CVI.—*The Determination of the Parachors of Substances in Solution.*

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It has hitherto been possible to determine the parachors only of such substances as are capable of stable existence above their melting points. This limitation would be removed if it could be shown that the parachors of substances unstable in the pure liquid state can be calculated from the surface tensions and densities of their solutions in solvents of known parachor. Numerous data as to the surface tensions and densities of liquid mixtures exist, but they are by no means equally trustworthy as to surface tensions. We have therefore determined the surface tensions of a preliminary series of liquid mixtures, using Sugden's apparatus (J., 1924, **125**, 27) standardised with pure benzene; our data are thus on the same basis as Sugden's, being dependent upon the surface tension of benzene as determined by Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827) and confirmed by Sugden (J., 1921, **119**, 1483) using his own form of apparatus with jets of experimentally determined diameter. The surface tension of benzene at 25° was taken as 28·23 dynes/cm.

In choosing the components of our mixtures, we have sought to vary not only their chemical nature but also the difference between the surface tensions of the pure substances, in order that any effects due to surface absorption might be detected. The mixtures examined will be seen to include cases of non-associated liquids with non-associated, associated with associated, and non-associated with associated.

Parachors of solutes have been calculated from our results by first finding the parachor P_m of a solution containing a molecular fraction x of solute in a solvent of known parachor P; P_m is equal to $M_m\gamma^{\frac{1}{4}}/(D - d)$, where γ and D are the surface tension and density of the solution, and M_m is the mean molecular weight of the mixture*; d, the density of the vapour, is negligible at 25°. On the assumption that parachors obey the straight-line mixture law, P_x, the parachor of the solute, is found from P and P_m by means of the relation $P_m = P(1 - x) + P_x . x$.

EXPERIMENTAL.

It is clear that the above method of calculation, particularly when it is applied to dilute solutions, requires that all experimental data should be as accurate as possible. All the liquids used were therefore very carefully purified by distillation or freezing out, particular care being taken with the benzene (m. p. 5·40°) used for standardising the apparatus employed in the determination of surface tensions. This was of the usual Sugden type (*loc. cit.*, p. 28), used in conjunction with a water or xylene manometer immersed in the thermostat (25°) that also contained the bubbler. This arrangement was found to give more concordant bubble-pressure readings than an alcohol manometer in an athermostatic water-bath as used by Sugden. The irregularities noticed by Sugden in the working of water manometers due to fouling of the water surface (*ibid.*, p. 28) were prevented by introducing tubes containing activated charcoal between the manometer and the bubbler. Pressure differences were measured by means of a cathetometer reading to 0·01 mm.; successive readings were consistent to at most 0·2%. The apparatus was restandardised before each mixture was investigated.

The following constants were used in the calculation of the parachors of solvent liquids:

H = 17·1, C = 4·8, N = 12·5, O = 20·0, Cl = 54·3, double bond = 23·2, semipolar bond = − 1·6, 6-membered ring = 6·1, carboxyl O_2 = 60·0.

Densities were determined by means of a 10 c.c. specific gravity bottle.

Our experimental results (at 25°) and calculations are summarised in the following tables, which include data (marked S. and J.) due to Sugden and W. W. Jones (private communication) for mixtures of chloroform and benzene, nitrobenzene and benzene, and nitrobenzene and carbon tetrachloride at 25·5°.

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* $M_m = M_s(1 - x) + M_x . x$, where M_s is the molecular weight of the solvent, M_x that of the solute, and x is the molecular fraction of solute.

