

The Effect of Tetraalkylammonium Ions and Hydroxy Compounds on the Voltammetric Behavior of Azobenzene in Aprotic Dipolar Solvents. Part A. The Substrate–Anion Radical Redox Couple

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Wang, H., Ingemann, S., Ulstrup, J. and Hammerich, O., 1992. The Effect of Tetraalkylammonium Ions and Hydroxy Compounds on the Voltammetric Behavior of Azobenzene in Aprotic Dipolar Solvents. Part A. The Substrate–Anion Radical Redox Couple. – Acta Chem. Scand. 46: 178–185.

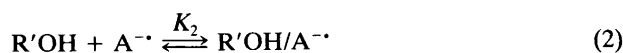
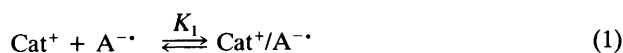
The equilibrium constants, K_i [eqn. (i)], for ion-pair formation between R_4N^+ ($R = \text{Me, Et, Pr}$ and Bu) and the azobenzene anion radical ($AZ^{\cdot-}$) in *N,N*-dimethylformamide (DMF), acetonitrile and propylene carbonate are too small to be determined by cyclic voltammetry. A small positive shift of approximately 10 mV observed for the reduction peak in passing from $R_4N^+ = \text{Me}_4N^+$ to $R_4N^+ = \text{Bu}_4N^+$ was attributed to liquid junction and interfacial effects.



The equilibrium constants, K_{ii} [eqn. (ii)], for hydrogen-bond formation between $R'OH$ ($R' = \text{H, Me, Et}$ and *i*-Pr) and $AZ^{\cdot-}$ in the same solvents were found to be in the range $0.4\text{--}1.6 \text{ M}^{-1}$ and for the alcohols to decrease with increasing size of R' . The effect of the structure of R_4N^+ on K_{ii} was small as demonstrated for water in DMF for which it was found that the magnitude of K_{ii} increased from 0.53 to 0.57 M^{-1} on passing from $R_4N^+ = \text{Me}_4N^+$ to $R_4N^+ = \text{Bu}_4N^+$. The deuterium equilibrium isotope effects for hydrogen-bonding were slightly larger than unity.

The results from this and earlier studies indicate that the magnitudes of the equilibrium constants for hydrogen-bonding between $R'OH$ and anion radicals derived from aromatic nitro, carbonyl and azo compounds are determined by both electrostatic and orbital interactions.

The stability and reactivity of anion radicals ($A^{\cdot-}$) and dianions (A^{2-}) in aprotic dipolar solvents depend strongly on the nature of the counter ions (Cat^+) and the presence of hydroxylic compounds ($R'OH$), such as water and aliphatic alcohols. Owing to work reported by the research groups of Szwarc,^{1–6} Parker,^{7–17} and Stevenson,^{18–34} as well as number of Polish workers^{35–45} and others,^{46–57} the effects of equilibria (1) and (2) on the thermodynamic and kinetic properties of a variety of anion radicals are now well established and as a result of this extensive work a number of general trends relevant to the present work have emerged. (In the following the slash, /, indicates a weak interaction for example a hydrogen-bond or that between the ions in an ion-pair).



First, the formation and dissociation of $\text{Cat}^+/A^{\cdot-}$ and $R'OH/A^{\cdot-}$ are generally fast processes^{25,26,32–34} with rate constants in the range $5 \times 10^7\text{--}1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (formation) and $10^7\text{--}10^8 \text{ s}^{-1}$ (dissociation). Accordingly, reactions (1) and (2) behave as equilibrium processes during cyclic voltammetry (CV) at voltage sweep rates up to at least 1000 V s^{-1} . Values of K ($= K_1$ or K_2) may be determined from eqn. (3), where ΔE_p is the peak potential shift for the reversible $A|A^{\cdot-}$ couple caused by addition of an excess of X ($= \text{Cat}^+$ or $R'OH$) to the voltammetry solution.^{8–13,41,42,44,57,58}

$$\Delta E_p \approx \frac{RT}{nF} \ln (1 + K[X]) \quad (3)$$

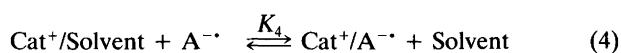
Secondly, K has been observed to depend strongly on the nature of the solvent.^{8–13,19,24,27,41,42,45,47,54,56} This indicates

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that eqns. (1) and (2) are oversimplifications of the more general equations (4) and (5). Values of ΔG° , ΔH° and ΔS° have been measured in a number of cases,^{8,11,12,19,20,22,29-31,46,52} but it is difficult to see definite trends related to structural properties of $A^{-\cdot}$ in the data.



