η'_a, but also on its actual viscosity η_a. Although compounds Nos. 40 and 17 have almost the same value of η'_a, their temperature coefficients of viscosity differ considerably. This must be due to the difference in η_a which the effect of chemical structure brings about. The same may be said in the comparison of the viscosity-temperature coefficients of compounds Nos. 15, 28, and 51 having almost the same value of η'_a. Of these three compounds equally with eighteen paraffinic carbon atoms the one having normal chain has the lowest temperature coefficient of viscosity owing to its lowest viscosity. That compounds Nos. 32, 17, and 51, having nearly the same viscosity at 25°C., also differ much in the viscosity-temperature coefficient, is due to differences in the values of η'_a. As a rule, for such compounds of comparable viscosities, the greater η'_a, the lower the viscosity-temperature coefficient, whence it follows that the longer the molecule, the smaller the temperature coefficient of viscosity.

Since η'_a is related by equations (7) and (1′) to the temperature coefficient of viscosity in the form

$$\frac{1}{1.23\eta'_a} = \frac{1000}{\nu_a}\left[0.00366+\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45^\circ\mathrm{C.}}\right] \qquad (7'),$$

an index that is expressed by $\frac{1000}{\nu_a}\left[0.00366+\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45^\circ\mathrm{C.}}\right]$, if it be calculated for high-molecular-weight hydrocarbons, must be inversely proportional to their values of η'_a. Therefore, the relation of their chemical structure to their values of this index may at once be found, provided we have complete information on the effects of their chemical structure on their values of η'_a. Fig. 6 shows the variation in $(\Delta\nu/\Delta t)_{25-45^\circ\mathrm{C.}}$ and in the index for compounds Nos. 26, 15, and 16 with the number of carbon atoms in the side chain, indicating that the index decreases with length of side chain, whereas $(\Delta\nu/\Delta t)_{25-45^\circ\mathrm{C.}}$ increases.

The above mentioned conclusions are in some respects comparable with those made by Mikeska(9) on the relation between the chemical

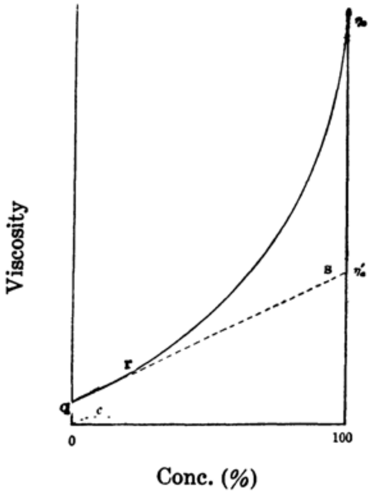


Fig. 1.

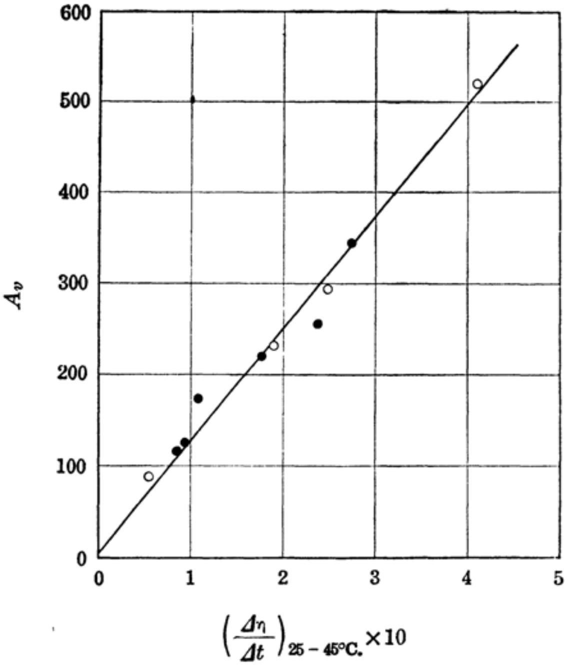


Fig. 2.

