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On the Viscosity of Liquid Selenium

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The viscosities of liquid selenium and partially-chlorinated liquid selenium were measured in the temperature range from 235°C to 305°C using an Ubbelohde-type tilting viscometer. The "intrinsic" viscosities, η_0, were estimated by extrapolating the values of the viscosities, η_θ, of various rates of shear to a zero rate of shear. The "intrinsic" viscosities of the liquid selenium were estimated to be 20.18, 13.46, 9.11, 6.32, 3.67 and 2.30 poise at 235, 245, 255, 265, 285, and 305°C respectively. The viscosities of the chlorinated liquid selenium decreased with an increase in the chlorine content, but they varied discontinuously at a chlorine content of 0.0125% and then decreased linearly. The apparent activation energy for the viscous flow of the liquid selenium was estimated to be 17.9 kcal/mol. The apparent activation energies for the viscous flow of the chlorinated selenium varied discontinuously at a chlorine content of about 0.0125%, as in the case of the viscosity. The average-chain length of the selenium molecules was considered not to be changed, but the radicals at both ends of the linear chain vanish in forming the bonds with chlorine atoms with an increase in the chlorination below a chlorine content of 0.0125%. Therefore, it is concluded that the presence of radicals at the molecular ends would have an influence upon the viscosity and the apparent activation energy for the viscous flow of selenium. The notable large value of the apparent activation energy of such a non-branched polymer as selenium was attributed to the large amount of energy needed to transport the segments into the holes.

Liquid selenium is considered to be a mixture of Se_8 ring molecules and long chains.[1] The properties of the liquid selenium should be governed by those of the long-chain molecules, since the liquid selenium contains few ring molecules. The number of selenium atoms in a chain of average length was calculated to be 7200 at 230°C by the thermodynamic theory developed by Eisenberg and Tobolsky.[1] The linear chains are considered to be diradical molecules with an unpaired electron at each end of the chain. The presence of radicals in the amorphous selenium was confirmed by Abdullaev *et al.*[2] and Sampath *et al.*[3] on the basis of their ESR studies. Sampath[4] reported that the results obtained by Eisenberg and Tobolsky were supported by the value of the spin concentration in the amorphous selenium. In this study, the effect of radicals on the viscous flow of the liquid selenium was studied.

Experimental

Materials. The selenium and the partially-chlorinated selenium samples were prepared in the manner described in a previous paper.[5]

Procedure. An Ubbelohde-type tilting viscometer[6] was used for the measurements of the viscosities of the liquid samples. The viscosity, η_θ, at the tilting angle, θ, of the viscometer was calculated by the following equation:

$$\eta_\theta = A_\theta \rho t$$

where A_θ, ρ, and t are the parameter of the viscometer, the density of the liquid sample, and the efflux time respectively. The tilting angle, θ, is the angle of the capillary of the viscometer to the vertical line. The parameter, A_θ, of the viscometer was estimated by means of the measurement of the efflux time of glycerol of a known viscosity at 25°C and at various tilting angles, θ. The viscosities, η_θ, of the liquid samples were measured at several tilting angles. The " intrinsic " viscosity, η_0, was estimated graphically by extrapolating the values of the viscosities, η_θ, to a ninety-degree tilting angle, *i.e.*, to a zero rate of shear. The viscosities and the densities of the liquid samples were measured at specified temperatures within an accuracy of ± 0.1°C in an electric furnace.

The densimeter is shown in Fig. 1. The volume between the fixed lines, and the diameters of both the capillaries were measured using mercury at 30°C. The height of the liquid selenium column in the capillary was measured with a measuring microscope to an accuracy of 1/100 mm. The linear expansion coefficient of the densimeter is 7.95×10^{-7}°C^{-1} over the temperature

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[1] A. Eisenberg and A. V. Tobolsky, *J. Polymer Sci.*, **46**, 19 (1960).

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[3] P. I. Sampath and R. C. Keezer, *Bull. Am. Phys. Soc.*, **10**, 613 (1965).

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[5] S. Hamada, T. Sato and T. Shirai, This Bulletin, **41**, 135 (1968).

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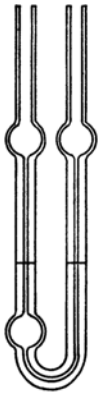

Fig. 1. Densimeter.

range from 20°C to 50°C, and those of the liquid selenium and of the chlorinated liquid selenium are calculated to be from 1.06×10^{-4} to 1.22×10^{-4}°C^{-1} over the temperature range from 230°C to 305°C. Therefore, the expansion of the densimeter is negligible compared with those of the liquid samples.

