cepts δ_0 increase as a function of α [14]. To illustrate the former point compare the ratio of the slopes $(\Delta\delta/\Delta N)_{\alpha\simeq 0.95}/(\Delta\delta/\Delta N)_{\alpha\simeq 0}$ for say, the bromide ion with that of the OH^- ion in aqueous solutions. The ratios were 1.04 and 1.26 – 1.32 for the Br^-, and OH^- ion, respectively [15]. Our results demonstrate, therefore, that there is no significant protium-deuterium fractionation in the hydration shells of these halide anions, i.e., ϕ_{X^-} is close to unity.

In order to solve Eq. (3) for ϕ_{X^-}, the values of δ_{M^+}, δ_{X^-} and ϕ_{M^+} are needed. The fractionation factors of the alkali metal ions are known (0.98 for Na^+, 0.97 for K^+) [2] and single ion chemical shifts can be obtained as follows. In water ($\alpha = 0$) Eq. (3) is given by:

$$\delta = \delta_0 + N_{MX}(\delta_{M^+} + \delta_{X^-}) . \tag{4}$$

The slope of the δ vs. N_{MX} plot can then be split into single ion contributions by using the ratios $(\delta_{M^+}/\delta_{X^-})$ from the data of Symons et al. [17]. Employing this procedure, and the data of Table 1, the following values were calculated: $\phi_{Br^-} = 0.96 \pm 0.05$, and $\phi_{I^-} = 0.97 \pm 0.04$ [18].

The obtained fractionation factors will now be discussed. It should be emphasized that the values of ϕ_{X^-} were found to be negligibly sensitive to variations of the $(\delta_{M^+}/\delta_{X^-})$ ratios which were used to obtain the single ion chemical shifts [19]. Consequently, one can vary these ratios by ca. 25% without affecting the values of ϕ_{X^-}. Our data can also be handled in a different manner. From Table 1 it is possible to calculate values of ϕ_{X^-} and $(\delta_{M^+}/\delta_{X^-})$ simultaneously by slightly changing the slopes of the plots at the discrete α values (one at a time). Examination of the obtained results showed that all the chemically acceptable solutions were within the error limits of the determined fractionation factors [20].

Our result for the bromide ion is in agreement with Albery's ϕ_{Br^-} value if the latter is considered to arise from the contribution of 8 water molecules in its solvation shell [21]. Significantly, these directly determined fractionation factors are practically the same as that recently obtained for the aqueous chloride ion. The present results are also in line with what is known about the solvation of the halide ions in water. The picture that emerged from this, as well as from other spectroscopic studies [7 – 9], is that the H-bonds in the hydration shells of these ions are only slightly weaker than those formed by bulk water.

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Acid Base Reactions Between Acridine Orange and Substituted Phenols in Benzonitrile
Part I. Thermodynamics of Association and Ionic Equilibria

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Ionization / Molecular Interactions / Solutions / Thermodynamics

Proton transfer reactions of the five substituted phenols 3-Cl-4-nitrophenol *CNP*, 4-nitrophenol *NP*, 3-methyl-4-nitrophenol *MNP*, 4-Cl-3,5-dimethylphenol *CMP*, and 3,5-dimethylphenol *DMP* with acridine orange, and the formation of hydrogen bonded complexes AHA^- of the anions A^- of *CNP*, *NP*, and *MNP* with the respective phenols AH in benzonitrile solution were investigated by means of absorption spectroscopy. Thermodynamic data for the formation of the complexes AHA^- and of the ionic reactions (1) and (2) of *CNP*, *NP*, and *MNP* with the acridine orange base B

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$$n\,\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{A(AH)}_{n-1}^{-} + \mathrm{HB}^{+} \qquad \begin{array}{lr} n = 1 & (1)\\ n = 2 & (2)\\ n = 3 & (3)\end{array}$$

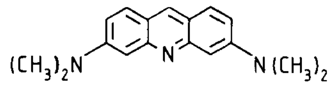
and for the reactions (2) and (3) of *CMP* and *DMP* with B were determined. The reactions (1)–(3) are exothermic. The absolute values of ΔH_1 increase with the acidity of the phenols. The formation enthalpies of the hydrogen bonded anions AHA^- are much larger than ΔH_1, so that ΔH_2 is mainly determined by this association. On the other hand there is no significant difference between ΔH_2 and ΔH_3; thus the hydrogen bond formed between a phenol and a complexed anion AHA^- is very weak. Substituent effects on the acidity of phenols are about twice as large in benzonitrile as in aqueous solution.

1. Introduction

The properties of acids and bases in solution are determined as much by the solvent as by the structure of the solute molecules themselves [1, 2]. Therefore, to obtain information about the reactivities of the acids and about solvation processes, it is necessary to study acid base reactions in different solvents. Interest in such data has increased in recent years, with the publication of thermodynamic data of solvation-like molecule-ion interactions in the gas phase [3].

