

398. *Partial Vapour Pressures and Refractivities of Binary Mixtures of Benzene and some of its Polar Derivatives.*

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IN investigating the part which dipole moment and dielectric constant play in determining the properties of polar liquids, useful data are obtained by determining the effect of increasing concentration of polar molecules in an inert liquid on their activity. Profound interaction between the polar molecules may be detectable by changes in refractivity. For simplicity, the polar liquid should contain but one symmetrically placed dipole per molecule, and the non-polar liquid should, except for lack of polarity, be of similar chemical structure and molecular size to the polar liquid. These requirements are, as nearly as possible, fulfilled by binary mixtures of benzene and polar monosubstituted benzenes. The polar liquids used were chloro- and bromo-benzene, anisole, aniline, dimethylaniline, benzonitrile, and phenol (refractivities only are reported for the last). The vapour pressures were measured at 70°, in order that they might be of convenient magnitude, and the refractivities at 25°, in order to avoid error due to evaporation in the refractometer.

EXPERIMENTAL.

Partial Vapour Pressures.—The method used by Zawidski (*Z. physikal. Chem.*, 1900, **35**, 129) is open to the objection that the comp. of the mixture changes during the distillation. This error is particularly large if the com-

ponents are very different in volatility. The same criticism applies to the bubbling method, and here there may be, in addition, error due to failure to obtain saturation of the gas stream with vapour (Berkeley and Hartley, *Proc. Roy. Soc., A*, 1906, **77**, 156). Rosanoff's method (*J. Amer. Chem. Soc.*, 1909, **31**, 448, 953) seems to be unsuitable for pairs of liquids of very different volatility, owing to the difficulty of controlling the addition of the more volatile component. The most promising method appears to be that of Sameshima (*J. Amer. Chem. Soc.*, 1918, **40**, 1482), which is similar to Zawidski's except that the distillate, after filling the receiver, flows back to the still containing the boiling mixture. When equil. has been attained by adjusting the press. in the apparatus until the temp. of the boiling mixture remains const. at the value at which measurements are required to be made, the comp. and quantity of vapour leaving the still and of returning distillate are equal. Error due to change in comp. of the mixture during distillation is thus eliminated. A large sample of distillate (in the present work about 9 c.c.) can be collected, thus permitting an accurate analysis. By rejecting the first filling of the receiver, error due to the presence of moisture from glass surfaces in the first portion of distillate may be avoided. However, if the volatilities of the pure components of the mixture are very different, as in the present work, the distillate from mixtures rich in the less volatile component is so rich in the more volatile component that it boils on its way back to the still through the thermostat. The returning distillate consequently does not mix thoroughly with the contents of the still, but to a large extent passes straight through as vapour, thus vitiating the method. This difficulty was overcome by the following modification of Sameshima's apparatus.

The apparatus (Fig. 1) was supported by clamps from vertical steel rods bolted 4 in. from a wooden framework securely fastened to the wall, floor, and ceiling of the laboratory. The still *S* (containing 75–150 c.c. of liquid) was immersed to the level of the ground-glass stoppers in a glass-sided thermostat (covered with paraffin wax) kept just over 1° above the boiling temp. The ground part of the stoppers was about 3 cm. long, and it was unnecessary to use a mercury seal. The temp. of the boiling liquid was read through a telescope on a thermometer suspended by a Pt wire from a hook on the stopper of the still. The thermometer was of short range, graduated in 0.2°, and was compared at intervals with a standard recently calibrated at the N.P.L.

Superheating was avoided by means of an auxiliary heater *H* (shown in a side view). In order to function properly, the electrical heater must provide a highly localised and fairly intense source of heat, which will produce bubbles of vapour that will agitate the whole of the liquid in the still. It consisted of three short closely-wound coils of Pt wire (0.07 mm. diam.) supported on a glass framework and connected in parallel with five accumulators, which provided a current of just less than 1 amp. through each coil. If the wire is thicker, or if it forms a long uncoiled loop, it tends merely to heat the liquid without forming bubbles of vapour; if it is too thin, it is easily burnt out. Mixtures were less prone to superheat than pure substances.