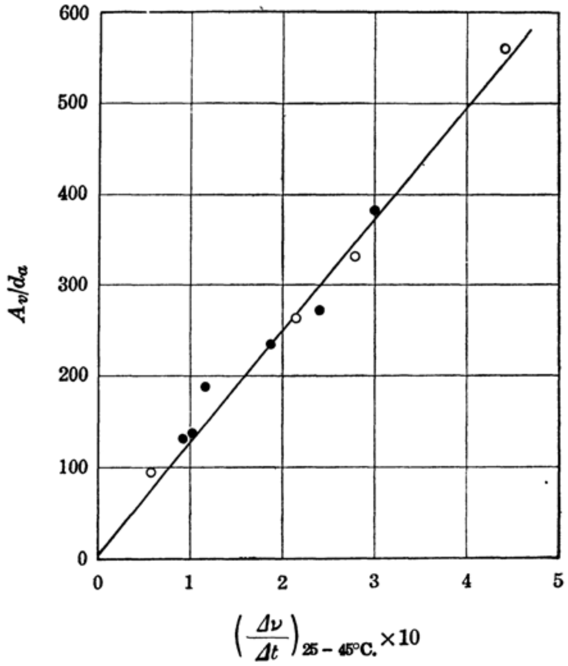


Fig. 3.

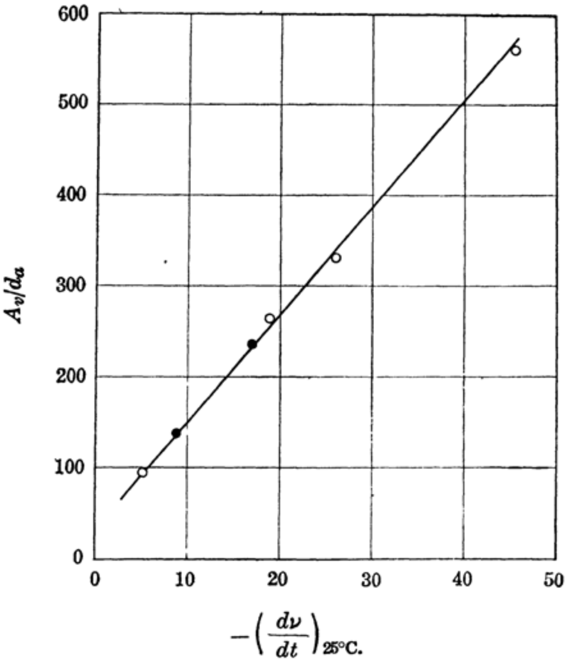


Fig. 4.

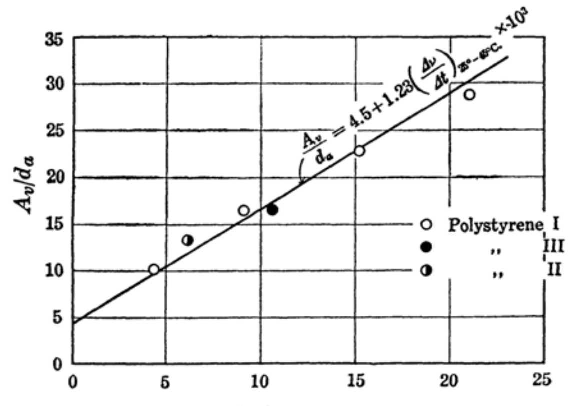
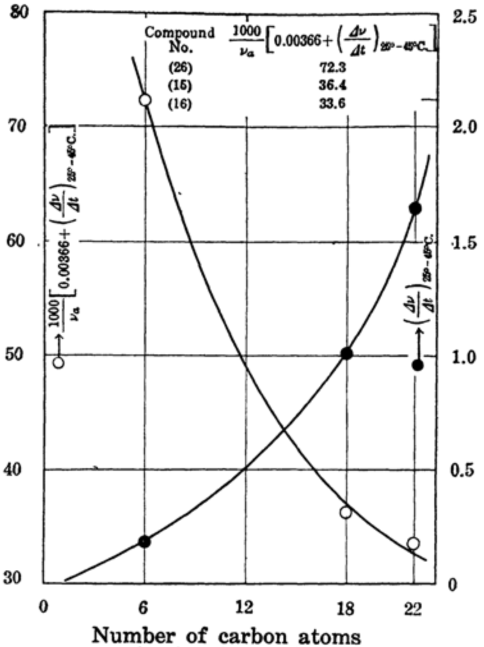


