146. *The Freezing Points of Some Benzene Solutions.*

By C. R. Bury and H. O. Jenkins.

The depression of the freezing point of benzene by 19 solutes has been determined by an equilibrium method in order to test recent views as to the importance of two of the factors that are believed to be responsible for the departure of solutions from ideal behaviour, *viz.*, internal-pressure differences and the dipole moments of the molecules.

EXPERIMENTAL.

Previous investigators of the f. p.'s of solutions in organic solvents, almost without exception, have used the Beckmann or some other modification of the supercooling method. This method is subject to a number of objections: (*a*) Thermal equilibrium is never established. (*b*) The concentration of the solution is uncertain owing to the separation of solvent on freezing. (*c*) The ease with which benzene solutions can be supercooled seems to depend on the concentration of the solute (Jones and Bury, J., 1925, **127**, 1947; Sidgwick and Sutton, J., 1930, 1461); the difference between true and observed f. p.'s, which always exists when this method is used but is unimportant as long as it remains constant, is likely to increase with concentration as the result of this phenomenon. (*d*) The solute may be adsorbed at the solid–liquid interface that is formed on freezing.

The last objection has not been raised before and must therefore be discussed. The discussion will be limited to the best established case—adsorption of acetic acid at the benzene solid–liquid interface. The evidence for this is, first, that pure benzene freezes without supercooling in large transparent blocks which adhere to the walls of the containing vessel, while the addition of 0·2% of acetic acid causes it to freeze after considerable supercooling in long needles, radiating inwards from the containing walls. Such changes of crystal habit are usually attributed, and in some cases can be proved to be due, to the preferential adsorption of an impurity on certain faces of the crystal (Milligan, *J. Physical Chem.*, 1929, **33**, 1363; Marc and Wenk, *Z. physikal. Chem.*, 1910, **68**, 104). Marc and Wenk also show that the presence of adsorbable impurities favours supercooling. The frequency with which the crystal habit of organic solvents is altered by solutes indicates that adsorption is a common occurrence.

Secondly, van Bijlert's method of detecting the formation of solid solutions (*Z. physikal. Chem.*, 1891, **8**, 343) can also be used to detect adsorption; the method, indeed, is incapable of distinguishing between the two phenomena. This method, which is identical in principle with Schreinemakers's method of indirect analysis, consists in adding an inert reference substance (X) to a solution in benzene of the substance (Y) which is suspected of being adsorbed by, or forming mixed crystals with, solid benzene. The mixture is partially frozen, the mother-liquor poured off, and both mother-liquor and moist solid analysed. Mixed-crystal formation or adsorption is indicated if the product $P = [X]_L[Y]_S/[X]_S[Y]_L > 1$, where brackets indicate concentrations, and the subscripts L and S refer to mother-liquor and moist solid respectively.

Beckmann (*Z. physikal. Chem.*, 1897, **22**, 609) performed a series of three experiments with acetic acid in benzene, using bromoform as reference substance, which gave an average value for P of 1·05. He was investigating the possibility of mixed-crystal formation, which usually gives rise to much greater values of P, and therefore attributed his results to experimental error. A similar series of four experiments by Dr. E. R. Jones, working in these laboratories, gave 1·03 as the mean value of P. While the amount of acetic acid separating out with the solid is small, and accurate analysis difficult, these results indicate that P is definitely greater than unity, and that acetic acid is adsorbed from a benzene solution on the surface of solid benzene: the other alternative, mixed-crystal formation, is improbable with substances of such diverse structure.

If, in the determination of degrees of association from freezing-point measurements, solutions are prepared synthetically, and the removal of solute by adsorption neglected, the results obtained will be too great. Comparison, however, of our results for acetic acid, in which this source of error is avoided, with those of previous investigators (see below) makes it probable that the error is small.

In order to avoid the errors of the supercooling method, freezing points have been determined by an equilibrium method, in which the temperature and concentration of a solution in equilibrium with solid benzene are determined, errors due to adsorption being avoided since the concentration is determined after the solute has been adsorbed. The apparatus and procedure were based on those employed in previous work on aqueous solutions (Jones and Bury, *Phil. Mag.*, 1927, **3**, 1032), but the application of the method to non-aqueous solutions necessitates several important modifications.

First, organic liquids generally have much smaller latent and specific heats than water: this makes it necessary to reduce to a minimum the passage of heat from the room to the inside of the vacuum flask in which the freezing points are determined. This was achieved by sinking the flask in a well-stirred outer bath whose temperature was maintained within 0·1° of that of the contents of the flask. Without this precaution a continual temperature drift was observed.

