866. *Molecular Polarisation in Ternary Systems comprising Benzene, Pyridine, and an Alcohol.*

By D. Cleverdon, G. B. Collins, and J. W. Smith.

The apparent molecular polarisations of *n*- and *tert.*-butyl alcohol and of diphenylmethanol at zero concentration in various benzene–pyridine mixtures, and of pyridine at zero concentration in various mixtures of benzene with the alcohols, have been determined. By assuming that the active masses of the alcohols, pyridine, and association complexes can be represented satisfactorily by their concentrations in mole/c.c., the approximate equilibrium constants for the association of pyridine with the monomeric alcohol molecules, and the effective molecular polarisations of the association complexes, have been calculated. The results are discussed in relation to the probable electron distibutions in the alcohol molecules.

The fact that the presence of pyridine modifies considerably the courses of the reactions of certain alcohols with, *e.g.*, acetyl chloride, suggests that pyridine may associate with these alcohols. In 1947 it was pointed out [1] that any such association should cause the dielectric polarisation of a solution containing both an alcohol and pyridine in an inert solvent to be greater than the value calculated from the molecular polarisations of the components. An effect of the type predicted was observed for a number of alcohols in benzene solution, and the augmentation of the polarisation above the value calculated from the amounts of alcohol and pyridine present was shown to increase progressively with the concentrations of both the alcohol and pyridine.[2] On the grounds of the chemical behaviour of their derivatives, a series of alkyl and substituted alkyl groups was arranged in the order of their electron-releasing properties, and it was thought possible that the increases in polarisation observed for the alcohols derived from these groups, when studied under comparable conditions, might follow a similar order.[1] This aspect of the subject has had to be deferred, however, until the effect has been studied in more detail for simple alcohols so as to elucidate the quantitative aspects of the increment of the polarisation. With this object in view the dielectric polarisations of mixtures of benzene and pyridine with *n*- and *tert.*-butyl alcohol and with diphenylmethanol have now been studied in detail.

To investigate systems comprising two solutes A and B, which associate with one another but not with the solvent S, it is desirable to determine the limiting values of the molecular polarisation of A at zero concentration in various mixtures of B and S, and also of the molecular polarisation of B at zero concentration in mixtures of A and S. The study of the systems from the two points of view, however, does not necessitate complete duplication of the experimental work, as once data have been obtained for solutions of A in a number of mixtures of B and S these can be used to provide corresponding data for solutions of B in mixtures of A and S. If the weight fractions of the three components are w_A, w_B, and w_S, then $w_A + w_B + w_S = 1$. If a mixture is regarded as a solution of A in a solvent $B + S$, then w_B', the weight fraction of B in the solvent mixture, is $w_B/(w_B + w_S)$, and therefore $w_B = w_B'(1 - w_A)$. Alternatively, if the system is regarded as a solution of B in a solvent $A + S$, it follows that $w_A = w_A'(1 - w_B)$, where w_A' is the weight fraction of A in the solvent. Combining these expressions we obtain:

$$w_A = w_A'\frac{1 - w_B'}{1 - w_A'w_B'} \quad \text{and} \quad w_B = w_B'\frac{1 - w_A'}{1 - w_A'w_B'}$$

If solutions of A in constant mixtures of B and S have been studied, the values of w_B' have been fixed when making the solvent mixtures. If a set of convenient values be chosen for w_A' the corresponding values of w_A may be calculated for each mixture, and the specific polarisations of the solutions of those concentrations determined by interpolation of the

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[1] Cleverdon, Ph.D. Thesis, London, 1947.

[2] Cleverdon and Smith, *Chem. and Ind.*, 1948, 29.

existing data. It remains only to calculate the set of values of w_B to complete the polarisation data equivalent to those for a series of solutions of B in mixtures of A and S in the chosen proportions.

The general case of two substances A and B, which form an unstable compound AB but do not react with the solvent S, has been discussed previously.[3] If the active masses of these substances can be represented by their concentrations in mole/c.c., the apparent limiting value of the molecular polarisation of A at zero concentration in a constant mixture of B and S, $(P_{A_\infty})_{BS}$, is given by:

$$\frac{\Delta P}{(P_{A_\infty})_{BS} - (P_{A_\infty})_S} = \frac{M_B}{Kw_B'd_{BS}} + 1$$

where M_B is the molecular weight of B, d_{BS} the density of the solvent mixture, K the association constant of the complex AB, and $\Delta P = (P_{AB_\infty})_S - (P_{A_\infty})_S - (P_{B_\infty})_S$, the last three functions being the limiting values of the molecular polarisations of AB, A, and B, respectively, at zero concentration in the solvent S. It follows, therefore, that a plot of $1/\{(P_{A_\infty})_{BS} - (P_{A_\infty})_S\}$ against $M_B/w_B'd_{BS}$ should be linear, with a slope $1/K\Delta P$ and an intercept on the axis for the former of $1/\Delta P$. Further, this should superpose upon the corresponding plot of $1/\{(P_{B_\infty})_{AS} - (P_{B_\infty})_S\}$ against $M_A/w_A'd_{AS}$ derived from data for solutions of B in solvents comprising mixtures of A and S.

