Absorbing and Reflecting Powers of H2SO4 Solutions in the Far Infrared

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Absorbing and Reflecting Powers of H_2SO_4 Solutions in the Far Infrared

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(Received April 3, 1936)

The reflecting and absorbing powers, and hence dispersion, of H_2SO_4 solutions were determined as a function of concentration and of wave-length between 50μ and 150μ. Pure H_2SO_4 reflects and absorbs the far infrared less than water as is to be expected from the Debye theory on dipole orientation. A broad band around 60μ, similar to the 60μ band in water, was observed in both concentrated and dilute H_2SO_4. This band appears to be of interatomic origin and possibly a fundamental vibration frequency of the sulphate radical, SO_4, due to bending. The reflecting and absorbing powers of H_2SO_4 solutions are much greater than of pure H_2O or H_2SO_4. This is accounted for by the presence of ions which move in translation to follow the alternations of the electromagnetic waves in the far infrared. The structure of these ions is discussed in reference to other physical properties observed in H_2SO_4 solutions. It is suggested that in adding less than 5 percent water to H_2SO_4 possibly ions of SO_4^{--} and OH_4^{++} might be formed; on further dilution, ions of H^- and H_3SO_5 are formed (hydrated HSO_4^-, with the water making stable six-ring of $S-O-H-O-H-O-S$); on still further dilution, ions of H^+ and SO_4^{--} become most abundant.

Introduction

THE measurements of Rubens[1] for the reflecting power of strongly concentrated H_2SO_4, 2 parts $H_2SO_4 + 1$ part H_2O, 2 parts $H_2O + 1$ part H_2SO_4 (measured by volume) and of H_2O are given in Table I. Rubens' data show

TABLE I. *Reflecting power.*

Solution	23μ	33μ	52μ	63μ	83μ	94μ	117μ	313μ
H_2SO_4	8.8	7.9	16.9	18.7	17.7	17.7	18.4	21.7%
2 $H_2SO_4 + H_2O$ (Vol)	9.2	10.9	19.4	20 6	22.3	—	—	28.8%
2 $H_2O + H_2SO_4$ (Vol)	8 1	9.6	14.2	17.0	19.0	—	—	26.5%
H_2O	6.5	7.2	9.3	10.6	10.9	11.1	12.7	15.1%

that the reflecting powers of H_2SO_4 solutions are considerably greater than those of pure water or concentrated H_2SO_4. In the present investigation we have increased the number of concentrations and have also measured their absorption thus permitting the dispersion to be calculated.

In Fig. 1 are shown for H_2SO_4 solutions the freezing point, F.P., specific gravity, S.G., specific electrical conductivity, κ, and the viscosity, η.[2] The electrical conductivity of the solutions must of course be attributed to the formation of ions and the Raman spectrum indicates that at least three types of ions exist. In the region of the spectrum investigated, these ions can be expected to follow in translation the alternations of the electromagnetic waves and cause a reflection and absorption considerably in
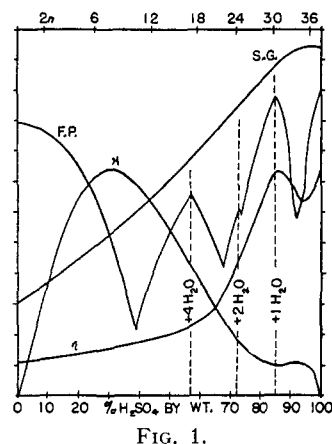

FIG. 1.

excess to that produced by a turning of the polar molecules or of any active infrared bands.[3]

Although many physical properties of H_2SO_4 solutions have been studied, the structures of the compounds formed have not been established. The present investigation of the far infrared dispersion of these solutions was undertaken with the hope of giving additional data and a new tool for analyzing the structures of molecules in solutions.

Experimental Procedure

Monochromatic radiations of 52, 63, 83, 100, 117 and 152μ were obtained by the method of reststrahlen with suitable filters for purification. A Wellsbach mantle was used as a source of radiation and the energy was finally detected by a special compensated vacuum thermocouple and

[1] H. Rubens, Verh. d. D. Phys. Ges. **17**, 315 (1915).
[2] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. X, and Fr. Ephraim, *Anorganische Chemie*.
[3] C. H. Cartwright, Phys. Rev. **49**, 101 (1936).

statically-balanced galvanometer which was read by a semi-automatic device. The reststrahlen plates and the specimens were enclosed in a case containing dry air and were changed mechanically from the exterior. For reflection measurements, the solutions were contained in a separate compartment of dry air.