Results

The Stability of the Chlorinated Liquid Selenium. Figure 2 shows the relationship between the chlorine content of the chlorinated selenium and the heating time at 265°C. The chlorine content decreased linearly with an increase in the heating time until about 3 hr, but the chlorinated selenium was stabilized after 3 hr. Because the escape of chlorine from the chlorinated selenium is considered to be negligible after 3 hrs' heating at 265°C, the viscosities and the densities were measured after 4 hrs' heating at 265°C.

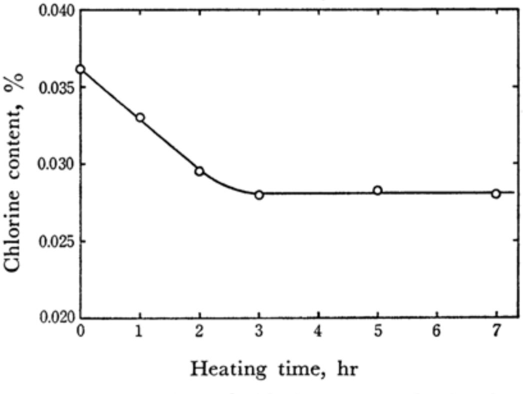

Fig. 2. Variation of chlorine content by heating at 265°C in chlorinated selenium.

The Densities of the Liquid Selenium and of the Chlorinated Liquid Selenium. The density of the liquid selenium was estimated to be 3.9850 g/cm^3 at 235°C, and the linear expansion coefficient was calculated to be 1.09×10^{-4}°C^{-1} in the temperature range from 230°C to 305°C, from the temperature dependence of the density. The densities of the chlorinated selenium were estimated to be from 3.9835 to 3.9770 g/cm^3 at 235°C in the chlorine-content range from 0.0033 to 0.0257%, and their linear expansion coefficients were calculated to be from 1.08×10^{-4} to 1.19×10^{-4}°C^{-1} in the temperature range from 230°C to 305°C.

The Viscosities of the Liquid Selenium and of the Chlorinated Liquid Selenium. The viscosities, η_θ, of the liquid samples at several tilting angles were measured at temperatures from 230°C to 305°C. Figure 3 shows the dependence of the viscosities, η_θ, of the liquid selenium on the tilting angle, θ, of the viscometer. The viscosity of the liquid selenium decreased with a decrease in the tilting angle of the viscometer, *i. e.*, with an increase in the rate of shear. The viscosities of the chlorinated liquid selenium showed the same appearance as that of the liquid selenium. Both the liquid selenium and the chlorinated liquid selenium are considered to behave as non-Newtonian liquids. Therefore, the "intrinsic" viscosities, η_0, of the liquid samples were estimated by extrapolating the viscosity values, η_θ, to a zero rate of shear in order to discuss the behavior of their viscous flow.

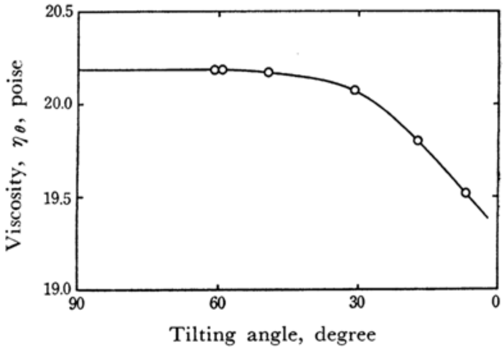

Fig. 3. Dependence of viscosity of liquid selenium on tilting angle.

The "intrinsic" viscosities, η_0, of the liquid samples are given in Table 1.

The dependence of the logarithm of the viscosity, $\log \eta_0$, on the chlorine content at 235°C is shown in Fig. 4. The $\log \eta_0$ values decreased continuously to a chlorine content of 0.0125%, and then more rapidly and linearly with an increase in the chlorine content.

The chlorine content of 0.0125% corresponds to the state when all the radicals at both ends of the linear-chain molecules of selenium vanish in forming bonds with chlorine atoms.[5] The radicals vanish more and more with an increase in the chlorination until 0.0125%, and the average chain length of the chlorinated selenium molecules

TABLE 1. VISCOSITIES OF LIQUID SELENIUM AND OF CHLORINATED LIQUID SELENIUM

Chlorine Content, %	Viscosities, η_0, poise 235°C	245°C	255°C	265°C	285°C	305°C
0	20.18	13.46	9.11	6.32	3.67	2.30
0.0033	17.22	12.40	8.93	6.61	3.76	2.35
0.0053	16.31	11.76	8.48	6.40	3.68	2.20
0.0092	15.95	11.43	8.45	6.25	3.64	2.26
0.0113	15.41	11.11	8.18	6.04	3.54	2.13
0.0126	15.31	10.94	8.06	5.97	3.52	2.10
0.0134	14.83	10.51	7.73	5.82	3.45	2.12
0.0146	14.61	10.19	7.66	5.88	3.39	2.07
0.0197	12.46	8.90	6.73	5.17	3.26	2.06
0.0257	9.84	7.40	5.62	4.28	2.67	1.69