Finally, in solvents such as hexamethylphosphoramide (HMPA), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and acetonitrile (MeCN) complexes higher than 1:1 seem to be of only minor importance for anion radicals whereas both 1:1 and 1:2 complexes have been observed for dianions.^{1-6,8,9,11,13,40,50}

The present work originated from our observation that the rate constant for electron transfer *from* the anion radicals of different aromatic hydrocarbons *to* the anion radicals of azobenzene (AZ) and halogen-substituted azobenzene in DMF increased significantly upon addition of water⁵⁹ or aliphatic alcohols⁶⁰ to the voltammetry solutions. Moreover, the electron transfer rate was found to depend significantly on the structure of the tetraalkylammonium salt used as the supporting electrolyte.⁶⁰ These observations were suggested to reflect the participation of ion-paired and/or hydrogen-bonded species in the electron transfer steps and for this reason it became of interest to explore the effect of Cat^+ and $\text{R}'\text{OH}$ on the voltammetric behavior of AZ in more detail. In the present study Cat^+ was a tetraalkylammonium ion, R_4N^+ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}$ or Bu) and $\text{R}'\text{OH}$ was water ($\text{R}' = \text{H}$) or an aliphatic alcohol ($\text{R}' = \text{Me}, \text{Et}$ or *i*-Pr). The solvents were DMF, MeCN and propylene carbonate (PC).

Results and discussion

The effect of R_4N^+ on the $\text{AZ}|\text{AZ}^{-\cdot}$ redox couple. The peak-to-peak separation for the $\text{AZ}|\text{AZ}^{-\cdot}$ redox couple at a voltage sweep rate (ν) of 1 V s^{-1} and $T = 297 \text{ K}$ was approximately 59 mV and the ratio of anodic to cathodic peak current was close to unity for all four supporting electrolytes independent of the solvent. The values of the half-peak width, $E_{p/2} - E_p$, and the quarter-peak width, $E_{p/4} - E_p$, for the reduction peak were 57 and 81 mV, respectively, where $E_{p/2}$ and $E_{p/4}$ are the potentials at $i = i_p/2$ and $i_p/4$. These values are close to those, 56.5 and 80.8 mV, predicted by theory^{61,62} for a reversible one-electron transfer reaction at 297 K and our results thus agree with earlier reports concerning the voltammetric reduction of AZ to $\text{AZ}^{-\cdot}$.^{37,63-67} Values of E_p and of $E_{p/2} - E_p$ and $E_{p/4} - E_p$ for the reduction peak in DMF are listed in Table 1.

From these data it is seen that reduction of AZ becomes increasingly difficult in the order $\text{Bu}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Et}_4\text{N}^+ < \text{Me}_4\text{N}^+$. Although the total effect amounts to only 10 mV we were initially puzzled by this trend, since it is the oppo-

Table 1. Peak potentials and peak widths for the reversible one-electron reduction of azobenzene in DMF containing different tetraalkylammonium salts as supporting electrolytes.^a

Supporting electrolyte	$-E_p/\text{mV}^b$	$(E_{p/2} - E_p)/\text{mV}$	$(E_{p/4} - E_p)/\text{mV}$
Bu_4NBF_4	1162.1	57.2	81.2
Pr_4NBF_4	1162.9	57.5	81.3
Et_4NBF_4	1167.1	57.1	80.9
Me_4NBF_4	1171.8	57.4	81.5
Bu_4NBF_4	1162.2	57.2	81.1
Pr_4NBF_4	1163.5	57.5	81.3
Et_4NBF_4	1168.2	57.7	81.5
Me_4NBF_4	1172.0	57.6	81.6
Bu_4NBF_4	1162.0	57.1	81.0
Pr_4NBF_4	1163.0	57.2	81.0
Et_4NBF_4	1167.5	57.6	81.5
Me_4NBF_4	1171.6	57.3	81.4

^aData from three different series of measurements at a supporting electrolyte concentration of 0.1 M and $C_{\text{AZ}} = 1.0 \text{ mM}$, $T = 297 \text{ K}$ and $\nu = 1.0 \text{ V s}^{-1}$. ^bPotentials versus an Ag-wire reference electrode (see the Experimental section).

site of that expected for formation of contact ion-pairs between R_4N^+ and $\text{AZ}^{-\cdot}$ considering the decreasing size of R_4N^+ in passing from Bu_4N^+ to Me_4N^+ . The possibility that the trend in the data might be an experimental artifact was ruled out by the following observations. First, the data were highly reproducible as seen in Table 1, which summarizes results obtained for three separate measurement series. Secondly, the peak shapes were independent of the structure of R_4N^+ as judged by the values of $E_{p/2} - E_p$ and $E_{p/4} - E_p$ (Table 1) which made it unlikely that the potential shift was caused by insufficient electronic compensation of the solution resistance.

