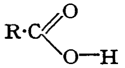
146. *The Effect of Moisture on the Hydrogen Bond in Carboxylic and Sulphinic Acids.*

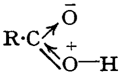
By (Mrs.) W. G. Wright.

The association of both carboxylic and sulphinic acids is shown to be increased by the presence of moisture. Sulphinic acids are more highly associated than carboxylic acids, and evidence points to the fact that they exist in solution as trimers and hexamers. In solution in dry nitrobenzene, association of sulphinic acids appears to be similar to that exhibited by alcohols.

Carboxylic Acids.—If the structure of a carboxylic acid molecule in solution in a non-aqueous solvent can be represented as lying between the extreme forms (I) and (II), then the approach of a molecule such as a water molecule, which could interact with the hydrogen atom of the carboxylic group, would modify the structure towards structure (II). This might be expected to have some influence on the degree of association of the acid, and, for small quantities of moisture, this effect should be more marked in very dilute solutions, and decrease as the proportion of acid to water increases.

(I.)



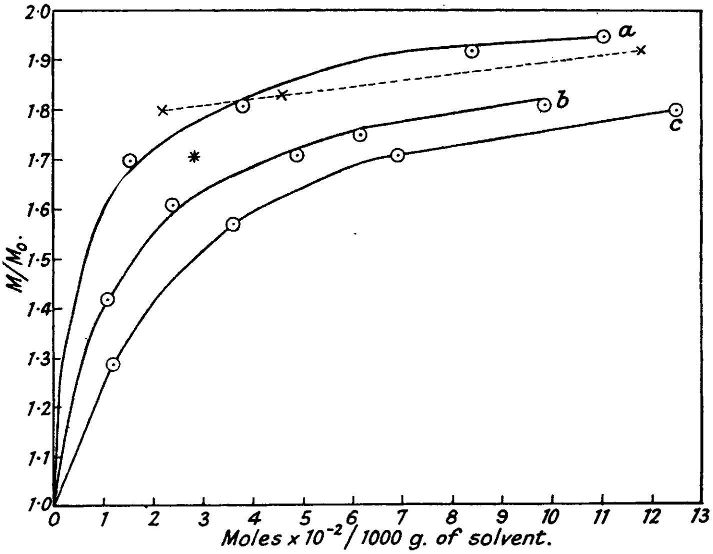


(II.)

Measurements of the freezing-point depressions in very dry solvents were made, and compared with those in solvents containing moisture. The curves obtained by plotting the degree of association against the concentration in moles per 1000 g. are shown in Figs. 1—8. In every case the degree of association in the dry solvent was lower than in the solvent containing moisture.

Fig. 1.

Association of benzoic acid in benzene.



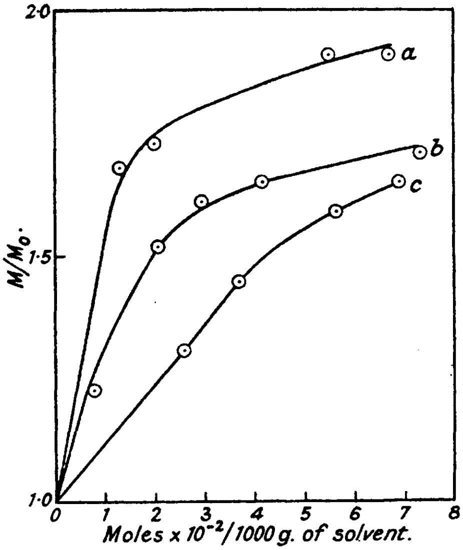
(a) " *AnalaR* " *benzene containing* 0·0043 *mole of water*/1000 *g. of solvent.*
(b) *Dry* " *AnalaR* " *benzene.*
(c) *Dry pure benzene.*
* " *AnalaR* " *benzene containing* 0·0023 *mole of water*/1000 *g. of solvent.*
×——× *Beckmann's experiment.*

It is noteworthy that, in the case of benzyl alcohol where no such ionic hybrid is possible, the presence of water causes a decrease in the degree of association, as would be expected from the rise in dielectric constant (Brown and Bury, *J. Physical Chem.*, 1926, **30**, 694).

Benzoic acid. A detailed examination of the association of this acid was made, at lower concentrations than heretofore. The results are shown in Figs. 1 and 7.

FIG. 2.