The solutions of H_2SO_4 investigated were 2, 6, 12, 18, 24, 30, 36 and 37.4 normal and were kindly prepared by Dr. Hauss. To facilitate comparison with other investigations, the concentrations expressed as percentage by weight of H_2SO_4 were 9.3, 25.0, 44.0, 59.2, 72.1, 83.4, 96.1 and 100 percent or expressed as percentage by volume of H_2SO_4 they were 5.3, 15.4, 30.0, 43.7, 58.5, 73.3, 92.9 and 100 percent. The most concentrated H_2SO_4 was fuming as it was taken from the bottle but all of the SO_3 gas that would escape at room temperature was allowed to do so in a dry atmosphere before the acid was used for measurements.

For absorption measurements, the solutions were contained between two crystalline quartz plates and the absorption coefficient, $n\alpha$, was calculated by the usual formula:

$$I = I_0^{-4\pi n\alpha d/\lambda}, \qquad (1)$$

where I is the transmission of the cell with the solution of thickness d and I_0 is the transmission of a quartz comparison plate of thickness, 4 mm, having the same thickness of quartz as in the cell. The index of refraction, n, of all the solutions was found to be so nearly that of crystalline quartz for the same wave-lengths, that the loss by reflection from the two surfaces, quartz-liquid and liquid-quartz was negligible. The tabulated thickness, d, of the solutions was determined by measuring the absorbing power of all the solutions at $\lambda = 117\mu$ in a cell of thickness $d = 34.6\mu$. This thickness was too great to give a suitable transmission for shorter wave-lengths so thinner spacers of platinum were used and the thickness, d, was calculated from Lambert's law, formula (1).

The reflection measurements were made on the free surface of the solutions and compared with the reflection from an evaporated tin mirror having 100 percent reflecting power for the wave-lengths used.

The index of refraction, n, was calculated from the reflecting and absorbing power ac-

cording to the well-known formula:

$$R = 100\frac{(n-1)^2 + n^2\alpha^2}{(n+1)^2 + n^2\alpha^2}. \qquad (2)$$

EXPERIMENTAL RESULTS

In Table II are recorded the percentage reflection, R, the percentage transmission, T ($T = 100 I/I_0$, for a solution of thickness d), the calculated absorption coefficient, $n\alpha$, and the index of refraction, n.

Some of the data in Table II are shown graphically in Figs. 2 and 3, both as a function of wave-length and of concentration.

DISCUSSION

To facilitate a general interpretation of the data in Table II and Figs. 2 and 3, it may be well to recall the different ways in which absorption might occur in the spectral region from 50μ to 150μ: (1) Characteristic absorption bands due to fundamental atomic vibration frequencies of small binding forces, (2) characteristic absorption bands due to combination made up of differences

TABLE II.

