THE MOLECULAR STATE OF INORGANIC LIQUIDS.

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Although the osmotic properties of inorganic substances in aqueous solution have been the subject of extensive investigation, few measurements have been made upon non-aqueous solutions of non-polar and dipolar inorganic compounds. In connection with other investigations in this laboratory we were led to examine the properties of arsenic trichloride, phosphorus trichloride, sulphur monochloride, phosphorus oxychloride, sulphuryl chloride and thionyl chloride for the purpose of ascertaining the molecular condition of these substances in non-polar media. Inasmuch as the ebullioscopic measurements of previous workers [1] led to erroneous results owing to the volatility of the solute, the cryoscopic method was employed in the present determinations.

Experimental.

Since the liquids suffer ready hydrolysis on exposure to the atmosphere they were allowed to stand for a short time over freshly activated silica gel (in order to adsorb traces of free hydrogen chloride) prior to distillation in an all-glass apparatus, which incorporated a long Dufton column and

TABLE I.

Substance.	Weight of Solute (g).	Depression.	Molecular Weight.
Arsenic trichloride M = 181·3	0·583	0·96	180
	1·214	1·97	182
	0·445	0·72	182
	0·986	1·58	184
			Mean 182
Phosphorus trichloride M = 137·4	0·308	0·60	152
	0·664	1·31	150
	1·175	2·31	150
	1·006	2·01	148
	1·389	2·73	150
			Mean 150
Sulphur monochloride M = 135·0	0·730	1·55	139
	0·983	2·07	140
	0·369	0·80	136
	0·885	1·90	137
	1·434	3·06	138
			Mean 138
Phosphorus oxychloride M = 153·4	0·223	0·39	169
	0·623	1·09	169
	0·958	1·70	167
	0·481	0·89	160
	1·187	2·15	163
			Mean 166
Sulphuryl chloride M = 135·1	1·079	2·26	141
	1·367	2·82	143
	0·442	0·95	137
	0·702	1·49	139
			Mean 140
Thionyl chloride M = 119·1	0·246	0·56	130
	0·610	1·41	127
	1·060	2·45	128
	0·765	1·88	120
	1·310	3·16	122
			Mean 125

condensing unit provided with guard-tubes of anhydrous calcium chloride and silica gel. Each liquid was subjected to at least three fractionations under ordinary pressure, but sulphur monochloride was fractionated under reduced pressure in order to avoid thermal decomposition. The boiling-points and densities of the pure liquids were as follows: arsenic trichloride, b.p. 129·0°/771 mm., $d_{4^\circ}^{25^\circ}$ 2·1497; phosphorus trichloride, b.p. 75·7°/758 mm., $d_{4^\circ}^{25^\circ}$ 1·5659; sulphur monochloride, b.p. 42·0°/23 mm., $d_{4^\circ}^{25^\circ}$ 1·6714; phosphorus oxychloride, b.p. 105·9°/762 mm., $d_{4^\circ}^{25^\circ}$ 1·6676; thionyl

[1] Oddo and Serra, *Gazz. Chim. Ital.*, 1899, **31**, 222.

chloride, b.p. 76·5°/766 mm., $d_{4°}^{25°}$ 1·6290 ; sulphuryl chloride, b.p. 69·2°/754 mm., $d_{4°}^{25°}$ 1·6570. Benzene (purified for molecular weight determinations) was distilled over phosphorus pentoxide (free from trioxide) before use as solvent.

The cryoscopic apparatus consisted of a Beckmann tube provided with a three-holed rubber stopper carrying a calibrated thermometer, a delivery tube for the admission of nitrogen, and a glass stirrer. The stirrer was arranged to operate through an air-tight device, while a slow stream of rigorously dried nitrogen was passed through the apparatus. The gas was led out through the side-tube of the Beckmann vessel, which was also fitted with a guard-tube of calcium chloride to prevent backward diffusion of moisture. The measurements were carried out in accordance with the orthodox procedure with due regard to the precautions adopted in the case of highly reactive solutions.[2] The final concentrations employed, however, were rather higher than is customary in cryoscopic work in order to detect, if possible, the incidence of association. The cryoscopic constant of benzene was determined from the depressions produced by pure naphthalene under the same experimental conditions. The mean value, $K = 52·3$, was employed in calculating the results shown in Table I.

Discussion.

The molecular state of the pure liquids has been studied by Vaubel,[3] but as may be seen from Table II, the values of the association factor

TABLE II.—ASSOCIATION FACTORS.

	Vaubel.	Ramsay and Shields.	Walden.	Longinescu.	Present Work.
$AsCl_3$	1·50	—	0·83	0·83	1·00
PCl_3	1·48	1·02	0·97	1·17	1·09
S_2Cl_2	1·37	0·95	1·27	1·44	1·02
$POCl_3$	—	1·00	0·99	0·99	1·08
$SOCl_2$	—	1·08	0·80	1·09	1·05
SO_2Cl_2	—	0·97	1·09	0·80	1·03

obtained by this investigator are higher than would be anticipated from the general properties of the liquids. The association factors calculated from the surface energy equations of Ramsay and Shields [4] and Walden [5] are in good agreement in the case of all the liquids with the exception of sulphur monochloride. The values computed from the empirical equation of Longinescu [6] correspond fairly well with those obtained by the other methods.

The cryoscopic measurements show that the observed molecular weight does not change appreciably with the concentration of the solution. Although the calculation of the association factors on this basis depends on the premise that no interaction occurs between solvent and solute, there is little doubt that these values are more reliable than those calculated from the surface energy relations. In fact, we find no discrepancy in the case of sulphur monochloride, which behaves as a perfectly normal liquid. The depressions produced by phosphorus

[2] Bowden, *J. Chem. Soc.*, 1939, 37.
[3] Vaubel, *J. prak. Chem.*, 1904, **69**, 138.
[4] Ramsay and Shields, *J. Chem. Soc.*, 1893, **63**, 1089.
[5] Walden, *Z. physik. Chem.*, 1909, **65**, 129.
[6] Longinescu, *J. Chim. physique*, 1903, **1**, 289.

trichloride and phosphorus oxychloride are slightly lower than the ideal, and these deviations may be due to internal pressure differences between solvent and solute or to slight association of the solute.

It has been found by Sugden and his co-workers [7] that the parachor of several of the above substances is independent of the temperature of measurement and that these liquids, therefore, are essentially normal. Moreover, measurements in this laboratory reveal that the variation of viscosity with temperature conforms to the Andrade exponential formula [8] in the case of arsenic trichloride, sulphur monochloride and phosphorus oxychloride. Although such conformity does not in itself prove that association is absent, it does imply that there is no change of association with temperature. In the case of phosphorus trichloride, sulphuryl chloride and thionyl chloride, however, there is appreciable departure from the exponential relation, and this is doubtless to be referred to the difference in the associative tendency of the molecules at different temperatures.

Summary.

Molecular weight determinations on non-polar and dipolar inorganic chlorides in benzene solution indicate that the liquids behave as normal solutes with the exception of phosphorus trichloride and phosphorus oxychloride which show slight deviations from ideality. The results are briefly discussed in the light of the various formulæ for calculating association factors, and also from the standpoint of the exponential formula for the variation of viscosity with temperature.

[7] Sugden, Reed and Wilkins, *J. Chem. Soc.*, 1925, **127**, 1525.
[8] Andrade, *Phil. Mag.*, 1934, **17**, 497, 698.