332. *The Association of Acetic Acid, of its Three Chlorinated Derivatives, and of* n-*Butyric and Hexoic Acids, dissolved in Benzene : Dielectric Polarisation compared with Cryoscopic Measurements.*

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The carboxylic acids are a series for which—presumably because of their polymerised state in most solutions—measured physical properties frequently appear to be contradictory or inconclusive. This is true of all available dipole-moment data.

In the present paper a study of the association of the acids mentioned in the title has been made by dielectric polarisation methods. No previous work of this type exists for the chlorinated acetic acids, and our measurements for the three unsubstituted fatty acids cover regions of considerably greater dilution than those hitherto investigated. For these dilute solutions departures from rectilinear relationships between the dielectric constants and the concentrations have been observed, indicating the occurrence of dissociation of double molecules into more polar single molecules. In the case of trichloroacetic acid this phenomenon has been treated quantitatively by using the methods outlined in the preceding paper; it is concluded that the dimeric form is not non-polar but has a moment of *ca.* 1·1 D., *i.e.*, of the same general magnitude as the values found by Zahn and Briegleb for the dimeric fatty acids. This result is subject to limitation by the intervention of solvent and atomic polarisation effects to unknown extents.

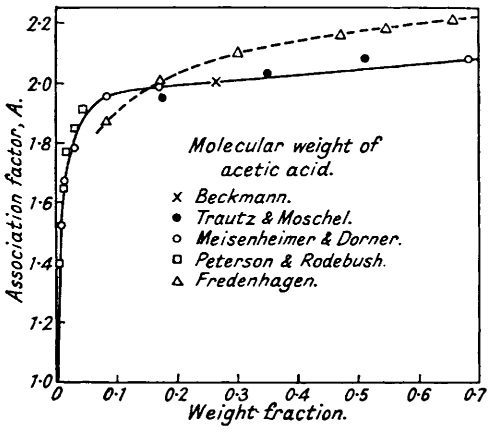
(1) *Previous Studies of Association, other than Dielectric-constant Measurements.*—Beckmann (*Z. physikal. Chem.*, 1897, **22**, 610) carried out cryoscopic measurements on some carboxylic acids and found that the molecular weight of acetic acid in benzene corresponded to double molecules. Herz and Fischer (*Ber.*, 1905, **38**, 1138) also investigated the partition of acetic and monochloroacetic acids between water and various aromatic hydrocarbons, showing that the concentration of the acid in the organic liquid was proportional to the square of that in water; hence, assuming the acids to consist of single molecules in water, they deduced that they were associated to double molecules in the organic liquid.

Trautz and Moschel (*Z. anorg. Chem.*, 1926, **155**, 13), also from molecular-weight determinations, concluded that the carboxylic acids were all completely associated to double molecules in benzene, even in dilute solutions. These authors, however, observed that in nitrobenzene the apparent molecular weights began to decrease when dilute solutions were reached. They also investigated the vapour densities of several of the aliphatic acids at different temperatures, and found (as a few earlier experiments by other authors had also shown) that in the gas phase the dimers dissociated into single molecules to an increasing extent as the temperature was raised. They were able to calculate the equilibrium constants and heats of association in each case, and although their values were not in good mutual agreement, they agree approximately with more accurate values since obtained for formic (Coolidge, *J. Amer. Chem. Soc.*, 1928, **50**, 2166) and acetic (Fenton and Garner, J., 1930, 694; MacDougall, *J. Amer. Chem. Soc.*, 1936, **58**, 2585) acids.

Brown and Bury (*J. Physical Chem.*, 1926, **30**, 694) used nitrobenzene as a cryoscopic solvent for phenylacetic, propionic, benzoic, and cinnamic acids, which were found to dissociate partly in dilute solutions, and they examined the effect of small quantities of water. If the solvent were not thoroughly dried, some of the dissociated molecules combined with the water, so that the net number of dissolved molecules, and consequently the freezing point depressions, were reduced. In these circumstances, dissociation of the complexes would not be detected. Meisenheimer and Dorner (*Annalen*, 1930, **482**, 138) also investigated the molecular weights of benzoic and phenylacetic acids in nitrobenzene, with similar results.

