Complexation Thermodynamics of Cyclodextrins

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I. Introduction

Naturally occurring α-, β-, and γ-cyclodextrins and their higher homologues are truncated cone-shaped molecules with a hollow, tapered cavity of 7.9-Å depth. The top and bottom diameters of the cavity of most widely used cyclodextrins are 4.7 and 5.3 Å for α-cyclodextrin, 6.0 and 6.5 Å for β-cyclodextrin, and 7.5 and 8.3 Å for γ-cyclodextrin, respectively.[1] Possessing a hydrophobic central cavity suitable for the inclusion of various organic molecules, cyclodextrin was one of the first receptor molecules whose ability to bind organic molecules was recognized and extensively studied by various experimental techniques.[2−7]

The most probable mode of binding involves the insertion of the less polar part of the guest molecule into the cavity, while the more polar—and often charged—group of the guest is exposed to the bulk solvent just outside the wider opening of the cavity. This picture is derived from both thermodynamic and NMR studies.[2,5,8−16] The inclusion complexation of guest molecules by cyclodextrins in aqueous solutions results in a substantial rearrangement and removal of the water molecules originally solvated to both the cyclodextrin and guest molecules, and this process also induces the release of water molecules from the cyclodextrin cavity into the bulk water. The principal factors involved in binding are believed to be primarily van der Waals and hydrophobic interactions,[3,8,9,11,17−22] although hydrogen bonding and steric effects also have certain roles to play.[9,10] The thermodynamic quantities obtained for the inclusion complexation by cyclodextrins are a consequence of the weighted contributions of these interactions.

Complexation reactions involving cyclodextrins are highly important to drug delivery systems technology and also to the separation and food industries.[2,23−27] These reactions also serve as excellent models for understanding general inclusion phenomena, as well as enzyme−substrate interactions.[3] Several classes of compounds which can be included in natural α-, β-, and γ-cyclodextrins have been subjected to systematic thermodynamic studies. These cover almost every class of compound such as hydrocarbons,[28,29] aliphatic alcohols,[8,11,17,30−32] diols,[31,33] amines and acids,[9] cyclohexane derivatives,[12] amino acids,[34,35] origopeptides,[36] sugars,[37] phenols,[38−40] aromatic amines,[13] azo compounds,[41−44] naphthalene derivatives and other aromatic compounds,[14,45−47] and various drugs.[48−53] However, only a limited number of systematic thermodynamic studies using modified cyclodextrins have been reported.[54−57]

It should be noted that the thermodynamic properties of cyclodextrins themselves, such as the heat capacity both in the solid state and in solution,[58] standard enthalpies, entropies, and free energies of solution,[43,59−63] enthalpies of hydrolysis,[64] and thermodynamic quantities of acid−base dissociation,[65,66] have been studied by various experimental methods. Attempts to apply molecular mechanics calculations have also been made to investigate the solute−solvent interactions between cyclodextrin and water[67] and the molecular interactions in inclusion complexes of cyclodextrins.[68] Electrostatic potentials of the inside of the cyclodextrin cavity have also been calculated to elucidate the role of dipole−dipole interactions between host and guest.[69]

In some papers,[14,55,68] large amounts of thermodynamic data were collected to examine the validity of the enthalpy−entropy compensation relationship in the complexation reactions of natural and modified cyclodextrins. However, until now, no comprehensive

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review has been published on the thermodynamics of these reactions. Accordingly, the main aims of this review are to expand and update the thermodynamic data collected in our previous papers[14,55] and to discuss the data obtained for a wide variety of organic and some inorganic guests from a more global point of view. Such a global treatment will lead us to a better and deeper understanding of the nature of the inclusion complexation by natural and modified cyclodextrins, as well as the factors involved in controlling the supramolecular interactions.

II. Scope and Limitations

All of the thermodynamic data published or in press up until October 1997 are collected in the tables. In this review, we deal primarily with papers containing the equilibrium constants and the enthalpies and entropies of complex formation with 1:1 host−guest stoichiometry.

In some cases, an unsatisfactory description or unsuccessful fit of the experimental data to a simple 1:1 host−guest complex model has led researchers to apply more sophisticated models with 1:2 or 2:1 stoichiometry.[33,71−78] However, it should be noted that the physicochemical origins of these apparent deviations from the simple 1:1 model are quite divergent from case to case. For example, at high concentrations, the activity coefficients for anions and cations—and even for neutral molecules—could deviate significantly from unity or those values observed at low concentrations. Also, critical micelle concentrations of some amphiphilic guests could be low when there are cyclodextrins present in the solution. Moreover, the possibility of dimerization of simple 1:1 complexes should not be excluded, and one should take into account all of the possibilities before deviating from the simple 1:1 model to a more complicated model.

