

The Influence of the Solvent on Organic Reactivity. Part 4.¹ Spectroscopic Parameters of Lewis Basicity and Acidity of Hydroxylic Solvents. A Comprehensive Correlation Analysis of the $\log k$ Values for the Reactions of Diazodiphenylmethane with Benzoic Acid in Aprotic and Hydroxylic Solvents at 37 °C

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Solvent Lewis basicity parameters B , and solvent Lewis acidity parameters E , are presented for 23 alcohols, including 2-methoxyethanol. The Lewis basicity parameters were derived from the effect of the hydroxylic compound on ν_{OH} for phenol in dilute solution in carbon tetrachloride, and the Lewis acidity parameters were derived from the Dimroth-Reichardt E_{T} values. Rate coefficients at 37.0 °C for the reactions of diazodiphenylmethane with benzoic acid in the same solvents are also presented. All these results, combined with the corresponding results for 44 aprotic solvents obtained previously, permit a successful comprehensive correlation analysis of the solvent effect for the above reaction in both aprotic and hydroxylic solvents, along the lines used previously with the aprotic solvents alone (Koppel-Palm analysis). The most satisfactory procedure, however, involves the separate consideration of the Lewis acidity parameters of the two classes of solvent, so that terms in E_{OH} and E_{AP} may acquire characteristic coefficients in the multiple regression. The direct use of E_{T} , rather than the separate use of E and dielectric $[(\epsilon - 1)/(2\epsilon + 1)]$ parameters, is also examined.

PART 3¹ dealt with the correlation analysis, by multiple regression on solvent parameters, of $\log k_0$ values at 37 °C for the reactions of diazodiphenylmethane with benzoic acid in 43 aprotic solvents. (k_0 is the limiting second-order rate coefficient at [acid] = 0.) The most important analysis was of the type advocated by Koppel and Palm,² the solvent parameters being the Lewis basicity (or nucleophilicity) parameter B , the Lewis acidity (or electrophilicity) parameter E , the dielectric function $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$, and the refractive index function (Na light) $f(n^2) = (n^2 - 1)/(2n^2 + 1)$. Other papers^{3,4} have dealt with multiple regression analysis of $\log k$ values at 30 °C for the corresponding reactions in up to 22 alcohols. For these systems the solvent parameters were the above dielectric function, Taft's⁵ polar

substituent constant σ^* for the alkyl group of the alcohol, and $n_{\gamma\text{H}}$, the number of γ -hydrogen atoms in the alcohol molecule.

To permit a comprehensive correlation analysis for the reactions in both aprotic and hydroxylic solvents, we have, first, measured the rate coefficients at 37.0 °C for the reactions in 23 alcohols, including 2-methoxyethanol (Table). Secondly, we have determined values of the solvent basicity parameters B for the hydroxylic solvents, by a procedure based on certain findings of Koppel and Paju⁶ (Table). In order to make available a complete set of solvent Lewis acidity parameters E it has also been necessary to determine the Dimroth-Reichardt⁷ E_{T} value for some of the hydroxylic solvents (Table) and one of the aprotic solvents (see below).

Rate coefficients ($l \text{ mol}^{-1} \text{ min}^{-1}$) for the reaction between benzoic acid and diazodiphenylmethane in various alcohols at 37.0 °C, and solvent parameters for the same alcohols

