SYSTEM SULPHURIC ACID-ETHERS.

PART II. SYSTEM SULPHURIC ACID PROPYL ETHER.

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INTRODUCTION.

There is increasing evidence to show the existence of the oxonium compounds $H_2SO_4R_2O$ and $H_2SO_42R_2O$ in the liquid state from the measurement of viscosity, freezing point, vapour pressures, heats of formation, and, temperature co-efficient of viscosity and electrical conductivity. Although such data are more complete in the case of the system H_2SO_4,H_2O and $H_2SO_4Et_2O$ there are no data for the mixtures of sulphuric acid with other ethers.

Viscosity determinations have been extensively employed for demonstrating the existence of complexes in binary mixtures. A maximum point in the viscosity concentration curve indicates complex formation and establishes its composition. In Part I (*This Journal,* **20A**, 87–93), we discussed the viscosities of the mixtures of sulphuric acid with water, methyl ether and ethyl ether. In the case of sulphuric acid water mixtures, it is well known that there is a maximum in the viscosity composition curve at 50% molar. In the case of mixtures with ethyl ether, although the earlier results of Pound (*J.C.S.*, 1911, **99**, 698) definitely established the position of maximum at 50% molar, Sabinina (*Jour. Gen. Chem. U.S.S.R.*, 1933, **3**, 87) showed that the maxima was displaced to 56% molar, and did not change with temperature. There are numerous theories to explain the displacement of maxima in the viscosity curve based upon the ternary character of the system according to which the maximum is shifted towards the side of the component having higher viscosity, and depends upon the temperature. It is, therefore, untrustworthy to deduce from the position of the maximum the chemical composition of the complex. The discrepancy in the above case may, however, be due to chemical reactions between ether and sulphuric acid as the corresponding conductivity data quantitatively fit in with the assumption that dialkyl sulphate and water are formed as suggested by us (*loc. cit.*), depending upon the method of preparing the mixtures.

In the case of mixtures with methyl ether, we found that although the tendency towards formation of a molecular aggregate was shown by a very strikingly flat maximum the chemical composition of the complex could not be deduced. The mean position of the maximum was also shifted very much towards the sulphuric acid side owing to wide difference in the viscosities of the two components.

In this paper we have extended our researches to the study of the system sulphuric acid propyl ether and found that very high maximum occurs at 50% molar composition showing the formation of the compound $H_2SO_4\ Pr_2O$. It appears, therefore, that the failure of direct viscosity composition diagram in indicating the composition of the complex in the case of methyl ether may be either due to the fact that the affinity between sulphuric acid and methyl ether is not sufficient to bring about combination, or to the increased difference in the relative viscosities of the two components.

EXPERIMENTAL.

The apparatus employed for measurements of viscosity and conductivity was same as that described in Part I. Propyl ether was prepared by passing pure *n*-propyl alcohol over potassium alum as the catalyst at 190° (*cf.* Gajendragad and Jatkar, *Jour. Ind. Chem. Soc.*, 1935, **12**, 486).

The results of experiments with propyl ether are given in Table I which shows the various values for density, relative viscosity and specific conductivity for the various mixtures, and are showed graphically in Fig. 1.

TABLE I.

System Sulphuric Acid and Propyl Ether.

Expt. No.	% H_2SO_4	Density	Relative Viscosity	Sp. Conductivity 10^4
1	100·0	1·829	282·4	109·9
2	97·3	1·781	266·3	523·1
3	94·9	1·743	290·4	661·1
4	92·6	1·701	247·4	696·7
5	87·9	1·622	248·5	685·8
6	86·1	1·636	234·8	666·0
7	81·4	1·570	242·3	546·2
8	76·8	1·511	256·9	403·3
9	70·3	1·446	282·6	242·9
10	64·3	1·383	341·5	146·5
11	58·6	1·321	393·0	85·8
12	53·1	1·268	434·2	46·2

TABLE I—*Contd.*

Expt. No.	% H_2SO_4	Density	Relative Viscosity	Sp. Conductivity 10^4
19	50·9	1·156	341·0	34·6
13	48·0	1·219	439·0	26·4
14	41·3	1·160	383·5	19·8
18	40·7	1·057	156·4	16·5
16	28·0	0·941	38·4	9·9
17	26·6	0·930	35·0	9·9
15	00·0	0·748	6·8	..

