Determination of the Complexes between Dimethylphenols and Pyridine by a Dielectric Constant Method in Non-polar Solvents

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The apparent equilibrium constants for the association of pyridine with dimethylphenols in benzene and in cyclohexane at 25 °C have been measured by the method of dielectric constant variation, in order to check and extend the results obtained by spectroscopic methods. Solvent effects were detected. Excess of dipole moments have been derived and related with pK_a values from the literature. The influence of the relative positions of the methyl substituents on complex formation are discussed qualitatively.

To determine the equilibrium constant for complex formation in solution ($m\text{A} + n\text{B} \rightleftharpoons \text{A}_m\text{B}_n$) it is necessary to ascertain the ratio m/n (usually by some form of Job's method[1]) and then to measure the actual concentration of one species, *viz.* A, B, or A_mB_n, the initial concentrations of two of these being known.

The available methods for measuring concentrations are all of limited usefulness; however, electric dipole moment measurements can, in principle, be applied to study chemical interactions between molecules. From the change in moment when a multimolecular complex is formed, information about the nature and the extent of perturbation can be derived. Except for stable co-ordination complexes, this method has not been applied extensively, because, for less stable complexes, it is necessary to know the association constant before the electrical polarisation measurements can be fully interpreted.

For the particular case of complex formation through hydrogen bonding,[2] the most commonly used methods are i.r. and u.v. spectroscopy.

It is not generally practicable to derive both the association constant and the dipole moment of the complex from polarisation data alone,[3,4] though this may be done in special cases.[5] However, Jungers *et al.*[6] have developed a method based on the variation of dielectric constant of the system with its composition. The method is not as quick and possibly not as accurate as the spectroscopic method, but it can be applied to solutions in any non-polar solvent. In addition, and because the apparent dipole moment of the complex can be obtained, this method may give some information about the stoicheiometry of the complex and the electronic perturbations therein.[7]

In this work, the method has been applied to study the equilibrium between pyridine and the isomeric dimethylphenols in benzene and in cyclohexane solutions, at 25 °C, in order to assess the influence of the positions of the methyl substituents on complex formation.

The observed enhancement of dipole moment, $\Delta\mu$, of H-bonded complexes may be explained on the basis of proton-transfer and charge-transfer effects.[8,9] The state of prototropic equilibrium depends on the concentration ranges of the acid and base involved, the extent of self-association of either or both moieties, and the extent of formation of homoconjugate and heteroconjugate ions.[10]

In the present study the influence of both inductive and mesomeric effects on the strength and polarity of H-bonds has been analysed.

Experimental

The details of the purification of the dimethylphenols and the solvents benzene and cyclohexane, and of the apparatus used, have been reported previously.[11]

Pyridine (analytical reagent grade) was supplied by Merck, and further purified by the method of Leis and Currans[12] and by passage over molecular sieves (4Å).

Method

Jungers *et al.*,[6] extending Job's method, showed that if two solutes A and B form an unstable compound AB, but do not associate with the solvent S ($m\text{A} + n\text{B} \rightleftharpoons \text{A}_m\text{B}_n$), it is possible to determine simultaneously the dipole moment μ_{AB} and stability constant K_{AB} of the complex A_mB_n from dielectric polarisation measurements alone.

The fundamental assumptions are (i) that only one complex, with defined stoicheiometry, can be formed from specific interactions between A and B, (ii) that the activity coefficients of the molecular species taking part in the reaction are unity, and (iii) that the complex is of the simple 1:1 type.

Assumption (i) implies that the excess function property of the system will reach the highest value at the maximum concentration of the complex AB; therefore, the values of the corresponding property of solutes A and B, do not affect the value of the excess function property of the system. The condition (ii) requires that the forces of interaction between A and B which lead to complex formation are of very short range. The assumption (iii) implies that these forces are specific and capable of saturation.

