Part II

CHEMICAL ENGINEERING
INORGANIC CHEMISTRY
PHYSICAL CHEMISTRY

Effect of Hydrogen Sulfide on the Viscosity of Sulfur

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Certain chemical substances have the ability to reduce profoundly the viscosity of elemental sulfur over the temperature range in which polymerization occurs. Of these substances, hydrogen sulfide is particularly interesting because of its common occurrence in molten sulfur and because of its potential application to process systems requiring viscosity control of sulfur above 160°C. Heretofore, no reliable data have been available for quantitatively correlating the viscosity and hydrogen sulfide content of elemental sulfur. This investigation used a specially designed capillary viscometer to obtain viscosity data for molten sulfur containing various quantities of dissolved hydrogen sulfide. *Measurements were made over the range 177–288°C. and* 0.18–0.35% by weight of H_2S (H_2S saturation pressures of 1.20–4.61 atm.).

THE VISCOUS behavior of molten elemental sulfur has received considerable attention because of its somewhat anomalous temperature dependency as shown in Figure 1. Monoclinic sulfur containing only S_λ melts at 119° C., and at this temperature has a viscosity of 10–11 centipoises (*7*). Upon heating, a sudden rise in viscosity begins at 158–159° C., and a maximum value of 93,000 centipoises is reached at 188–189° C. (*1*). Heating beyond this point results in a gradual decrease in viscosity with a value of only 100 centipoises being observed at the boiling point (*1*). The accepted explanation for this behavior is that as sulfur is heated above 158° C., the eight-membered rings (S_λ) begin to rupture, and the resultant short fragments polymerized to form chains of very high molecular weight (*5*, *6*). As sulfur is heated beyond 188° C., thermal activity becomes predominant, and the mean molecular weight of the polymerized chains begins to decrease.

Many chemical substances, by interfering with the polymerization of sulfur chains, exhibit a pronounced ability to suppress viscosity at temperatures above 158° C Thus, small amounts (less than 1%) of halogens, organic sulfides, metallic sulfides, hydrogen sulfide, and other organic compounds (*2*) are able to reduce the maximum viscosity of sulfur from 93,000 centipoises to a few hundred centipoises or less. It is generally agreed that these materials are effective in reducing viscosity because they attach to the terminal positions of the chains so that polymerization cannot occur (*1*, *3*, *4*). Of all the chemical substances which are effective in controlling sulfur viscosity, hydrogen sulfide is the most important, because it is a very common impurity in nearly all Frasch sulfur, it exhibits the greatest influence for a given concentration, and it has the greatest potential as a practical means of controlling sulfur viscosity in chemical processing applications.

To date, the only extensive information available on the viscosity of the sulfur–hydrogen sulfide system has been that published by Bacon and Fanelli in 1943 (*1*), and by Fanelli in 1946 (*3*). In his studies, Fanelli measured the viscosity of pure sulfur which had been treated with a weighed quantity of hydrogen sulfide or hydrogen persulfide (*3*). Measurements were made in both open and closed systems, but in no case was the resultant hydrogen sulfide content of the sulfur sample quantitatively determined. Since a large portion of the hydrogen sulfide added to the sulfur was lost as a gas, there is no way to correlate Fanelli's viscosity data with the actual hydrogen sulfide content of the sulfur. Using Fanelli's data to predict the viscosity of a sulfur of known hydrogen

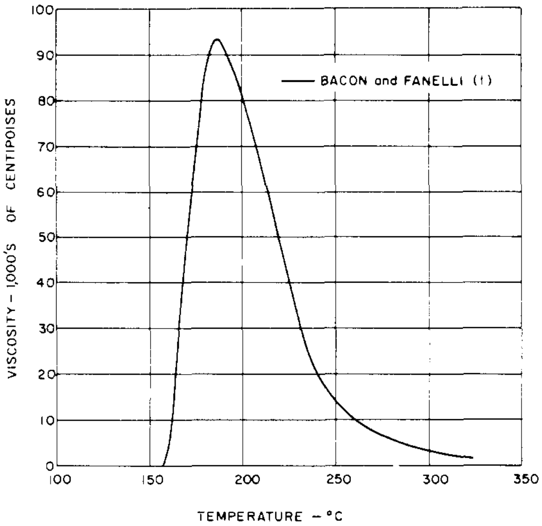

Figure 1. Viscosity-temperature diagram for elemental sulfur (*1*)

sulfide content, therefore, would give values considerably higher than the true values.