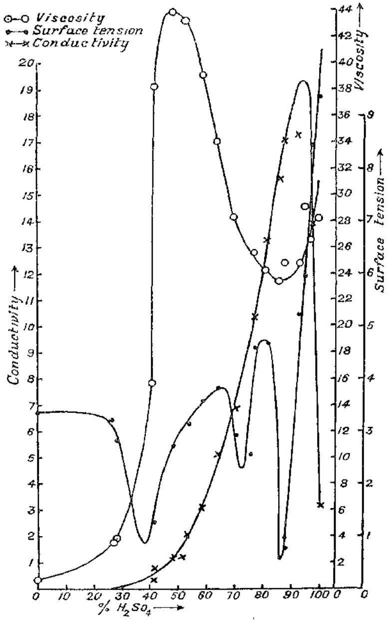

FIG. 1 System Sulphuric Acid N. Propyl Ether.

On addition of propyl ether to sulphuric acid there was a very rapid drop in viscosity which showed a minima at 86%. The discordant values before the minima was reached, were found to be due to the fact that these results changed with time indicating chemical reactions. The viscosity of the mixture in experiment No. 5 containing 88% acid changed from 249 units to 264 units in 17 hours. There is also a rapid fall in relative surface tension which, although not measured with any accuracy, still shows a sharp minima at 86%. (*cf.* Fig. 1). With further addition, the viscosity attained a maximum value at 50%, which was one and half times that of pure sulphuric acid, indicating the formation of a compound $H_2SO_4Pr_2O$.

Experiments 15–19 were done starting from propyl ether side. The figure (1) shows the sharp rise to the maximum at 50%, the value of which was, however, not the same as that obtained when starting from the sulphuric acid side. There was no change in the viscosity of the mixture containing 51% sulphuric acid even after seventeen hours (Expt. No. 19). But a mixture containing 41% acid (Expt. No. 14) which was prepared starting from sulphuric acid side showed a change in viscosity from 384 to 389 units in the same time.

The values for surface tension which are very approximate, however, do not show any indication of the formation of the 50% compound. It is interesting to recall here a similar conclusion of Pound (*loc. cit.*) in the case of the system sulphuric acid-ethyl ether.

In the case of the conductivity of the mixtures of sulphuric acid and propyl ether, the values near minima were erratic. The maximum conductivity is shown at 92.6% acid, while there is rapid fall in conductivity at 86%, which, when calculated on the basis of chemical reaction of the ether, gives 96.5% as the composition of the aqueous sulphuric acid, is in fair agreement with value obtained for water. The conductivity however is only 0.069 when compared to 0.1100 for water, owing to the dilution and change of medium as in the case of the system sulphuric acid and ethyl ether.

The comparative viscosities of the mixtures of water, methyl ether, ethyl ether and propyl ether with sulphuric acid are shown in Fig. 2 which shows that, with increase in the molecular weight of the ethers, the viscosity of the intermediate compound $H_2SO_4\ R_2O$ increases to a high value. In the region where the compound $H_2SO_4\ 2R_2O$ might exist the slope of the curve of viscosity against composition is also high, but there is no direct indication of compound formation.

A great many of the workers hold the view that although the formation of maximum does imply molecular aggregation, it is untrustworthy to deduce from the position of the maximum the chemical composition of the complex since, as already pointed out, the position

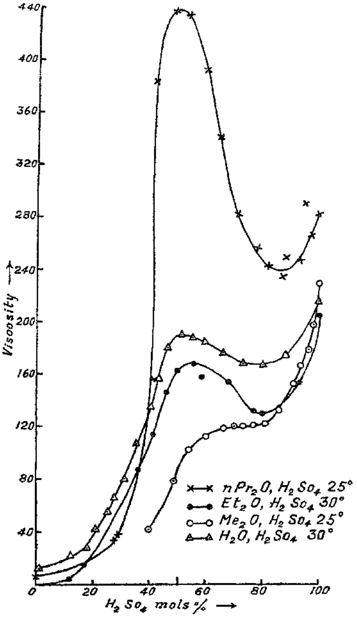

FIG. 2. Viscosity of Mixtures of Ethers and Sulphuric Acid.

depends upon the relative viscosities of the two components and frequently alters with temperature. The nature of the complex should be determined by the maximum deviation from the mixture law, rather than from the position of the maximum itself.

