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H-Bond Acceptor Parameters for Anions

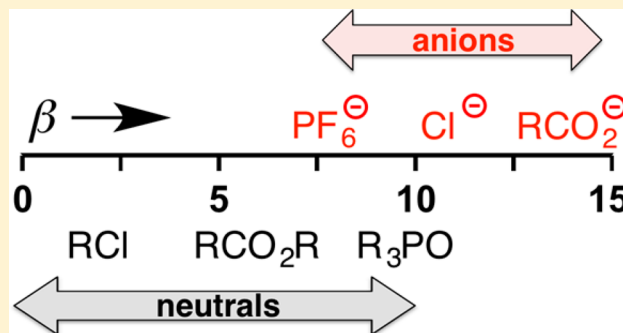
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Supporting Information

ABSTRACT: UV/vis absorption titrations have been used to investigate the formation of H-bonded complexes between anionic H-bond acceptors (HBAs) and neutral H-bond donors (HBDs) in organic solvents. Complexes formed by three different HBDs with 15 different anions were studied in chloroform and in acetonitrile. The data were used to determine self-consistent HBA parameters (β) for chloride, bromide, iodide, phosphate diester, acetate, benzoate, perchlorate, hexafluorophosphate, hydrogen sulfate, methyl sulfonate, triflate, and perfluorobutyl sulfonate. The results demonstrate the transferability of H-bond parameters for anions between different solvents and different HBD partners, allowing reliable prediction of anion recognition properties in other scenarios. Carboxylates are the strongest HBAs studied, with β parameters (≈ 15) that are significantly higher than those of neutral organic HBAs, and the non-coordinating anion hexafluorophosphate is the weakest acceptor, with a β parameter comparable to that of pyridine. The effects of ion pairing with the counter-cation were found to be negligible, provided small polar cations were avoided in the less polar solvent (chloroform). There is no correlation between the H-bonding properties of the anions and the pK_a values of the conjugate acids.



INTRODUCTION

Molecular recognition events involving anions are fundamental to a wide range of biological processes.¹ The regulation of non-covalent interactions formed in a specific but transient manner between biomolecules is widely exploited within the body to perform essential tasks and achieve function.² Synthetic systems have extensively employed the formation of H-bonding interactions to anions as a key molecular recognition motif in supramolecular chemistry,^{3,4} finding applications in a wide range of processes including catalysis,⁵ responsive materials,⁶ ion extraction,⁷ transportation,⁸ and sensing.⁹ However, there are numerous factors that influence the properties of non-covalent interactions, complicating the analysis of the operational basis of complex systems. In order to gain a deeper insight into the factors which govern molecular recognition, a quantitative approach to non-covalent interactions is required. Despite the importance of H-bonding to anions, the development of a quantitative analysis of the behavior of charged species in solution has been slow to emerge.

Abraham developed quantitative scales for the H-bond acceptor (HBA) and H-bond donor (HBD) strengths of neutral organic functional groups.¹⁰ These scales were established through analysis of experimentally determined association constants (K) for formation of H-bonded complexes in carbon tetrachloride solution.^{10–12} The H-bonding properties of neutral molecules were described using eq 1.

$$\log K = c_1 \alpha_2^H \beta_2^H + c_2 \quad (1)$$

where c_1 and c_2 are constants related to the solvent, and α_2^H and β_2^H represent the HBD and HBA properties of the solutes.

H-bond descriptors α_2^H and β_2^H have been measured for a wide range of different compounds^{10–12} and have been used to construct linear free energy relationships (LFERs) to predict the behavior of neutral solutes in a number of biological and physicochemical processes.¹³ We have extended this approach to explicitly include the influence of solvent on solution-phase equilibria between H-bonded solutes. The solvent competition model illustrated in Figure 1 is based on a comparison of the relative stabilities of pairwise contacts between solvent and solute.¹⁴

Provided HBD and HBA parameters are available for the solutes (α and β) and the solvent (α_s and β_s), eq 2 can be used to predict the Gibbs free energy change (ΔG°) for formation of a H-bonded complex in any solvent.¹⁵

$$\Delta G^\circ = -(\alpha - \alpha_s)(\beta - \beta_s) + 6 \quad (2)$$

where the adverse free energy associated with formation of a bimolecular complex in solution has been experimentally determined to be 6 kJ mol⁻¹ in carbon tetrachloride and is assumed to be a constant in other solvents.