Secondly, the tendency of benzene to absorb moisture cannot be neglected (Sidgwick, J., 1920, **117**, 1340). To avoid this, a gentle current of dry air, first cooled by passage through a metal coil immersed in the outer bath, was passed into the flask; also, whenever possible, a small amount of phosphoric oxide was placed in the solution (Roberts and Bury, J., 1923, **123**, 2037; Jones and Bury, J., 1925, **127**, 1947). Unfortunately, the device of using phosphoric oxide to keep solutions dry is inapplicable with solutes containing hydroxyl or other reactive groups (Brown and Bury, *J. Physical Chem.*, 1925, **29**, 1312).

To obviate difficulties that arise from the small latent heat of benzene, and to avoid unnecessary exposure of it to the air, about 200 ml. of the freshly distilled solvent were placed directly in the vacuum flask and frozen *in situ* by a current of cold brine which circulated through two concentric tubes immersed in the solvent. After determining the freezing point of the solvent, a suitable amount of the solute was added and the freezing process repeated, and so on.

A disadvantage of the method is the large quantity of solvent required, although apparatus and procedure were designed to economise its use. Each series required about 350 ml. of carefully purified benzene, obtained by fractionation from about four times the quantity of commercial " pure " benzene. Altogether about 50 series of experiments were performed, two at least being done with each solute.

The chief disadvantage of the method, however, is the difficulty of analysing the solutions with sufficient accuracy; this difficulty has played an important part in restricting the choice of solutes. Direct volumetric methods were used whenever possible, *i.e.*, in estimating phenol, *o*- and *p*-cresol, and pyridine; but for the majority of the solutes some indirect method based on determinations of some physical property had to be used. Measurement of the refractive indices with a Pulfrich refractometer was tried in some preliminary experiments, but the volatility of the solutions, and the unsatisfactory temperature control of the instrument made this method impracticable. Density determinations were therefore used. Samples of about 30 ml. were taken from the freezing-point apparatus and shaken with a few ml. of water at 25° to remove any phosphoric oxide held in suspension; the density of these moist solutions was determined at 25° with an accuracy of about ± 0·003%. Concentrations were deduced by comparison with the densities of solutions of known concentration which had also been saturated with water at 25°. When, for reasons stated above, phosphoric oxide could not be used, densities of dry solutions were compared.

The accuracy of analysis depends on the difference between the densities of solvent and solute. Under favourable conditions, the molality could be determined with an uncertainty of less than 0·0005 unit, but with other solutes the possible error was about twice as great. This uncertainty as to the concentration was the most serious source of error in the work. There are, of course, a number of solutes whose densities are so close to that of benzene that this method of analysis is useless; for such solutes no method of analysis of sufficient accuracy could be devised.

Temperatures were measured with a Beckmann thermometer which had been standardised at the National Physical Laboratory. Although more accurate methods are available, further refinement in the measurement of temperatures is useless unless solutions can be analysed more accurately. Peterson and Rodebush (*J. Physical Chem.*, 1928, **32**, 709) devised an apparatus, based on the equilibrium principle, for the accurate determination of the freezing points of very dilute benzene solutions; in practice the analysis of these dilute solutions was found impossible, and their concentration was determined by synthesis, before freezing. This involves the sacrifice of one of the essential features of the equilibrium method, to which it owes its superiority.

Benzene was purified by shaking with sulphuric acid until a negative indophenin test was given; it was then washed, distilled from phosphoric oxide, and fractionally frozen five times. Commercial benzene (and *cyclo*hexane also) seems to contain some impurity that influences its crystal habit in the same way that acetic acid does, and the appearance of the solid changes remarkably as fractionation proceeds. Purified benzene was stored over water and distilled from phosphoric oxide as required. All solutes used were carefully purified by appropriate methods.

TABLE I.

Carbon tetrachloride.

θ.	*m.*	*θ/m.*	*a.*	*γ.*	*γ'.*
0·603°	0·1184	5·093°	1·000	0·992	0·991
0·883	0·1737	5·083	0·999	0·988	0·987
0·883	0·1740	5·075	1·001		0·986
1·761	0·3499	5·031	1·000	0·975	0·973
2·457	0·4917	4·997	1·000	0·966	0·963
2·801°	0·5630	4·975°	1·000	0·960	0·958
4·005	0·8166	4·904	1·001	0·943	0·940
4·503	0·9218	4·885	0·999	0·935	0·933
4·972	1·026	4·848	1·002	0·928	0·926
5·620	1·166	4·818	1·000	0·918	0·917

Chloroform.		*Bromoform.*		p-*Dichlorobenzene.*		*Ethylene dichloride.*	
θ.	*m.*	*θ.*	*m.*	*θ.*	*m.*	*θ.*	*m.*
0·495°	0·0973	0·819°	0·1611	0·435°	0·0851	0·937°	0·1847
0·713	0·1398	1·334	0·2638	0·875	0·1724	1·297	0·2563
0·945	0·1871	2·053	0·4081	1·100	0·2167	1·345	0·2662
1·547	0·3073	3·045	0·6122	2·820	0·5673	2·920	0·5871
2·125	0·4251	3·995	0·8125	3·353	0·6761	3·370	0·6812
2·810	0·5658	4·675	0·9579	4·624	0·9471	4·194	0·8549
4·885	1·0033	4·899	1·0067	4·830	0·9914	4·664	0·9560
5·515	1·1403	5·173	1·0656	5·273	1·0859	5·111	1·0536