The effect was not specific for the $\text{AZ}|\text{AZ}^{-\cdot}$ redox couple as demonstrated by the data for the reversible one-electron reductions of three aromatic hydrocarbons, anthracene (AN), perylene (PE) and triphenylene (TP). These data are summarized in Table 2 together with data for AZ in DMF at $T = 263 \text{ K}$ and in MeCN and it is noted that the effect is practically independent of the temperature and substrate structure. In contrast, an appreciable difference was observed between the results obtained for DMF and MeCN solutions. The average potential shift on passing from Bu_4N^+ to Me_4N^+ was 10.3 mV for DMF, while a value of 21.3 mV was observed for MeCN.

Petersen and Evans⁶⁸ have reported similar results for the reduction of a variety of compounds in MeCN containing tetraheptylammonium (Hep_4N^+) or tetraethylammonium perchlorate as supporting electrolytes. It was observed that the values of E_p were uniformly shifted in the positive direction when the supporting electrolyte was changed from Et_4NClO_4 to $\text{Hep}_4\text{NClO}_4$ and the potential shift was essentially independent of the substrate structure. The average shift for 26 compounds was $21 \pm 8 \text{ mV}$.

Thus, there seems no doubt that the effect of the struc-

Table 2. Peak potentials for the reversible one-electron reductions of azobenzene, anthracene, perylene and triphenylene in DMF or MeCN containing different tetraalkylammonium salts as supporting electrolytes.^a

Supporting electrolyte	$\Delta E_p/mV^b$						
	DMF					MeCN	
	AZ	AZ ^c	AN	PE	TP	AZ	PE
Bu ₄ NBF ₄	0	0	0	0	0	0	0
Pr ₄ NBF ₄	1.1	0.7	0.4	0.1	0.6	5.3	1.0
Et ₄ NBF ₄	5.5	5.8	5.8	5.6	4.5	8.6	6.4
Me ₄ NBF ₄	9.7	10.2	10.2	10.9	18 ^d	20.0	22.5

^aIn solvent containing R₄NBF₄ (0.1 M) at C_{substrate}^o = 1.0 mM, T = 297 K and v = 1.0 V s⁻¹. ^bE_p(Bu₄NBF₄) - E_p(R₄NBF₄). ^cAt T = 263 K and v = 0.05 V s⁻¹. ^dUncertain value due to background interference.

ture of R₄N⁺ on E_p is real. It has been pointed out⁶⁸ that part of the potential shift must be due to different liquid junction potentials, E_j, between the reference electrode and the voltammetry solutions. Values of E_j may be estimated from the Lewis-Sargent equation,⁶⁹ eqn. (6), where $\Lambda_{R_4NBF_4}^o$ (= $\Lambda_{R_4N^+}^o + \Lambda_{BF_4^-}^o$) is the limiting conductivity of R₄NBF₄.

$$E_j = \frac{RT}{F} \ln \frac{\Lambda_{Bu_4NBF_4}^o}{\Lambda_{Me_4NBF_4}^o} \quad (6)$$

The values of $\Lambda_{Bu_4N^+}^o$ (25.4 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [DMF]; 64.1 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [MeCN]), $\Lambda_{Me_4N^+}^o$ (38.8 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [DMF]; 94.5 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [MeCN]) and $\Lambda_{BF_4^-}^o$ (108.5 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [MeCN]) are available in the literature⁷⁰ and $\Lambda_{BF_4^-}^o$ in DMF (47.5 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) was determined from the Walden equation,⁷¹ eqn. (7), using $\Lambda_{BF_4^-}^o$ for MeCN and the appropriate viscosities, η (0.80 cP [DMF]; 0.35 cP [MeCN]).⁷⁰

$$\Lambda^{DMF} \times \eta^{DMF} = \Lambda^{MeCN} \times \eta^{MeCN} \quad (7)$$