It is also possible to use eq 2 to determine H-bond parameters for solutes or solvents on the basis of experimentally measured association constants for H-bond formation.^{14–19} For

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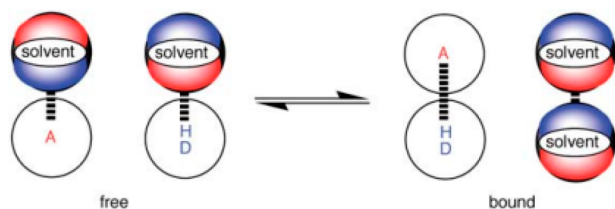


Figure 1. Solvent competition model for the formation of a H-bonded complex between two solutes. The position of equilibrium is determined by the energies of the solute–solvent interactions in the free state, and the solute–solute and solvent–solvent interactions in the bound state. DH represents a H-bond donor solute, and A is a H-bond acceptor solute.

example, if the α , α_s , and β_s parameters for a particular system are known, then experimental determination of the association constant (K) for formation of a complex between the HBD and any HBA can be used to determine the β value through rearrangement of eq 2 to give eq 3.

$$\beta = \beta_s + (RT \ln K + 6)/(\alpha - \alpha_s) \quad (3)$$

This approach has been used to quantify the HBA strength of a wide range of neutral organic functional groups.^{19–22} To date, trialkyl amine oxide and trialkyl phosphine oxide are two of the strongest neutral organic HBAs on the H-bond acceptor scale, with β values of 11.6 and 10.7, respectively.^{22,23} The HBA properties of neutral organometallic compounds have been determined in the same way, and a β value of 12.1 was measured for *trans*-[Ni(F)(2-C₅NF₄)(PEt₃)₂].²³ Here, this approach is used to add anionic species to the β H-bond scale.

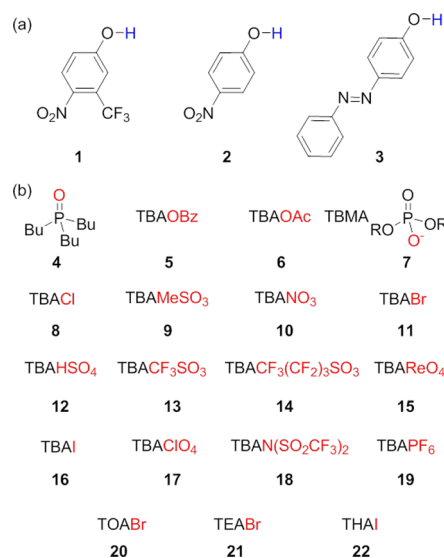
Marcus and co-workers have utilized the Gibbs free energy of transfer (ΔG_{tr}°) and enthalpy (ΔH_{tr}°) of ions from water to other solvents and correlated the values with properties of the solvents using multiple linear regression analysis.²⁴ Linear solvation energy relationships (LSERs) constructed from these data were employed to elucidate information about interactions of the ions with the first solvation shell in aqueous and nonaqueous solvents. The LSER approach has also been used to derive H-bond descriptors for the solvation properties of ionic species.²⁵

Several groups have reported association constants for H-bonded complexes between quaternary ammonium halide salts and HBDs (phenols, trihaloalkanes, and alcohols),^{26–29} and Abraham and co-workers used these results to estimate β_2^H values for halide anions.³⁰ As the H-bond scales of Hunter and Abraham can be interconverted,²³ estimates of β values for halides can be obtained from these results: 11.3–12.7 (Cl[−]), 10.2–10.7 (Br[−]), and 8.7–9.9 (I[−]). Here, we describe measurement of the HBA parameters (β) of a diverse series of monovalent anions using experiments in three different solvents and titrations with three different HBDs. The influence of ion pair formation on the HBA properties of the anions has also been quantified through systematic variation of the counter-cation.

RESULTS

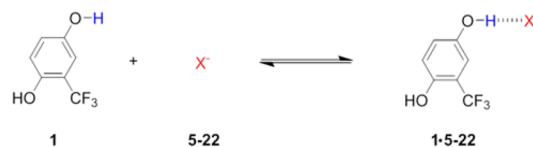
Three donors of differing HBD strength—4-nitro-3-trifluoromethylphenol (**1** $\alpha = 5.1$), 4-nitrophenol (**2** $\alpha = 4.7$), and 4-phenylazophenol (**3** $\alpha = 4.3$)—and 18 HBAs (**5–22**, Scheme 1) were selected to study the formation of H-bonded complexes between neutral donors and charged acceptor species (Scheme 2). The three HBD all have an absorption

Scheme 1. (a) H-Bond Donors and (b) H-Bond Acceptors Employed in This Study^a



^aCounter-cations: TBA = tetrabutylammonium, TBMA = tributylmethylammonium, THA = tetrahexylammonium, and TOA = tetraoctylammonium.

Scheme 2. Formation of a H-Bonded Complex between a Neutral Donor and a Charged Acceptor, X[−]



maximum in the UV/vis region that changes significantly on formation of a H-bond, facilitating measurement of association constants. In addition, the HBD parameters span a range of values that are all near the top of the α scale, and so stable complexes are formed even with less polar anions in competitive solvents. Phosphine oxide **4** was additionally employed as a HBA to align with previous studies undertaken for neutral solutes.^{20,21} The 15 distinct anions selected as HBAs include a series of halides and sulfonates, acetate, benzoate, phosphate diester, perchlorate, nitrate, and perchlorate (**5–19**, Scheme 1). Titration experiments were also carried out with the TBA salts of succinimide, tetrafluoroborate, cyanate, and nitrite, but problems relating to deprotonation of the HBD, overlapping signals, or lack of appreciable binding precluded use of these data for determination of β parameters for these anions.