EXPERIMENTAL PROCEDURE

This present investigation was designed to yield an accurate quantitative relationship between the viscosity and hydrogen sulfide content of elemental sulfur. To do this, samples of high purity sulfur were saturated with hydrogen sulfide under various conditions of temperature and hydrogen sulfide partial pressure. When system equilibrium was attained, the viscosity and hydrogen sulfide content of the sample were measured as functions of temperature and pressure. The sulfur used in this investigation was a commercial grade of distillate sulfur analyzing 99.98% sulfur, 0.02% carbon, and no more than 30 p.p.m. of ash. No attempt was made to further purify this sulfur, since it was quite certain that the high concentrations of hydrogen sulfide used in the test work would completely obscure the viscosity modifying effects of any other impurities. The hydrogen sulfide used was a technical grade material supplied by Matheson Co. in steel cylinders. Independent chromatographic analysis showed its purity to be 99.0 ± 0.5% (by volume) with the principle impurities being carbon dioxide and nitrogen. Partial pressures of hydrogen sulfide in the test system were computed on the basis of ideal gas behavior assuming a value of 0.99 for the volume fraction.

The equipment used in this study is shown schematically in Figure 2 and consisted primarily of two stainless steel autoclaves interconnected by a precision bored metering tube and quick-opening ball valve. ASTM 316 stainless steel was used throughout, since it was known from past experience that this material would give excellent service under the anticipated test conditions. The autoclaves, tube and ball valve were immersed in an agitated oil bath used to control system temperature up to 300° C. In operation, the primary autoclave was completely filled with elemental sulfur, and then pure hydrogen sulfide was introduced as a portion of the sulfur was drained out. Temperature and hydrogen sulfide pressure were maintained at specific values, and the autoclave charge was agitated for a sufficient time to assure a condition of equilibrium. At the end of this period, the secondary autoclave was pressurized with nitrogen to some pressure slightly less than the pressure in the primary autoclave. The pressure difference between the two autoclaves was then read on a mercury manometer connected between the vapor spaces. A small amount of silicone oil in each arm of the manometer served to isolate the mercury interface and prevent reaction with the hydrogen sulfide. Once the pressure differential had been adjusted to the desired value, the agitator was stopped, and time was allowed for any dispersed gas to disengage from the autoclave charge. The ball valve was then opened, and sulfur was allowed to flow through the metering tube from the primary autoclave to the secondary autoclave, where the sample was collected in a tared container. The viscosity of the sample was calculated from Poiseuille's equation:

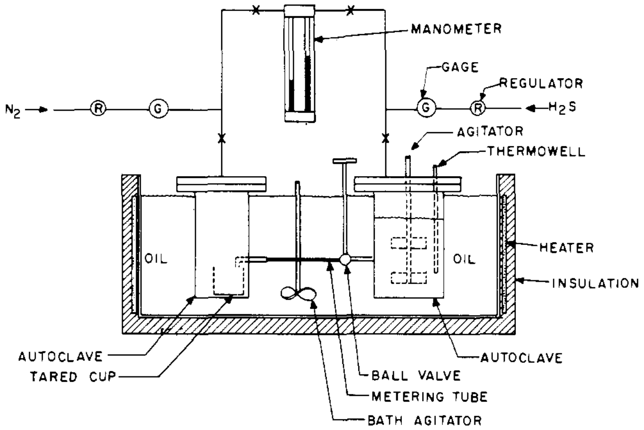

Figure 2. Schematic diagram of capillary viscometer

$$\mu = \frac{(\Delta P)\, D_T^2}{32\, L_T U_T} \tag{1}$$

where ΔP is the manometer differential plus the hydrostatic sulfur head above the tube centerline in dyne/cm.^{2} (1 mm. Hg = 1333 dyne/cm.^{2}), L_T is the viscometer tube length (30.48 cm.), and U_T is the mean velocity (cm./sec.) based on viscometer tube diameter D_T (0.3124 cm.). In Equation 1, the viscosity μ is expressed in units of dyne-sec./cm.). The system was so designed and operated that all other sources of flow resistance in the transfer line were insignificant relative to the frictional resistance of the viscometer tube itself.

Table I. Viscosity of Sulfur as a Function of Temperature and H_2S Saturation Pressure

H_2S Press., Atm.	Temp., °C.	Average Viscosity, Centipoises	Std. Dev. for Three Determinations
1.20	177	35.4	0.5
1.20	204	72.3	0.5
1.20	232	109.1	0.9
1.20	260	135.4	2.2
1.20	291	122.3	0.8
2.01	177	34.6	0.3
2.01	204	60.6	0.5
2.01	232	77.6	1.5
2.01	260	86.8	1.1
2.01	288	79.3	2.0
3.05	177	30.7	0.1
3.05	204	49.0	0.5
3.05	232	58.3	1.0
3.05	260	61.8	0.6
3.05	288	60.7	3.2
4.61	171	20.7	0.3
4.61	204	44.0	0.7
4.61	232	45.4	0.5
4.61	260	49.6	0.6
4.61	288	48.8	0.6

To be sure that Poiseuille's equation accurately described the fluid flow in the viscometer, additional runs were made with a petroleum oil whose viscosity had been determined with a Brookfield Model LVF rotational viscometer. A comparison of the two methods of measurement showed a deviation of only 2.0%, which is well within the estimated accuracy of the test data.

