330. *Partial Vapour Pressures and Refractivities of Mixtures of Benzene with Nitrobenzene, Phenol, Benzyl Alcohol, or* p-*Dichlorobenzene.*

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The work of Martin and Collie (J., 1932, 2658) on mixtures of benzene with some of its polar derivatives has been extended to two hydroxylic compounds, a substance of large dipole moment, and one whose moment is zero owing to the opposition of two equal moments.

The method was the same as that of Martin and Collie (*loc. cit.*). The partial vapour pressures of the polar compounds investigated form a very small fraction of the total pressure, and consequently the chief source of error lies in the analyses of the distillates, which were carried out by means of density measurements. In order to obtain accurate data for dilute solutions, the density of the pure benzene used as solvent in each run must be checked. The analysis of mixtures so rich in phenol and *p*-dichlorobenzene that solid separated on cooling was carried out by first diluting a known weight with a known weight of benzene, sufficient to bring the solid into solution. In the experiments with benzyl alcohol the air in the apparatus was replaced by carbon dioxide in order to minimise oxidation. The vapour pressures of pure nitrobenzene and benzyl alcohol, which were inclined to superheat, were verified by a static method.

Purification of Materials.—Benzene and phenol. These were purified as described by Martin and Collie (*loc. cit.*).

Benzyl alcohol. The B.D.H. product was thoroughly shaken with aqueous potassium hydroxide and extracted with ether which had been freed from peroxides by silver nitrate and sodium hydroxide. After being washed, the extract was treated with saturated sodium hydrogen sulphite, filtered, washed, and dried over potassium carbonate. After removal of ether, the alcohol was distilled under reduced pressure and the middle fraction dried over lime which had been burnt in an atmosphere of nitrogen. Before use, it was again distilled in a vacuum. All the above operations were carried out in an atmosphere of nitrogen. Schiff's reagent indicated a barely detectable quantity of benzaldehyde, and this quantity was not increased during the vapour-pressure experiments with the material.

Nitrobenzene. Benzene, purified by Richards and Shipley's method (*J. Amer. Chem. Soc.*, 1919, **41**, 2007), was nitrated, the temperature not being allowed to rise above 50°. After thorough washing, the nitrobenzene was dried first over potassium carbonate and calcium chloride and then over phosphoric oxide. Finally it was distilled twice under reduced pressure, the middle fractions being collected.

p-*Dichlorobenzene.* B.D.H. " purified " material was recrystallised four times from aqueous alcohol and dried by passing pure dry air under reduced pressure through a column of the powdered substance packed in a wide glass tube. Finally, it was fractionated through a four-pear column and the fraction boiling over a range of 0·02° collected; m. p. 53·2°.

Results.—The densities ($d_{4°}^{25°}$), refractive indices ($n_{\alpha}^{25°}$), and the refractivities $[R_L]_{6563}$ of mixtures containing a molar fraction c of the polar component are recorded in Table I. The refractivities are calculated for a molecular weight $cM_1 + (1 - c)M_2$, where M_1 is the molecular weight of the polar component and M_2 that of benzene. The differences, Δ, are equal to $R_{calc.} - R_{obs.}$, where $R_{calc.} = R_1c + R_2(1 - c)$, R_1 being the refractivity of the pure polar component and R_2 that of benzene. For *p*-dichlorobenzene, $R_{calc.}$ was read off the best straight line through the observed points. The data for phenol mixtures have already been recorded (Martin and Collie, *loc. cit.*).

TABLE I.

c.	$d_{4°}^{25°}$.	$n_{\alpha}^{25°}$.	$[R_L]_{6563}$.	Δ.	c.	$d_{4°}^{25°}$.	$n_{\alpha}^{25°}$.	$[R_L]_{6563}$.	Δ.
				Nitrobenzene–Benzene Mixtures.					
0·02844	0·88360	1·49476	26·170	+0·004	0·48464	1·04414	1·51950	29·050	+0·042
0·06856	0·89843	1·49705	26·418	+0·013	0·54639	1·06312	1·52270	29·477	+0·009
0·14298	0·92609	1·50140	26·894	+0·012	0·65311	1·09687	1·52780	30·151	+0·018
0·24861	0·96388	1·50714	27·554	+0·027	0·82758	1·14910	1·53609	31·285	+0·003
0·33572	0·99399	1·51183	28·114	+0·025	1·00000	1·19849	1·54348	32·388	—
0·34552	0·99786	1·51225	28·157	+0·044					
				Benzyl Alcohol–Benzene Mixtures.					
0·05162	0·88372	1·49561	26·292	+0·020	0·41644	0·95182	1·51250	28·570	+0·023
0·09838	0·89231	1·49825	26·615	−0·008	0·54908	0·97451	1·52001	29·488	−0·067
0·11056	0·89502	1·49833	26·670	+0·012	0·67562	0·99489	1·52296	30·186	+0·026
0·13298	0·89923	1·49889	26·837	−0·015	0·86285	1·02230	1·52935	31·376	+0·005
0·25792	0·92306	1·50557	27·569	+0·133	1·00000	1·04127	1·53359	32·238	—
0·27048	0·92481	1·50631	27·694	−0·033					
				p-*Dichlorobenzene–Benzene Mixtures.*					
0·02907	0·88824	1·49451	26·260	±0·00	0·21853	0·98100	1·50520	28·159	±0·00
0·05184	0·90102	1·49574	26·450	+0·04	0·31960	1·02655	1·51012	29·158	±0·00
0·09951	0·92379	1·49855	26·965	±0·00	0·35521	1·04152	1·51164	29·519	±0·00
0·12285	0·93483	1·49968	27·156	+0·03	0·49095	1·09917	1·51819	30·851	±0·00
0·14462	0·94541	1·50088	27·418	±0·00					

