

# THE SYSTEM SULPHURIC ACID—ETHERS.

## PART I. SYSTEM SULPHURIC ACID—METHYL ETHER.

By S. K. Kulkarni Jatkar and N. G. Gajendragad.

### INTRODUCTION.

Ethyl ether is an important solvent in many technical processes, but cannot be used in India owing to its great volatility and risk of explosion when the vapour gets mixed with air. One of the efficient methods of recovering the vapours is to use concentrated sulphuric acid as absorbing medium, forming additive compounds having low vapour pressure with one and two mols. of ether. The ether can be recovered by diluting the mixture and distilling.

In the course of our work on the catalytic production of ethers (This *Journal*, 1932, 15A, 59) sulphuric acid was used to absorb the methyl ether. One volume of sulphuric acid can absorb 600 volumes of the gas, most of which can be liberated by adding water. It was interesting to find out if methyl ether also forms additive compounds like ethyl ether.

The system sulphuric acid and ethyl ether was first studied by Pound (*Jour. Chem. Soc.*, 1911, 99, 698) who as a result of measurement of density, viscosity, surface tension and conductivity came to the conclusion that the complex  $(C_2H_5)_2O, H_2SO_4$  was definitely formed. He further extended his studies (*Jour. Chem. Soc.*, 1922, 110, 944) to ternary mixtures of sulphuric acid, water and ethyl ether and concluded that the complexes (1)  $H_2SO_4 \cdot H_2O$ , (2)  $H_2SO_4 \cdot Et_2O$ , (3)  $3H_2SO_4 \cdot 2Et_2O$ , (4)  $H_2SO_4 \cdot H_2O$  and (5)  $H_2SO_4 \cdot H_2O \cdot Et_2O$  were formed. Of these (1), (2) and (3) have been isolated.

Tschelinceo and Kozloo (*Jour. Russ. Phys. Chem. Soc.*, 1914, 46, 708) studied the thermochemical changes accompanying the compound formation and showed perfectly definite heat development which come to a sharp end after the introduction of each of the two molecules of ether in the case of ethyl ether and isoamyl ether. The amount of heat generated in Calories per mol. are  $H_2SO_4 + Et_2O \rightarrow 6.83$ ,  $H_2SO_4 \cdot Et_2O + Et_2O \rightarrow 1.74$ . These values are analogous to the values in case of water  $H_2SO_4 + H_2O \leftarrow 6.38$  and  $H_2SO_4 \cdot H_2O + H_2O \rightarrow 3.04$ .

*Viscosity.*—In the case of the system  $H_2SO_4 \cdot H_2O$  it is well known that in the viscosity composition curve a maxima occurs at the 50% molar composition and minima at 80% molar.

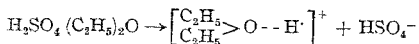
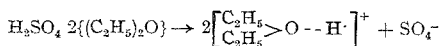
L. Sabinina (*Jour. Gen. Chem. U.S.S.R.*, 1933, 3, 87–90) studied the viscosities of mixtures of ether and sulphuric acid at 0°, 10°,

20° and 30°. While Pound (*loc. cit.*) found a maximum in viscosity at 50 per cent. molar, Sabinina (who does not mention Pound's work) found the maxima at about 56% molar sulphuric acid at all the temperatures. But the curve showing dependence of the temperature coefficient of viscosity on the composition shows a clear maxima at 50 molar; but the second compound is not clearly indicated in the data found both by Pound and Sabinina.

*Conductivity.*—The high electrical conductivity of the mixtures of ethyl ether and sulphuric acid discovered by Plontnikov in 1908 has been a puzzle to scientists for a long time. The suggestion that ethyl ether, in solution of a substance of high dielectric constant, (80) is dissociated into ions is *a priori* improbable. One of the difficulties of interpretation of the conductivity composition curves lies in the fact that no simple relation exists between the conductivities of these mixtures and the composition of the complexes, the presence of which has been indicated by other methods of investigation such as viscosity, freezing point and thermo-chemical data.

Pound (*loc. cit.*) noted the sharp descent to a mixture of minimum conductivity which is *analogous to the case of sulphuric acid water mixture* at 99.7%. As more ether was added there is a maximum conductivity (.0855) at 89% acid.

M. Usanovich (*Jour. Gen. Chem. U.S.S.R.*, 1934, 4, 215) who also does not quote Pound, measured the electrical conductivity of the mixtures of sulphuric acid with ethyl ether at 0° and 25°. The two isotherms of specific conductivity pass through a maximum at 90–92% sulphuric acid, which he ascribed to the dissociation of the oxonium compounds:



Usanovich found that the temperature coefficient of electrical conductivity passed through a minimum at 50% and through a maximum at 33% molecular composition coinciding with the composition of the compounds obtained by Tschelinceo and Kozloo (*loc. cit.*).

