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PHYSICO-CHEMICAL PROPERTIES OF SULFUR

II Effects of Different Types of Reagent on Viscosities of Liquid Sulfur

BY TSUNESUKE DOI

The changes of the viscosity of liquid sulfur were measured, in the temperature range 120 to 210°C, by adding to sulfur different types of reagents, which react with sulfur in different degrees. From the results of measurements the reagents could be classified into three groups according to different viscosities of sulfur.

The viscosities of liquid sulfur resulting from adding any reagent of the first group were stable against heat. At first, up to a certain point, the temperature of liquid sulfur of the lowest viscosity decreases as the quantity of added reagent increases, but then it increases with further addition of the reagent.

The viscosities of liguid sulfur resulting from adding any reagent of the second group were also stable against heat, but as the quantity of the reagent increased the temperature of liquid sulfur of the lowest viscosity rose steadily.

The viscosities of liquid sulfur resulting from adding any of the third group reagent were unstable against heat and changed considerably with time. The author will gives an inclusive interpretation of these phenomena.

Introduction

It is known that the temperature of liquid sulfur of the lowest viscosity changes by adding to sulfur different types of reagents, which react with sulfur in different degrees, and that the viscosities of sulfur have been discussed in the preceding works[1][2][3]. But there are no known data to interprete these results systematically.

The author measured, in the temperature range 120 to 200°C, the changes of the viscosity of liquid sulfur at the lowest viscosity area by adding to sulfur different types of reagents, which resulted in different reactions with sulfur, and classified these reagents into three groups and put a reasonable interpretation on each group.

Experiments and Results

Apparatus

The experiments were carried out in an Ostwald viscometer which was dipped in a glycerin bath. The temperature of the bath was regulated within ±0.1°C. The range of water refflux time of the Ost-

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1) R. F. Bacon and F. Fanelli, *J. Am. Chem. Soc.*, **65**, 639 (1943)

2) J. Furukawa and S. Nishida, *J. Rubber Soc. Japan*, **29**, 384 (1956)

3) F. Fairbrother, G. Gee and G. T. Merall, *J. Poly. Sci.*, **16**, 466 (1955)

wald viscometers used in this experiment, was 70 to 110 sec. The tops of each viscometer were connected by a joint pipe in order to keep the sulfur and reagent from evaporation (see Fig. 1).

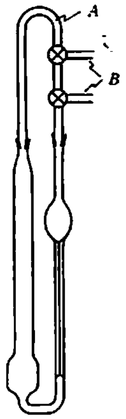

Fig 1 Ostwald viscometer

A : joint pipe
B : suction pipe

Materials

The sulfur which was used in this experiment was purified by the same method as in the previous paper[4], and the reagents were of a chemically pure grade.

Methods

After the heating medium, starting from the high temperature side, reached a certain temperature, the sample was kept at this temperature for twenty minutes. The measurements were carried out subsequently. It had been confirmed by the pre-experiments that twenty minutes were sufficient to reach thermal equilibrium. The viscosities were measured in the temperature range 120 to 210°C. Each sample was a mixture of about 18 g of sulfur and a certain amount of a reagent. Furthermore, the measurements

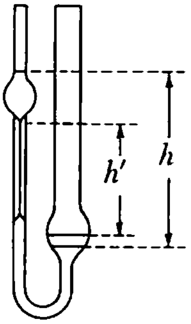

Fig. 2 Mean difference of liquid surfaces ; $1/2(h+h')$

h : difference of the liquid surfaces when the upper liquid surface just falls through the upper etched line.
h' : difference of the liquid surfaces when the upper liquid surface just falls through the lower etched line.

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[4] F. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942)

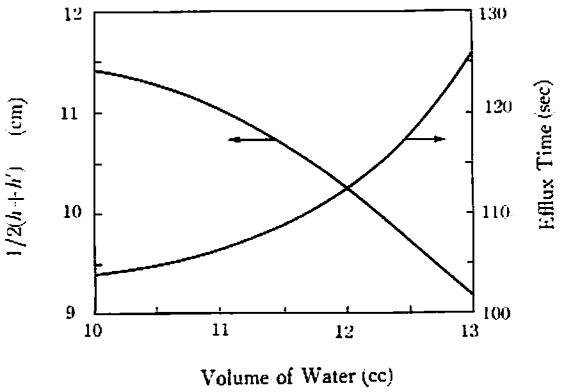

Fig. 3 Effect of volumes of water to the mean differences of liquid surfaces and the efflux time