We may take into account the simplest of ideal law for the properties of liquid solutions, *viz.*, that fluidity is the additive property so that $F = n_1F_1 + n_2F_2$ where F is the fluidity and n the mol fraction. If the deviations from this rule are plotted against molar composition a maximum deviation should be shown at the 33.3% molar and 50% molar in the case of the system sulphuric acid and ethers. The results of such calculations for the mixtures of sulphuric acid with water, methyl ether, ethyl ether and propyl ether are given in Tables II, III, IV and V and shown graphically in Fig. 3 in which the negative deviations of the observed fluidities from those calculated by the above formulæ are plotted against molar composition.

TABLE II.

Fluidity of the System Sulphuric Acid Water.

	Mols. %	Calc.	Obs.	Diff.
1	0·00	130·00	130·00	0·00
	0·03	129·97	85·47	44·5
2	0·06	129·95	70·42	59·53
3	12·2	114·71	43·45	71·26
4	18·5	106·81	33·84	72·97
5	20·5	104·52	24·15	80·37
6	25·1	98·54	17·77	80·77
7	27·3	95·78	15·41	80·37
8	30·6	91·90	12·42	79·48
9	35·2	85·88	9·35	76·53
10	39·7	80·25	7·41	72·84
11	42·9	76·24	6·38	69·86
12	46·5	71·72	5·54	66·18
13	51·2	65·83	5·25	60·58
14	54·8	61·33	5·33	56·00
15	59·3	55·68	5·44	50·24
16	66·2	47·04	5·71	41·33
17	72·2	39·52	5·91	33·61
18	80·4	29·41	5·97	23·44
19	87·8	19·97	5·80	14·17
20	99·6	5·18	4·68	0·50
21	100·0	4·68	4·68	0·00

Table III.

Fluidity of the System Sulphuric Acid Methyl Ether

	Mols. %	Calc.	Obs.	Diff.
1	0·00	440·0	440·00	0·00
2	39·64	266·9	24·45	242·45
3	40·72	262·6	21·74	240·86
4	47·91	231·3	12·72	218·58
5	53·96	204·9	9·79	195·11
6	59·72	179·8	8·88	170·92
7	65·09	152·0	8·47	143·53
8	66·69	149·4	8·40	141·00
9	67·83	144·4	8·36	136·04
10	69·32	138·0	8·33	129·67
11	71·46	128·7	8·30	120·40
12	73·17	121·2	8·28	112·92
13	74·72	114·4	8·26	106·14
14	76·05	108·7	8·26	100·44
15	77·02	104·5	8·20	96·30
16	80·33	90·06	8·13	81·93
17	82·98	78·53	7·87	70·66
18	83·30	77·14	7·81	69·33
19	84·50	71·78	7·81	63·97
20	85·61	67·08	7·81	59·27
21	85·86	65·99	7·75	58·24
22	86·53	63·07	7·58	55·49
23	88·58	54·14	6·89	47·25
24	89·54	49·96	6·76	43·20
25	90·94	43·86	6·62	37·24
26	91·84	39·94	6·02	33·92
27	93·65	32·06	6·02	26·04
28	93·74	31·66	6·00	25·66
29	94·21	29·62	5·94	23·68
30	95·60	23·56	5·78	17·78
31	95·97	21·95	5·59	16·36
32	97·57	14·98	5·29	9·69
33	97·77	14·11	5·26	8·85
34	100·00	4·40	4·40	0·00

Table IV.

Fluidity of the System Sulphuric Acid and Ethyl Ether (Pound).

	Mols. % acid	Fluidity		
		Obs.	Calc.	Diff.
1	0	468·6	468·6	0
2	5·09	366·3	445·02	108·72
3	7·60	323·0	433·34	110·34
4	13·21	229·4	407·33	177·93
5	17·37	172·7	388·03	215·33
6	24·04	101·8	357·09	255·29
7	32·68	45·47	317·01	271·44
8	36·82	28·74	297·81	269·07
9	39·82	21·05	283·89	262·84
10	42·41	14·9	271·9	257·0
11	45·10	11·4	259·4	248·0
12	51·37	7·46	230·3	222·9
13	55·25	6·51	212·3	205·8
14	58·23	6·19	198·5	192·3
15	63·14	6·23	175·7	169·5
16	66·00	6·38	162·5	156·1
17	72·90	7·25	130·5	123·2
18	81·94	7·87	88·5	80·7
19	88·08	7·25	60·1	52·8
20	90·88	6·89	47·1	40·2
21	91·16	5·91	45·8	39·9
22	94·77	5·34	29·0	23·7
23	96·58	5·27	20·6	15·4
24	98·24	4·90	12·9	8·0
25	99·15	4·83	8·7	3·9

TABLE V.