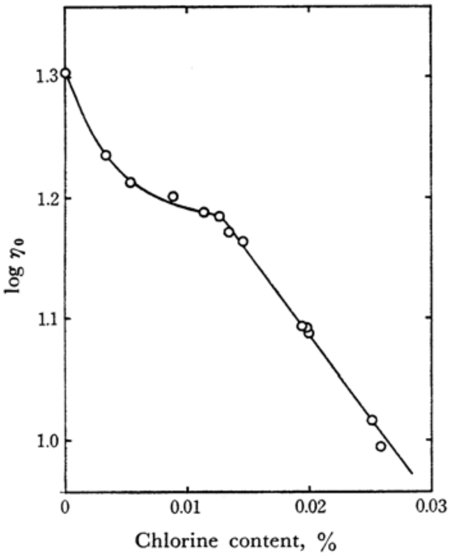

Fig. 4. Plot of log η_0 against chlorine content at 235°C.

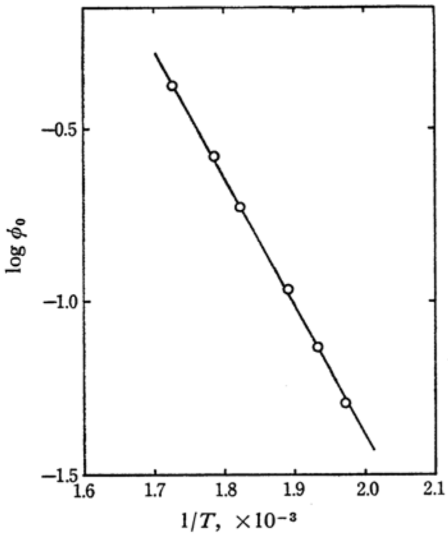

Fig. 5. Temperature dependence of fluidity of liquid selenium.

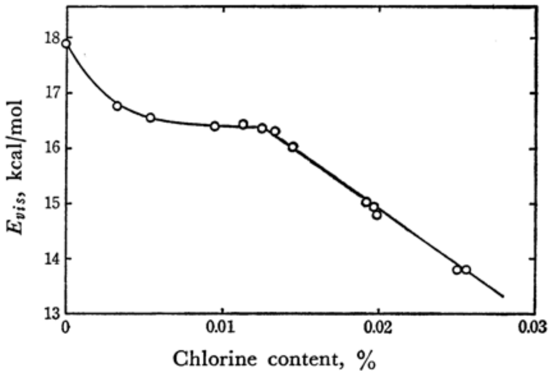

Fig. 6. Dependence of E_{vis} on chlorine content.

will not be changed. Therefore, the discontinuous variation in the viscosity at the chlorine content of 0.0125% suggests the influence of the fulfilment of the radicals of the chain ends.

The decreases in the viscosity of the chlorinated selenium above 0.0125% are considered to be due to a cut-off of the chain molecules by chlorine.

The Apparent Activation Energies for the Viscous Flow of the Liquid Selenium and of the Chlorinated Liquid Selenium. Figure 5 shows the relationship between the fluidity, ϕ_0, *i. e.*, $1/\eta_0$, of the liquid selenium and the temperature, T. The log ϕ_0 varied linearly with $1/T$. The temperature dependences of the log ϕ_0 of the chlorinated selenium were similar to that of the liquid selenium. Since the dependences of the log ϕ_0 on the temperature showed an Arrhenius-type variation, the apparent activation energies for the viscous flow, E_{vis}, were estimated from the following equation:

$$E_{vis} = -\boldsymbol{R}\mathrm{d}(\ln \phi_0)/\mathrm{d}T$$

The apparent activation energy for the viscous flow of the liquid selenium was estimated to be 17.9 kcal/mol. The dependence of the E_{vis} of the chlorinated selenium on the chlorine content is shown in Fig. 6. The E_{vis} decreased abruptly with an increase in the chlorine content. The E_{vis} varied discontinuously near the chlorine content of 0.0125%, and then decreased linearly above 0.0125%.

Discussion

The liquid organic-chain polymers, in general, show comparatively small values of E_{vis}, though they increase with an increase in the bulk of the side chains. The E_{vis} values for some organic chain polymers are shown in Table 2.[7] The value of E_{vis} is considerably larger for selenium, though it has no branched chain.

