THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 33, NO. 2, 1963

PHYSICO-CHEMICAL PROPERTIES OF SULFUR

1. Pressure Effects on Viscosity of Liquid Sulfur

BY TSUNESUKE DOI

The viscosities of the temperature range 130 to 230°C and for the pressure range 1 to 100 atm are given for pure liquid sulfur by the Rolling Ball Viscometry. The pressure effects on the viscosity are obtained in the temperature range above 160°C, and the lower the temperature of liquid sulfur, the greater the effect of pressures at 160–230°C. The pressure effects on the viscosity in the temperature range below 160°C are negligible, being close to zero at approximately 130°C. The results obtained, however, are not in quantitative agreement with the predictions of E. Powell and H. Eyring. The author's results are satisfactorily interpreted in terms of the quantitative thermodynamic theory and an equilibrium polymerization theory which was published by G. Gee and his coworkers, and A. V. Tobolsky and his coworkers.

It is also found that the equation of viscosity for the Rolling Ball Method previously published by this author is satisfactory in the wide range of centipoise to several hundreds poise.

Introduction

It is well known that sulfur melts to become a pale yellow, mobile liquid at approximately 120°C, and that the mobile liquid changes into an extremely viscous, dark brown liquid when molten sulfur is further heated above 160°C. Many authors have studied this liquid sulfur to know its characteristic behavior. R. F. Bacon and F. Fanelli¹⁾ measured the viscosity of liquid sulfur carefully through the temperature range of 120–300°C. It has been believed that the viscosity of liquid sulfur suddenly increases to become linear chain polymers above 160°C, and that internal equilibria exist between the S_8 ring and the linear chain polymers. Attempts to estimate these internal equilibria have been made by R. E. Powell and H. Eyring²⁾, G. Gee³⁾ and A. V. Tobolsky and A. Eisenberg⁴⁾, *et al.* But the pressure effects on the equilibria (that is, on the viscosity) have been theoretically estimated only by R. E. Powell and H. Eyring²⁾, and there is no published data concerning these effects.

In this paper the viscosities are given for pure sulfur through the temperature range of 130–230°C for pressures of 1, 50 and 100 atmospheres, and theoretical analysis of the effect of pressures is given by this author.

(*Received February 1, 1964*)

1) R. F. Bacon and F. Fanelli, *J. Am. Chem. Soc.*, **65**, 639 (1943)
2) F. E. Powell and H. Eyring, *J. Am. Chem. Soc.*, **65**, 648 (1943)
3) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952)
4) A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, **81**, 780 (1959)

Calculation of Pressure Effects for the Equilibria

For the calculation of the pressure effects it is necessary that the melting viscosity of sulfur is represented as a function of the temperature, the concentration of polymer, and the degree of polymerization. Such a function is derived using equations[3] introduced by G. Gee.
That is:

$$(\eta)=AP^{2/3} \tag{1}$$

$$\eta/\eta_0=1+(\eta)\phi+k(\eta)^2\phi^2 \tag{2}$$

$$-\log\eta_0=0.68-2940/T \tag{3}$$

where,

(η): intrinsic viscosity
P: degree of polymerization (S_8 units)
η: viscosity of melting sulfur
η_0: viscosity of environment of linear chain polymers in melting sulfur
ϕ: weight fraction of polymer molecule in melting surfur
T: absolute temperature

In this case the melting sulfur is assumed to be a polymer solution in which the polymer molecules of sulfur are dissolved in the solvent of S_3 rings. The first two terms on the right side of eq. (2) become negligible when the degrees of polymerization are assumed to be great and are accordingly dropped.

$$\eta/\eta_0=k(\eta)^2\phi^2 \tag{4}$$

combining eqs. (1), (3) and (4), gives finally:

$$\log\eta=a+b/T+4/3\log P+2\log\phi \tag{5}$$

where,

$a=\log kA^2-0.4343\times9.67$
$b=0.4343\times2940$

In order to calculate the effect of pressure for the equilibria using viscosity, only a knowledge of functional relations between P and pressure, and between ϕ and pressure is required.