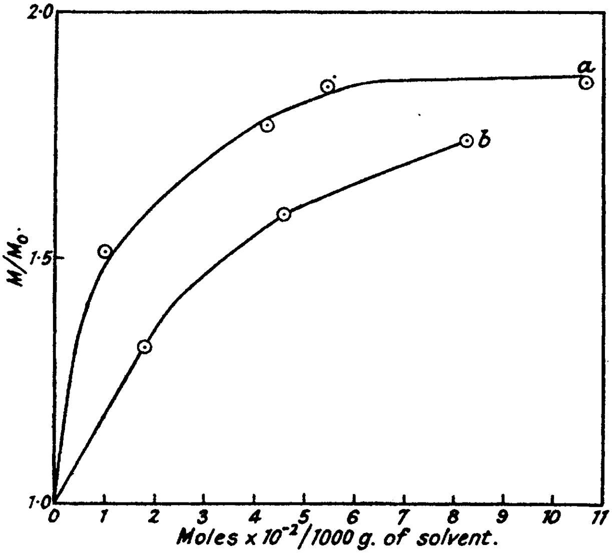
Association of o-*toluic acid in benzene.*



(a) *Containing* 0·0197 *mole of water*/1000 *g. of solution.*
(b) *Dry " AnalaR " benzene.* (c) *Dry pure benzene.*

FIG. 3.

Association of m-*toluic acid in benzene.*

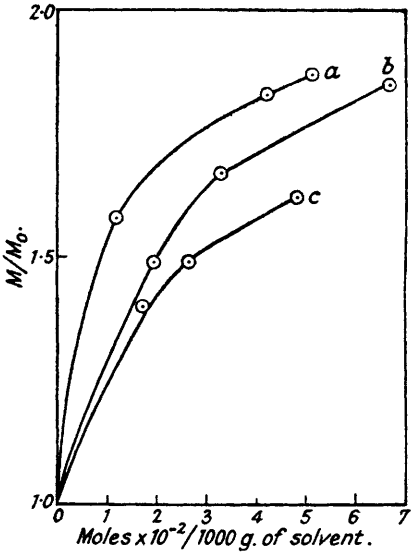


(a) *Containing* 0·0098 *mole of water*/1000 *g. of solvent.* (b) *Dry.*

Beckmann (*Z. physikal. Chem.*, 1888, **2**, 715) used Kahlbaum benzene, dried, and distilled over sodium. By drying " AnalaR " benzene and distilling over sodium, the results shown in Fig. 1, curve *a*, were obtained. It will be seen that the results of Beckmann, marked x—x—x, lie very near this curve. The same benzene was then dried for 2 weeks over phosphoric oxide and distilled from fresh phosphoric oxide, and the results shown by curve *b* were obtained.

FIG. 4.

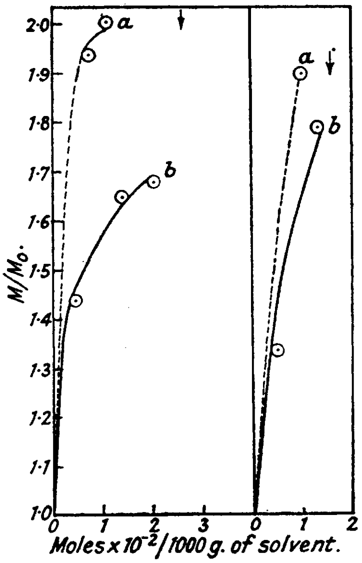
Association of p-*toluic acid in benzene.*



(a) *Containing* 0·0162 *mole of water*/1000 *g. of solvent.*
(b) *Containing* 0·0080 *mole of water*/1000 *g. of solvent.*
(c *Dry.*

FIG. 5. FIG. 6.