θ.	*m.*	*θ/m.*	*a.*	*γ.*	*θ.*	*m.*	*θ/m.*	*a.*	*γ.*
p-*Cresol.*					o-*Cresol.*				
0·420°	0·0861	4·878°	1·045	0·917	0·790°	0·1612	4·901°	1·040	0·915
1·100	0·2341	4·699	1·078	0·833	0·989	0·2078	4·759	1·065	0·878
1·305	0·2906	4·490	1·125	0·781	1·407	0·3041	4·627	1·090	0·834
1·663	0·3867	4·300	1·170	0·724	1·692	0·3662	4·621	1·089	0·819
2·539	0·6389	3·974	1·254	0·619	2·690	0·6300	4·271	1·165	0·714
3·483	0·9951	3·501	1·409	0·502	3·105	0·7618	4·076	1·215	0·666
3·773	1·143	3·301	1·489	0·461	4·505	1·241	3·631	1·342	0·545
4·405	1·466	3·006	1·625	0·397	4·885	1·396	3·501	1·383	0·514
4·780	1·691	2·827	1·722	0·361	5·040	1·460	3·451	1·404	0·502
5·002	1·852	2·700	1·795	0·338					
Carbon disulphide.					*Quinoline.*				
0·638	0·1264	5·047	1·008	0·980	1·542	0·3084	4·999	1·008	0·943
2·173	0·4411	4·926	1·016	0·932	2·350	0·4826	4·870	1·026	0·902
2·615	0·5410	4·834	1·030	0·916	2·838	0·6038	4·700	1·057	0·860
3·123	0·6517	4·792	1·033	0·900	3·300	0·7078	4·662	1·062	0·845
3·425	0·7201	4·756	1·038	0·891	3·602	0·7865	4·580	1·076	0·824
4·153	0·8815	4·711	1·039	0·866	4·159	0·9228	4·506	1·086	0·800
4·405	0·9434	4·669	1·045	0·858	4·664	1·049	4·445	1·095	0·781
5·440	1·193	4·560	1·058	0·822	5·053	1·149	4·397	1·102	0·765
5·634	1·241	4·539	1·060	0·816	5·116	1·167	4·383	1·104	0·766
o-*Nitrophenol.*					*Chlorobenzene.*				
0·660	0·1304	5·061	1·005	0·969	0·833	0·1642	5·073	1·001	0·986
0·980	0·1968	4·980	1·018	0·953	1·133	0·2236	5·067	0·999	0·980
1·899	0·3915	4·851	1·034	0·910	1·430	0·2843	5·030	1·002	0·973
2·342	0·4897	4·784	1·044	0·888	2·208	0·4414	5·002	1·000	0·961
3·538	0·7705	4·592	1·073	0·829	3·127	0·6320	4·948	1·001	0·944
3·900	0·8608	4·531	1·083	0·811	3·713	0·7596	4·888	1·007	0·933
4·648	1·058	4·393	1·107	0·772	4·586	0·9459	4·848	1·006	0·917
5·098	1·183	4·310	1·123	0·749	5·357	1·120	4·784	1·010	0·902
Ethylene dibromide.					p-*Nitrophenol.*				
0·900	0·1781	5·053	1·004	0·974	0·203	0·0472	4·301	1·188	0·726
1·339	0·2678	5·000	1·010	0·962	0·230 *	0·0546 *	4·212	1·213	0·690
1·940	0·3911	4·960	1·011	0·944	0·233 *	0·0547 *	4·260	1·199	0·689
2·586	0·5296	4·883	1·021	0·924	*Bromobenzene.*				
3·040	0·6323	4·808	1·031	0·910					
3·619	0·7545	4·797	1·027	0·894	1·600	0·3176	5·037	1·000	0·974
4·555	0·9779	4·658	1·047	0·862	2·828	0·5708	4·956	1·003	0·954
4·810	1·039	4·629	1·050	0·856	3·131	0·6346	4·933	1·004	0·949
5·051	1·093	4·621	1·048	0·848	4·788	0·9910	4·832	1·007	0·920
					5·190	1·079	4·811	1·006	0·913

Benzoic acid.

θ.	m.	θ/m.	a.
0·182°	0·0691	2·634°	1·941
0·245	0·0937	2·615	1·954
0·445	0·1697	2·622	1·944
0·501	0·1941	2·581	1·974
0·609	0·2391	2·547	1·998
0·644	0·2531	2·544	1·999
0·702	0·2749	2·554	1·990
0·725	0·2860	2·535	2·006
0·885	0·3505	2·525	2·009
1·044	0·4152	2·514	2·015
1·098 *	0·4374 *	2·510	2·017

Acetic acid.