It has been found in recent years by a number of investigators that dissociation occurs in dilute benzene solution as well as in nitrobenzene. Cryoscopic measurements have been made on acetic acid and its homologues by Peterson and Rodebush (*J. Physical Chem.*, 1928, **32**, 709), by Fredenhagen (*Physikal. Z.*, 1935, **36**, 321), and by Meisenheimer and Dorner (*Annalen*, 1936, **523**, 299), using very dilute solutions and carefully dried materials. Some of the results for acetic acid are shown in Fig. 1. Berger's ebullioscopic measurements on benzoic and other aromatic acids in benzene (*Z. physikal. Chem.*, 1933, *B*, **22**, 283) also show a very rapid increase in the molecular weight with concentration in the most dilute solutions, until the stage of dimeric molecules is reached.

Fig. 1.



In contrast to these results, Bell, Baughan, and Vaughan-Jackson (J., 1934, 1969) found that the molecular weights of mono-, di-, and tri-chloroacetic acids, determined cryoscopically in *p*-chlorotoluene, are double throughout the whole range of concentrations which can be examined, and Bell and Arnold (J., 1935, 1432) found that trichloroacetic acid is also completely associated in benzene. Bell (*Proc. Roy. Soc.*, 1934, *A*, **143**, 377) had observed that the catalytic power of several acids, notably mono-, di-, and tri-chloroacetic acids, in bringing about the transformation of *N*- into *p*-bromoacetanilide in chlorobenzene and in benzene solution was considerably diminished as the concentration of the catalyst increased, and he had suggested that the increasing degree of association was the cause. The same phenomenon occurs in the catalysis of diene syntheses by trichloroacetic acid (Dr. A. Wassermann; private communication).

That the halogenated acids should be more strongly associated than acetic acid itself is to be expected in a solvent which does not facilitate dissociation, because the strong electron-attracting action of the — CCl_3 group can operate only to promote association by increasing the stability of the dimers, and the solvent molecules are not involved as proton acceptors, as they would be were the medium an "ionising" one. Thus, the increasing degree of ionisation (acid strength) found as one proceeds from acetic to trichloroacetic acid in *aqueous* solution would be essentially in agreement with an increase of stability of the dimeric forms in benzene solutions. However, the results of the present work, as will be seen, are in disagreement with the cryoscopic measurements on this point.

(2) *Previous Dielectric-polarisation Measurements.*—Owing to the association of the carboxylic acids, the many dipole-moment investigations which have been made on them provide a somewhat confused and inconclusive mass of data. Each acid has two dipole moments, that of the single and that of the double molecules, and values obtained in the usual manner lie between these two.

Williams made measurements on benzoic and *cyclo*hexanecarboxylic acids (*J. Amer. Chem. Soc.*, 1927, **49**, 2417; 1930, **52**, 1831) in benzene, and Wolf on the first five of the aliphatic series (*Physikal. Z.*, 1930, **31**, 227). Piekara (*Compt. rend.*, 1934, **198**, 1018) studied acetic and propionic acids in hexane.

Due consideration was given to association by Smyth and Rogers (*J. Amer. Chem. Soc.*, 1930, **52**, 1824) in relation to the polarisation of benzene solutions of acetic and butyric acids, but they used insufficiently dilute solutions to detect any effect of the dissociation into single molecules, and their values, extrapolated to infinite dilution, were taken as the polarisations of the double molecules. They concluded, but without real justification, that the double molecules had zero moment. They also measured the polarisation of acetic acid in ether, and observed normal behaviour. Extrapolation gave the value 61·7 c.c. for the total polarisation at infinite dilution at 20° and 1·53 D. for the dipole moment.

