Cucurbit[7]uril host–guest complexes with small polar organic guests in aqueous solution

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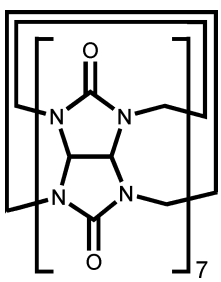
The host–guest stability constants for the inclusion of a series of small neutral polar organic guests in cucurbit[7]uril (CB[7]) have been determined in aqueous solution by ^{1}H NMR titrations. The dependence of the stability constant on the nature of the guests indicates that hydrophobic and dipole–quadrupole interactions are responsible for the binding. The complexation-induced chemical shift changes in the guest proton resonances, coupled with energy-minimization calculations, suggest that the guests are located such that their dipole moment is aligned perpendicular with the quadrupole moment of the CB[7] host. The stability constants for acetone and acetophenone decrease in the presence of Na^+ or K^+ cations as a result of cation capping of the CB[7] portals.

Introduction

The cucurbit[*n*]urils (CB[*n*], n = 5–8, 10) are a family of cyclic host molecules comprised of n glycoluril units bridged by $2n$ methylene groups.[1] The portals of the hydrophobic cavity are lined with ureido carbonyl groups which afford ion–dipole, dipole–dipole, and hydrogen-bonding interactions with the guest. There has been increasing research interest in their host–guest chemistry during the past several years since improved methods for preparing the minor CB[*n*] products, where n = 5, 7, 8, and 10, were reported.[2] The CB[6], CB[7], and CB[8] hosts have comparable cavity volumes to the well studied cyclodextrins, α-CD, β-CD, and γ-CD, respectively.[1] In general the stability constants of the cucurbit[*n*]urils are larger than those of the corresponding cyclodextrins with the same guest, and can be several orders of magnitude larger when the guest is a dication. The CB[7] host (Scheme 1) in particular has demonstrated remarkably strong binding ($K_{CB[7]}$ = 10^8–10^{15} dm^3 mol^{-1}) towards guests such as cationic substituted ferrocenes[3] and organic dications.[4]



Scheme 1 Cucurbit[7]uril.

While the majority of guests studied with the CB[*n*] hosts have been cationic, binding to neutral and anionic guests have been observed. The smallest member of the family, CB[5] (and its Me_{10}CB[5] derivative) bind small neutral gas and solvent molecules.[5] Very recently, it has been shown that these hosts also bind anions such as Cl^- and NO_3^-.[6] With CB[6], aliphatic alcohols $CH_3(CH_2)_mOH$, exhibit very little dependence of the stability constant ($\log K_{CB[6]}$ = 2.53–2.73 in 50% (v/v) aqueous formic acid) on the aliphatic chain length (m = 1–5).[7] With CB[7] capped by Na^+ on each portal, the selectivity towards $CH_3(CH_2)_mOH$ is somewhat greater, with $K_{CB[7]}$ = 90, 710, 1220, and 410 dm^3 mol^{-1} (in 0.05 mol dm^{-3} NaCl) for m = 1, 2, 3, and 4, respectively.[8] The binding of alkali metal cations on the portal(s) of cucurbiturils has been demonstrated to significantly reduce the binding of a variety of guest molecules.

The vast majority of guests investigated with the larger CB[7] and CB[8] host molecules have been cationic, including neutral molecules which become protonated upon inclusion, due to complexation-induced increases in the guest pK_a values.[9] In this study, the host–guest interactions between cucurbit[7]uril and a series of common neutral polar organic solvents, including ketones, amides, sulfoxides and nitriles, have been investigated. The host–guest stability constants were determined from ^{1}H NMR titrations and are compared to values reported previously for β-cyclodextrin. The effects of Na^+ and K^+ cations on the stability constants of the CB[7] host–guest complexes of acetone and acetophenone have also been studied.