The resulting E_j amounts to approximately -4 mV (DMF) and -5 mV (MeCN) for measurements carried out using a reference electrode containing Bu₄NBF₄ immersed in voltammetry solutions containing Me₄NBF₄. The origin of the remaining 6 mV for DMF and 15 mV for MeCN is unknown at present, but the fact that compounds of very dissimilar structure⁶⁸ give similar results indicates that the potential shifts are related to different properties of the electrode-solution interface rather than different bulk properties of the solvent-supporting electrolyte mixture. Our observation that the effect is more pronounced in MeCN than in DMF supports this view, since cations are generally better solvated in DMF than in MeCN,⁷² in accordance with expected stronger adsorption of the long-chain R₄N⁺ ions in MeCN. A clue to the effect could rest on the different size match between the substrates and

R₄N⁺. Azobenzene and the hydrocarbons are notably larger than Me₄N⁺ and in the presence of this cation the anion radicals are likely to be released from the electrode surface immediately after electron transfer. On the other hand, A and A^{-•} might be temporarily 'trapped' by the much larger Bu₄N⁺ at the surface located in partly solvent-filled regions between the Bu₄N⁺ ions adjacent to the electrode. If this should happen the charged A^{-•} state would be stabilized by favorable image charge or electron exchange interactions with the metal resulting in a positive shift of the reduction peak.

Our data do not warrant further conclusions regarding the nature of the phenomenon, but we wish to emphasize that the potential differences are small and likely to pass unnoticed at a measurement precision of e.g. ± 10 mV typical for much of the earlier work referred to above. In this light our results agree with previous studies where it was found that the reduction potential for AZ and related azo compounds in DMF was essentially the same for Cat⁺ = Et₄N⁺, K⁺ and Na⁺.^{37,38,63} Thus, it is concluded that the values of K₈, eqn. (8), for the formation of R₄N⁺/AZ^{-•} in commonly applied aprotic dipolar solvents are too small to be detected by voltammetry.



These results are not exceptional. Other aromatic compounds for which ion-pairs with R₄N⁺ in aprotic dipolar solvents could not be detected include benzophenone (DMF^{35,40}), fluorenone (DMF^{35,36}), 1,2,3-indanetrione (DMF³⁶), benzil (DMF and DMSO³⁹ and DMF⁵⁷), azoxybenzene (DMF⁴³), nitrosobenzene (DMF⁴⁴), and cyano compounds such as cyano- and dicyano-benzenes (DMF⁵¹) and tetracyanoquinodimethane (MeCN⁵⁵). In contrast, appreciable values of K₈ have been observed for nitrobenzene (DMF⁴¹ and DMSO-MeCN mixtures⁴⁵). The reason for this difference is not clear.

The effect of R'OH on the AZ|AZ^{-•} redox couple. Evaluation of the equilibrium constant, K, for hydrogen-bonding through measurements of ΔE_p is often complicated by protonation, that is by the complete transfer of the proton from R'OH to A^{-•}, eqn. (9), followed by further reaction of AH[•]. However, it is possible in many cases to outrun reaction (9) by proper choice of v. In this study we used v = 10 V s⁻¹ for DMF, while v = 100 V s⁻¹ was required for MeCN and PC.



Another issue to be considered is whether the residual water always present in so-called non-aqueous solvents affects the results. In this work the solvent-supporting electrolyte mixtures were carefully dried by being passed through a column of activated alumina immediately before the measurements were made (see the Experimental sec-

tion). The concentrations of residual water in the resulting solutions are typically less than 5 mM.⁸ The fact that stoichiometric concentrations of R'OH of 40 mM or more were necessary in most experiments to bring about a measurable peak potential shift thus led to the conclusion that the effect of residual water was negligible.

In discussions of R'OH effects on the formal potentials for reduction of A to A^{-•} it is usually assumed that the observed E_p changes are related only to A^{-•}. However, the stability of the parent compound, A, might also be affected by the composition of the solvent-supporting electrolyte mixture, in particular for substrates containing hydrogen-bond accepting oxygen or nitrogen atoms, eqn. (10).