Association of α- *and* β-*naphthoic acids in benzene.*

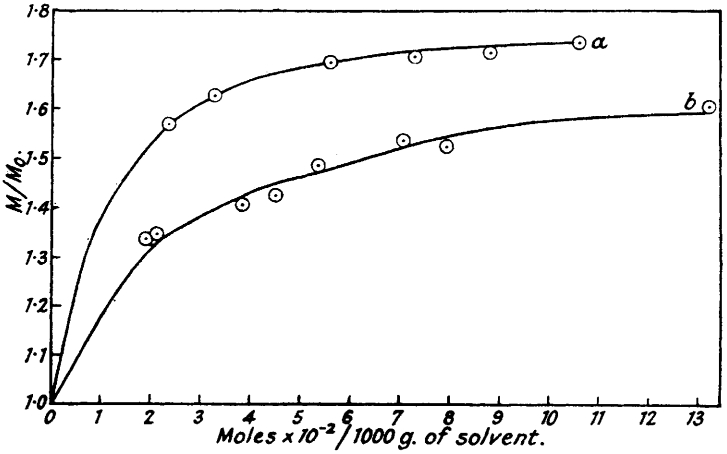


α-*Acid.* β-*Acid.*

FIG. 5. (a) *Containing* 0·0244 *mole of water*/1000 *g. of solvent.* (b) *Dry.*
FIG. 6. (a) *Containing* 0·0244 *mole of water*/1000 *g. of solvent.* (b) *Dry.*
↓ *Indicates point at which solution was saturated.*

FIG. 7.

Association of benzoic acid in nitrobenzene.



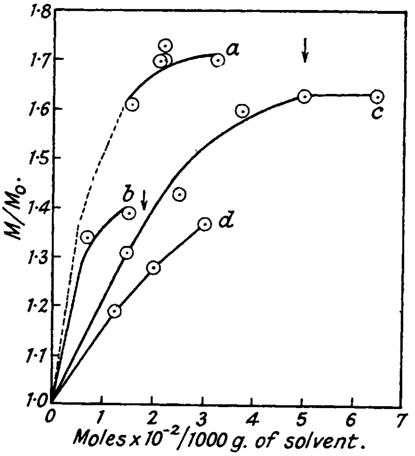
(a) *Containing* 0·0107, 0·0428, 0·1360 *mole of water*/1000 *g. of solvent (all on same curve).*
(b) *Dry and containing* 0·0026 *mole of water*/1000 *g. of solvent (on same curve).*

The difference in the number of water molecules present was calculated from the rise in freezing point of the benzene. Finally, benzene purified by recrystallisation many times, and dried and distilled from phosphoric oxide, was used, and the results shown in curve *c* were obtained.

It is obvious that the degree of association is sensitive to very small amounts of water. It is also raised by the presence of other impurities (curve *b*).

FIG. 8.

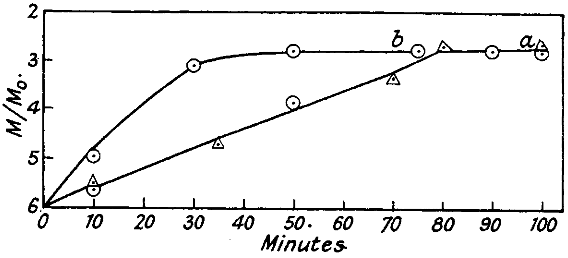
Association of α- and β-naphthoic acids in nitrobenzene.



(a) *β-Naphthoic acid, containing* 0·0366 *mole of water*/1000 *g. of solvent.*
(b) *β-Naphthoic acid, dry.*
(c) *α-Naphthoic acid, containing* 0·0386 *mole of water*/1000 *g. of solvent.*
(d) *α-Naphthoic acid, dry.*

FIG. 9.

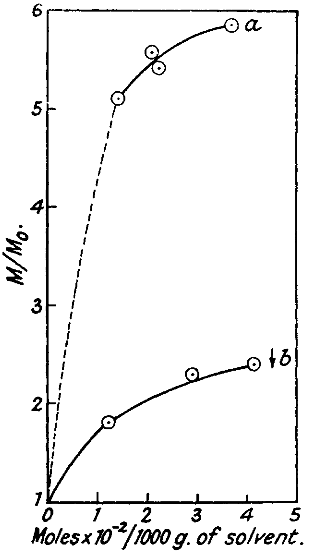
α- and β-Naphthalenesulphinic acids : rate of degradation of hexamer.



(a) ○ *α-Acid, concentration* 0·0104 *mole* /1000 *g. of solvent.*
△ *β-Acid, concentration* 0·0087 *mole*/1000 *g. of solvent.*
(b) *α-Acid, concentration* 0·0128 *mole*/*per* 1000 *g. of solvent.*

FIG. 10.

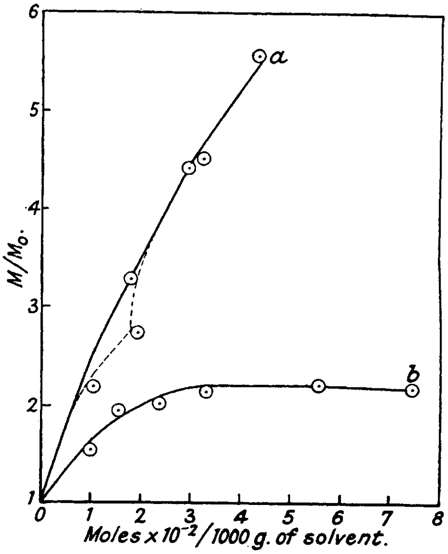
Association of benzenesulphinic acid in benzene.