θ.	m.	θ/m.	a.
0·253	0·0967	2·616	1·952
0·608	0·2375	2·560	1·987
0·950	0·3815	2·490	2·035
1·254	0·5095	2·461	2·053
1·659	0·6847	2·423	2·077
2·410	1·024	2·353	2·121
2·689	1·152	2·335	2·131
3·166	1·386	2·285	2·167
3·644	1·626	2·241	2·197
4·715	2·197	2·146	2·267
5·202	2·481	2·097	2·310

Nitrobenzene.

θ.	m.	θ/m.	a.
0·490°	0·1016	4·823°	1·058
0·507	0·1045	4·852	1·050
0·796	0·1652	4·818	1·054
0·960	0·2027	4·736	1·071
1·226	0·2602	4·712	1·073
1·722	0·3725	4·623	1·088
1·921	0·4157	4·621	1·087
2·220	0·4854	4·574	1·094
2·675	0·5960	4·488	1·109
3·178	0·7142	4·450	1·113
3·265	0·7342	4·447	1·113
3·806	0·8684	4·383	1·123
3·940	0·9008	4·374	1·122
4·653	1·089	4·272	1·141
4·980	1·174	4·240	1·145
5·313	1·271	4·181	1·156
5·387	1·293	4·166	1·160

Phenol.

θ.	m.	θ/m.	θ.	m.	θ/m.
1·430°	0·594	2·407°	3·638°	1·888	1·927°
2·720	1·261	2·157	4·701	2·764	1·701
3·150	1·540	2·045	5·001	3·160	1·583

Pyridine.

θ.	m.	θ/m.	θ.	m.	θ/m.
1·200°	0·275	4·364°	4·004°	0·965	4·175°
1·225	0·282	4·344	4·146	0·994	4·171
2·659	0·624	4·261	4·886	1·186	4·119

* Eutectic point.

The results obtained are given in Table I, where θ is the depression of the freezing point, and m the concentration in mols. per 1000 g. of benzene. Association factors are the molality (m) divided by that of an ideal solution which would have the same freezing point. Activity coefficients (γ) have been calculated when possible by the methods of Lewis and Randall (" Thermodynamics," 1923, chap. XXIII); for acetic and benzoic acids and for nitrobenzene, however, these cannot be calculated without further data at lower concentrations. As a general rule, measurements cover the range $\theta = 0{\cdot}5°—5{\cdot}0°$. In order to save space, a selection only of our results is given.

DISCUSSION.

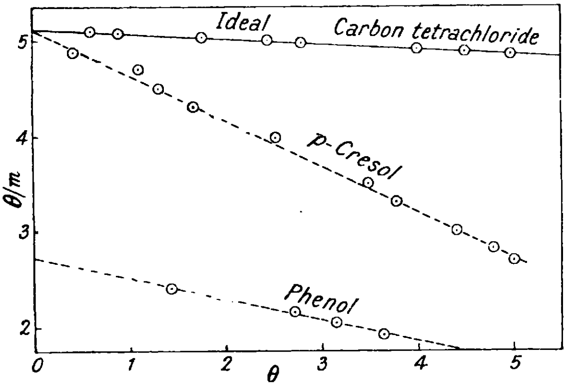
1. *The Freezing Points of Ideal Solutions.*—Since an ideal solution is defined as one in which the activities of the components are equal to their mol.-fractions, their freezing points can be calculated by replacing the activity of the solvent by its mol.-fraction in Lewis and Randall's equation XXIII—17 (*op. cit.*). On introducing numerical values for the freezing point of the solvent (278·6° K., Richards, Carver, and Schumb, *J. Amer. Chem. Soc.*, 1919, **41**, 2019), its molal heat of solidification (— 2349·4 g.-cals.; Huffman, Parks, and Daniels, *ibid.*, 1930, **52**, 1547), and the molal heat capacities of solid and liquid benzene (28·3 and 31·0 g.-cals.; Maass and Waldbauer, *ibid.*, 1925, **47**, 1; Huffman, Parks, and Daniels, *loc. cit.*), an equation is obtained from which the mol.-fraction, and hence m, corresponding to any desired value of θ, can be calculated. The figures obtained can be represented ($\pm$ 0·002°) by the interpolation formula $\theta = 5{\cdot}122m - 0{\cdot}261m^2$, valid for the range $m = 0—1$.