A type of system which conforms to most of these requirements is that in which A is a substance bearing a moderately acidic hydrogen atom *e.g.*, a dimethylphenol, B is pyridine, and S is a non-polar solvent such as benzene or cyclohexane.

Investigation of hydrogen bonding in such systems is interesting for its own sake. Accordingly, we have examined the series of systems in which A is a dimethylphenol (2,3-, 2,4-, 2,5-, 2,6-, 3,4-, or 3,5-isomer).

Consider the case of two binary solutions, I and II, where C_A° and C_B° are the total concentrations (in mol l^{-1}) of solutes A and B, respectively, in the solvent S. If v_I and v_{II} are the volumes (in litres) of solutions I and II, respectively, ternary systems can be obtained from I and II, and the composition of the ternary solution can be related to those of the binary ones through the volume fractions Y_I and Y_{II}.

The balance equations for solutes and solvent in ternary systems are (1)—(3), where X_A, X_B, and X_{AB} are the molar

$$C_A^\circ(1 - Y_{II}) = X_A + X_{AB} \tag{1}$$

$$C_B^\circ Y_{II} = X_B + X_{AB} \tag{2}$$

$$C_S^\circ V_S^\circ = 1 - C_A^\circ(1 - Y_{II})V_A^\circ - C_B^\circ Y_{II} V_B^\circ \tag{3}$$

concentrations of free A and B, and bound A (or B) respectively: C_S° is the total concentration of solvent (in mol l^{-1}); and V_A°, V_B°, and V_S° are, respectively, the molar volumes of solutes A and B and solvent S (in l mol^{-1}).

From the balance equations for solutes in the ternary system and the equilibrium constant K_{AB}, equation (4) can be obtained.

$$C_A^\circ(1 - Y_{II}) = X_A + K_{AB}X_A C_B^\circ Y_{II}/(1 + K_{AB}X_A) \quad (4)$$

On the other hand, on the basis of Onsager–Kirkwood theories,[13,14] the apparent dipole moment of the complex, μ_{AB}, may be given by equation (5), where k is the Boltzman constant,

$$<\mu_{AB}> = |27kT\,V_{AB}^\circ/4\pi N_o(2\varepsilon_S + 1)^2|\cdot|(2\varepsilon_S + n_{AB}{}^2)/(n_{AB}{}^2 + 2)|^2\cdot[|(2\varepsilon_S{}^2 + 1)/3\varepsilon_S{}^2|\cdot(\mathrm{d}\varepsilon/\mathrm{d}Y_{AB})_0 - (2\varepsilon_S + 1)^2(n_{AB}{}^2 - \varepsilon_S)/3\varepsilon_S(2\varepsilon_S + n_{AB}{}^2)] \quad (5)$$

N_o is the Avogadro number, T is the absolute temperature (in K); V_{AB}° is the apparent molecular volume of the complex (assumed $= V_A^\circ + V_B^\circ$, where V_A° and V_B° are the apparent molar volumes of A and B, respectively, determined from the corresponding binary systems[11]). The parameter ε_S is the dielectric permittivity of the solvent; n_{AB} is the refractive index at the i.r. frequency, related to the corresponding refractive index at the sodium D-line frequency by Cauchy's relationship (6).[15]

$$|(n^2 - 1)/(n^2 + 2)|_{\text{i.r.}} = |(n^2 - 1)/(n^2 + 2)|_D/1.007 \quad (6)$$

The value of n_{AB} at the sodium D-line frequency can be derived from the values of the apparent molar refraction of A and B, assuming the additivity law (7) to be fulfilled, and the apparent

$$R_{AB} = R_A + R_B \quad (7)$$

molar refractions of the solutes are derived from those of the corresponding binary systems.[11] The value of the parameter $(\mathrm{d}\varepsilon/\mathrm{d}Y_{AB})_0$ can be obtained from the apparent dielectric permittivity of the complex, ε_{AB}, and the dielectric constant of solvent ε_S by using the relation (8).

