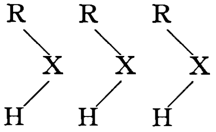
331. *The Association of* p-*Toluenesulphonmethylamide and Related Compounds in Solution : a Comparison of Dielectric Polarisation and Cryoscopic Measurements.*

By R. J. W. LE FÈVRE and H. VINE.

The polymerisation of various aryl sulphonamides in a number of solvents has been studied by dielectric polarisation measurements. The dependence of the dielectric constant upon concentration for *p*-toluenesulphonmethylamide, in all its solutions, has given qualitative indications of a dissociation of a less polar double molecule into a more polar single variety. From the observed specific polarisations the association factors, *A* (defined as the ratios of the apparent to the true molecular weights), have been calculated. They are compared with the corresponding values obtained by Hunter (J., 1937, 320) and Hunter and Chaplin (*ibid.*, p. 1114) using cryoscopic methods. The divergences demonstrate that the dimeric forms of these compounds are not non-polar, and suggest that more than one mode of association may be operative.

THE polymerisation (association) which many organic molecules containing oxygen, nitrogen, or sulphur, etc., undergo in the liquid or the dissolved state (cf. Turner, " Molecular Association," 1915, Ch. V), at first represented as involving the co-ordination of hydrogen (Sidgwick, " The Electronic Theory of Valency," 1927, p. 134), is now commonly recognised as a special application of the Hund–Pauling theory of resonance (cf. Hinshelwood, *Ann. Reports*, 1933, **30**, 44; Sidgwick, *ibid.*, p. 112; 1934, **31**, 37; Ingold, J., 1933, 1120; Sidgwick, J., 1936, 533). According to this, the *real* state of a system composed of the molecular species RXH is intermediate between the *unreal* extremes described by the formulæ



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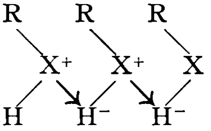
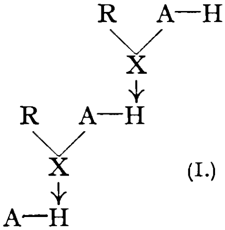
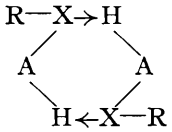


The power of hydrogen to effect such molecular unions depends primarily upon the nature of X; for what follows, it need only be noted that the readiness with which this resonance occurs is greatest when R is attached to hydrogen through oxygen, less when through nitrogen or sulphur, and least when through carbon (*Ann. Reports*, 1934, **31**, 43). Association complexes of this type arise from molecules, like those of water and the alcohols, in which the " donor " and " acceptor " atoms are directly linked. With more complicated structures, in which these atoms are separated by others, *two* modes of polymerisation can be plainly foreseen, one (I) to produce a chain in which theoretically many constituent molecules could be linked, and the other (II) to give a ring form containing two only.



(I.)



(II.)

In the past, association has been studied by a variety of physical measurements (cf. Turner, *op. cit.*) but, where solutions are concerned, chiefly by molecular-weight and partition-coefficient determinations. The cryoscopic method has been much used (and is probably the best available) to give a quantitative measure of the association, the results being frequently expressed by plotting against concentration the " association factor " (in these papers denoted by A), *i.e.*, the ratio of the apparent to the true molecular weight.

The types (I) and (II), however, should differ widely in an easily investigated physical property : from considerations of symmetry, the apparent dipole moment of a dimeride such as (II) might reasonably be expected to be several D. units less than one such as (I) (where analogies with the dipolar " Zwitter-ionen " are obvious) so that the existence, nature, and dependence upon concentration or temperature of such aggregates in a solution should be discernible by dielectric-polarisation studies.

This paper and the succeeding one report investigations of groups of compounds whose dimers may *a priori* take either of the forms (I) and (II), *viz.*, (1) diazoaminobenzene and derivatives, (2) certain aryl sulphonamides, and (3) acetic acid and its three chloro-substitution products.

The Theory of the Method.—The system under consideration is a solution. A simple relation between the association and the apparent polarisation of a solute can be derived if it is assumed that an equilibrium exists between single molecules and a definite species of double molecules. (In this connection it is more logical to use specific polarisations and weight fractions—written p and w with appropriate subscripts—rather than molar quantities, because the molecular weight of the dissolved substance is—in these cases—often an indeterminable quantity.)