Fractionation was eliminated by circulating thermostat water through the jacket *J*. *C*₁ and *C*₂ were Davies double-surface condensers 2 ft. long, through which either tap or ice-cooled water could be circulated (it is not necessary for *C*₂ to be more than 6 in. long). The two condensers *A* and *B* (*A* was in series with *C*₁, and *B* with *C*₂) kept the returning distillate cool

and liquid until it had mixed thoroughly with the liquid in the still. The two small bulbs *D* served a double purpose: (1) to take up strain in the glasswork and (2) to facilitate mixing. Condenser *A* was surrounded with an air-jacket in order to prevent (1) the cooling water from becoming too warm and (2) undue cooling of the thermostat. It was impracticable, owing to glass-blowing difficulties, to place a similar jacket round condenser *B*. The short lengths of tubing *E* and *F*, which were unavoidably exposed directly to the thermostat, were lagged with split corks. It was sometimes necessary to immerse the receiver *R* in a cooling mixture.

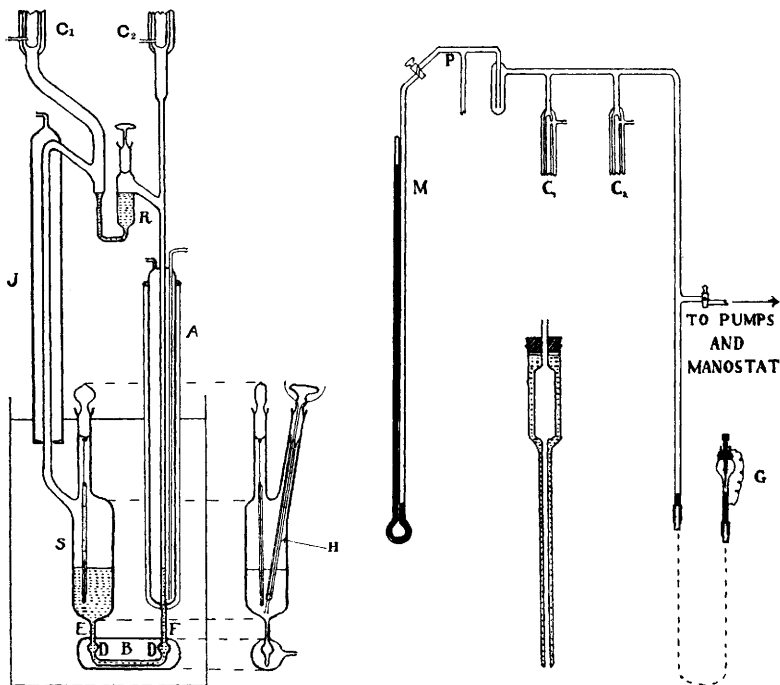


FIG. 1.

FIG. 2.

A lagged 10-gallon metal drum was used as a manostat. The press. in the apparatus was regulated to within 0.1 mm. by means of an electrical make-and-break, adjustable by screw, at the open end of the auxiliary manometer *G*, which, through a relay, controlled a Hyvac pump. By using a small pulley and a resistance in series with the armature of the shunt-driving motor, the speed of the pump was reduced. The setting of such a regulator varies with atm. press.; however, changes in the latter are negligibly small over the period during which it is necessary to keep the press. const. In order to accelerate press. equalisation in the apparatus, all tubing was of at least 1 cm. internal diameter. The total press. in the apparatus was read to 0.2 mm. with a magnifying glass on the manometer *M*, which was fitted with a glass mirror-backed scale. For pumping large vols. of air out of the apparatus, a Geryk oil pump was used. By admitting pure dry air to the

apparatus at the point P , the risk of sweeping vapour into the manometer was avoided.

The receiver R usually filled in about 3 mins. Boiling was maintained for 20—30 mins. after equil. had apparently been reached. For withdrawing samples of the hot mixture in the still for analysis, a pipette jacketed with H_2O at room temp. (Fig. 2) was used in order to cool the sample rapidly and thus minimise change in its comp.

The most reliable method of analysing the mixtures was by determining their densities at 25° in either 5 or 10 c.c. pycnometers, fitted with ground-glass caps. If the difference in density of the two pure liquids was 0.15, the composition of a mixture could be determined to 0.0005 mol.-fraction. For preparing mixtures of known comp., it is necessary to use long narrow-necked flasks with especially well-ground stoppers, filled almost to the neck with liquid.