Carbon tetrachloride is a typical ideal solute, at least in the range of concentrations used in this work. As can be seen from Fig. 1, in which θ/m is plotted against θ, the experimental points lie close to the line calculated for an ideal solute. Within the limits of experimental error, association factors are equal to 1, and activity coefficients agree closely with those calculated for the formula for those of an ideal solute, $\gamma' = 1000/(Mm + 1000)$, where M is the molecular weight of the solvent. This equation is determined by the conditions that the activity of an ideal solute ($\gamma' m$) must be proportional to its mol.-

fraction and must also, in the limiting case $m = 0$, be equal to its molality (m). Chloroform, bromoform, *p*-dichlorobenzene, and ethylene dichloride are similar, so calculations of θ/m, α, and γ are omitted.

2. *The Freezing Points of Non-ideal Solutions.*—*p*-Cresol is typical of many non-ideal solutes. As can be seen from Fig. 1, the values of θ/m lie on a straight line which extrapolates ($\theta = 0$) to the normal value of θ/m characteristic of an ideal solute, but with substances of this type the slope of the line depends on the solute and varies from substance to substance. *o*-Cresol, carbon disulphide, *o*- and *p*-nitrophenols, ethylene dibromide, and quinoline are also members of this class of solute: chlorobenzene and bromobenzene are almost ideal solutes, but appear also to belong to this class.

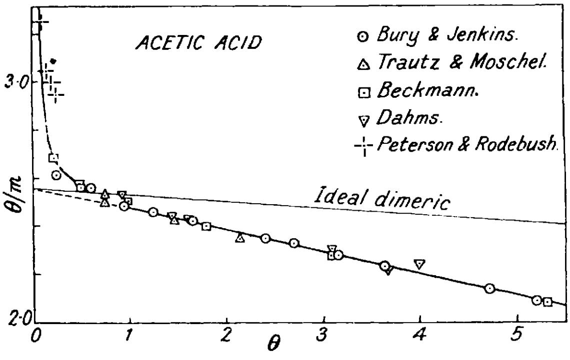
Fig. 1.



Benzoic and acetic acids are examples of another type of non-ideal solute. As can be seen from Fig. 2, in which the results for acetic acid are plotted as in Fig. 1, θ/m first falls rapidly to about half its limiting value and thereafter falls much less rapidly. The experiments barely touch the initial part of the line where θ/m is changing rapidly, though measurements with these two solutes were extended to lower concentrations than usual; the work of Peterson and Rodebush (*loc. cit.*), however, shows the behaviour of acetic acid in this region.

Our results for acetic acid are compared in Fig. 2 with those of previous investigators, the most important of which are Beckmann (*Z. physikal. Chem.*, 1888, **2**, 729), Dahms (*Wied. Ann.*, 1895, **54**, 499; 1897, **60**, 120), Trautz and Moschel (*Z. anorg. Chem.*, 1926, **155**, 13), and Peterson and Rodebush (*loc. cit.*). The remarkably close agreement of our results with those of the first three observers indicates that adsorption does not cause appreciable errors.

Fig. 2.



The "ideal dimeric" line in Fig. 2 has been drawn by plotting half the calculated value of θ/m for an ideal solute against θ. If acetic acid was an equilibrium mixture of the monomeric and dimeric forms, and if this was the only cause of its abnormal behaviour, the experimental curve should approach this line asymptotically with increasing concentration. Actually, however, it crosses this line and approaches asymptotically another line which is related to the ideal dimeric line just as the *p*-cresol line is related to the ideal line (Fig. 1). It appears, therefore, that the dimeric form of acetic acid belongs to the *p*-cresol class of non-ideal solutes, and that acetic acid is practically completely associated to the dimeric form at all concentrations greater than about 0·4*m*. The same conclusions appear to apply to benzoic acid also, though with this solute measurements are restricted to dilute solution on account of its low solubility. Since acetic acid is almost completely transformed into the dimeric form at all concentrations greater than about 0·4*m*, it is improbable that the abnormal properties of pure acetic acid at low temperatures can be accounted for by the assumption that it is a mixture of a monomeric and a dimeric form.

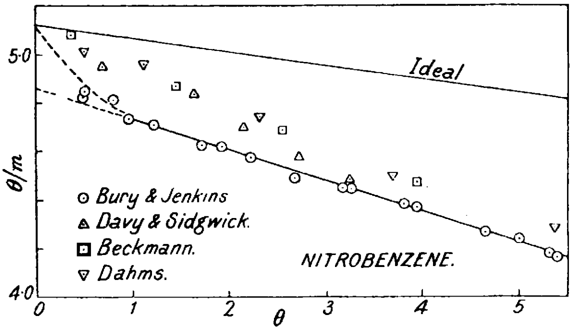
p-Cresol and acetic acid are representatives of the two common classes into which "associated" substances can be divided (Auwers, *Z. physikal. Chem.*, 1899, **30**, 300;

Brown and Bury, *J. Physical Chem.*, 1926, **30**, 694). The facts described above, and the behaviour in the gaseous state, make it probable that the abnormality of acetic acid is mainly, but not entirely, due to association to a dimeric form. The abnormality of the *p*-cresol type of solute has not yet been satisfactorily explained.

