Binding Forces Contributing to the Complexation of Organic Molecules with β-Cyclodextrin in Aqueous Solution

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Formation constants of weak inclusion complexes between β-cyclodextrin (CD) and a number of organic solutes in aqueous solution were measured by the spectrophotometric measurement of the inhibitory effect of the solutes on the complexation of CD with phenolphthalein. Types and relative strengths of various intermolecular forces between CD and the guest affecting the stability of inclusion complexes were studied based upon the linear solvation energy relationship (LSER). It was found that increasing guest molecular size stabilizes the complex by virtue of increasing dispersive interactions between the hydrophobic interior of the CD cavity and the guest whereas increasing guest dipolarity and hydrogen bond (HB) acceptor basicity lead to a decrease in the stability of the complex due to the stronger dipolar and hydrogen bonding interactions with water, which is more dipolar and HB acidic than CD.

Cyclodextrins (CD) are cyclic oligosaccharides traditionally formed by the action of *Bacillus macerans* amylose on starch. CDs contain six to twelve glucose units which are bonded through α-(1,4) linkages. Among them, the three smallest homologues are commercially available.[1] They have the shape of a hollow truncated cone, the interior of which forms a relatively hydrophobic cavity. The ability of CDs to form inclusion complexes with a variety of compounds has been extensively utilized in many industrial, pharmaceutical, agricultural, and other related applications.[1,2] CDs have also been extensively employed in separation science and their applications in liquid chromatography have recently been reviewed by several researchers.[3-5]

Although numerous papers have been published on binding forces affecting inclusion complexation of CD with the guest the nature of the driving forces of complexation have not yet been fully understood. However, it is widely accepted that the stabilities of CD inclusion complexes are governed by several forces such as hydrogen bonding, hydrophobic interactions, dispersive interactions, dipolar interactions, release of distortional energy of and extrusion of high energy water from CD upon inclusion of guest, and the guest molecular size and shape.[1,2] To date only a few works have been devoted to characterize the cavity of the CDs with regard to their polarity.[6-8] CDs have, depending upon their size, 18–24 primary and secondary hydroxy groups on their upper and lower rims, which may undergo hydrogen bonding (HB) interactions with incoming guest molecules. We have recently reported Kamlet–Taft solvatochromic HB donor acidity values (α) of CDs.[9] Despite the relevance of CD–guest interactions to several important areas of chemistry and biology the types and quantitative estimation of relative importance of CD–guest interactions influencing the stabilities of CD inclusion complexes in aqueous media have not been studied in detail. In the present work we have measured the complexation constants of β-CD with a number of organic solutes in water and examined them to get better insight into the type and relative strength of CD–analyte interactions affecting the stabilities of the complexes based upon the linear solvation energy relationships (LSERs).[10,11]

Kamlet, Taft and their co-workers have applied the LSER approach and their solvatochromic parameters, π^* (dipolarity/polarizability), β (HB acceptor basicity) and α (HB donor acidity), to some 600 processes[10,11] and have shown that many disparate physicochemical, biochemical, toxicological, pharmacological properties of organic non-electrolytes that depend on solute–solvent interactions and aqueous solubilities in a variety of media can be correlated, rationalized, and predicted by the application of this methodology.[12-27]

According to the LSER formalism, when applied to phase-transfer processes, a general solute or solvent property (SP) can be correlated *via* the use of three types of terms [eqn. (1)].[10,11]

$$\mathrm{SP} = \mathrm{SP}_0 + \text{cavity term} + \text{dipolar term} + \text{HB term(s)} \quad (1)$$