The results of Zawidski (*loc. cit.*) for $C_6H_6-CCl_4$ at 50° were satisfactorily repeated.

Refractive Indices.—These were measured for the H_α line (λ 6563) at 25° with a Pulfrich refractometer, and are accurate to 0.0001.

Purification of Materials.—*Chlorobenzene.* Fractionation with an "evaporator" still-head gave a product boiling over 0.1° . This was washed 3 times with $NaOH$ aq. and H_2O , and dried first over K_2CO_3 and then over $CaCl_2$. Finally, it was distilled under reduced press.

Bromobenzene. This was washed twice with $NaOH$ aq., and then steam-distilled 5 times to remove dibromobenzene. Two fractionations through a four-pear column gave a product boiling over 0.2° . This was dried over $CaCl_2$ and distilled under reduced press.

Anisole. Fractionation twice through a four-pear column after washing with $NaOH$ aq. reduced the b. p. range to 0.2° . After drying over stick KOH it was distilled under diminished press.

Aniline. Two fractionations of A.R. aniline gave a product boiling over 0.2° . This was dried over stick KOH and distilled in vac. immediately before use.

Dimethylaniline. An A.R. product, in which no $NHMePh$ could be detected by the Ac_2O test, was subjected to the same treatment as aniline.

Benzonitrile. This was purified by the method of Martin (*J.*, 1928, 3275).

Phenol. Commercial "absolute" phenol was freed from cresols by freezing out the hydrate 4 times. It was dried by fractionation 3 times through a four-pear column (the final product boiled over 0.1°).

Benzene. A. R. Benzene was purified by the method of Richards and Shipley (*J. Amer. Chem. Soc.*, 1919, 41, 2007).

Alcohol. The alcohol used for washing was refluxed over CaO and distilled.

Results.

In Table I are given the densities, refractive indices, and v. p.'s of the pure substances used. Partial v. p.'s of the polar component are recorded as p (in mm. of Hg at 0°) in Table II; c represents the composition as a mol.-fraction of the polar component.

Table III gives, for mixtures of known mol.-fraction of the polar component, c , the densities (d_4^{25}), the refractive indices (n_D^{25}), the observed mol. refractivities $[R_L]_{6563} = R_{\text{obs.}} - \text{calc.}$ for a mol. wt. of $cM_1 + (1 - c)M_2$, where M_1 is the mol. wt. of the polar component and M_2 that of C_6H_6 , and the difference

TABLE I.

Substance.	d_4^{25} .	n_D^{25} .	V. p. (70°).
Benzene	0.87288	1.49312	545.3 *
Chlorobenzene	1.10113	1.51697	99.3
Bromobenzene	1.48903	1.55287	43.0
Aniline	1.01749	1.57662	10.6
Dimethylaniline.....	0.95185	1.54923	8.2
Anisole	0.98924	1.50992	39.8
Benzonitrile	1.00105	1.52096	10.32

* The International Critical Tables give 545.6.

TABLE II.

Chlorobenzene.			Bromobenzene.			Dimethylaniline.		
c.	Total press.	p.	c.	Total press.	p.	c.	Total press.	p.
0.0285	535.2	3.60	0.0263	533.3	1.88	0.0182	536.1	0.07
0.0497	525.2	5.64	0.0604	514.4	3.51	0.0618	509.6	0.87
0.1115	493.5	13.12	0.1061	481.4	6.76	0.1197	474.7	1.33
0.2256	435.0	26.28	0.2839	401.9	14.12	0.1990	431.3	2.34
0.3938	367.1	42.28	0.3690	349.7	18.77	0.2441	403.3	2.43
0.4138	347.2	45.99	0.3913	338.8	19.35	0.2549	397.9	2.36
0.5052	315.5	52.95	0.4615	296.8	22.51	0.2938	375.6	2.75
0.6242	251.3	65.47	0.6144	223.3	28.66	0.3444	349.6	3.37
0.7272	206.7	76.03	0.6165	214.2	27.68	0.3537	341.9	3.36
0.8161	169.7	84.25	0.7407	166.5	32.45	0.4529	288.9	4.32
0.8372	166.9	85.78	0.8424	115.9	37.54	0.6066	205.0	5.80
0.9213	128.8	93.63	0.9419	68.6	42.10	0.7417	129.9	7.09
0.9320	126.1	95.63	0.9565	62.9	42.28	1.0000	8.2	8.2
1.0000	99.3	99.3	1.0000	43.0	43.0			