To permit direct comparison of the HBA properties of the anions in Scheme 1, the same tetrabutylammonium counterion was used in **5–19**. The influence of the counterion on H-bonding interactions with Br[−] and I[−] was investigated through variation of the alkyl group of the quaternary ammonium cation: butyl (**11**), octyl (**20**), and ethyl (**21**) for Br[−]; butyl (**16**) and hexyl (**22**) for I[−] (Scheme 1).

Two different solvents were used for the titration experiments: acetonitrile and chloroform. These solvents have quite different H-bonding and dielectric properties: chloroform has a dielectric constant of 4.8 and is primarily a HBD, whereas acetonitrile has a dielectric constant of 37.5 and is primarily a HBA.¹⁵ The tetraalkylammonium salts used as guests in the titration experiments have good solubility in both solvents. The

neutral H-bond scales were originally developed on the basis of measurements made in carbon tetrachloride and trichloroethane,^{10–12} so to test interchangeability with the more polar solvents used here, UV/vis absorption titration experiments were also carried out for the neutral HBA 4 in carbon tetrachloride, chloroform, and acetonitrile. The effect of the water content of the solvent was also investigated.

Association Constants. Compounds 1–3 all have a UV/vis absorption band that is sensitive to formation of H-bonds, providing a convenient method to monitor binding.^{15,17,20} Accordingly, UV/vis absorption titration experiments were carried out by adding each of the HBAs, 4–22, to each of the HBDs, 1–3, in acetonitrile and in chloroform. Representative UV/vis absorption spectra from the titrations are shown in Figure 2. Upon the addition of increasing quantities of 4–22 to

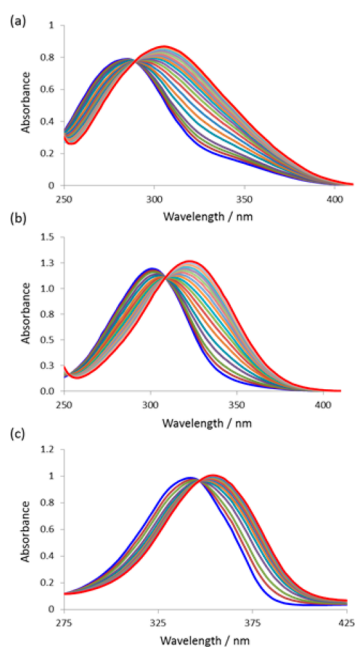


Figure 2. UV/vis absorption spectra for titration of 8 into (a) 1 (0.13 mM), (b) 2 (0.11 mM), and (c) 3 (0.049 mM) in chloroform at 298 K. The initial spectra of unbound 1, 2, and 3 are shown in blue, and the final spectra corresponding to the bound complexes 1·8, 2·8, and 3·8 are shown in red.

1–3, bathochromic shifts of the UV/vis bands were seen: typically 284–306 nm for 1, 300–322 nm for 2, and 344–358 nm for 3 in chloroform (Figure 2).

In general, the data for the anion titrations fit well to a 1:1 binding isotherm, and the resulting association constants are shown in Table 1. In some cases (15, 16, and 22), UV/vis absorption of the guest prevented acquisition of suitable data due to overlap with the spectrum of the host, 1 or 2 (see Supporting Information). However, 3 absorbs at significantly longer wavelengths than 1 and 2 (Figure 2), so it was possible to measure association constants with this HBD. In acetonitrile at high concentrations of guest (9 and 11), proton transfer was observed in some cases. Formation of phenolate anions is associated with the appearance of absorption bands at 405 nm for 1, 420 nm for 2, or 476 nm for 3 (see Supporting Information).^{20c,21} However, it was possible to obtain a reasonable degree of saturation (55–70%) before deprotonation became significant, and so association constants could be determined. For the neutral HBA 4, the titration data were fit

to an isotherm that allowed for a second weaker binding interaction, as described previously.¹⁵

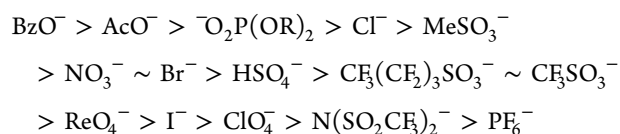
The association constants measured for the complexes span 3 orders of magnitude (Table 1). The relative polarities of the solvents and solutes determine the stabilities of the H-bonded complexes (Table 2). Consequently, the largest association constants are observed in the carbon tetrachloride, followed by chloroform, with the lowest association constants in acetonitrile. For example, the stability of the 2·4 complex goes from 99 000 M⁻¹ in carbon tetrachloride to 1400 M⁻¹ in chloroform and 110 M⁻¹ in acetonitrile. For the weaker HBAs (13–19 and 22), the association constants were too low to be measured in acetonitrile.