of the viscosity of each mixture were repeated after several hours and also on the following day in order to confirm whether the viscosities of the sample had not changed. The specific gravity of a sample changes when a reagent is added to sulfur. And it decreases as the amount of the reagent is increased. Therefore, it was convenient to make a diagram of the relation between the volume and the mean height surface level of liquid $\left(\frac{h'+h}{2}\right)$ measured by water at 20°C to find out the volume of a sample (see Figs. 2 and 3). The specific gravities are calculated from these volumes and the weights of the samples. The specific gravities of naphthalene, diphenyl and *p*-dichlorobenzene at 120°C were measured as 0.9502, 0.9545 and 1.175, respectively.

The equation[5] of the specific gravity of naphthalene is known as follows:

$$\rho=0.9779-0.767\times10^{-3}(t-80)-0.755\times10^{-6}(t-80)^2 \qquad (1)$$

The specific gravity at 120°C which was calculated by eq. (1) was 0.9468. It was almost the same as the measured one. Therefore, the specific gravities of naphthalene above 120°C were calculated by eq. (1). On the other hand, the specific gravities of diphenyl and *p*-dichlorobenzene above 120°C were calculated respectively by each of the corrected equations derived by changing the constant of eq. (1), so that each of the specific gravities calculated by eq. (1) at 120°C should be the same as the observed one.

Furthermore, the observed specific gravities of the liquid sulfur to which approximately 10 weight % of naphthalene, *p*-dichlorobenzene or diphenyl was added, coincided respectively with the values calculated by using both eq. (1) and the specific gravities of pure sulfur assuming the additivity of the volume between sulfur and the reagent. Therefore, the specific gravities of each sample at any temperature were obtained by the calculations mentioned above. The specific gravities of sulfur were derived from the data relating to the specific volumes of sulfur obtained by Shirai[6]. There was an apprehension that the added reagent would evaporate into the space of the viscometer though both tops of each viscometer were connected by a joint pipe. But it was confirmed that the analytical results of bromine and iodine changed neither before nor after the measurement of viscosities when they were added approximately 5 weight % to sulfur, respectively.

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[5] D. I. Zhuravlev, *J. Phys. Chem.* (U. S. S. R.), **9**, 375 (1937)

[6] T. Shirai, *J. Chem. Soc. Japan* (*pure chemistry section*), **72**, 698 (1951)

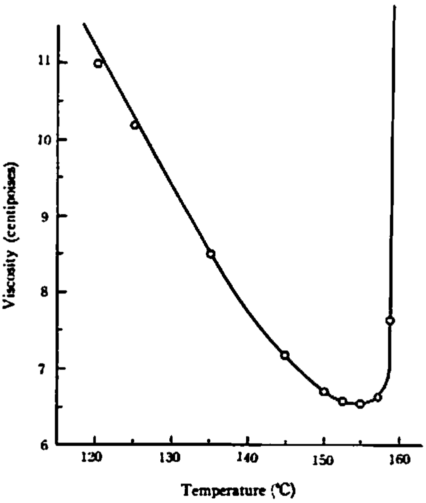
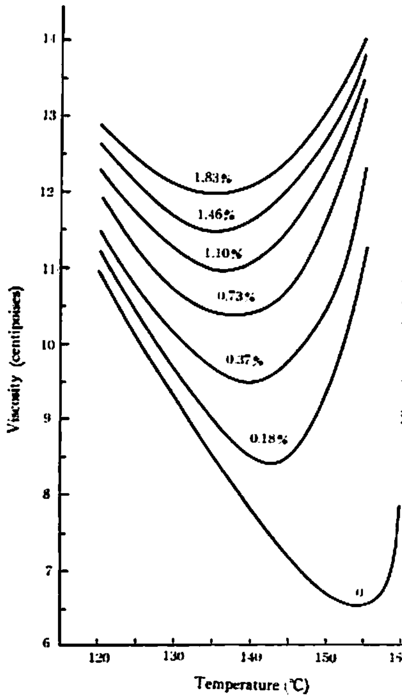