| Solvent | k | B'^a | B'^b | B^c | E_{T}^d | E_{T}^e | E^c |
|---------------------|-------|---------|--------|-------|------------------|------------------|-------|
| Methanol | 4.15 | 219 ± 3 | 218 | 114 | | 55.5 | 14.9 |
| Ethanol | 1.80 | 229 ± 3 | 235 | 117 | | 51.9 | 11.6 |
| Propan-1-ol | 1.97 | 232 ± 2 | | 119 | | 50.7 | 10.6 |
| Propan-2-ol | 1.17 | 240 ± 3 | 236 | 122 | | 48.6 | 8.7 |
| Butan-1-ol | 1.70 | 234 ± 3 | 231 | 119 | | 50.2 | 10.3 |
| Butan-2-ol | 1.19 | 242 ± 3 | 240 | 122 | | 47.1 | 7.4 |
| 2-Methylpropan-1-ol | 2.65 | 233 ± 3 | 230 | 119 | 48.6 | 48.8 | 7.4 |
| 2-Methylpropan-2-ol | 0.404 | 249 ± 3 | 247 | 125 | | 43.9 | 5.2 |
| Pentan-1-ol | 1.52 | 235 ± 3 | | 120 | 49.2 | 49.1 | 9.7 |
| Pentan-3-ol | 0.963 | 245 ± 3 | | 124 | | 45.7 | 6.2 |
| 2-Methylbutan-2-ol | 0.244 | 253 ± 3 | 261 | 127 | 40.7 | 41.7 | 5.1 |
| Hexan-1-ol | 1.31 | 235 ± 2 | | 120 | 49.0 | 48.8 | 9.6 |
| Heptan-1-ol | 1.17 | 235 ± 2 | | 120 | 48.5 | | 9.6 |
| Octan-1-ol | 1.03 | 237 ± 2 | | 121 | 48.7 | 48.3 | 10.1 |
| Decan-1-ol | 0.932 | 236 ± 2 | | 120 | 47.7 | | 10.1 |
| Dodecan-1-ol | 0.891 | 237 ± 2 | | 121 | 46.7 | | 9.6 |
| Cyclopentanol | 1.33 | 243 ± 2 | | 123 | 47.0 | 47.7 | 7.7 |
| Cyclohexanol | 1.29 | 247 ± 2 | 242 | 124 | 47.4 | 46.9 | 7.4 |
| Benzyl alcohol | 16.3 | 214 ± 3 | 208 | 112 | 50.4 | 50.8 | 10.5 |
| 1-Phenylethanol | 6.85 | 223 ± 3 | | 115 | 46.7 | | 8.0 |
| 2-Phenylethanol | 4.99 | 228 ± 3 | | 117 | 49.5 | | 9.7 |
| 3-Phenylpropan-1-ol | 4.54 | 228 ± 3 | | 117 | 48.5 | | 8.9 |
| 2-Methoxyethanol | 1.08 | 232 ± 3 | 238 | 119 | | 52.3 | 12.5 |

^a This work. $B' = \nu_{\text{OH}}(\text{phenol}) - \nu_{\text{OH}}(\text{phenol-base complex})$; $\nu_{\text{OH}}(\text{phenol})$ 3 611 cm^{-1} . ^b Ref. 6. ^c Calculated as described in text. ^d This work, in kcal mol^{-1} ; 1 cal = 4.184 J. ^e Ref. 7

DISCUSSION

The Basicity Parameter B for Hydroxylic Solvents.—For aprotic solvents B is based on the wavenumber shift $\Delta\nu_{OD}$ on transfer of CH_3OD from the gas phase to solution in a given solvent.^{2,8,9} A B value for an alcohol cannot be measured directly in this way because the deuteron of CH_3OD rapidly exchanges with the hydroxylic proton of the alcohol ROH , and $\Delta\nu_{OD}$ no longer has a clear-cut significance. ν_{OH} For phenol in dilute solution in carbon tetrachloride is, however, changed by the addition of aprotic or hydroxylic solvents in low concentration and $\Delta\nu_{OH}$ may be regarded as a measure of the Lewis basicity of the additive. We may conveniently designate this quantity B' , and for a set of 54 aprotic solvents Koppel and Paju⁶ have shown that the B and B' values conform to equation (1) with a correlation coefficient r 0.987. If

$$B = 0.382B' + 30 \quad (1)$$

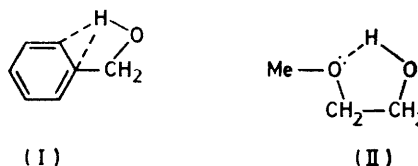
we assume that this equation should apply also to the hydroxylic solvents, the experimentally inaccessible B values for these may be calculated from the observed values of B' .*

We have determined B' values for 23 alcohols, including 2-methoxyethanol (Table). B' values for eleven of the alcohols, including 2-methoxyethanol, were included in Koppel and Paju's compilation⁶ and these are also in the Table, along with values of B calculated as above from our own results. The agreement between our values and Koppel and Paju's⁶ is in several cases not very good. The earlier values involve considering results obtained in various laboratories with different instruments. All our values have been obtained by a standard procedure using a single high precision instrument, and moreover most of the trends with change in structure are consistent with the generally accepted electronic effects of the substituents in the alcohols.⁵