It has also been noted that the analysis of experimental titration data by more sophisticated models other than a 1:1 stoichiometry may lead to a nonunique numerical solution in the mathematical treatments, which is often encountered in solving thermodynamic equations dealing with the equilibrium constants in the range typical for the complexation reactions of cyclodextrins.[70] Appropriate precautions should therefore be exercised to obtain reliable and unique data from these more sophisticated models.

Having considered the complications concerning individual nonstoichiometric host−guest systems, the apparent lack of information about more sophisticated data treatments and the required physicochemical data (e.g., activity coefficient) in most cases, we finally decided not to include the thermodynamic data reported for more complicated 1:2 or 2:1 host−guest systems in this review. Readers interested in these systems should refer to the original papers.[33,71−78]

Additionally, thermodynamic data obtained under conditions allowing the coexistence of both neutral and ionized species derived from the same original guest molecule in the solution are not quoted, unless the method employed can clearly discriminate between the complexation reactions of both species. In such mixed systems, only apparent equilibrium constants and thermodynamic quantities are usually obtained,[79] and these values depend critically upon the pH of the solution as exemplified in the literature.[49,80−82] Similarly, thermodynamic complexation data obtained from mixtures of polymeric hosts of different molecular weights[83,84] are not included in the tables. In some spectroscopic or kinetic measurements, thermodynamic data for metastable, or transient, complexes are reported,[41,85−87] but only the data for the final, stablest complexes are cited in the tables. Experiments performed above the critical micelle concentration[88] cannot be treated by

a simple 1:1 model, and these results are also not included in the tables.

Although the thermodynamic quantities for complexation reactions may be derived indirectly by dealing with the relevant exchange reactions, only the thermodynamic quantities reported for direct complexation reactions with cyclodextrins are discussed in this review. For instance, the results of calculations derived from thermodynamic quantities have been reported for the exchange reactions of an organic guest between α- and β-cyclodextrin cavities[12,39] or the exchange of 1-alkyl to *sec*-alkyl guests in the same cyclodextrin cavity.[9] Finally, data from experimental studies in which only differential thermodynamic quantities ($\Delta\Delta G°$, $\Delta\Delta H°$, or $\Delta\Delta S°$) for two competitive complexation reactions are reported[24,26] are not included in the tables, although these data may elucidate regularities in thermodynamic results.

III. Determination of Thermodynamic Quantities

A wide variety of experimental methods have been employed in the determination of thermodynamic quantities for the complexation reactions of cyclodextrins. These include several different types of microcalorimetry (batch microcalorimetry,[89−91] flow microcalorimetry,[17,31] titration "macro" calorimetry,[18] and titration microcalorimetry[8,9,92,93]), electronic absorption (UV−vis),[11,38,94−96] circular dichroism (CD),[97−100] fluorescence (steady-state[34,36,76,101,102] and time-resolved[103−106]), nuclear magnetic resonance (NMR)[25,107−112] and electron spin resonance (ESR) spectroscopy,[85,113,114] gas-[26,115] and liquid-phase[80,116−119] chromatography, capillary electrophoresis,[120−122] pH potentiometry,[38,71,72] the use of ion selective electrodes (ISE),[123,124] kinetic experiments,[125−127] and solubility determinations.[128−132] Vapor pressure,[28,29] conductivity,[76,133] and surface tension[134] measurements constitute experimental methods that are only rarely employed in the thermodynamic investigation of cyclodextrin complexation. Detailed descriptions of the principles and experimental procedures of the various methods mentioned above can be found in the papers cited.

Calorimetry is the only direct method for determination of the reaction enthalpy. However, despite a long history as an established methodology,[135,136] it is not the most widely used method for studying the complexation thermodynamics of cyclodextrins. This may be due to a combination of the need for a relatively large amount of sample, sophisticated and delicate equipment, and some expertise required to obtain reliable results.[19] Performing "test" reactions is strongly recommended to ensure correct and precise microcalorimetric determinations.[8,9,92,93] Of the various types of calorimetry mentioned above, titration microcalorimetry is the most modern and sensitive method available at the present time.