Taking equilibrium (10) into consideration leads to the more general equation, (11), which reduces to eqn. (3) for $K_{10} = 0$. It is also noted that no E_p shift is expected for an A|A^{-•} redox system for which K_2 and K_{10} are equal.

$$\Delta E_p \approx \frac{RT}{nF} \ln \frac{1 + K_2[\text{R'OH}]}{1 + K_{10}[\text{R'OH}]} \quad (11)$$

Information about K_2 and K_{10} is available for only few substrates. One such case is A = ninhydrin and R'OH = EtOH for which K_2 and K_{10} have been measured in HMPA.³¹ It was found that K_{10} was not only significant but, in fact, 4.5 times larger than K_2 . The enthalpy of formation, ΔH° , was more negative for R'OH/A^{-•} than for R'OH/A, as intuitively expected considering the increased affinity of the anion radical relative to the neutral compound for the partially positive hydrogen in R'OH. This effect, however, was more than cancelled by a large negative entropy change, ΔS° , associated with hydrogen-bond formation to the anion radical. We do not draw general conclusions concerning the relative magnitudes of K_2 and K_{10} from

Table 3. Reversible peak potential shifts, ΔE_p , for the voltammetric reduction of azobenzene as a function of the concentration of added water, and equilibrium constants, $K_{\text{water}}^{\text{DMF}}$, for the formation of the H₂O/AZ^{-•} hydrogen-bond complex in DMF.^a

$C_{\text{water}}^\circ/\text{mM}$	$\text{R}_4\text{N}^+ = \text{Bu}_4\text{N}^+$		$\text{R}_4\text{N}^+ = \text{Me}_4\text{N}^+$	
	$\Delta E_p/\text{mV}^b$	$K_{\text{water}}^{\text{DMF}}/\text{M}^{-1}^c$	$\Delta E_p/\text{mV}^b$	$K_{\text{water}}^{\text{DMF}}/\text{M}^{-1}^c$
100	1.6	0.65	1.3	0.52
200	2.8	0.58	2.9	0.60
300	3.9	0.55	3.6	0.51
400	4.7	0.51	4.6	0.50
	av. 0.57 ± 0.06		av. 0.53 ± 0.05	

^aIn solvent containing R_4NBF_4 (0.1 M) at $T = 295 \text{ K}$, $\nu = 10 \text{ V s}^{-1}$ and $C_{\text{AZ}}^\circ = 1.0 \text{ mM}$. ^bRelative to E_p for azobenzene in the absence of added water. ^cFrom eqn. (3).

Table 4. Reversible peak potential shifts, ΔE_p , for the voltammetric reduction of azobenzene as a function of the concentration of added methanol and equilibrium constants, $K_{\text{MeOH}}^{\text{MeCN}}$, for formation of the MeOH/AZ^{-•} hydrogen-bond complex in MeCN.^a

$C_{\text{MeOH}}^\circ/\text{mM}$	$\Delta E_p/\text{mV}^b$	$K_{\text{MeOH}}^{\text{MeCN}}/\text{M}^{-1}^c$
20	3.1	6.5
40	5.9	6.6
60	8.6	6.7
80	10.9	6.8
100	12.9	6.7
	av. 6.7 ± 0.1	

^aIn solvent containing Bu_4NPF_6 (0.1 M) at $T = 292 \text{ K}$, $\nu = 100 \text{ V s}^{-1}$ and $C_{\text{AZ}}^\circ = 1.0 \text{ mM}$. ^bRelative to E_p for azobenzene in the absence of added methanol. ^cFrom eqn. (3).

these data since ninhydrin in HMPA may not be typical, but just point out that K_2 values obtained from eqn. (3) should be considered as minimum values as long as the corresponding values of K_{10} are not known. To the best of our knowledge, values of K_{10} for the hydrogen-bond formation between AZ and the hydroxy compounds used in this study are not available for DMF, MeCN or PC. However, it has been reported⁷³ that K_{10} for BuOH/AZ in chloroform is 0.28 M^{-1} . Owing to the much stronger hydrogen-bond accepting properties of the solvents applied in our study the values of K_{10} for these solvents are expected to be smaller, but not necessarily negligible. For this reason we restrict our discussion to general trends in the data and to comparison with reports on related substrates. Two typical sets of data for K_{12} [eqn. (12)] are shown in Tables 3 and 4. (Here and in the following the sub- and super-scripts refer to the particular R'OH and solvent, respectively).



The values of ΔE_p were usually quite small, which raised the question as to whether the data for K_{12} might be affected by the structure of the supporting electrolyte ions. For this reason $K_{\text{water}}^{\text{DMF}}$ was determined in the presence of either Bu_4NBF_4 or Me_4NBF_4 and the results in Table 3 show that the average value for Me_4N^+ , 0.53 M^{-1} , is only slightly smaller than the value, 0.57 M^{-1} , for Bu_4N^+ . The same tendency, that the smaller cation gives rise to a slightly smaller equilibrium constant, has been observed for PhCOCH_3 for which K_{12} for Bu_4NBF_4 and Et_4NBF_4 was 20.2 M^{-1} and 16.6 M^{-1} , respectively.⁹ In both cases the effect is small, which suggests that K_{12} is not affected significantly by the structure of R_4N^+ and in the following we report results for Bu_4N^+ only. Larger differences between other cations have, however, been observed. The value of K_{12} for the $\text{H}_2\text{O}/\text{PhNO}_2^{-\bullet}$ complex in DMF was for example found to be 2.3 M^{-1} in the presence of Bu_4N^+ ,¹² while the value was only 0.31 M^{-1} for Na^+ .⁴² We did not observe any