The assumptions on which this method is based should be roughly true for the case of an alcohol in a series of constant mixtures of pyridine and benzene. When the alcohol approaches zero concentration in these A-in-BS systems the conditions become such that interaction occurs only between pyridine and monomeric alcohol molecules. When the $(P_{B_\infty})_{AS}$ values for pyridine in constant mixtures of an alcohol and benzene ("B-in-AS" systems) are studied, however, the alcohol is present both as single molecules and as associated molecules of various degrees of complexity. As the extent of this association differs from one solvent mixture to another the results obtained in different series of measurements relate to the interaction of pyridine molecules with alcohols in different states of complexity. Hence the plots for the B-in-AS systems cannot be expected to superpose upon those for the A-in-BS systems.

The polarisation results obtained for the systems studied are summarised in Table 1, where α and β are the limiting values of $d\epsilon/dw$ and dv/dw, respectively, at zero concentration. The values of $(P_{A_\infty})_{BS}$ and $(P_{B_\infty})_{AS}$ shown are the mean figures from at least three methods of extrapolation, and the maximum divergences from the mean values are indicated. The results for the series of solutions of *n*-butyl alcohol in a pyridine–benzene mixture fall well in line with the remaining data for this system, derived by the indirect procedure.

In each system the apparent molecular polarisation values at zero concentration increase progressively with increasing concentration of pyridine or alcohol in the solvent mixture. On the other hand the association does not seem to affect appreciably the refractivities of the mixtures, as the apparent values of the molecular refractions of the solutes show no systematic change with the composition of the solvent. The effective specific volumes of the solutes, as given by $v_{BS} + \beta$ or $v_{AS} + \beta$, indicate that in each system the association is accompanied by a decrease in volume. A decrease in effective specific volume also accompanies the association of alcohols alone in benzene solution.[4]

If P_{E+A} is assumed to be represented by $[R_D]$, the results for solutions of pyridine in benzene lead to a dipole moment of 2·20 D, in accordance with previous values[5-7] obtained from measurements on benzene solutions (2·23, ~2·2, 2·20) and close to the value (2·15 D) obtained from microwave-absorption measurements on the vapour.[8]

[3] Few and Smith, *J.*, 1949, 2781.
[4] Boud, Cleverdon, Collins, and Smith, *J.*, 1955, 3893.
[5] Goethals, *Rec. Trav. chim.*, 1935, **54**, 299.
[6] Hückel, *Ber.*, 1944, **77**, 810.
[7] Leis and Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 79.
[8] De More, Wilcox, and Goldstein, *J. Chem. Phys.*, 1954, **22**, 876.

TABLE 1. *Summary of polarisation data.*

$100w_B$	v_{BS}	α	β	$(P_{A\infty})_{BS}$ (c.c.)	$(P_{A\infty})_{BS} - (P_{A\infty})_S$ (c.c.)	$[R_D]_A$ (c.c.)
			n-*Butyl alcohol in benzene–pyridine.*			
0·000	1·14458	3·77	0·133	81·0 ± 0·3	—	22·0
1·000	1·14328	—	—	94·3 ± 0·1	13·3	—
2·000	1·14192	—	—	103·9 ± 0·2	22·9	—
2·833	1·14083	6·15	0·130	109·5 ± 0·3	28·5	22·1
3·000	1·14059	—	—	110·6 ± 0·2	29·6	—
4·000	1·13926	—	—	115·2 ± 0·3	34·2	—
5·000	1·13793	—	—	118·7 ± 0·2	37·7	—
6·000	1·13660	—	—	121·4 ± 0·1	40·4	—
			tert.-*Butyl alcohol in benzene–pyridine*			
0·000	1·14458	3·65	0·206	80·5 ± 0·2	—	22·6
1·244	1·14286	4·18	0·207	87·2 ± 0·3	6·7	22·7
2·440	1·14133	4·64	0·206	92·3 ± 0·4	11·8	22·6
3·738	1·13957	5·06	0·206	96·4 ± 0·3	15·9	22·7
6·541	1·13587	5·69	0·206	100·7 ± 0·3	20·2	22·6
6·871	1·13547	5·86	0·204	102·2 ± 0·4	21·7	22·6
9·166	1·13242	6·20	0·205	103·1 ± 0·3	22·6	22·6
			Diphenylmethanol in benzene–pyridine.			
0·000	1·14458	1·780	−0·246	111·0 ± 0·2	—	57·7
1·477	1·14260	3·157	−0·249	155·6 ± 0·2	44·6	57·7
1·907	1·14205	3·422	−0·249	163·4 ± 0·2	52·4	57·5
2·763	1·14089	3·850	−0·249	175·3 ± 0·3	64·3	57·5
4·266	1·13884	4·364	−0·250	187·9 ± 0·1	76·9	57·6