Usanovich says that when ether was added to sulphuric acid having a conductivity of  $0.9 \times 10^{-2} - 1.5 \times 10^{-2}$ , the maximum was reached at 90% after which the curve *coincides* with that found by Kohlrausch (*Pogg. Ann.* 1876, 159, 233) for *aqueous* solution. Further addition led to the fall in conductivity which was more pronounced than in the case of water.

P. Walden has shown that sulphuric acid is a very difficult substance for electro-chemical investigations. Although Plotnikov

discovered the high electrical conductivity of mixtures of sulphuric acid and ethyl ether in 1908, he did not succeed in obtaining constant values as he found that the magnitude of conductivity changed with time. Our experience with methyl and propyl ether showed changes in the physical properties particularly when starting with mixtures from sulphuric acid side.

### EXPERIMENTAL.

The densities, viscosity and electrical conductivity were measured in a specially constructed apparatus (Fig. 1). Pure sulphuric acid

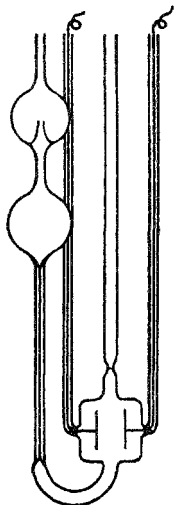


FIG. 1

was prepared in the cell itself by adding fuming acid to 96% acid until minimum conductivity was obtained (Hantzsch, *Z. Physikal Chem.*, 1907, **61**, 257). Methyl ether was prepared by passing vapours of methyl alcohol through sulphuric acid at 127°, the gas being absorbed in cold sulphuric acid from which it was liberated by adding water and after being passed through caustic soda and calcium chloride was led into the apparatus through the capillary side. The results of the measurements are given in Table I and shown graphically (Fig. 2) where relative viscosities and relative conductivities are plotted against percentage composition of the mixture.

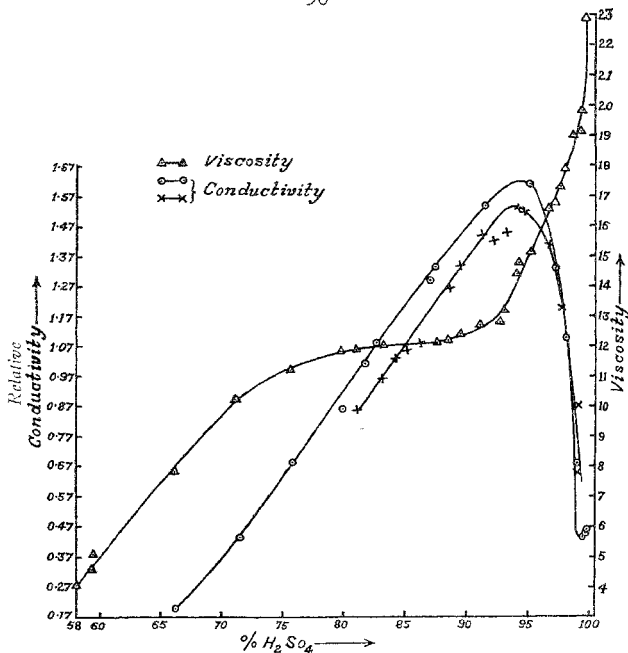


FIG. 2  
System Methyl ether—Sulphuric acid

TABLE I.  
System Sulphuric acid and Methyl ether.

Expt. No.	% Composition : Acid	Specific Conductivity $\times 10^4$	Density 25°	Relative Viscosity
19	100.6	159	..	..
1	100	121	..	..
20	99.8	134	..	..
27	99.8	203	1.838	22.91
43	99.6	201	..	..
28	99.6	173	1.838	22.91
29	99.4	223	1.826	19.82
1a	99.1	456	1.825	19.10

TABLE I—*Contd.*

Expt. No.	% Composition: Acid	Specific Conductivity $\times 10^4$	Density 25°	Relative Viscosity
21	98.9	343	1.820	19.00
30	98.8	361	1.818	18.90
31	98.1	614	1.810	17.90
2	97.9	694	1.795	17.30
32	97.2	798	1.791	16.84
33	96.9	856	1.785	16.67
3	96.9	851	1.785	16.60
44	96.0	823	1.770	16.60
34	95.5	1068	1.765	15.10
4	94.8	1031	1.750	14.80
5	94.3	1060	1.740	14.45
6	93.2	1100	1.725	13.20
7	92.9	1104	..	..
35	92.8	..	1.717	12.87
45	92.7	1082	1.730	12.80
8	92.1	1109	1.710	12.80
36	91.4	..	1.692	12.84
22	91.4	107	..	..
9	91.2	1100	1.640	12.70
10	89.8	1074	1.665	12.45
11	89.7	1063	..	..
12	88.7	1021	1.650	12.30
13	88.5	1013	..	..
46	87.7	1097	1.620	12.15
14	87.4	985	..	..
37	87.1	..	1.618	12.13
15	86.3	896	1.605	12.10
23	85.4	893	..	..
16	85.3	876	1.590	12.08
24	85.0	799	..	..
17	85.2	853	1.570	12.05
18	83.1	804	..	..
47	82.8	906	1.555	12.90
25	82.7	779	..	..
38	81.8	..	1.527	11.96
26	81.0	725	1.520	11.90
48	79.9	733	..	11.80
39	75.9	..	1.437	11.26
49	72.8	445	..	..
40	71.4	..	1.370	10.21
41	66.2	..	1.295	7.86
50	65.1	167	..	..
51	59.4	84	1.265	4.60
42	58.3	..	1.195	4.09