Zahn made measurements of the dielectric polarisation of formic, acetic, and propionic acids as vapours (*Physical Rev.*, 1930, **35**, 1047; 1931, **37**, 1516). Using Coolidge's vapour densities for formic acid (*J. Amer. Chem. Soc.*, 1928, **50**, 2166), he calculated the moments of the single and the double molecules as 1·51 D. and 0·99 D. The limiting values of the apparent dipole moments of acetic and propionic acids at different temperatures were 1·73 D. and 1·74 D., respectively.

Wilson and Wenzke (*J. Chem. Physics*, 1934, **2**, 546; *J. Amer. Chem. Soc.*, 1935, **57**, 1265) measured the dipole moments of several carboxylic acids in dioxan, in which they are not associated; the values of P_∞ and μ given in Table I were obtained for the simpler acids. Under the heading μ_{ester} are given the dipole moments of the corresponding ethyl esters, determined in the usual manner in benzene or quoted from the "Table of Dipole Moments" (*Trans. Faraday Soc.*, 1934, Appendix).

TABLE I.

Acid.	P_∞, c.c.	$[R_L]_D$, c.c.	μ, D.	μ_{ester}, D.	Acid.	P_∞, c.c.	$[R_L]_D$, c.c.	μ, D.	μ_{ester}, D.
Formic	90·5	8·6	2·07	1·94	Benzoic	94·5	34·1	1·75	1·82
Acetic	75·9	13·0	1·74	1·82	Phenylacetic	100·1	37·0	1·71	—
Propionic ...	80·8	17·5	1·75	1·74	Stearic.........	149·9	86·9	1·74	—

There is quite good agreement between the moments of acetic and propionic acids in the vapour state and in dioxan, and those of their esters. (The concordance with the data obtained in dioxan may be fortuitous, however, since they *may* merely represent properties of a complex with the solvent.) Zahn's value for monomeric formic acid (1·55) is low in comparison with Wilson and Wenzke's and with the moment of ethyl formate, and it may therefore be that his value for the dimeric form (0·99) is high.

Briegleb (*Z. physikal. Chem.*, 1930, *B*, **10**, 205) made a systematic study of the polarisation of formic, acetic, propionic, butyric, *iso*valeric, and benzoic acids in benzene, and Hrynakowski and Zochowski (*Ber.*, 1937, **70**, 1739) extended these measurements to the higher fatty acids, hexoic, heptoic, octoic, palmitic, and stearic, working at 71°. For all these acids, therefore, data exist for concentrations from *ca.* 10 to 100%. Extrapolation of the values to zero concentration gives no indication of what occurs in the dilute solutions, but shows roughly the polarisation of the double molecules. The polarisations found in this way, together with molecular refractions obtained from various sources, are contained in Table II. In each case the molecular weight of the single molecules has been taken in calculating the molar polarisation.

TABLE II.

Acid.	P_∞, c.c.	$[R_L]_D$., c.c.	$P_\infty - [R_L]_D$, c.c.	Acid.	P_∞, c.c.	$[R_L]_D$, c.c.	$P_\infty - [R_L]_D$, c.c.
Formic	29·3	8·5	20·8	Hexoic	40·8	31·4	9·4
Acetic	24·3	12·8	11·5	Heptoic	45·2	36·0	9·2
Propionic	24·4	16·0	8·4	Octoic	50·1	40·7	9·4
Butyric	31·0	21·9	9·1	Palmitic	89·0	77·7	11·3
*iso*Valeric	34·4	26·2	8·2	Stearic	99·0	86·9	12·1

