Sugden's Parachors. Part V. Mercaptans.

By Balwant Singh and Ram Singh.

Liquids can be classified broadly into two groups, which are usually distinguished by the terms "normal" and "associated". The latter show a number of abnormalities in their physical properties, which are usually explained by the formation of aggregates of simple molecules to give an easily dissociated complex.

According to Sidgwick ("The Electronic Theory of Valency", *pp.* 134-154) in the case of associated liquids, there is a combination between the molecules through the formatibn of co-ordinate links.

Taking Richards and Carver's results for the surface tension of ethyl alcohol at 20° (*J. Amer. Chem. Soc.*, 1921, **43**, 827), Jones (*J. Chem. Soc.*, 1928, *p.* 1197) calculated its parachor, which has been found to be 126·7, while the theoretical value is 132·2. There is a contraction of −5·5 units at 20° for the single molecule, or −11 units for the double. This result is consistent with the view that association of alcohol takes place by co-ordination through hydrogen and it is accomplished by a singlet link, *i.e.*, C_2H_5-OH...OH-C_2H_5. One such bond requires a contraction of 12·4 units; this would the dimeric form. Thus it mean, apparently that the ethyl alcohol at 20° is on the average in is possible to account for these large contractions on the assumption that association involves single electron linkings (Sugden, *J. Chem. Soc.*, 1927, *p.* 1173).

Sidgwick and Bayliss (*J. Chem. Soc.*, 1930, *p.* 2031) from study of the parachors of *ortho*-phenols, have shown that the co-ordination of a hydrogen atom to form the group $=O\rightarrow H-$ involves a decrease of 14·4 units in the parachor of the single molecule. If this decrease represents the effect of the conversion of $>O+H-$ into $>O\rightarrow H-$, it should occur also in associated hydroxylic compounds in general.

Sulphur belongs to the same group of elements in the Periodic Table as oxygen. Each has six valency electrons and hence they possess analogous chemical properties. Oxygen, when it is present in combination with hydrogen as a hydroxy group —O-H, brings about association in hydroxylic compounds. The present work was undertaken to ascertain if sulphur in combination with hydrogen as the sulphydryl group —S-H would behave in the same way.

The parachors of a number of mercaptans have been determined in the fused state. Associated liquids, such as alcohols, phenols, fatty acids, etc., give parachors 4 to 8 units lower than the calculated values (Sugden, *J. Chem. Soc.*, 1924, **125**, 37; Jones, *loc. cit.*, Hunten and Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 161; Bhatnagar and Singh, *J. Indian Chem. Soc.*, 1930, 7, 666).

Experimental.

p-Chlorophenyl mercaptan, m. p. 50°, *p*-bromophenyl mercaptan, m. p. 75°, *p*-tolylmercaptan, m. p. 42·5°, *p*-methoxy-*m*-tolyl mercaptan, m. p. 39° were prepared for this investigation by the method of Stewart (*J. Chem. Soc.*, 1922, **121**, 2555).

The parachor is then calculated by the formula: $P = y^{\frac{1}{4}} M/D$, in which M is the molecular weight, y is the surface tension in dynes/cm.; D is the density of the liquid at a given temperature. Densities were determined with a **U**-shaped pyknometer (Sugden, *J. Chem. Soc.*, 1924, **125**, 1171) and the surface tensions by the method of maximum bubble pressure using the apparatus described by Bhatnagar and Singh (*J. Chim. phys.*, 1928, **25**, 21). The results are given in Table I.

Table I.

Substance.	Temp. (°C).	Density (g./c.c.).	Surface tension dynes/cm.	Parachor observed $P_{obs.}$	Parachor calculated $P_{calc.}$
1. Ethyl mercaptan*	2·0	0·8582	23·63	159·6	160·4
	16·7	0·8428	21·62	159·0	
			Mean	159·3	
2. Phenyl mercaptan†	16·9	1·080	38·46	254·0	
	25·5	1·074	37·67	253·9	
	35·0	1·059	36·31	255·4	255·3
	58·0	1·037	33·58	255·7	
	76·4	1·015	31·39	256·8	
			Mean	255·2	

* Ethyl mercaptan (Ramsay and Shields, *J. Chem. Soc.*, 1893, **63**, 1089).