Let a_1 and a_2 denote single and double molecules of the substance a, and suppose that there exists the equilibrium $2a_1 \rightleftharpoons a_2$. The specific orientation polarisations are related by the equation ${}_{O}p_a w_a = {}_{O}p_{a_1} w_{a_1} + {}_{O}p_{a_2} w_{a_2}$. Let the degree of association, γ, be defined as w_{a_2}/w_a, then $w_{a_2} = \gamma w_a$ and $w_{a_1} = (1 - \gamma) w_a$. Therefore ${}_{O}p_a w_a = {}_{O}p_{a_1} w_a (1 - \gamma) + {}_{O}p_{a_2} \gamma w_a$, from which

$$\gamma = ({}_{O}p_{a_1} - {}_{O}p_a)/({}_{O}p_{a_1} - {}_{O}p_{a_2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

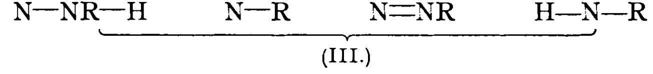
If the double molecules are non-polar, then ${}_{O}p_{a_2} = 0$, and

$$\gamma = ({}_{O}p_{a_1} - {}_{O}p_a)/{}_{O}p_{a_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is easily seen that the association factor, A, is equal to $2/(2 - \gamma)$.

A number of applications of these considerations will now be given. In these, the specific orientation polarisations (${}_{O}p$) are estimated from the experimental measurements by subtracting the specific refractions from the related specific total polarisations.

Diazoaminobenzene.—Hunter (J., 1937, 320) found that the cryoscopically determined apparent molecular weights of diazominobenzene and derivatives containing an unsubstituted —N_3H— group in benzene showed increases with a rise of concentration, whereas the behaviour was normal when the hydrogen was replaced by alkyl groups. In the former case values of A rose to as much as 1·24 in the concentration range examined (up to *ca.* 10 g. per 100 g. of benzene). A cyclic double molecule (III) was regarded as the most probable, although the possibility was envisaged that the formation of an open-chain polymer might occur. The real form of (III), being centrosymmetric, should have



(III.)

no resultant dipole moment. However, measurements on diazoaminobenzene over a wide concentration range (made when work reported in J., 1937, 1805, was in progress), did not reveal any exceptional decreases in the polarisation; within experimental error the usual rectilinear relationship between the dielectric constant and the weight fraction was found, and a value of the polarisation at infinite dilution (*i.e.*, the polarisation of the single diazoaminobenzene molecules) obtained. By using this in equation (2) above, values of A have been calculated. They are shown in Fig. 1 (curve II), against Hunter's values (curve I) for comparison. The non-agreement suggests that the dimeric form is not entirely non-polar, and that although some of it may be adequately represented by (III), part of it is probably in the more highly polar open-chain form.

The case is not a good one to study, however, for, in addition to the fact that association does not occur to a very large extent within the limitations imposed by solubility, the orientation polarisation is only a small fraction of the total and the accuracy of measurement is therefore not great. (The specific refractions are, of course, not affected by the association.)

FIG. 1.

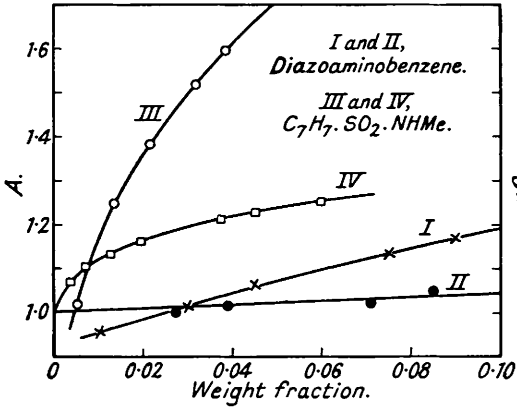
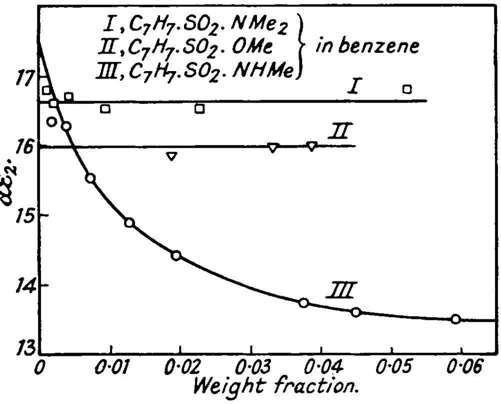
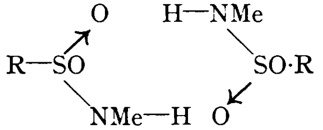