Except for formic acid, they all have apparent orientation polarisations of *ca.* 10 c.c., corresponding (since the molecules are double) to dipole moments of *ca.* 1·0. In view, however, of the structure of these dimers, it is not impossible that atomic polarisation or solution effects may account for the apparent orientation polarisations. It may be observed, for comparison, that the extrapolated polarisations given in Table II are nearly the same as the corresponding values measured by us at $w_1 =$ *ca.* 0·01. Our present measurements also show that $P - [R_L]_D$ calculated in the same way as in Table II (*i.e.*, by taking molecular weights of single molecules) does not become zero at infinite dilution. As examples, the following may be quoted :

	Acetic acid.	Butyric acid.	Hexoic acid.
Extrapolated value from present work	10·7	11·4	12·7
Ditto from previous measurements *	11·5 (B)	9·1 (B)	9·4 (H)

* (B) = Briegleb (*loc. cit.*). (H) = Hrynakowski and Zochowski (*loc. cit.*).

Reference to the results expressed in Figs. 1—5 shows that it is only at much lower concentrations than those which have been investigated previously that dissociation to any appreciable extent occurs in benzene.

(3) *Present Investigations.*—The densities and dielectric constants of benzene solutions of acetic, *n*-butyric, *n*-hexoic, and mono-, di-, and tri-chloroacetic acids have been measured, especially in the region of the lowest possible concentrations. With trichloroacetic acid there is a very large deviation from the rectilinearity of a plot of ε with w_1 at first, after which the line becomes straight. In dichloroacetic acid the deviation is also quite large; at higher concentrations the rate of increase of *D.C.* with weight fraction becomes greater as it does in acetic acid and (to a smaller extent) in the other fatty acids. Monochloroacetic acid shows a small but definite deviation in the lowest concentrations; this substance is not very soluble in benzene. The dielectric constants of acetic, butyric, and hexoic acid solutions are much smaller than those of corresponding solutions of the other acids, but the accuracy of measurement is sufficient to show up small departures from the straight-line relationship below the concentration $w_1 = 0·02$.

The similarity of these relations to those obtained for *p*-toluenesulphonmethylamide in benzene and chloroform (see preceding paper) shows very clearly that a change in the molecular state of the solutes occurs as the concentration varies. The inflexion and upward trend of the ε–w_1 curves for acetic and dichloroacetic acids is somewhat surprising, but the polarisation is the more fundamental quantity, and this affects the density also.

The experimental observations are recorded in Table III, together with the polarisations calculated from them, and, in the case of trichloroacetic acid, values of the degree of association obtained on the basis of certain assumptions, as described below. The measurements have been made in the usual way, with benzene dried over sodium. The acids were distilled before use in order to remove water. The specific orientation polarisation ${}_{0}p_1$ is, as in the previous paper, the difference between the total polarisation and the refraction for the Na-*D* line.

TABLE III.

$w_1 \times 10^5$.	$\epsilon^{25°}_{1200}$.	$d^{25°}_{4°}$.	p_{12}.	${}_{0}p_1$.
0	2·2725	0·87378	0·34086	—
		Chloroacetic acid.		
296	2·2823	0·87472	0·34233	0·649
653	2·2918	0·87592	0·34363	0·576
1053	2·3032	0·87715	0·34526	0·570
1213	2·3068	0·87765	0·34573	0·553
2877	2·3472	0·88304	0·35095	0·503
4997	2·3984	0·88999	0·35723	0·480
5982	2·4240	0·89331	0·36025	0·476
		Dichloroacetic acid.		
198	2·2783	0·87458	0·34163	0·551
354	2·2823	0·87512	0·34217	0·533
771	2·2913	0·87669	0·34324	0·472
1006	2·2966	0·87759	0·34387	0·462
1189	2·3004	0·87824	0·34431	0·453
1805	2·3111	0·88068	0·34533	0·411
3164	2·3348	0·88589	0·34759	0·376
7710	2·4146	0·90391	0·35450	0·340
13249	2·5175	0·92674	0·36247	0·326
32663	2·9723	1·01773	0·38975	0·313
52043	3·6751	1·12912	0·41747	0·310
		Acetic acid.		
331	2·2748	0·87414	0·34115	0·213
648	2·2777	0·87448	0·34156	0·233
1177	2·2803	0·87507	0·34182	0·207
1532	2·2820	0·87543	0·34200	0·199
2325	2·2868	0·87631	0·34255	0·198
3347	2·2916	0·87740	0·34301	0·189
5238	2·3014	0·87949	0·34401	0·185
7593	2·3161	0·88215	0·34566	0·188
11295	2·3419	0·88659	0·34859	0·193
		n-*Butyric acid.*		
847	2·2777	0·87431	0·34163	0·183
2369	2·2830	0·87523	0·34226	0·151
3674	2·2871	0·87606	0·34270	0·142
7138	2·2982	0·87830	0·34388	0·1343
14247	2·3218	0·88301	0·34637	0·1306
28248	2·3768	0·89285	0·35232	0·1326
		n-*Hexoic acid.*		
605	2·2754	0·87397	0·34133	0·149
1194	2·2773	0·87420	0·34160	0·133
2224	2·2807	0·87464	0·34206	0·125
5882	2·2905	0·87603	0·34335	0·1132
8699	2·2984	0·87722	0·34434	0·1109
14793	2·3154	0·87962	0·34653	0·1092

