ULTRAVIOLET ABSORPTION OF AQUEOUS SULFUR SOLUTIONS

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INTRODUCTION

The kinetics of the formation of monodispersed sulfur hydrosols by the acid decomposition of sodium thiosulfate has been extensively studied by La Mer and others (1–5). The homogeneous part of the reaction can be followed by optical absorption measurements at 300 mμ. If the absorption is interpreted as due to molecular sulfur, it is necessary to know the extinction coefficient of sulfur in water in order to determine the concentration of sulfur at any stage of the reaction.

The extremely low solubility of sulfur in water precludes the direct determination of the extinction coefficient. La Mer and Kenyon (1) have measured the absorption of sulfur in carbon tetrachloride, chloroform, and acetone and have used the average of the extinction coefficients in these solvents as an approximation to the value in water.

We have determined the extinction coefficient of sulfur in ethanol–water mixtures as well as a number of transparent organic solvents and will present an empirical relation between extinction coefficient and solvent refractive index which will permit us to estimate the extinction coefficient of sulfur in water.

EXPERIMENTAL PROCEDURE

Optical densities of sulfur solutions were measured for wavelengths of 225–380 mμ using a Beckman model DU quartz spectrophotometer with 1-cm. and 10-cm. quartz cells. The sulfur solutions, whose concentrations varied from 0.00012 to 0.012 g. atoms of sulfur/l., were compared with the pure solvents as standards of absorption. The solvents used were chloroform, ethanol, ethanol–water mixtures, glycerol, *n*-hexane, and methanol.

The solutions were prepared by adding small amounts of sulfur to the solvents and heating. It was found inexpedient to determine the concentrations by direct weighing because of the small quantities of sulfur to be handled. Furthermore, sulfur did not dissolve completely in the cases of chloroform and *n*-hexane. Preparations in which a suspension appeared

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were filtered. The extinction coefficients for the glycerol solutions are not reported because such small amounts of sulfur dissolved that analysis was unsuccessful. Aliquot portions of the solutions were used for making dilutions. It was found that much of the solubility data in standard

TABLE I

Extinction Coefficients of Sulfur in Various Solvents

λ	Extinction coefficients						
	CHCl₃	C₂H₅OH	95%C₂H₅OH	90%C₂H₅OH	n-Hexane	CH₃OH	Water
mμ							
380	2.2	2.3	2.3	3.6	2.2	3.2	2.6
370	5.5	4.7	4.7	6.2	4.5	5.8	5.2
360	11.8	10.4	10.1	12.2	9.8	11.2	10.9
350	25.0	21.6	21.3	23.8	20.7	20.8	20.9
340	51.9	43.3	42.9	46.2	42.7	41.3	41.6
330	102	83.2	82.9	86.0	83.2	80.2	80.7
320	186	154	154	158	156	149	150
310	314	264	263	270	276	257	258
300	494	428	426	431	451	411	414
295	615	536	540	544	571	521	524
290	727	649	658	658	696	637	640
285	818	739	755	752	796	732	735
280	864	790	807	800	845	789	792
275	875	812	824	819	860	802	805
270	895	828	830	832	864	812	815
265	920	842	847	848	880	829	832
260	904	820	830	827	859	813	816
258	869	795	805	801	831	790	792
256	846	764	769	772	797	761	763
254	818	732	735	740	766	724	727
252	803	707	708	710	738	699	702
250	823	698	690	693	718	680	683
248	854	703	692	697	725	676	682
246	883	732	717	722	756	697	702
244	—	775	766	770	810	745	749
242	—	844	836	839	892	806	812
240	—	936	935	932	987	901	907
235	—	1182	1191	1182	1256	1161	1166
230	—	1363	1378	1375	1435	1351	1357
225	—	1458	1477	1474	1504	1435	1440

references was not reliable. Brooke (6) has pointed this out and has suggested this topic for undergraduate research projects.

The solutions were analyzed for sulfur content both by evaporation and by gravimetric analysis of sulfur as barium sulfate. The sulfur was first oxidized to sulfate by bromine and then precipitated and weighed as

$BaSO_4$ (7). The analysis was the largest source of error, for the quantities of sulfur and $BaSO_4$ were quite small. A microbalance was used for all weighings.