SP_0 denotes the value of SP when all the three terms in the equation are zero. The cavity term is usually taken as the product of the solute van der Waals molar volume (V_I) and the square of the Hildebrand solubility parameter (δ_H) of the solvent. V_I is computer-calculated intrinsic molecular volume of the solute.[28] V_I is scaled by 1/100 so that it should cover roughly the same range as the other independent variables. The dipolar term is the product of the solute π^* and the solvent π^*. The π^* parameter measures a combination of dipolarity/polarizability of a compound. The hydrogen bonding (HB) terms are written as a cross product of the solute α and the solvent β (type B HB) and the product of the solute β and the solvent α (type A HB). In the case of the host–guest inclusion complexation in water, which involves the transfer of the guest molecule from water into the CD cavity, SP in eqn. (2) denotes a logarithmic complex formation constant and the relevant LSER can be written as eqn. (2). The subscript 2

$$\log K_f = \log K_{f,o} + M(\delta^2_{H,c} - \delta^2_{H,w})V_{I,2}/100 + S(\pi^*_c - \pi^*_w)\pi_2{}^* + B(\alpha_c - \alpha_w)\beta_2 + A(\beta_c - \beta_w)\alpha_2 \quad (2)$$

denotes the solute property. The subscripts c and w denote the CD and water, respectively. The coefficients M, S, A and B are the fitting parameters that are independent of solutes and solvents considered.

When K_f values of a number of different guests in a given CD in water are considered, the parameters for CD and water in eqn. (2) are fixed and subsumed into the constants in eqn. (2). Then eqn. (2) can be reduced to eqn. (3). The coefficients m, s, b

$$\log K_f = \log K_{f,o} + mV_{I,2}/100 + s\pi^*_2 + b\beta_2 + a\alpha_2 \quad (3)$$

and a are obtained by multiple linear regression of log K_f *vs.* the solute parameters. The sign and magnitude of the coefficients

Table 1 Properties of selected solutes[a]

Solute	$V_1/100$	π^*	β	α
Acetaldehyde	0.283	0.67	0.42	0
Acetone	0.380	0.71	0.48	0.04
Acetonitrile	0.271	0.75	0.31	0.15
Tetrahydrofuran	0.455	0.58	0.55	0
Benzene	0.491	0.59	0.10	0
Toluene	0.592	0.55	0.11	0
Nitrobenzene	0.631	1.01	0.30	0
Benzaldehyde	0.606	0.92	0.44	0
Aniline	0.562	0.73	0.50	0.16
Benzyl alcohol	0.634	0.99	0.52	0.35
Methanol	0.205	0.40	0.42	0.35
Ethanol	0.305	0.45	0.45	0.33
Propan-2-ol	0.401	0.40	0.51	0.31
Butan-1-ol	0.499	0.40	0.45	0.33
Cyclohexanol	0.636	0.45	0.51	0.31
Trichloromethane	0.427	0.58	0.10	0.35
Tetrachloromethane	0.514	0.28	0.10	0
Diethylamine	0.535	0.25	0.70	0
Dimethylsulfoxide	0.466	1.00	0.76	0
Dimethylformamide	0.444	0.88	0.69	0

[a] Data from ref. 14.

measure the direction and relative strength of different types of solute–solvent interactions affecting complexation. Twenty compounds of widely varying chemical properties are chosen in order to ensure that all the possible types of intermolecular interactions are accounted in the LSER. In the selection of the guest compounds molecular sizes of the guests are also considered to ensure that they are all compatible with the size of the β-CD cavity. The properties of the selected organic compounds are listed in Table 1.

Experimental

Chemicals.—β-CD from Aldrich (Milwaukee, USA) was purified by recrystallization from water and dried *in vacuo* at 80 °C. Phenolphthalein and all the organic compounds of reagent grade were obtained from various sources and were purified according to known procedures.[29]

Apparatus.—Absorption spectra were measured in a 10 mm cell at 25 ± 0.2 °C with a Hitachi Model 320 UV–VIS spectrophotometer set at 550 nm. The pH of the aqueous solution was measured using a Corning Model 135 pH/Ion meter.

Spectrophotometric Determination of Complexation Constants.—The equilibrium constant for complexation between β-CD and the guest were determined by spectrophotometric measurements of the inhibitory effect of the guest molecule on the complexation of β-CD with phenolphthalein (PHT).[30,31] Upon addition of β-CD to a purple coloured alkaline solution of PHT, the absorbance decreases due to the formation of a colourless PHT–CD complex. Upon addition of another potential guest molecule, a fraction of added guest is included by CD to expel PHT to a bulk solution, resulting in an increase in absorbance.