Phenol is known to form solid solutions with benzene (Garelli, *Z. physikal. Chem.*, 1896, **21**, 122), and it was studied as an example of such substances and because we desired to test a method of detecting the formation of solid solutions. The proposed method proved useless so it is not described. As can be seen from Fig. 1, the values of θ/m lie on a straight line, but this does not extrapolate to the normal value of θ/m when $\theta = 0$. From the limiting value of θ/m (2·73) it follows that the distribution coefficient of phenol between solid and liquid benzene is 0·47 (van 't Hoff, " Lectures on Theoretical and Physical Chemistry," 1899, vol. II, p. 75).

Pyridine is suspected of forming solid solutions with benzene; Bruni (*Gazzetta*, 1898, **28**, i, 259) studied solid solutions of pyridine and piperidine in benzene, but owing to analytical difficulties recorded no data for pyridine. It was important, however, to compare, if possible, the degree of association from freezing points with that determined from polarisation measurements by Rolinski (*Physikal. Z.*, 1928, **29**, 658). The results obtained show that pyridine belongs to the same class as phenol, and gives a distribution coefficient of 0·14; a direct determination by Dr. E. R. Jones, using van Bijlert's method, gave a value of 0·18. The great difficulty of determining pyridine accurately in the presence of benzene makes van Bijlert's method very uncertain, and the discrepancy between the two methods is well within the limits of experimental error.

FIG. 3.



Our results for nitrobenzene are compared with those of previous observers (Beckmann, *loc. cit.*; Dahms, *loc. cit.*; Davy and Sidgwick, J., 1933, 281) in Fig. 3, in which the results are plotted as before. This method of plotting emphasises the divergence between different observers much better than that employed by Davy and Sidgwick. Our results differ considerably from these, which is remarkable in view of the close agreement of our results for acetic acid with those of Beckmann and of Dahms. The discrepancy was first attributed to the presence of some impurity of higher molecular weight in the nitrobenzene, but this was disproved by the fact that two different samples of nitrobenzene gave identical results. The first sample (m. p. 5·678°) was obtained from commercial nitrobenzene by fractional distillation and freezing, the second (m. p. 5·699°) by the nitration of pure benzene at a low temperature. The similarity of our figures for nitrobenzene to those of phenol and pyridine suggests that it forms mixed crystals with benzene. The distribution coefficient would be about 0·05. The low concentration of nitrobenzene in the mixed crystals indicated by freezing-point measurements and the impossibility of analysing with sufficient accuracy mixtures of benzene, nitrobenzene, and some inert reference substance, make it impracticable to confirm this suggestion by van Bijlert's method. The three determinations at the lowest concentrations, which, however, are most liable to experimental error, suggest another possibility—that the curve may turn up and that θ/m may have a normal value at infinite dilution. This would imply, however, that nitrobenzene was different from all other solutes examined.

3. *Internal Pressure and Deviations from the Law of Ideal Solutions.*—Hildebrand (*J. Amer. Chem. Soc.*, 1921, **43**, 500) defines internal pressure as the function $T(\partial P/\partial T)_v$; he has proved that unless liquids have equal internal pressures, their mixtures cannot obey Raoult's law, and has put forward the hypothesis that deviations from this law are approximately proportional to differences in internal pressure of the components, for certain simpler types of systems. This rule is not applicable to mixtures of polar and

non-polar molecules, which, according to Hildebrand, should give abnormally large deviations.

The relevant data for judging the value of this hypothesis are collected in Table II,

TABLE II.

	$\mu \times 10^{18}$.	$T(\partial P/\partial T)_v$, atm.	$a(m = 1)$.
C_6H_6	0	3716	—
Ideal solute	—	—	0·928
CCl_4	0	3368	0·930
$(CH_3{\cdot}CO_2H)_2$	0	3444	0·758
$CHCl_3$	1·05	3693	0·930
CS_2	0	3725	0·850
C_6H_5Cl	1·5	3799	0·913
$C_2H_4Cl_2$	1·2	4183	0·930
$C_2H_4Br_2$	0·9	4455	0·860
$CHBr_3$	1·0	4490	0·930
$C_6H_5{\cdot}NO_2$ ...	4·0	4921	—

which includes data for those solutes the internal pressures of which are known. The second column contains the dipole moments (μ) (Smyth, " Dielectric Constant and Molecular Structure," 1931), and the third internal pressures (in atmospheres) at 20°, calculated from Tyrer's measurements of adiabatic compressibility (J., 1914, **105**, 2540), determinations of $(\partial P/\partial T)_v$ by Westwater, Frantz, and Hildebrand (*Physical Rev.*, 1928, **31**, 135), and measurements of the velocity of sound in liquids by Freyer, Hubbard, and Andrews (*J. Amer. Chem. Soc.*, 1929, **51**, 759). The three methods agree closely, 3731, 3687, and 3728 atm. respectively being the values for benzene. Tyrer's measurements enable the internal pressure to be calculated for a range of temperatures, and it was found that changes of internal pressure with temperature were nearly proportional to the internal pressure itself, so that it is justifiable to compare differences of internal pressure at 20° with deviations from the ideal at 0—5°. In the fourth column are the activities at $m = 1$, obtained by interpolation from the data given in Table I, which are the most convenient criteria of the abnormality of the solutions. It seems desirable, for reasons given above, to regard acetic acid as existing in the dimeric form, and the activity was calculated on this assumption. The dipole moment follows from the measurements of Smyth and Rogers (*J. Amer. Chem. Soc.*, 1930, **52**, 1824).