According to A. V. Tobolsky and A. Eisenberg, the conditions at equilibrium at any temperature for the polymerization of sulfur may be assumed to be:

$$\left.\begin{array}{l} M \xrightleftharpoons{K_1} M^* \\ M^*+M \xrightleftharpoons{K_3} M_2^* \\ M_{n-1}^*+M \xrightleftharpoons{K_3} M_n^* \end{array}\right\} \tag{6}$$

where

M: a S_8 ring (mole/kg)

M^*, M_2^*,…… M_n^*: a diradical of monomer, dimer and n-mer, respectively (mole/kg)

K_1, K_3: equilibrium constants for the ring opening reaction of S_8, and the polymerization reaction, respectively.

A. V. Tobolsky and A. Eisenberg derived the following two equartions from conditions (6) as follows:

$$P=\frac{1}{1-K_3\mathrm{M}}\ , \tag{7}$$

$$\mathrm{M}_0=\frac{P-1}{PK_3}+\frac{K_1}{K_3}\times P(P-1)\ , \tag{8}$$

where M_0 is moles of S_8 ring per 1 kg (3.90 moles/kg).

ϕ is given from the definition as

$$\phi=\frac{\mathrm{M}_0-\mathrm{M}}{\mathrm{M}_0}\ . \tag{9}$$

Substitution of M from eq. (7) into eq. (9) gives

$$\phi=\frac{\mathrm{M}_0-\frac{1}{K_3}}{\mathrm{M}_0}\ . \quad (\because \quad P\fallingdotseq P-1) \tag{10}$$

P is given from eq. (8) as

$$P=\sqrt{\left(\mathrm{M}_0-\frac{1}{K_3}\right)\frac{K_3}{K_1}}\ . \quad (\because \quad P\fallingdotseq P-1) \tag{11}$$

Finally, ϕ is given as a function of K_3 and P is given as a function of K_1 and K_3. The effects of pressure for K_1 and K_3 are calculated by the following equation[5].

$$\ln K_n=-\frac{\Delta V_n}{\mathrm{R}T}\pi+\text{const.} \tag{12}$$

where,

K_n: K_1 or K_3

$-\Delta V_n$: volume difference between the start and the completion of the reaction per one mole corresponding to K_1 or K_3

π: pressure

We can rewrite eq. (12) as eq. (13) in order to drop the constant.

$$\ln\frac{K_n'}{K_n}=\frac{-\Delta V_n}{\mathrm{R}T}(\pi'-\pi) \tag{13}$$

It is assumed that $-\Delta V_3$ is independent of pressure. Unfortunately, there is no published data about $-\Delta V_n$, but it can be derived from the data about specific volume of sulfur which were measured by T. Shirai[6] in the temperature range of 90–360°C. In the temperature range from 120 to 160°C, in which only the existence of S_8 ring is assumed, the specific volume of sulfur V_0 is

$$V_0=0.5242+0.000242t \tag{14}$$

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[5] S. Sasaki, "*Kagakuhannoron*", 458, Kyoritsu shuppan

[6] T. Shirai, *Nihon kagaku zasshi*, 72, 698 (1951)

where t is temperature (°C). It is assumed that there is the additivity of specific volume between the S_8 ring and the linear chain polymer of sulfur. (Perhaps the end groups of the polymer have an opposite effect[7] upon the above assumption. If this assumption is correct, such an effect decreases according to the degree of polymerization and becomes negligibly small.)

$$V = V_0(1-\phi)+V_p\phi \ , \tag{15}$$

where V and V_p are the specific volumes of the melting sulfur and the linear chain polymers of sulfur, respectively. Table 1 is obtained using the results of the published calculation of ϕ of A. V. Tobolsky and A. Eisenberg, and the published data of V by T. Shirai.