Table 5. Equilibrium constants, $K_{R'OH}^{Solvent}$, and deuterium equilibrium isotope effects, $K_{R'OH}^{Solvent}/K_{R'OD}^{Solvent}$, for the formation of the hydrogen-bonded complexes, $R'OH/AZ^{-}$, between azobenzene anion radical and hydroxylic compounds in aprotic dipolar solvents.^a

R'OH	DMF ^b		MeCN ^c		PC ^d	
	$\frac{K_{R'OH}^{DMF}}{M^{-1}}$	$\frac{K_{R'OH}^{DMF}}{K_{R'OD}^{DMF}}$	$\frac{K_{R'OH}^{MeCN}}{M^{-1}}$	$\frac{K_{R'OH}^{MeCN}}{K_{R'OD}^{MeCN}}$	$\frac{K_{R'OH}^{PC}}{M^{-1}}$	$\frac{K_{R'OH}^{PC}}{K_{R'OD}^{PC}}$
H ₂ O	0.6		4.4		5.2	
D ₂ O	0.5	1.2	4.0	1.1	4.9	1.1
CH ₃ OH	1.6		6.7		6.9	
CH ₃ OD	1.5	1.1	5.8	1.2	5.5	1.3
CH ₃ CH ₂ OH	0.9		4.4		4.6	
(CH ₃) ₂ CHOH	0.4		2.3		2.8	

^aIn solvent containing Bu₄NPF₆ (0.1 M); C_{AZ}²⁻ = 1.0 mM. The values of C_{R'OH}⁰ were, in most cases, kept between 40 and 200 mM. ^bAt $v = 10 \text{ Vs}^{-1}$ and $T = 294 \text{ K}$. ^cAt $v = 100 \text{ Vs}^{-1}$ and $T = 292 \text{ K}$. ^dAt $v = 100 \text{ Vs}^{-1}$ and $T = 294 \text{ K}$.

influence of the supporting electrolyte anion which was either BF₄⁻ or PF₆⁻.

A slight trend in the data was occasionally observed as, for example, seen in Table 3. These trends were not reproducible and are likely to be incidental considering that the standard deviations for the potential measurements were typically $\pm 0.6 \text{ mV}$ (see the Experimental section). Only 1:1 complexes therefore seem to be important for AZ²⁻ in line with the work cited in the introduction.

The values of K_{12} obtained for all four hydrogen-bond donors in three different solvents are summarized in Table 5.

The data show that K_{12} varies with R'OH in the order MeOH > EtOH \approx H₂O > *i*-PrOH independently of the solvent. This agrees with the trend reported by Parker⁸ for PhCHO and aliphatic alcohols in DMF. The effect was thought to reflect mainly the size of the alkyl group as almost identical values of K_{12} were found for primary alcohols. Similar effects of the structure of R₄N⁺ have been found in studies of PhCHO,¹¹ PhCOPh¹² and PhNO₂.^{12,19}

The equilibrium isotope effect, $K_{R'OH}^{Solvent}/K_{R'OD}^{Solvent}$, was found to be between 1.1 and 1.3 for all the systems (Table 5). This is in keeping with data reported for PhCOCH₃⁹ and PhCHO¹¹ in DMF. The small values have been regarded as indicative of the same type of binding forces in R'OH/A²⁻ and R'OH/Solvent.⁹

So far the available data are too scarce to warrant a detailed discussion of the relation between K_{12} and the structure of the substrate. For the substituted nitrobenzenes and benzophenones it has been found¹² that K_{12} for H₂O/A²⁻ and MeOH/A²⁻ in DMF increased with increasing electron donating ability of the substituent, but that the Hammett plots based on σ_p are not linear. On the other hand, almost linear Hammett plots were observed for MeOH/ArNO₂²⁻ in HMPA if the substituents were limited to being electron withdrawing and σ_p^+ was used instead of σ_p .²⁴ The largest set of published data relate to H₂O/A²⁻ (A = ArCHO, PhCOCH₃, ArCOAr and ArNO₂) in DMF^{9,11-13} and we have found that $\log K_{12}$ for this series of

compounds correlate linearly (Fig. 1, $r = -0.971$) with the electron affinity (E_{ea}) of A. (Values of E_{ea} have been determined experimentally⁷⁴ only for the 11 compounds included in Fig. 1). However, the data point for AZ (●) resulting from this work and a recently published⁷⁵ value of E_{ea} deviates significantly from the correlation line. Essentially the same pattern was observed for the relation between $\log K_{12}$ for MeOH/A²⁻ in DMF and E_{ea} .