TABLE 2. E_{vis} FOR SOME ORGANIC CHAIN POLYMERS AT A ZERO RATE OF SHEAR

	Ethylene	Propylene	Isobutylene	Styrene
E_{vis} kcal/mol	6.5—7.0	9.0—9.6	12.0—16.2	22.6

The apparent activation energy for the viscous flow consists of two parts. One of them is the energy necessary to produce holes. The other is the energy, ΔE_f which is necessary to drive the segments into the holes. If ϕ_1 and ϕ_2 are the fluidities at a constant volume, that is, the iso-state of a free volume, at temperatures of T_1 and T_2 respectively, ΔE_f can be expressed by the following equation:[8]

$$-\Delta E_f(1/T_1-1/T_2) = \boldsymbol{R}\ln(\phi_1/\phi_2) + \ln(T_1/T_2)/2$$

The relationship between the specific volume of the liquid selenium and the temperature at the specified pressures can be calculated using the values of the thermal expansion coefficient of liquid selenium, $\alpha=3.27\times10^{-4}$, and of the compressibility of liquid selenium,[9] $\beta=1.53\times10^{-5}$ bar^{-1}. From this relationship, certain conditions, *i. e.*, the temperature and the pressure, under which the compressed liquid selenium possesses an iso-volume state can be estimated graphically. Harrison[9] reported the viscosity of liquid selenium over the temperature range from 260°C to 350°C under a compressed system in the range from 1 bar to 1500 bar. The viscosities of the compressed liquid selenium in an iso-volume state at the corresponding temperatures and pressures can be deduced from Harrison's results.

Table 3 shows the viscosities in the case of the iso-volume state of 0.2533 cm^3/g, as an example. The ΔE_f value was calculated to be 11.5 kcal/mol from the data in Table 3. The ΔE_f value for ordinary liquids is, in general, assessed to be within the range from one-tenth to one-fifth of the total apparent activation energy for the viscous flow. A larger amount of energy, however, is necessary to drive the segments into the holes for the viscous flow of the liquid selenium than those of ordinary liquids; this must cause the larger E_{vis} value for the liquid selenium. Moreover, the apparent activation energy for the viscous flow of the liquid selenium shows the character of a "structure activation energy," as in the case of water.

TABLE 3. VISCOSITIES AT ISO-VOLUME STATE $v=0.2533$ cm^3/g

Press., bar	1	500	1000	1500
Temp., °K	533	556	581	605
η, poise	5.69	3.74	2.39	1.61

Bondi[10] expressed the viscosity of the liquid in connection with the v_f and the ΔE_f as follows:

$$\eta = (v_f^{1/3}/v_L)(2\pi m\boldsymbol{k}T)^{1/2}\exp(\Delta E_f/\boldsymbol{R}T)$$

where v_f is the free volume; v_L, the molecular volume in the liquid; m, the mass per molecule, and $\boldsymbol{k}$, the Boltzmann constant. The fraction of v_f at T_g, f_g, defined by Williams, Landel and Ferry,[11] is well known to be 2.5×10^{-2} in usual organic and inorganic polymers. The abnormality of the f_g of the amorphous selenium has been shown by the volume relaxation phenomenon.[5] The f_g value of the amorphous selenium is 6.33×10^{-2}; it is larger than those of the usual polymers, but it decreases with an increase in the chlorination, reaching the normal value, 2.5×10^{-2}, at a chlorine content of more than 0.0125%. Therefore, the free volume of the liquid selenium would be larger than that of the chlorinated liquid selenium. However, the contribution of the free volume term, $(v_f^{1/3}/v_L)$, on the viscosity is not very large. The ΔE_f of the chlorinated selenium could not be established, for the dependence of the viscosity of the chlorinated selenium on the pressure was obscure. However, a decrease in ΔE_f upon the chlorination was suggested by the dependence of the E_{vis}, of the chlorinated selenium on the chlorine content below 0.0125%, as is shown in Fig. 6 (assuming that the chain length of selenium molecules does not change at chlorine contents below 0.0125%). The abrupt decrease in the viscosity of the chlorinated liquid selenium at chlorine contents below 0.0125% is due to the decrease in ΔE_f, in spite of the decrease in the f_g upon chlorination.

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[9] D. E. Harrison, *J. Chem. Phys.*, **41**, 844 (1964).

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The decreases in the viscosity and E_{vis} value of the chlorinated selenium at chlorine contents above 0.0125% are probably due to the shortening of the chain molecules with an increase in the chlorination.