Thus B' rises with the carbon chain-length in the n -alkanols, from 219 for methanol to a limiting value of ca. 236 for chains of more than about six carbon atoms. Also, branching at the α -carbon atom increases B' by ca. 10 wavenumbers for each additional methyl group. These and other details for the alkanols in the Table are in agreement with the electron-releasing properties of alkyl groups as they are usually manifested for processes in solution.⁵ Further, B' for benzyl alcohol would be expected to be lower than the value for methanol, in view of the electron-attracting properties of the benzyl group. However, the effect on B' of introducing a phenyl group is in no case as large as might have been expected from the σ^* values of alkyl and aralkyl groups.⁵ The minute effect of introducing the electron-attracting

* It would, of course, be possible to use values of B' directly for the correlation analysis of solvent effects on reactivity.⁶ Unfortunately the ν_{OH} band for the phenol-base- CCl_4 system is sometimes rather broad and complex in the case of aprotic solvent additives, and precise values of B' are difficult to assign in such cases. The wide bands are probably due to there being more than one basic centre in the molecule. At present we prefer to avoid giving too much weight to individual values of B' for aprotic solvents and to smooth out their idiosyncracies by the application of equation (1).

2-OMe into ethanol is also rather surprising. It seems possible that the unexpectedly high Lewis basicities both of the phenyl-substituted alcohols and of 2-methoxyethanol are connected with internal hydrogen-bonding favouring conformations in which π - or p -electrons respectively are rather close to the hydroxylic oxygen atom,^{10,11} e.g. (I) and (II).



The Lewis Acidity Parameter E for Hydroxylic Solvents.—Koppel and Palm's² solvent parameter E may be calculated from the corresponding Dimroth-Reichardt E_T value⁷ through equation (2)¹² where $Y = (\epsilon - 1)/(\epsilon + 2)$ and $P = (n^2 - 1)/(n^2 + 2)$. We have therefore determined E_T values for those of our alcohols which

$$E = E_T - 25.10 - 14.84Y - 9.59P \quad (2)$$

had not been studied by Reichardt and his colleagues. To provide a desirable calibration of our work against Reichardt's, we also included several alcohols for which E_T values were already known. The Table contains the E_T values (Reichardt's and/or ours) for the 23 alcohols involved in the present work (including 2-methoxyethanol). The discrepancies between our values and Reichardt's vary between 0.2 and 1.0 kcal mol⁻¹, and the agreement may be considered satisfactory.

The structural influences on E_T previously indicated for the alkanols¹³ are further illustrated by the new values. The matter most meriting comment, however, is the effect of introducing phenyl. Reichardt has demonstrated a rectilinear relationship between E_T and σ^* for the alkanols, but benzyl alcohol does not conform to this.¹³ Thus butan-1-ol and benzyl alcohol have very similar E_T values. The anomaly is now seen to occur with other phenyl-substituted alcohols, the E_T value for 1-phenylethanol being similar to the values for secondary alkanols, and values for 2-phenylethanol and 3-phenylpropan-1-ol lying close to those for butan-1-ol and pentan-1-ol. Further the E_T value of 2-methoxyethanol might be expected to lie considerably above that for ethanol, whereas the values are actually very similar. The anomalously low Lewis acidities of the phenyl-substituted alcohols and of 2-methoxyethanol complement their anomalously high Lewis basicities referred to above, and internal hydrogen-bonding may likewise provide a possible explanation.

In calculating E values we have normally used Reichardt's values of E_T when available, in order to adhere to those values which are commonly employed in studies of solvent effects.⁷ However for the unbranched alkan-1-ols from pentan-1-ol upwards and for the phenyl-substituted alcohols we have preferred to use our own values consistently. We have also used our own value

for cyclohexanol, for which we took special care over purity (see Experimental section).

E_T Values were already available for all the aprotic solvents involved in this work except 2,4-dimethylpentan-3-one.¹ In earlier work we had been unable to prepare a stable solution of the relevant *N*-phenolpyridinium betaine in this solvent. However, this has now been accomplished and $E_T = 38.5$ (Reichardt has recently found 38.7¹⁴). We have also re-determined the E_T values for three aprotic solvents: cyclopentanone, 39.4 (cf. 40.3^{1,7}); *m*-dichlorobenzene, 36.4 (cf. 37.0^{1,7}); diethyl carbonate, 37.0 (cf. 36.2^{1,7}). Corresponding new E values are: 2,4-dimethylpentan-3-one, -1.3; cyclopentanone, -0.2; diethyl carbonate, 4.1.

