the desylamine, namely, α-phenyl-α-(p-ethylanilino)ace-tophenone, $C_2H_5C_6H_4NHCHPh\cdot CO\cdot Ph$, rather than the reported hydroxy imine, $C_2H_5C_6H_4N = CPh\cdot CHOH\cdot Ph$.

EXPERIMENTAL

Mixtures of 8.5 grams (0.04M) of benzoin with 5.5 grams (0.04M) of each of the three aminobenzoic acids were heated without solvent in an oil bath to 180°. All three mixtures lost water at as low a temperature as 130°, rapidly at 160–170°. The crude o- and p-(desylamino)benzoic acids solidified in the bath, the meta isomer on cooling. After two crystallizations from glacial acetic acid the o-, m- and p-(desylamino)benzoic acids were obtained in yields of 5.9, 5.6, and 5.9 grams, respectively (48, 46, 48%). For analysis, the para compound was recrystallized once more from acetic acid, the ortho compound from methanol, and the meta compound from a mixture of benzene and methanol. p-(Desylamino)phenylacetic acid, m.p. 189°, was obtained in a similar reaction. Our m.p. and analyses agreed with the melting point reported (1) and with the theoretical composition.

Small samples of the three (desylamino)benzoic acids and of p-(desylamino)phenylacetic acid were heated with an excess of phenylhydrazine in acetic acid. On cooling, all of the solutions gave abundant precipitates of yellow, crystalline benzoin phenylosazone, m.p. 229–230°. Mixed melting points with pure, authentic benzoic phenylosazone were not depressed.

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Viscosity of Sulfur Dioxide at 200°C. for Pressures Up to 3500 P.S.I.

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Experimental viscosities for sulfur dioxide have been determined at 200°C. and pressures ranging from 250 to 3500 p.s.i.g. using a transpiration type viscometer. The temperature of 200°C. was arbitrarily selected since it is somewhat above the critical temperature of sulfur dioxide (T_c = 430.7°K.). The pressure was varied beyond the critical pressure of the substance, P_c = 1143 p.s.i.a., so that the viscosity behavior of sulfur dioxide in the critical region would be well defined.

INCREASING interest in the area of transport properties makes it necessary that viscosities, thermal conductivities, and self-diffusivities be established both at normal pressures and at the high pressures required to define the dense phase region. Investigations of this type have been conducted by Lohrenz (8), who measured viscosities of light hydrocarbons in their liquid state with a falling cylinder viscometer, and by Comings, Mayland, and Egly (4), who determined viscosity values for a number of gases at elevated pressures by the use of a transpiration-type viscometer.

Individual viscosity correlations have been presented in the literature for several pure substances at high pressures in the dense gaseous and liquid phases (2, 11). This information is largely restricted to substances of a nonpolar nature. Theiss (13) has developed a reduced state viscosity correlation for water in the gaseous and liquid states from the experimental data available in the literature for this substance. Shimotake (10) used a transpiration-type viscometer to establish the viscosity of ammonia for temperatures of 100°, 150°, and 200°C. and pressures up to 5000

p.s.i. and used these data to develop a reduced state viscosity correlation for this substance.

To expand the information on the viscosity behavior of polar substances, experimental viscosities for sulfur dioxide have been determined in this study. Such measurements are desirable, since the only viscosity values reported for sulfur dioxide at high densities are those of Awbery and Griffiths (1) and Stakelbeck (12) for the liquid region and meager and scattered data presented by the latter investigator for the gaseous region. The present study was particularly concerned with the establishment of the viscosity behavior of sulfur dioxide in the vicinity of the critical point, since no experimental viscosities have been reported for this region.

EXPERIMENTAL PROCEDURE AND RESULTS

A transpiration-type viscometer was used with an approach similar to that described previously (10) to determine experimental viscosities of sulfur dioxide at 200°C.

and pressures ranging from 250 to 3500 p.s.i.g. Altogether, nine experimental runs were conducted. The temperature of 200° C. (473.2° K.) was arbitrarily selected, since it is somewhat above the critical temperature of sulfur dioxide (T_c = 430.7° K.). The pressure was varied beyond the critical pressure of the substance, P_c = 1143 p.s.i.a., so that the viscosity behavior of sulfur dioxide in the critical region could be well defined. The results of the experimental runs are presented in Table I.

INTERPRETATION OF DATA

The internal consistency of the viscosity values of sulfur dioxide has been checked by plotting the difference between the experimental viscosity value and the viscosity at the same temperature and atmospheric pressure, $\mu - \mu^*$, vs. the corresponding reduced density, ρ_R, obtained from the reduced density correlation developed by Meyer (9). Relationships of this type have proved to be useful for understanding more effectively the behavior not only of viscosity, but also of thermal conductivity and self-diffusivity (7). The residual viscosities resulting from this study and the corresponding density values are presented in Table I. The viscosity of sulfur dioxide at normal pressures at 200° C., μ^* = 2060 × 10^{-5} centipoise, was obtained from the data of Trautz and Weizel (14) and Trautz and Zink (15).