$100w_A$	v_{AS}	α	β	$(P_{B\infty})_{AS}$ (c.c.)	$(P_{B\infty})_{AS} - (P_{B\infty})_S$ (c.c.)	$[R_D]_B$ (c.c.)
			*Pyridine in benzene–*n-*butyl alcohol.*			
0·000	1·14455	6·67$_5$	−0·133	123·2 ± 0·2	—	24·1
0·923	1·14577	7·79	−0·140	138·4 ± 0·2	15·2	24·1
1·250	1·14616	8·14$_5$	−0·142	143·2 ± 0·3	20·0	24·0
1·866	1·14698	8·90	−0·146	153·0 ± 0·3	29·8	24·0
2·538	1·14777	9·69	−0·150	163·7 ± 0·5	40·5	24·1
3·564	1·14895	10·92	−0·154	177·9 ± 0·5	54·7	24·0
4·350	1·14983	11·83	−0·157	188·8 ± 0·6	65·6	24·0
			*Pyridine in benzene–*tert.-*butyl alcohol.*			
1·000	1·14659	—	—	130·2 ± 0·2	7·0	—
2·000	1·14850	—	—	137·2 ± 0·3	14·0	—
3·000	1·15034	—	—	144·4 ± 0·4	21·2	—
4·000	1·15214	—	—	151·6 ± 0·4	28·4	—
5·000	1·15388	—	—	159·1 ± 0·5	35·9	—
			Pyridine in benzene–diphenylmethanol.			
1·000	1·14210	—	—	139·3 ± 0·1	16·1	—
2·000	1·13964	—	—	153·0 ± 0·0	29·8	—
3·000	1·13718	—	—	165·1 ± 0·1	41·9	—
4·000	1·13472	—	—	175·5 ± 0·3	52·3	—
5·000	1·13226	—	—	184·1 ± 0·3	60·9	—
6·000	1·12980	—	—	190·5 ± 0·5	67·3	—

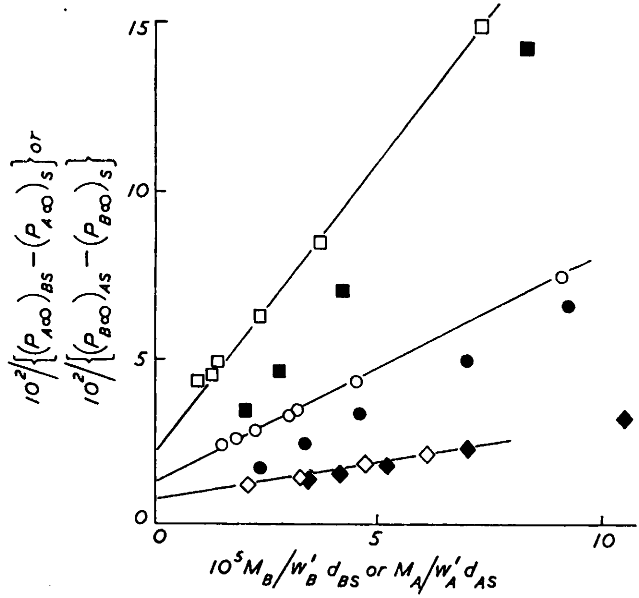
The results of plotting $1/\{(P_A)_{BS} - (P_A)_S\}$ against $M_B v_{BS}/w_B'$ are shown in the Figure. For each of the A in BS systems the points are satisfactorily linear, although there are slight indications of deviations at low values of $M_B v_{BS}/w_B'$, corresponding to high pyridine concentrations, where the assumptions regarding the ideality of behaviour are less justified. The best straight lines as deduced by the least-squares method have the slopes and intercepts shown in Table 2. The values of K and of the dipole moments μ_{AB} of the complexes deduced from these results are also included in the Table.