Correlation Analysis of the Solvent Effect on the Rate Coefficients for the Reactions of Diazodiphenylmethane with Benzoic Acid in Aprotic and Hydroxylic Solvents at 37 °C.—In Part 3¹ we presented a correlation analysis for the reaction in 43 aprotic solvents by means of equation (3).

$$\log k_0 = -3.190 + 4.463f(\epsilon) + 12.330f(n^2) + \\ (\pm 0.346) \quad (\pm 1.544) \\ 0.210E - 0.0181B \quad (3) \\ (\pm 0.020) \quad (\pm 0.0008) \\ N = 43 \quad R = 0.979 \quad s = 0.176$$

We can now update this analysis (albeit rather trivially) by including the data for 2,4-dimethylpentan-3-one. The resulting expression is (4). As expected the changes

$$\log k_0 = -3.131 + 4.584f(\epsilon) + 11.96f(n^2) + \\ (\pm 0.368) \quad (\pm 1.60) \\ 0.1949E - 0.0181B \quad (4) \\ (\pm 0.0201) \quad (\pm 0.0008) \\ N = 44 \quad R = 0.976 \quad s = 0.188$$

in the regression coefficients [except in that of the least important term, $f(n^2)$] and in the measures of goodness of fit are very small.

A comprehensive Koppel–Palm correlation analysis of the results for 44 aprotic solvents, 22 alcohols, and 2-methoxyethanol gives equation (5). (For the aprotic

$$\log k = -2.850 + 4.434f(\epsilon) + 11.27f(n^2) + \\ (\pm 0.425) \quad (\pm 1.50) \\ 0.1068E - 0.0180B \quad (5) \\ (\pm 0.0072) \quad (\pm 0.00096) \\ N = 67 \quad R = 0.955 \quad s = 0.224$$

solvents the symbol k has the same significance as k_0 used previously, *i.e.* the limiting second-order rate coefficient at [acid] = 0.) Comparison of equation (4) and equation (5) shows that the increase in the number of data-points from 44 to 67 through the incorporation of the hydroxylic solvents has been accompanied by only a small decrease in R and a small increase in s . This seems rather satisfactory. Further, the corresponding regression coefficients in the two equations have very similar values, except in the case of E , whose coefficient is greatly reduced in (5) compared with (4). The close correspond-

ence for B is particularly satisfying and suggests that the B values for hydroxylic solvents as derived by us really are on the same scale as those for aprotic solvents.

The change in the coefficient of E as between equations (4) and (5) suggests that the Lewis acidity of the two classes of solvent may not have the same impact on the rate coefficient of the reaction between diazodiphenylmethane and benzoic acid. We therefore venture to separate the two classes of solvent in this respect, so that the term involving E_{AP} for aprotic solvents and that involving E_{OH} for hydroxylic solvents may each acquire its own characteristic coefficient in the regression. Equation (6) is obtained. The coefficient of E_{AP} is very close to

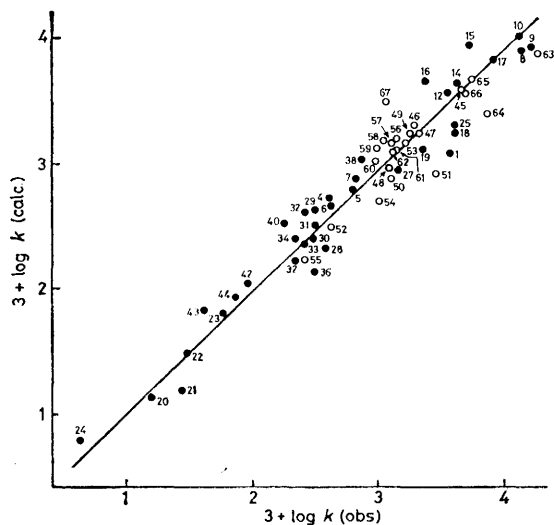
$$\log k = -3.387 + 4.675f(\epsilon) + 12.92f(n^2) + \\ (\pm 0.378) \quad (\pm 1.38) \\ 0.1921E_{AP} + 0.1089E_{OH} - 0.01772B \quad (6) \\ (\pm 0.00205) \quad (\pm 0.0064) \quad (\pm 0.00084) \\ N = 67 \quad R = 0.966 \quad s = 0.197$$

that of E in equation (4) for the aprotic solvents only; that of E_{OH} in (6) is very close to that of E in (5), since the E term in (5) is dominated by the relatively large values of E for most of the hydroxylic solvents.