Some insight into the origin of the deviation of the AZ point from the correlation lines was gained through a series of AM1 calculations.⁷⁶ The results for the anion radicals derived from the aromatic nitro and carbonyl compounds show that the highest electron density is found at the oxygen atom(s) in all cases and the values, which are in the range -0.46 to -0.51 , show remarkably small dependence on the structure of A²⁻. Thus, the electrostatic contribution to the energy of the hydrogen-bond for these anion radicals

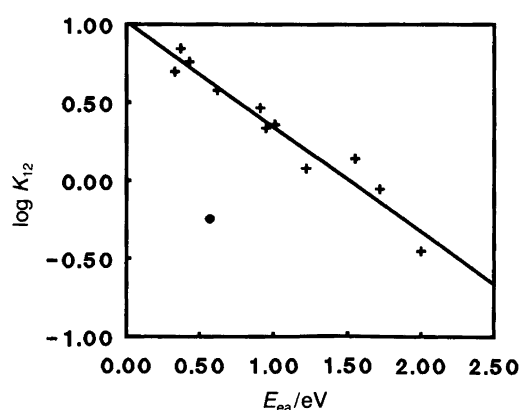


Fig. 1. $\log K_{12}$ as a function of E_{ea} for C₆H₅COCH₃, *p*-CH₃C₆H₄CHO, C₆H₅CHO, C₆H₅COC₆H₅, *p*-CH₃OC₆H₄NO₂, *p*-CH₃C₆H₄NO₂, C₆H₅NO₂, *p*-NCC₆H₄CHO, *p*-CH₃COC₆H₄NO₂, *p*-O₂NC₆H₄CN and *p*-O₂NC₆H₄NO₂ (listed in order of increasing E_{ea}). The values for K_{12} are taken from Refs. 9, 11 and 12 and those for E_{ea} are from Ref. 74. The data point given by a filled circle (●) is for the anion radical of C₆H₅N=NC₆H₅ (this work and Ref. 75).

is essentially constant and the observed variation in K_{12} with structure appears to be determined mainly by orbital interactions. The calculations for AZ^{--} show that the negative charge is more evenly distributed in this anion radical with values close to -0.2 for the electron densities at the two nitrogen atoms and the carbon atoms in the 4- and 4'-positions. Accordingly, the electrostatic contribution to the hydrogen-bond energy is smaller for AZ^{--} than for the anion radicals derived from aromatic nitro and carbonyl compounds and we suggest this to be the major reason for the relatively small values of K_{12} observed for H_2O/AZ^{--} and $MeOH/AZ^{--}$. A more detailed study of these effects is in progress.

When the results for the different solvents are compared it is seen that the values of K_{12} for DMF are uniformly smaller than for MeCN and PC, which are very similar. The same trend was observed⁹ for the $H_2O/PhCOCH_3^-$ complex for which K_{12} was determined to be $5 M^{-1}$ in DMF and $21 M^{-1}$ in MeCN. The effect of the solvent has been attributed to differences in the $R'OH/Solvent$ interactions,⁹ eqn. (5), which are smaller for MeCN and PC than for DMF. A similar dependence has been noticed for the observed rate constants for protonation of the anthracene anion radical by substituted phenols.⁷⁷ The rate constants were found to vary in the order $DMSO < DMF \ll PC < MeCN$ and it was shown that the major factor controlling the solvent attenuation was indeed the strength of the $ArOH/Solvent$ interactions.