The relationship between residual viscosity and reduced density obtained from the viscosity values determined in this study is presented in Figure 1. Residual viscosities resulting from the investigations of Awbery and Griffiths (1) and Stakelbeck (12) are also included in this figure. It can be seen from Figure 1 that the relationship obtained from the data of this study is continuous and, when extended, properly coincides with the values resulting from the viscosities reported by these investigators for the liquid region. The relationship of Figure 1 also passes through the several scattered points resulting from the data of Stakelbeck for the gaseous region.

Figure 1 enables the direct establishment of the viscosity of sulfur dioxide at the critical point. From this figure, the residual viscosity at p_R = 1.00 is $(\mu - \mu^*)_c$ = 1710 × 10^{-5} centipoise. The corresponding viscosity at atmospheric pressure and the critical temperature was found to be μ_c^* = 1880 × 10^{-5} cp. Consequently, the viscosity of sulfur dioxide at the critical point is μ_c = (1710 × 1880) × 10^{-5} = 3590 × 10^{-5} cp. The equation obtained by Hougen and Watson (6)

$$\mu_c = 77.0 \times 10^{-5} \frac{(M)^{1/2} P_c^{2/3}}{T_c^{1/6}} \qquad (1)$$

produces a critical viscosity of μ_c = 4090 × 10^{-5} cp. for sulfur dioxide from the values M = 64.066, T_c = 430.7° K.

and P_c = 77.8 atm. Thus, the critical viscosity of sulfur dioxide calculated from Equation 1 is 13.9% higher than that resulting from the experimental values of this study.

APPLICATION OF ENSKOG THEORY

The data of this study can be treated in a comprehensive manner by use of the theoretical treatment of viscosity developed by Enskog (5). For the effect of pressure on viscosity, Enskog proposed the following relationship, assumin a rigid sphere model:

$$\frac{\mu}{\mu^*} = b\rho \left[\frac{1}{b\rho\chi} + \frac{4}{5} + 0.7614 \, b\rho\chi \right] \qquad (2)$$

For rigid spheres $b\rho\chi$ is equal to the compressibility factor minus 1. For real gases Enskog suggested that this quantity
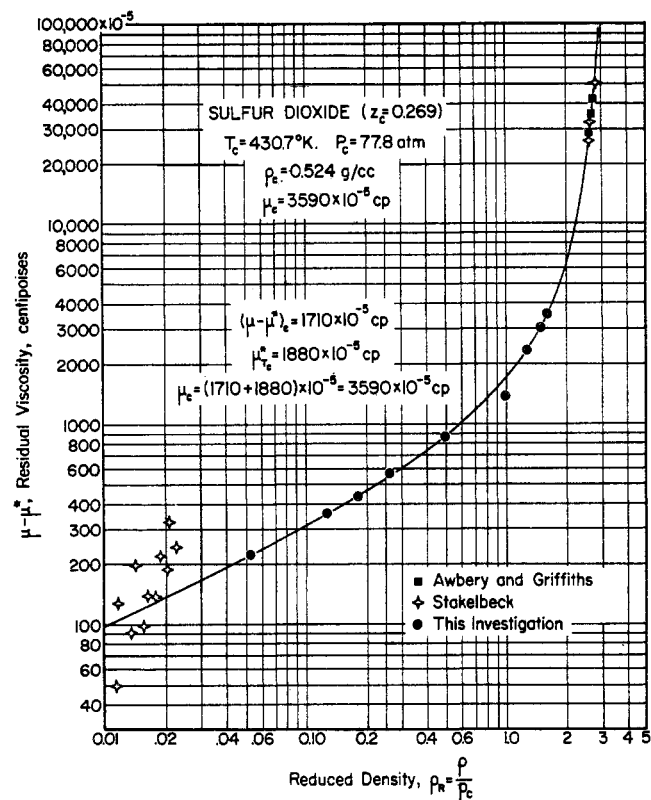

Figure 1. Relation between residual viscosity and reduced density for sulfur dioxide

Table I. Experimental Viscosity Values, Corresponding Densities, and Derived Quantities

200° C. (T_R = 1.099) μ^* = 2060 × 10^{-5} cp.