Table 1 Calculations of $-\Delta V_3$

t (°C)	M (mole/kg)	$1-\phi$	V (cc/g)	V_0 (cc/g)	V_p (cc/g)	$-\Delta V_3$ (V_p-V_0) (cc/g)
167	3.65	0.936	0.5642	0.5647	0.5578	0.0069
177	3.36	0.862	0.5660	0.5671	0.5597	0.0074
187	3.14	0.805	0.5672	0.5695	0.5560	0.0135
197	2.89	0.741	0.5680	0.5720	0.5563	0.0158
207	2.69	0.690	0.5693	0.5744	0.5580	0.0164
217	2.52	0.646	0.5709	0.5768	0.5603	0.0165
227	2.37	0.608	0.5723	0.5792	0.5620	0.0172
237	2.21	0.566	0.5739	0.5817	0.5640	0.0177
247	2.08	0.533	0.5758	0.5841	0.5660	0.0181
257	1.96	0.502	0.5778	0.5865	0.5692	0.0173
267	1.86	0.477	0.5799	0.5889	0.5718	0.0171
277	1.76	0.451	0.5821	0.5913	0.5742	0.0171
287	1.68	0.431	0.5842	0.5937	0.5770	0.0167
297	1.60	0.410	0.5862	0.5961	0.5795	0.0166
307	1.52	0.390	0.5887	0.5985	0.5823	0.0162

Mean 0.0154

$-\Delta V_3$ below 187°C in Table 1 is extremely small. The author is of the opinion that this is due to experimental error. It is reasonable to assume that $-\Delta V_3$ is almost constant throughout 167 to 307°C. But the author has adopted the mean value of $-\Delta V_3$ throughout 167–307°C, including the extreme values. $-\Delta V_3$ is 0.0154 cc/g (3.8 cc/mole).

This value of $-\Delta V_3$ is the volume change corresponding to K_3. The volume change corresponding to K_1, that is, the volume change of the ring opening reaction of the S_8 ring is unknown. But fortunately, it is obvious from eq. (11) that the changes of K_3 contribute almost exclusively to P, and the changes of K_1 do not contribute to P because the term $\left(M_0-\frac{1}{K_3}\right)$ is the most important. That is, the effect of pressure itself acts equally upon not only K_3, but also K_1 ; however, the change of viscosity is almost exclusively due to K_3.

We can rewrite eq. (5) as eq. (16) at the same temperature.

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7) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1068 (1940)

$$\log \eta'/\eta = 4/3 \log P'/P + 2 \log \phi'/\phi \qquad (16)$$

where P' and ϕ' are P and ϕ under pressure, respectively. Substitution of K_3' and K_1' of eq. (13) into eq. (11) gives P'. M′ and ϕ' are obtained by eq. (7) and eq. (9): respectively. Finally, we obtain η'/η from eq. (16). The results are summarized in Tables 2 and 3. By assuming $-\Delta V_1=0$ the value η'/η in Table 2 is almost the same as the value of η'/η in Table 3 which was obtained by assuming $-\Delta V_1=0.0154$. The calculation is restricted to the range 167–307°C in which eq. $P \fallingdotseq P-1$ is valid.

In general there are terms other than P and ϕ which give the pressure effects on viscosity. Such other terms, however, are negligible when pressures as low as in this report are found, and are therefore dropped from the author's calculations.

Table 2 The calculation results of η'/η by assuming $-\Delta V_1=0$ and $-\Delta V_3=0.0154$ cc/g