|	λ (μ) ν (cm^{-1})		52 192	63 159	83 120	100 100	117 85	152 (μ) 66 (cm^{-1})
H_2O		R	9.2	10 7	11.6	12.0	12.7	13 0%
	$d \approx 19.7\mu$	T	11.5	14.7	24 4	40.2	49.0	53.3%
		$n\alpha$	0.46	0.49	0 48	0.37	0.34	0.39
		n	1.68	1.77	1.89	2.01	2.04	2.09
$2n\ H_2SO_4$		R	10.7	11.8	12 8	13.8	15.1	15.8%
	$d = 21.0\mu$	T	7.0	8.5	15 5	29.2	38.5	44.0%
		$n\alpha$	0 53	0.59	0.59	0.47	0.42	0.47
		n	1.75	1.78	1.87	2.07	2.17	2 19
$6n\ H_2SO_4$		R	13.1	14.7	16.2	17 0	18.5	19.7%
	$d \approx 21.4\mu$	T	3.7	4.7	13 0	23.5	31.2	35.2%
		$n\alpha$	0 64	0 72	0.63	0.54	0.51	0 59
		n	1.85	1.88	2.11	2 27	2 38	2.42
$12n\ H_2SO_4$		R	16.8	18.7	19 6	21.0	22.5	23.6%
	$d \approx 21.0\mu$	T	2.0	3 2	10 3	18.8	26.9	29.9%
		$n\alpha$	0.77	0.82	0.71	0.63	0.58	0.70
		n	2.02	2 13	2.33	2.53	2.66	2.69
$18n\ H_2SO_4$		R	19.9	20 2	22.0	23 6	24.5	25.3%
	$d = 16.0\mu$	T	7.0	9 8	18 2	34.1	40.4	45.4%
		$n\alpha$	0.69	0.73	0 71	0.54	0 53	0.60
		n	2.37	2.37	2 54	2.79	2.85	2 89
$24n\ H_2SO_4$		R	21.7	22.1	22.1	23.0	24.0	25.4%
	$d = 22.4\mu$	T	2 7	3.2	11.5	20.5	33 0	37 8%
		$n\alpha$	0 67	0.77	0.64	0.56	0 46	0 52
		n	2.53	2 53	2.60	2 73	2.84	2.92
$30n\ H_2SO_4$		R	21 9	20.5	20.1	20 6	22 6	24 1%
	$d = 20.6\mu$	T	6.6	7.2	15.1	30.0	40.2	44.9%
		$n\alpha$	0.55	0.64	0 61	0.55	0.41	0.47
		n	2.62	2.46	2.45	2 54	2.74	2 85
$36n\ H_2SO_4$		R	13.3	15.9	16.8	17.4	18.3	19 0%
	$d = 21.6\mu$	T	7.4	8.1	19.8	37.5	46.8	51.8%
		$n\alpha$	0.50	0 58	0.49	0 36	0.32	0 37
		n	2.01	2.12	2.25	2.37	2.45	2.47
H_2SO_4		R	8.1	9.7	9.8	10 5	10.6	11.3%
	$d = 21.5\mu$	T	20 5	21.0	38.7	59.5	66.0	71 8%
		$n\alpha$	0 30	0.36	0.30	0.20	0.18	0.19
		n	1.72	1.80	1.84	1.96	1.99	2.00
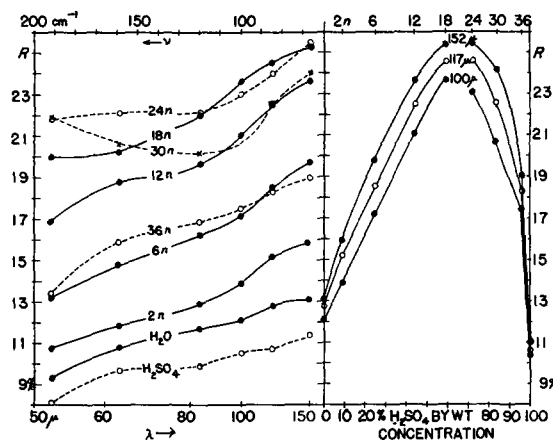
FIG. 2.
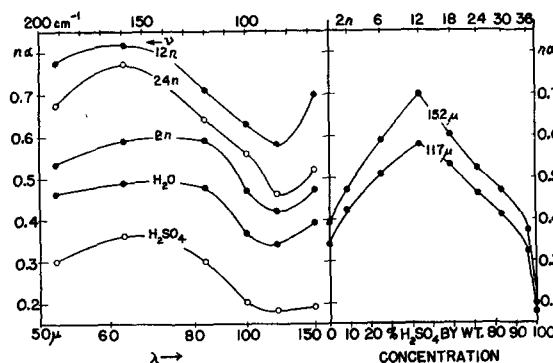
FIG. 3.

of near infrared vibration frequencies, (3) characteristic absorption bands produced by the polar molecules oscillating in a quasi-crystalline structure formed by the intermolecular fields, (4) general absorption due to an orientation of the permanent dipoles, and (5) rather general absorption due to·ions following the alternations of the electromagnetic radiation.

1. On 100 percent H_2SO_4

From a study of the absorbing and reflecting powers of more than twenty different liquids,[4] which illustrate the above types of absorption, it was found that the general absorption in water is exceptionally strong. This is explained by the strong permanent dipole, small molecular radius and the low viscosity of liquid water. We should therefore expect pure H_2SO_4 to have a general absorption that is considerably less than that of water. The fact that Rubens (Table I) observed a greater reflecting power for H_2SO_4 than for

water suggests that there were ions present. From our data, it can be estimated that the most concentrated H_2SO_4 measured by Rubens was about 36 normal. 100 percent H_2SO_4 is 37.4 normal but it is extremely hygroscopic and difficult to obtain. The most concentrated H_2SO_4 we measured was obtained by allowing fuming H_2SO_4 to give off the dissolved SO_3 gas in a dry atmosphere, so it seems probable that the most concentrated H_2SO_4 we measured contained some dissolved SO_3 rather· than H_2O. The especially rapid drop in the curves in Figs. 2 and 3 from 96 percent to 100 percent might therefore be due to SO_3 diluting the H_2SO_4 to give a lower reflecting and absorbing power than would be observed for 100 percent H_2SO_4. On the other hand, although the reflecting and absorbing powers of our strongest acid are less than for water, in view of its·being a much more viscous fluid and the molecules having a smaller permanent dipole and a larger radius than water, one might expect still smaller values for the reflecting and absorbing powers for 100 percent H_2SO_4 than we obtained.[5] In fact, our values give a relaxation time of less than 7×10^{-13} sec. and a radius of less than 0.3×10^{-8} cm which are obviously too small and they indicate that in our strongest acid there was a general absorption due to more than an orientation of the permanent dipoles of the H_2SO_4 molecules.