Fig. 5.



Number of carbon atoms in the side chain.

Fig. 6.

Table 1.

Oils	Conc. of benzene solution in % (C_p)	Density (d)	η_r	K_p		η'_a in poises	A_v	$\frac{A_v}{d_a}$	Mean viscosity-temperature coefficient between 25 and 45°C.	
									$\frac{\Delta\eta}{\Delta t}$	$\frac{\Delta\nu}{\Delta t}$
Mobile Oil S.R.N. (Mixed base)	2.525	0.8743	1.052	0.0238	0.0240	0.0195	520	561	0.410	0.441
	4.183	0.8751	1.087	0.0238						
	4.943	0.8755	1.105	0.0243						
Mobile Oil W. N. (Naphthenic)	2.706	0.8745	1.046	0.0195	0.0195	0.0169	87.9	94.9	0.0536	0.0577
	4.062	0.8752	1.070	0.0197						
Gargoyl Aero. H. (S. A. E. 60) (Paraffinic)	1.282	0 8733	1.035	0.0314	0.032	0.0232	294	331	0.248	0.279
	2.001	0.8734	1.056	0.0322						
	2.873	0.8735	1.083	0.0332						
	4.120	0.8737	1.121	(0.0336)						
Gargoyl Aero. W. (S. A. E. 50) (Paraffinic)	2.112	0.8731	1.054	0.0293	0.0311	0.0226	232	264	0.189	0.214
	3.015	0.8731	1.083	0.0315						
	3.949	0.8731	1.112	0.0325						

Table 2.

Oils	Density at 25°C. (d_a)	Viscosity			Mean viscosity-temperature coefficient between 25 and 45°C.		Constants in Walther's formula		$-\left(\frac{d\nu}{dt}\right)$ at 25°C. in centistokes	Viscosity index
		Temp. (°C.)	Kinematic visc. in stokes (ν)	Absolute visc. in poises (η)	$\frac{\Delta\nu}{\Delta t}$	$\frac{\Delta\eta}{\Delta t}$	m	$\log k_1$		
Mobile Oil S. R. N.	0.9272	25	10.94	10.14	0.441	0.410	4.073	10.56	45.5	14
		45	2.133	1.952						
		90	0.2214	0.1966						
Mobile Oil W. N.	0.9253	25	1.609	1.489	0.0577	0.0536	4.266	10.90	5.13	58
		45	0.456	0.417						
		90	0.0815	0.0723						
Gargoyl Aero. H. (S. A. E. 60)	0.8871	25	7.680	6.813	0.279	0.248	3.427	8.948	26.0	109
		45	2.109	1.847						
		90	0.3043	0.2585						
Gargoyl Aero. W. (S. A. E. 50)	0.8790	25	5.953	5.233	0.214	0.189	3.403	8.864	19.0	97
		45	1.680	1.457						
		90	0.2538	0.2136						

Table 3.