Aniline.			Anisole.			Benzonitrile.		
c.	Total press.	p.	c.	Total press.	p.	c.	Total press.	p.
0.0339	526.4	0.83	0.0330	528.7	1.94	0.0359	525.9	0.86
0.0750	506.7	1.18	0.0795	503.2	4.34	0.0798	503.6	1.61
0.1542	472.2	2.17	0.1425	468.4	7.22	0.1228	481.2	2.40
0.2610	429.9	4.40	0.3666	347.8	18.51	0.1835	451.3	2.95
0.3899	376.5	5.85	0.5195	271.4	23.96	0.2659	403.2	4.05
0.5410	319.1	6.88	0.6831	185.4	29.57	0.3506	369.3	4.89
0.5850	292.9	7.23	0.9083	76.4	37.67	0.4164	335.8	5.49
0.6808	244.1	7.91	1.0000	39.8	39.8	0.4888	295.7	6.71
0.7718	176.1	8.76				0.5563	259.7	7.48
0.7804	173.6	9.25				0.7146	164.8	8.90
0.8156	143.1	9.29				0.7914	121.0	9.46
1.0000	10.6	10.6				1.0000	10.32	10.32

$\Delta = R_{\text{calc.}} - R_{\text{obs.}}$ where $R_{\text{calc.}} = R_1c + R_2(1 - c)$, R_1 being the refractivity of the pure polar component and R_2 that of C_6H_6 . For PhOH, which is solid and not miscible in all proportions with C_6H_6 at 25° , the extrapolated value 27.699 was assigned to R_1 . For pure benzene, $R_{\text{obs.}} = 25.992$.

Discussion.

The close agreement between $R_{\text{obs.}}$ and $R_{\text{calc.}}$ (Table III) shows that the partial molal refractivities of the polar liquids are constant over the whole concentration range. The only approach to a systematic departure from constancy is in the case of benzonitrile.

TABLE III.