FIG. 2.



p-*Toluenesulphonmethylamide and Related Compounds.*—Extending the earlier work of von Auwers and others, Chaplin and Hunter (J., 1937, 1114) measured the molecular weights of a series of *N*-substituted amides and sulphonamides cryoscopically in benzene over a sufficient range of concentration to show clearly that molecular association (indicated by a steep concentration–molecular weight curve) is general in amides and sulphonamides possessing a free amide hydrogen atom, but that replacement of both amide hydrogen atoms effectively checks association (producing a flat or gently-sloping curve). *p*-Toluenesulphonmethylamide is a good example of the associating compounds, for A rises to 1·60 at a concentration corresponding to $w_1 = 0{\cdot}04$, whereas the dimethylamide only shows a small increase. If, as Hunter and Chaplin (*loc. cit.*) suggest, association in this series is due to resonance between



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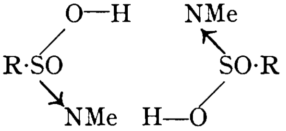


the dimerides should have dipole moments which—although probably not zero, for the structures are complicated—will be very considerably smaller than those of the single molecules, which contain polar $S \rightarrow O$ links; and, in any one case therefore, the increasing degree of association with concentration should be clearly revealed by a parallel *decrease* of the orientation polarisation of the solute.

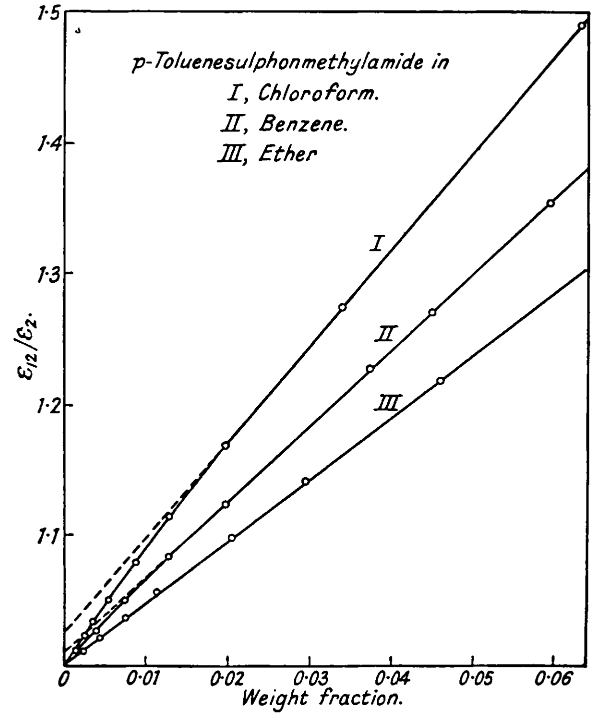
In the present work comparisons have been made between *p*-toluenesulphonmethylamide, *p*-toluenesulphondimethylamide, and methyl *p*-toluenesulphonate, and benzene, chloroform, and ether have been used as the solvents. *p*-Toluenesulphonamide itself is very sparingly soluble in benzene.

It is clear that, within experimental error, ϵ is a linear function of w_1 in the non-associating compounds, but the line curves off in the more dilute solutions when there is association. The difference is brought out clearly in Fig. 2, which refers to benzene solutions; the coefficient $\alpha\epsilon_2$ (see Le Fèvre and Vine, J., 1937, 1805) is plotted against w_1, so that the curvature of the ϵ–w_1 graph is much exaggerated.