TABLE 2. *Association constants in benzene solution, and dipole moments of complexes of pyridine with alcohols.*

Alcohol	$1/K\Delta P$ ($\times 10^8$)	$1/\Delta P$ ($\times 10^4$)	K ($\times 10^{-2}$)	ΔP (c.c.)	$(P_{AB\infty})_S$ (c.c.)	$[R_{AB}]_S$ (c.c.)	μ_{AB} (D)
n-Butyl alcohol	683	135	20	74	278	46	3·37
tert.-Butyl alcohol	1745	210	12	48	252	47	3·16
Diphenylmethanol	239	77	32	130	364	82	3·71

The results for the pyridine–diphenylmethanol *B*-in-*AS* system lie on the same line as those for the corresponding *A*-in-*BS* system so long as the concentration of alcohol is low, under which conditions the alcohol is essentially monomeric.[4] This seems to confirm the essential validity of the method for studying such association by molecular polarisation measurements. At the highest diphenylmethanol concentrations used, however, association of the alcohol becomes appreciable, and divergences from collinearity with the *A*-in-*BS* data occur. It is not surprising that the results for the *B*-in-*AS* systems involving *n*- and *tert.*-butyl alcohol show much greater divergences from those for the corresponding *A*-in-*BS* system, as their association is considerable even in 1% solutions in benzene. The data fall on lines which are almost parallel to those for the *A*-in-*BS* systems, with slopes 708 and 1700 × 10^{-7}, respectively. For each *B*-in-*AS* system the $(P_{B\infty})_{AS} - (P_{B\infty})_S$ values are greater than would be expected from the data for the *A*-in-*BS* system by an amount which increases progressively with increasing concentration of alcohol in the solvent mixture. As the association of alcohols in benzene solution seems to lead to the production of polymeric rather than dimeric molecules,[4] pyridine would be expected to associate more readily with dimeric and polymeric alcohol molecules than with monomeric molecules. This would account qualitatively for the results observed, although the matter is further complicated by the fact that association with dimeric and polymeric molecules will lead to aggregates of different average moment from those formed with monomeric alcohol molecules.

Plots of $1/\{(P_{A\infty})_{BS} - (P_{A\infty})_S\}$ *against* $M_B/w_B'd_{BS}$ *and of* $1/\{(P_{B\infty})_{AS} - (P_{B\infty})_S\}$ *against* $M_A/w_A'd_{AS}$.



○ n-*Butyl alcohol in benzene–pyridine.*
□ tert.-*Butyl alcohol in benzene–pyridine.*
□ *Diphenylmethanol in benzene–pyridine.*
● *Pyridine in benzene–*n-*butyl alcohol.*
■ *Pyridine in benzene–*tert.-*butyl alcohol.*
◆ *Pyridine in benzene–diphenylmethanol.*

The values of the product $K\Delta P$, being obtained from the slopes of the plots for the

A-in-*BS* systems, should be fairly accurate. The separate *K* and ΔP values, however, are subject to much greater error, and the values of μ_{AB} calculated from the latter have a probable error of about $\pm 0{\cdot}05$ D. The values of *K* obtained indicate that *n*-butyl alcohol tends to associate with pyridine to a slightly greater extent than does *tert.*-butyl alcohol. This behaviour is parallel to the association of the alcohol molecules with one another in benzene solution. On the other hand, although only slightly associated itself at low concentrations in benzene solution, diphenylmethanol associates with pyridine more readily than do either of the butyl alcohols. Further, the ΔP value, which gives the difference between the molecular polarisation of the complex and the sum of the molecular polarisations of the two separate compounds, is also greatest for diphenylmethanol and least for *tert.*-butyl alcohol.

In the association complex the axis of the pyridine dipole is collinear with the H–O bond of the alcohol molecule and hence, if no electron displacements occur within the molecules as a result of the association, the dipole moment of the complex should be given by $\mu_{AB}^2 = \mu_A^2 + \mu_B^2 + 2\mu_A\mu_B \cos\theta$, where θ is the angle of inclination of the dipole axis of the alcohol molecule to the O–H bond. The values obtained for μ_A, μ_B, and μ_{AB} lead to angles θ of 60°, 72°, and 29° in the *n*-butyl alcohol, *tert.*-butyl alcohol, and diphenylmethanol molecule, respectively.

Although the oxygen bond angle in the alcohols (110¼° in methyl alcohol) is greater than that in water (104½°), in which the effective bond moment is 1·5 D, the forms of the lone-pair orbitals are such that the contributions of the lone-pair electrons to the dipole moments are almost equal in water and in the alcohols. On the other hand the change in state of hybridisation of the bonding orbitals should lead to a slightly smaller H–O bond moment in an alcohol compared with that in water. The value of θ found for *n*-butyl alcohol can be accounted for by effective components to the moment of 1·55 and 1·38 D along the C–O and H–O bonds respectively. The above considerations together with an inductive effect in the alkyl group render these values not unreasonable.

