XLIV.—*Association of Phenols in the Liquid Condition.*

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IT is a well recognised fact that substances containing hydroxyl groups usually form associated molecules when in the liquid condition, the results obtained in this direction being mainly due to the researches of Ramsay and his co-workers (Ramsay and Shields, *Phil. Trans.*, 1893, **184**, 655; *Trans.*, 1893, **63**, 1089; Aston and Ramsay, *Trans.*, 1894, **65**, 167; *Zeitsch. physikal. Chem.*, 1893, **12**, 433; 1894, **15**, 89; Ramsay, *ibid.*, **15**, 106).—These authors applied a method indicated by Eötvös (*Wied. Annalen*, 1886, **27**, 452), and although the method of calculation employed has been fully explained in the papers quoted, a short reference seems desirable here, as the original expression was subsequently modified.

The assumption made by Ramsay and Shields in their first paper was that

$$K = \frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt}$$

should be the same for different liquids when γ is the surface tension, M the molecular weight of substance, v the specific volume, and t the temperature. This expression holds for substances which are non-associated in the liquid state, and a large number of compounds gave a mean value of this coefficient equal to 2.121. This number is not appreciably exceeded except in particular cases where experimental errors are likely to arise. A lower value is, however, frequently found and in such cases the molecular complexity may be deduced. For if K' be the coefficient found experimentally, the assumed molecular weight, M , in the calculation should be multiplied by

$$\left(\frac{2.121}{K'}\right)^{\frac{3}{2}} = x$$

in order to obtain the mean molecular weight of the liquid. The quantity x was at first described as the factor of association, but has since been shown to be probably greater than the average complexity. Van der Waals (*Zeitsch. physikal. Chem.*, 1894, **13**, 657) substituted the expression

$$x^{\frac{2}{3}} = \frac{k(\tau' - \tau) + \sigma'_M}{\sigma_M}$$

for that given by Ramsay; whilst Ramsay (*Proc. Roy. Soc.*, 1894, **56**, 175, and *Zeitsch. physikal. Chem.*, 1894, **15**, 112), finding that the values for the molecular surface energy are generally well satisfied by the expressions of the form

$$\gamma(Mv)^{\frac{2}{3}} = \frac{k(\tau - d)}{1 + \mu\tau}$$

where τ is the temperature expressed in degrees below the critical point, deduces the equation

$$x = \left[\frac{2.121}{k} (1 + \mu\tau) \right]^{\frac{3}{2}}$$

for calculating the factor of association. The effect of these corrections, is shown in the annexed table :

Substance.	Ramsay and Shields (uncorrected).	Van der Waals (corrected).	Ramsay (corrected).
Water	3.8 (0—10°)	1.9 (0°)	1.707 (0°)
Methyl alcohol ...	3.43 (16—46)	2.1 (20)	2.32 (20)
Ethyl „	2.74 (16—46)	1.61 (20)	1.65 (20)
Acetic acid	3.62 (16—46)	—	2.13 (20)

Subsequent workers who have used this method for the determination of molecular complexity have simply used the uncorrected expression: reference may be made to the papers of Bottomley (who points out that his results on account of being uncorrected are probably too high, *Trans.*, 1903, **83**, 1421) on the molecular formulæ of fused salts and of G. Carrara and G. Ferrari (*Gazzetta*, 1906, **36**, 419) on the complexity of various aliphatic compounds.

Amongst the hydroxylic compounds examined by Ramsay and Shields (*loc. cit.*) are a number of alcohols and fatty acids; one notices that these substances are always associated, but the greatest deviations are observed with the substances of lowest molecular weight (as deduced from vapour density); namely, the larger the groups attached to carbinol or carboxyl, the less is the tendency towards association.

Of phenolic compounds but little is known as to the degree of association. Ramsay and Shields's paper (*Trans.*, 1893, **63**, 1101) contains measurements for guaiacol; these furnish association factors of 1.08 between 19.6° and 46.0°, and of 0.96 between 46° and 78°, whilst phenol, on the other hand, exhibits very considerable association (*Trans.*, 1894, **65**, 168). Evidently the methoxyl group is responsible for this hindering of association, whilst the association of phenol itself must be referred to its hydroxyl group, seeing that the parent substance, benzene, is non-associated (*loc. cit.*, p. 1100). But whether the action of the methoxyl group is specific or due also to its position in the molecule cannot immediately be determined from the data given, although the work of Auwers on the molecular weight of phenols in benzene and naphthalene solutions would lead to the conclusion that orientation must have a decided influence.