The pH of the solutions was adjusted with 4×10^{-3} mol dm^{-3} sodium carbonate. Spectral measurements were made within 2 h of the preparation of PHT/sodium carbonate reagent. Solutions of organic compounds with this reagent were prepared just before making the spectral measurements. In preliminary experiments for the determination of molar absorption coefficient of PHT and complexation constant for PHT–CD, the PHT concentration was kept at 3.0×10^{-5} mol dm^{-3} and the β-CD concentration was varied from 8.3×10^{-5} to 1.1×10^{-3} mol dm^{-3}. In experiments for the determination of equilibrium constants for the 1:1 complexes between CD and organic solutes, the concentrations of PHT and β-CD were kept at 3.0×10^{-5} and 1.5×10^{-4} mol dm^{-3}, respectively and known concentrations of the solutes were added (see Table 2, but their concentrations were kept constant during a series). Details of the procedure for determination of K_f can be found in the literature.[32]

Results and Discussion

The K_f values for the 1:1 complexes between β-CD and the organic guests obtained are listed in Table 2. Average deviations of K_f values in replicate measurements were in the order of 8%. Measured K_f values for a number of solutes are compared with available literature values in Table 3. The measured values are generally in good agreement with the corresponding literature values. The values for benzene and cyclohexanol are quite different from the literature values. However, these literature values are not in agreement with each other. It remains to be seen which values are correct.

The multiple linear regression equation for log K_f values of 20 compounds is given by eqn. (4). The coefficient for the α term is statistically zero, indicating that the type B HB interaction is, in essence, not affecting the stability of CD–guest complexes. This seems reasonable because water is a much stronger HB donor ($\alpha = 1.17$)[33] than all the guest molecules (Table 1) and the hydroxy groups on β-CD ($\alpha = 0.14$–0.21).[9] For any solute to act as an HB donor in aqueous solution it must usually do so at the expense of a water molecule acting as an HB donor at the same site. Thus if there can occur hydrogen bonding on the HB acceptor sites of β-CD the HB donors are to be water molecules which exist in a great excess over the solute, rendering the hydrogen bonding between the solute and CD not possible. We thus excluded the α parameter and the log K_f values were regressed using a three-parameter equation which includes V_1, π^* and β. The resulting LSER equation is given as eqn. (5).

$$\log K_f = -1.37\,(\pm 0.31) + 7.61\,(\pm 0.50)V_1/100 - 0.91\,(\pm 0.28)\pi^* - 1.27\,(\pm 0.32)\beta - 0.08\,(\pm 0.42)\alpha \quad (4)$$
$$n = 20, r = 0.972, \mathrm{SD} = 0.27$$

$$\log K_f = -1.40\,(\pm 0.27) + 7.62\,(\pm 0.48)V_1/100 - 0.90\,(\pm 0.26)\pi^* - 1.27\,(\pm 0.31)\beta \quad (5)$$
$$n = 20, r = 0.972, \mathrm{SD} = 0.26$$

From the magnitude of each coefficient in eqn. (5) we can see that the leading term influencing the stabilities of the 1:1 complexes between CD and organic guests is the cavity formation, which is followed by the hydrogen bonding and dipolar interactions.

The positive sign for the coefficient *m* indicates that increasing solute size (V_1) leads to increasing stability of the complexes in water. Does this mean, as usually interpreted in other LSER studies,[10,11] that since water is a more cohesive solvent than CD, increasing V_1 leads to increasing solubility in the CD over water, and in turn leading to increased stability of the complex? We speculate that the cavity formation process does not necessarily occur during the transfer of the solute from water to β-CD for the formation of the complex since a cavity already exists in β-CD for the incoming solute if its size is compatible with the size of the cavity. The CD cavities are known to be hydrophobic[34] and therefore the energetically unfavourable polar/apolar interactions between the included water and the CD cavity are readily substituted without an