Relative to 100 percent H_2SO_4, we can only conclude that our measurements show qualitatively that the absorbing and reflecting powers of 100 percent H_2SO_4 are less than those of water.

2. Raman spectra results

The Raman spectra of H_2SO_4 solutions have been studied by several investigators.[6] Let us review here the interpretation as given by Woodward and Horner[7] which seems to be generally accepted: (1) The characteristic unsymmetrical Raman band of water begins to show in 75 percent H_2SO_4 solutions (volume concentrations are used) and increases rapidly.

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[5] C. H. Cartwright and J. Errera, Proc. Roy. Soc. A154 138 (1936).

[6] Nisi, Jap. J. Phys. 5, 119 (1929); Woodward, Physik. Zeits. 32, 212 (1931); R. Rao, Ind. J. Phys. 8, 123 (1933); S. Rao, Ind. J. Phys. 9, 195 (1934); R. M. Bell and M. A. Jeppesen, J. Chem. Phys. 3, 245 (1935); N. G. Pai, Phil. Mag. 134, 616 (1935).

[7] L. A. Woodward and R. G. Horner, Proc. Roy. Soc. A144, 129 (1934).

with dilution. (2) The Raman bands 381, 555, 910, 978, and 1121 cm⁻¹ are characteristic of the H_2SO_4 molecule and their intensities diminish rapidly with dilution. (3) The Raman bands 595, 895 and 1036 cm⁻¹ are characteristic of an HSO_4^- ion. They are not present in concentrated H_2SO_4 but appear in all solutions and their intensity is a maximum in 25 percent H_2SO_4. (4) The Raman bands 452 and 982 cm⁻¹ are characteristic of an SO_4^{--} ion. These bands begin with 50 percent H_2SO_4 and get stronger with dilution.

The Raman spectra are therefore interpreted as successive dissociations from H_2SO_4 to $H^+ + HSO_4^-$ and from HSO_4^- to $H^+ + SO_4^{--}$. The existence of HSO_4^- ions is based on a comparison with the spectra of $KHSO_4$ solutions; but, this does not deny the hypothesis that one molecule of water is combined with HSO_4^- to form an ion of $H_3SO_5^-$. The maxima of the freezing point curve and the viscosity curve in Fig. 1 are strong evidence for the latter as well as the fact that the Raman band of water only appears in more dilute solutions than one molecule of water per molecule of H_2SO_4. In the following we shall assume that ions of $H_3SO_5^-$ rather than HSO_4^- are formed.

Pfund has studied the near infrared reflecting power of several H_2SO_4 solutions[8] and found variations which appear to be in accord with the Raman data. Several of the characteristic bands are seen to be both infrared and Raman active.

3. Characteristic absorption band at about 60μ

The broad absorption band around 60μ in liquid water can be attributed to a movement of the water molecules as a whole in a quasi-crystalline structure.[9, 10] The fact that H_2SO_4 has a band at about 60μ, as shown in Fig. 3, can hardly be interpreted as evidence that the structure of H_2SO_4 is a water molecule loosely attached to a SO_3 molecule, although the transition from SO_3 to H_2SO_4 is continuous with the addition of H_2O to SO_3. Both the Raman and ultraviolet[11] spectra of H_2SO_4 deny such an hypothesis. Since this band is present in both

concentrated and dilute solutions, it is probably due to intramolecular rather than intermolecular motions, for the intermolecular fields are a function of concentration. It seems likely that its origin is due to a characteristic frequency of the sulphate radical, SO_4. The intensity of the absorption further suggests that it is a fundamental band rather than due to a combination of near infrared frequencies. That this band has not been observed in the Raman spectra of H_2SO_4 and its solutions might be due to its not being Raman active or it might be due to the experimental difficulties encountered in observing Raman bands of such low frequency. Indeed, the active Raman band in water around 60μ is not mentioned in the Raman investigations on H_2SO_4 solutions.