TABLE II.

$c_{soln.}$.	$c_{dist.}$.	P.	p.	$c_{soln.}$.	$c_{dist.}$.	P.	p.	$c_{soln.}$.	$c_{dist.}$.	P.	p.
Nitrobenzene–Benzene Mixtures.				*Phenol–Benzene Mixtures.*				*Benzyl Alcohol–Benzene Mixtures.*			
0·0316	0·00057	528·7	0·30	0·0298	0·00174	530·0	0·92	0·03486	0·00079	525·1	0·42
0·0510	0·00056	517·6	0·29	0·0322	0·00207	530·1	1·10	0·06339	0·00153	516·4	0·79
0·0653	0·00120	510·5	0·61	0·0670	0·00347	511·9	1·78	0·07083	0·00138	513·9	0·71
0·1280	0·00179	483·6	0·87	0·0812	0·0040	508·4	2·03	0·1129	0·00213	499·3	1·06
0·2001	0·00365	444·8	1·62	0·1136	0·0057	495·9	2·81	0·2464	0·00365	458·6	1·67
0·2390	0·00421	423·7	1·78	0·1291	0·00522	487·7	2·54	0·3903	0·00404	409·4	1·65
0·4577	0·00971	308·1	2·99.	0·1425	0·00630	482·2	3·04	0·4600	0·00455	389·1	1·77
0·6138	0·0157	223·5	3·52	0·2215	0·0077	459·8	3·54	0·4899	0·00444	370·1	1·64
0·6732	0·0218	181·4	3·96	0·4033	0·01164	405·8	4·74	0·6195	0·00760	300·7	2·28
0·8134	0·0480	99·6	4·78	0·4231	0·0120	392·2	4·71	0·8272	0·0118	147·8	1·75
0·8381	0·0587	77·3	4·53	0·5885	0·01905	319·5	6·08	1·0000	—	2·1	2·1
1·0000	—	5·1	5·1	0·7300	0·0304	236·0	7·18				
				1·0000	—	8·4	8·4				
				p-*Dichlorobenzene–Benzene Mixtures.*							
0·01710	0·00096	533·4	0·51	0·2123	0·01255	425·4	5·34	0·5089	0·0472	259·8	12·25
0·04834	0·00243	515·1	1·25	0·2306	0·01365	415·6	5·66	0·6162	0·0705	202·0	14·24
0·1119	0·00599	481·4	2·88	0·3608	0·02718	339·2	9·20	0·8043	0·1820	100·9	18·36
								1·0000	—	21·6	21·6

Table II gives the partial vapour pressures of the polar components (p) and the total pressures (P) (in mm. of mercury at 0°), and the compositions of the solutions ($c_{\text{soln.}}$) and distillates ($c_{\text{dist.}}$) in molar fractions of the polar components, all at 70°.

DISCUSSION.

The values of the differences Δ in Table I show that the only approach to a systematic departure of the partial molal refractivities from constancy occurs in the case of nitrobenzene mixtures. In the work of Martin and Collie (*loc. cit.*) similar behaviour was observed only with benzonitrile. Of all the substances investigated, these two have the largest dipole moments, and therefore are the two in which mutual deformation of the molecules is most likely to occur at higher concentrations.

Intermolecular forces in liquids may be of three kinds: (1) van der Waals cohesive forces of wave-mechanical origin, (2) inter-dipole (or more generally inter-multipole) forces, and (3) co-ordinate links between donor and acceptor atoms in different molecules. It appears likely that in order to account for the thermodynamic properties of liquid mixtures both (1) and (2), and perhaps in some cases (3), must be considered.