Salts are likely to be strongly solvated by adventitious water present in nonpolar solvents. The water content of the acetonitrile used in these experiments was determined to be 0.02%.³¹ In order to determine whether this quantity of water is sufficient to perturb the association constants reported in Table 1, water was deliberately added to the acetonitrile stock solvent, and the titrations were repeated. The results are illustrated in Figure 3.

In the presence of increasing quantities of water, the association constant of the 1·TBABr complex falls, but relatively large amounts of water are required to have a significant effect (similar behavior was observed for the 1·TOABr and 1·TEABr complexes, see Supporting Information). It is clear from Figure 3 that small amounts of water have a negligible effect on the association constant, and so the results in Table 1 are not perturbed by water content.

The variation in association constant with HBD follows the same trend for all HBAs. The complex formed with 1 is more stable than the corresponding complex formed with 2, which is more stable than the 3 complex, in agreement with HBD parameters ($\alpha = 5.1, 4.7, \text{ and } 4.3$, respectively). The differences in association constants are most marked in chloroform, where the 1 complexes are up to 2 orders of magnitude more stable than the corresponding 3 complexes.

The variation in association constant with HBA follows the same trend for all HBDs:



The carboxylates, BzO⁻ and AcO⁻, form the most stable complexes with all of the HBD, and the complexes formed with PF₆⁻ have the lowest association constants, which is consistent with the use of PF₆⁻ as a non-interacting anion. The ranking of the anions is the same as the Hofmeister series (Cl⁻ > NO₃⁻ ~ Br⁻ > I⁻ > ClO₄⁻), which orders anions by their ability to induce the precipitation of proteins from aqueous solution.^{32–34} For the halide series, Cl⁻, Br⁻, and I⁻, the stabilities of the complexes decrease on moving down the group, in agreement with the literature.^{26,27} For the sulfonate ion series, the stabilities of the complexes follow the inductive effect of the substituent. The methyl group in MeSO₃⁻ increases the association constants compared with HSO₄⁻, which has a hydroxyl group. The more electron-withdrawing fluoroalkyl groups in CF₃SO₃⁻ and CF₃(CF₂)₃SO₃⁻ have the opposite effect.

H-Bond Acceptor Parameters. To determine whether a self-consistent set of H-bond parameters can be obtained in a

Table 1. Association Constants (K/M^{-1}) Measured by UV/Vis Absorption Titration Experiments at 298 K^a

cation	anion	HBA	HBD/solvent					
			1		2		3	
			MeCN	CHCl ₃	MeCN	CHCl ₃	MeCN	CHCl ₃
–	–	4	300 ± 98	5400 ± 1700	110 ± 36	1400 ± 110	69 ± 9	240 ± 15
TBA ⁺	BzO [–]	5	/ ^b	/ ^b	/ ^b	/ ^b	/ ^b	11000 ± 5700
TBA ⁺	AcO [–]	6	/ ^b	/ ^b	/ ^b	/ ^b	/ ^b	10000 ± 2200
TBMA ⁺	–O ₂ P(OR) ₂	7	/ ^b	/ ^f	15000 ± 6000	18000 ± 3100	3500 ± 1400	4100 ± 780
TBA ⁺	Cl [–]	8	2400 ± 700	23000 ± 4700	920 ± 150	5800 ± 140	320 ± 57	870 ± 33
TBA ⁺	MeSO ₃ [–]	9	510 ± 160 ^b	16000 ± 4300	/ ^b	2600 ± 640	80 ± 30 ^b	/ ^b
TBA ⁺	NO ₃ [–]	10	/ ^c	6300 ± 440	/ ^c	1600 ± 240	/ ^c	220 ± 45
TBA ⁺	Br [–]	11	230 ± 84	4600 ± 450	120 ± 10	1200 ± 110	59 ± 13	260 ± 82
TBA ⁺	HSO ₄ [–]	12	150 ± 49	4100 ± 400	68 ± 22	1600 ± 85	34 ± 2	250 ± 14
TBA ⁺	CF ₃ SO ₃ [–]	13	/ ^d	970 ± 260	/ ^d	360 ± 55	/ ^d	/ ^b
TBA ⁺	CF ₃ (CF ₂) ₃ SO ₃ [–]	14	/ ^d	1100 ± 380	/ ^d	320 ± 61	/ ^d	93 ± 7
TBA ⁺	ReO ₄ [–]	15	/ ^e	/ ^e	/ ^e	/ ^e	/ ^d	84 ± 12
TBA ⁺	I [–]	16	/ ^e	/ ^e	/ ^e	/ ^e	/ ^d	58 ± 5
TBA ⁺	ClO ₄ [–]	17	/ ^d	320 ± 140	/ ^d	/ ^c	/ ^d	/ ^c
TBA ⁺	–N(SO ₂ CF ₃) ₂	18	/ ^d	120 ± 18	/ ^d	42 ± 4	/ ^d	16 ± 6
TBA ⁺	PF ₆ [–]	19	/ ^d	74 ± 11	/ ^d	35 ± 9	/ ^d	10 ± 2
TOA ⁺	Br [–]	20	230 ± 27	5200 ± 370	120 ± 28	1500 ± 84	47 ± 3	210 ± 64
TEA ⁺	Br [–]	21	240 ± 67	2900 ± 200	110 ± 13	750 ± 240	65 ± 32	200 ± 41
THA ⁺	I [–]	22	/ ^e	/ ^e	/ ^e	/ ^e	/ ^d	68 ± 7