Fig. 4 Viscosities of pure sulfur

—— : Fanelli's data
○ : Author's data



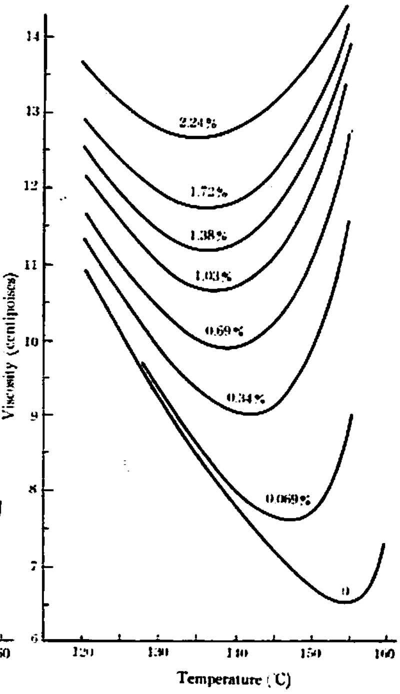


Fig. 5 Effect of S_2Cl_2 on the viscosities of sulfur

Fig. 6 Effect of Br_2 on the viscosities of sulfur

The calculations of viscosities were carried out by using the well known formula⁷⁾ with a velocity correction term for the Ostwald viscometer.

Results

The viscosities of pure sulfur, in the temperature range 120°C to 160°C, observed by the author almost coincided with the values observed by Bacon and Fanelli¹⁾ (see Fig. 4). The changes of the viscosities of liquid sulfur were measured in the temperature range 120 to 210°C by adding to sulfur different types of reagents, which react in different degrees with sulfur; some of them are shown in Figs. 5, 6, 7, 8, 9, 10, 11 and 12. From the results of measurements the reagents were classified into three

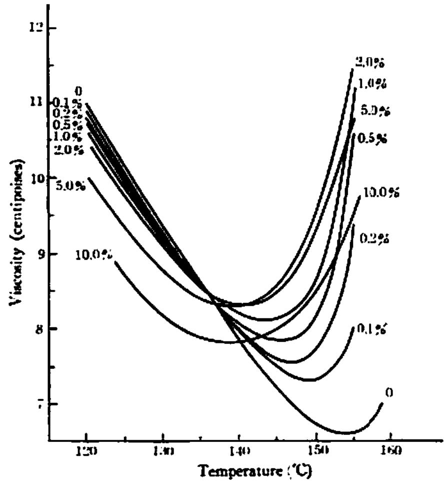


Fig. 7 Effect of I_2 on the viscosities of sulfur

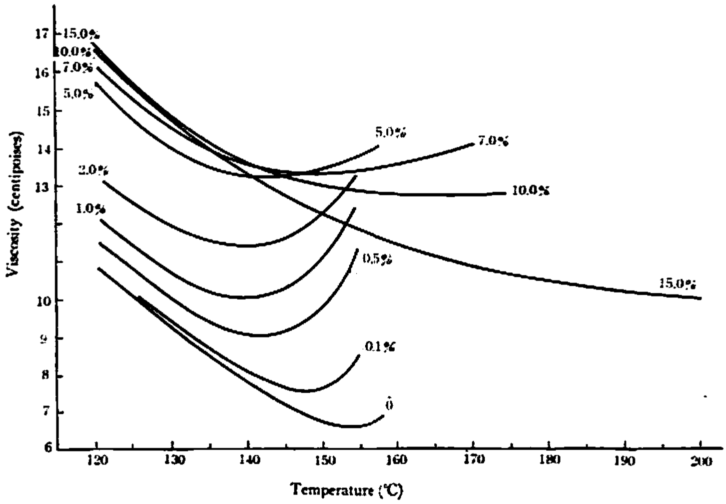


Fig. 8 Effect of dibenzothiazyl disulfide on the viscosties of sulfur

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7) H. Mizutani, "Kobunshi no Jugodosokutei" 39, Kyoritsu Shuppan

groups according to the different viscosities of sulfur.

Group 1 : The viscosities of liquid sulfur resulting from adding any of the reagents of this group were stable against heat. At first, up to a certain point, the temperature in the case of the lowest viscosity decreases as the quantity of the reagent added increases, but then it increases with further addition of the reagent. "Being stable against heat" means that the viscosities of liquid sulfur at any temperature added with each reagent of this group are unchangeable by the heating for several hours in the temperature range 120 to 200°C, and the viscosities redetermined after cooling it to room temperature for one day were reproducible under the same conditions. Halogen and dibenzothiazyl disulfide belong to this group. The viscosity-temperature curves of liquid sulfur added with sulfur monochloride, bromine, iodine or dibenzothiazyl disulfide are shown in Figs. 5, 6, 7 and 8, respectively. The added quantities of reagents