Trichloroacetic acid.

$w_1 \times 10^5$.	$\epsilon^{25°}_{1200}$.	$d^{25°}_{4°}$.	p_{12}.	${}_{0}p_1$.	γ.	γ'.
135	2·2772	0·87432	0·34153	0·665	0·194	0·215
353	2·2835	0·87536	0·34230	0·577	0·301	0·333
824	2·2927	0·87713	0·34332	0·467	0·434	0·480
1091	2·2961	0·87818	0·34354	0·415	0·497	0·550
1482	2·3006	0·87973	0·34377	0·365	0·558	0·617
2303	2·3117	0·88317	0·34446	0·325	0·606	0·671
3872	2·3292	0·88988	0·34503	0·277	0·664	0·735
4358	2·3342	0·89192	0·34513	0·267	0·676	0·749
6646	2·3561	0·90195	0·34515	0·234	0·716	0·792
8147	2·3703	0·90870	0·34505	0·221	0·732	0·810
13010	2·4127	0·93901	0·34390	0·197	0·761	0·843
17107	2·4500	0·95058	0·34278	0·181	0·781	0·864
33324	2·5993	1·03736	0·33520	0·150	0·818	0·906

The dipole moments of the ethyl esters of mono-, di-, and tri-chloroacetic acids in benzene have also been measured, in order to afford a comparison with the acids. The usual straight-line relationship of ε and d with w_1 has been found in each case, so the coefficients $\alpha\varepsilon_2$ and β have been obtained and the dipole moments calculated from them. The results are given in Tables IV and V. In Table VI are listed the values taken for the molecular and specific refractions. That of acetic acid was recorded by Briegleb; the others were obtained from it by taking 4·6 for the CH_2 group and 5·1 for chlorine.

TABLE IV.

$w_1 \times 10^5$.	$\epsilon^{25°}_{1200}$.	$d^{25°}_{4°}$.	$\alpha\epsilon_2$.	β.
0	2·2725	0·87378	—	—
		Ethyl trichloroacetate.		
981	2·3075	0·87696	3·56	0·371
1915	2·3418	0·87997	3·62	0·370
2760	2·3733	0·88263	3·65	0·367
5206	2·4651	0·89078	3·70	0·374
11274	2·7047	0·91164	3·83	0·384
		Ethyl chloroacetate.		
1523	2·3639	0·87691	6·00	0·235
2635	2·4325	0·87925	6·07	0·237
3481	2·4831	0·88104	6·05	0·239
		Ethyl dichloroacetate.		
631	2·3011	0·87569	4·53	(0·346)
1458	2·3395	0·87784	4·60	0·319
2631	2·3940	0·88111	4·62	0·319
4582	2·4871	0·88665	4·68	0·321

TABLE V.