Results and discussion

Host–guest stability constants

The host–guest stability constants and stoichiometries were determined from ^{1}H NMR titrations with cucurbit[7]uril, by monitoring the integrations of the free and bound guest proton resonances (slow exchange) or the chemical shift changes in guest resonances (fast exchange). For all of the guests investigated, with the exceptions of the larger ketones pentan-3-one and 3,3-dimethylbutan-2-one, the guest exchanges were fast on the ^{1}H

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NMR timescale (400 MHz). The host–guest stability constants for fast-exchanging guests may be determined from chemical shift titrations (Fig. 1).

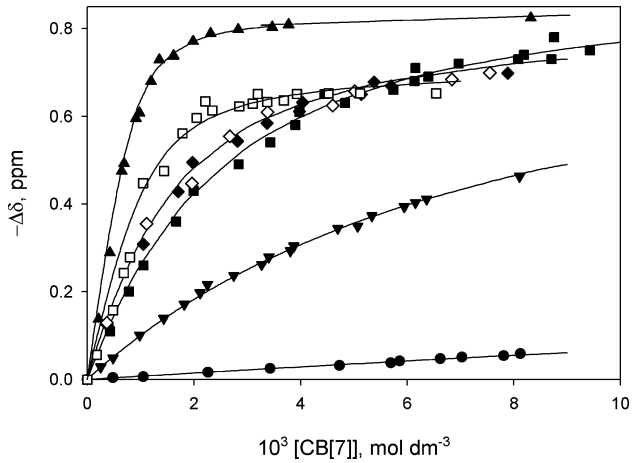


Fig. 1 ^{1}H NMR chemical shift titrations for cucurbit[7]uril with (■) acetone, (□) 2-butanone, (▲) acetophenone, (◆) dimethylformamide, (◇) methyl acetate, (▼) dimethylsulfoxide, and (●) acetonitrile (guest concentrations 0.90–1.0 mmol dm^{-3}) in aqueous solution at 25 °C.

The limiting chemical shifts of the aliphatic proton resonances of the guests ($\Delta\delta = \delta_{bound} - \delta_{free}$) provide an indication of the preferred orientation of the guest in the cucurbituril host cavity.[1] Upfield shifts ($\Delta\delta < 0$) are associated with guest protons located within the shielding hydrophobic cavity, whilst guest protons located at the deshielding carbonyl-laced portals result in downfield shifts ($\Delta\delta > 0$). For pentan-3-one and 3,3-dimethylbutan-2-one, the addition of CB[7] resulted in broadening of the proton resonances and the formation of bound and free signals, indicating slow guest exchange on the ^{1}H NMR timescale. Mezzini *et al.*[10] have recently reported that 1-phenylbutan-2-one and 3,3-dimethyl-1-phenylbutan-2-one bind to CB[7], with intermediate and slow exchange behaviour, respectively. With the slower-exchanging guests the stability constants were determined from integrations of the proton resonances for the bound and free guests. The host–guest stability constants $K_{CB[7]}$ determined in this study and that of Mezzini *et al.*,[10] along with previously reported values for β-cyclodextrin with these guests, are presented in Table 1.

The host–guest stability constants for the neutral guests with CB[7] are about two orders of magnitude greater than those of the corresponding guests with β-cyclodextrin (Table 1).[11–15] The stability constants for the binding of dimethylsulfoxide, dimethylformamide, and acetonitrile with β-CD have not been reported, however the corresponding values with α-CD are very

Table 1 Stability constants ($K_{CB[7]}$) and limiting complexation-induced chemical shifts ($\Delta\delta$) for the CB[7] host–guest complexes with small polar organic guests in aqueous solution at 25 °C (no added electrolyte), along with available literature values for the β-CD stability constants