The experimental system incorporated two autoclaves so that the transfer pressure differential (100–130 mm. Hg) could be controlled independently of the total system pressure, and hydrogen sulfide flashing could be prevented in the viscometer tube. If the primary autoclave had been permitted to discharge directly to ambient pressure, so much hydrogen sulfide would have been released in the viscometer tube, that it would have been impossible to determine viscosity by Poiseuille's equation. The described system performed quite satisfactorily, and made it possible to control transfer pressure differentials to within ±1.25 mm. of mercury.

Hydrogen sulfide solubility measurements were made independently of any viscosity determinations, and different autoclave charges were used. Samples were flashed directly through a short small-bore tube into a tared container which had previously been purged with nitrogen. Entrance of the tube was through a gastight seal so that any gas released by depressurization of the sample was forced to flow into the tared container. At the time of sample taking, the outlet tube from the tared container was already connected to the hydrogen sulfide absorption train which consisted of two iodine filled bubbling flasks. Thus any hydrogen sulfide released from the sample could leave the system only through the absorption flasks. To quantitatively recover the hydrogen sulfide, 1% refined lead sulfide catalyst was added to the sample, and the sample was purged with nitrogen for two hours at 130° C. Excess iodine in the absorption flasks was finally determined by titration with thiosulfate, and the weight of sample was determined by reweighing the tared container at the end of the analysis. This procedure for determining hydrogen sulfide in molten sulfur resulted from a research study conducted by Freeport Sulphur Co. and has heretofore not been published. Although the procedure has not been verified by independent investigators, it has been exhaustively tested by members of the Freeport Sulphur Co. organization and is presently employed as a routine analytical procedure in Freeport's operations.

DATA AND DISCUSSION

Viscosity measurements were made over the range from 177° to 288° C. and at hydrogen sulfide partial pressures of 1.20 to 4.61 atm. At each condition of temperature and pressure, determinations were made in triplicate, and the values were averaged. Standard deviation was computed for each set of three determinations, and these standard deviations are presented in Table I along with the averaged viscosity values. In addition to computing the standard deviation for each set of determinations, the data as a whole were examined to determine if they could be grouped into one statistical population. Analysis revealed that the data do belong to a single log-normal population with a mean standard deviation of 1.55% of the viscosity value.

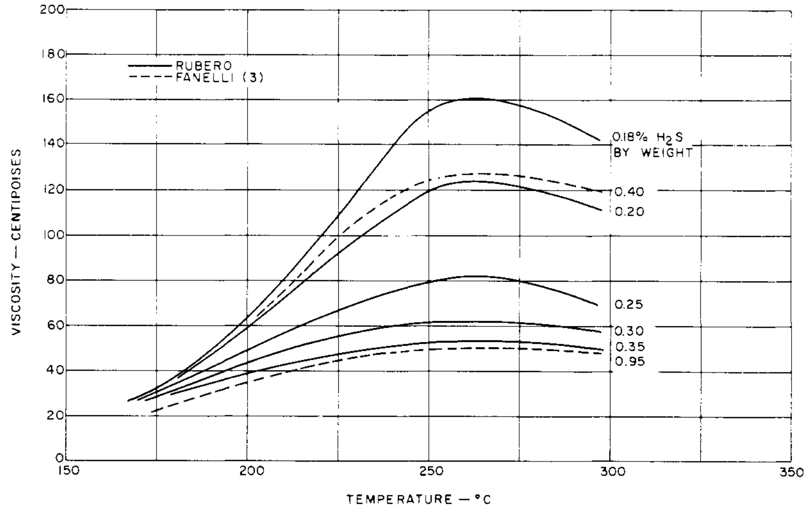

Figure 3. The effect of H_2S on the viscosity of sulfur. Comparison with Fanelli's data