Acid base equilibria in the polar organic solvents dimethylsulfoxide, dimethylformamide, propylene carbonate, and acetonitrile have been extensively studied [4–11]. In a study of the kinetics of acid base reactions in acetonitrile we recently found that the recombination of the p-nitrophenolate ion with the triethylammonium ion to form the ion pair is kinetically hindered, whereas there is no energy barrier for the proton transfer within the reaction complex [12]. Similar results had previously been obtained [13]. We describe here related work on acid base systems in benzonitrile solution. Many of the chemical and solvent properties of benzonitrile are similar to those of acetonitrile, since they are for the most part determined by the C-N-functional group. The molecules of both solvents possess dipole moments of about equal magnitude (μ = 4.05 and 3.85 D, resp.), whereas the dielectric constant of benzonitrile (ε_{25} = 25.2) is significantly smaller than that of acetonitrile (ε_{25} = 36). In recent years benzonitrile has frequently been used as a solvent in electrochemical studies of ionic reactions. To our knowledge no equilibrium or kinetic data about acid base reactions in benzonitrile have been reported.

In part I data are presented on acid base and association equilibria in benzonitrile solution involving the indicator base acridine orange *AO* and 3-Cl-4-nitrophenol *DNP*, 4-nitrophenol *NP*, 3-methyl-4-nitrophenol *MNP*, 4-Cl-3,5-dimethylphenol *CMP*, and 3,5-dimethylphenol *DMP*. In the following paper kinetic data for these systems will be presented [14]. The systems were chosen because of the convenience of using the strong absorption of the protonated acridine orange AOH^+ at 20000 cm^{-1} ($\varepsilon = 6.97 \cdot 10^7\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) for the spectroscopic determination of equilibrium and kinetic data with low concentrations of the indicator. Thus some of the complications of hydrogen bond association or base stacking expected at higher base concentrations could be avoided. The titration curves revealed the existence of three different acid base equilibria.



1. At low concentrations of both the phenol AH and the base B free ions are formed in the acid base reaction

$$\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{A}^- + \mathrm{HB}^+;\ K_1 = \frac{c_{\mathrm{A}^-} \cdot c_{\mathrm{HB}^+}}{c_{\mathrm{AH}} \cdot c_{\mathrm{B}}}. \tag{1}$$

2. Under these conditions we also found hydrogen bonded anions AHA^- formed in the reaction

$$2\,\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{AHA}^- + \mathrm{HB}^+;\ K_2 = \frac{c_{\mathrm{AHA}^-} \cdot c_{\mathrm{HB}^+}}{c_{\mathrm{AH}}^2 \cdot c_{\mathrm{B}}}. \tag{2}$$

3. Further association of the anion occurs at phenol concentrations above 10^{-3} M:

$$3\,\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{A(AH)}_2^- + \mathrm{HB}^+;\ K_3 = \frac{c_{\mathrm{A(AH)}_2^-} \cdot c_{\mathrm{HB}^+}}{c_{\mathrm{AH}}^3 \cdot c_{\mathrm{B}}}. \tag{3}$$

Most of the measurements were performed at a constant ionic strength 0.1 M. Thermodynamic data were obtained by measuring at different temperatures. Salt effects were investigated by changing the concentration of inert salt added to the solutions.

The association constants and thermodynamic data for the homoconjugation [15] of the anions of *CNP*, *NP*, and *MNP*, i.e. their hydrogen bond association with the corresponding phenol according to

$$\mathrm{A}^- + \mathrm{AH} \rightleftharpoons \mathrm{AHA}^-;\ K_4 = \frac{c_{\mathrm{AHA}^-}}{c_{\mathrm{A}^-} \cdot c_{\mathrm{AH}}} \tag{4}$$

were also derived from spectrophotometric titrations of tetraalkylammoniumphenolates with the phenols. This was done in order to ascertain the values of K_4 derived from the titration curves with acridine orange.

2. Experimental

2.1. Chemicals and Sample Solutions

The acridine orange free base was prepared from the hydrochloride (Fluka) and purified as described in Ref. [16]. The purity of the base was checked by thin layer chromatography.

4-nitrophenol *NP*, 3-$\mathrm{CH_3}$-4-nitrophenol *MNP*, 4-Cl-3,5-dimethylphenol *CMP*, and 3,5-dimethylphenol *DMP* were commercial products (Ega and Merck). 3-Cl-4-nitrophenol *CNP* was prepared by nitration of 3-Cl-phenol [17]. All the phenols were recrystallized several times from water (*CNP*, *NP*, *MNP*), toluene (*NP*), or petroleum ether 90–100°C bp. (*CMP*, *DMP*). The final step in the purification of *MNP*, *CMP*, and *DMP* was sublimation at ca. 0.1 Pa. The melting points agreed with the literature values.

The tetrabutylammoniumsalts of *CNP*, *NP*, and *MNP* were prepared by reacting a solution of the phenol in methanol with an equimolar amount of a freshly prepared aqueous tetrabutylammoniumhydroxide solution and recrystallization from acetone/ether. The purity of the salts was verified by regenerating the phenol with perchloric acid and measuring its UV-absorption. With *CMP* and *DMP* a mixture of the normal salt and an acid salt with stochiometry $\mathrm{Bu_4N \cdot AHA}$ is obtained. By starting with the reactants in a 1 : 2 ratio the acid salts were obtained in pure form, whereas it was impossible to prepare the normal salts.