A. *Non-associated solutes in non-associated solvents.*

Carbon tetrachloride in benzene.*

x.	D.	γ.	P_m.	P_x.
0·3419	1·130	27·69	211·1	219·2
0·4512	1·208	27·74	213·3	220·8
0·7326	1·405	26·98	216·8	220·2
0·8527	1·487	26·64	218·0	220·0
1·0000	1·585	26·20	—	(219·5)

Mean P_x = 220·1, $P_{\mathrm{CCl_4}}$ = 219·5, $P_{\mathrm{calc.}}$ = 222·0.

m-Xylene in benzene.

x.	D.	γ.	P_m.	P_x.
0·3969	0·8626	28·00	238·4	286·3
0·4655	0·8615	27·92	243·2	284·5
0·6918	0·8579	28·11	261·5	285·6
0·8428	0·8569	27·85	272·6	284·7
1·0000	0·8557	30·45	—	(285·1)

Mean P_x = 285·3, $P_{m\mathrm{-C_8H_{10}}}$ = 285·1, $P_{\mathrm{calc.}}$ = 285·1.

* Parachor of benzene = 207·1.

*cyclo*Hexane in benzene.

0·2963	0·8330	26·41	217·1	240·9
0·3790	0·8230	25·81	219·9	240·8
0·4508	0·8168	25·84	222·3	240·9
0·5240	0·8097	25·65	225·6	240·3
0·6207	0·8007	25·36	229·1	242·5

Mean P_x = 241·1, $P_{\mathrm{C_6H_{12}}}$ = 240·1.

Chloroform in benzene.

0·2474	1·008	27·78	201·0	182·4
0·3501	1·067	27·64	198·9	183·3
0·5343	1·177	27·10	193·9	182·5
0·7365	1·303	27·34	190·4	184·3
0·9020	1·409	26·53	185·6	183·2
1·0000	1·476	26·73	—	(183·4)

Mean P_x = 183·1, $P_{\mathrm{CHCl_3}}$ = 183·4, $P_{\mathrm{calc.}}$ = 184·8.

Ethyl acetate in carbon tetrachloride.†

0·1755	1·461	25·59	219·2	215·4
0·3196	1·360	25·02	218·4	215·1
0·4758	1·252	24·39	217·6	216·0
0·6884	1·105	23·96	217·4	216·1
1·0000	0·8938	23·42	—	(216·1)

Mean P_x = 215·7, $P_{\mathrm{CH_3\cdot CO_2Et}}$ = 216·1, $P_{\mathrm{calc.}}$ = 216·0.

Chloroform in benzene (S. and J.).

0·2068	0·9866	28·06	—	184·7
0·3966	1·0958	27·36	—	181·6
0·4892	1·1506	27·32	—	183·5
0·7096	1·2882	26·91	—	183·5
1·0000	1·4794	26·43	—	(183·0)

Mean P_x = 183·3, $P_{\mathrm{CHCl_3}}$ = 183·0, $P_{\mathrm{calc.}}$ = 184·8.

† Parachor of carbon tetrachloride = 220·0.

B. *Associated solutes in non-associated solvents.*

Ethyl alcohol in benzene.

0·237	0·8578	27·38	187·8	125·5
0·421	0·8422	25·40	172·1	124·1
0·564	0·8304	25·00	161·4	126·0
0·758	0·8163	23·84	145·4	125·7
1·000	0·7898	21·90	—	(126·0)

Mean P_x = 125·3, P_{EtOH} = 126·0, $P_{\mathrm{calc.}}$ = 132·2.

Acetic acid in benzene.

0·279	0·9005	28·08	186·6	133·5
0·510	0·9329	27·04	168·9	132·0
0·820	0·9965	27·78	145·6	132·1
1·000	1·051	28·52	—	(132·2)

Mean P_x = 132·5, P_{HAc} = 132·2, $P_{\mathrm{calc.}}$ = 141·2.

Acetone in benzene.

x.	D.	γ.	P_m.	P_x.
0·2993	0·8507	26·82	193·1	159·5
0·5283	0·8318	25·52	182·4	160·3
0·7034	0·8163	24·52	174·5	160·6
0·8563	0·8017	23·67	167·6	161·1
1·0000	0·7867	22·72	—	(161·1)

Mean P_x = 160·5, $P_{\mathrm{C_3H_6O}}$ = 161·1, $P_{\mathrm{calc.}}$ = 160·2.