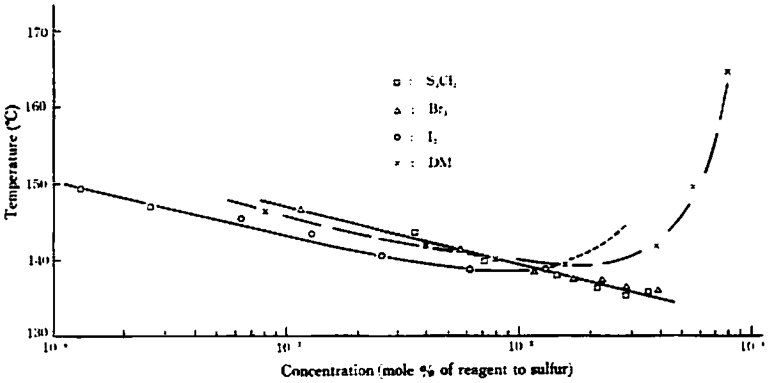

Fig. 9 Relation between concentrations of reagents in sulfur and temperaturs at lowest viscosity.

Table 1 Temperatures at lowest viscosities of sulfur added with reagents

Quantity added of S_2Cl_2	Weight % to sulfur	0	0.18	0.37	0.73	1.10	1.46	1.83	—	—
	Mole % to sulfur × 10^3	0	3.71	7.02	14.04	21.05	28.03	35.02	—	—
Temperature at lowest viscosity °C		154.5	143.5	140.0	138.0	136.5	135.5	136.0	—	—
Quantity added of Br_2	Weight % to sulfur	0	0.069	0.344	0.688	1.032	1.376	1.270	2.408	—
	Mole % to sulfur × 10^3	0	1.104	5.52	11.04	16.64	22.09	27.60	38.64	—
Temperature at lowest viscosity °C		154.5	146.5	141.5	138.5	137.5	137.5	136.5	136.0	—
Quantity added of I_2	Weight % to sulfur	0	0.1	0.2	0.5	1.0	2.0	5.0	10.0	—
	Mole % to sulfur × 10^4	0	1.261	2.522	6.305	12.61	25.11	63.05	126.1	—
Temperature at lowest viscosity °C		154.5	149.5	147.0	145.5	143.5	140.5	139.0	139.0	—
Quantity added of DM	Weight % to sulfur	0	0.1	0.5	1.0	2.0	5.0	7.0	10.0	15.0
	Mole % to sulfur × 10^4	0	7.69	38.45	76.90	152.6	184.5	538.3	768.3	1155.0
Temperature at lowest viscosity °C		154.5	147.0	142.0	140.0	139.5	142.0	150.0	165.0	230?

Table 2 Temperatures at lowest viscosities of sulfur added with reagents

Quantity added (% to sulfur)		0	0.5	1.0	2.0	5.0	7.0	10.0	15.0
Sulfur in naphthalene	mole/kg	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
	mole/*l*	6.95	6.88	6.81	6.67	6.28	6.06	5.73	5.26
Temperature at lowest viscosity(°K)		431.5	432.5	434.0	436.5	445.5	451.0	459.5	472.0
Sulfur in *p*-dichlorobenzene	mole/kg	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
	mole/*l*	6.95	6.89	6.84	6.72	6.42	6.22	5.94	5.54
Temperature at lowest viscosity(°K)		431.5	431.5	433.5	435.0	441.5	446.5	453.5	462.0
Sulfur in diphenyl	mole/kg	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
	mole/*l*	6.95	6.88	6.81	6.67	6.28	6.06	5.74	5.28
Temperature at lowest viscosity(°K)		431.5	432.5	434.0	438.0	445.0	452.0	460.0	472.5

and their corresponding temperature in the case of the lowest viscosity in these figures are assembled in Table 1 and are shown in Fig. 9. The added quantities of each reagent are shown in the weight percentage to sulfur.

Group 2: The viscosities of liquid sulfur resulting from adding any of the reagents of this group were also stable against heat, but as the quantity of the reagent increased the temperature in the case of the lowest viscosity increased steadily. Naphthalene, *p*-dichlorobenzene, diphenyl and *m*-cresol belong to this group. The viscosity-temperature curves of liquid sulfur mixed with naphthalene, *p*-dichlorobenzene or diphenyl are shown in Figs. 10, 11 and 12, respectively. Table 2 shows the temperatures in the case of the lowest viscosity obtained from Figs. 10, 11 and 12. The concentrations in these figures, instead of the added quantities of the reagents, are expressed by the concentrations of the sulfur contents which are shown in both mole kg^{-1} and mole l^{-1}. Figs. 13 and 14 are shown in mole kg^{-1} and mole l^{-1}