The same behaviour has been observed in chloroform as in benzene, but in ether, *p*-toluenesulphonmethylamide as well as the methyl sulphonate, gives a practically straight line for the dielectric constant. The slight deviation is not more than the experimental error, which is somewhat increased on account of ethereal solutions being more difficult to handle. In order to show the difference in behaviour in the three solvents, the ratios of the dielectric constants of the solutions to those of the pure solvents have been plotted against the weight fraction in Fig. 3.

Fig. 4 shows the specific orientation polarisations of the three substances. The curves for *p*-toluenesulphonmethylamide in benzene (III) and chloroform (VI) become much steeper below a concentration of *ca.* 4% and thus afford positive evidence of the dissociation of less polar complexes. In ether, on the other hand, the substance must be completely dissociated throughout (curve VIII).

FIG. 3.



The power of oxygenated compounds to break down complexes involving hydrogen bonds has been studied by various workers (Higasi, *Bull. Inst. Phys. Chem. Res., Tokyo,* 1933, **12**, 773; Thomson, this vol., p. 460; Wilson and Wenzke, *J. Chem. Physics,* 1934, **2**, 546; *J. Chem. Amer. Soc.*, 1935, **57**, 1265). The solute molecules become associated with those of the solvent instead of with molecules of their own type, and this must occur in the case of *p*-toluenesulphonmethylamide in ether. The measured polarisation is therefore that of the ether–amide complex, and it is noticeable that there is a larger difference between the polarisations of *p*-toluenesulphonmethylamide and methyl *p*-toluenesulphonate in ether than there is in benzene and chloroform (see Fig. 4), which is probably due to this fact.

The experimental observations at 25° are recorded in Table I, and the results for benzene solutions are summarised in Table II. The benzene used was prepared in the usual way; the chloroform and ether were "AnalaR" specimens, which were dried and distilled before use. Standard values were taken for the dielectric constants of benzene and chloroform, and that of ether was found by comparison with the chloroform. Incidentally, the dipole moments of the three substances in benzene have been calculated, that of the associating substance by graphical extrapolation, and the others by means of the usual equation

$$p_\infty = p_2(1 - \beta) + c\alpha\varepsilon_2.$$

FIG. 4.

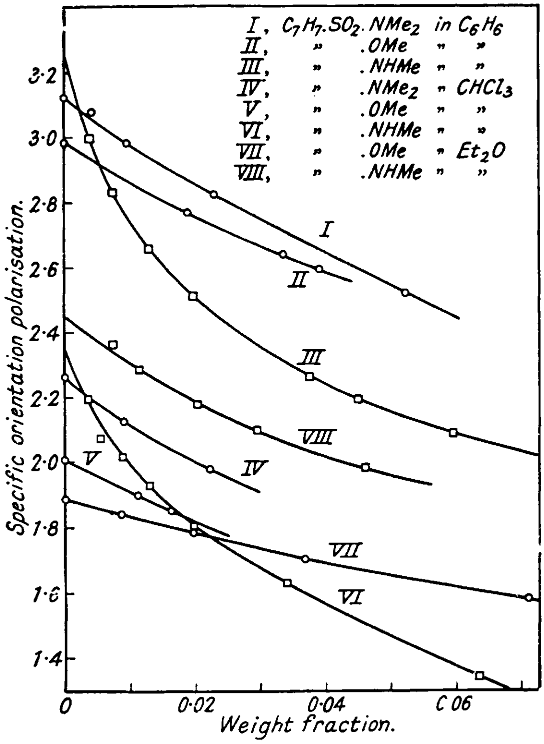


TABLE I.