Tetrabutylammonium-hexafluorophosphate *TBHP* (Fluka, p. A.) was used as an inert salt for regulating the ionic strength. As purchased, it contains acid impurities. It was recrystallized several times and carefully dried.

Benzonitrile was purified by a procedure which is an improved modification of that in Ref. [18]. The solvent was stirred for two days with H_3PO_4 (85%), decanted, and after a first rapid distillation again twice distilled over CaH_2, and the middle fraction collected each time. The solvent was stored in brown flasks, and handled under nitrogen. The content of acid impurities in the solvent was checked by the visible absorption of acridine orange, and was below $5 \cdot 10^{-7}$ M.

The total amount of protic impurities (water) in our sample solutions could not be measured directly. Some conclusions, however, can be drawn from the effects of added methanol on the spectra. Whereas the extinctions of acridine orange, as base and protonated, and of the phenols were only negligibly influenced, the spectra of the phenolate anions changed completely because of their heteroassociation with methanol in analogy to the homoconjugation described in the text. In several experiments we measured the extinction coefficient ε_A of a phenolate anion and, after adding a small amount of perchloric acid, the extinction coefficient ε_{AH} of the phenol as well. The apparent ratio $\varepsilon_A/\varepsilon_{AH}$ is a sensitive indicator for protic impurities in the phenolate solution. In a typical set of experiments the scatter of four ratios $\varepsilon_A/\varepsilon_{AH}$ was 0.6%. If this is ascribed to the presence of impurities, then the maximum possible difference of their concentrations was $6 \cdot 10^{-4}$ M. The impurity level is believed to be much lower because the experimental scatter of $\varepsilon_A/\varepsilon_{AH}$ corresponds to only 2 – 3 times the reading accuracy of our spectrometer.

The effect of methanol on the anion spectra is temperature dependent. At 5°C the absorbance of the anion of *MNP* at 22700 cm^{-1} is reduced by 35.5% in a solution containing $6 \cdot 10^{-2}$ M methanol. The effective absorption coefficient is 18% higher at 40°C. Thus in the presence of protic impurities the apparent extinction coefficient of the anion increases with increasing temperature. No such effect was observed with our sample solutions.

2.2. Spectrophotometric Measurements and Treatment of Data

Visible and UV spectra were measured with a Zeiß spectrophotometer DMR 21. The solutions were made up by weight and titrated in a storage vessel fused to a quartz cuvet [16]. The temperature was measured in the cuvet with a Si-diode, and was kept constant to within ± 0.1°C. The extinction coefficients of the homoconjugated anions were measured by adding a small amount of tetrabutylammoniumsalt to a 0.1 M solution of the corresponding phenol whereby practically all phenolate ions are converted into the hydrogen bonded complexes. It was assumed that the extinction coefficients of the hydrogen bonded complexes at the analytical wavelength are identical. The extinction coefficients and analytical wavelengths are given in Table 1.

The densities of the salt solutions at 25°C were separately determined. The thermal expansion of the solutions was taken to be equal to that of benzonitrile [16, 19].

In addition to the equilibria (1) – (3) several other mechanisms were considered as possible explanations of the titration curves [16]. For the mechanisms discussed in the text the correlation coefficients r^2 of linear plots of all titration curves were better than 0.95. The corresponding Van t'Hoff plots for K_2 had $r^2 > 0.99$ in all systems. Other mechanisms led either to physically meaningless parameters, or low r^2 values, or curved Van t'Hoff plots.

As a rule 7 to 9 points were taken per titration. Between 6 and 8 series of titrations in the temperature range 5 – 55°C served to determine thermodynamic data.

3. Results

3.1. Hydrogen Bond Association (Homoconjugation) of Nitrophenols

The long wavelength absorption bands of tetrabutylammoniumsalts of *CNP*, *NP*, and *MNP* are blue shifted on addition of the corresponding phenol because of the formation of homoconjugate anions according to Eq. (4). The association constant K_4 is obtained from a plot of $\log \frac{c_{AHA^-}}{c_{A^-}}$ vs. $\log c_{AH}$ according to

$$\log \frac{c_{AHA^-}}{c_{A^-}} = \log c_{AH} + \log K_4 \,. \qquad (6)$$

Although the extinction coefficients of the hydrogen bonded anions at the analytical wavelength are small, it is necessary to evaluate Eq. (6) by an iterative procedure, using the independently determined value ε_{AHA^-}. Typical results are shown in Fig. 1.