(a) *Containing* 0·1863 *mole of water*/1000 *g. of solvent.*
(b) *Dry.*

FIG. 11.

*Association of toluene-*p*-sulphinic acid in benzene.*



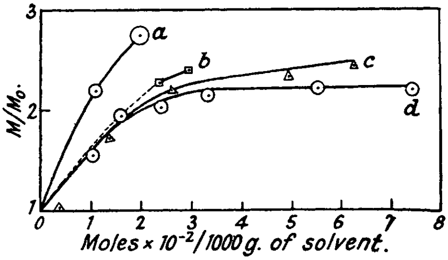
(a) *Containing* 0·0244 *mole of water*/1000 *g. of solvent.*
(b) *Dry.*

In nitrobenzene (Fig. 7) the degree of association is raised by the presence of water, but is not so sensitive to small amounts. 0·0026 Mole. of water per 1000 g. of solvent had no effect on association.

The solvation of benzoic acid in undried benzene is extremely slow, whereas it is practically instantaneous in the very dry solvent. Sidgwick has stated that an intermolecular hydrogen bond causes a decrease in the solubility in benzene (Sidgwick and Callow, *J.*, 1924, 527; Sidgwick, *J.*, 1925, 907).

FIG. 12.

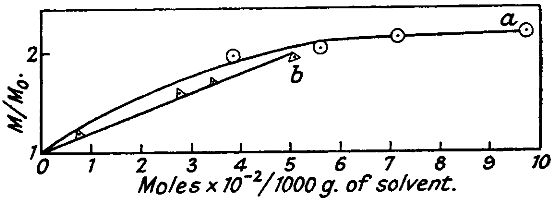
*Association of toluene-*p*-sulphinic acid in benzene.*



Containing (a) 0·0244, (b) 0·0123, (c) 0·0113 *mole of water*/1000 *g. of solvent.* (d) *Dry.*

FIG. 13.

Association of benzenesulphinic acid in nitrobenzene.



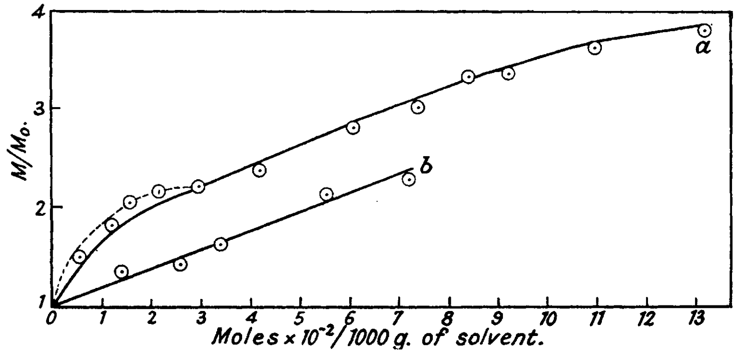
(a) *Containing* 0·1360 *mole of water*/1000 *g. of solvent.* (b) *Dry.*

In the moist solvent the dimer may be formed on the solid–liquid interface, thus inhibiting solvation. All carboxylic acids so far examined show this characteristic.

Toluic acids. In pure dry benzene, *p*-toluic acid gave a curve identical with that of benzoic acid, and the effect of adding water was similar (Fig. 4). *o*-Toluic, on the other hand, gave a slightly different curve in the pure dry solvent. The association was not quite so great, owing, probably, to a small degree of chelation between the methyl and the carboxyl group (Fig. 2). Curve *b* shows the association in dry " AnalaR " benzene. The presence of impurities had the same effect as on the association of benzoic acid. In the presence of traces of moisture *o*- and *p*-toluic acids and benzoic acid all gave similar curves, M/M_0 (where M = apparent molecular weight and M_0 = formal molecular weight), reaching 1·9 at 0·07 mole per 1000 g. of solvent (Figs. 1, 2, 4, curves *a*).

FIG. 14.