Oils	Density at 25°C.	Kinematic viscosity		Absolute viscosity		$\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45°C.}$	$\left(\frac{\Delta\eta}{\Delta t}\right)_{25-45°C.}$	$-\left(\frac{d\nu}{dt}\right)_{25°C.}$ in centistokes	A_v	$\frac{A_v}{d_a}$
		25°C.	45°C.	25°C.	45°C.					
Shell C. 2A.	0.8867	2.711	0.8663	2.404	0.7580	92.2×10^{-3}	82.3×10^{-3}	—	117	132
Aero Shell	0.9110	2.934	0.8990	2.673	0.8070	102×10^{-3}	93.3×10^{-3}	8.61	126	138
Mobile Oil A.	0.9215	3.212	0.8945	2.960	0.8140	116×10^{-3}	107×10^{-3}	—	174	189
Voltol	0.9359	5.013	1.263	4.692	1.172	187×10^{-3}	176×10^{-3}	16.9	220	235
Flugol	0.9405	6.594	1.800	6.202	1.491	240×10^{-3}	237×10^{-3}	—	256	272
Germ Oil	0.9039	7.755	1.747	7.010	1.560	300×10^{-3}	273×10^{-3}	—	345	382

Table 4.

Polystyrenes	Dilute solution in benzene				Dilute solution in ethyl acetate			
	Conc. in % (C_p)	Density (d)	η_r	K_∞	Conc. in % (C_p)	Density (d)	η_r	K_∞
No. I	0.0945	0.8737	1.070	0.848 } 0.84	0.0992	0.8931	1.038	0.429 } 0.42
	0.1922	0.8738	1.143	0.852	0.2146	0.8934	1.083	0.433
	0.2459	0.8739	1.178	0.828	0.4018	0.8938	1.157	0.437
No. II	0.3075	0.8739	1.0961	0.358 } 0.36	0.2476	0.8935	1.046	0.208 } 0.20
	0.5056	0.8742	1.153	0.348	0.3981	0.8938	1.080	0.218
	0.7069	0.8746	1.231	0.374				
No. III	0.4251	0.8746	1.0552	0.149 } 0.15	0.4943	0.8939	1.047	0.106 } 0.11
	0.6755	0.8746	1.0901	0.153	0.6630	0.8941	1.066	0.109
	0.9242	0.8751	1.126	0.155				

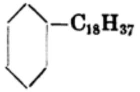
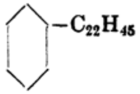
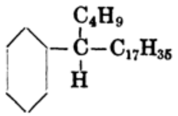
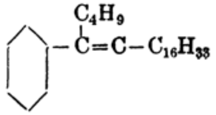
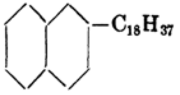
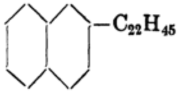
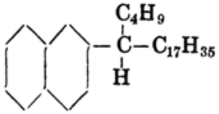
Table 5. Comparison of K_p of Mobile Oil S.R.N. in ethyl acetate and benzene.

Solvent	C_p (%)	Density (d)	η_r	K_p
Ethyl acetate	2.902	0.8931	1.064	0.0247 } 0.0248
	4.898	0.8932	1.109	0.0249
Benzene	2.525	0.8743	1.051	0.0238 } 0.0240
	4.183	0.8751	1.087	0.0238
	4.943	0.8755	1.105	0.0243

Table 6. Viscosity characteristics of viscous polystyrene solutions in benzene.

Solution No.	Polystyrenes	Conc. (%)	Density at 25°C. (d_a)	Kinematic viscosity in stokes		$\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45°C.}$	K_∞ in ethyl acetate	η'_a	$\frac{A_v}{d_a}$
				25°C.	45°C.				
1	I	10.83	0.8915	0.3105	0.2244	0.00431	0.42	0.0306	10.2
2		13.82	0.8966	0.6168	0.4350	0.00909		0.0375	16.5
3		16.01	0.9007	0.9722	0.6690	0.0152		0.0426	22.8
4		17.62	0.9035	1.335	0.9147	0.0210		0.0464	28.8
5	III	36.82	0.9352	0.3130	0.1910	0.00610	0.11	0.0235	13.3
6	II	27.92	0.9193	0.6168	0.4043	0.0106	0.20	0.0371	16.6

Table 7 (a). Viscosity characteristics of aromatic hydrocarbons.

