like" characteristics that have been attributed to polyalcohols relative to monohydric alcohols (*4*). This point is the same for HCl transfer to ethylene glycol at $X_3 \approx 0.13$ (*10*).

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RECEIVED for review October 23, 1970. Accepted February 5, 1971. Work supported by National Science Foundation.

Solubility of Sulfur in Liquid Sulfur Dioxide, Carbon Disulfide, and Carbon Tetrachloride

JANE M. AUSTIN, DAN JENSEN, and BEAT MEYER[1]
Chemistry Department, University of Washington, Seattle, Wash. 98105

The solubility of sulfur in liquid sulfur dioxide, carbon disulfide, and carbon tetrachloride is reported. In liquid sulfur dioxide the solubility increases with rising temperature. Between 25° and 65° C there is indication of solvent-solute interaction. At 95° C, the transition temperature between orthorhombic and monoclinic sulfur, a definite change in solubility is noted. In carbon disulfide, the solubility increases logarithmically with rising temperature. In carbon tetrachloride, the solubility also increases with rising temperature. However, between 140° and 170° C, a reaction takes place.

The solubility of sulfur in liquid gases and solvents is not well known. It is often much larger than expected. The purpose of this study was to explore the solubility of sulfur in liquid sulfur dioxide and to extend the temperature range for the sparse and old data on carbon disulfide and carbon tetrachloride.

References regarding the solubility of sulfur in liquid sulfur dioxide are all qualitative (*1, 6, 8, 11*). They suggest that there is only a slight solubility which increases with rising temperature. The solubility of sulfur in carbon disulfide, as measured by five different experimenters, has been critically summarized (*2*) for the range between −116° and +98° C. Data for the solubility of sulfur in carbon tetrachloride (*3, 5*) obtained at four temperatures indicate that the solubility changes smoothly with temperature up to 58° C with no reactions taking place. However, it is known (*10*) that above 150° C, carbon tetrachloride reacts with sulfur.

EXPERIMENTAL

Reagent grade carbon disulfide from Allied Chemical Co., and carbon tetrachloride and phosphorus pentoxide, both from J. T. Baker Chemical Co., were used. Sulfur of 99.99% purity was donated by the Freeport Sulphur Co. CP grade sulfur dioxide was drawn from Matheson Chemical Co. cylinders.

Sulfur dioxide was further purified by passing it through two columns of phosphorus pentoxide drying agent and subjecting the dried gas to two freeze-pump-thaw cycles. All other chemicals were used without further purification.

Since the solubility of sulfur in sulfur dioxide was measured up to the critical point, sealed sample tubes were necessary. Sample tubes were made from 7-mm o.d. pyrex tubing which was closed at one end and annealed. Approximately 4 in. from the sealed end, a constriction was made and the entire tube was joined to an $^{18}/_{7}$ ball joint attached to a vacuum system. The bulb served as a container for gaseous sulfur dioxide dried by passing through phosphorus pentoxide drying tubes. This procedure was similar to that reported before (*9*).

For safety reasons, sample tubes were made from medium-wall, annealed glass tubing selected from standard stock. Hot tubes were handled only with mechanical fingers to lessen the danger from explosion due to the high vapor pressures of the solvents. Protective face guards were worn, and the experiment was carried out in screen-enclosed beakers behind explosion-proof glass. However, only one or two out of a dozen sample tubes burst around the critical point of SO_2, and in most cases the failures occurred above critical conditions.

Throughout all experiments, the same basic procedure was followed to measure solubilities. We observed, within a 5° C range, when the last traces of sulfur dissolved. For this purpose, tubes were immersed in constant temperature baths and were rotated mechanically or shaken to enhance equilibration. In the cases of both liquid sulfur dioxide and carbon tetrachloride, equilibrium was approached both by raising and lowering the temperature of the bath used.

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[1] To whom correspondence should be addressed.

Table I. Solubility of Elemental Sulfur in Three Solvents

SO_2		CS_2		CCl_4	
Wt %, sulfur	Temp range where soluble, ° C	Wt %, sulfur	Temp range where soluble, ° C	Wt %, sulfur	Temp range where soluble, ° C
0.0039	15–20	24.16	22	0.1087	–20––17
0.0078	20–25	28.45	32	0.1975	–8––5
0.0153	30–35	32.76	38–40	0.3942	5–10
0.0207	40–45	34.89	44	0.6552	20–22
0.0237	50–55	37.49	45–46	1.302	45–50
0.0284	55–60	40.23	46–48	1.940	55–62
0.0382	60–65	44.34	50	2.570	60–65
0.0766	70–75	48.62	52–53	3.193	70–75
0.1619	75–80	50.06	55–56	6.188	95–100
0.2436	80–85	52.29	57–59	11.65	129–131
0.3891	110–115	55.66	59–61	20.88	198+[a]
0.4226	120–125	59.99	63–64	34.54	198+[a]
0.4617	135–140	63.66	66–69		
0.6131	152+[b]	71.44	75		
0.7742	152+[b]	79.00	85		
		83.34	90		
		90.84	102		

[a] Reaction has taken place. [b] Critical point = 152° C.