^aAverage of at least two titrations. Errors are quoted at the 95% confidence limit. In all cases, greater than 55% saturation of the binding isotherm was achieved. ^bDeprotonation of the H-bond donor was observed upon addition of guest. ^cThe salt was not sufficiently soluble to obtain a saturation binding isotherm. ^dThe association constant was too low to be measured. ^eThe absorption of the solute obscured the spectrum. ^fAssociation constant too high to be measured using UV/vis spectroscopy.

Table 2. H-Bond Parameters for Neutral Solutes and Solvents

compound	α	β	α_s	β_s
1	5.1			
2	4.7 ^a			
3	4.3 ^a			
4		10.7 ^b		
CCl ₄			1.4 ^c	0.6 ^c
MeCN			1.5	5.1 ^c
CHCl ₃			2.2 ^c	1.3

^aValue from ref 16. ^bValue from ref 22. ^cValue from ref 17.

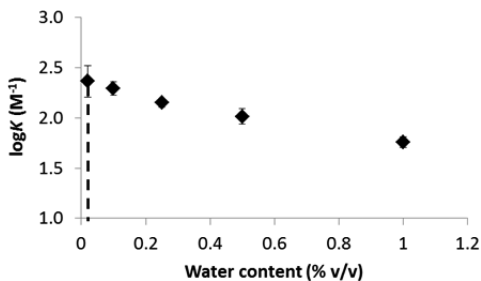


Figure 3. Effect of water on the association constant of the 1:11 complex in acetonitrile. The vertical dotted line represents the water content of acetonitrile without addition of water (0.02%).

three different solvents, the association constants for the neutral HBA, 4, were analyzed using eq 2. Figure 4 shows that the association constants measured for 4 are consistent with eq 2 if the H-bond parameters in Table 2 are used. The values in Table 2 were obtained by optimizing to fit the experimental data, but in most cases they are identical or very close to values deduced from the literature.³⁵ The exception is the β value for

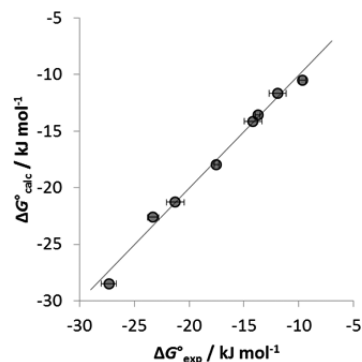


Figure 4. Comparison of experimental free energies of complexation ($\Delta G^{\circ}_{\text{exp}}$) with values calculated using eq 2 ($\Delta G^{\circ}_{\text{calc}}$) for complexes formed with the neutral HBA 4 in carbon tetrachloride, chloroform, and acetonitrile. The line represents $\Delta G^{\circ}_{\text{calc}} = \Delta G^{\circ}_{\text{exp}}$.

chloroform, where the theoretical value of 0.8, which was obtained from a semiempirical calculation of the molecular electrostatic potential surface, is slightly too low to account for the experimental association constants in Table 1.¹⁴

The results for the neutral HBA in Figure 4 suggest that the association constants in Table 1 can be used the H-bond parameters from Table 2 to determine β values for the anions in 5–22. Table 3 shows the values of β derived from the association constants in Table 1 using eq 3. Remarkably good agreement is found for β values measured with different HBDs in different solvents. For example, the six independent measurements of β for 8 (TBACl) all fall between 12.0 and 12.3. Thus, the data for each HBA can be combined to obtain a representative average value that can be used with different HBDs in different solvent environments. In addition, we can be reasonably confident that the values obtained for HBAs, where