Although the dipole moment of *tert.*-butyl alcohol is about the same as that for *n*-butyl alcohol, it is probable that the electron-density distribution is very different in the two molecules. This is shown, for instance, by the difference between the modes of interaction of the two compounds with hydrogen chloride. As compared with *n*-butyl alcohol there is likely to be an effective increase of the component of the moment along the C–O bond and a corresponding decrease in the component of the moment along the H–O bond.

These effects will cause the axis of the dipole in the *tert.*-butyl alcohol molecule to have a greater angle of inclination to the H–O bond than has the axis of the moment of *n*-butyl alcohol. Although the results are not sufficiently accurate to be used as a real measure of θ they suggest that in the formation of the complexes of these alcohols with pyridine there is no appreciable modification of the electron-density ditribution originally present in the separate molecules.

It seems highly improbable, however, that the dipole in the diphenylmethanol molecule is inclined to the H–O bond at an angle as small as 29°, as this would correspond with components of 1·70 and 0·83 D along the H–O and the C–O bond, respectively, in the isolated molecule. A much more plausible explanation for the relatively high value found for the moment of the complex with pyridine is that in this system the association between the molecules causes a modification of the electron distribution in the component molecules. It has been shown [9] that the apparent molecular polarisations of primary and secondary aromatic amines in dioxan solution are greater than in benzene, whilst for aliphatic amines the values obtained in the two solvents are almost equal. As dioxan itself has zero dipole moment, hydrogen bonding between an oxygen atom of a dioxan molecule and an amino-hydrogen atom would not, *per se*, lead to an increase in the dielectric polarisation of the system. Hence polarisation measurements do not prove the non-existence of association between dioxan and aliphatic amines, but simply indicate that, if this association occurs, it is not accompanied by any appreciable change in the electron-density distribution in the two molecules. For aromatic amines the difference between the apparent dipole

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[9] Few and Smith, *J.*, 1949, 753; Smith, *J.*, 1950, 3532; 1953, 109.

moments in dioxan and in benzene solution must be a consequence of the hydrogen bonding, and can be correlated with the readiness with which mesomeric displacements can occur in the amine molecule. Similar displacements may account for the results now obtained with diphenylmethanol. Since this compound reacts with hydrochloric acid by the same mechanism as *tert.*-butyl alcohol, it is probable that in the isolated molecule there is a tendency for electron density to be donated from the benzene rings towards the adjoining carbon atom. This leads to an increased component to the moment directed roughly along the C–O bond, as in *tert.*-butyl alcohol. On association with a pyridine molecule, however, this effect will be easily reversed, leading to a resultant moment for the complex in excess of the value which would be expected from vector addition of the values for the separate molecules.

Since this work was completed, Sutton and his co-workers[10] have used partitioning between the liquid and vapour phases to investigate complex formation between a volatile reactant and an involatile one in a volatile solvent. For *cyclo*hexane solutions of trimethylamine and *n*-heptyl alcohol the association constant for hydrogen-bond formation was found to be 35×10^2 (mole/c.c. units) which is comparable with our values for the butyl alcohols and pyridine, whilst for trimethylamine and triphenylmethanol it was found to have a higher value (120×10^2), as is to be expected from our result for diphenylmethanol. The finding that when K values determined in this way are combined with polarisation data for systems involving phenols and trimethylamine there is an increase in moment ($\Delta\mu$) as compared with the vector sum of the moments of the reactants parallels our observation with diphenylmethanol and pyridine. Further, the fact that $(\Delta\mu)^2$ is a fairly linear function of K appears to be somewhat analogous to the rough proportionality shown between the values of K and ΔP in Table 2.

EXPERIMENTAL

Materials.—Benzene, *n*- and *tert.*-butyl alcohol, and diphenylmethanol were purified as described previously.[4] Laboratory-reagent pyridine was dried (NaOH) and distilled through a 20-plate column; the middle fraction was refluxed from three successive portions of potassium permanganate and then from freshly ignited barium oxide; it was finally distilled from barium oxide in dry nitrogen and had b. p. 115·5°/762 mm., d_4^{25} 0·97786, n_D^{25} 1·5071.

Apparatus and Methods.—The dielectric constants were measured with the resonance apparatus described by Few, Smith, and Witten[11] relative to a value of 2·2725 for the dielectric constant of benzene at 25°. The use of the more recent value[12] of 2·2741 makes no perceptible difference to the conclusions. The refractive indices were measured with a Hilger Abbé refractometer. In the systems involving *tert.*-butyl alcohol and diphenylmethanol the measurements were concentrated on series of solutions of the alcohol in various pyridine–benzene mixtures, but, to facilitate interpolation of the results, most of the measurements on the system containing *n*-butyl alcohol were made on series of solutions of pyridine in mixtures of benzene with the alcohol. All measurements were made at 25·0°. The results are recorded in Table 3.