However, in the case of carbon disulfide solutions, all values are for increasing temperature only, because in this system cooking leads easily to supersaturated solutions. Fixed temperatures were established by using baths of Dry Ice–acetone, chloroform slush, and carbon tetrachloride slush. In the temperature range between –20° and 0° C calcium chloride–ice was used. The range 0–100° C was established with a water bath, and mineral oil was used between 100° and 200° C.

The samples were prepared by introducing a known amount of sulfur by pipetting a solution of sulfur in carbon disulfide of known concentration into the pyrex tube. The carbon disulfide solution was pumped off on the vacuum line. In some preliminary experiments, the sulfur was further purified by vacuum sublimation. This procedure, however, proved unnecessary.

Sulfur dioxide, after drying by passing through a double column of phosphorus pentoxide drying agent, was carried through two freeze-pump-thaw cycles to remove traces of noncondensable gases. A known volume of sulfur dioxide at a given pressure was condensed into the sample tube, and the tube was sealed.

Carbon disulfide and carbon tetrachloride were introduced into the sample tubes with pipets; they were frozen and degassed, and the tubes were sealed.

Light has been reported to affect the solubility of sulfur in various solvents by precipitating insoluble sulfur (*13*). Therefore, all experiments were carried out under similar lighting conditions in a dark hood. An experiment using medium intensity uv light showed that under our experimental conditions, light did not precipitate sulfur to any noticeable extent.

RESULTS AND DISCUSSION

Table I shows that sulfur is soluble in all the solvents and that solubility increases with temperature. Figure 1 summarizes the results as a graph of log weight percent sulfur soluble in the solvent vs. 1/*T*.

Sulfur Dioxide. Sulfur is slightly soluble in sulfur dioxide with the solubility increasing with rising temperature from 3.9×10^{-3} wt % sulfur at 15–20° C to 0.46 at 135–140° C. The weight percentage of sulfur in each sample is accurate to ±2%, and the temperatures are recorded to an accuracy of ±5° C. The uncertainty in temperature reading is due to the difficulty in determining when the last traces of sulfur particles dissolve. For all systems below the critical point, the net transfer of solvent from the liquid to the gas phase is insignificant, because even at the highest observed pressure, the gas contained less than 3% of all material.

Solubility increases logarithmically with temperature to the temperature range 25–65° C. A marked inflection point, between 55° and 65° C, seems to be caused by solvent-solute interaction. A phase or structure change of sulfur can be ruled out because the free energy vs. temperature curve of the sulfur exhibits no discontinuities (*12*). Above 65° C, the solubility increases at the same rate as below 25° C. This indicates that the chemical composition is not changed. A discontinuity or change in the solubility takes place at the temperature, 95° C, of transition between orthorhombic and monoclinic sulfur. An examination of the plot shows that the solubility increases less for monoclinic sulfur than for orthorhombic sulfur. The solubility curve has no inflection at the melting point of sulfur.

Carbon Disulfide. Sulfur is extremely soluble in carbon disulfide, the solubility increasing logarithmically with temperature and approaching 100 wt % near 100° C. Our data confirm earlier work (*3*). In this system, experimental problems are significant. It was difficult to see small sulfur crystals in the highly colored solutions, and the solutions supersaturated easily. The weight percent of sulfur in each sample is accurate to ±2%. The temperature range was ±1–3° C.

Carbon Tetrachloride. In carbon tetrachloride, the solubility of sulfur is moderate and increases logarithmically with temperature up to 140° C. Above this temperature, the lower liquid sulfur phase darkens, bubbles continuously, and does not dissolve at the expected temperature, thus suggesting that a chemical reaction takes place. The weight percent sulfur data are accurate to ±2%, and the temperatures are accurate to ±5° C.

Above 159° C, sulfur becomes largely polymeric and dirad-

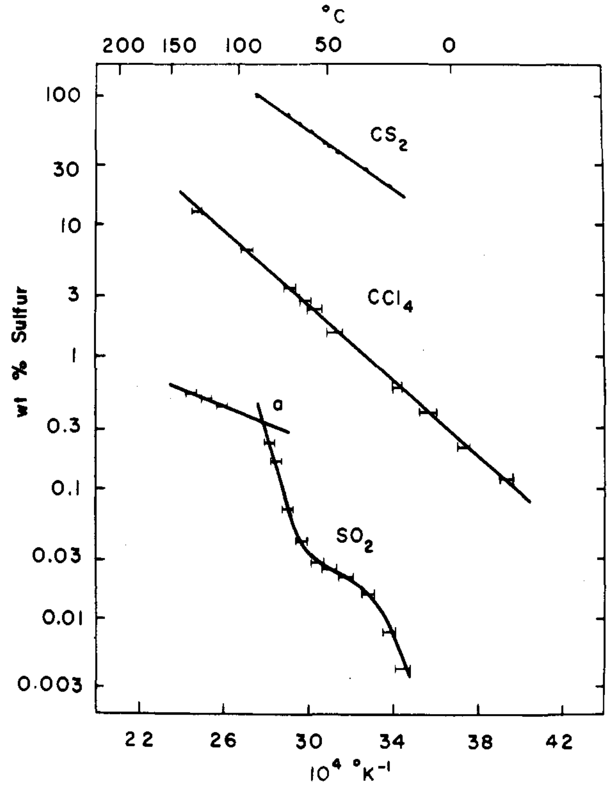

Figure 1. Solubility of sulfur in CS_2, CCl_4, and liquid SO_2
(a) Transition temperature of orthorhombic-monoclinic sulfur