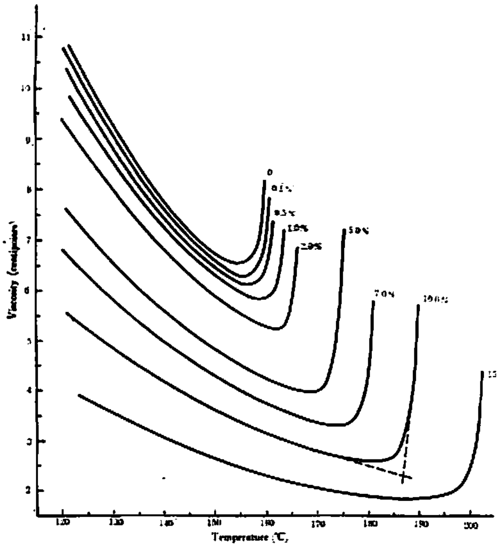

Fig. 10 Effect of naphthalene on the viscosities of sulfur

as the abscissa, respectively. The numerical values of specific viscosity which are necessary for trans-calculation from mole kg^{-1} to mole l^{-1} were selected at 157°C for convenience. The author regarded the intersecting point of the tangent of both sides of the sharp curvature of each viscosity-temperature curve as the temperature at which the viscosities reached the lowest point. This temperature in the case of the lowest viscosity would be considered as the critical transition temperature of the polymerization of sulfur. Phenol and *m*-cresol could not be measured satisfactorily, because they could not be easily dissolved by sulfur.

Group 3: The viscosities of liquid sulfur resulting from adding any of the reagents of this group were unstable against heat and changed considerably with time. Pyrogallol, *p*-benzoquinone, *α*-naphthol, tetramethyl thiuram disulfide, 2-mercaptbenzothiazole and diphenylguanidine belong to this group. The

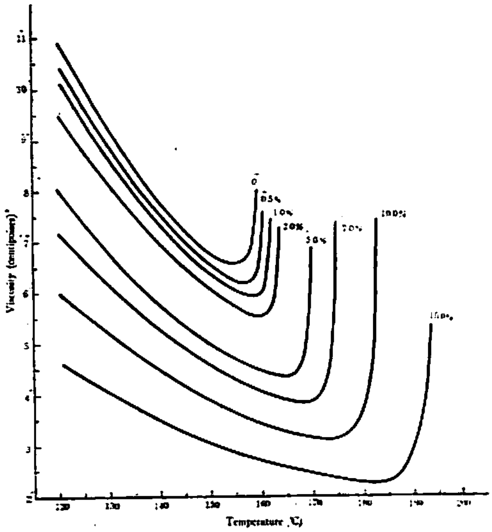

Fig. 11 Effect of *p*-dichlorobenzene on the viscosities of sulfur

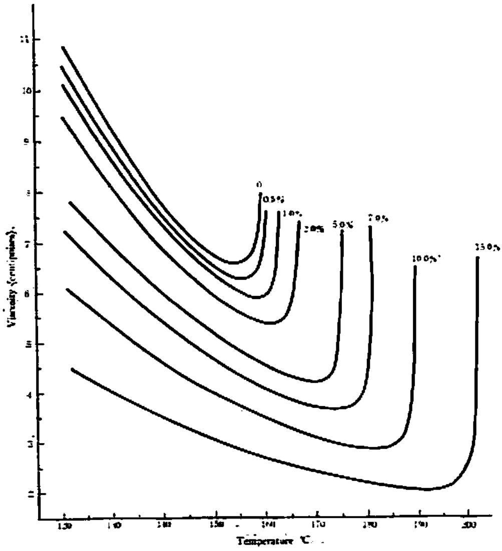

Fig. 12 Effect of diphenyl on the viscosities of sulfur

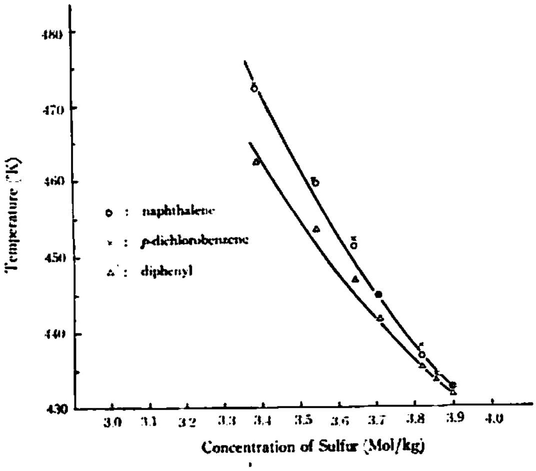

Fig. 13 Relation between sulfur concentrations which is shown in mole/kg and temperatures at lowest viscosity