$$(\mathrm{d}\varepsilon/\mathrm{d}Y_{AB})_0 = \varepsilon_{AB} - \varepsilon_S \quad (8)$$

To determine the value of the parameter ε_{AB}, we may use the value of the parameter δ_{AB} obtained from the experimental relation between the excess function property $\Delta\varepsilon$ and the ternary system composition, or from the values of dielectric permittivities of solutes in the binary system.[11] The value of ε_{AB} is given by equation (9).

$$\varepsilon_{AB} = (\delta_{AB} + \varepsilon_A V_A^\circ + \varepsilon_B V_B^\circ)/V_{AB}^\circ \quad (9)$$

If ε_{exp} and ε_{th} are the formal and additive permittivities respectively of the ternary solution given by equations (10) and (11), it can be shown that, if the excess function property,

$$\varepsilon_{exp} = \varepsilon_S C_S^\circ V_S^\circ + \varepsilon_A X_A V_A^\circ + \varepsilon_B X_B V_B^\circ + \varepsilon_{AB} X_{AB} V_{AB}^\circ \quad (10)$$

$$\varepsilon_{th} = \varepsilon_S C_S^\circ V_S^\circ + \varepsilon_A C_A^\circ(1 - Y_{II})V_A^\circ + \varepsilon_B C_B^\circ Y_{II} V_B^\circ \quad (11)$$

denoted $\Delta\varepsilon$, is the difference between formal and additive permittivities of this solution, the value of δ_{AB} will be given by equation (12), where the value of X_{AB} is given by equation (13).

$$\delta_{AB} = \Delta\varepsilon/X_{AB} \quad (12)$$

$$X_{AB} = K_{AB}X_A C_B^\circ Y_{II}/(1 + K_{AB}X_A) \quad (13)$$

The value of the parameter δ_{AB} will be a characteristic of the complex formation, and will be constant for a system formed by solutes A and B in a particular solvent S, if the temperature remains unchanged.

Apparently there are two indeterminates, *viz.* K_{AB} and δ_{AB}, and these can be elucidated by an iterative process which calculates the values of the constants from a series of experimental measurements of dielectric permittivity of the ternary solutions. The process described above can be summarised as follows. From equations (4) and (13), the values of X_{AB} at each ith value of the volume fraction Y_{II_i} may be obtained for an appropriate range of K_{AB} values, for the first series of ternary solutions denoted by the curve $j = 1$. By using equation (12), the first approximate value of the parameter δ_{AB} at the highest value of $\Delta\varepsilon$ can be determined for a particular value of K_{AB}. Then, with the values of K_{AB} and δ_{AB} determined and by using equations (4), (12), and (13), a value of the excess function property, denoted as $\Delta\varepsilon_i^{\text{calc}}$, may be calculated for each Y_{II_i} value, at the jth series of ternary solutions. The optimal values for the parameters K_{AB} and δ_{AB} will be obtained when the new parameter $\bar{\pi}$ defined as in equation (14) attains its minimum

$$\bar{\pi} = \sum_{j=1}^{l}\sum_{i=1}^{n}|\Delta\varepsilon_i^{\text{calc}} - \Delta\varepsilon_i|/l \quad (14)$$

value at the 0.95 significance level.

For the calculation of $\Delta\mu$ equation (15)[16] was used; the values

$$\Delta\vec{\mu} = |\vec{\mu}_{AB} - \Sigma\vec{\mu}_{\text{components}}| \quad (15)$$

of $\Sigma\vec{\mu}_{\text{components}}$ were obtained from the corresponding vectorial combination of dipole moments, making certain tacit assumptions: that the nitrogen lone pair orbital is directed along the hydrogen bond, *i.e.* the C_{2v} axis of the pyridine coincides with the O–H ··· N axis, that the COH angle for dimethylphenols is 115°, and that there is free rotation around the O–H ··· N axis in the complexes studied. If the dipole moments μ_A and μ_B are considered to form angles α and β with respect to the O–H ··· N axis, respectively, $\Delta\mu$ can be given as equation (16), where the values of μ_A and μ_B are taken as the