π (atm.)	T (°K)	t (°C)	K_1	K_3	P (S_8 unit)	M (mole/kg)	ϕ	η (poise)	η'/η
1	440	167	5.40×10^{-12}	0.2739	112300	3.65	0.064	290	
	450	177	1.23×10^{-11}	0.2976	113900	3.36	0.138	775	
	460	187	2.71×10^{-11}	0.3185	94500	3.14	0.195	931	
	470	197	6.08×10^{-11}	0.3460	75800	2.89	0.259	850	
	490	217	2.59×10^{-10}	0.3968	46000	2.52	0.354	536	
	510	237	9.47×10^{-10}	0.4524	28400	2.21	0.433	264	
	540	267	5.70×10^{-9}	0.5376	13870	1.86	0.523	84	
	580	307	4.73×10^{-8}	0.6578	5750	1.52	0.610	22	
			K_1'	K_3'	P'	M′	ϕ'	η'	
50	440	167	5.40×10^{-12}	0.2753	116900	3.632	0.0687	353	1.218
	450	177	1.23×10^{-11}	0.2992	116500	3.342	0.1430	788	1.106
	460	187	2.71×10^{-11}	0.3201	95800	3.124	0.1990	789	1.062
	470	197	6.08×10^{-11}	0.3477	76500	2.878	0.2621	882	1.037
	490	217	2.59×10^{-10}	0.3988	46330	2.509	0.3568	549	1.024
	510	237	9.47×10^{-10}	0.4545	28580	2.201	0.4358	269	1.019
	540	267	5.70×10^{-9}	0.5399	13940	1.853	0.5249	85.2	1.015
	580	307	4.73×10^{-8}	0.6605	5770	1.514	0.6118	22.3	1.011
100	440	167	5.40×10^{-12}	0.2768	121500	3.615	0.0734	423	1.459
	450	177	1.23×10^{-11}	0.3008	118700	3.327	0.1470	928	1.198
	460	187	2.71×10^{-11}	0.3218	97040	3.110	0.2028	1043	1.120
	470	197	6.08×10^{-11}	0.3495	77220	2.862	0.2661	922	1.085
	490	217	2.59×10^{-10}	0.4007	46600	2.498	0.3597	564	1.051
	510	237	9.47×10^{-10}	0.4567	28720	2.190	0.4384	274	1.039
	540	267	5.70×10^{-9}	0.5424	13990	1.844	0.5270	86.3	1.027
	580	307	4.73×10^{-8}	0.6633	5790	1.508	0.6131	22.5	1.020

Table 3 The calculation results of η'/η by assuming $-\Delta V_1 = 0.0154$ cc/g and $-\Delta V_3 = 0.0154$ cc/g

π (atm.)	T (°K)	t (°C)	K_1'	K_3'	P' (S_8 unit)	M′ (mole/kg)	ϕ'	η' (poise)	η'/η
50	440	167	5.428×10^{-12}	0.2753	116600	3.632	0.0687	352	1.215
	450	177	1.237×10^{-11}	0.2992	116200	3.342	0.1430	855	1.104
	460	187	2.724×10^{-11}	0.3201	95500	3.124	0.1990	985	1.058
	470	197	6.110×10^{-11}	0.3477	76320	2.878	0.2621	878	1.033
	490	217	2.602×10^{-10}	0.3988	46200	2.509	0.3568	548	1.022
	510	237	9.512×10^{-10}	0.4545	28500	2.201	0.4358	267	1.017
	540	267	5.725×10^{-9}	0.5399	13900	1.853	0.5249	85	1.012
	580	307	4.750×10^{-8}	0.6605	5760	1.514	0.6118	22.2	1.007
100	440	167	5.458×10^{-12}	0.2768	120700	3.615	0.0734	421	1.451
	450	177	1.243×10^{-11}	0.3008	118100	3.327	0.1470	924	1.192
	460	187	2.738×10^{-11}	0.3218	96520	3.110	0.2028	1035	1.113
	470	197	6.142×10^{-11}	0.3495	76800	2.862	0.2661	910	1.071
	490	217	2.615×10^{-10}	0.4007	46400	2.498	0.3597	559	1.043
	510	237	9.559×10^{-10}	0.4567	28600	2.190	0.4384	272	1.032
	540	267	5.750×10^{-9}	0.5424	13930	1.844	0.5270	85.8	1.022
	580	307	4.770×10^{-8}	0.6633	5770	1.508	0.6131	22.3	1.015