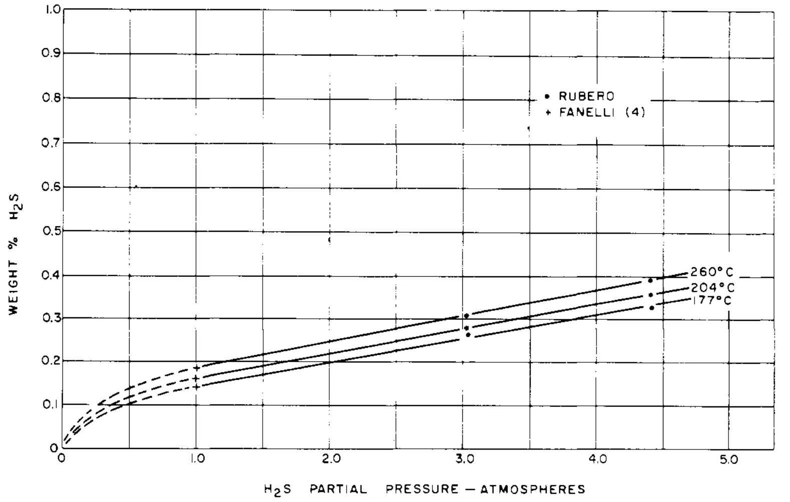

Figure 4. Solubility isotherms for the H_2S–sulfur system

The absolute accuracy of the experimental data is estimated to be approximately ±5% with the major sources of error being the fluctuations in transfer differentials and variations in tube bore measurements.

By combining the data in Table I with the data on hydrogen sulfide solubility, it is possible to plot viscosity *vs.* temperature with hydrogen sulfide content as the parameter as shown in Figure 3. This is the method of presentation originally used by Fanelli (*3*), and some of Fanelli's data are included in Figure 3 for purposes of comparison. Figure 4 shows the solubility of hydrogen sulfide in sulfur as a function of temperature and pressure. The values for solubility at one atmosphere are those reported by Fanelli in 1949 (*4*).

An inspection of Figure 3 immediately reveals that dissolved hydrogen sulfide strongly suppresses the viscosity of elemental sulfur above 158° C., and also progressively shifts the region of maximum viscosity from 188° C. to higher temperatures (a characteristic of virtually all viscosity suppressants for sulfur). It is obvious that the viscosity values predicted from Fanelli's data of 1946 are significantly higher than those obtained in this study. As has been explained, this discrepancy is due to the fact that the nominal concentrations reported by Fanelli only represent the total amount of hydrogen sulfide added to the system and not the actual amount dissolved in the sulfur.

It is believed that the viscosity data obtained in this study are considerably more accurate and reliable than those that have been available in the past. The new data may be applied with confidence to the design of engineering systems in which hydrogen sulfide is used to control the viscosity of molten elemental sulfur at temperatures in the viscous range.

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Viscosity of Methane–*n*-Butane Mixtures

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Data are presented for methane–*n*-butane mixtures containing nominally 25, 50, 70, and 90 mole per cent methane. Each mixture is shown to have a viscosity field similar to that of a pure component and the data for each can be correlated by use of a residual plot. Use of molar densities in the residual plot is shown to simplify the presentation of the composition dependence of viscosity.

PREVIOUSLY REPORTED investigations have defined the viscosity behavior of ethane (*11*), propane (*18*), and *n*-butane (*7*) for significant ranges of pressure and temperature. Detailed studies of the viscosity behavior in the critical region for ethane, propane, and *n*-butane have been reported (*17*).

In this investigation, the objective was to obtain sufficient data on the viscosity of mixtures of methane and *n*-butane to permit study of the effects of composition on viscosity behavior. These data have been used in a definitive test of the applicability of the residual viscosity concept in correlating mixture viscosity data. The residual concept was used also to extrapolate the data on individual mixtures.

A search of the literature revealed only one previous investigation of the viscosity of a binary hydrocarbon system for an extensive pressure-temperature field. Bicher and Katz (*2*) presented values of viscosity for the pure components and mixtures in the system methane-propane. Pressures were between atmospheric and 5000 p.s.i.a. Temperatures ranged from 77° F. to 437° F. The accuracy claimed was ±3%, average. These data were used in preliminary trials of several concepts and for comparison of behavior trends. No data were found on methane–*n*-butane mixtures.

APPARATUS AND MATERIALS

The viscometer employed in this investigation operated on the same principle as the instrument imployed previously in pure component investigations (*9*, *18*). As a normal operating procedure, check runs on nitrogen at several conditions were carried out before and after each experimental measurement of hydrocarbon systems to insure that the instrument behaved properly.

Auxiliary vessels and manifolding have been added to permit preparation and mixing of samples of specified composition. The sampling system has been modified to permit obtaining representative samples for analysis. The result of this change in installation is to completely isolate the test sample within the thermostat, thus eliminating the possibility of condensation or diffusion due to temperature gradients.

A schematic diagram of the complete system is shown in Figure 1. Samples were prepared by displacing a certain volume of each component from vessel *B* to vessel *C* at constant pressure and temperature. The volume of each component determines the mass and thus the composition of the sample. To mix the sample, the system exterior to vessel *C* is evacuated. The sample confined in vessel *C* is then flashed to fill the viscometer and vessel *B*. Mixing of

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