The effect of temperature on K_{12} for H_2O/AZ^{--} was measured in all three solvents. The data followed eqn. (13) in the temperature ranges given in Table 6 which also gives the values of ΔG° , ΔH° and ΔS° .

$$\ln K_{12} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

It is noteworthy that ΔH° is negative in all three solvents. The values, given in parentheses as $\Delta H^\circ/kcal mol^{-1}$, for MeCN (-2.0) and PC (-2.0) are lower than that for DMF (-1.1) and identical to within experimental error. This accounts for the similar behavior of these two solvents. Small negative values of ΔH° seem to be general for reactions in $DMF-Bu_4N^+$, which is the only solvent- R_4N^+ sys-

Table 6. Thermochemical data for the formation of the H_2O/AZ^{--} hydrogen-bond complex in aprotic dipolar solvents.^a

Solvent	ΔG° kcal mol ⁻¹	ΔH° kcal mol ⁻¹	ΔS° cal mol ⁻¹ K ⁻¹
DMF	0.26	-1.1	-4.5
MeCN	-0.8	-2.0	-4.3
PC	-1.0	-2.0	-3.3

^aAt $C_{AZ}^\circ = 1.0$ mM in solvents containing Bu_4NPF_6 (0.1 M). The temperature ranges were the following: DMF (255–294 K), MeCN (225–296 K) and PC (273–295 K).

tem for which data have been published for a range of H_2O/A^- . For comparison the following values have been found: $PhCHO$ (-0.64),¹¹ $PhNO_2$ (-0.44)¹² and $PhCOPh$ (-1.43).¹² ΔS° depends less on the solvent, and it thus appears that K_{12} is determined mainly by enthalpy. It should be noticed that appreciable substituent effects have been observed for ΔH° in the $PhNO_2$ and $PhCOPh$ series and it is difficult to identify definitive trends in the data. The same relates to ΔS° , which may take both negative and positive values. However, this lack of a relationship between structure and ΔH° or ΔS° may only be apparent, since even eqn. (5) is an oversimplification and does not include contributions from the solvation of A^- , which may be subject to separate substituent effects.

The general conclusion with respect to the thermodynamic stability of AZ^{--} in the three aprotic dipolar solvents in this study is that ion-pairing with R_4N^+ is insignificant, whereas hydrogen-bonding effects can be detected, but are small. The observation that hydrogen-bond formation stabilizes AZ^{--} relative to ion-pair formation with R_4N^+ has been observed in a number of related cases.^{19,25,40}

Experimental

Reagents, electrolytes and solvents. Azobenzene (Fluka, *purum*), anthracene (Rhône-Poulenc, *Prolabo pur*), perylene (Aldrich, 99+ %) and triphenylene (Fluka, *purum*) were used as received. Tetramethylammonium tetrafluoroborate (Fluka, *purum*), tetraethylammonium tetrafluoroborate (Fluka, *puriss.*), tetrapropylammonium tetrafluoroborate (Fluka, *purum*) and tetrabutylammonium tetrafluoroborate (Fluka, *puriss.*) were all used without further purification. Tetrabutylammonium hexafluorophosphate was prepared from tetrabutylammonium hydrogensulfate (Aldrich) and hexafluorophosphoric acid (Fluka, *tech.* 75 % solution in water) by a procedure similar to that described earlier for tetrabutylammonium tetrafluoroborate.⁷⁸ *N,N*-Dimethylformamide (Riedel deHaën) was distilled at reduced pressure prior to use. Acetonitrile (Romil Chemicals, far UV) and propylene carbonate (Fluka, *purum*) were used as received. The solvent/supporting electrolyte mixtures were passed through a column filled with activated neutral alumina (Woelm, W 200) immediately before the voltammetric measurements were made.

Instrumentation. The electrochemical instrumentation, cells and electrodes were the same as described earlier.^{59,78} The reference electrode was an Ag-wire in contact with a 0.1 M solution of Bu_4NBF_4 in DMF, MeCN or PC.

Peak potential measurements. Peak potentials, E_p , for the reduction of azobenzene were recorded by linear sweep voltammetry applying a linear extrapolation of the baseline.⁷⁸ The values given are averages of 6 to 12 measurements for the hydrogen-bond effects and of 20 to 30 measurements for the ion-pair effect. The standard deviations were typically ± 0.6 mV.

Quantum chemical calculations. The charge distributions of the anion radicals were estimated by means of AM1 calculations (J. J. P. Stewart, *QCPE #455*, MOPAC, version 4.02) carried out on an IBM 6151-115 desk computer equipped with an Advanced Floating Point Accelerator.

Acknowledgements. The authors thank The Danish Natural Science Research Council and The Carlsberg Foundation for financial support and Henan Normal University for making the stay of H.W. possible. Dr. Peter Sommer-Larsen is acknowledged for helpful discussions on the semi-empirical calculations and Dr. Andrej Mendkovich for providing us with the results of Ref. 73.

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Received May 2, 1990.