TABLE 3. *Polarisation data.*

Pyridine in benzene.

$100w_2$	ε	v	n_D	p	P_2	R_2
0·0000	2·2725	1·14458	1·4979	0·34089	—	—
0·7945	2·3258	1·14353	1·4981	0·35048	122·5	24·6
2·2190	2·4228	1·14166	1·4983	0·36727	121·0	24·3
3·8926	2·5386	1·13946	1·4984	0·38628	119·2	24·0
4·4362	2·5771	1·13868	1·4985	0·39234	118·7	24·1
5·0702	2·6218	1·13784	1·4986	0·39927	118·0	24·1
6·4325	2·7197	1·13601	1·4987	0·41393	116·8	24·0

$\varepsilon = 2{\cdot}2725 + 6{\cdot}675w_2 + 4{\cdot}26w_2^2$.

$v = 1{\cdot}4458 - 0{\cdot}133w_2$. $n_D^2 = 2{\cdot}2437 + 0{\cdot}04w_2$.

P_2 by direct extrapolation = 123·2 c.c.; from parameters = 123·16 c.c. $[R_D]_2 = 24{\cdot}05$ c.c.
Taking $P_{E+A} = [R_D]$, $\mu = 2{\cdot}20_2$ D.

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[10] Denyer, Gilchrist, Pegg, Smith, Tomlinson, and Sutton, *J.*, 1955, 3889; Hulett, Pegg, and Sutton, *J.*, 1955, 3901.

[11] Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211.

[12] Hartshorn, Parry, and Essen, *Proc. Phys. Soc.*, 1955, **68**, *B*, 422.

TABLE 3. (*Continued.*)

n-*Butyl alcohol in pyridine–benzene.*

100w_B	100w_A	ε	v	n_D	p	P_A	R_A
4·410	0·0000	2·5758	1·13872	—	0·39215	—	—
	2·1650	2·7343	1·14095	—	0·41796	117·4	—
	4·0562	2·8756	1·14299	—	0·43970	115·9	—
	6·1995	3·0227	1·14528	—	0·46122	111·4	—
	7·9983	3·1589	1·14707	—	0·48003	110·5	—
2·833	0·0000	2·4650	1·14083	1·4981	0·37432	—	—
	0·9843	2·5270	1·14204	1·4970	0·38522	109·9	22·7
	2·8924	2·6530	1·14429	1·4946	0·40651	110·2	22·2
	2·9991	2·6598	1·14436	1·4943	0·40762	110·1	21·9
	3·0916	2·6662	1·14449	1·4941$_5$	0·40867	110·1	21·9
	4·5501	2·7627	1·14607	1·4926	0·42417	109·0	22·2
	4·8752	2·7840	1·14647	1·4922	0·42753	108·7	22·2

Pyridine in n-*butyl alcohol–benzene.*

100w_A	100w_B	ε	v	n_D	p	P_B	R_B
0·9233	0·0000	2·3085	1·14577	1·4967	0·34797	—	—
	0·6650	2·3600	1·14483	1·4968$_5$	0·35711	136·2	24·4
	1·3439	2·4118	1·14384	1·4969$_5$	0·36604	133·9	24·0
	2·1411	2·4718	1·14280	1·4970$_5$	0·37613	131·6	24·0
	2·9471	2·5323	1·14168	1·4972	0·38598	129·5	24·0
	4·7860	2·6694	1·13921	1·4974$_5$	0·40729	125·6	24·1
	6·4394	2·7933	1·13698	1·4977	0·42538	122·6	24·1
1·250	0·0000	2·3222	1·14616	1·4962	0·35062	—	—
	0·9771	2·4009	1·14487	1·4963	0·36444	139·6	23·9
	1·8384	2·4688	1·14362	1·4964	0·37589	136·4	23·8
	2·9127	2·5512	1·14218	1·4966	0·38929	132·7	24·0
	3·7391	2·6142	1·14103	1·4968	0·39917	130·4	24·0
	5·0759	2·7156	1·13918	1·4970	0·41445	127·2	24·0
	5·7741	2·7686	1·13825	1·4971	0·42215	125·7	24·0
1·866	0·0000	2·3479	1·14698	1·4955	0·35558	—	—
	0·6028	2·4016	1·14608	1·4956	0·36495	151·1	23·7
	1·2421	2·4557	1·14518	1·4957	0·37414	146·4	23·9
	2·2688	2·5409	1·14366	1·4959$_5$	0·38809	141·5	24·0
	2·9854	2·5981	1·14268	1·4961	0·39715	138·3	24·1
	5·0322	2·7601	1·13988	1·4964	0·42148	131·7	24·0
	6·2873	2·8582	1·13813	1·4966$_5$	0·43532	128·5	24·1
2·538	0·0000	2·3766	1·14777	1·4946	0·36102	—	—
	0·5823	2·4325	1·14693	1·4947	0·37067	159·6	24·0
	1·3289	2·5009	1·14583	1·4949	0·38210	154·0	24·1
	2·1123	2·5698	1·14473	1·4950	0·39324	149·2	24·0
	2·8671	2·6341	1·41366	1·4952	0·40329	145·2	24·0
	4·5834	2·7757	1·14124	1·4955	0·42434	137·8	24·1
	6·7647	2·9508	1·13822	1·4958$_5$	0·44850	130·8	24·1
3·564	0·0000	2·4211	1·14895	1·4934$_5$	0·36932	—	—
	0·6522	2·4907	1·14794	1·4936	0·38106	171·6	23·7
	1·2361	2·5500	1·14709	1·4937	0·39077	166·5	23·8
	2·3167	2·6530	1·14554	1·4939	0·40695	157·7	23·9
	2·8161	2·6992	1·14483	1·4941	0·41396	154·6	24·1
	4·5346	2·8500	1·14236	1·4944$_5$	0·43574	145·1	24·0
	6·9125	3·0490	1·13901	1·4948$_5$	0·46223	135·5	24·1
4·350	0·0000	2·4545	1·14983	1·4924	0·37544	—	—
	0·5816	2·5217	1·14892	1·4925	0·38665	182·1	23·6
	1·3242	2·6028	1·14780	1·49275	0·39969	174·5	24·0
	2·0719	2·6790	1·14676	1·4929	0·41150	167·4	24·1
	3·2037	2·7886	1·14508	1·4931	0·42770	158·7	24·0
	4·6780	2·9225	1·14292	1·4934$_5$	0·44637	149·6	24·0
	6·7755	3·1042	1·13997	1·4938$_5$	0·46995	140·0	24·0