Experiments and Results

Apparatus

The experiments were carried out in a Rolling Ball Viscometer (Fig. 1). It is well known that sulfur is corrosive and that some impurity is present which has a marked effect on its viscosity. In setting up of the apparatus, a corrosion resistant material must be needed. It was found that a stainless steel designated SUS-32 is highly resistant. Therefore, the experimental apparatus was built of SUS-32 and a Pyrex type glass tube. This glass tube has a 10 mm inner diameter and 20 mm outer diameter, is circular in bore, has an equal diameter over the entire length, has a smooth inner surface, and it has been selected from among many special tubes manufactured by Shibata Kagaku Kikai Corporation. The ball, consisting of 60 percent gold and 40 percent platinum which has a specific gravity of 20.166, must correspond to the diameter of the tube, and the ball was made with the same accuracy as of a ball bearing. Teflon (tetrafluoroethylene) was used for packing to fasten the glass tube. Both SUS-32 stainless steel chips and Teflon chips were heated for several hours in sulfur, but this had no effect on the viscosity of the sulfur. In order to pump sulfur, a hand pump and a glycerin medium were used. A long stainless steel tube (150 cm long) and a stainless steel cylinder containing a small plug of Teflon as a valve was used between the pump and the experimental apparatus to prevent diffusion of glycerin into the sulfur in the glass tube (See Fig. 1). Two heating medium were used :

(1) glycerin, for temperatures below 160°C, and (2) a salt mixture consisting of 7 percent sodium nitrate, 53 percent potassium nitrate, and 40 percent sodium nitrate, for temperatures above 160°C. Both coiled element and city gas were used to heat the medium, and the temperature of the bath was regulated within ±0.3°C.

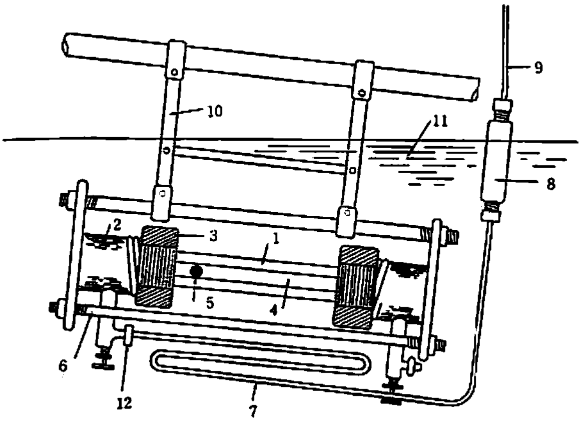

Fig. 1 Measuring apparatus of viscosity of melting sulfur by Rolling Ball Method

1 : Pyrex type glass tube
2, 3 : Nut and bolt which fasten glass tube (inner packing is Teflon)
4 : Melting sulfur
5 : A ball consisting gold and platinum
6 : Stainless steel frame
7 : Stainless steel pipe containing melting sulfur
8 : Stainless steel cylinder containing a small Teflon plug as a value
9 : Stainless steel pipe containing glycerin for pumping
10 : Stainless steel frame for supporting apparatus
11 : Heating medium
12 : A joint for the stainless steel pipe

Sample Preparation

The sulfur employed was a chemically pure grade manufactured by Kanto Kagaku Corporation. This sulfur was purified by the procedure developed by R. F. Bacon and F. Fanelli[1]. The high purity of this sample was confirmed by measurements of viscosity by the Rolling Ball Viscometer at the atmospheric pressure. The equation[8] published by this author was used for the calculation of the viscosity by the Rolling Ball Viscometer. As a precaution the absolute value of viscosity by the Rolling Ball Viscometer was checked by the viscosity standard sample JS-2000 (18.77 poises, 0.9023 g/cm^3 at 20°C) kindly supplied by Dr. Kawada, Keiryo Kenkyujo. The result obtained was very satisfactory. The viscosity of purified sulfur for the temperature range 160 to 230°C agreed with that of R. F. Bacon and F. Fanelli. The viscosity of purified sulfur for the temperature range below 160°C by an Ostwald Viscometer also agreed with R. F. Bacon and F. Fanelli's observations.