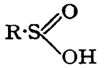
*Association of toluene-*p*-sulphinic acid in nitrobenzene.*

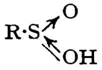


(a) *Containing* 0·1360 *mole of water*/1000 *g. of solvent.* (b) *Dry.*

Naphthoic acid. Association was increased by the presence of water in both these acids (Figs. 5 and 6). In view of the low solubility of these acids in benzene, the experiments were repeated in nitrobenzene, with similar results. β-Naphthoic is a little more highly associated than the α-acid.

Sulphinic Acids.—The effect of moisture on the association exhibited by these acids is even more marked than on the association of carboxylic acids. Phillips, Hunter, and Sutton (*J.*, 1945, 146) have shown that the dative bond S→O of sulphones should be amended to S=O. If a similar structure be considered for sulphinic acids, possible resonance hybrids, the relative importance of which may be affected by the presence of water, are shown in (III) and (IV).

(III.)



(IV.)

In nitrobenzene, in the presence of traces of water, trimers are formed (Figs. 13—16). In the case of α- and β-naphthalenesulphinic acids, the freezing point depressions indicate the formation of hexamers on solvation, which break down slowly, in the course of 1—1½ hours, to trimers. At approximately the same concentration α- and β-acids gave identical time curves (Fig. 9, curve *a*), and the rate of degradation increased with concentration (Fig. 9, curve *b*).

In very dry nitrobenzene the association of sulphinic acids is evidently of quite a different nature. A linear relationship between association and concentration is shown, similar to that exhibited by alcohols (Figs. 13—16). Since the acidity of carboxylic acids is attributed by Pauling (" The Nature of the Chemical Bond ") to the existence of the ionic hybrid, without which " the acid strength would differ by only a small amount from that of an alcohol ", it may be that in a very dry solvent of high dielectric constant the ionic structure contributes little or nothing towards the resultant, and the acids do, in fact, behave, as far as association is concerned, like alcohols. This change in the nature of the association in intensively dried solvent was shown by all sulphinic acids examined:

FIG. 15. FIG. 16.

Association of α- and β-naphthalenesulphinic acids in nitrobenzene.

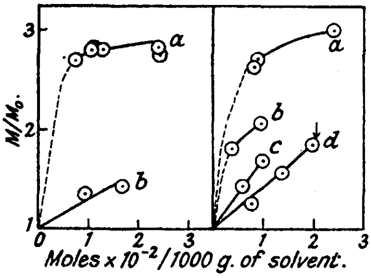
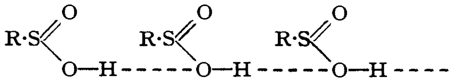


FIG. 15. *α-Acid :*
(a) *Containiing* 0·1360 *mole of water*/1000 *g. of solvent.*
(b) *Dry.*

FIG. 16. *β-Acid :*
Containing (a) 0·1360, (b) 0·0157, (c) 0·0059 *mole of water*/1000 *g. of solvent.*
(d) *Dry.*



In benzene, no lag in the stabilising of the freezing point occurred, but the degree of association was very high in the damp solvent (Figs. 10—12), indicating the presence of stable hexamers in undried solvents and of trimers in intensively dried solvent. No change in the nature of the association was indicated in dry benzene.

The high dielectric constant of nitrobenzene probably accounts for the lack of stability of the hexamers in this solvent.

The solubilities of β-naphthoic, β-naphthalenesulphinic, and benzenesulphinic acids were found to be greater in damp nitrobenzene than in the dry solvent.

Benzenesulphinic acid, at 0·04 mole per 1000 g. concentration, gave M/M_0 2·4, in dry benzene, whereas in the damp solvent, at the same concentration, the figures rose to 5·9 (Fig. 10).

Toluene-*p*-sulphinic acid at the same concentration gave 2·2 in the dry solvent, and 5·2 in the solvent containing moisture (Fig. 11). The association of this acid is sensitive to very small increments in the amount of water present (Fig. 12).

α-Naphthalenesulphinic, which was very sparingly soluble in both solvents, gave $M/M_0 = 3{\cdot}3$ in dry benzene, and 5·6 in damp benzene; 1·3 in dry, and 2·8 in damp nitrobenzene, all at 0·01 mole concentration (Fig. 15).

β-Naphthalenesulphinic acid was too insoluble in benzene for reliable observation, but in nitrobenzene gave $M/M_0 = 1·85$ in dry and 2·94 in damp solvent, both at 0·02 mole concentration (Fig. 16). β-Naphthalenesulphinic acid was slightly more associated than the α-acid (compare β- and α-naphthoic acids, see earlier).