In conjunction with Bartsch, Beveridge, Dohrn, Ewing, Gierig, Innes, Mann, Orton, Smith, and Walker, Auwers has carried out extensive cryoscopic investigations on the molecular weights of alcoholic and phenolic compounds dissolved in non-hydroxylic solvents (*Zeitsch. physikal. Chem.*, 1893, **12**, 689; 1894, **15**, 33; 1895, **18**, 595;

1896, 21, 337; 1899, 30, 300; 1900, 32, 39; 1903, 42, 51; *Ber.*, 1895, 28, 2878; 1898, 31, 3037). The results obtained have proved conclusively that alcohols and phenols generally form associated molecules in benzene and naphthalene solutions, and also that the association may be inhibited partially or entirely by introduction of substituents ortho to the hydroxyl group in the case of phenolic compounds.

It is consequently a matter of interest to learn whether this non-association is true in the limiting case, namely, when the compound in question is simply fused but not dissolved in another liquid. The results obtained were of such a character as amply to demonstrate the inhibiting influence of ortho-substituents. In calculating the results the original formula given by Ramsay and Shields has been adopted; the results are consequently probably too high in those cases where association occurs, nevertheless the existence of association is indicated and corrections could not very well be applied, as the critical points of the substances examined have only been determined in a few cases, whilst in others they would be indeterminable owing to the decomposition which occurs at higher temperatures.

EXPERIMENTAL.

(a) *Apparatus*.—The apparatus employed in these experiments is of a modified description; on the one hand the errors due to contact with air had to be avoided, on the other the apparatus designed by Ramsay and Shields was inapplicable on account of the fact that several of the substances examined undergo considerable decomposition when raised to their boiling points. A piece of capillary tubing of uniform bore was bent and fused to a larger piece of tubing with a diameter of 2 cm. The wider tube was fitted with a sound rubber stopper through which a tube was inserted, this and the end of the capillary tube being connected with rubber pressure tubing to a T-piece. The third arm of the T-piece was joined by rubber tubing, capable of being closed by a pinch-cock, with a tube connected on the one hand with a gauge, on the other with a Fleuss pump, washing bottles being placed between the pump and the apparatus. The pump was thoroughly overhauled prior to the experiments and was lubricated with an oil of very low vapour-pressure, so that the air-pressure in the whole system could be reduced to a few millimetres. Evacuation was effected when the portion of the apparatus in which the capillary rise was determined was already warm, in this way any air error may be reduced to a negligible amount. The results obtained in the case of phenol itself show a fair agreement with those published by Ramsay, Aston, and Shields, although our numbers for the density deviate somewhat from those given

by Kopp. Before an experiment the apparatus was cleaned with alcohol, water, fuming nitric acid, and water, in succession, and was then dried by a current of air at 100° . Before taking a reading of the capillary rise with the cathetometer, the apparatus was tilted so as to ensure complete wetting of the sides of the capillary tube.

The capillary tube was carefully calibrated by measurement of the lengths of several different threads of mercury, and only such tubing was employed as proved to have an even bore.

For a bath, a beaker containing approximately $1\frac{1}{2}$ litres of liquid was employed, the liquids used being water, glycerol, or paraffin; on one occasion concentrated sulphuric acid was employed. With this quantity of liquid and regulation of the heating flame it was possible to keep

the temperature within 0.1° for at least fifteen minutes. The temperature was read with two thermometers graduated in tenths of degrees; these had been calibrated by means of the ice point, steam point and the boiling point of bromobenzene.

The densities were measured at some definite temperature by comparison with an equal volume of water and the densities at other temperatures deduced by measurement of the expansion in dilatometers made of glass the coefficient of expansion of which had been determined. Two dilatometers were employed, one with a capacity of about 5 c.c., the other of about 9 c.c., the larger dilatometer being employed in all cases where the amount of material sufficed for the purpose.

Materials Examined.—The source of the materials and guarantee of their purity is briefly stated below.

Phenol.—"Synthetic" phenol of Kahlbaum.

o-Cresol.—Obtained from Schuchardt. Refractionated with a rod and disc column (15 discs) and distilled again immediately before use. The substance shows supercooling to a marked extent. For 20° below its melting point the supercooled liquid contracts regularly.

m-Cresol.—Merck's "extra pure." The substance gave a benzoyl derivative by the Schotten-Baumann method, which, without any recrystallisation, melted within 1.5° of the correct value. The cresol was fractionated with a rod and disc column and then twice rapidly distilled.

p-Cresol.—Obtained from Kahlbaum, fractionated with a rod and disc column, a fraction boiling within 0.25° being collected.

o-Nitrophenol.—Prepared from redistilled "absolute" phenol. The product was distilled three times in steam and then dried. On account of the numbers obtained the specimen was once more distilled in a current of steam; recrystallised from methyl alcohol and dried in a vacuum. A repetition of the density and capillarity determinations gave the same value for K .

m-Nitrophenol.—Purchased from Schuchardt and recrystallised from benzene.

p-Nitrophenol.—Prepared at the same time as the ortho-isomeride. The substance was recrystallised from (a) concentrated hydrochloric acid, (b) water with addition of animal charcoal, (c) slightly acidified water.

o-Chlorophenol.—Purchased from Schuchardt, once fractionated with rod and disc column, and then rapidly distilled twice. The determinations of density and capillarity were twice effected with practically identical results.

m-Chlorophenol.—Purchased from Schuchardt and fractionated (column), boiling point constant.

p-Chlorophenol.—Purchased from Schuchardt, fractionated and twice rapidly distilled; the boiling point was within 0.25° .

m-Bromophenol.—Prepared by the diazo-reaction from Kahlbaum's pure *m*-bromoaniline; the boiling point of the specimen was constant.

p-Bromophenol.—Purchased from Kahlbaum; the melting point was within 1° .