The spectrophotometer was thermostated at 25°C. by circulating water in order to keep the cells from being heated by the hydrogen lamp, thus minimizing evaporation and thermal currents. Narrow slit widths were used for maximum sensitivity and reproducibility. Sulfur was purified by the method of Bacon and Fanelli (8). Commercial 95% alcohol was used for the 90 and 95% ethanol runs. The absolute ethanol was prepared by the method of Weissberger and Proskauer (9). Hexane from
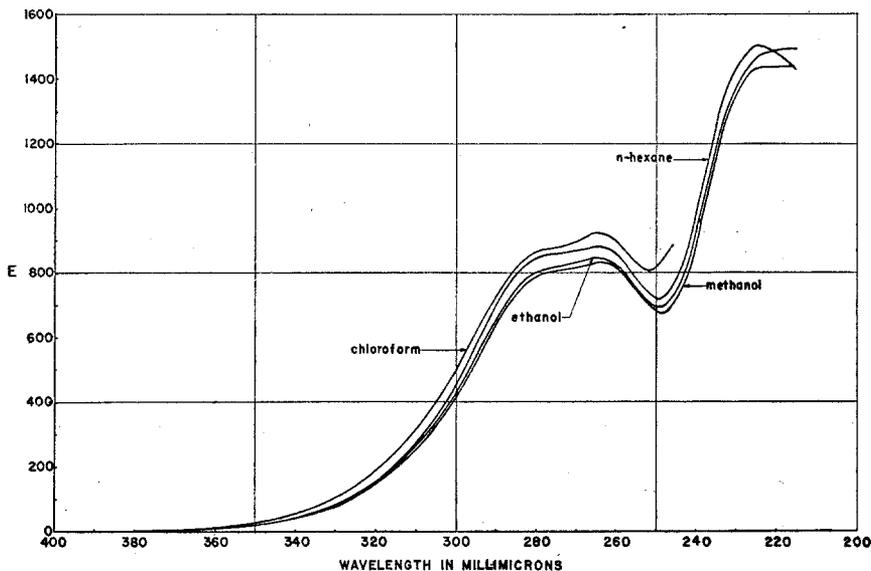
FIG. 1. Absorption curves for sulfur in various solvents. Extinction coefficient, $E = \log_{10}(I_0/I)$ for 1 M concentration and 1-cm. path length.

petroleum was purified for optical use by the method of Weissberger and Proskauer. A hydrocarbon mixture whose index of refraction was 1.3815, rather than 1.3750 for pure n-hexane, was produced. Merck's reagent-grade chloroform and Baker's C.P. reagent-grade methanol were used. All refractive indexes are for the sodium D line and 20°C.

RESULTS AND DISCUSSION

The extinction coefficients[1] are found in Table I and are plotted as a function of wavelength in Fig. 1. The curves show a maximum in the

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[1] The extinction coefficient, E, is defined by $\log_{10}(I/I_0) = -Elc$, where I/I_0 = transmission, c = molar concentration, and l = light path in centimeters. This differs from the value of La Mer and Kenyon (1) by the factor 2.303.
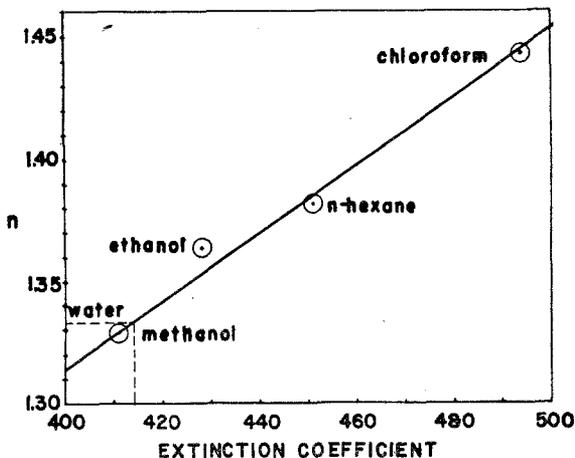
FIG. 2. Variation of extinction coefficient at 300 mμ with the index of refraction of the solvent (sodium D line).

vicinity of 265 mμ and a minimum in the region of 250 mμ. This is in agreement with the findings of Ford and La Mer (10).