C. *Non-associated liquid in associated solvent.*

Ethyl acetate in acetic acid.

x.	D.	γ.	P_{m}.	P_x.
0·0000	1·0510	28·52	132·2	—
0·1273	1·0200	27·49	142·8	216·0
0·3031	0·9844	26·56	157·9	217·2
0·5429	0·9471	25·21	178·0	216·5
0·6890	0·9288	25·05	191·1	217·6
1·0000	0·8938	23·42	—	(216·1)

Mean $P_x = 216{\cdot}8$, $P_{CH_3\cdot CO_2Et} = 216{\cdot}8$, $P_{\mathrm{calc.}} = 216{\cdot}0$.

D. *Associated liquids in associated solvents.*

Acetic acid in ethyl alcohol.

x.	D.	γ.	P_{m}.	P_x.
0·0000	0·7898	21·90	126·0	—
0·2262	0·8540	24·06	127·7	133·5
0·4241	0·9062	25·75	129·3	133·8
0·5550	0·9384	26·07	129·3	131·9
0·7414	0·9868	27·10	130·4	131·9
1·0000	1·051	28·52	—	(132·2)

Mean $P_x = 132{\cdot}8$, $P_{HAc} = 132{\cdot}2$, $P_{\mathrm{calc.}} = 141{\cdot}2$.

Acetone in ethyl alcohol.

x.	D.	γ.	P_{m}.	P_x.
0·0000	0·7898	21·90	(126·0)	—
0·1879	0·7902	22·12	132·6	161·2
0·4508	0·7900	22·85	142·4	162·4
0·6874	0·7892	22·63	150·1	161·1
1·0000	0·7882	23·07	—	(161·4)

Mean $P_x = 161{\cdot}6$, $P_{\mathrm{calc.}} = 160{\cdot}2$.

Acetone in acetic acid.

x.	D.	γ.	P_{m}.	P_x.
0·0000	1·0510	28·52	(264·4)	—
0·2909	0·9996	27·79	234·0	160·8
0·4998	0·9547	26·74	212·1	160·3
0·6183	0·9247	26·14	199·8	160·2
0·7288	0·8921	25·53	188·5	160·5
1·0000	0·7867	22·72	—	(161·1)

Mean $P_x = 160{\cdot}5$, $P_{C_3H_6O} = 161{\cdot}1$, $P_{\mathrm{calc.}} = 160{\cdot}2$.

In the last example the molecule of acetic acid has been taken as $(CH_3{\cdot}CO_2H)_2$, for which the parachor is 2 × 132·2 = 264·4.

In all the examples so far quoted it will be noticed that the parachor of the solute, as calculated by application of the mixture law from the mean parachor of the solution, is in good agreement with the experimentally determined parachor of the pure solute; it is, moreover, independent of the dilution. We have, however, found cases where the value of the solute parachor falls off linearly with dilution. Data for these cases are given below and are plotted in Fig. 1.

Nitrobenzene in benzene.

x.	D.	γ.	P_{m}.	P_x.
0·2129	0·9517	30·26	215·9	249·0
0·3707	1·0070	31·99	223·8	252·0
0·4822	1·0435	33·15	229·6	253·7
0·6109	1·0860	35·24	236·8	255·7
0·7063	1·1130	36·51	242·6	257·4
1·0000	1·1988	42·87	—	(262·5)

$P_{\mathrm{calc.}} = 264{\cdot}1$.

Nitrobenzene in benzene (S. and J.).

x.	D.	γ.	P_{m}.	P_x.
0·0000	0·8722	28·23	(207·1)	—
0·1650	0·9334	30·22	—	256·4
0·3000	0·9929	31·64	—	246·9
0·5176	1·0538	34·30	—	257·2
0·7669	1·1308	38·12	—	259·6
1·0000	1·1986	43·25	—	(263·0)

$P_{\mathrm{calc.}} = 264{\cdot}1$.