A wide variety of spectroscopic methods are frequently employed to determine equilibrium constants for cyclodextrin complexation. The choice of the spectroscopic method and the experimental procedure depends on the spectral properties of the guest and/or host used. In the case of aliphatic guests lacking in intense absorption bands in the accessible UV−vis region, some chromophoric compounds (e.g., azo dyes) are added to the cyclodextrin solution as a competitive binder, and the binding constants are determined by differential UV spectroscopy.[11] The interaction of cyclodextrins with aromatic guest compounds—which possess strong absorption bands in the UV−vis region—can be studied without adding any chromophoric dyes. When using spectroscopic methods, the equilibrium constants determined at several different temperatures are analyzed by the van't Hoff equation to give the thermodynamic quantities for the complexation reaction, assuming an invariant heat capacity throughout the temperature range employed. Exactly the same data treatment can be applied to steady-state fluorescence spectroscopy,[34,101,102,132,137−144] while the equilibrium constants are calculated from the rate constants determined by fluorescence lifetime measurements.[103−106,145]

NMR titration is also used to obtain the thermodynamic quantities for cyclodextrin complexation. A mathematical approach similar to that employed in the absorption[11,94] and fluorescence[101,102] spectroscopic determinations is used. NMR spectroscopy is widely utilized in chiral discrimination studies using cyclodextrins.[25,107−112]

ESR spectroscopy is employed in the measurement of equilibrium constants between stable radicals (e.g., nitroxide) and cyclodextrins.[85,113,114] No comparisons of the thermodynamic quantities obtained can be made because these guests have been studied only by ESR spectroscopy.

CD spectroscopy is one of the best methods for the observation of the complexation behavior of chromophoric guests with cyclodextrins, since all natural cyclodextrins are inherently chiral and the spectral changes caused by the inclusion of guest molecules are often more exaggerated in the CD spectra than the UV spectra.[97−100] However, like microcalorimetry, this method is not the most widely used method for the determination of thermodynamic quantities for cyclodextrin complexation, probably due to the low availability of the instrument.

Two essentially equivalent potentiometric techniques, the use of ion selective electrodes (ISE)[123,124] and pH potentiometry,[71,72] have been adopted in the studies of the complexation thermodynamics of cyclodextrins. In the case of ISE, a direct measurement of the free guest concentration (or activity) in the solution can be made.[123,124] To evaluate the concentrations of reaction components from raw pH data, sophisticated mathematical procedures are used.[71,72]

Thermodynamic quantities have been evaluated by gas-[26,115] and liquid-phase[80,116−118] chromatography from the temperature dependence of the retention time of the guest molecule interacting with cyclodextrins bound to the stationary phase or added to the mobile phase. In recent years, chromatographic methods have been widely employed in the determination of differential thermodynamic quantities for various enantiomers upon their interaction with cyclodextrins.[24,146,147]

Capillary electrophoresis has also been employed in some thermodynamic studies of chiral recognition by cyclodextrins.[120,121] Using this method, the rela-

tive concentrations of free and complexed guest molecules—each of which possesses different migrating speeds in the presence of cyclodextrin added to the electrolyte solution—can be determined.

Complexation equilibrium constants between some esters and cyclodextrins can be determined from the change in the rate constant of ester hydrolysis in the presence of cyclodextrins, since cyclodextrins are known to accelerate the rate of hydrolysis in buffer solutions.[126] Competitive inhibition studies allow us to obtain the complexation thermodynamic quantities for guests that are not directly involved in the cyclodextrin-catalyzed reaction, but which interfere with the ester's hydrolysis through competitive complexation. For instance, thermodynamic quantities for the complexation reaction between cyclodextrins and the adamantanecarboxylate ion can be determined from the temperature-dependent study of the competitive inhibition of cyclodextrin-accelerated hydrolysis of 3-nitrophenyl acetate by adamantanecarboxylate.[125]

Solubility determinations, in which the complexation equilibrium constants are evaluated from the solubility changes upon addition of cyclodextrins, were often used in the 1960s for organic guests with low water solubilities, such as some pharmaceuticals.[128−132] Some modifications of this method have recently been employed.[48]

All of the experimental methods mentioned above should be used with the proper precautions and with appropriate skills of the investigator to obtain reliable thermodynamic data. It should be noted that, even within the same article, the equilibrium constants determined by different experimental methods for the same reaction can significantly deviate from one another.[53,148]

We emphasize again that calorimetric methods, in which the equilibrium constant and reaction enthalpy are directly and simultaneously determined by using the data at a single constant temperature, have advantages over other methods, in which the thermodynamic quantities are determined from the van't Hoff equation, assuming an invariant heat capacity over the temperature range employed. This is because the heat capacity has been demonstrated in some cases to vary even over a relatively narrow temperature range in the complexation reactions of cyclodextrins,[28,149] cyclophanes,[150,151] and ribonuclease A.[149] With only a few exceptions,[28,151] heat capacity changes for cyclodextrin complexation reactions are determined by calorimetry.[8,10,12,21,33,152]

The accuracy of the equilibrium thermodynamic data determined using various experimental methods has been compared and reviewed.[153−155] As demonstrated in some cases,[153,154] van't Hoff treatment of experimental data often leads to a significantly larger uncertainty than direct microcalorimetric determination of the reaction enthalpy.