Guest	$\Delta\delta_{CB[7]}$/ppm	$K_{CB[7]}$/dm^3 mol^{-1}	$K_{\beta\text{-CD}}$/dm^3 mol^{-1}
Acetone	−0.92 (CH_3)	580 ± 50[a]	2.7 ± 0.4[b]
Butan-2-one	−0.91 (CH_3)	3100 ± 500[a]	9.3 ± 0.2[b]
	−1.05 (CH_2)		
	−0.70 (CH_2CH_3)		
Pentan-3-one	−0.53 (CH_3)	2060 ± 550[c]	18 ± 1[b]
	−0.97 (CH_2)		
3,3-Dimethylbutan-2-one	−0.83 (CH_3)	6740 ± 620[c]	585 ± 55[b]
	−0.76 ($C(CH_3)_3$)		64–343[d]
Acetophenone	−0.29 (CH_3)	9600 ± 700[a]	123 ± 9[b]
	−0.82 (*o*-CH)		
	−0.86 (*m*-CH)		
	−0.65 (*p*-CH)		
1-Phenylbutan-2-one[e]	−0.73 (CH_2Ph)	4600[e]	—
	−0.68 (CH_2CH_3)		
	−0.34 (CH_2CH_3)		
	−0.62 (*o*-CH)		
	−0.81 (*m*-CH)		
	−0.83 (*p*-CH)		
3,3-Dimethyl-1-phenylbutan-2-one[e]	−0.75 (CH_2Ph)	27340[e]	6238–18300[d]
	−0.79 ($C(CH_3)_3$)		
	+0.29 (*o*-CH)		
	+0.01 (*m*-CH)		
	−0.05 (*p*-CH)		
Methyl acetate	−0.85 (CH_3)	1020 ± 100[a]	11.8 ± 1.2[f]
	−0.80 (OCH_3)		
Dimethylsulfoxide	−0.91 (CH_3)	140 ± 20[a]	<1[g]
			0.41 ± 0.04[h]
Dimethylformamide	−0.78 (CH_3)	1000 ± 80[a]	3.1[g]
	−0.80 (CH_3)		
	−0.80 (COH)		
Acetonitrile	−0.67 (CH_3)	11 ± 1[a]	4.6[g]
			5.6 ± 0.1[h]

[a] Determined from ^{1}H NMR chemical shift titrations. [b] Ref. 11. [c] Determined from relative integrations of bound and free guest proton resonances. [d] Ref. 12. The values of $K_{\beta\text{-CD}}$ were dependent on the host or guest proton resonance monitored. [e] Ref. 10. [f] At 22 °C, ref. 13. [g] For α-CD, ref. 14. [h] For α-CD, ref. 15.

small (<1, 3.1, and 4.6 $dm^3\ mol^{-1}$, respectively).[14] The stability constants for acetone (also butan-2-one) with α-CD (2.94 ± 0.05 and 2.0 $dm^3\ mol^{-1}$) and β-CD ($2.72 \pm 0.35\ dm^3\ mol^{-1}$) are very similar[11] and therefore these other solvents would be expected to show similar stability constants with β-CD. For the ketones, the magnitudes of both $K_{CB[7]}$ and $K_{\beta\text{-CD}}$ generally increase with the hydrophobicity of the alkyl groups (Table 1). We observe no change in the methyl resonance of the more hydrophilic methanol upon addition of CB[7], even up to 10 mmol dm^{-3} host.

The cucurbituril, with two polar carbonyl-laced portals at opposite ends of the cavity, has a quadrupolar moment. With small polar molecules, such as acetone, we anticipate that the carbonyl oxygen would prefer to align with the center of cavity, such that the two methyl groups would be deep within the hydrophobic cavity. While the quadrupole–dipole interaction is not expected to provide a large portion of the stabilization of the host–guest complex, it could have a significant influence over the position and orientation of these small molecules in the CB[7] cavity. This should manifest itself in a significant upfield complexation-induced shift in the methyl proton resonance. Mock and Shih observed that the stability constant of CB[6] with the 1,5-pentanediammonium dication ($K_{CB[6]} = 2.4 \times 10^6\ dm^3\ mol^{-1}$) decreases by factors of 6 and 460 when the central methylene group was replaced by thioether S and ether O atoms, respectively.[16] They related this decrease in the stability constant to the trend of $CH_2 > S > O$ in the hydrophobicities of the central atom in the guest molecule.