$$\Delta\mu = \pm(\mu_{AB}^2 - \mu_A^2\sin^2\alpha - \mu_B^2\sin^2\beta - 2\mu_A\mu_B\sin\alpha\,\sin\beta)^{1/2} - \mu_A\cos\alpha - \mu_B\cos\beta \quad (16)$$

corresponding values of dipole moments of solutes A and B, respectively, determined for binary solutions in the corresponding solvent, using an equation similar to expression (5).[11] If the value of the angle β is taken as zero in all cases, equation (16) can be simplified to (17). The angle α has been taken as 22°

$$\Delta\mu = \pm(\mu_{AB}^2 - \mu_A^2\sin^2\alpha)^{1/2} - \mu_A\cos\alpha - \mu_B \quad (17)$$

for all cases, as stated for phenol;[16,17] a variation of 5° would not change the main qualitative conclusions.

Results and Discussion

Up to three different series of experiments, denoted $j = 1$, 2, or 3, depending on the relative solubility of the dimethylphenols in the solvent at 25 °C were performed. For the curves denoted by $j = 1$, $j = 2$, and $j = 3$, the values of C_A° and C_B° are related as follows: $C_A^\circ = C_B^\circ$, $C_A^\circ < C_B^\circ$, and $C_A^\circ > C_B^\circ$, respectively. For each titration curve, the sum of molar concentrations of the two solutes A and B was kept constant.

Figure 1 shows the change in the excess function property $\Delta\varepsilon$ at various volume fractions referred to pyridine (Y_{II}) for all the complexes formed between pyridine and each dimethylphenol isomer in benzene as solvent at 25 °C; similar representations at