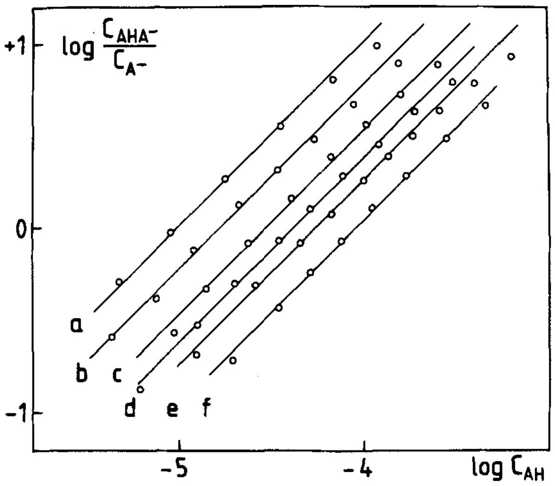


Fig. 1

Plots of Eq. (6) for the titration of tetrabutylammonium-p-nitrophenolate with *NP* in benzonitrile, ionic strength 0.1 M. Temperatures (°C): a) 4.5; b) 11.7; c) 18.7; d) 25.9; e) 30.7; f) 41.2. The straight lines are drawn with the theoretical slope 1

At the end of the titrations small systematic deviations between the calculated concentration terms and the correlation of Eq. (6) occur. They may be caused by an underestimation of ε_{AHA^-} in our measuring method (see experimental part). Another possible reason is the onset of a second association of the anions according to

$$AH + AHA^- \rightleftharpoons A(AH)_2^- \,; K_5 = \frac{c_{A(AH)_2^-}}{c_{AH} \cdot c_{AHA^-}} \,. \qquad (5)$$

Table I

Extinction coefficients of nitrophenols AH, their anions $A^\ominus$, and of homoconjugated anions $AHA^\ominus$ at the analytical wavelengths

Phenol	AH		$A^\ominus$		$AHA^\ominus$
	$\tilde{\nu}$ max cm^{-1}	ε 10^6 cm^2 mol^{-1}	$\tilde{\nu}$ cm^{-1}	ε 10^6 cm^2 mol^{-1}	ε 10^6 cm^2 mol^{-1}
CNP	30000	6.15	23000	24.1	0.83
NP	32100	10.5	22500	30.7	0.90
MNP	30200	8.06	22500	25.1	0.41

Table II
Thermodynamic data of the acid base reactions (1) and (2) of nitrophenols with *AO*, and of the hydrogen bond formation (4) of nitrophenolate ions[a])

Phenol	$AH + B \rightleftharpoons A^{\ominus} + HB^{\oplus}$			$2\,AH + B \rightleftharpoons AHA^{\ominus} + HB^{\oplus}$			$A^{\ominus} + AH \rightleftharpoons AHA^{\ominus}$		
	$-\Delta H_1$ kJ mol^{-1}	$-\Delta S_1$ JK^{-1} mol^{-1}	K_1[b])	$-\Delta H_2$ kJ mol^{-1}	$-\Delta S_2$ JK^{-1} mol^{-1}	K_2[b]) M^{-1}	$-\Delta H_4$ kJ mol^{-1}	$-\Delta S_4$ JK^{-1} mol^{-1}	K_4[b]) M^{-1}
CNP	23.3 (1.7)	82 (6)	0.66 (0.06)	60.1 (0.85, 6.0)	121 (2.8)	$1.56 \cdot 10^4$ $(0.14 \cdot 10^4)$	36.9 (0.8, 5.8)	39.1 (2.7)	24500 (1800)
NP	18.9 (1.9)	94 (7)	0.0276 (0.002)	61.2 (1.1, 6.5)	151 (3.6)	690 (22)	42.3 (0.8, 4.0)	57.0 (2.8)	25000 (1500)
MNP	14.5 (2.2)	90 (8)	$6.4 \cdot 10^{-3}$ $(0.7 \cdot 10^{-3})$	50.4 (0.9, 6.2)	127 (2.9)	155 (16)	35.9 (1.3, 6.3)	36.5 (4.2)	25200 (1700)
NP[c])	17.3 (0.6)	88 (1.8)	0.025 (0.004)	52.3 (0.7, 5.0)	136 (1.8)	117 (17)	34.7 (0.8, 6.0)	46.0 (2.5)	4590 (360)

[a]) At ionic strength 0.1 M. The standard errors are given in parenthesis. For ΔH_2 and ΔH_4 the 95% confidence limits are also given. ΔH_1 was derived from ΔH_2 and ΔH_4.
[b]) At 25°C. [c]) In acetonitrile.

Table III
Equilibrium constants K_1 and K_4 for *MNP* at different ionic strengths *I*, 25°C

I M	$\log K_4$	$\log K_1$	$\log K_1$, calc.[a])
0.025	4.42	−2.52	−2.55
0.05	4.42	−2.40	−2.37
0.1	4.34	−2.20	−2.18
0.2	4.33	−1.95	−1.97

[a]) Dependence of K_1 on the ionic strength calculated with the parameters $\log K_1^0 = -3.20$ and $r = 0.40$ nm.

This association plays a principal role at phenol concentrations above 10^{-3} M, which, however, were not reached in the titrations. At the present time neither of the possibilities can be excluded. In either case the values of K_4 derived from that part of the titration which agrees with the theoretical line are not affected by these deviations.