Compound No.	Structure	Empirical formula	Densiny at 25°C. (d_a)	Kinematic viscosity*		$\left(\frac{\Delta v}{\Delta t}\right)_{25-45°C.}$	$\frac{A_v}{d_a}$	η'_a	$K_p \cdot d_a$	Viscosity index
				25°C.	45°C.					
1		$C_{24}H_{42}$	0.8540*	0.133	0.0770	0.0028	7.94	0.0168	0.0178	196
2		$C_{28}H_{50}$	0.8513	0.197	0.115	0.0041	9.5	0.0207	0.0243	164
3		$C_{28}H_{50}$	0.8554	0.274	0.131	0.0073	13.5	0.0203	0.0236	138
5		$C_{28}H_{48}$	0.8675	0.228	0.117	0.0056	11.4	0.0200	0.0231	162
15		$C_{28}H_{44}$	0.906	0.378	0.177	0.0101	16.9	0.0224	0.0271	140
16		$C_{32}H_{52}$	0.8987	0.599	0.270	0.0165	24.8	0.0242	0.0300	144
17		$C_{32}H_{52}$	0.898*	0.630	0.265	0.0183	27.0	0.0233	0.0286	122

* Extrapolated values.

Table 7 (a).—(*Concluded*)

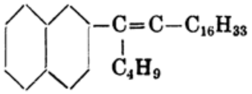
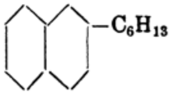
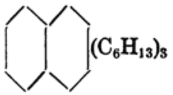
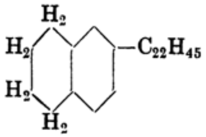
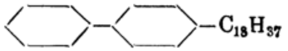
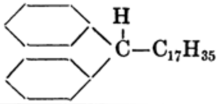
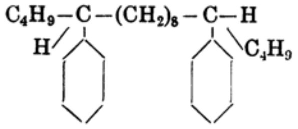
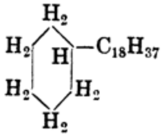
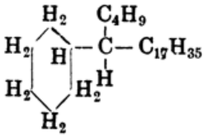
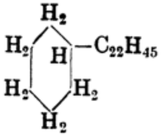
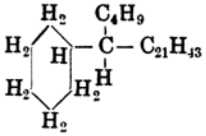
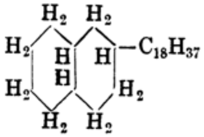
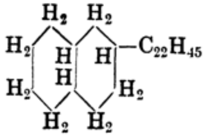
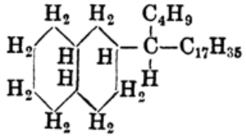
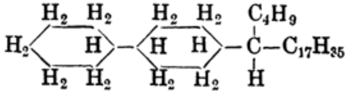
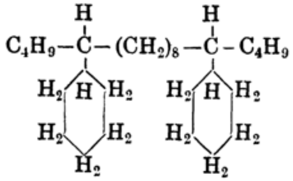
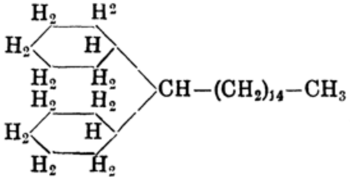
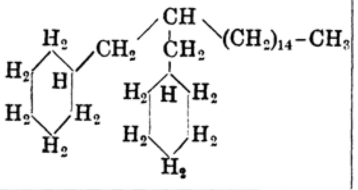
Compound No.	Structure	Empirical formula	Density at 25°C. (d_a)	Kinematic viscosity*		$\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45°C.}$	$\frac{A_v}{d_a}$	η'_a	$K_p \cdot d_a$	Viscosity index
				25°C.	45°C.					
18		$C_{32}H_{50}$	0.9081	0.555	0.237	0.0159	24.1	0.0230	0.0281	116
26		$C_{16}H_{20}$	0.9575	0.0752	0.0396	0.00178	6.69	0.0112	0.0085	−66
28		$C_{28}H_{44}$	0.911	0.600	0.241	0.0180	26.6	0.0226	0.0274	98
32		$C_{32}H_{56}$	0.8786	0.629	0.286	0.0172	25.7	0.0245	0.0305	145
40		$C_{30}H_{46}$	0.9138*	0.452	0.213	0.0120	19.3	0.0234	0.0282	131
48		$C_{30}H_{46}$	0.9260*	0.467	0.199	0.0134	21.0	0.0222	0.0267	96
51		$C_{30}H_{46}$	0.9051	0.630	0.245	0.0193	28.2	0.0223	0.0269	92