Table 3. β Values for Anions

cation	anion	HBA	HBD/solvent ^a						average β^b
			1		2		3		
			MeCN	CHCl ₃	MeCN	CHCl ₃	MeCN	MeCN	
TBA ⁺	BzO ⁻	5	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	15.1 ± 0.6	15.1 ± 0.6
TBA ⁺	AcO ⁻	6	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	15.0 ± 0.2	15.0 ± 0.2
TBMA ⁺	⁻ O ₂ P(OR) ₂	7	/ ^c	/ ^c	14.4 ± 0.3	13.4 ± 0.2	14.4 ± 0.4	14.0 ± 0.2	14.3 ± 0.5 ^d
TBA ⁺	Cl ⁻	8	12.1 ± 0.2	12.0 ± 0.2	12.3 ± 0.1	12.3 ± 0.1	12.3 ± 0.2	12.1 ± 0.1	12.1 ± 0.3
TBA ⁺	MeSO ₃ ⁻	9	11.1 ± 0.2	11.6 ± 0.2	/ ^c	11.5 ± 0.2	11.1 ± 0.3	/ ^c	11.3 ± 0.5
TBA ⁺	NO ₃ ⁻	10	/ ^c	10.7 ± 0.1	/ ^c	11.0 ± 0.1	/ ^c	10.5 ± 0.2	10.7 ± 0.5
TBA ⁺	Br ⁻	11	10.5 ± 0.3	10.6 ± 0.1	10.7 ± 0.1	10.7 ± 0.1	10.8 ± 0.2	10.7 ± 0.4	10.6 ± 0.2
TBA ⁺	HSO ₄ ⁻	12	10.2 ± 0.2	10.4 ± 0.1	10.2 ± 0.3	11.0 ± 0.1	10.4 ± 0.1	10.7 ± 0.1	10.4 ± 0.6
TBA ⁺	CF ₃ SO ₃ ⁻	13	/ ^c	9.2 ± 0.2	/ ^c	9.5 ± 0.2	/ ^c	/ ^c	9.4 ± 0.4
TBA ⁺	CF ₃ (CF ₂) ₃ SO ₃ ⁻	14	/ ^c	9.4 ± 0.3	/ ^c	9.4 ± 0.2	/ ^c	9.5 ± 0.1	9.4 ± 0.1
TBA ⁺	ReO ₄ ⁻	15	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	9.4 ± 0.2	9.4 ± 0.2
TBA ⁺	I ⁻	16	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	8.9 ± 0.1	8.9 ± 0.1
TBA ⁺	ClO ₄ ⁻	17	/ ^c	8.3 ± 0.4	/ ^c	/ ^c	/ ^c	/ ^c	8.3 ± 0.4
TBA ⁺	⁻ N(SO ₂ CF ₃) ₂	18	/ ^c	7.4 ± 0.1	/ ^c	7.4 ± 0.1	/ ^c	7.2 ± 0.3	7.3 ± 0.2
TBA ⁺	PF ₆ ⁻	19	/ ^c	7.0 ± 0.1	/ ^c	7.3 ± 0.2	/ ^c	6.9 ± 0.2	7.0 ± 0.3
TOA ⁺	Br ⁻	20	10.5 ± 0.1	10.7 ± 0.1	10.7 ± 0.2	11.0 ± 0.1	10.6 ± 0.1	10.4 ± 0.4	10.6 ± 0.4
TEA ⁺	Br ⁻	21	10.5 ± 0.2	10.2 ± 0.1	10.6 ± 0.1	10.2 ± 0.3	10.8 ± 0.4	10.4 ± 0.2	10.6 ± 0.3 ^d
THA ⁺	I ⁻	22	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	9.1 ± 0.1	9.1 ± 0.1

^aErrors quoted at twice the standard deviation (2σ) of the individual titrations performed. ^bErrors at the 95% confidence limit. ^cNo experimental data available. ^d β values obtained in chloroform have been excluded for calculation of average β value.

multiple experimental measurements were not possible, are likely to be transferable to different systems. Figure 5 shows the agreement between the experimentally measured free energies of complexation (ΔG°) and the values calculated using eq 2 with the average β values from Table 3.

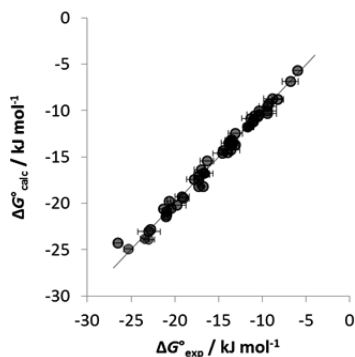


Figure 5. Comparison of experimental free energies of complexation ($\Delta G^\circ_{\text{exp}}$) with values calculated using eq 2 ($\Delta G^\circ_{\text{calc}}$) for H-bonded complexes formed with anions. The line represents $\Delta G^\circ_{\text{calc}} = \Delta G^\circ_{\text{exp}}$.