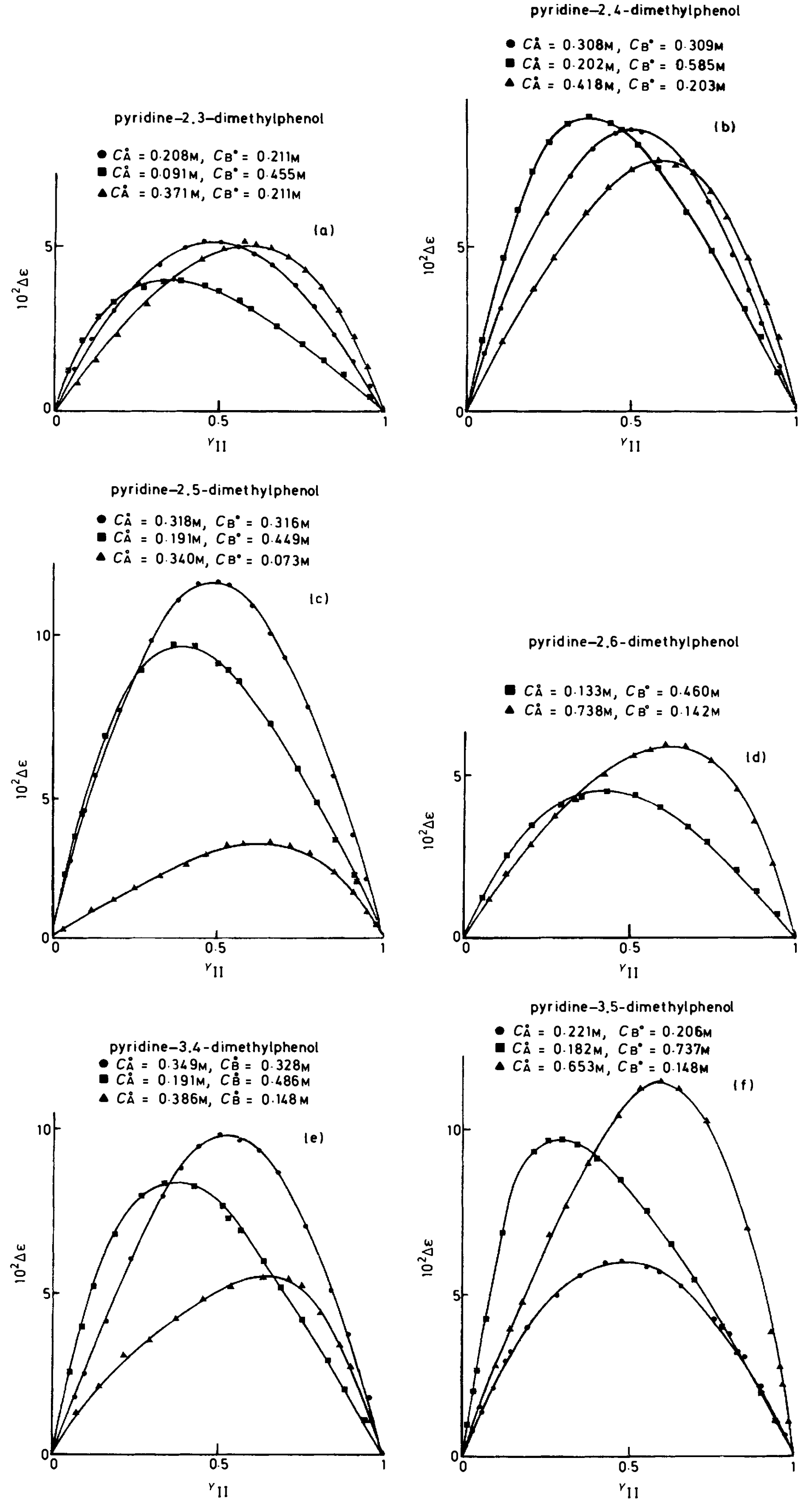

Figure 1. Excess function ($\Delta\varepsilon$) dependence on volume fraction (Y_{II}) for pyridine–dimethylphenol complexes in benzene at 25 °C, at different initial compositions