The first five results are for sulphuric acid water mixtures. The experiments have been arranged in order of the percentage of acid in the mixture. Experiments Nos. 1-18 were carried out using 100% sulphuric acid, Nos. 19-26 with 100.6%, Nos. 27-42 with 99.8% and Nos. 43-51 with 99.6% acid.

## DISCUSSION.

With increasing addition of methyl ether the viscosity drops very rapidly with composition and remains somewhat constant near 83% acid and falls with further addition until the concentration reached is 58%. There is no evidence to show the formation of a compound  $\text{H}_2\text{SO}_4(\text{CH}_3)_2\text{O}$  at 68% composition. The slope of the curve, however, changes at 81% and 76% corresponding to the formation of compounds  $(\text{CH}_3)_2\text{O} \cdot 2\text{H}_2\text{SO}_4$  and  $2(\text{CH}_3)_2\text{O} \cdot 3\text{H}_2\text{SO}_4$ . A compound of ethyl ether and sulphuric acid corresponding to the latter has been reported by Pound (*loc. cit.*).

In the case of conductivity we get a minima at 99.4% composition and maxima at 94% after correcting for viscosity. It is interesting to note that conductivity at both maxima and minima is the same as that of sulphuric acid water mixture which led us to suspect that we are in reality dealing with the same phenomenon. It appears that methyl ether has combined with sulphuric acid to form dimethyl sulphate and water and the actual conductivity is due to the system sulphuric acid and water. This is confirmed by calculating the relative amounts of the two components in the system on the basis of the above chemical reaction and it is found that the calculated minima and maxima occur at 99.6% and 96.6% which are in very good agreement with the values 99.7 and 96.7 found by Knietzsch in the case of the system sulphuric acid and water.

It is interesting to compare our above finding regarding conductivity to the studies of the system sulphuric acid and ethyl ether reported by Pound (*loc. cit.*) and Usanovich (*loc. cit.*). The minima occurs in this case at 98.4% of acid, which, on calculation, as in the case of methyl ether, comes to 99.6% being in good agreement with the value found in the case of water. The maxima occurs at 89%, which, on the basis of similar calculation works out as 96.7 and is in perfect agreement with the value of the system sulphuric acid and water. The magnitude of the specific conductivity is 0.085 which is naturally lower than that for the other two systems (.1100) owing to the effect of dilution and change in the dielectric constant of the medium. Pound has reported a conductivity maxima (.1092) when 94.7 gms. of 98.25% acid were mixed with 4.3% ethyl ether. This, on the basis of similar calculations, yields a value of 96.8% as the composition of the sulphuric acid water mixture, which taken along with the magnitude (.1092) of conductivity in this case, conclusively proves that chemical reaction takes place even when 98% acid is used for absorbing the ether. Thus the high conductivity of these systems attributed by Usanovich to the dissociation of the oxonium compound formed from ether and sulphuric acid, conform to the simple explanation that dialkyl sulphate and water are formed as the result

of chemical action, the conductivity being due to the system sulphuric acid and water.

The following table summarises the results for the minima and maxima in conductivity of mixtures of sulphuric acid with water, methyl ether and ethyl ether.

System	Minima			Maxima			Authors	
	Ether	H <sub>2</sub> O	Conductivity	Ether	H <sub>2</sub> O	Conductivity		
H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> O	..	..	99.7	.01	..	96.7	-1100	Knietsch (1901)
H <sub>2</sub> SO <sub>4</sub> Me <sub>2</sub> O	..	99.4	99.6	.03	94.0	96.6	-1100	Authors (1937)
H <sub>2</sub> SO <sub>4</sub> Et <sub>2</sub> O	..	98.4	99.6	.01	89.0	96.7	-.0835	} Pound (1911)
H <sub>2</sub> SO <sub>4</sub> (98.3%) Et <sub>2</sub> O	..	..	..	94.7	96.8	-1092		

### SUMMARY AND CONCLUSION.

A study of the viscosity of the system sulphuric acid-methyl ether at 25° did not reveal the maxima corresponding to the formation of the compound H<sub>2</sub>SO<sub>4</sub>R<sub>2</sub>O found in the case of mixtures of sulphuric acid with water and other ethers.

The electrical conductivities of the mixtures of sulphuric acid with methyl and ethyl ethers show that the conductivity observed is due to the water formed as a result of sulphonation following the formation of additive compounds.

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*Department of General Chemistry,  
Indian Institute of Science,  
Bangalore.*

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