Fluidity of the Sulphuric Acid Propyl Ether.

	Mols. % acid	Fluidity		
		Obs.	Calc.	Diff.
1	0	147·10	147·10	0
2	27·35	28·57	107·83	79·26
3	28·83	26·04	105·71	79·67
4	41·67	6·39	87·27	80·88
5	42·27	2·61	86·41	83·81
6	49·04	2·28	76·69	74·41
7	51·90	2·93	72·59	69·66
8	59·56	2·55	61·59	59·04
9	65·21	2·93	53·58	50·65
10	71·13	3·54	44·98	41·44
11	77·55	3·89	35·76	31·87
12	81·95	4·13	29·45	25·32
13	86·60	4·26	22·77	18·51
14	88·29	4·02	20·35	16·33
15	92·82	4·04	13·84	9·80
16	95·08	3·44	10·60	7·16
17	97·44	3·76	7·21	3·45
18	0	3·54	3·54	0

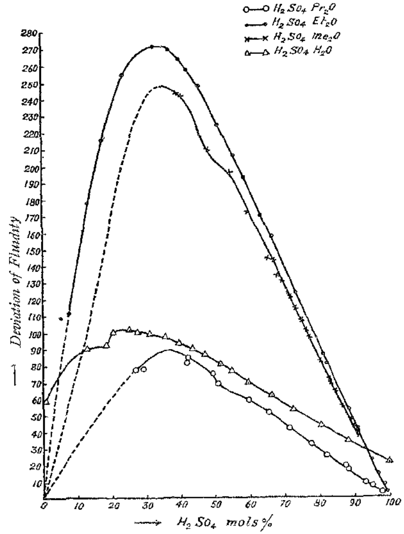

FIG. 3.

The maxima at 50 molar observed by Pound in the direct relationship between viscosity composition of the system H_2SO_4 Et_2O is not shown in the curve, while the maximum negative deviation is shown at 33% molar, corresponding to the compound H_2SO_4 $2Et_2O$ the existence of which has been proved by other methods of investigation. The viscosity data obtained by Sabinina (*loc. cit.*) showed a maximum in deviation of fluidity composition curve at 20% molar and a small inflection at 50% molar.

In the case of the system sulphuric acid methyl ether (the fluidity of which has been assumed to be one hundredth that of sulphuric acid) there is a small inflection in the fluidity deviation composition curve at 50 molar and the tendency to form a compound at 33% molar is quite evident although no experimental points are available at concentrations lower than 39% molar. It will be interesting to confirm the presence of this compound by measurements of viscosity at lower temperatures when more of the ether can dissolve in sulphuric acid.

The high maximum in the viscosity curve of the system $H_2SO_4nPr_2O$ is replaced only by a small inflection at 50 molar in Fig. 1 and the position of the maximum deviation at 33% molar is clearly evident.

The application of deviations of fluidity composition curve in the case of the system sulphuric acid-water results again in the total disappearance of the maxima at 50% observed in direct viscosity relationship and even the one at 33%, while the position of maximum deviation corresponds to $H_2SO_4\,3H_2O$, the existence of which has been very well established by several independent methods.

SUMMARY.

A comparative study of the viscosities of the mixtures of sulphuric acid, methyl ether, ethyl ether and *n*-propyl ether shows that the compounds $H_2SO_4R_2O$ and $H_2SO_42R_2O$ exist in the liquid mixtures, the first of which is indicated by maxima in direct viscosity composition curve and the second is shown by maximum negative deviation in the fluidity composition curve.

The conductivity of the system sulphuric acid propyl ether shows a maxima at 92.6% and rapid fall in conductivity from 86% which on the basis of quantitative reaction resulting in the formation of water and dialkyl sulphate, corresponds to 96.5% of the aqueous sulphuric acid.

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