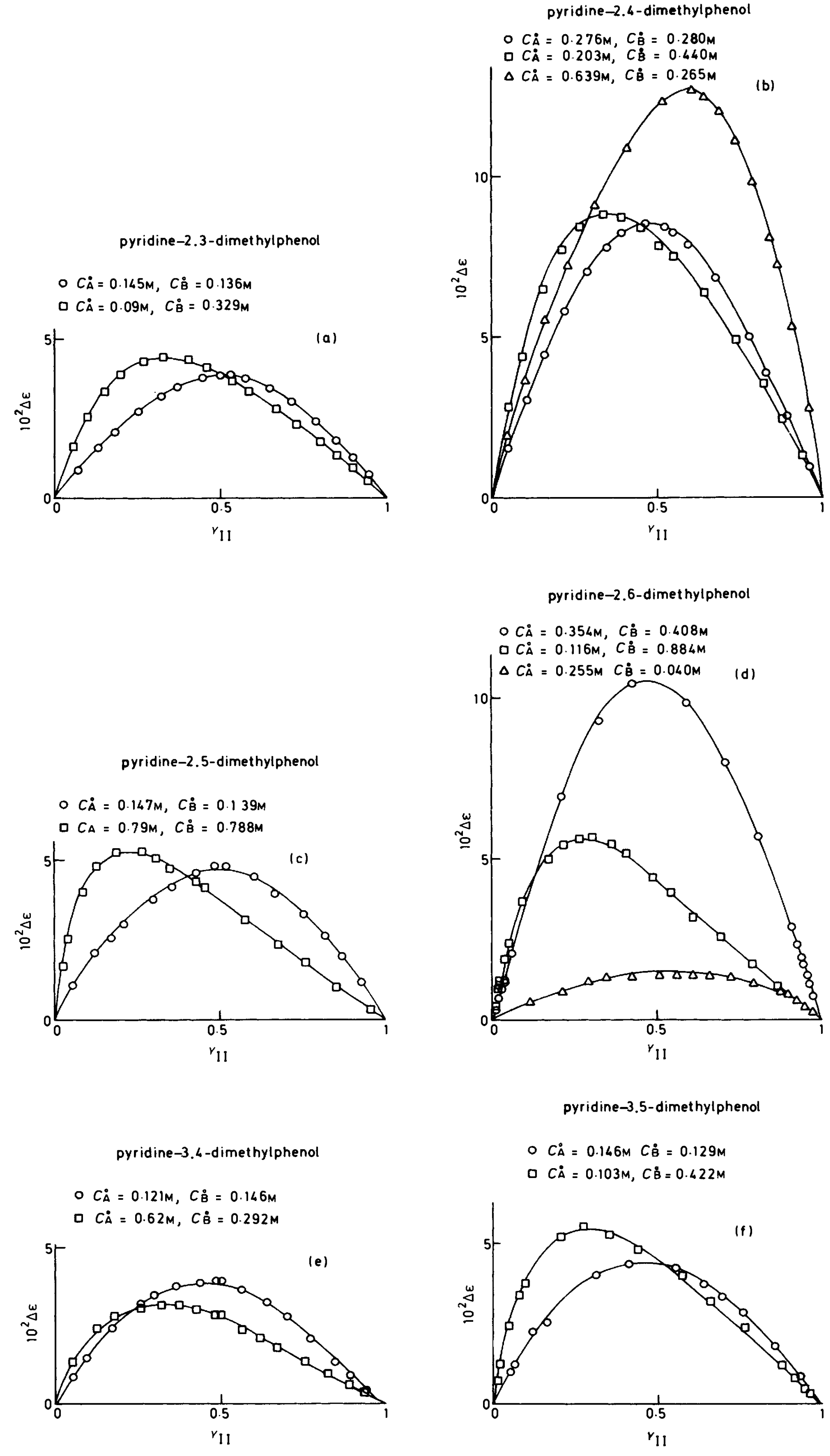

Figure 2. Excess function ($\Delta\varepsilon$) dependence on volume fraction (Y_{II}) for pyridine–dimethylphenol complexes in cyclohexane at 25 °C, at different initial compositions

Table 1. Apparent equilibrium constant (K_{AB}/l mol^{-1}) and parameters δ_{AB} and $\bar{\pi}$, for pyridine–dimethylphenol complexes in benzene (B) and cyclohexane (C) solutions at 25 °C

Isomer	Solvent	K_{AB}	δ_{AB}	$10^6\ \bar{\pi}$
2,3-	B	17.0 ± 0.8	1.026	3.1
	C	44.0 ± 2	0.940	0.8
2,4-	B	11.8 ± 0.4	1.150	2.5
	C	14.7 ± 1.0	1.219	2.6
2,5-	B	11.0 ± 0.6	1.452	1.4
	C	102 ± 12	0.967	8.7
2,6-	B	5.2 ± 0.2	1.284	3.0
	C	24.1 ± 2.0	0.892	8.5
3,4-	B	20.7 ± 1.0	0.989	8.8
	C	65.0 ± 6.0	0.965	3.7
3,5-	B	15.0 ± 1.0	1.215	9.3
	C	218 ± 20	0.866	7.5

the same temperature in cyclohexane solutions are shown in Figure 2.

For all the curves $j = 1$, the maximum value of $\Delta\varepsilon$ is reached at $Y_{II} = 0.5$, in good agreement with assumption (iii) previously mentioned.

The optimal values for the apparent equilibrium constant K_{AB} and the parameter δ_{AB}, along with the corresponding value of $\bar{\pi}$ at the minimum, are listed in Table 1 for the complexes in benzene and cyclohexane at 25 °C. The values of K_{AB} are greater in cyclohexane than in benzene, which may be attributable to differences in preferential sorption.