Table 2 Measured equilibrium constants for 1:1 complexation between β-CD and organic solutes at 25 °C

Solute	Conc. range mol dm^{-3}	K_f/dm^3 mol^{-1}				Average[a]	log $K_{f,meas}$	log $K_{f,calc}$[c]	Diff.[d]
		I	II	III	IV				
Acetaldehyde	0.20–0.73	0.21	0.24	0.21	0.25	0.23 (0.02)[b]	−0.64	−0.39	−0.25
Acetone	0.23–0.73	2.36	2.75	2.70	2.61	2.61 (0.17)	0.42	0.25	0.17
Acetonitrile	0.73–0.86	0.50	0.58	0.60	0.51	0.54 (0.05)	−0.27	−0.40	0.13
Tetrahydrofuran	0.10–0.96	27.29	31.15	31.24	28.70	29.60 (1.93)	1.47	0.85	0.61**
Benzene	0.007–0.009	65.71	62.66	73.07	67.38	67.21 (4.37)	1.83	1.68	0.14
Toluene	0.0042–0.0044	132.23	116.90	127.14	121.60	124.47 (6.66)	2.09	2.48	−0.38*
Nitrobenzene	0.0097–0.010	96.87	112.00	112.79	121.58	110.81 (10.2)	2.04	2.12	0.08
Benzaldehyde	0.004–0.025	55.87	60.08	63.74	59.12	59.70 (3.24)	1.78	1.83	−0.05
Aniline	0.0077–0.026	36.29	44.51	37.83	39.28	39.48 (3.57)	1.60	1.60	0.00
Benzyl alcohol	0.0034–0.0079	48.51	54.74	49.52	54.26	51.76 (3.20)	1.71	1.88	−0.16
Methanol	0.90–0.99	0.10	0.12	0.11	0.11	0.11 (0.01)	−0.96	−0.73	−0.23
Ethanol	0.58–0.70	0.93	0.87	0.90	1.05	0.94 (0.08)	−0.027	−0.052	0.025
Propan-2-ol	0.24–0.25	4.11	4.53	4.50	3.78	4.23 (0.36)	0.63	0.64	−0.02
Butan-1-ol	0.033–0.043	15.17	14.96	14.16	14.54	14.71 (0.45)	1.17	1.47	−0.30*
Cyclohexanol	0.022–0.032	576.08	571.38	570.39	572.83	572.67 (2.48)	2.76	2.39	0.36*
Trichloromethane	0.0066–0.0083	27.43	23.91	26.23	30.45	27.01 (2.72)	1.43	1.20	0.23
Tetrachloromethane	0.0029–0.0032	159.17	157.64	160.74	162.63	160.04 (2.13)	2.20	2.14	0.06
Diethylamine	0.14–0.15	21.52	23.15	25.26	22.63	23.14 (1.57)	1.36	1.56	−0.20
Dimethylsulfoxide	0.57–0.58	1.26	1.66	1.60	1.22	1.44 (0.23)	0.16	0.28	−0.12
Dimethylformamide	0.23–0.24	2.39	3.08	3.02	2.18	2.67 (0.45)	0.43	0.31	0.12

[a] Average of replicate measurements. [b] In parentheses are standard deviations. [c] Calculated using eqn. (5). [d] Measured minus calculated. One asterisk denotes difference of more than 1 standard deviation; two asterisks, two standard deviations of eqn. (5).