	$a\epsilon_2$.	β.	$P_{1\infty}$.	μ, D.
$CH_2Cl{\cdot}CO_2Et$	6·04	0·237	171·0	2·64
$CHCl_2{\cdot}CO_2Et$	4·62	0·320	172·9	2·61
$CCl_3{\cdot}CO_2Et$	3·64	0·371	172·2	2·55

TABLE VI.

	M.	$[R_L]_D$.	$[r_L]_D$.
$CH_3{\cdot}CO_2H$	60	12·8	0·213
$CH_2Cl{\cdot}CO_2H$	94·5	17·9	0·190
$CHCl_2{\cdot}CO_2H$	129	23·0	0·178
$CCl_3{\cdot}CO_2H$	163·5	28·1	0·172
$CH_2Cl{\cdot}CO_2Et$	122·5	27·1	0·221
$CHCl_2{\cdot}CO_2Et$	157·0	32·2	0·205
$CCl_3{\cdot}CO_2Et$	191·5	37·3	0·195
n-$C_3H_7{\cdot}CO_2H$	88	21·9	0·249
n-$C_5H_{11}{\cdot}CO_2H$	116	31·4	0·270

The specific orientation polarisations of mono-, di-, and tri-chloroacetic acids are plotted against the concentration in Figs. 2, 3 and 4. That of ethyl trichloroacetate is also included in Fig. 4. It is clear that the dimeric molecules of trichloroacetic acid have a small polarisation, but that below the concentration w_1 = *ca.* 0·04, considerable dissociation to more polar molecules occurs. The values approached by the polarisations of the mono- and the di-chloro-acid at higher concentrations correspond to double molecules with quite high dipole moments, but in the dilute solutions the proportion of more polar single molecules obviously increases.

FIG. 2.

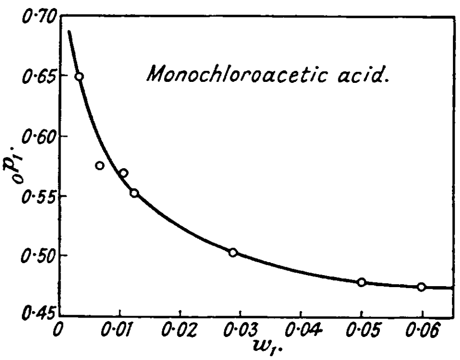
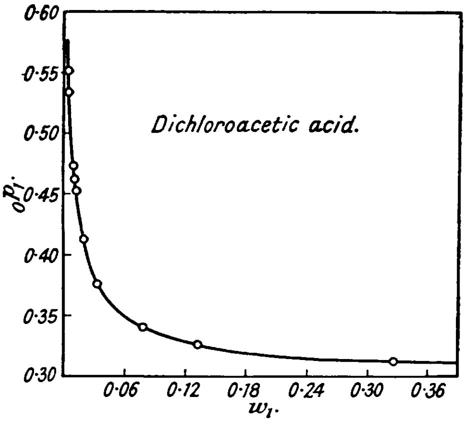


FIG 3.



The value for trichloroacetic acid at zero concentration (0·825) was derived by equating the moment of the acid to that of its ethyl ester. The values similarly calculated for mono- and di-chloroacetic acids (1·524 and 1·090 respectively) are much higher than the polarisations of the most dilute solutions that could be examined; dissociation, therefore, occurs to a smaller extent in these two than in trichloroacetic acid. The orientation polarisations of acetic, butyric, and hexoic acids only show a slight tendency to increase in most dilute solutions.