Table 7 (b). Viscosity characteristics of naphthenic hydrocarbons.

Compound No.	Structure	Empirical formula	Density at 25°C. (d_a)	Kinematic viscosity*		$\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45°C.}$	$\frac{A_v}{d_a}$	η'_a	$K_p \cdot d_a$	Viscosity index
				25°C.	45°C.					
11		$C_{24}H_{48}$	0.834*	0.204	0.106	0.0049	10.5	0.0194	0.0214	160
12		$C_{28}H_{56}$	0.8395	0.322	0.153	0.0085	15.0	0.0215	0.0255	140
13		$C_{28}H_{56}$	0.8327	0.313	0.156	0.0079	14.2	0.0220	0.0264	170
14		$C_{32}H_{64}$	0.8372	0.462	0.217	0.0123	19.6	0.0236	0.0290	149
37		$C_{28}H_{54}$	0.863	0.493	0.230	0.0132	20.7	0.0238	0.0294	144
38		$C_{32}H_{62}$	0.8673	0.772	0.339	0.0217	31.2	0.0247	0.0309	148

* Extrapolated values.

Table 7 (b).—(*Concluded*)

Compound No.	Structure	Empirical formula	Density at 25°C. (d_a)	Kinematic viscosity*		$\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45^\circ C.}$	$\frac{A_v}{d_a}$	η'_a	$K_p \cdot d_a$	Viscosity index
				25°C.	45°C.					
39		$C_{32}H_{62}$	0.8615	1.00	0.390	0.0305	42.0	0.0238	0.0294	114
46		$C_{34}H_{66}$	0.867	1.52	0.541	0.0490	64.8	0.0235	0.0288	110
52		$C_{30}H_{58}$	—	1.033	0.363	0.0335	45.7	0.0226	0.0274	88
53**		$C_{28}H_{54}$	0.8791 at 20°C.	η_{25° =0.532	η_{45° =0.213	$\left(\frac{\Delta\eta}{\Delta t}\right)_{25-45^\circ C.}$ =0.0160	A_v =24.2	0.0220	0.0264	98
54**		$C_{30}H_{58}$	0.8860 at 20°C.	η_{25° =0.481	η_{45° =0.197	$\left(\frac{\Delta\eta}{\Delta t}\right)_{25-45^\circ C.}$ =0.0142	A_v =22.0	0.0219	0.0262	103

** For the calculation of $\left(\frac{\Delta\eta}{\Delta t}\right)_{25-45^\circ C.}$, η'_a, and $K_p \cdot d_a$ of compounds Nos. 53 and 54, their values of absolute viscosity from Landa and Čech were used.

structure and the viscosity index of hydrocarbons, but none of his conclusions seem possible to explain the fact that compound No. 1, having a shorter side chain than compounds Nos. 2 and 13, is greater in viscosity index, as shown in the last column of Table 7, than the latter, whereas in the case of compounds Nos. 26, 15, 16, the shorter the side chain, the smaller is the viscosity index. No contradiction like this, however, is encountered in considering index $\frac{1000}{\nu_a}\left[0.00366+\left(\frac{\Delta\nu}{\Delta t}\right)_{25-45^\circ\mathrm{C.}}\right]$ in relation to their chemical structure, for the reason that in the above two series of compounds η'_a invariably increases with length of side chain.

Aeronautical Research Institute,
Tokyo Imperial University.