An examination of the results reveals that the extinction coefficients vary linearly with the index of refraction of the solvent. A plot of extinction coefficient at 300 mμ against solvent index of refraction (sodium D line) is shown in Fig. 2. A value of 414 for the extinction coefficient of a water solution (index of refraction, 1.33) was obtained by interpolation. When divided by the conversion factor 2.303, the average value obtained
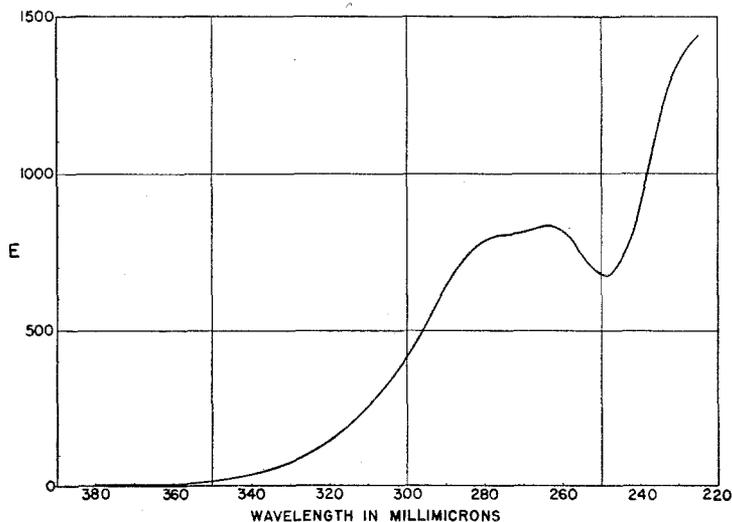

FIG. 3. Absorption curve for sulfur in water.

by La Mer and Kenyon for 300 mμ is 551. By similar interpolations the extinction coefficients of sulfur in water were obtained at other wavelengths and are tabulated in the last column of Table I. The extinction curve for sulfur in water is plotted in Fig. 3.

Variation of Wavelength of Maximum and Minimum of Absorption Curves with Solvent Refractive Index

Solvent	Maximum	Minimum	Refractive index[a]
Glycerol	266.0	251.0	1.4729
Chloroform	265.5	250.5	1.4432
n-Hexane	264.5	249.8	1.3815
Ethanol	264.0	249.3	1.3618
Methanol	263.5	249.0	1.3290

[a] The index of refraction data were obtained from the International Critical Tables, Vol. VII. McGraw-Hill Book Company, Inc., New York, 1933. The index of refraction of the n-hexane mixture was measured. All refractive indexes are for sodium D line and 20°C.

The addition of water to the ethanol solutions had no apparent effect upon the extinction coefficient. This is consistent with the above results since the index of refraction of 90 and 95% ethanol is very close to that of pure ethanol.
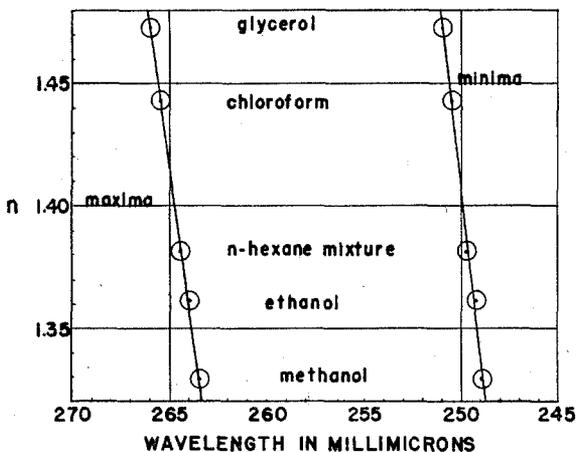

FIG. 4. Variation of position of maximum and minimum of absorption curves with solvent refractive index.

Beer's law was found to hold within the experimental limits. Each solvent was examined at at least three concentrations over at least a tenfold concentration range. There was an apparent failure of Beer's law in the range 340–380 mμ and at the lower wavelengths where the solvents absorb appreciably. The former can be attributed to the inaccuracy of the spectrophotometer in the region of low optical density. The apparent

failure of Beer's law near the transmission limits of solvents was studied by Vandenbelt, Henrich, and Bash (11) and is attributed to the influence of stray light.

The positions of the maximum and minimum of the absorption curves move toward higher wavelengths with solvents of increasing index of refraction. This is in agreement with Kundt's Rule (12) and the work of Le Rosen and Reid (13). The data are tabulated in Table II and plotted in Fig. 4.

The two principal sources of error in this research were in the analysis for sulfur concentration and the optical density readings. The average deviations of the analyses were about 2%. The average deviations of the optical density readings were within $\pm 1\%$ except in cases of very low optical density and near the transmission limit of the solvents.

ACKNOWLEDGMENT

SUMMARY

Absorption curves of sulfur in the solvents chloroform, ethanol, ethanol–water mixtures, n-hexane, and methanol were obtained for the range 225–380 mμ. The curves were found to be quite similar, but were displaced toward higher wavelength and extinction coefficients as the index of refraction of the solvent increased. The average of all extinction coefficients at 300 mμ was 440 $\pm$ 4.9%. Examination of these extinction coefficients with respect to solvent index of refraction permits estimation of a value of 414 for water solutions at 300 mμ. Beer's law holds for these solutions.

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