Energy-minimized structures (MM2) were determined for the host–guest complexes[17] (Fig. 2) and the resulting locations and orientations of the guest molecules in the CB[7] cavity are in agreement with the complexation-induced chemical shifts ($\Delta\delta$) of the guest protons. All of the guests which exhibit fast exchange on the NMR timescale are located with the C=O group pointing towards the center of the linkage between two glycoluril units and the plane of the O=CRR′ (or $O{=}SR_2$) guest lying more or less perpendicular to the major axis of the CB[7] cavity. As a result the alkyl proton resonances of the guests exhibit $\Delta\delta$ values in the −0.70 to −1.05 ppm range. With pentan-3-one, 3,3-dimethylbutan-2-one, and 3,3-dimethyl-1-phenylbutan-2-one,[10] which exhibit slow exchange on the NMR timescale, the C=O group is also pointing to the center of the bridge between the glycoluril groups, however the O=CRR′ plane is now parallel with the major axis of the host cavity. The methyl proton resonances in pentan-3-one, for example, shift upfield by only 0.53 ppm, suggesting that the methyl group is located closer to the portals than the methyl groups on butan-2-one.[10]

The CB[7] complex with acetophenone exhibited fast guest exchange, with $\Delta\delta$ values (Table 1) and the molecular modelling study (Fig. 2) indicating that the phenyl ring in fully included in the cavity. A recent study of the interaction of benzyl *tert*-butyl nitroxide and 2,2,6,6-tetramethyl-pyridinyl-*N*-oxyl (TEMPO) radicals also included measurements of the stability constants of the corresponding ketones as diamagnetic analogs. The 1-phenylbutan-2-one exhibited fast exchange on the NMR timescale, with significant upfield shifts in both the aliphatic and aromatic proton resonances, implying that the CB[7] is shifting back and forth over the entire guest molecule length. With the 3,3-dimethyl-1-phenylbutan-2-one guest, exchange is slow on the NMR timescale and the CB[7] is clearly located over the aliphatic portion with the hydrophobic *t*-butyl group.[10]

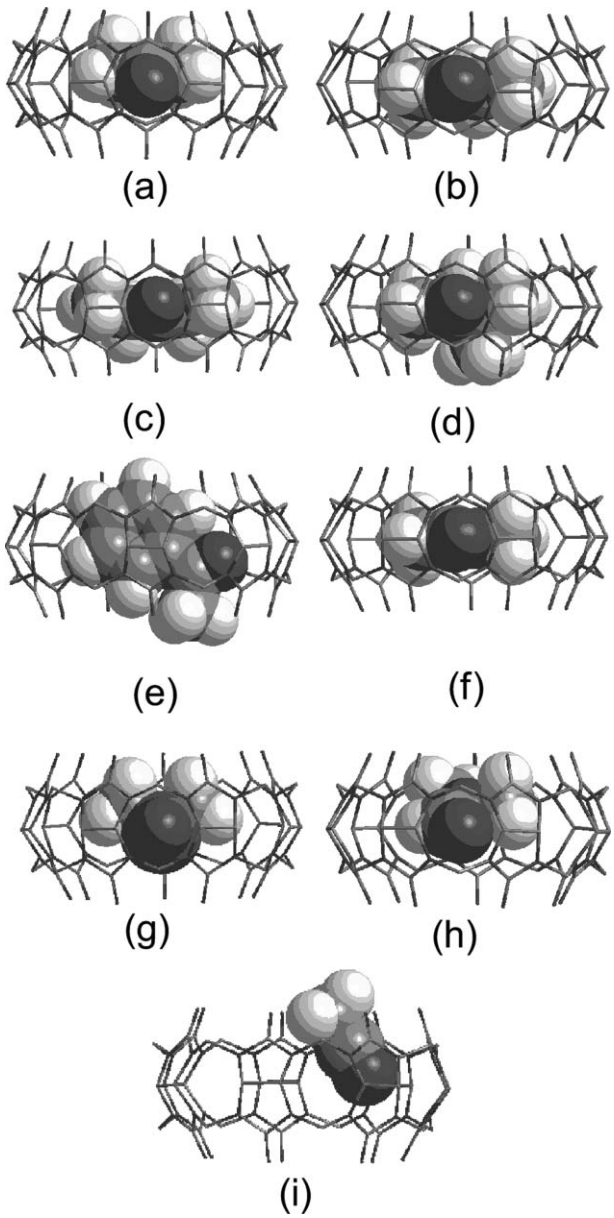
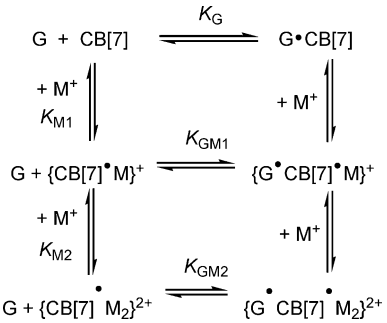