The data collected in Table II afford little support to Hildebrand's hypothesis. Carbon disulphide, the dipole moment of which is zero, and the internal pressure of which is practically identical with that of benzene, should approximate most closely of all the solutes examined to an ideal solution; it is, however, markedly abnormal. Bromoform, on the other hand, forms an ideal solution in benzene up to the highest concentration measured, though its internal pressure is considerably greater than that of benzene, and it has a dipole moment. No correlation between internal pressure and activities can be detected. It should be pointed out that the data are too few to enable a final opinion to be given, but the table includes all substances the internal pressures of which were known at the time this research was undertaken, except such substances as alcohol, the investigation of which was impracticable for analytical reasons.

4. *Association and Polarisation.*—Two distinct views as to the relation between association and polarisation have been proposed. Lange (*Z. Physik*, 1925, **33**, 169), Ebert (*Z. physikal. Chem.*, 1924, **113**, 1), and Debye (Marx, " Handbuch der Radiologie," VI, 1925, 633) suggest that the association of two or more molecules is caused by the attraction between them due to their dipole moments. In dilute solutions, two possibilities may be considered. First, a complex molecule of greater moment, capable of attracting further molecules, may be formed, in which case polarisation will increase with association and therefore with concentration, and association will not cease with the formation of double molecules. Secondly, a double molecule of zero dipole moment, incapable of attracting another molecule, may be formed; polarisation will then decrease with concentration.

Sidgwick (" Electronic Theory of Valency," Oxford, 1927, 132) suggests that association is due to the tendency of two molecules to unite by means of a co-ordinate link. Since the co-ordinate link has a large dipole moment, association should normally cause an increase in polarisation, but a symmetrical complex molecule containing two or more co-ordinate links may be formed, whereupon polarisation will decrease with association, since a symmetrical molecule must have a dipole moment of zero.

Increase of polarisation has only been observed with the alcohols, which were found unsuitable for freezing-point measurements on account of analytical difficulties. It is remarkable from the point of view of Sidgwick's hypothesis that this type of behaviour is so rare, for it might be expected to be the most general type of association.

In cases where polarisation decreases with concentration, both hypotheses lead to the conclusion that P, the molecular polarisation of a polar solute in a non-polar medium is the sum of two terms, one (A) due to the electronic and atomic polarisations, invariant with respect to temperature, association, and concentration, and the other due to the dipole orientation, which should depend on temperature (T), the degree of association (X), and hence on the concentration, and on a constant (B) proportional to the square of the dipole moment: $P = A + (1 - X)B/T$. Thus measurements of the polarisation of acetic acid in benzene by Smyth and Rogers (*loc. cit.*) show that the second term on the right of the above equation, due to orientation, is practically zero. Since the dipole moment is certainly not equal to zero, it follows that $X = 1$, and that acetic acid is almost completely associated at the lowest concentration studied (1·5*m*). This is in agreement with the conclusions derived from freezing-point measurements, but further measurements of the polarisation and freezing points at lower concentrations are desirable in order to test the equation completely.

Comparison of association factors derived from freezing points and from polarisations are given in Table III. In the second column are the dipole moments (Smyth, *op. cit.*), and in the third, the degrees of association (X_F) obtained by interpolation from freezing-point measurements. If the formation of double molecules only is assumed, association factors (α) in Table I are related to degrees of association by the formula $X_F = 2(\alpha - 1)/\alpha$. Degrees of association calculated from polarisation measurements (X_P) are given in the fourth column with the source. Comparisons are made at unit molality when possible.

TABLE III.