The results at constant ionic strength 0.1 M are given in Table 2. K_4 depends somewhat on the ionic strength (Table 3). Because the inert salt TBHP is not measurably associated in acetonitrile [20] it was assumed to be completely dissociated; tetra-alkylammoniumsalts are associated to about the same extent in benzonitrile as in acetonitrile [21–23]. The concentrations of the phenolate salts were in the range 10^{-5} to 10^{-4} M. At these low concentrations it is unlikely that incomplete dissociation might have influenced the results. The values of K_4 obtained by the titration depend on the dissociation constant of the salt

$$K_d = \frac{c_{A^-} \cdot c_{Bu_4N^+}}{c_{Bu_4NA}}$$

only if this is significantly lower than 10^{-3} (M). Reported dissociation constants of tetra-alkylammoniumsalts in benzonitrile are: Bu_4NClO_4, $K_d = 1.3 \cdot 10^{-2}$ (M) [24]; Et_4NJ, $K_d = 7.4 \cdot 10^{-3}$ (M) [25].

Thermodynamic data for the homoconjugation of *NP* were also determined in acetonitrile solution. In the literature values of the association constant at 25°C are given: $K_4^{NP} = 4.7 \cdot 10^3$, $3.3 \cdot 10^3$ (M^{-1}) [26], and $1.4 \cdot 10^3$ (M^{-1}) [27]. Our value K_4^{NP} (25°C) $= 4590 \pm 360\,(M^{-1})$ agrees well with the former.

The homoconjugation constants of the methyl-substituted phenols *CMP* and *DMP* could not be determined directly, because their anions absorb at only slightly longer wavelengths than the solvent. Some measurements in acetonitrile demonstrated that their association properties are similar to those of the more acidic phenols.

3.2. Acid Base Equilibria of Acridine Orange with Nitrophenols

Titration of a benzonitrile solution of acridine orange *AO* with a solution of a nitrophenol leads to similar changes in the spectrum of *AO* as protonation in aqueous solution. But the increase of the absorption band of AOH^+ at 20000 cm^{-1} is due not alone to the ionic equilibrium (1). A mechanism including both reactions (1) and (2) allows for a satisfactory description of the titration curves. By combining the expressions for the equilibrium constants K_1 and K_2 the relation

$$\frac{c^2_{BH^+}}{(c^0_B - c_{BH^+})\,c_{AH}} = K_2 \cdot c_{AH} + K_1 \qquad (7)$$

is derived. Here c^0_B is the initial concentration of *AO*, c_{BH^+} is the spectroscopically determined equilibrium concentration of AOH^+. Eq. (7) was evaluated by an iterative procedure, where in the first step the concentration of the homoconjugated anion c_{AHA^-} was neglected. The procedure converges after a few cycles. In our systems, however, the ratio between intercept and slope of plots according to Eq. (7) was between 10^{-4} and 10^{-5}. This means neither Eq. (7) nor any other relation provides accurate values of K_1. We preferred, therefore, to use the independently measured values of K_4 for calculating c_{AH} in Eq. (7). The values of K_1 determined by both methods agreed within the error limits.

The titration curves showed an isosbestic point at 22300 cm^{-1} indicating that only two forms of acridine orange were present in the solutions. In principle the formation of hydrogen bonded complexes

$$AH + B \rightleftharpoons AH..B, \quad K_8 = \frac{c_{AHB}}{c_{AH} \cdot c_B} \qquad (8)$$

and ion pairs

$$AH..B \rightleftharpoons A^-..HB^+, \quad K_9 = \frac{c_{A^-\,HB^+}}{c_{AHB}} \qquad (9)$$

may be expected. Because of the low concentrations of *AO* used in our experiments, significant amounts of these complexes would have been present only when

$$K_f = \frac{c_{A^-..HB^+}}{c_{AH} \cdot c_B} = K_8 K_9 > 500\,(M^{-1})\,.$$

Evaluating our data with a scheme including reactions (1), (2), and (8) + (9) resulted in small and scattered values of K_f with large standard deviations, whereas the results for the overall constant K_1 were unaffected. Thus the equilibrium data give no conclusive evidence for the existence of hydrogen bonded complexes AH..B and $A^-..HB^+$.

No other mechanism consisting of two or three steps combining ion pair formation with association of reactants or products with phenol or base yields a satisfactory description of the titration curves.

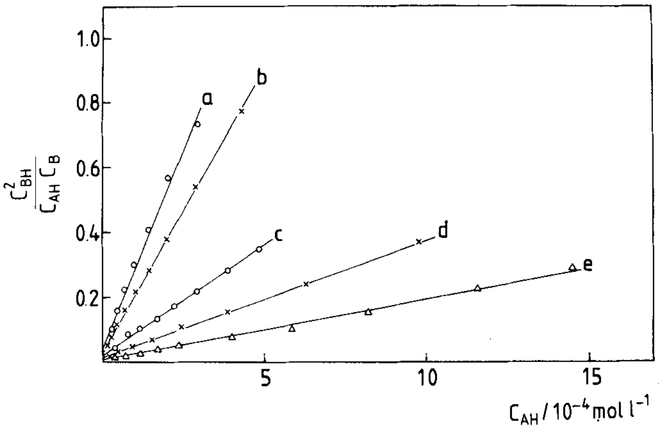


Fig. 2
Plots of Eq. (7) for the titration of *AO* with *NP* in benzonitrile, ionic strength 0.1 M. Temperatures (°C): a) 10.8; b) 14.6; c) 25.0; d) 32.1; e) 46.9