The van der Waals forces, which are responsible for the cohesion of such liquids as benzene and hexane, have been interpreted on a basis of wave mechanics by London (*Z. Physik*, 1930, **63**, 245; *Z. physikal. Chem.*, 1930, **11**, *B*, 222). In substances of similar structure under similar conditions their contribution to the free energy of a molecule increases additively as groups are added to the molecule. This additivity is probably the cause of the success of Langmuir's principle of independent surface action in describing the properties of liquid mixtures in cases where dipolar forces are either absent or roughly the same in both liquids (Smyth and Engel, *J. Amer. Chem. Soc.*, 1929, **51**, 2646, 2660; Butler, Thomson, and Maclennan, this vol., p. 674).

That dipolar forces are of the order of magnitude required to account for the properties of mixtures of a polar and a non-polar, but otherwise similar, liquid, appears probable from the present work and that of Martin and Collie (*loc. cit.*). The standard state adopted for the polar substance is that in extremely dilute solution in the non-polar solvent. Consequently, ideal partial vapour pressures are represented by the tangent to the partial vapour pressure–concentration curve of the polar liquid in the limit of zero concentration. The work of transferring the polar molecule from a medium of dielectric constant equal to that of the mixture (or pure liquid) considered to one of dielectric constant equal to that of the non-polar liquid is put equal to the work of transferring the molecule from the real to an ideal solution. The radius of the molecule required to give the correct result depends on the exact nature of the model adopted, but both the model of Martin (*Phil. Mag.*, 1929, **8**, 550) and that of Bell (*Trans. Faraday Soc.*, 1931, **27**, 799) give values of the correct order of magnitude (a and a' respectively in Table III).

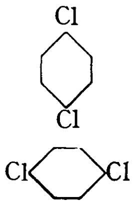
TABLE III.

Substance.	$\mu \times 10^{18}$.	D.	p/p_i.	a (Å.U.).	a' (Å.U.).
Nitrobenzene	3·85	27·5	0·654	4·71	3·98
Phenol	1·56	8	0·309	1·70	1·41
Benzyl alcohol	1·68	9·2	0·178	1·60	1·28
p-Dichlorobenzene	0·00	2·86	0·859	—	—
Chlorobenzene	1·57	5·2	0·849	3·04	2·37

In Table III, μ is the dipole moment, D the dielectric constant, and p/p_i the ratio of the observed to the ideal vapour pressure. The data for chlorobenzene are those of Martin and Collie (*loc. cit.*) and the value of 8 for the dielectric constant of phenol at 70° has been assumed. Dielectric-constant data are not yet available for performing the calculation for any of the mixtures.

Benzyl alcohol and phenol show a much bigger deviation from the ideal (*i.e.*, are more associated) than nitrobenzene, although they both have smaller dipole moments and dielectric constants. Consequently, the values of a and a' required for the first two substances are much smaller than would be expected. According to Sidgwick ("The Electronic Theory of Valency," 1927, p. 134) association in hydroxylic compounds takes place by the formation of co-ordinate links between oxygen and hydrogen atoms in different molecules. Whilst this affords a qualitative explanation of the behaviour of benzyl alcohol and phenol, it is incapable of quantitative expression. The screening effect of neutral groups on a dipole is recognised as an important factor, and an alternative explanation is provided by the somewhat isolated position of the O–H dipole due to the smallness of the group and the angle of about 90° between the valencies of oxygen. This view is supported by the trend of *a* and *a'* for the hydroxylic compounds towards the value for a hydroxyl group.

Since the dipole moment of *p*-dichlorobenzene is zero, it should, according to the simplest form of the dipole theory, form ideal mixtures with benzene. The small deviation observed may be due to van der Waals forces. However, these cannot be entirely responsible for the deviations of both *p*-dichlorobenzene and chlorobenzene, for if so the deviation of the former should, according to the additivity principle (p. 1415), be distinctly greater than that of chlorobenzene. Since the deviations are about the same, the dipolar forces in chlorobenzene compensate for the van der Waals forces being smaller, and therefore the former are, in chlorobenzene at least, comparable in importance with the latter. Complex orientation of the type shown in the inset may to a certain extent be responsible for the association of *p*-dichlorobenzene. If so, the rôle assigned to dipolar forces in chlorobenzene must be increased, not diminished.



SUMMARY.

1. Partial vapour pressures (at 70°) and refractivities (at 25°) of mixtures of benzene with nitrobenzene, phenol, benzyl alcohol, or *p*-dichlorobenzene have been measured.

2. The hydroxylic compounds are much more associated than the others, and *p*-dichlorobenzene is slightly associated.

3. The results are discussed from the point of view of dipolar and van der Waals forces.

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