Association of Benzoic Acid in Benzene (*see Fig.* 1).

Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Method of drying.
0·0121	0·048°	1·29	Dry, purified	P_2O_5, 2 weeks
0·0360	0·117	1·57		
0·0691	0·214	1·71		
0·1252	0·356	1·80		
0·0109	0·0395	1·42	Dry (" AnalaR ")	P_2O_5, 17 days
0·0240	0·0765	1·61		
0·0487	0·146	1·71		
0·0615	0·204	1·75		
0·0986	0·280	1·81		
0·1885	0·511	1·89		
0·0283	0·085°	1·71	0·0023 (" AnalaR ")	P_2O_5, 1 week
0·0153	0·046	1·70	0·0043 (" AnalaR ")	Na, 1 week
0·0382	0·108	1·81		
0·0841	0·224	1·92		
0·1104	0·290	1·95		
Beckmann (*Z. physikal. Chem.*, 1888, **2**, 715).				
0·0221	—	1·80	Kahlbaum	Na
0·0459	—	1·83		
0·1180	—	1·92		

Association of Toluic Acids in Benzene.

Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
See Fig. 2.				
Ortho-	0·0259	0·101°	1·31	Dry, purified
	0·0371	0·131	1·45	
	0·0567	0·183	1·59	
	0·0691	0·214	1·65	
	0·0081	0·034	1·23	Dry, " AnalaR "
	0·0208	0·070	1·52	
	0·0296	0·094	1·61	
	0·0419	0·132	1·65	
	0·0738	0·222	1·71	
	0·0128	0·039	1·68	0·0197
	0·0199	0·059	1·73	
	0·0551	0·148	1·91	
	0·0673	0·181	1·91	
See Fig. 3.				
Meta-	0·0103	0·051	1·04	Dry
	0·0181	0·070	1·32	
	0·0460	0·148	1·59	
	0·0826	0·244	1·74	
See Fig. **3**.				
Meta-	0·0099	0·033°	1·51	0·0098
	0·0425	0·021	1·77	
	0·0544	0·148	1·85	
	0·1064	0·288	1·86	
See Fig. 4.				
Para-	0·0173	0·059	1·40	Dry
	0·0263	0·089	1·49	
	0·0482	0·143	1·62	
	0·0193	0·066	1·49	0·0080
	0·0327	0·106	1·67	
	0·0670	0·185	1·85	
	0·0118	0·038	1·58	0·0162
	0·0421	0·118	1·83	
	0·0514	0·141	1·87	
	0·0764	saturated		

Association of Naphthoic Acids in Benzene.

Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
See Fig. 5.				
α-	0·0048	0·017°	1·44	Dry
	0·0140	0·043	1·65	
	0·0204	0·062	1·68	
	0·0072	0·019	1·94	0·0244
	0·0106	0·027	2·01	
	0·0263	saturated		
See Fig. 6.				
β-	0·0052	0·020°	1·34	Dry
	0·0133	0·038	1·79	
	0·0100	0·027	1·90	0·0244
	0·0164	saturated		

Association of Benzoic Acid in Nitrobenzene (*see Fig.* 7).

Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Method of drying.
0·0189	0·099°	1·34	Dry	P_2O_5, 13 days
0·0387	0·192	1·41		
0·0706	0·320	1·54		
0·1320	0·570	1·61		
0·0202	0·105	1·34	0·0026	P_2O_5, 9 days
0·0213	0·110	1·35		
0·0452	0·222	1·43		
0·0537	0·252	1·49		
0·0793	0·361	1·53		
0·0561	0·235°	1·70	0·0107	P_2O_5, 2 days
0·0327	0·140	1·63	0·0428	Moisture added
0·0732	0·300	1·71		
0·0882	0·361	1·72		
0·1057	0·426	1·74		
0·0236	0·105	1·57	0·1360	Moisture added

Association of Naphthoic Acids in Nitrobenzene (*see Fig.* 8).

Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
α-	0·0126	0·074°	1·19	Dry	β-	0·0071	0·037°	1·34	Dry
	0·0199	0·110	1·28			0·0149	0·075	1·39	
	0·0299	0·152	1·37			0·0200	saturated		
	0·0048	0·038	1·00	0·0386		0·0154	0·067	1·61	0·0366
	0·0147	0·078	1·31			0·0211	0·087	1·70	
	0·0249	0·122	1·43			0·0218	0·088	1·73	
	0·0375	0·164	1·60			0·0219	0·090	1·70	
	0·0498	0·214	1·63			0·0326	0·134	1·70	
	0·0646	0·276	1·63			0·0433	saturated		

Association of α- and β-Naphthalenesulphinic Acids (*see Fig.* 9).