Influence of the Counter-cation. Both the nature of the counterion and the polarity of the solvent are important factors in determining the type of ion pair formed in a salt solution.^{36–38} Bjerrum described the existence of three different types of ion pairs in solution: (i) contact ion pairs, which involve direct interaction between oppositely charged species; (ii) solvent-shared ion pairs, wherein oppositely charged species are separated by one layer of solvent molecules; and (iii) solvent-separated ion pairs, which have more than one layer of solvent separating the oppositely charged species.³⁷ The nature of the ionic species present in solution can be further complicated through the formation of higher aggregates of ions (triplets and quadruplets) at high salt concentrations.³⁸

To establish whether ion pairing of the salt has a significant effect on the H-bond parameters reported in Table 3, three different counter-cations were used for the bromide anion: tetraoctylammonium (20), tetrabutylammonium (11), and tetraethylammonium (21). A value of β was determined for each of these salts with each of the three HBDs in both chloroform and acetonitrile. The β values for all 18 measurements fall within the range 10.2–11.0, but there are some clear trends. In particular, the values measured for TEABr in chloroform are consistently lower than those of the other systems. Figure 6 shows the average β values for the three

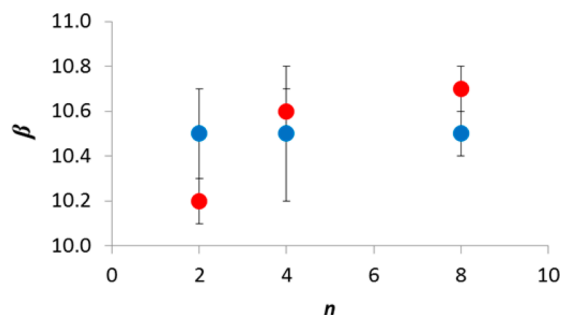


Figure 6. Influence of solvent and counterion on the H-bond acceptor parameter measured for Br⁻ (β). The counterions are N⁺(C_nH_{2n+1})₄. The red data points were measured in chloroform and the blue data in acetonitrile.

different HBD complexes as a function of solvent and counterion. There is a clear outlier with a β value about 0.5 lower than those of the other five systems. We ascribe this difference to stronger ion pairing of the TEABr salt in chloroform, which lowers the apparent β value by competing with H-bond formation.

The dielectric constant of a solvent is inversely proportional to the association constant for ion pairing of the salt.³⁹ Acetonitrile has a high dielectric constant (37.5),⁴⁰ so loose ion

pairs are most likely to be present in this solvent, i.e., solvent-separated or solvent-shared.³⁷ Chloroform has a low dielectric constant (4.8),⁴⁰ so contact ion pairs and higher aggregates are likely to predominate in this solvent.^{36,38} The counter-cation is therefore more likely to affect H-bonding interactions with anions in chloroform. It appears that the larger tetraalkylammonium cations do not interact sufficiently strongly with the anion to affect the measured association constants in either solvent, but the smaller, more polar tetraethylammonium cation forms a tighter ion pair with the bromide anion in chloroform, and this interaction competes with H-bond formation.

For more polar counter-cations, the effects of ion pairing are likely to be more important, but it appears that most of the measurements presented in Table 3 are not perturbed by such effects. The only other system where ion pairing plays a role is in the complexes formed by the TBMA salt 7. The methylammonium headgroup is relatively polar, and the complexes formed in chloroform result in significantly lower β values than the complexes in acetonitrile. The data obtained in chloroform were therefore not used in determining the average values of β for 21 or for 7 in Table 3.

DISCUSSION

The HBA properties of the anions are illustrated graphically in Figure 7. BzO^- and AcO^- are the strongest HBAs studied ($\beta =$

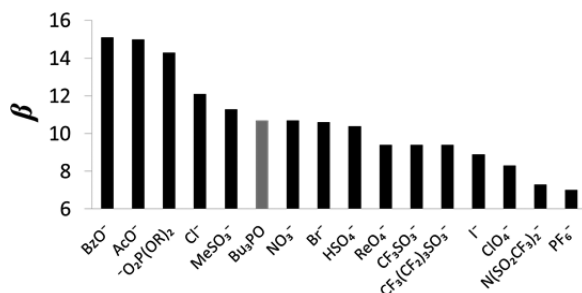


Figure 7. β values for anions (the neutral acceptor Bu_3PO is shown for comparison in gray).

15.1 and 15.0, respectively), and PF_6^- is the weakest ($\beta = 7.0$). The β values measured for the halides fall within the ranges estimated from the literature (see Introduction). The HBA properties of Br^- are similar to those of phosphine oxide 4, while I^- is comparable to a sulfoxide HBA.²³ Of the four sulfonate ions involved in this study, MeSO_3^- has the largest β value (11.3), while HSO_4^- has a β value of 10.4, and $\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$ and CF_3SO_3^- have lower β values (9.4). The substantial differences in β for these ions highlight the influence that the electronic nature of substituents can have on HBA properties. Nitrate has a β value of 10.7, which is similar to those of Br^- and 4. The β value of ReO_4^- (9.4) is comparable to that of the weakest halide, I^- , and lower β values of 8.4 and 7.3 were obtained for ClO_4^- and $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, respectively. The HBA capability of the perchlorate anion is similar to that of a urea functionality, while $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ is comparable to pyridine.¹⁴ The weakly coordinating anion PF_6^- has a β value of 7.0, which is significantly lower than that of the perchlorate ion on the HBA scale.