ical (*4*, *7*), and thus it is a good nucleophile able to attack carbon tetrachloride. Sosnovsky (*10*), in a discussion of the compound trichloromethanesulfenyl chloride, discusses the products which seem to result from this reaction.

A least-squares fit of the data for both the carbon disulfide-sulfur and the carbon tetrachloride-sulfur experiments gives straight lines whose slopes, using the equation

$$\log \epsilon/(1/T) = -\Delta H/2.303\ R \qquad (1)$$

where ϵ is the solubility, yields heat of solution ΔH_s values of 3.68 ± 0.05 kcal/mol for carbon disulfide and 6.4 ± 0.1 kcal/mol for carbon tetrachloride. On the basis of the fit of the curves, the solubility ϵ of the carbon disulfide-sulfur solution can be calculated using the equation

$$\log \epsilon = (-8.07 \times 10^2/T) + 4.16 \qquad (2)$$

for the temperature range 22–102° C, while for carbon tetrachloride-sulfur solutions it can be calculated using the equation

$$\log \epsilon = (-1.41 \times 10^3/T) + 4.58 \qquad (3)$$

for the temperature range −20° to 131° C.

For liquid sulfur dioxide-sulfur, the ΔH and ϵ cannot be given because points do not lie on a straight line.

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RECEIVED for review October 26, 1970. Accepted February 8, 1971. JMA was an undergraduate National Science Foundation Fellow. Also this work was in part supported by the National Air Pollution Control Administration.

Separation of Longifolene from Pine Oil

N. MASON JOYE, JR., ADRON T. PROVEAUX, and RAY V. LAWRENCE[1]
Naval Stores Laboratory, Olustee, Fla. 32072
EDWARD F. PALAGYI
Glidden-Durkee, Division of SCM Corp., Jacksonville, Fla. 32201

Pine oil obtained from extractives of ponderosa pine (*Pinus ponderosa Laws*) stumps was fractionally distilled to separate longifolene. The components of each fraction were determined by gas chromatography.

The pine oil obtained from a commercial size run of ponderosa pine stumps was examined by gas chromatography and found to contain about 20% of a sesquiterpene (longifolene) (*1*) not usually present in pine oil from southern pine stumps. Removal or separation of this component was necessary to market a pine oil equivalent to those already on the market.

This study on the separation of the components of pine oil was carried out to determine the feasibility of separating longifolene from pine oil.

Table I shows the composition of the starting pine oil and of each fraction of the distillation. The composition of fractions 1–6 combined and of a commercial pine oil are also included in Table I. Fractions 1–6 account for approximately 70% of the pine oil and contain only a trace of longifolene in the 6th fraction. Thirty-four percent of the longifolene is in fraction 7 and the remaining 66% in the pot residue. A bulb-to-bulb distillation of the residue gave longifolene of 98% purity.

EXPERIMENTAL

One drum of pine oil containing 336 lb was charged and distilled. The distillation column was 316 stainless steel, 5.75 in. i.d. with a 13-ft section packed with 1-in. pall rings. The charge was at total reflux for 1.5 hr prior to distillation. The pine oil was distilled at a 10:1 reflux ratio. Product temperature was maintained at 40–50° C to prevent crystallization of high-melting components such as borneol. An operating differential pressure of 25 mm Hg with 50 mm Hg top column pressure was maintained throughout the distillation. When the operating differential pressure began to drop, the run was stopped and the residue remaining in the pot removed.

Seven fractions weighing 35 lb each were taken and 53 lb of pot residue recovered. Approximately 38 lb were unaccounted for and assumed to have been carried over in the vacuum system. Each fraction, the pot residue, and the original pine oil were analyzed by gas chromatography. An F&M Model 700 gas chromatograph with dual columns and flame detector was used. The column was a 15-ft by 3/16-in. copper column packed with 5% Versamid 900 on 70/80 mesh diatoport S. The column temperature was 150° C, and the helium flow 100 ml/min. The peak areas were measured with a disc integrator equipped with an automatic printer.

The pine oil components were identified by comparison of retention times with known compounds and by collecting and recording the infrared spectra of the individual peaks. The infrared spectrum of longifolene is in Figure 1, and the infrared spectra of 11 other pine oil components are deposited with the ACS Microfilm Depository Service (*2*).

SUMMARY

Longifolene was separated from other pine oil components using commercial equipment available in most plants. The distilled pine oil contains the same components in approxi-

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[1] To whom correspondence should be addressed.