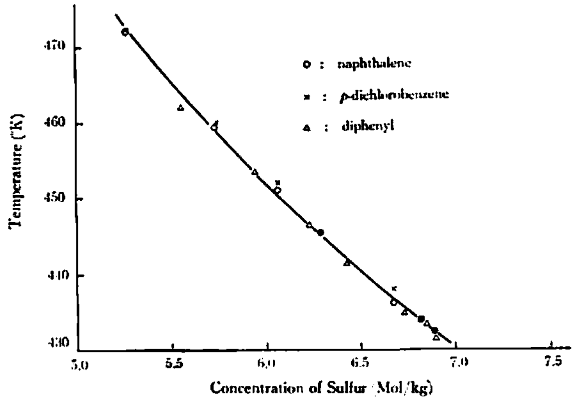

Fig. 14 Relation between sulfur concentrations which is shown in mole/kg and temperatures at lowest viscosity

viscosities of liquid sulfur just after addition of tetramethyl thiuram disulfide were greater than that of pure liquid sulfur but they decreased with time. In the case of the other reagents, the viscosities of liquid sulfur increased steadily with time.

Considerations

It is believed that halogen and dibenzothiazyl disulfide which belong to group 1 react with sulfur quickly and reach equilibria. The structure of S_2Cl_2 was determined as Cl–S–S–Cl by using the electron diffraction method by Guthrie[8].

This molecule, Cl–S–S–Cl, would produce Cl–S· radicals by the thermal cleavage of the S–S bond. The molecules of bromine and iodine would also produce Br–S· and I–S· radicals after their addition to liquid sulfur. Though $X\text{–}S_n\cdot$ (X; Cl, Br or I, $n=2$, 3, 4……8) radicals would also be produced, X–S· would be justifiable on behalf of the whole radicals which were produced initially. It would be necessary to identify these radicals by the electron spin resonance method in order to justify this assumption.

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8) G. B. Guthrie, *Acta Cryst.*, 3, 16 (1950)

The radicals produced by the thermal cleavage would react with ring sulfur and thus promote the sulfur polymerization. The viscosities of liquid sulfur increase because of the polymerized sulfur. In the case of dibenzothiazyl disulfide, the thiyl radicals produced by the thermal cleavage would promote the sulfur polymerization. Among these polymers there would be some polymers both ends of which are blocked by some of the above mentioned radicals. The different effects to the viscosities of liquid sulfur among different reagents are due to their different reactivities to sulfur. According to Fig. 9, the order of reactivities would become as follows:

$$\mathrm{Cl} \fallingdotseq \mathrm{Br} > \text{Dibenzothiazyl disulfide} > \mathrm{I}$$

It is believed that sulfur monochloride has the same effect on sulfur as chlorine. Almost all bromines, when added to liquid sulfur, would initially also produce Br–S· radicals, and then they would promote the sulfur polymerization. But dibenzothiazyl disulfide and iodine have less reactivity than both chlorine and bromine, and the more they are added, the more the diluting effects of their unreacted molecules increase. Therefore, the temperatures in the case of the lowest viscosity which have decreased initially, change to increase subsequently, when the added reagent has been added in excess of a certain quantity.

The aromatic reagents which belong to group 2 are stable in the temperature range 120 to 220°C and do not react with sulfur. The liquid sulfur is diluted by addition of these types of the reagents and its viscosities decrease. Therefore, the temperature in the case of the lowest viscosity increases by the retardation of polymerization due to dilution. In this case, it would be thought that the effect of the retardation of polymerization is independent of any type of the reagents. As a matter of fact, Fig. 14 shows that naphthalene, *p*-dichlorobenzene and diphenyl are plotted on the same line, if mole/l is taken instead of mole/kg as the unit of concentration.

The reagents which belong to group 3 would be gradually decomposed to radicals, or the produced radicals gradually would react with sulfur. If the reagents react with sulfur faster after the rapid decomposition to radicals, the terminal radicals of the reaction products would be unstable and would gradually decompose themselves. Tetramethyl thiuram disulfide would belong to the latter and the other reagents to the former.

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