The explanation of the different coefficients of E_{AP} and E_{OH} is not entirely clear. It may be that while the substantial E values which characterise most alcohols refer to the clearly defined Lewis acidity of OH , the much smaller values for aprotic solvents have no analogous clearly defined physical significance. E is actually negative for certain solvents (see Supplementary Publication No. SUP 22188 and discussion in ref. 1).

The degree of success of equation (6) is shown in the Figure by means of a plot of $\log k(\text{calc})$ versus $\log k(\text{obs})$. Although equation (6) appears overall to express the results for the hydroxylic solvents almost as well as it expresses those for the aprotic solvents, the detailed characteristic pattern for the hydroxylic solvents is not well given, and there are some strikingly deviant members. The attempt to subject the results for hydroxylic solvents by themselves to Koppel–Palm analysis is not satisfactory: the coefficient of B emerges as *ca.* -0.10, an absurd value (*cf. ca.* -0.02 for the aprotic solvents), while the coefficient of E is *ca.* -0.03 (note the negative sign) and this term is at a low level of significance. The trouble lies to some extent in a strong collinearity of B and E for the hydroxylic solvents; *r ca.* -0.75. Thus the possibility of a Koppel–Palm analysis for the data relating to hydroxylic solvents depends on fitting the data in a regression whose main lines are established by a much larger number of aprotic solvents. This process is able to place the various sub-classes of alcohols approximately in the right parts of the $\log k$ scale, but is incapable of dealing adequately with the reactivity patterns inside the sub-classes.

In Part 3¹ the problem of the parametrisation of solvent electrophilicity (Lewis acidity) was discussed. The limitations of the Koppel–Palm procedure for deriving the E values of aprotic solvents were pointed



og k (calc) as given by equation (6) versus $\log k$ (obs), for diazodiphenylmethane reacting with benzoic acid at 37 °C. Key: ● aprotic solvents; ○ alcohols; 1 benzene; 2 toluene; 3 *o*-xylene; 4 *m*-xylene; 5 *p*-xylene; 6 mesitylene; 7 tetrachloromethane; 8 chloroform; 9 dichloromethane; 10 1,2-dichloroethane; 11 fluorobenzene; 12 chlorobenzene; 13 bromobenzene; 14 iodobenzene; 15 *o*-dichlorobenzene; 16 *m*-dichlorobenzene; 17 nitrobenzene; 18 acetonitrile; 19 benzonitrile; 20 di-isopropyl ether; 21 di-*n*-butyl ether; 22 THF; 23 dioxan; 24 1,8-epoxy-*p*-menthane (cineole); 25 diphenyl ether; 26 anisole; 27 phenetole; 28 acetone; 29 butan-2-one; 30 pentan-3-one; 31 pentan-2-one; 32 3-methylbutan-2-one; 33 hexan-2-one; 34 3,3-dimethylbutan-2-one; 35 2,4-dimethylpentan-2-one; 36 cyclopentanone; 37 cyclohexanone; 38 acetophenone; 39 methyl acetate; 40 ethyl acetate; 41 diethyl carbonate; 42 DMF; 43 DMA; 44 DMSO; 45 methanol; 46 ethanol; 47 propan-1-ol; 48 propan-2-ol; 49 butan-1-ol; 50 butan-2-ol; 51 2-methylpropan-1-ol; 52 2-methylpropan-2-ol; 53 pentan-1-ol; 54 pentan-3-ol; 55 2-methylbutan-2-ol; 56 hexan-1-ol; 57 heptan-1-ol; 58 octan-1-ol; 59 decan-1-ol; 60 dodecan-1-ol; 61 cyclopentanol; 62 cyclohexanol; 63 benzyl alcohol; 64 1-phenylethanol; 65 2-phenylethanol; 66 3-phenylpropan-1-ol; 67 2-methoxyethanol (points for aprotic solvents nos. 2, 3, 11, 13, 26, 39, and 41 are omitted; they would be obscured by others)

out, and an alternative correlation analysis using E_T values directly was presented. The updated version (*i.e.* for 44 aprotic solvents) of equation (6) in the previous Part¹ is (7). [As explained in Part 3¹ the use of E_T

$$\log k = -5.489 - 0.01877B + 0.1357E_T + 8.03f(n^2) \quad (7)$$

$$(\pm 0.0009) \quad (\pm 0.0102) \quad (\pm 1.69)$$

$$N = 44 \quad R = 0.969 \quad s = 0.211$$

directly precludes any role for $f(\epsilon)$, since E_T is highly collinear with $f(\epsilon)$.