Rate of degradation of the hexamer after solvation.

Acid.	Moles per 1000 g.	Time (mins.).	ΔT.	M/M_0.	Acid.	Moles per 1000 g.	Time (mins.).	ΔT.	M/M_0.
α-	0·0104	10	0·102°	5·60	α-		75	0·032°	2·80
		50	0·019	3·83			200	0·032	—
		90	0·027	2·80	β-	0·0087	10	0·011	5·51
		100	0·027	2·80			35	0·013	4·66
		185	0·029	—			70	0·018	3·37
	0·0128	10	0·018	4·98			80	0·022	2·71
		30	0·029	3·09			100	0·022	2·71
		50	0·032	2·80			190	0·022	—

Association of Benzenesulphinic Acid in Benzene (*see Fig.* 10).

Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000.
0·0124	0·035°	1·81	Dry	0·0140	0·014°	5·11	0·1863
0·0291	0·065	2·29		0·0207	0·019	5·58	
0·0416	0·089	2·39		0·0221	0·021	5·40	
				0·0366	0·032	5·86	

Association of Toluene-p-*sulphinic Acid in Benezne* (*see Figs.* 11 *and* 12).

Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
0·0103	0·034°	1·55	Dry	0·0235	0·053°	2·27	0·0123
0·0157	0·041	1·96		0·0296	0·063	2·40	
0·0240	0·061	2·02		0·0107	0·025	2·19	0·0244
0·0333	0·079	2·15		0·0181	0·028	3·30	
0·0556	0·128	2·22		0·0197	0·029	2·76	
0·0746	0·173	2·20		0·0294	0·032	4·42	
0·0036	0·018	1·03	0·0113	0·0326	0·037	4·52	
0·0135	0·040	1·72		0·0433	0·037	5·58	
0·0260	0·061	2·19					
0·0496	0·108	2·35					
0·0625	0·131	2·44					

Association of Naphthalenesulphinic Acids in Benzene.

Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
α-	0·0051	0·010°	2·62	Dry	β-	0·0018	0·005°	1·81	Dry
	0·0087	0·008	5·75	0·1863		0·0095	saturated		
	0·0108	saturated							

Association of Benzenesulphinic Acid in Nitrobenzene (*see Fig.* 13).

Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
0·0073	0·042°	1·21	Dry	0·0384	0·100°	1·97	0·1360
0·0274	0·119	1·61		0·0561	0·140	2·05	
0·0346	0·143	1·69		0·0716	0·170	2·16	
0·0509	0·182	1·95		0·0976	0·227	2·20	
0·0933	saturated						

*Association of Toluene-*p*-sulphinic Acid in Nitrobenzene* (*see Fig.* 14).

Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
0·0140	0·093°	1·35	Dry, in presence of silica gel.	0·0296	0·094°	2·20	0·1360
0·0258	0·127	1·42		0·0418	0·123	2·38	
0·0337	0·145	1·63		0·0608	0·151	2·81	
0·0553	0·191	2·12		0·0737	0·173	2·99	
0·0719	0·220	2·28		0·0840	0·176	3·33	
0·0055	0·026	1·49	0·1360	0·0923	0·193	3·35	
0·0121	0·046	1·83		0·1096	0·214	3·59	
0·0156	0·053	2·06		0·1321	0·245	3·77	
0·0215	0·070	2·15					

Association of Naphthalenesulphinic Acids in Nitrobenzene.

Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.	Acid.	Moles per 1000 g.	ΔT.	M/M_0.	Water in moles per 1000 g.
See Fig. 15.					*See* Fig. 16.				
α-	0·0092	0·047°	1·36	Dry	β-	0·0076	0·042°	1·26	Dry
	0·0167	0·082	1·43			0·0138	0·062	1·56	
	0·0073	0·019	2·70	0·1360		0·0199	0·075	1·85	
	0·0104	0·029	2·80			0·0210	saturated		
	0·0109	0·027	2·83			0·0057	0·028	1·42	0·0059
	0·0128	0·032	2·80			0·0098	0·041	1·68	
	0·0240	0·059	2·83			0·0036	0·014	1·79	0·0157
	0·0243	0·062	2·75			0·0091	0·031	2·05	
						0·0080	0·021	2·63	0·1360
						0·0087	0·022	2·71	
						0·0240	0·056	3·00	

EXPERIMENTAL.