Measurements

The apparatus was evacuated through the joint which was disconnected from the stainless steel pipe (See No. 12, Fig. 1). After pre-heating to approximately 150°C, the apparatus was filled with the melting sulfur. It was found that the viscosity of sulfur in the apparatus decreases gradually according to heating for a long time (See Fig. 2). This is probably due to the glycerin. Therefore, the measuring time was restricted to be within 10 hours for low temperatures and 3 to 5 hours for high temperatures. After the heating medium reached a definite temperature, a sample of sulfur was kept at this temperature for thirty minutes. The measurement was subsequently carried out. The viscosities were calcula-

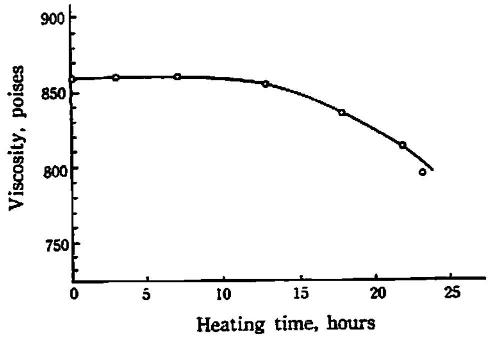

Fig. 2 The viscosity changes of sulfur in the apparatus during heating (at 180°C)

ted by the following equation[8].

$$\eta=\frac{2}{21\pi}\cdot g\cdot\sin\theta\cdot\frac{(\sigma_s-\sigma)t}{l}\cdot\frac{\alpha(\alpha^2D-d)^2}{D+d} \tag{17}$$

where,

η: viscosity of fluid (poise)
g: acceleration of gravity (980 cm/sec^2)
θ: angle of inclination of tube to the horizontal
σ: density of fluid (g/cm^3)
σ_s: density of ball (g/cm^3)
t: rolling time of ball (sec)
l: rolling distance of ball (cm)
d: diameter of ball (cm)
D: diameter of tube (cm)
α: correction factor (0.999)

As the viscosities of sulfur are remarkably different both above 160°C and below 160°C, the conditions of the measurements were separated in the two ranges.

Above 160°C

$D=1.006$ cm, $d=0.8202$ cm, $\sigma_s=20.166$
$l=5.60$ cm, $\theta=26°40'$, $\sigma=1.760$

Below 160°C

$D=1.006$ cm, $d=0.9288$ cm, $\sigma_s=20.166$
$t=15.09$ cm, $\theta=11°00'$, $\sigma=1.784$

Two definite values for the density of sulfur were taken, one above 160°C, and the other below 160°C, because the changes of the density of sulfur due to temperature is small. The inclination of the tube was adjusted by fixing the height and base of a triangle whose hypotenuse is the tube.

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[8] T. Doi, *This Journal* 32, 7 (1962)

Table 4 The viscosities of melting sulfur under pressure in the temperature range below 160°C

Temperature (°C)	Pressure (atm.)	Rolling time of a ball (sec.)	Viscosity (poise)
130	1	8.8	0.092
	50	8.8	0.092
	100	8.8	0.092
150	1 *a*	6.52	0.068
	1 *b*	6.78	0.071
	50	6.78	0.071
	100	7.03	0.074
155	1	6.39	0.067
	50	6.47	0.068
160	1	8.00	0.084
	50	9.04	0.095
	100	11.66	0.122

Note : Each value in the table is the average of 3 or 4 trials. The values indicated by *a* and *b* were recorded on different days.