Figure 8 compares the HBA parameters measured for the anions with the $\text{p}K_a$ values of the conjugate acids in water.⁴¹ There is no relationship between the covalent interaction of an anion with a proton and the non-covalent interaction with a

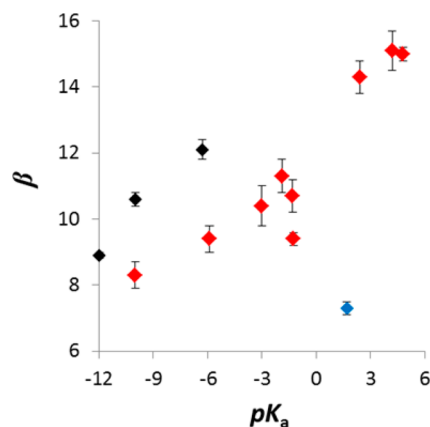


Figure 8. Comparison of the H-bond acceptor properties of anions (β) with the $\text{p}K_a$ of the conjugate acids in water. Halide acceptors are shown in black, oxygen acceptors in red, and the nitrogen acceptor in blue.

HBD, which means that $\text{p}K_a$ cannot be used for predicting HBA properties. There are some trends for anions within the same class, i.e., halides (black data points) and oxygen acceptors (red data points), but the correlations are weak. For example, CF_3SO_3^- and ReO_4^- have comparable HBA properties ($\beta = 9.4$) but very different $\text{p}K_a$ values (-5.9 and -1.3).

CONCLUSION

UV/vis absorption titrations have been used to characterize the H-bonded complexes formed between 15 different anions and three different H-bond donors in chloroform and in acetonitrile. The data are successfully described by the solvent competition model, allowing the determination of the H-bond acceptor parameter (β) for each of the anions. The transferability of the HBA parameters means that they can be used for estimating the properties of non-covalent complexes formed between anions and any HBD in any solvent environment.

Carboxylates are the strongest H-bond acceptors studied, with a HBA strength that surpasses those of all previously reported neutral species, and PF_6^- is the weakest charged HBA studied.¹⁴ The variation in β values measured for a series of sulfonate anions shows that the electronic effects of substituents are similar to those observed for neutral HBA. The influence of ion pairing on the measured β values was investigated through systematic variation of the counter-cation. Ion pairing only competes with H-bond formation for small polar counter-cations (tetraethylammonium) in less polar solvents (chloroform), and the β values reported here are not perturbed by the effects of ion pairing. There is no relationship between the H-bonding properties of the anions and the $\text{p}K_a$ values of the conjugate acids.

We anticipate that the quantification of HBA parameters for anions will be valuable in disentangling the roles of solvent and receptor in anion recognition and in facilitating the future design of complex supramolecular architectures.

EXPERIMENTAL SECTION

Standard Method for UV/Vis Absorption Titrations. Titrations were carried out on a Cary 3 Bio UV/vis spectrophotometer, using standard titration protocols.^{20c} A 10 mL sample of the host, 4-nitro-3-trifluoromethylphenol (1), 4-nitrophenol (2), and 4-(phenylazo)phenol (3), was prepared at a known concentration [typically between 0.092 and 0.14 mM in MeCN (1), 0.05 and 0.087

mM in MeCN (2), 0.022 and 0.043 mM in MeCN (3); 0.12 and 0.14 mM in CHCl₃ (1), 0.070 and 0.12 mM in CHCl₃ (2), and 0.035 and 0.049 mM in CHCl₃ (3)]. A 2 mL portion of this solution was removed and added to a quartz cuvette, and the UV/vis spectrum was recorded. The guest (4–22) was dissolved in 1–2 mL of the host solution. Aliquots of this solution were successively added to the cuvette, and the UV/vis absorption spectrum was recorded after each addition. The UV/vis absorption spectra were analyzed using a Microsoft Excel spreadsheet to fit the changes in absorption at fixed wavelengths to a 1:1 binding isotherm by optimizing the association constant and absorption of the free and bound host using purpose-written VBA macros.

Abbreviations. Following is a summary of abbreviations used herein: Ac = acetyl, Bz = benzoate, Et = ethyl, HBA = H-bond acceptor, HBD = H-bond donor, LFER = linear free energy relationship, LSER = linear solvation energy relationship, Me = methyl, R = pentyl, TBA = tetrabutylammonium, TEA = tetraethylammonium, THA = tetrahexylammonium, TOA = tetraoctylammonium, TBMA = tributylmethylammonium.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b02008.

Titration data (PDF)

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Notes

The authors declare no competing financial interest.

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