CXII.—*The Parachor of Tervalent Iodine.*

By NEVIL V. SIDGWICK and EDMUND D. P. BARKWORTH.

SUGDEN has shown (J., 1927, 1173) that compounds of quinquevalent phosphorus and antimony give anomalous parachor values, which he attributes to the formation of singlet links, although they may equally well be ascribed to the expansion of the valency group (see Sidgwick, "Electronic Theory of Valency," p. 128). The effect of an increase of valency could further be tested by means of compounds containing tervalent iodine, such as the dichloroiodides or the "esters" formed by iodoso-compounds with organic acids. On the analogy of phosphorus and antimony, we should expect such compounds to show a parachor defect of about 26 units.

Unfortunately, most of these compounds decompose before melting or just above their melting points, and they are not soluble enough for the parachor to be determined in solution by the method of Hammick and Andrew (J., 1929, 754). One substance, *viz.*, iodosobenzene propionate, $C_6H_5{\cdot}I(O{\cdot}CO{\cdot}C_2H_5)_2$, was found, however, which was sufficiently soluble, and its parachor was determined by this method in chlorobenzene solution. The result showed a parachor defect of 17·3 units.

Since this work was begun, Sugden and Henley (J., 1929, 1058) have determined the parachors of some selenium compounds, one of which, selenium oxychloride monohydrate, $SeCl_2(OH)_2$, has a structure exactly analogous to that of iodosobenzene propionate. Its observed defect was 22·5 units. Lowry and Gilbert (J., 1929, 2087), Sugden and Burstall (J., 1930, 229), and Simons (*J. Amer. Chem. Soc.*, 1930, **52**, 3488) have measured similar compounds of tellurium; if β-diethyl telluridibromide and tellurium tetrachloride, which are described by the respective authors as polar, are excluded, the average defect is 22·0 units. The slight differences between these values are too small to support any further conclusions, but they show a curious regularity, thus :

P				
26·7				
As (calc.)	Diff.	Se		
26·2	3·7	22·5		
Sb	Diff.	Te	Diff.	I
25·7	3·7	22·0	4·7	17·3

EXPERIMENTAL.

Willgerodt's method (*Ber.*, 1892, **25**, 3498) for the production of iodosobenzene propionate was modified, the solution of iodosobenzene in propionic acid being distilled under 12 mm., and the temperature not being allowed to rise above 60°. This process removes, first, the water formed during the reaction, and then the excess of propionic acid, and gives a much better yield. The residue when recrystallised once from ligroin (b. p. 60—80°) gave a yield of 70% of the theoretical. The material used in the parachor determination was recrystallised twice immediately before each experiment (Found : I, 36·45; available O, by titration, 4·6. Calc. : I, 36·27; av. O, 4·6%) and then melted and remelted at 67—70°, unaltered by further recrystallisation.

The solvent used in parachor determinations was chlorobenzene, in which iodosobenzene propionate dissolves with the absorption of considerable heat; it was purified by fractionation and distillation under reduced pressure.

Surface-tension Measurements.—The apparatus was essentially that of Sugden (J., 1924, **125**, 271) as modified by Hammick and Andrew (J., 1929, 754). It was calibrated with benzene before each determination, and was placed in a small thermostat containing water covered with a layer of paraffin. The manometer, containing xylene of $d_{4^\circ}^{25^\circ}$ 0·8576, was in a separate thermostat at 25°.

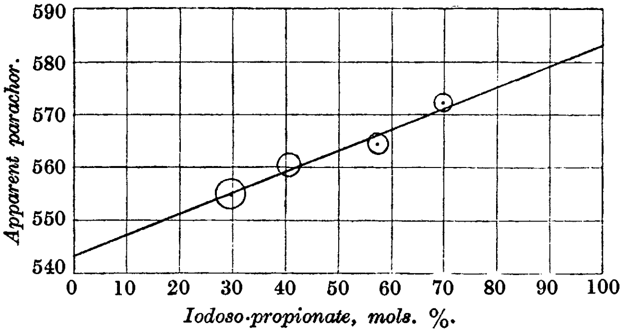
Density Measurements.—The densities were determined as described by Sidgwick and Bayliss (J., 1930, 2029).

The following table shows the results obtained :

	(i).	(ii).	(iii).	(iv).
Propionate, mols. %	29·46	40·34	57·40	69·85
Temp.	49·70°	50·07°	56·00°	60·20°
Surface tension, γ	32·42	33·99	34·88	35·97
Density	1·2965	1·3526	1·4126	1·4400
Apparent parachor of propionate	555·1	560·6	564·5	572·4

In the case of (iii) and (iv) the temperature had to be raised as shown to ensure solution. One determination of the parachor of the solvent chlorobenzene was also carried out at 50·09° and gave 244·9; in calculations the theoretical value of 244·3 was used. The apparent parachor of the propionate rises with the concentration of the solution (see Fig. 1) owing to the large difference in surface tension of the solvent and of the solute (compare Hammick and Andrew, *loc. cit.*). The values fall on a straight line, and were therefore extrapolated to 100% propionate by means of the formula

FIG. 1.



$$E = \frac{(N - \Sigma C)\Sigma(PC) + (\Sigma C^2 - \Sigma C)\Sigma P}{N\Sigma C^2 - (\Sigma C)^2}$$

derived by the method of the least squares. Here C represents the molar fractions and P the apparent parachors of the propionate; N is the number of determinations. This gives 583·5. The calculated value is 600·8 if —6·4 is allowed for the two ester groups. The defect is therefore 17·3.

Our thanks are due to Mr. D. Ll. Hammick for help and advice, and to Imperial Chemical Industries Ltd. for a grant towards the cost of the work.

DYSON PERRINS LABORATORY,
OXFORD.

[*Received, March 9th*, 1931.]
