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Dissociation of Phenols and Phenolate Salts and Homocomplexation in the corresponding Phenol–Phenolate Systems in Benzonitrile

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The acidities of 12 substituted phenols ($\mathrm{p}K_a^{\mathrm{BN}}$ relative to the $\mathrm{p}K_a^{\mathrm{BN}}$ of $HClO_4$) and the formation constants of the corresponding homocomplexes, K_{AHA}, in benzonitrile have been determined from e.m.f. measurements. Comparison with previous results reveals that the stability of homocomplexes increases in aprotic solvents in the order acetonitrile $\approx$ propylene carbonate $<$ benzonitrile $<$ acetone. Conductivity measurements have been carried out on the 12 tetrabutylammonium phenolates in benzonitrile. The data have been analysed using the Pitts equation and the limiting conductivities and dissociation constants of the salts have been calculated.

Phenols are known to form hydrogen-bonded complexes with their parent bases in aprotic solvents. This association depends on the strength of solute–solvent interactions because of the competition between the phenolate ions and the solvent for hydrogen bonding with the phenol. Studies of some electrolytes[1, 2] and the kinetics of proton transfer[3] in benzonitrile have been reported. However, too little is known about the acid–base and association properties of weak acids in benzonitrile. The purpose of this study was to collect suitable data on phenol–phenolate systems in benzonitrile and to make a comparison with the results obtained in acetonitrile,[4–7] propylene carbonate[8] and acetone.[9]

Benzonitrile (BN) is a protophobic[10] dipolar solvent with a dielectric permittivity $\varepsilon = 25.2$, dipole moment 4 D, viscosity 0.0122 P and density 1.0008 g cm^{-3} at 298 K.[11]

EXPERIMENTAL

Benzonitrile (Riedel de Haen) was dried with $CaSO_4$ and distilled in nitrogen under reduced pressure. Redistillation was carried out after 1 h refluxing with P_2O_5 and the middle fraction of *ca.* 70% of the distillate was used. The specific conductivity of BN purified in this way was $\kappa = 2.9 \times 10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Tetrabutylammonium perchlorate prepared from perchloric acid and tetrabutylammonium hydroxide in water was crystallized from the reaction mixture and then from ethyl acetate and dried. Elementary analysis was 56.00% C (calc. 56.21), 10.82% H (calc. 10.61), 4.21% N (calc. 4.10). All other salts were obtained and analysed as described previously.[12] Anhydrous $HClO_4$ solution in BN (containing acetic acid) was prepared as described by Kolthoff and Coetzee.[13]

Potentiometric measurements were carried out at 25 ± 0.05 °C using a N-517 Mera Elwro pH-meter and are accurate to within ±0.5 mV. When not in use, the Radelkis glass electrode was stored under water. The reference electrode was a modified calomel electrode in which the aqueous KCl solution was replaced by 0.1 mol dm^{-3} tetrabutylammonium chloride solution in BN. The glass sensor electrode was calibrated in buffer solutions containing tetrabutylammonium perchlorate and $HClO_4$.

For pH measurements 20 cm^3 of a 10^{-3} mol dm^{-3} salt solution was placed in the cell and appropriate volumes of a solution containing 10^{-3} mol dm^{-3} salt and 6×10^{-3} mol dm^{-3} acid were added. Thus the ionic strength was kept practically constant. After each addition of the titrant, the potential reached an equilibrium value within 2–8 min. The system was carefully dried. Two independent titrations were made with each system.

The conductances of 8–10 samples of each quaternary salt in BN in the range $(0.3\text{–}5) \times 10^{-3}$ mol dm^{-3} were measured using a bridge of type K-58-23/18 at 1 kHz (accuracy, 0.2–0.5%; cell constants, 0.0189 and 0.2950 cm^{-1}).

RESULTS AND DISCUSSION

POTENTIOMETRIC MEASUREMENTS

In fig. 1 the dependence of the e.m.f. on the ratio c_{HA}/c_A is shown for four systems characterized by different strengths of homoconjugation. The p_aH values were calculated from the Nernst equation

$$E = E_0 - Sp_aH, \qquad (1)$$

where $E_0 = 1280$ mV [based on $pK_a^{BN}(HClO_4) = 2.795$[1]] and $S = 61$ mV (obtained in the calibration of the glass electrode). The pK_a^{BN} values were determined from E_{aq} (e.m.f. for $c_{HA} = c_A$) values:

$$pK_a^{BN} = (E_0 - E_{eq})/S - \log f_{\pm} \qquad (2)$$

and are listed in table 1. The pK_a^{BN} of picric acid found in this way (11.1) is close to that (11.0) determined by Kolthoff and Chantooni in acetonitrile.[6a] The pK_a values in acetonitrile of 3-nitrophenol, $pK_a^{AN} = 23.8$, and of 4-nitrophenol, $pK_a^{AN} = 20.9$,[6b] are also very close to the pK_a^{BN} values reported here. However, the absolute pK_a values in both solvents are uncertain since they are based on the pK_a values of $HClO_4$ determined in the mixed solvent systems acetonitrile + acetic acid and benzonitrile + acetic acid. It has been shown that in the system $HClO_4$ + acetic acid + acetonitrile the dissociation of $HClO_4$ is due mainly to the protonation of the acetic acid.[14] The similarity of the measured pK_a values of the phenols in both solvents indicates that the same holds for the system $HClO_4$ + acetic acid + benzonitrile. Even if the reference points of the pK_a scales in both solvents are uncertain, the slopes of the plots of pK_a^{BN} and pK_a^{AN} against pK_a^{water} are still the correct measure of the difference between the solvent–solute interactions in the respective solvents. There is a linear correlation between the pK_a^{BN} and pK_a^{water} values of the phenols with a slope of 1.7, which denotes that BN is (like acetonitrile) a solvent which is better able to differentiate between the acidity of the phenols than water.

Homoconjugation constants K_{AHA} were calculated from the titration curves using the relation[5,7,8]

$$K_{AHA} = [AHA]/(C_{AH} - [AHA])(C_S - [AHA]) \qquad (3)$$

where $$[AHA] = (K_a C_{AH} - a_{H^+} f_{A^-} C_S)/(K_a - a_{H^+} f_{A^-})$$

and C_{AH} and C_S denote the total concentrations of acid and salt, respectively. In eqn (3) the very small H^+ activity a_{H^+} is neglected.

One might expect that the formation of homocomplexes will increase, in general, with decreasing acidity of the parent phenols, because the more basic anions compete more favourably with the solvent for hydrogen-bond formation. This is confirmed by

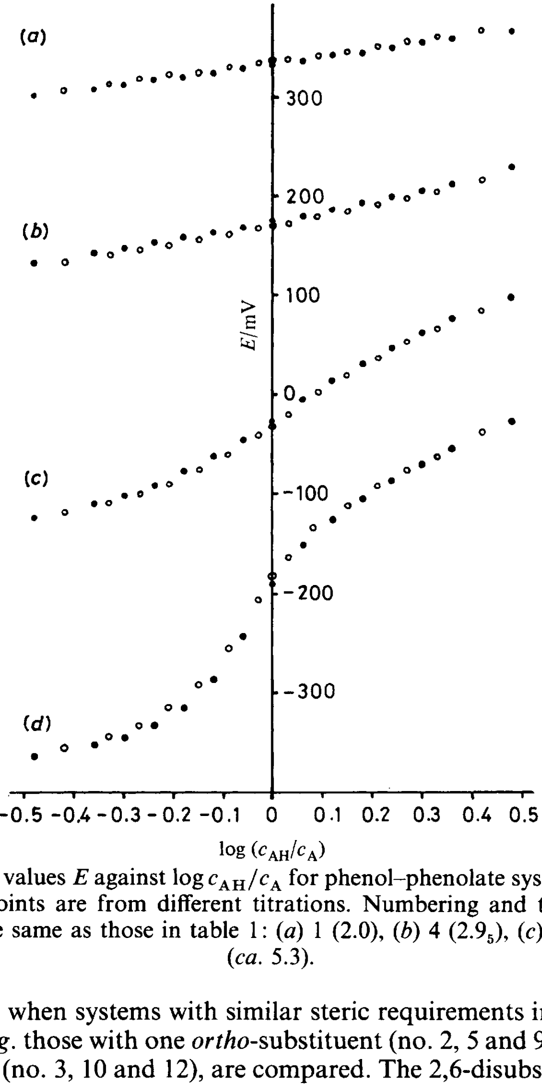

Fig. 1. Plot of e.m.f. values E against $\log c_{AH}/c_A$ for phenol–phenolate systems in benzonitrile. Open and closed points are from different titrations. Numbering and the $\log K_{AHA}$ values (in brackets) are the same as those in table 1: (*a*) 1 (2.0), (*b*) 4 (2.9_5), (*c*) 10 (4.4) and (*d*) 12 (*ca.* 5.3).

the data in table 1 when systems with similar steric requirements in proximity to the hydrogen bond, *e.g.* those with one *ortho*-substituent (no. 2, 5 and 9) or those without *ortho*-substituents (no. 3, 10 and 12), are compared. The 2,6-disubstitued compounds (no. 1, 4, 6, 7, 8 and 11) show a much weaker interaction, as expected from steric considerations. The same result was also obtained for analogous systems in propylene carbonate[8] and acetonitrile.[7]

In fig. 2 $\log K_{AHA}$ for phenol–phenolate systems in BN, propylene carbonate and acetone is plotted as a function of $\log K_{AHA}$ in acetonitrile. Slightly stronger homocomplexation in BN arises from the lower permittivity of BN and its smaller hydrogen-bond accepting power compared with acetonitrile and propylene carbonate.[15] In acetone the effect of lower permittivity is of greater importance than the increase in basicity.