Table 3 Comparison of K_f values obtained in this work with literature values

Solute	This work	Lit. (ref.)
Benzene	67.21	120 (38), 196 (39)
Aniline	39.48	50 (39)
Benzyl alcohol	51.76	50.12 (32)
Methanol	0.11	0.32 (32), 0.40 (40)
Ethanol	0.94	0.93 (32), 1.2 (40)
Propan-2-ol	4.23	3.80 (32)
Butan-1-ol	14.71	16.60 (32), 17 (37), 27.6 (40)
Cyclohexanol	572.67	501.2 (32), 470 (37)

appreciable expense of energy by the more favoured apolar/apolar interaction between the guest and the CD cavity.[35] This might be an indication that extrusion of 'high energy water' plays a role in determining the stabilities of the β-CD complexes with organics. Increasing stability of the complex with increasing solute size can be indicative of the fact that non-polar dispersive interactions between the solute and the CD cavity is an important factor affecting the stability. It is known that polarizability and hence dispersive interaction strength of a molecule increases with its size.[21] This indicates that the coefficient *m* is a measure of non-polar (hydrophobic) dispersive interactions between the CD cavity and the solute. A much greater magnitude of the coefficient *m* than the other two coefficients then indicates that the formation of inclusion complexes of CDs is dominated by non-polar (hydrophobic) dispersive interactions between the CD cavity and the solute.

The sign for the coefficient *b* is negative, indicating that increasing solute β leads to decreasing stabilities of the CD complexes. Because water is a stronger HB donor acid (α = 1.17) than β-CD (α = 0.14–0.21), the hydrogen bonding between the solute and the hydroxy groups on β-CD in water is highly improbable and thus increasing solute β should lead to increased hydrogen bonding with water, resulting in increased solubility of the solute in water and thus decreased complexation to occur between CD and the solute. This is in agreement with Kano *et al.*[36] that no evidence for hydrogen bonding was found in complex formation between alkyl phenols and β-CD. The magnitude of the coefficient *b* (1.27) is much smaller than the coefficient *m* (7.62), indicating the contribution of hydrogen bonding interactions to the formation of inclusion complexes are minor.

The sign for the coefficient *s* is also negative, indicating that increasing solute dipolarity leads to a decrease in the stabilities of the CD complexes. Since water is more dipolar (π^* = 1.09)[33] than β-CD (π^* = 0.43),[9] increasing solute π^* should lead to increased dipolar interactions with the more dipolar water, resulting in increased solubility of the solute in water and thus decreased complexation to occur between CD and the solute. The magnitude of the coefficient *s* (0.90) is again much smaller than the coefficient *m* (7.62), indicating that the contribution of dipolar interactions to the formation of inclusion complexes is minor.

In summary, the driving forces involved in the formation of weak inclusion complexes of β-CD and organic solutes studied in this work seems to depend on many factors such as hydrogen bonding, hydrophobic interactions, dispersive interactions, dipolar interactions, release of distortional energy of and extrusion of high energy water from CD upon inclusion of guest, and the guest molecular size. The study based on the linear solvation energy relationships has shown that for solutes whose sizes are small enough to be included in the cavity of β-CD, increasing guest molecular size stabilizes the complex by virtue of increasing dispersive interactions between the hydrophobic interior of the CD cavity and the guest, whereas increasing guest hydrogen bond acceptor basicity and dipolarity lead to a decrease in the stability of the complex due to stronger dipolar and hydrogen bonding interactions with water, which is more dipolar and hydrogen bond acidic than CD.

It should be noted that besides the relevance of the guest size with the strength of non-polar dispersive interactions of the solute with CD, the size of the guest is an important factor determining the stability of the CD complex, in that good matching of the solute size and that of the CD cavity is essential for efficient intermolecular contacts leading to increased stability of the inclusion complex. The solute size term in LSER is not sensitive enough to recognize whether the tight spatial fit is achieved between the CD cavity and the guest. However, it is capable of recognizing if the solute size is too big to fit in the cavity. The data point for any solute having incompatible size with the CD cavity would appear as an outlier from the LSER model fit. Nevertheless the LSER has been demonstrated to be very useful in deconvoluting the types and relative strengths of various intermolecular forces affecting the stability of inclusion complexes.

Calculated K_f values using eqn. (5) are listed in Table 2. For only four out of 20 instances differences between calculated and experimental values are greater than one standard deviation of eqn. (5). The LSER equation [eqn. (5)] may be utilized to estimate K_f for the other solutes whose molar volume and solvatochromic parameters are known, if their sizes are compatible with the CD cavity.

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