† Phenyl mercaptan (Morgan and Chazal, *J. Amer. Chem. Soc.*, 1913, **38**, 1821).

	Substance.	Temp. (°C).	Density (g./c.c.).	Surface tension (dynes/cm.)	Parachor observed $P_{obs.}$	Parachor calculated $P_{calc.}$
3.	*p*-Chlorophenyl mercaptan.					
		60·0	1·224	36·80	291·1	
		70·0	1·214	35·90	291·7	
		80·0	1·204	34·52	291·2	292·5
		100·0	1·186	32·36	290·9	
				Mean	291·2	
4.	*p*-Bromophenyl mercaptan.					
		82·5	1·526	36·51	304·5	
		100·0	1·512	35·34	304·8	306·2
		116·5	1·494	33·79	305·0	
				Mean	304·8	
5.	*p*-Tolyl mercaptan.	50·5	1·022	33·84	292·8	
		64·4	1·010	32·48	293·3	294·3
		80·1	1·001	31·65	294·1	
				Mean	293·4	
6.	*p*-Methoxy-*m*-tolyl mercaptan.					
		44·6	1·093	36·48	346·5	
		59·7	1·081	35·51	348·0	353·3
		75·5	1·067	34·10	349·1	
				Mean	347·9	
7	Benzyl mercaptan.	18·5	1·058	39·26	293·6	
		30·0	1·047	37·96	294·1	294·3
		41·2	1·038	36·84	294·5	
				Mean	294·1	

From the above results, it is evident that the parachors calculated are in good agreement with the observed parachors except in case of *p*-methoxy-*m*-tolyl mercaptan where the values differ by 5·4 units owing to the presence of a methoxy-group (Bhatnagar and Singh, *loc. cit.*). The mercaptans, therefore, are not associated in the liquid or in the fused state. They behave as normal liquids. This is supported by the work of Auwers (*Z. phys. Chem.*, 1893, 12, 689; *ibid.*, 1899, **30**, 529). From the determination of the molecular weights of a large number of mercaptans, alcohols and phenols in benzene and napthalene by the cryoscopic method, he has shown that the mercaptans are cryoscopically normal substances as compared with the alcohols and the phenols. This fact is clearly borne out by the results given in Table II, where in the first five cases benzene is the solvent, while in the last two cases napthalene is the solvent.

TABLE II.

Substance.	Mol. weight.	Substance in 100 g. of solvent (g.).	Observed depression (°C).	Mol. weight (calc.).
1. Methyl alcohol	32	0·32	0·360	43
		0·66	0·612	53
		1·80	1·265	70
		4·42	1·978	110
		7·29	2·475	144
2. Benzyl alcohol	108	0·35	0·170	101
		0·74	0·310	106
		2·82	1·038	132
		5·12	1·510	165
3. Phenol	94	0·30	0·100	145
		1·27	0·410	152
		2·98	0·925	158
		3·93	1·175	164
4. β-Naphthol	144	0·38	0·135	137
		1·06	0·365	142
		2·32	0·740	154
5. Thiophenol	110	0·51	0·236	106
		1·01	0·453	110
		2·08	0·930	110
		4·30	1·928	109
6. *p*-Chlorothiophenol	144·5	1·10	0·541	140
		2·50	1·180	146
		4·98	2·350	146
		9·06	4·257	146
7. *p*-Methoxy thiophenol	140	0·82	0·402	141
		3·31	1·597	143
		5·72	2·665	148
		7·19	3·370	147

Molecular weights calculated as well as observed by the cryoscopic method in the case of the mercaptans are in fair agreement whilst the alcohols and the phenols give abnormal molecular weights in solution. Hence the presence of a sulphydryl group in mercaptans does not promote association.

The authors desire to thank Prof. S. S. Bhatnagar for advice and guidance.

UNIVERSITY CHEMICAL LABORATORIES,
LAHORE AND KHALSA COLLEGE, AMRITSAR.

Received March 9, 1931.