	$\mu \times 10^{18}$.	$X_F(m = 1)$.	$X_P(m = 1)$.	
Carbon disulphide	0	0·091	0	Rolinski, *loc. cit.*
Carbon tetrachloride ...	0	0	0	,, ,,
p-Dichlorobenzene	0	0	0	Smyth, Morgan, and Boyce, *J. Amer. Chem. Soc.*, 1928, **50**, 1536.
Benzoic acid	0·8	2·0 *	0 *	Williams and Allgeier, *ibid.*, 1927, **49**, 2416.
Ethylene dibromide ...	0·9	0·090	0·297	Smyth and Kamerling, *ibid.*, 1931, **53**, 2988.
Bromoform	1·0	0	0	Smyth and Rogers, *ibid.*, 1930, **52**, 2227.
Chloroform	1·05	0	0	Williams and Krchma, *ibid.*, 1927, **49**, 1676.
Ethylene dichloride ...	1·2	0	—	
o-Cresol	1·4	0·430	0·121	Philip and Haynes, J., 1905, **87**, 998.
p-Cresol	1·64	0·584	0·050	,, ,, ,, ,,
Bromobenzene	1·5	0·004 *	0·113 *	Højendahl, Thesis, Copenhagen, 1928.
Chlorobenzene	1·5	0·016	0·054	Rolinski, *loc. cit.*
Phenol	1·7	—	0	Williams and Allgeier, *loc. cit.*
Pyridine	2·1	—	0·42	Lange, *Z. Physik*, 1925, **33**, 169.
Quinoline	2·25	0·168	0·15	Rolinski, *loc. cit.*
Nitrobenzene	4·0	0·20—0·24	0·264	Davy and Sidgwick, *loc. cit.*
o-Nitrophenol	3·1	0·086 *	0·078 *	Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1930, **52**, 1356.
p-Nitrophenol	5·0	0·54 †	0 †	,, ,, ,, ,, ,,

* *m* = 0·5. † *m* = 0·1.

Table III shows that agreement is only satisfactory for certain non-associated substances (carbon tetrachloride, *p*-dichlorobenzene, bromoform, and chloroform) and possibly also for quinoline, *o*-nitrophenol, and nitrobenzene; for this last substance, however, the accuracy and interpretation of the freezing-point data are doubtful. Lack of agreement in certain cases may be due to inaccuracy of the polarisation measurements and, in the case of ethylene dibromide, is probably due to variation of the dipole moment of the substance itself with changing conditions (Smyth and Kamerling, *loc. cit.*), but there remain a number of substances for which it is clear that the two methods do not agree.

The table also shows that there are a number of substances (bromoform, chloroform, ethylene dichloride, and phenol) that have appreciable dipole moments but do not show any sign of association. Distribution measurements (Philip and Clark, J., 1925, **127**, 1274) confirm the conclusions of polarisation measurements for phenol. This is contrary to what would be expected from the Lange–Ebert–Debye hypothesis. On the other hand, carbon disulphide has zero moment but is shown by freezing-point measurements to be markedly associated.

It is interesting to note that chlorobenzene has a dipole moment and is slightly associated, while the symmetrical *p*-dichlorobenzene has a zero dipole moment and is not associated. This is what would be expected from the Lange-Ebert–Debye hypothesis, but is contrary to what would be expected from most other points of view.

p-Nitrophenol is much more associated than *o*-nitrophenol, in accordance with the views of Sidgwick and Callow (J., 1924, **125**, 527), who concluded that the substituent groups in the *o*-compound were united by means of a co-ordinate link to form a ring. With the *p*-compound, this was impossible for stereochemical reasons, but the union of substituent groups of neighbouring molecules caused association. Two consequences of this view are, however, contrary to observed facts. The presence of a co-ordinate link due to ring formation should make the dipole moment of the *o*-compound abnormal, whereas it is close to what would be expected from a knowledge of the dipole moments of phenol, nitrobenzene, and the other two nitrophenols. Secondly, if the mechanism of the association of the *p*-compound was that postulated by Sidgwick and Callow, association should be detectable by polarisation measurements.

The results quoted in Table III do not support the assertion of Rolinski (*loc. cit.*) that there is a direct parallelism between the dipole moment and association of a solute. This is not a consequence of the Lange–Ebert–Debye hypothesis, for, according to these authors, association should depend, not only on the magnitude of the dipole moment of the solute, but also on the shape of the molecule and position of the dipole.

In conclusion, it appears that the union of separate molecules by a chemical bond to form an associated molecule is a rare phenomenon. Some loose association and orientation of neighbouring molecules, such as that suggested by Lange, Ebert, and Debye, seems far more probable, but it seems reasonable to suppose that the component dipoles of the individual bonds rather than the resultant molecular dipoles play a predominant part, since the molecules in a liquid are so close and since the force between dipoles falls off so rapidly as the distance between them increases. Many circumstances, including the fact that the apparent dipole moment of a molecule depends on its surroundings, as is shown by recent work on ethylene dibromide (Smyth and Kamerling, *loc. cit.*) and nitrobenzene (Jenkins, *Nature*, 1934, **133**, 106), show that the polarisation of a solution is a more complex phenomenon than was first thought.

We desire to thank Dr. E. R. Jones for much valuable preliminary work, without which this research would not have been possible. One of us (H. O. J.) thanks the Senate of this College for the award of a Sir Garrod Thomas Fellowship.

EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

[*Received, March 14th*, 1934.]