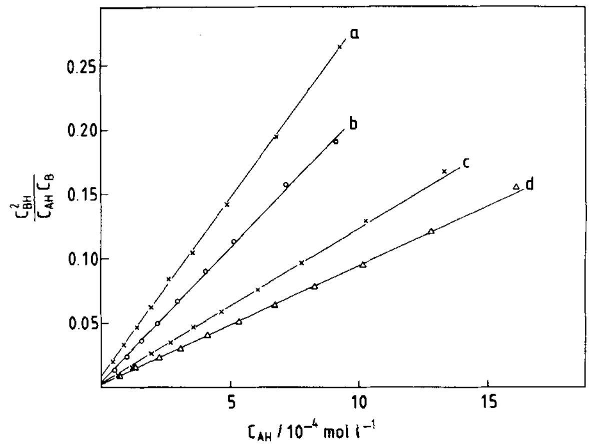


Fig. 3
Plots of Eq. (7) for the titration of *AO* with *MNP* at different ionic strengths I (M): a) 0.2; b) 0.1; c) 0.05; d) 0.025. Temperature 25°C

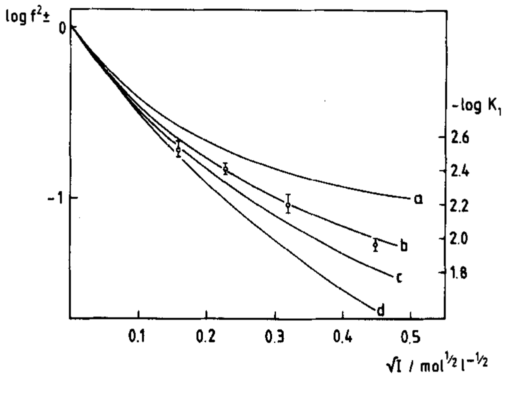


Fig. 4
Dependence of K_1 for *MNP* on the ionic strength. Left scale: square of the ionic activity coefficient $f^\pm$ on a logarithmic scale. Theoretical lines are calculated with the extended Debye-Hueckel theory using the ionic radius r (nm): a) 0.6; b) 0.4; c) 0.3; d) 0.2. Points: experimental values of K_1, right scale

One example of a plot of Eq. (7) is given in Fig. 2. Thermodynamic data were derived from the temperature dependence of the equilibrium constants (Table 2). The dependence of K_1 and K_2 on the ionic strength was investigated in the case of *MNP*. The corresponding plots of Eq. (7) are presented in Fig. 3. Values of K_1 were fitted to the extended Debye-Hückel formula for the ionic activity coefficients

$$\log f_\pm = -\frac{A\cdot z_A\cdot z_B\cdot\sqrt{I}}{1+B\cdot r\cdot\sqrt{I}}$$

where A and B have the usual meaning [28]. The parameters of the best fit are the thermodynamic equilibrium constant $K_1^0 = 6.3\cdot 10^{-4}$ and the ionic radius $r = 0.40$ nm. A plot of log K_1 vs. $\sqrt{I}$ is shown in Fig. 4. In Table 3 a comparison is made of calculated and experimental values of K_1.

In titrations of *AO* with *NP* in acetonitrile solution the same reaction scheme consisting of reactions (1) and (2) was established. Thermodynamic data for this system were derived by titrations at 6 different temperatures between 11°C and 43°C. They are listed in Table 2.

3.3. Acid Base Equilibria of Acridine Orange with Methylphenols

CMP and *DMP* are so weakly acidic that acridine orange is significantly protonated only when the phenol is in more than hundredfold excess. It is reasonable to assume that under these conditions all the anions are hydrogen bonded. The dependence of the concentration of protonated *AO* on the phenol concentration indicates the presence of two equilibria. A mechanism consisting of reactions (2) and (3) allows for a satisfactory description of the titration curves. A combination of the expressions for both equilibrium constants, K_2 and K_3, leads to the equation

$$\frac{c^2_{\mathrm{HB}^+}}{(c^0_{\mathrm{B}} - c_{\mathrm{HB}^+})\cdot c^2_{\mathrm{AH}}} = K_3\cdot c_{\mathrm{AH}} + K_2\,. \qquad (10)$$

It is a good approximation here to take $c_{\mathrm{AH}} = c^0_{\mathrm{AH}} - 2\,c_{\mathrm{HB}^+}$. The value of $K_5 = K_3/K_2$ obtained with this approximation was used to calculate the concentrations of both types of hydrogen bonded anions AHA^- and $\mathrm{A(AH)}_2^-$, and the calculation repeated. In both systems K_2 is smaller by 4 to 5 orders of magnitude than K_5, and is much smaller than K_3. Therefore the error limits for both constants K_2 and K_5 are relatively large, whereas K_3 was obtained with good accuracy from the slope of the plot of Eq. (10). The data for the *DMP/AO* system are shown in Fig. 5.