Nitrobenzene in carbon tetrachloride (S. and J.).

0·0000	1·5839	26·10	—	—
0·2246	1·4978	28·35	—	249·5
0·4276	1·4188	30·68	—	251·9
0·6551	1·3302	34·54	—	256·2
0·8181	1·2668	37·91	—	259·1
1·0000	1·1986	43·25	—	(263·0)

$P_{\text{calc.}} = 264{\cdot}1$.

Acetophenone in benzene.

0·1538	0·9030	29·94	219·1	284·7
0·2966	0·9279	31·13	230·4	285·6
0·4668	0·9548	32·63	244·5	287·4
0·7749	0·9975	36·06	271·6	290·4
1·0000	1·0243	38·77	—	(292·4)

$P_{\text{calc.}} = 294{\cdot}1$.

Nitromethane in benzene.

0·2327	0·9120	29·14	188·8	128·0
0·3737	0·9396	29·35	177·6	128·1
0·5594	0·9822	30·04	163·3	128·9
0·7362	1·0317	31·76	150·8	130·6
1·0000	1·1315	35·80	—	(131·8)

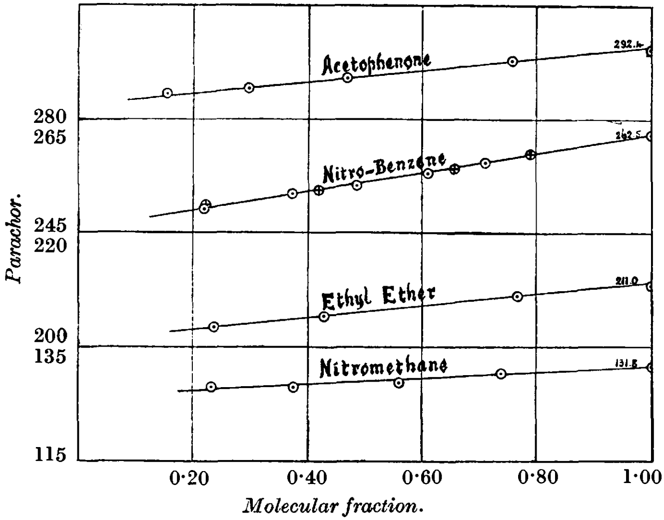
$P_{\text{calc.}} = 130{\cdot}2$.

Ethyl ether in benzene.

0·2356	0·8321	24·53	206·3	203·7
0·4267	0·7996	21·81	206·5	205·5
0·7464	0·7475	18·49	208·4	208·8
1·0000	0·7069	16·47	—	(211·0)

$P_{\text{calc.}} = 210{\cdot}2$.

FIG. 1.



The open circles in the above diagram refer to our values for solute parachors in benzene solution; Sugden and Jones's data for nitrobenzene in carbon tetrachloride are shown with crossed circles. In all cases the straight line through the solute parachor values passes through the parachor value of the pure solute to within less than 1%.

It will be seen from the above tables that the mixtures from which we have obtained solute parachor values that are independent of dilution are characterised by the fact that the surface tensions of the pure components do not differ by more than about 5—6 dynes/cm. at most. The smallest deviation from the rigid straight-line mixture law is found in the case of nitromethane and benzene, where the difference in surface tension between the two components is nearly 7 dynes/cm.; the greatest deviation occurs with nitrobenzene and benzene, where the difference in surface tensions is about 14·5 dynes/cm. It is thus probable that the deviation is connected with the Gibbs surface absorption effect, and we are at present investigating the point. On the purely practical side, however, the position appears to be as follows: Application of the mixture law to the mean parachor of a series of solutions will give either the parachor of the pure solute or a series of values from which a value for the pure solute can be obtained by straight-line extrapolation. (With water as solvent anomalous results are obtained; these are being investigated.)

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