Run	Pressure, P.S.I.A.	μ, Cp.	$\mu - \mu^*$, Cp.	ρ, G./Cc.	$b\rho\chi$	$b\rho$	b
1	265	2282 × 10^{-5}	222 × 10^{-5}	0.0278	0.165	0.159	5.72
2	515	2420	360	0.0597	0.310	0.276	4.62
3	765	2498	438	0.0959	0.475	0.371	3.87
4	1015	2631	571	0.1362	0.61	0.440	3.23
5	1515	2930	870	0.2725	0.91	0.549	2.02
6	2015	3456	1396	0.5135	1.19	0.659	1.28
7	2515	4418	2358	0.6812	1.45	0.827	1.21
8	3015	5110	3050	0.7940	1.71	0.923	1.16
9	3515	5653	3593	0.8541	1.93	0.984	1.15

Sulfur dioxide. T_c = 430.7° K P_c = 77.8 atm. (1143 p.s.i.a.) ρ_c = 0.524 g./cc.
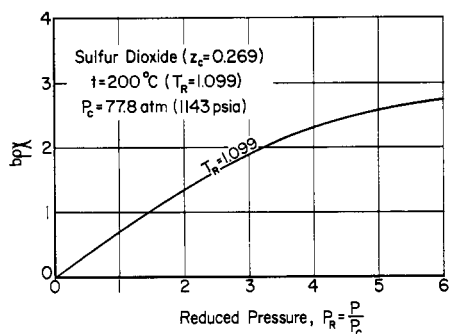
Figure 2. Relation between $b\rho\chi$ and reduced pressure for sulfur dioxide at 200° C.
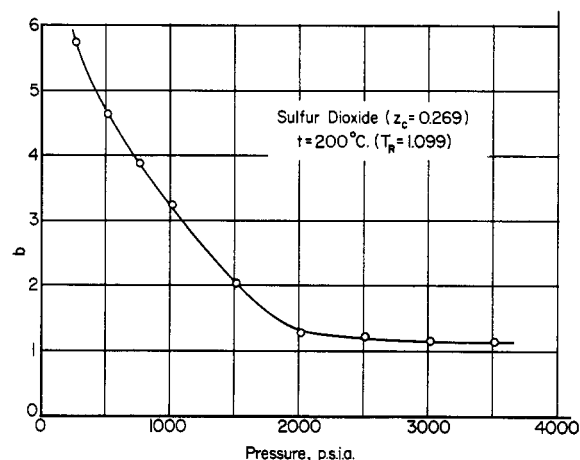
$(T_R = 1.099)$

Figure 3. Relation between Enskog coefficient b and pressure for sulfur dioxide at 200° C.

T_R = reduced temperature, T/T_c
V = molar volume, cc./g.-mole

Greek Letters

μ = viscosity, centipoises
μ^* = viscosity at normal pressures, cp.
μ_c = viscosity at critical point, cp.
μ_R = reduced viscosity, μ/μ_c
$\mu_{T_c}^*$ = viscosity at normal pressures and critical temperature, cp.
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c
χ = probability of nearness, Equation 2

be established from experimental PVT data by use of the following relationship resulting from the Enskog equation of state (3):

$$b\rho\chi = \frac{V}{R}\left(\frac{\partial P}{\partial T}\right)_v - 1 \qquad (3)$$

Values of $b\rho\chi$ for sulfur dioxide at 200° C. (T_R = 1.099) were calculated from Equation 3 by the use of the PVT data compiled by Meyer (9) and are presented in Figure 2 for reduced pressures up to P_R = 6.0. The $b\rho\chi$ values for the experimental conditions are presented in Table I.

Enskog suggested that the value of b for use in Equation 2 be determined for a real gas from the minimum value of $(\mu/\mu^*)/\rho$ as a function of $b\rho\chi$. For sulfur dioxide at 200° C., a minimum value of $(\mu/\mu^*)/\rho$ = 2.75 was obtained at $b\rho\chi$ = 1.60; while Equation 2 indicates that the minimum should occur at $b\rho\chi$ = 1.146. The use of the resulting value of b and the established values of $b\rho\chi$ produced viscosity values for sulfur dioxide from Equation 2 which were considerably lower than the corresponding experimental values, especially at low pressures.

From the $b\rho\chi$ values presented in Table I and the values of the viscosity ratio, μ/μ^*, obtained in this study, values of b were calculated from Equation 2 for the nine experimental runs and are also presented in Table I, along with the corresponding values of b. These values of b were related to pressure, as shown in Figure 3. It can be seen from this figure that at high pressures a constant value of b = 1.15 is approached. Similar behavior was found to exist for ammonia at 100°, 150°, and 200° C. (10). Since in the derivation of Equation 3 the assumption was made that b is independent of temperature, the relationship of Figure 3 should be applicable for the calculation of viscosity values at any temperature from Equation 2.

NOMENCLATURE

b = constant for Enskog viscosity relationship, Equation 2
M = molecular weight
R = gas constant
P = pressure
P_c = critical pressure
P_R = reduced pressure, P/P_c
T = absolute temperature, ° K.
T_c = critical temperature, ° K.

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