Purity of Materials.—May and Baker's benzene was fractionally crystallised 7 times, and then kept over phosphoric oxide for at least 2 weeks, with frequent shaking and changing of the drying agent. As required it was distilled direct from fresh phosphoric oxide into the freezing point tube (f. p. of benzene, 5·51—5·52°).

This benzene crystallised in hexagons on the sides of the vessel, and this hexagonal formation of crystals was retained on the addition of both water and solute. It is evidently not so much a sign of purity as of the absence of such substances as are adsorbed on the solid–liquid interface. Where this occurs there is a definite change in crystal form. Acetic acid causes benzene to freeze in long needles, owing to preferential adsorption of the impurity on certain faces of the crystal (Milligan, *J. Physical Chem.*, 1929, **33**, 1363; Marc and Wenk, *Z. physikal. Chem.*, 1910, **68**, 104). It is well known that coloured impurities are always deposited on the first batch of crystals, indicating that this adsorption is a common occurrence.

"AnalaR" Nitrobenzene was dried over phosphoric oxide and fractionated. The fraction boiling at 210—211° was kept over phosphoric oxide for 2 weeks; the freezing point was found to be unchanged by further drying (f. p. of nitrobenzene, 5·72°).

All solutes were purified by recrystallisation and kept over phosphoric oxide, except benzenesulphinic acid. This compound cannot be dried in this way, as it decomposes. It was therefore dried in a current of warm dry air, and cooled in a desiccator containing phosphoric oxide, immediately before use.

The sulphinic acids were prepared from the corresponding sulphonyl chlorides. Benzenesulphonyl chloride was reduced to the sulphinic acid by being shaken with a saturated solution of sodium sulphite for ½ hour at room temperature. α- and β-Naphthalenesulphinic acids were purified by crystallisation from chloroform. Benzenesulphinic was crystallised from ether, and subsequently precipitated from the ammonium salt. Toluene-*p*-sulphinic acid was treated in the same manner as benzenesulphinic acid. These precautions were necessary to remove traces of the sodium hydrogen sulphinate which is always precipitated with these acids, and is stable in acid solution. Absence of inorganic matter was verified by combustion in a weighed platinum crucible.

Method.—The required solvent was distilled into the freezing-point tube. Dry air, or, in the case of sulphinic acids, nitrogen to prevent oxidation, was bubbled through dried solvent containing phosphoric oxide at the freezing point of the solvent, and was then passed through the top of the freezing-point tube. Measurements of freezing point showed that this current of air or nitrogen, saturated with dry solvent, removed any traces of moisture which may have entered the apparatus during manipulation.

As soon as a steady freezing point was reached the solute was introduced. The passage of dry solvent vapour was continued throughout the experiment, thus removing any water which may have entered during the addition of the solute.

This current of solvent vapour not only prevented loss of weight from the solvent, which a current of dry air alone would cause, but was itself a far more effective drying agent than dry air. All observations were carried out on very dilute solutions to eliminate inaccuracies due to large differences in internal pressure. The depressions in freezing point (ΔT) were correspondingly small, and, to obtain as accurate results as possible, all conditions were kept constant, *i.e.* the temperature of the cooling bath, the depth of the freezing point tube in the bath, the depth of the bulb of the thermometer in the solution, the degree of super-cooling, and the rise in temperature while the crystals were being melted. The temperature of the cooling bath was kept at 1·5° below the freezing point of the solution. Super-cooling was kept between 0·05° and 0·1°; thus comparatively few crystals were formed, and the strength of the solution was not materially increased on crystallisation.

Solvents containing the required amount of moisture were prepared by mixing dry solvent with solvent saturated at room temperature. Freezing-point observations in the damp solvent were made in a current of air or nitrogen, which had been first dried, and then passed through some of the same solvent, at its freezing point; thus no more moisture was introduced. Measurement of the freezing point of the solvent in the bubbler both before and after the experiment showed that it was not appreciably dried during the course of the experiment. A fairly large volume was used.

For purposes of calculation the freezing-point lowering constant was taken as 5·12° for benzene and 6·99° for nitrobenzene.

Thanks are due to Dr. J. Kenyon, F.R.S., for his interest in this work.

BATTERSEA POLYTECHNIC. [*Received, March 22nd*, 1948.]