4. Structure of ions in H_2SO_4 solutions

According to the theory of valency, the two structures of H_2SO_4 and H_2SO_4 plus one molecule of H_2O shown in Fig. 4 should be considered.[12] The stability of $H_2SO_4 \cdot H_2O$, as is shown by the freezing point curve and the viscosity curve in Fig. 1 is rather strong evidence for structures (A) and (A') which form a stable six-ring with the water molecule. The electrical conductivity of the solutions must of course be accounted for by the presence of ions and in Fig. 5 are shown some possible structures as the dilution is increased. It is, however, probable that many of the ions are more than singly hydrated because of the small maximum in the freezing point curve and the sudden change in the index of refraction of visible light[13] for $H_2SO_4 \cdot 2H_2O$. Also the freezing point curve shows that there is a strong tendency for four water molecules to unite with H_2SO_4, although it is not certain that such an association would be stable at room temperature.

Professor Lowry and Professor Pauling have suggested that the structure of $H_2SO_4 \cdot H_2O$ shown in Fig. 6 should be considered. Pauling suggests that both SO_4^{--} and OH_4^{++} would have a tetrahedral structure and intermolecular forces would cause these radicals to form a quasi-

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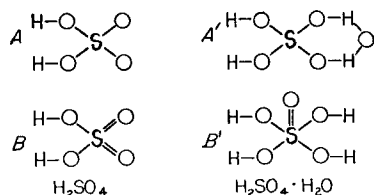[13] J. L. R. Morgan and C. E. Davis, J. Am. Chem. Soc. **38**, 555 (1916).
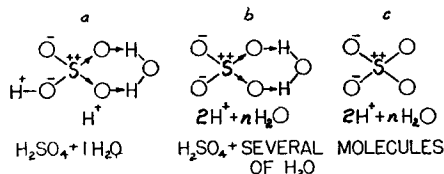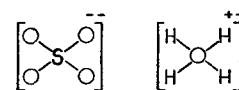
FIG. 4.

FIG. 5.

FIG. 6.

crystalline structure in the liquid. The rapid increase in the electrical conductivity curve in Fig. 1 and the reflecting and absorbing powers in Figs. 2 and 3 in the neighborhood of 100 percent H_2SO_4 seem most easily explained in terms of this structure which gives doubly charged ions and therefore a high electrical conductivity in spite of the large viscosity (see formula (4)). However, the behavior of the electrical conductivity as well as the results of Raman spectra (and the breaks at 95 percent concentration in Figs. 2 and 3, if we assume them to be real) indicate that the structure shown in Fig. 6 is probably only present in very strongly concentrated H_2SO_4.

5. Ionic absorption

The large increase in the general reflecting and absorbing powers of the solutions over pure water and H_2SO_4, as shown in Figs. 2 and 3, is due to the presence of ions which follow the alternations of the electromagnetic waves in this region of the spectrum. The wave-length, λ_0 (in μ) for which inertia begins to play a small part in hindering the motion of an ion is given by the formula:[3]

$$\lambda_0 = 1.65 M/\eta r, \qquad (3)$$

where M is the molecular weight of an ion of radius r (in A) and η is the specific viscosity of the solution. For the ions in H_2SO_4 solutions λ_0 is probably less than 50μ and their general absorption, as derived from Maxwell's equations, should be given approximately by the relation:

$$n\alpha \approx Ze^2\lambda/n\eta r, \qquad (4)$$

where Z is the number of ions of charge e per unit of volume and n is the index of refraction of the solution. Too many factors are involved to draw more than qualitative conclusions at present concerning the number and structure of the ions in as complicated an electrolyte as a solution of H_2SO_4; for, as the Raman spectra

show, at room temperature several types of ions are present and their respective concentrations are not well defined as might be suggested by the freezing point curve. From a rather extended study of the reflecting and absorbing powers of different concentrations of electrolytes of HCl, LiCl, NaCl, KCl, KBr, LiI, KI, ZnI_2, $MgSO_4$, and KOH, it was found that the increase in the reflecting and absorbing powers of water by the addition of H_2SO_4 is well accounted for by the formation of two hydrogen ions and one negative ion of SO_4^{--} until a concentration of about 12 normal is reached. Then ions of hydrogen and $H_3SO_5^-$ begin to predominate—a result that is in harmony with the Raman spectra findings. The rapid decrease in the reflecting and absorbing powers as well as the electrical conductivity from 36 normal to 37.4 normal (100 percent H_2SO_4) suggests that ions of OH_4^{++} and SO_4^{--} are first formed when water is added to H_2SO_4 and they reach a maximum concentration in 36 normal solutions. On further dilution, however, they must be replaced by ions of H^+ and $H_3SO_5^-$ to account for the change in electrical conductivity, infrared reflecting and absorbing powers, and the Raman spectra results.