Fig. 2 Energy-minimized structures (MM2) of the host–guest complexes of CB[7] with (a) acetone, (b) butan-2-one, (c) pentan-3-one, (d) 3,3-dimethylbutan-2-one, (e) acetophenone, (f) methyl acetate, (g) dimethylsulfoxide, (h) dimethylformamide, and (i) acetonitrile. The hydrogens on CB[7] have been removed for clarity.

Host–guest–cation complexes

A number of studies of the host–guest complexes of cucurbit[*n*]urils have demonstrated that the stability constants are dependent on the nature and concentration of the cations which make up the background electrolyte.[8,10,18–20] This arises from binding of cations to the portals, modulating the formation and dissociation rate constants and therefore the overall stability constant for the host–guest complex. With CB[6], stepwise stability constants of 1560 and 60 $dm^3\ mol^{-1}$ for $\{CB[6]{\cdot}Na\}^+$ and $\{CB[6]{\cdot}Na_2\}^{2+}$ and 560 and <20 $dm^3\ mol^{-1}$ for $\{CB[6]{\cdot}K\}^+$ and $\{CB[6]{\cdot}K_2\}^{2+}$, respectively, have been reported.[18b] Mezzini *et al.*[10]

have observed that for 1-phenylbutan-2-one, the stability constant drops from 2.50×10^4 dm^3 mol^{-1} for inclusion in CB[7] to a value of 6.15×10^3 dm^3 mol^{-1} for inclusion in K$^+$-capped CB[7]. From the dependency of the stability constant on the concentration of K$^+$, they have determined binding constants of $K_{M1} = 600$ and $K_{M2} = 53$ dm^3 mol^{-1} for $\{CB[7]\cdot K\}^+$ and $\{CB[7]\cdot K_2\}^{2+}$ respectively. The relationships between the equilibria of host–guest, host–cation, and host–guest–cation binding are illustrated in Scheme 2.



Scheme 2 The CB[7] host–guest–cation equilibria.

The ^{1}H NMR chemical shift titrations of acetone (Fig. 3) and acetophenone (Fig 4) with CB[7] in the presence of 0.20 mol dm^{-3} Na$^+$ and K$^+$ have been carried out. With both guests, the presence of the cations results in a reduction in the magnitude of the host–guest stability constants compared to the titrations in the absence of added cations. For acetone, the value of $K_{CB[7]}$ is reduced from 580 to 370 and 250 dm^3 mol^{-1} in the presence of 0.20 mol dm^{-3} Na$^+$ and K$^+$, respectively.

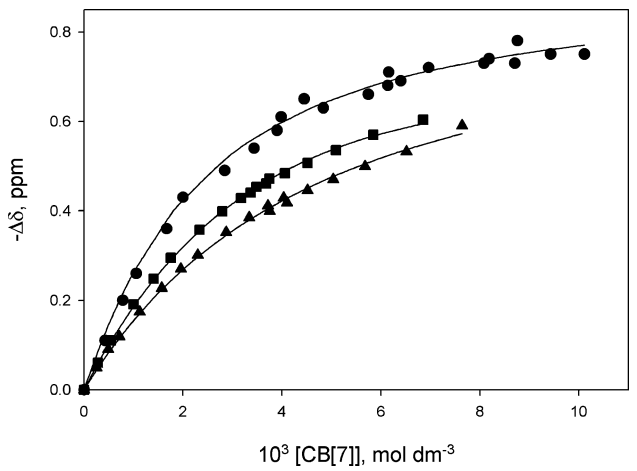


Fig. 3 Dependences of the complexation-induced chemical shift $\Delta\delta_{obs}$ for the methyl resonance of acetone (0.7–0.8 mmol dm^{-3}) on the concentrations of CB[7] in the (●) absence and presence of 0.20 mol dm^{-3} (■) Na$^+$ and (▲) K$^+$.