The agreement between the calculated and the experimental data was not improved if it was assumed that, in addition to the species involved in the equilibria (2) and (3), hydrogen bonded complexes or free anions were present in the solutions. The results are given in Table 4. Thermodynamic data for the second association of the anion are not listed in

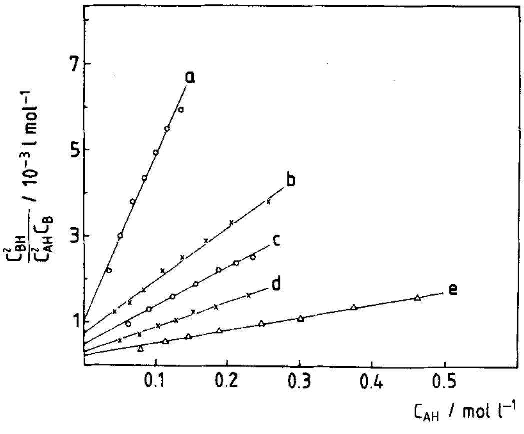


Fig. 5
Plots of Eq. (10) for the titration of *AO* with *DMP* in benzonitrile, ionic strength 0.1 M. Temperatures (°C): a) 6.6; b) 18.1; c) 24.2; d) 31.9; e) 43.1

Table IV
Thermodynamic data of the acid base reactions (2) and (3) of methylphenols with *AO*[a])

Phenol	$2\,AH + B \rightleftharpoons AHA^{\ominus} + HB^{\oplus}$			$3\,AH + B \rightleftharpoons A(AH)_2^{\ominus} + HB^{\oplus}$		
	$-\Delta H_2$ kJ mol^{-1}	$-\Delta S_2$ JK^{-1} mol^{-1}	K_2[b]) M^{-1}	$-\Delta H_3$ kJ mol^{-1}	$-\Delta S_3$ JK^{-1} mol^{-1}	K_3[b]) M^{-2}
CMP	47.6 (1.8, 13.4)	199 (6)	$8.3 \cdot 10^{-3}$ $(1.5 \cdot 10^{-3})$	44.8 (0.5, 3.1)	157 (1.4)	0.45 (0.04)
DMP	43.2 (0.9, 6.5)	208 (3)	$4.97 \cdot 10^{-4}$ $(0.8 \cdot 10^{-4})$	44.9 (0.5, 3.8)	190 (2)	$8.56 \cdot 10^{-3}$ $(0.4 \cdot 10^{-3})$

[a]) At ionic strength 0.1 M. The standard errors are given in parenthese s. For ΔH the 95% confidence limits are also given.

Table 4, because the limited accuracy of the titration data did not allow us to derive numerical values with acceptable reliability. The reaction enthalpy and entropy of this association are both small.

The mechanism discussed so far is not the only one in good agreement with the titration data of *AO* with *CMP* and *DMP*. We also calculated the dependence of the concentration of protonated *AO* on the phenol concentration in the ionic reaction (1) followed by association of the anion with two molecules of phenol:

$$2\,AH + A^- \rightleftharpoons A(AH)_2^-;\quad K_{11} = \frac{c_{A(AH)_2^-}}{c_{A^-} \cdot c_{AH}{}^2}. \tag{11}$$

With appropriate values of K_1 and K_{11} we obtained titration curves which deviated by less than 0.6% from theoretical curves calculated with Eqs. (2) and (3) in the range between 10% and 90% protonation of *AO*. Thus it is almost impossible to distinguish between these reaction schemes by equilibrium methods. Since the species involved in the two mechanisms and the types of equilibria are different the kinetic rate laws for the equilibration of the acid base system are also different. The kinetic measurements described in the following paper [14] revealed that the rate law of the coupled reactions (2) and (3) fits the concentration dependence of the relaxation times very well, whereas there was no correlation with the rate law of reactions (1) and (11). Therefore, the latter mechanism was disproved.

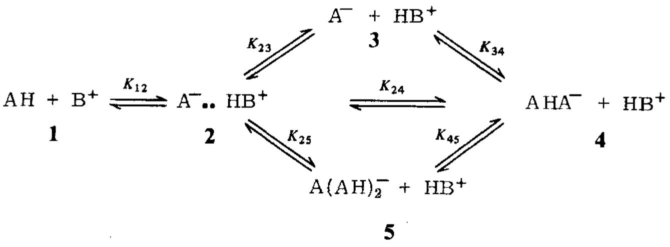
4. Discussion

Solutions in benzonitrile containing partly ionized phenols have complex equilibrium properties. In a solution with as little as $5 \cdot 10^{-6}$ M of phenol and phenolate ions the homoconjugation amounts to about 10%, becoming increasingly important at higher concentrations. Further association is negligible at concentrations up to 10^{-3} M. Ion pairs are typical intermediates in acid base reactions in aprotic solvents. These were not found in our systems. Data on ionic equilibria in acetonitrile allow one to derive a general rule that organic cations have little tendency to form ion pairs if their charges are delocalized. This is the case with the protonated acridine orange. Accordingly, the same rule apparently holds for benzonitrile as well. Ion pair formation is expected to contribute significantly to the equilibrium properties of solutions containing cations with localized charges. From the fact that the agreement between calculated and experimental titration curves is not improved by taking ion pairs into consideration, we can set an upper limit of $K_f = 500$ M^{-1} for the formation constant of the ion pairs in all systems studied. The existence of ion pairs in these systems was indeed clearly demonstrated by the kinetic measurements [14]. A value $K_f = 16$ M^{-1} was derived as a lower limit in the *AO/NP* system.