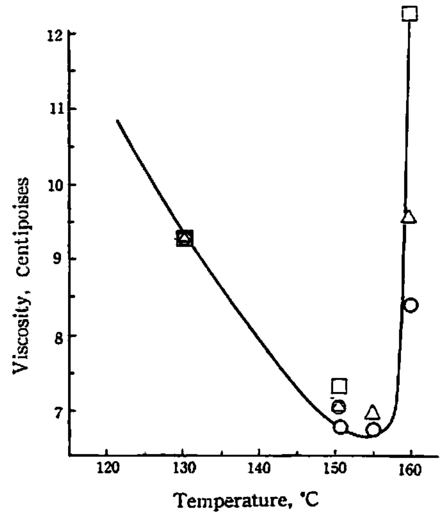

Fig. 3 A graph of the values of the viscosity of sulfur found in Table 4

○ 1 atm.
△ 50 atm. } Observed values
□ 100 atm.

—— Solid line indicates the values of the viscosity by using Ostwald Viscometer and this graph coincides with the values of R. F. Bacon and F. Fanelli

Results

The viscosity values are given in Tables 4 and 5 for pure sulfur in the temperature range 130–230°C for pressures of 1, 50 and 100 atmosphere, and are plotted in Figs. 3 and 4. The solid line of Figs. 3 and 4 were observed by R. F. Bacon and F. Fanelli. The solid line of Fig. 3 was also observed by this author using the Ostwald Viscometer. The symbols (○) of Figs. 3 and 4 were observed by this author using the Rolling Ball Viscometer at atmospheric pressure and coincided with the solid line. The theoretically predicted lines at 50 and 100 atmosphere of pressure are shown in Fig. 5 as symbols

Table 5 The viscosities of melting sulfur under pressure in the temperature range above 160°

Temperature (°C)	Pressure (atm.)	Rolling time of a ball (sec.)	Viscosity (poise)	Viscosity ratio η'/η
170	1	673	447	1,000
	50	724	482	1,075
	100	865	576	1,285
180	1	1,279	851	1,000
	50	1,375	915	1,073
	100	1,488	990	1,164
180.5	1	1,290	859	1,000
	50	1,426	950	1,105
	100	1,511	1,006	1,171
190	1	1,409	937	1,000
	50	1,443	960	1,025
	100	1,531	1.019	1,087
200	1	1,219	815	1,000
	50	1,263	840	1,036
	100	1,338	890	1,100
200	1	1,201	800	1,000
	50	1,234	822	1,027
	100	1,321	880	1,100
215	1	832	554	1,000
	50	838	558	1,008
	100	890	592	1,071
230	1	526	350	1,000
	50	528	351	1,004
	100	548	369	1,041

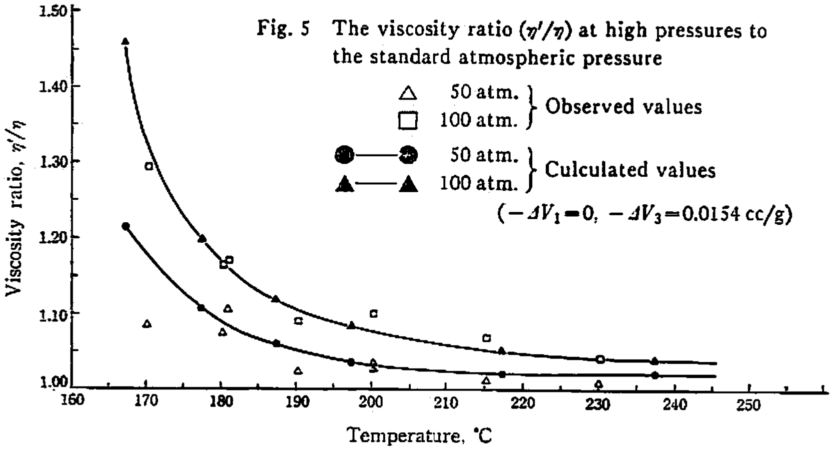

Fig. 5 The viscosity ratio (η'/η) at high pressures to the standard atmospheric pressure

(△) and (□) respectively. The viscosity ratios at 50 and 100 atmosphere to 1 atm are shown in relation to the theoretically predicted values indicated by the solid line curves in Fig. 5.