tert.-*Butyl alcohol in pyridine–benzene.*

100w_B	100w_A	ε	v	n_D	p	P_A	R_A
1·244	0·0000	2·3565	1·14286	1·4980	0·35585	—	—
	0·5432	2·3793	1·14397	1·4972	0·36031	87·1	22·9
	0·9696	2·3975	1·14481	1·4965$_5$	0·36381	87·2	22·8
	1·8620	2·4360	1·14655	1·4953	0·37116	87·3	23·0
	2·9705	2·4827	1·14858	1·4936	0·37990	86·4	22·7
	4·1819	2·5315	1·15076	1·4919	0·38892	85·0	22·8
	5·4530	2·5801	1·15299	1·4900	0·39777	83·4	22·6

TABLE 3. (*Continued.*)

tert.-*Butyl alcohol in pyridine-benzene.*

$100w_B$	$100w_A$	ε	v	n_D	p	P_A	R_A
2·440	0·0000	2·4382	1·14133	1·4983	0·36985	—	—
	0·4540	2·4594	1·14219	1·4976	0·37379	91·8	22·4
	1·0004	2·4854	1·14326	1·4967$_5$	0·37860	92·3	22·5
	1·7855	2·5232	1·14477	1·4956	0·38550	92·4	22·6
	2·3921	2·5518	1·14595	1·4947	0·39068	92·0	22·6
	3·9556	2·6235	1·14876	1·4925$_5$	0·40338	90·2	22·7
	5·1362	2·6749	1·15082	1·4909$_5$	0·41232	88·7	22·8
3·738	0·0000	2·5282	1·13957	1·4984	0·38459	—	—
	0·5667	2·5571	1·14066	1·4975$_5$	0·38975	96·0	22·7
	1·0785	2·5838	1·14168	1·4968	0·39447	96·4	22·7
	1·5541	2·6089	1·14262	1·4961	0·39888	96·6	22·8
	2·6278	2·6648	1·14460	1·4946	0·40850	95·9	22·8
	3·8606	2·7266	1·14688	1·4928	0·41894	94·5	22·8
	5·5571	2·8090	1·14981	1·4904$_5$	0·43252	92·4	22·7
6·541	0·0000	2·7284	1·13587	1·4987	0·41521	—	—
	0·5172	2·7581	1·13691	1·4980	0·42009	100·7	23·4
	0·9789	2·7846	1·13775	1·4973	0·42437	100·2	22·8
	1·6789	2·8263	1·13916	1·4962$_5$	0·43107	100·8	22·8
	2·6182	2·8821	1·14087	1·4947$_5$	0·43982	100·5	22·5
	3·7618	2·9489	1·14293	1·4932	0·45009	99·5	22·5
	5·3449	3·0387	1·14574	1·4910	0·46358	97·9	22·6
6·871	0·0000	2·7510	1·13547	1·4986	0·41848	—	—
	0·5059	2·7808	1·13646	1·4980	0·42332	102·0	23·9
	1·0360	2·8126	1·13747	1·4972	0·42842	102·1	23·2
	1·7573	2·8575	1·13882	1·4961	0·43549	102·8	22·8
	2·6889	2·9120	1·14056	1·4947	0·44396	101·3	22·7
	3·5443	2·9624	1·14209	1·4934	0·45164	100·4	22·5
	5·6388	3·0832	1·14581	1·4904	0·46958	98·2	22·5
9·166	0·0000	2·9202	1·13242	1·4991$_5$	0·44195	—	—
	0·5689	2·9557	1·13354	1·4983	0·44734	103·0	22·6
	1·3042	3·0023	1·13497	1·4972	0·45431	103·0	22·6
	1·6229	3·0231	1·13557	1·4967	0·45736	103·2	22·5
	2·6476	3·0892	1·13748	—	0·46696	102·8	—
	3·8051	3·1616	1·13957	1·4936	0·47723	101·5	22·6
	4·9980	3·2391	1·14165	1·4918	0·48792	100·9	22·5