Calculations of the Degree of Association of Trichloroacetic Acid.—Equations (1) and (3) (preceding paper, pp. 1791 and 1795) can be applied more readily to trichloroacetic acid than to *p*-toluenesulphonmethylamide, because the concentration range is greater. In order to calculate γ it is necessary to know $_0p_a$ and $_0p_{a_1}$. Since the measurements become less accurate as the concentration decreases, it is not possible to obtain a satisfactory value of $_0p_{a_1}$ by extrapolation, so this has been estimated in the manner described above (justified by the good agreement between the moment of ethyl acetate and that of acetic acid measured in the gas phase). The correct value for $_0p_{a_2}$ will depend upon the configuration of the dimeric form; if this is a resonance hybrid, such as is formulated in (II) in the previous paper, $_0p_{a_2}$ will be zero; if, however, an unsymmetrical structure such as that suggested for formic acid by Hengstenberg and Brú (*Anal. Fis. Quim.*, 1932, **30**, 341)—in which the four oxygen atoms are at the corners of a tetrahedron—is correct, then the dimeric form will be polar and ${}_0p_{a_1}$ will have a finite value.

Accordingly, γ has been calculated by assuming ${}_0p_{a_1}$ to be zero. It can be seen from equation (3) that the fraction $\gamma/d(1 - \gamma)^2$ should be proportional to w_1. Fig. 5 (curve I) shows these two quantities plotted against one another. A rectilinear relationship is not displayed. If it is assumed that ${}_0p_{a_1}$ is equal to 0·150, γ is 1 for the most concentrated

Fig 4.

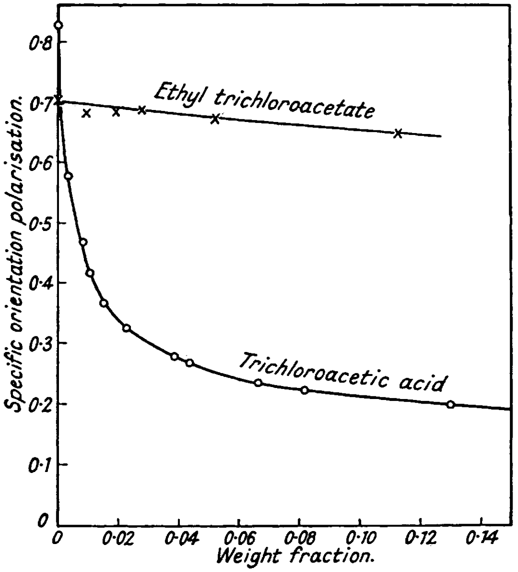
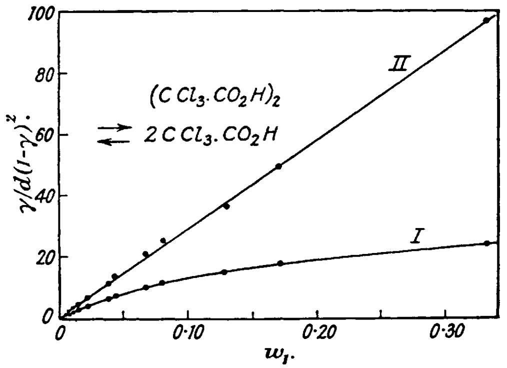


Fig. 5.



solution, and $\gamma/d(1 - \gamma d)^2$ approaches infinity. Therefore for some value of ${}_0p_{a_1}$ between 0 and 0·150 the curve must become nearly straight. By solving for two concentrations, the value 0·080 has been obtained, and the association factor γ' worked out with this figure. Curve II (Fig. 5) corresponds with curve I, but is derived from γ' instead of γ; it is a straight line, from whose slope it can be deduced that the equilibrium constant K is 24 l. mol.$^{-1}$. When ${}_0p_{a_1}$ is 0·080, ${}_0P_{a_1}$ is 26·0 c.c., and the apparent moment of the double molecule is 1·1 D. This result is in satisfactory agreement with the estimates quoted above (for other acids) from the papers of Zahn and Briegleb; whether it is false and arises from solvent or atomic polarisation effects, further work over a wide temperature interval might decide.

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