c.	$d_4^{25^\circ}$.	$n_D^{25^\circ}$.	$R_{obs.}$	Δ .	c.	$d_4^{25^\circ}$.	$n_D^{25^\circ}$.	$R_{obs.}$	Δ .
C ₆ H ₅ Cl-C ₆ H ₆ Mixtures.					C ₆ H ₅ -NMe ₂ -C ₆ H ₆ Mixtures.				
0-04095	0-88351	1-49400	26-181	+0-012	0-04103	0-87747	1-49634	26-586	+0-001
0-06985	0-89103	1-49471	26-318	+0-017	0-10620	0-88444	1-50136	27-538	-0-007
0-11537	0-90263	1-49589	26-540	+0-019	0-17136	0-89086	1-50635	28-506	-0-031
0-14715	0-91013	1-49677	26-712	+0-003	0-18428	0-89210	1-50693	28-678	-0-016
0-16443	0-91481	1-49724	26-788	+0-012	0-21553	0-89510	1-50910	29-134	-0-019
0-25771	0-93763	1-49982	27-258	+0-001	0-30450	0-90319	1-51478	30-424	-0-020
0-34176	0-95781	1-50193	27-671	+0-001	0-37785	0-90945	1-51941	31-496	-0-029
0-39808	0-97115	1-50327	27-945	+0-004	0-45819	0-91592	1-52396	32-658	-0-027
0-44497	0-98187	1-50441	28-170	+0-009	0-56951	0-92438	1-53019	34-285	-0-041
0-56517	1-00925	1-50722	28-766	+0-004	0-79318	0-93955	1-54061	37-499	-0-014
0-68606	1-03578	1-51002	29-363	+0-001	0-89552	0-94587	1-54511	38-981	-0-013
0-80654	1-06148	1-51271	29-951	+0-005	0-93004	0-94812	1-54643	39-461	+0-007
0-87587	1-07593	1-51423	30-294	+0-003	1-00000	0-95185	1-54923	40-482	—
0-94889	1-09083	1-51585	30-657	-0-001					
1-00000	1-10113	1-51697	30-907	—					
C ₆ H ₅ -NH ₂ -C ₆ H ₆ Mixtures.					C ₆ H ₅ Br-C ₆ H ₆ Mixtures.				
(The values of d and n are interpolated.)									
0-08574	0-88640	1-50082	26-360	+0-001	0-05000	0-9094	1-49666	26-368	+0-011
0-22112	0-90747	1-51292	26-946	-0-003	0-10000	0-9442	1-50006	26-773	-0-008
0-38822	0-93262	1-52755	27-673	-0-011	0-20000	1-0143	1-50665	27-513	+0-026
0-46817	0-94428	1-53435	28-020	-0-014	0-30000	1-0803	1-51300	28-301	+0-011
0-59155	0-96214	1-54466	28-551	-0-014	0-40000	1-1446	1-51919	29-074	+0-012
0-71177	0-97907	1-55447	29-065	-0-011	0-50000	1-2070	1-52520	29-844	+0-015
0-78628	0-98925	1-56500	29-391	-0-016	0-60000	1-2672	1-53097	30-613	+0-019
0-89170	1-00330	1-56867	29-843	-0-015	0-70000	1-3253	1-53644	31-381	+0-025
1-00000	1-01749	1-57662	30-294	—	0-80000	1-3810	1-54165	32-156	+0-023
					0-90000	1-4354	1-54714	32-940	+0-013
					1-00000	1-48903	1-55287	33-726	—
C ₆ H ₅ ·OMe-C ₆ H ₆ Mixtures.					C ₆ H ₅ ·OH-C ₆ H ₆ Mixtures.				
(The values of d and n are interpolated.)									
0-05000	0-88004	1-49414	26-321	+0-005	0-08590	0-89066	1-49776	26-126	+0-013
0-10000	0-88700	1-49515	26-655	+0-005	0-09043	0-89174	1-49809	26-134	+0-012
0-20000	0-90021	1-49713	27-327	+0-001	0-23653	0-92179	1-50631	26-388	+0-011
0-30000	0-91311	1-49905	27-996	-0-001	0-28108	0-93068	1-50864	26-465	+0-007
0-40000	0-92542	1-50082	28-660	+0-003	0-37384	0-94936	1-51365	26-630	±0-000
0-50000	0-93720	1-50251	29-328	+0-003	0-39741	0-95420	1-51496	26-672	-0-002
0-60000	0-94848	1-50412	29-995	+0-004	0-43543	0-96197	1-51693	26-734	+0-001
0-70000	0-95927	1-50566	30-663	+0-004	0-56014	0-98692	1-52330	26-946	+0-002
0-80000	0-96962	1-50714	31-330	+0-004	0-56047	0-98682	1-52335	26-951	-0-003
0-90000	0-97955	1-50857	32-000	+0-003	1-00000	—	—	27-699	—
1-00000	0-98924	1-50992	32-670	—					
C ₆ H ₅ ·CN-C ₆ H ₆ Mixtures.					C ₆ H ₅ ·OH-C ₆ H ₆ Mixtures.				
0-07543	0-88461	1-49550	26-373	+0-023	0-44008	0-93505	1-50647	28-317	+0-030
0-09701	0-88805	1-49622	26-482	+0-029	0-55560	0-94967	1-50976	28-943	+0-023
0-14828	0-89545	1-49793	26-758	+0-028	0-56821	0-95113	1-51010	29-015	+0-018
0-20560	0-90375	1-49974	27-060	+0-032	0-63912	0-95978	1-51196	29-395	+0-018
0-23865	0-90835	1-50062	27-231	+0-038	0-85754	0-98532	1-51752	30-574	+0-008
0-31304	0-91847	1-50294	27-635	+0-032	0-86299	0-98588	1-51765	30-605	+0-006
0-39255	0-92893	1-50520	28-064	+0-029	1-00000	1-03105	1-52096	31-344	—

If the figures for this compound are treated by the method of intercepts (Lewis and Randall, "Thermodynamics," 1923, p. 38), it is found that the partial molal refractivity increases from about 30.05 in dilute solution to 31.35 at mol.-fraction 0.2, after which it remains constant. Since this is the most polar liquid investigated, it is not surprising that in it a certain amount of mutual deformation of the molecules occurs at higher concentrations. In phenol (and perhaps in aniline) molecular association by co-ordination occurs according to Sidgwick ("The Electronic Theory of Valency," 1927, p. 134). If the argument of Smyth, Engel, and Wilson (*J. Amer. Chem. Soc.*, 1929, 51, 1736) be accepted, such co-ordination should

be reflected in refractivity changes, since association increases with increasing concentration. However, no such effect is detectable (cf. similar results of Smyth, Engel, and Wilson for alcohols, *loc. cit.*).