(1) Methyl *p*-toluenesulphonate in benzene.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25°}$.	$_0p_1$.
0	2·2725	0·87378	2·983
1870	2·5691	0·87881	2·766
3346	2·8072	0·88267	2·639
3889	2·8948	0·88407	2·591

(2) *p*-Toluenesulphondimethylamide in benzene.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25°}$.	$_0p_1$.
0	2·2725	0·87378	3·115
417	2·3422	0·87476	3·077
931	2·4263	0·87600	2·981
2286	2·6500	0·87952	2·819
5230	3·1503	0·88659	2·519

(3) *p*-Toluenesulphonmethylamide in benzene.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25°}$.	$_0p_1$.
0	2·2725	0·87378	3·25
383	2·3348	0·87478	2·997
734	2·3870	0·87571	2·833
1274	2·4625	0·87716	2·658
1960	2·5552	0·87901	2·512
3751	2·7875	0·88382	2·261
4500	2·8853	0·88585	2·192
5948	3·0766	0·88953	2·086

(4) Methyl *p*-toluenesulphonate in chloroform.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25°}$.	$_0p_1$.
0	4·724	1·47910	2·003
289	4·838	1·47842	1·932
1120	5·177	1·47642	1·897
1633	5·385	1·47492	1·848

(5) *p*-Toluenesulphondimethylamide in chloroform.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25°}$.	$_0p_1$.
0	4·724	1·47910	2·262
907	5·136	1·47610	2·123
2260	5·751	1·47163	1·976

(6) *p*-Toluenesulphonmethylamide in chloroform.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25°}$.	$_0p_1$.
0	4·724	1·47910	2·35
245	4·837	1·47852	2·219
353	4·886	1·47825	2·193
543	4·961	1·47775	2·074
868	5·098	1·47705	2·014
1282	5·261	1·47583	1·928
1977	5·520	1·47400	1·805
3402	6·021	1·47028	1·628
6326	7·042	1·46270	1·341

(7) Methyl *p*-toluenesulphonate in ether.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25}$.	$_0p_1$.
0	4·136	0·70678	1·884
872	4·274	0·70936	1·841
1976	4·448	0·71326	1·783
3685	4·717	0·71922	1·704
7089	5·265	0·73219	1·580

(8) *p*-Toluenesulphonmethylamide in ether.

$w_1 \times 10^5$.	$\epsilon_{1200}^{25°}$.	$d_{4°}^{25°}$.	$_0p_1$.
0	4·136	0·70678	2·45
236	4·188	0·72972	2·508
431	4·230	0·73182	2·487
739	4·290	0·73711	2·362
1128	4·366	0·74364	2·287
2033	4·541	0·75781	2·175
2945	4·718	0·77104	2·096
4595	5·041	0·79278	1·984

TABLE II.

Dipole moments in benzene.

Substance.	M.	P_∞.	$[R_L]_D$.	μ.
$C_7H_7 \cdot SO_2 \cdot OMe$	186	600	45	5·18
$C_7H_7 \cdot SO_2 \cdot NMe_2$	199	672	52	5·48
$C_7H_7 \cdot SO_2 \cdot NHMe$	185	648	47	5·4

In the case of *p*-toluenesulphonmethylamide in benzene, γ and A have been calculated for the various concentrations by assuming that the dimeric molecules have zero moment. Association to a quite large extent is indicated, but the values of A found in this way, shown in Fig. 1, curve IV, are lower than those obtained cryoscopically by Chaplin and Hunter (curve III). The quantitative significance of this is uncertain, but it should be noticed that the present results refer to measurements at 25° whereas the others were at the freezing point of benzene (*ca.* 4°). It is probable that the degree of association varies considerably with temperature, and it is intended to investigate this point experimentally.

The divergence between the two series of results is, however, most probably due to polarity of the dimeric form. If the mass law applies to the present case, $K = n_{a_2}/(n_{a_1})^2$, where n_{a_1} and n_{a_2} are the molar concentrations of the single and the double molecules respectively. Then

$$K = M\gamma/[2000dw_1(1-\gamma)^2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Values of γ and A are recorded in Table III, together with those of K derived from them by (3). The inconstancy of K is again probably due to the assumption regarding the dipole moment of the double molecules, but it could also be due to a departure from the mass law, such as would occur if there were more than one mode of association operative at the same time.

TABLE III.

$w_1 \times 10^5$	383	734	1274	1960	3751	4500	5948
γ	0·144	0·191	0·241	0·282	0·354	0·374	0·405
A	1·078	1·106	1·137	1·164	1·215	1·230	1·254
K	5·4	4·2	3·46	2·92	2·37	2·21	2·00

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[*Received, July 22nd,* 1938.]