The comprehensive correlation analysis for aprotic and hydroxylic solvents can also be done with B , E_T , and $f(n^2)$, equation (8) being obtained. The coefficient of E_T

$$\log k = -5.000 - 0.01779B + 0.1113E_T + 9.609f(n^2) \quad (8)$$

$$(\pm 0.00092) \quad (\pm 0.0054) \quad (\pm 1.465)$$

$$N = 67 \quad R = 0.956 \quad s = 0.220$$

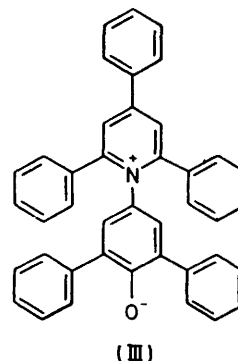
differs appreciably as between (7) and (8), but when the aprotic and hydroxylic solvents were treated separately in respect of their E_T values, there was no ensuing advantage.

EXPERIMENTAL

Solvents.—The general procedures used for purifying solvents for kinetic studies have been described previously.^{3,4,16} For the measurement of E_T values in cyclohexanol, 2,4-dimethylpentan-1-one, 1-phenylethanol, and 3-phenylpropan-1-ol it was necessary to include, as a final purification stage, percolation through 15 cm of alumina (Merck aluminium oxide 90, active neutral, activity state I). Failure to include this procedure resulted either in no absorption spectrum being observed or in gradual fading in the intensity of the spectrum.

Kinetic Studies.—Adequate accounts of the preparation and purification of the reagents, and of the spectrophotometric determination of rate coefficients have been given previously.⁴

Spectroscopic Procedure.—Measurements of ν_{\max} , the wavenumber of the absorption maximum, were made for the lowest frequency band in the electronic absorption spectrum of the solvatochromic dye (III)⁷ when dissolved in each of the solvents under study. The concentrations of



the solutions were not more than $10^{-4}M$ and, in solvents in which the dye was only sparingly soluble, saturation concentrations of *ca.* $10^{-5}M$ or less were used.

The solutions were examined in matched Infracil[®] cells of 20 mm path length, the reference cell containing the pure solvent only. Spectra were recorded on a Unicam SP 700 spectrophotometer at scan speed 4 ($750 \text{ cm}^{-1} \text{ min}^{-1}$) and minimum damping. This instrument (as indeed any instrument incorporating a silica prism monochromator) is prone to small variations of the wavenumber calibration (particularly at the lower end of the range) with quite small changes in ambient temperature. In order to ensure the required accuracy it therefore became our standard procedure to record a wavenumber calibration spectrum immediately after the recording (in duplicate) of each betaine solution spectrum. The calibration standard was didymium oxide glass and the wavenumber values of Acquista and Plyler¹⁶ were taken as reference values.*

For measurement of the basicity parameter, B' (after Koppel and Paju⁶), the following procedure was adopted. A $0.04M$ solution of the solvent in carbon tetrachloride was

* Maintenance of critical damping was most important. Inadvertent overdamping produced a shift of ν_{\max} in the direction of scan.

prepared. Two 4 ml portions of this solution were measured out. To one of these was added 4 ml of a 0.012M solution of phenol in carbon tetrachloride, and to the other 4 ml of carbon tetrachloride. These solutions were then transferred to the sample and reference cells respectively. The final concentration of the solvent in carbon tetrachloride in each cell was thus 0.02M, and the final concentration of phenol in the sample cell 0.006M.

I.r. absorption spectra were recorded in the wavenumber range 3 100—3 650 cm^{-1} at a scan rate of 20 $\text{cm}^{-1} \text{min}^{-1}$. Matched 20 mm Infrasil® cells were again found to be most convenient in this wavenumber region for the specified concentrations of basic solvent and phenol. The instrument used was a Unicam SP 100 (Mk II) spectrophotometer, and the best signal : noise ratio was achieved by using the silica prism monochromator option rather than the sodium chloride prism plus diffraction grating arrangement. Each spectrum was recorded at least twice, and the wavenumber ν_{OH} of the absorption maximum of the O—H stretching band of the phenol—basic solvent complex was measured with respect to the 3 297 cm^{-1} calibration band in the indene spectrum. An indene spectrum was recorded immediately after recording the spectra of each sample in order to ensure optimum accuracy. The difference between the wavenumber of the O—H stretching band for monomeric phenol in carbon tetrachloride (3 611 cm^{-1}) and ν_{OH} for the phenol—basic solvent—carbon tetrachloride mixture was taken as B' .

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