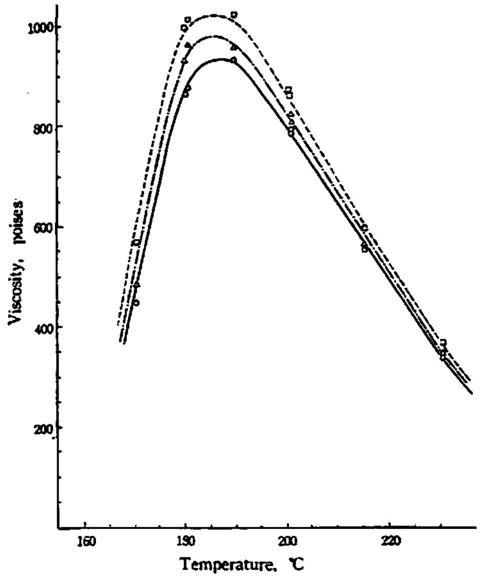

Fig. 4 A graph of the values of the viscosity of sulfur found in Table 5

○ 1 atm. ⎫
△ 50 atm. ⎬ Observed values
□ 100 atm. ⎭
—— 1 atm. Published values (R. F. Bacon aud F. Fanelli)
- - - 50 atm. ⎫ Calculated values
- - - - 100 atm. ⎭

Considerations

It was found (1) that the greater the increase in pressure, the higher the viscosities of melting sulfur in the temperature range above 160°C, in which an assumption $P \fallingdotseq P-1$ is applied to derive eqs. (10) and (11); and (2) that the viscosity ratio (η'/η) at high pressure to the standard atmospheric pressure becomes greater with decreasing temperature. The results obtained, however, are not in quantitative agreement with the predictions of E. Powell and H. Eyring2). The author's results are well interpreted in terms of the quantitative thermodynamic theory and an equilibrium polymerization theory which was published by G. Gee and his coworker and A. V. Tobolsky and his coworker. As for the values of $-\Delta V$ which is the source of the pressure effects, the value of $-\Delta V_3$ corresponding K_3 was obtained by the published data, but there was no published data about the value of $-\Delta V_1$ corresponding K_1. The lack of the value of $-\Delta V_1$, however, was not an obstacle to quantitative calculation because the value of $-\Delta V_3$ is the most important. This is recognized by the evidence that the values of the viscosity ratio in Fig. 2, calculated when zero is used for $-\Delta V_1$, are almost the same as those of the viscosity ratio in Fig. 3, calculated when 0.0154 cc/g is used for $-\Delta V_1$.

It is also found that there are almost no pressure effects in the temperature range below 160°C, in which it is difficult to recognize linear chain polymers, and therefore the assumption $P \fallingdotseq P-1$ cannot be applied. This is due to K_3 which is close to zero. Concerning the value of K_3, this author is of the opinion that the published values of A. V. Tobolsky and A. Eisenberg4) are too large in this range, and that the corresponding degrees of polymerization are too large. It is found, however, even in this range that the pressure effects become barely recognizable with rising temperature in spite of the absence of pressure effect in the lower temperature range.

In this work the Rolling Ball Method was adopted for the measurements of viscosity, and the viscosities were calculated by the equation5) published by this author. This equation agrees with experimental results in the wide range of centipoise to hundreds poise.

Acknowledgment

The author would like to thank Professor Dr. J. Osugi for his guidance and Dr. H. Teranishi, Dr. T. Makita, Dr. K. Inoue and Dr. K. Shimizu for their valuable discussions throughout this work. The author expresses his thanks also to Mr. K. Tamura, the General Manager of Rayon Plant of Asahi Chemical Industry Ltd., and Mr. K. Kubota for their aid to this research. The author is also indebted to Dr. H. Kawata of the Keiryo Kenkyujo for his generous gift of the viscosity standard sample.

Resident Representative (Europe)
Asahi Chemical Industry Ltd.