Diphenylmethanol in pyridine–benzene.

$100w_B$	$100w_A$	ε	v	n_D	p	P_A	R_A
1·477	0·0000	2·3724	1·14260	1·4980$_5$	0·35864	—	—
	0·5942	2·3910	1·14110	1·4986	0·36148	154·1	57·7
	1·4323	2·4170	1·13901	1·4993$_5$	0·36541	153·1	57·7
	2·4494	2·4475	1·13651	1·5002$_5$	0·36989	150·7	57·7
	3·5960	2·4808	1·13369	1·5012	0·37466	148·2	57·5
	4·4428	2·5049	1·13163	1·5020	0·37803	146·5	57·7
	5·6949	2·5400	1·12853	1·5030	0·38281	144·3	57·3
1·907	0·0000	2·4018	1·14205	1·4983	0·36370	—	—
	0·5143	2·4193	1·14077	1·4987	0·36637	162·8	56·4
	1·5728	2·4548	1·13816	1·4996$_5$	0·37169	160·6	57·3
	2·2371	2·4762	1·13645	1·5003	0·37479	158·4	57·5
	3·0757	2·5029	1·13439	1·5010	0·37861	156·4	57·5
	4·5423	2·5483	1·13076	1·5021	0·38492	153·1	56·9
	5·9192	2·5892	1·12735	1·5033$_5$	0·39039	150·1	57·1
2·763	0·0000	2·4600	1·14089	1·4983	0·37347	—	—
	0·2931	2·4712	1·14012	1·4985$_5$	0·37515	174·1	56·7
	0·5458	2·4809	1·13949	1·4987$_5$	0·37659	174·1	56·7
	2·0408	2·5366	1·13581	1·5000$_5$	0·38471	170·3	57·3
	3·6932	2·5952	1·13172	1·5015	0·39287	165·6	57·3
	4·5092	2·6235	1·12969	1·5022$_5$	0·39668	163·6	57·5
4·266	0·0000	2·5649	1·13884	1·4985	0·39041	—	—
	0·2728	2·5769	1·13815	1·4987$_5$	0·39213	188·2	58·2
	0·6439	2·5929	1·13723	1·4991	0·39441	186·6	57·8
	0·8541	2·6018	1·13672	1·4993	0·39567	185·5	57·8
	1·8917	2·6457	1·13418	1·5001	0·40177	182·6	57·1
	3·1605	2·6978	1·13103	1·5013	0·40875	178·9	57·3
	4·6501	2·7568	1·12745	1·5026	0·41639	174·9	57·5

In none of the mixtures studied was ε a linear function of w_A (or w_B) and hence, to minimise errors in the relative values of $(P_{A_\infty})_{BS}$ or $(P_{B_\infty})_{AS}$ derived, the methods used in the extrapolation to zero concentration included, not only the determination of the limiting value of $(\Delta\varepsilon/w_A)_{BS}$ and $(\Delta v/w_A)_{BS}$, but also the limiting values of $(\Delta\varepsilon/w_A)_{BS} - (\Delta\varepsilon/w_A)_B$, $(P_A)_{BS} - (P_A)_S$, $(P_A)_{BS'} - (P_A)_{BS}$ for successive solvent mixtures and $(P_A)_{BS'}/(P_A)_{BS}$ for successive solvent mixtures. A series of extrapolated values of $(P_{A_\infty})_{BS}$ were thereby obtained, the spread indicating the probable error in the final average value taken. For the derived data only the functions involving the molecular polarisation values were used.

Battersea Polytechnic, London, S.W.11.
Bedford College, London, N.W.1.

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