The relative methyl substituent positions influence the apparent equilibrium constant, as can be seen from the first column in the Table. This effect is probably due to steric hindrance, since in cyclohexane solution 3,5-dimethylphenol, with three substituents furthest apart, has the highest value of K_{AB}. For the other isomers, having either two methyl groups in adjacent positions (2,3- and 3,4-dimethylphenols) or *ortho*-methyl groups with respect to the hydroxy group (2,3-, 2,4-, 2,5-, and 2,6-dimethylphenols), the respective K_{AB} values are in the order: 2,5- > 3,4- > 2,3- > 2,6- > 2,4-dimethylphenol. From this point of view three comparisons are of interest. In the first (3,5- and 2,5-dimethylphenols) moving a methyl group from *meta*- to *ortho*-position with respect to the hydroxy group lowers K_{AB} by about 100 units. In the second (3,4- and 2,3-dimethylphenols), with two methyl groups on adjacent positions in each case, K_{AB} for 3,4-dimethylphenol is about 20 units greater than the corresponding value for 2,3-dimethylphenol. In the third pair (2,6- and 2,4-dimethylphenol) removal of a methyl from *ortho*- to *para*-position with respect to the hydroxy group lowers the K_{AB} value by about 10 units.

In benzene solution, the influence of relative methyl substituent positions on the value of K_{AB} is not as clear as in cyclohexane solution, because the range of the apparent equilibrium constants is much less, probably owing to specific interactions between the solvent and the complexes.

The values of δ_{AB} listed in the fourth column in Table 1 are greater in benzene than in cyclohexane solutions (except for the complex of 2,4-dimethylphenol, for which they are of the same order). Thus, the values of the apparent dipole moments will be higher in benzene than in cyclohexane solution.

The values of the parameter $\bar{\pi}$ (Table 1) are connected to the statistical parameters, and the values of K_{AB} obtained lie within the experimental error.

The values of R_{AB}, $V_{AB}{}^{\circ}$, ε_{AB}, and μ_{AB} for the complexes in benzene and cyclohexane solutions at 25 °C, derived from appropriate equations or the corresponding values for solutes A and B in binary solutions,[11] are listed in Table 2, along with the corresponding values for pyridine remeasured by us in both solvents at the same temperature. As expected, the values of μ_{AB} are greater in benzene than in cyclohexane solution, except for 2,4-dimethylphenol–pyridine and 3,4-dimethylphenol–pyridine, where they are of the same order. This fact can be attributed to the greater polarisability of benzene, which stabilises molecular associations of greater polarity; nevertheless a considerable increase in the apparent dipole moment in this type of complexes leads to a significant increase in basicity of the hydroxy group oxygen atom, enhancing solvent effect

Table 2. Polarisation data for dimethylphenol complexes, and pyridine alone, in benzene (B) and cyclohexane (C) solutions at 25 °C

Isomer	Solvent	$R_{AB}{}^{a}$	$V_{AB}{}^{\circ b}$	ε_{AB}	$\mu_{AB}{}^{c}$
2,3-	B	62.4 ± 0.2	198.8 ± 0.2	11.5 ± 0.1	3.94 ± 0.05
	C	62.4 ± 0.2	207.8 ± 0.4	10.4 ± 0.3	3.94 ± 0.05
2,4-	B	61.3 ± 0.2	201.2 ± 0.3	12.3 ± 0.1	4.14 ± 0.05
	C	62.0 ± 0.2	208.6 ± 0.5	11.7 ± 0.3	4.28 ± 0.05
2,5-	B	61.3 ± 0.2	201.8 ± 0.3	13.7 ± 0.1	4.42 ± 0.05
	C	63.4 ± 0.2	200.8 ± 0.5	10.4 ± 0.3	3.99 ± 0.05
2,6-	B	62.4 ± 0.2	201.3 ± 0.4	12.9 ± 0.1	4.27 ± 0.05
	C	61.7 ± 0.2	209.8 ± 0.5	10.0 ± 0.3	3.91 ± 0.05
3,4-	B	61.3 ± 0.2	199.5 ± 0.3	11.5 ± 0.1	3.99 ± 0.05
	C	63.4 ± 0.2	209.4 ± 0.5	10.7 ± 0.3	4.05 ± 0.05
3,5-	B	62.6 ± 0.2	202.2 ± 0.4	12.7 ± 0.1	4.23 ± 0.05
	C	63.6 ± 0.2	210.2 ± 0.5	10.1 ± 0.3	3.91 ± 0.05
Pyridine	B	24.3 ± 0.1	79.9 ± 0.1	7.38 ± 0.05	2.24 ± 0.02
	C	24.7 ± 0.3	84.5 ± 0.2	6.59 ± 0.05	2.22 ± 0.05