The stability constant for acetophenone decreases from 9600 to 1350 and 350 dm^3 mol^{-1} in the presence of 0.20 mol dm^{-3} Na$^+$ and K$^+$, respectively (Fig. 4). The much larger decreases in $K_{CB[7]}$ in the presence of the cations with this guest is consistent with both the methyl and phenyl groups protruding somewhat from the cavity of the host into the portals and being more hindered from binding by the presence of the cations at the portals.

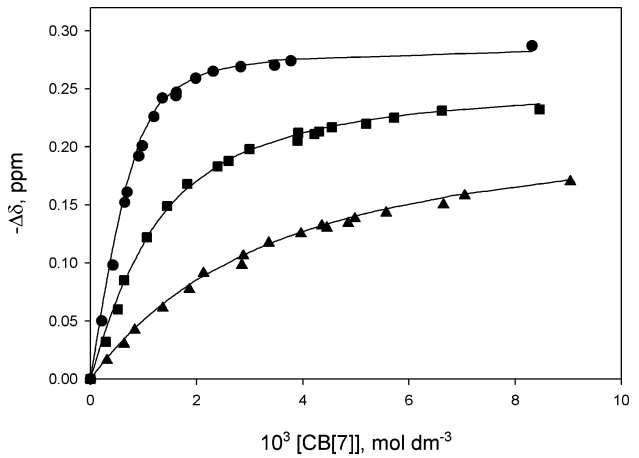


Fig. 4 Dependences of the complexation-induced chemical shift $\Delta\delta_{obs}$ for the methyl resonance of acetophenone (0.7–0.8 mmol dm^{-3}) on the concentrations of CB[7] in the (●) absence and presence of 0.20 mol dm^{-3} (■) Na$^+$ and (▲) K$^+$.

With acetone, the limiting chemical shift of the methyl proton resonance (−0.92 ppm) is very similar in the absence (Table 1) and presence of 0.20 mol dm^{-3} cation, as are the aromatic proton resonances of acetophenone. The methyl proton resonance of acetophenone has a somewhat lower limiting chemical shift change in the presence of the cations (−0.26 and −0.23 ppm with Na$^+$ and K$^+$, respectively) than in the absence of the cations (−0.29 ppm), likely as a result of the presence of the methyl group near the portal where the cations would bind.

The changes in the chemical shifts of the acetone and acetophenone proton resonances, in the presence of an excess of CB[7] (4–5 mole equivalents), with increasing cation concentrations have been measured (Fig. 5). If it is assumed that the chemical shift of the resonances of the host–guest complexes (G·CB[7]) do not change upon binding of the cations (M$^+$), then the change in $\Delta\delta_{obs}$ is simply the result of decreases in the stability constants of the $\{G\cdot CB[7]\cdot M\}^+$ and $\{G\cdot CB[7]\cdot M_2\}^{2+}$ complexes. The plot in Fig. 5 for acetone and acetophenone in the presence of K$^+$ (similar for Na$^+$, not shown) clearly exhibits the effects of a stronger binding

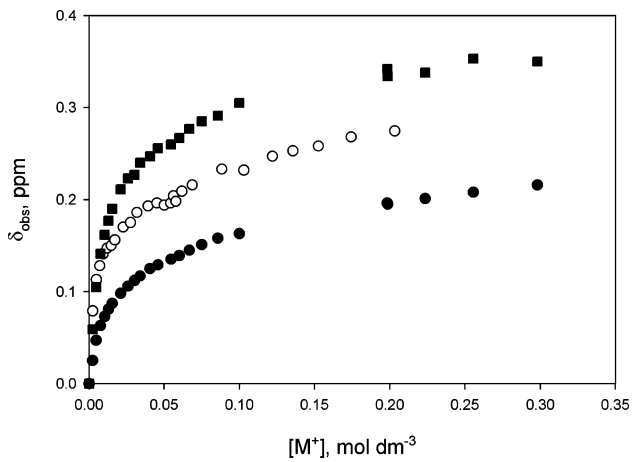


Fig. 5 Dependences of the chemical shift changes of the guest proton resonances (in the presence of 4–5 mole equiv. CB[7]) on K$^+$ concentration; (○) acetone, (●) acetophenone methyl, (■) acetophenone *o*-phenyl.

of the first cation, followed by a weaker second cation binding, resulting in progressively weaker inclusion of the organic guests.