We shall define as "perfect" a solution in which the restraining force on a polar molecule is the same as in an infinitely dilute solution in benzene, where interaction between the polar molecules is negligible. Perfect solutions are then represented by the tangent to the partial vapour pressure-mol.-fraction curve of the polar liquid at the limit of zero concentration. Interaction between the polar molecules will cause deviations from this tangent. There is usually no difficulty in drawing the tangent. To take deviations from Raoult's law as measures of imperfection is unsatisfactory, since to do so implies that all pure liquids are perfect, whilst admitting that mixtures may be imperfect.

If the interaction between a polar molecule and the surrounding liquid arises from the Coulomb forces due to the electrical charges on the molecule, and if the surrounding liquid may be represented by a medium of uniform dielectric constant, then it may be possible approximately to account for deviations from ideal behaviour on the lines previously indicated by one of us (*Nature*, 1931, **128**, 456). It was shown that the following relation should hold

$$p/p_i = e^{-\frac{\mu^2}{3a^3kT} \left(\frac{1}{D_i} - \frac{1}{D} \right)}$$

where, at a given concentration, p is as defined on p. 2661, p_i = ideal vapour pressure, μ = dipole moment of the polar molecule, D_i = dielectric constant of benzene, D = dielectric constant of the solution, a = "radius" of the molecule, k = Boltzmann's constant, and T = absolute temperature.

At present, we lack the dielectric-constant data necessary to test this relation completely, but work is in progress to remedy this defect. Meanwhile, we can apply it to pure chlorobenzene, aniline, and benzonitrile. In Table IV are the values of a (in Å.U.) required to give the observed values of p/p_i and also the values of a' , the corresponding molecular radius if the model of a dipolar molecule used by Bell (*Trans. Faraday Soc.*, 1931, **27**, 799) be adopted.

TABLE IV.

Substance.	$\mu \times 10^{18}$	D .	p/p_i .	a .	a' .
Chlorobenzene	1.57	5.2	0.849	3.04	2.37
Aniline	1.39	6.2	0.625	2.05	1.69
Benzonitrile	3.84	22.0	0.490	3.92	3.30

Both a and a' are of the correct order of magnitude. Preliminary results indicate that p/p_i for pure phenol is of the order 0.25, leading to values of $a = 1.8$ and $a' = 1.5$ Å.U. These values are much

smaller than would be expected, showing that the work of vaporising a phenol molecule from pure phenol is much greater than would be anticipated from its molecular size and dielectric properties. There are two possible interpretations: (1) extra work is required to overcome co-ordination between the molecules, and (2) owing to the acute angle between the valencies of the oxygen atom, the dipole of a hydroxyl group is somewhat isolated and neither pole is much screened by the radical attached to the hydroxyl group: the value of a for a hydroxylic compound therefore approximates to that for a hydroxyl group. The great power of hydroxylic solvents in promoting electrolytic dissociation may be due to the fact that both anions and cations can approach closely to an oppositely charged pole of the solvent molecule. When dielectric-constant and vapour-pressure data are available over the whole concentration range for phenol, it is hoped to be able to decide between these two possibilities, since according to (1) a should vary with concentration, whilst according to (2) it should remain constant.

The observation (p. 2659) that pure substances were more prone to superheat than mixtures may have a bearing on some effects attributed to intensive drying.

Summary.

1. The partial vapour pressures and refractivities of mixtures of benzene and chlorobenzene, bromobenzene, aniline, dimethylaniline, anisole, benzonitrile, and phenol (refractivities only) have been measured.

2. An apparatus suitable for determining the partial vapour pressures of binary mixtures of liquids of very different volatility has been described.

3. An interpretation of the results has been attempted in terms of the dipole moment and molecular radius of the polar molecules and the dielectric constant of the medium.

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