[a] In cm^3. [b] In cm^3 mol^{-1}. [c] In debye.

Table 3. Values of $\Delta\mu$/D for dimethylphenol complexes in benzene and cyclohexane solutions; pK_a values from ref. 18.

Isomer	$\Delta\mu$ (benzene)	$\Delta\mu$ (cyclohexane)	pK_a
2,6-	0.586	0.353	10.63
2,4-	0.438	0.722	10.60
2,3-	0.408	0.457	10.54
2,5-	0.773	0.437	10.41
3,4-	0.213	0.312	10.36
3,5-	0.456	0.258	10.19

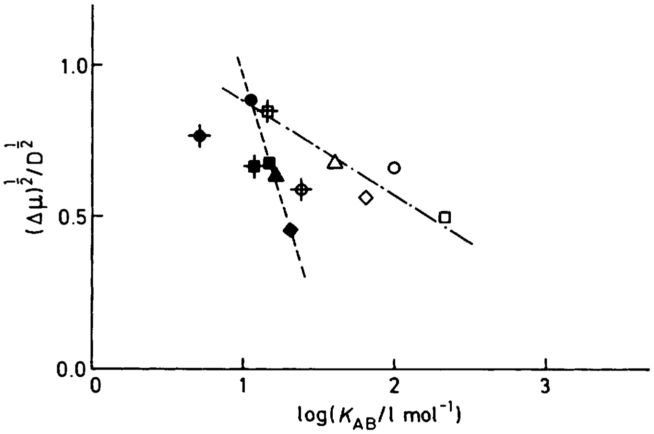

Figure 3. The relation between $(\Delta\mu)^{1/2}$ and log K_{AB} for pyridine–dimethylphenol complexes in benzene and cyclohexane solutions at 25 °C. 2,3-dimethylphenol in benzene (B) (▲) and cyclohexane (C) (△); 2,4-dimethylphenol in (B) (✚) and (C) (⊕); 2,5-dimethylphenol in (B) (●) and (C) (○); 2,6-dimethylphenol in (B) (◆) and (C) (⊕); 3,4-dimethylphenol in (B) (◆) and (C) (◇); and 3,5-dimethylphenol in (B) (■) and (C) (□)

interactions and additional disturbances of charge distribution in the complexes.

The values of $\Delta\mu$ obtained and the pK_a values from reference[18] are listed in Table 3. Since $\Delta\mu$ is less than 1.00 D in the complexes studied, the interacting components must form H-bonds of the type O–H $\cdots$ N; the possibility of formation of proton-transfer complexes is negligibly small; moreover the decrease in $\Delta\mu$ (in cyclohexane) with increasing acid strength of the dimethylphenol (fall in pK_a) can only be interpreted on the basis of H-bond formation, which becomes more and more predominant as the pK_a decreases, and the apparent association constant increases.

Figure 3 shows the decrease in $\Delta\mu^{1/2}$ with increasing log K_{AB} in benzene and cyclohexane solutions. The abnormal variation of 2,6-dimethylphenol–pyridine in both solvents is attributed to loss of planarity due to the presence of the two *ortho*-methyl groups.

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