No absolute p*K* scale exists in the benzonitrile solvent, although the existence of ionic acid base equilibria would allow for this possibility. The acidities of the phenols in benzonitrile may be defined on a relative scale with respect to the reference base *AO* by the equilibrium constants K_1. The determination of K_1 was possible for the nitrophenols only. It is assumed that the values of the association constants K_4 are similar for all the five phenols, since they are equal for *CNP, NP,* and *MNP* at 25°C (Table 2). This is in agreement with the fact that in acetonitrile K_4 for various acids depends very little on the acidity [5]. With the assumption K_4 = const. we can use K_2 instead of K_1 as a measure of the relative phenol acidities. The K_2 values span a range of 7.5 p*K* units in benzonitrile, compared with the aqueous acidity range of these phenols of 3.35 p*K* units. This demonstrates the differentiating power of benzonitrile. Substituent effects on the acidity are about twice as large in benzonitrile as in water. As expected, no self dissociation of the phenols was observed. In fact, the appearance of the anion spectrum in a phenol solution is a proof of the presence of basic impurities in the solvent. This is useful as a sensitive test for the purity of benzonitrile.

The acid base and association reactions in benzonitrile solution may be put together in one scheme including the ion pair.

Scheme 1



According to scheme I the observed acid base equilibria are characterised by $K_1 = K_{12} \cdot K_{23}$, $K_2 = K_{12} \cdot K_{24}$, and $K_3 = K_{12} \cdot K_{25}$. The thermodynamically very stable homoconjugated anion AHA$^-$ plays a central role in the equilibria.

In the systems studied the formation of the free ions in reaction (1) is exothermic, but cancellation of the negative ΔH_1 by large negative reaction entropies results in positive ΔG_1 values (Table 2). With decreasing acid strength of the phenol ΔH_1 increases from -23.3 kJ mol^{-1} (*CNP*) to -14.5 kJ mol^{-1} (*MNP*). Similar results have been obtained in dimethylsulfoxide [29]. Analogously the reaction enthalpies ΔH_2 decrease with decreasing acidity of the phenol, whereas ΔS_2 is more negative in the systems *CMP/AO* and *DMP/AO* than in the case of the nitrophenols. There is no significant difference between ΔH_2

and ΔH_3; thus the hydrogen bond formed between a phenol and a homoconjugated anion is very weak.

The heat evolved in the formation of the first hydrogen bond between a phenolate ion and a phenol ΔH_4 is significantly larger than that of the proton transfer from the phenol to the acridine orange base (Table 2). Therefore, the energetics of reaction (2) are mainly determined by this association. The association tendency of the phenolate ions in benzonitrile is much stronger than in acetonitrile. This is due to a larger reaction enthalpy ΔH_4. The difference of about 8 kJ mol^{-1} between ΔH_4 in these solvents may be ascribed to different hydrogen bond energies of hydrogen bonds between the phenol monomers and the solvents since benzonitrile is a weaker hydrogen bond acceptor than acetonitrile.

The solvent dependence of the *AO/NP* system reveals a surprising effect of the homoconjugation. At the ionic strength 0.1 M, K_1 has almost the same value in both solvents. This is a fortuitous coincidence, since the dependence of K_1 on the ionic strength in these solvents is quite different. The concentration of ions in a benzonitrile solution of *AO* and *NP* at the ionic strength 0.1 M is significantly larger than in a solution with the same starting concentrations in acetonitrile. This is due solely to the stronger anion association which shifts the overall equilibrium to the side of the ions in spite of the smaller dielectric constant of benzonitrile.

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Acid Base Reactions Between Acridine Orange and Substituted Phenols in Benzonitrile Part II. Kinetics: An Extended Eigen Mechanism of Proton Transfer

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Chemical Kinetics / Elementary Reactions / Molecular Interactions / Solutions

The kinetics of proton transfer between five substituted phenols (AH) and the acridine orange base (B) are studied in benzonitrile solution using the temperature jump method. In the overall reactions (1) – (3)

$$n = 1 \qquad (1)$$

$$n\,\mathrm{AH} + \mathrm{B} \underset{k_{bn}}{\overset{k_{fn}}{\rightleftharpoons}} \mathrm{A}^-(\mathrm{AH})_{n-1} + \mathrm{HB}^+; \quad n = 2 \qquad (2)$$

$$n = 3 \qquad (3)$$

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