Ethyl Salicylate.—Prepared from salicylic acid, absolute alcohol, and concentrated sulphuric acid. The boiling point was constant within 0.25° . The densities found, being appreciably lower than those given by Delffs (*Jahresb.*, 1854, 26), were re-determined and their values confirmed.

Ethyl m-Hydroxybenzoate.—Prepared like the salicylate and recrystallised successively from light petroleum and benzene.

Ethyl p-Hydroxybenzoate.—Prepared like its isomerides and recrystallised once from absolute alcohol and twice from benzene.

Benzyl Alcohol.—Made from benzaldehyde by the Cannizzaro reaction, twice fractionated with a rod and disc column, and then twice rapidly distilled.

Benzhydrol.—From benzaldehyde and magnesium phenyl bromide, recrystallised twice from alcohol.

Triphenylcarbinol.—Purchased from Schuchardt; the specimen melted within 1°. As the fused substance slowly darkens, the point of solidification was noted, but no appreciable decomposition had taken place.

Results.

The following record of the results given, the substance, its molecular weight, the temperature (t), the observed capillary rise (h), the radius of the capillary tube (r) and the density (ρ). For economy of space the quantities calculated from these determinations are omitted with the exception of

$$K = \frac{[\gamma(Mv)^{\frac{2}{3}}]_t}{t' - t} \quad \text{and} \quad x = \left(\frac{2 \cdot 121}{K} \right)^{\frac{2}{3}}.$$

Substance.	M. W.	t .	h .	r .	ρ .	K .	x .
Phenol	94	53.3°	2.0830	0.03396	1.0434	—	—
		83.0	1.9465	,,	1.0172	1.79	1.30
<i>o</i> -Cresol	108	39.6	2.0827	,,	1.0290	—	—
		67.4	1.9545	,,	1.0040	1.97	1.12
		99.7	1.7985	,,	0.9750	2.04	1.06
<i>m</i> -Cresol	108	19.1	2.1010	,,	1.0324	—	—
		57.6	1.9550	,,	1.0037	1.63	1.48
		99.9	1.7820	,,	0.9683	1.73	1.33
<i>p</i> -Cresol	108	45.5	1.9695	,,	1.0149	—	—
		73.8	1.8690	,,	0.9920	1.54	1.62
		99.8	1.7560	,,	0.9713	1.82	1.26
<i>o</i> -Nitrophenol	139	53.2	1.8635	,,	1.1745	—	—
		79.7	1.7425	,,	1.1486	2.42	0.84
<i>m</i> -Nitrophenol	139	116.0	2.5193	0.02788	1.3464	—	—
		147.0	2.4130	,,	1.3153	1.62	1.48
<i>p</i> -Nitrophenol	139	129.7	2.1000	0.03396	1.2613	—	—
		162.5	1.9840	,,	1.2329	1.83	1.25
<i>o</i> -Chlorophenol ...	128.5	12.7	1.9415	,,	1.2623	—	—
		45.2	1.8010	,,	1.2293	2.20	} 1.0
		73.3	1.6550	,,	1.1985	2.00	
<i>m</i> -Chlorophenol ...	128.5	33.0	2.3445	0.02788	1.2573	—	—
		78.6	2.1755	,,	1.2089	1.62	1.49
		138.5	1.8845	,,	1.1522	1.98	1.11
<i>p</i> -Chlorophenol ...	128.5	51.6	1.9060	0.03396	1.2504	—	—
		72.4	1.8255	,,	1.2417	1.86	1.22
		99.8	1.7220	,,	1.2026	2.03	1.08
<i>m</i> -Bromophenol ...	173	44.5	1.5330	,,	1.6221	—	—
		69.5	1.4780	,,	1.5900	1.65	1.45
		100.1	1.3955	,,	1.5542	1.79	1.29