The K_{AHA} value of 4-nitrophenol has also been determined by visible spectroscopy at an ionic strength of 0.1 mol dm^{-3}, giving $\log K_{AHA} = 4.40$, in full agreement with the value given in table 1.[16] The dependence of K_{AHA} on the ionic strength was shown to be very small, as expected.[16]

Table 1. Dissociation constants of the phenols (K_a) and homoconjugation constants (K_{AHA}) of the corresponding phenol–phenolate systems and dissociation constants (K_d) and limiting conductances (Λ_0) of the tetrabutylammonium phenolates in benzonitrile at 298 K

no.	phenol, phenolate salt or phenol–phenolate system	pK_a^{BN}	$\log K_{AHA}^{BN}$	$\bar{\sigma}^a$	$K_d^{BN}/10^{-2}$ mol dm^{-3}	Λ_0/Ω^{-1} cm^2 mol^{-1}
1	2,6-dibromo-4-nitro-	15.6	2.0	0.12	1.68	39.9
2	2,4-dinitro-	16.9	2.4	0.13	2.68	40.0
3	3,4-dinitro-	18.1	4.1	0.08	1.83	41.0
4	pentachloro-	18.25	2.95	0.05	1.80	41.3
5	2,5-dinitro-	19.15	3.30	0.06	1.56	39.1
6	2,4,6-tri-iodo-	19.9_5	2.7	0.16	0.75	41.1
7	2,4,6-tribromo-	20.6	2.9	0.09	0.97	37.4
8	2,4,6-trichloro-	21.0	3.1	0.03	0.82	38.8
9	2,3,5-trichloro-	21.1	5.0	0.25	0.91	40.8
10	4-nitro-	21.55	4.4	0.04	1.55	37.7
11	2,6-dichloro-	22.4	2.9	0.10	1.08	42.0
12	3-nitro-	24.1	5.3	0.42	1.25	38.7

[a] Average of the standard deviations of two measurements using 14 points of each titration curve.

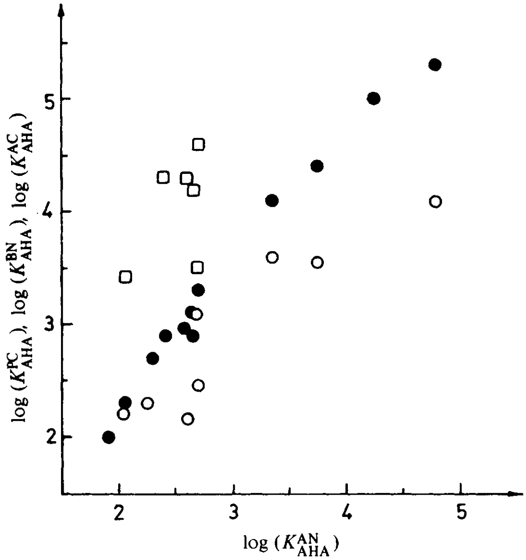

Fig. 2. Log K_{AHA} values in benzonitrile (●), propylene carbonate (○) and acetone (□) as a function of log K_{AHA} in acetonitrile for phenol–phenolate systems. Data for benzonitrile from this work, the rest from ref. (7)–(9).

CONDUCTIVITY MEASUREMENTS

The concentration dependence of the conductivity of tetrabutylammonium phenolates was evaluated using the Pitts equations for an incompletely dissociated electrolyte with a distance parameter $R = 10$ Å.[17] The equations were solved by an iterative procedure.[18]

The molar conductances Λ fell below the limiting Onsager slope, indicating incomplete dissociation. Values of the dissociation constants K_d are *ca.* 10^{-2} mol dm^{-3}, in close agreement with published values for other tetra-alkylammonium salts in BN.[11] There is no systematic substituent dependence of K_d. The limiting conductances Λ_0 fall within a relatively narrow range (table 1). With the value $\lambda_0 = 15.7\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ for the limiting conductance of the tetrabutylammonium ion in BN, the ionic conductances λ_0 for the substituted phenolate ions range from 21.7 to 26.3 Ω^{-1} cm^2 mol^{-1}. There is no direct relation between λ_0 and the sizes of the ions. Instead the degree of charge delocalization and polar interactions with the solvent seem to play some role.

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