If it is assumed that the limiting chemical shift change experienced by the guest protons in the CB[7] cavity is not significantly affected by the presence of the cations, and that the free concentrations of the cations are approximately equal to their respective total concentrations (because of the low relative concentration of the host and host–guest species), the dependence of the observed stability constant (K_{obs}, which may be calculated from the $\Delta\delta_{obs}$ and $\Delta\delta_{lim}$ values[21]) on the cation concentration may be fit to eqn 1.

$$K_{obs} = \frac{K_G + K_{GM1}K_{M1}\left[M^+\right] + K_{GM2}K_{M1}K_{M2}\left[M^+\right]^2}{1 + K_{M1}\left[M^+\right] + K_{M1}K_{M2}\left[M^+\right]^2} \quad (1)$$

Using $K_G = 580$ dm^3 mol^{-1}, the fit of the data for acetone in Fig. 5 to eqn 1 gives values of $K_{GM1} \approx 400$ dm^3 mol^{-1} and $K_{GM2} \approx 150$ dm^3 mol^{-1}, using the reported values for K^+ binding constants of $K_{M1} = 600$ dm^3 mol^{-1} and $K_{M2} = 53$ dm^3 mol^{-1}.[10] For the acetophenone, with $K_G = 9600$ dm^3 mol^{-1}, values of $K_{GM1} \approx 2000$ dm^3 mol^{-1} and $K_{GM2} \approx 500$ dm^3 mol^{-1} were obtained from a fit to the *o*-phenyl proton resonance. These specific stability constants have similar trends to the values of $K_G = 4600$ dm^3 mol^{-1} and $K_{GM1} = 470$ dm^3 mol^{-1} for 3,3-dimethyl-1-phenylbutan-2-one with CB[7] in the presence of K^+, reported by Mezzini *et al.*[10] The more the guest protrudes from the cavity into the portal, the greater the effect of cation binding on the magnitude of the host–guest stability constant.

The two solvents which exhibited the weakest interaction with the CB[7] cavity in aqueous solution are acetonitrile (11 dm^3 mol^{-1}) and dimethylsulfoxide (140 dm^3 mol^{-1}). The CB[7] is reasonably soluble in both solvents and the use of these solvents, or mixtures with water, represent alternative media for studying the host–guest chemistry of cucurbit[7]uril and other members of the host family.[22] The small host–guest stability constants for these solvents would allow for substantial stability constants for competitive guests in these non-aqueous media.

Experimental

Cucurbit[7]uril was prepared and characterized by the method of Day.[2b] The guest compounds were used as received (anhydrous, Aldrich). The ^{1}H NMR spectra were measured on a Bruker Avance 400 MHz instrument using D_2O as the solvent. The host–guest stability constants were determined from least-squares fitting of $\Delta\delta_{obs}$ for the guest proton resonances as a function of [CB[7]] to a 1 : 1 binding isotherm (fast guest exchange), as described previously,[23] or from the integrations of the bound and free guest proton resonances (slow guest exchange). The values of $\Delta\delta_{lim}$ and $K_{CB[7]}$ for acetonitrile were determined from the intercept and intercept–slope ratio, respectively, of a plot of $(\Delta\delta_{obs})^{-1}$ against $[CB[7]]^{-1}$. The energy-minimized structures of the host–guest complexes were determined using the MM2 program of the Chem3D software (CambridgeSoft).[17]

Conclusions

Small neutral polar organic guests form complexes with the cucurbit[7]uril host through hydrophobic effects and dipole–quadrupole interactions in aqueous solution. The host–guest stability constants for the ketones increase with the hydrophobicity of the guest and decrease upon the complexations of the portals with sodium or potassium cations.

Acknowledgements

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