Substance.	M.W.	<i>t.</i>	<i>h.</i>	<i>r.</i>	<i>p.</i>	<i>K.</i>	<i>α.</i>
<i>p</i> -Bromophenol ...	173	74.4	1.5390	0.03396	1.5967	—	—
		99.9	1.4640	,,	1.5667	1.88	1.20
Ethyl salicylate ...	166	20.5	1.9420	,,	1.1448	—	—
		61.1	1.8255	,,	1.1141	2.27	0.90
		85.6	1.6870	,,	1.0787	2.30	0.89
Ethyl <i>m</i> -hydroxy- benzoate.	166	85.8	1.8720	,,	1.1079	—	—
		115.4	1.7675	,,	1.0828	2.14	0.99
		143.5	1.6560	,,	1.0606	2.17	0.97
Ethyl <i>p</i> -hydroxy- benzoate.	166	119.7	1.7800	,,	1.0984	—	—
		149.3	1.6775	,,	1.0722	2.06	1.04
		172.8	1.5920	,,	1.0495	2.10	1.01
Benzyl alcohol	108	13.0	2.1960	,,	1.0523	—	—
		47.6	2.0775	,,	1.0250	1.51	1.66
		82.0	1.9470	,,	0.9976	1.64	1.45
Benzhydrol	184	73.55	2.5667	0.02788	1.0636	—	—
		90.9	2.4974	,,	1.0483	2.10	1.01
Triphenylcarbinol.	260	165.8	2.0810	,,	1.0313	—	—
		190.5	2.0001	,,	1.0128	2.11	1.01

Discussion of the Results.

From the measurements recorded in this paper it will be seen that phenolic compounds like the alcohols of the fatty series exhibit association in the liquid condition. It is evident that this association is conditioned by the hydroxyl group, and that such association may undergo steric hindrance by the introduction of groups in the ortho-position. The results obtained for the molecular complexity by the capillarity method closely follow the results of Auwers, using the freezing point method with non-hydroxylic solvents for the detection of the formation of complex molecules.

In the prevention of association two factors have to be taken into account, first the position and secondly the nature of the protecting group. It will be noted in the table of results that in the case of isomerides the effect is most marked (namely, the degree of association is least) when an ortho-compound is examined, and that generally the para-derivatives are more nearly normal than the corresponding meta-isomerides; one naturally arrives at the conclusion that the relative nearness of the positions is represented by the order ortho, para, meta.

The second factor with regard to the substituent is its intrinsic nature. The maximum effect amongst the group examined is exerted by the nitro- and carbethoxy-groups, followed by the halogens, and finally methyl. One might be inclined to attribute the effect to the negativity of the entrant group were it not that if this is the only quality necessary to prevent association the cresols should show much the same degree of association as phenol itself, whereas experiment proves that *o*-cresol gives very nearly normal α for the constant *K*. We are inclined, in agreement with Viscari and Thorpe, to attribute the effect, at least partly, to the steric hindrance of the

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group, and it was in the hope of confirming our views that we extended the investigation to the phenol carbinols. It might again be argued that the negative nature of the phenyl group was responsible, and an examination of similarly constituted aliphatic alcohols would have been desirable, had not G. Carrara and G. Ferrari (*Gazzetta*, 1906, **36**, 419) already determined the constants for various alcohols which are in favour of the views set forth in this communication. The following table is extracted from their work and gives the association factors for normal primary, secondary, and tertiary butyl alcohols :

Normal alcohol.		Secondary alcohol.		Tertiary alcohol.	
Temperature.	α .	Temperature.	α .	Temperature.	α .
22—30°	2·978	24—34°	2·191	26—36°	1·934
30—40	2·728	34—41	1·589	36—40	1·515
40—50	1·99	41—52	1·306	40—45	1·268

One peculiar result which attracted attention is the value for α obtained in the case of *o*-nitrophenol. This led to a very careful purification of the compound and a redetermination of its constants ; the result was, however, not affected. We may point out that Carrara and Ferrari (*loc. cit.*) observed similar abnormalities in the case of nitromethane, a substance also of acidic or pseudo-acidic character. The α -values they obtain for this compound vary from 0·935 in the temperature interval 20—31° to 0·809 between 54° and 59°.

The densities of the substances call for little comment, except that the molecular volume of *o*-nitrophenol is markedly greater than that of its isomerides ; in fact, the molecular volume of the nitrophenols appears to be greater the less the association.

Evidently since the hydroxyl groups are responsible for the association, a certain amount of "residual affinity" must be ascribed to them, and two possible formulæ immediately suggest themselves, namely :

The second of these formulæ would (as Dr. George Young pointed out to one of the authors) correspond to a hydrate of an ether, and must consequently be rejected.

Experiments were instituted to determine the capillarity values of fused azophenols, but had to be abandoned on account of the decomposition these substances undergo above their melting point. Could the research have been further extended in this direction, there is but little doubt that the results of Auwers and Orton would have been confirmed, and the *p*-hydroxyazo-compounds would have exhibited slight association, the *o*-derivatives none. Such behaviour would be in accordance with the formulation of the hydroxyazo-compounds of both series as quinone-hydrazones.