IV. Weak Interactions Involved in Inclusion Complexation

Molecular recognition phenomena in chemistry and biology involve only noncovalent interactions, such as electrostatic (ion−ion, ion−dipole, dipole−dipole, dipole−induced dipole, and higher order terms), van der Waals, hydrophobic, hydrogen bonding, charge-transfer, $\pi-\pi$ stacking interactions, and steric effects. It is interesting to note that each weak interaction in general is not sufficient enough individually to lead to the specific association of two molecules. Usually, molecular association is made possible not by a single weak interaction but through the simultaneous cooperation of several weak interactions.[4,156,157] Thus, chemical and biological molecular recognition phenomena may be unified as the chemistry of cooperative weak interactions.[158]

In molecular recognition processes, particularly those occurring in biological supramolecular systems, cooperativity plays a central role in controlling the structure and function of the host−guest complexes, enabling the "on/off" switching of supramolecular functions. For instance, the numerous, highly ordered hydrogen bonds that form the backbone of a DNA duplex are made or broken not independently but synchronously in an apparently single step, enabling the "all-or-none" association−dissociation control over a very narrow temperature range.[158] However, cyclodextrins are not so "preorganized", or flexible enough to allow allosteric conformational changes that are permissible in biological supramolecular systems. Indeed, in the case of cyclodextrin inclusion complexes, weak forces which work locally are not always cooperative in nature, but instead may act independently, or sometimes even counteract one another.

The most important contributions to the complexation thermodynamics of cyclodextrins are believed to originate from (a) penetration of the hydrophobic part of the guest molecule into the cyclodextrin cavity and (b) dehydration of the organic guest.[8,9,10] Since the cyclodextrin cavity is highly hydrophobic,[3,11,19,20] the transfer of the hydrophobic part of the guest molecule from water into the cyclodextrin cavity—a process which suffers the combined effects of the contributions a and b above—may be compared with typical hydrophobic interaction processes, i.e. the transfer of an organic molecule from an aqueous to organic phase such as hexane,[159] which is quantitatively evaluated by Hansch's hydrophobicity parameter (π).[160] Usually the sum of the contributions a and b is considered to be the entity of the hydrophobic effect, although occasionally contribution a is separated from the total effect as a "pure" van der Waals interaction.[8]

As indicated above, charged groups, such as ammonium and carboxylate,[10] or hydrophilic groups, such as hydroxyl, amino, and carboxyl,[8] remain exposed to the bulk solvent even after the inclusion of the hydrophobic moiety. An exception to this general rule is the aromatic hydroxyl group, which can penetrate deeply into the cyclodextrin cavity where it hydrogen-bonds to one of cyclodextrin's peripheral hydroxyl groups.[10] For guest molecules such as 4-hydroxyphenethylamine (tyramine),[10] the simple "hydrophilic outside−lipophilic inside model" described above cannot be applied. Thus, hydrogen-bonding interactions may function as a third factor (c) contributing to the stabilization of cyclodextrin

complexes with such guest molecules. Other examples of hydrogen-bond formation include the complexation reactions of short alkanediols[33] and ephedrines.[13] It is also certain that water molecules can form hydrogen bonds to the inside of cyclodextrin's cavity.

There are two more factors that contribute to the complexation thermodynamics of cyclodextrins, which differ from the classical hydrophobic effect,[159] and these are (d) the release of the water molecules originally included in the cyclodextrin cavity to bulk water[8,17,18] and (e) the conformational changes or strain release of the cyclodextrin molecule upon complexation.[3,11,19] It is not known exactly how many water molecules (*h*) exist in the cavity of natural cyclodextrins, nor how many water molecules (*i*) are released from the cavity upon complexation, but for α-cyclodextrin, these numbers (*h* and *i*) are estimated to be 2 or 3 and ≤2, respectively.[8,17,18] X-ray crystal structures show five to six water molecules residing in the cavity of α-cyclodextrin, two of which are hydrogen-bonded to peripheral hydroxyl groups.[161] In the case of *β*-cyclodextrin,[162] six to seven water molecules are distributed within the cavity, even though the cavity is big enough to accommodate up to 11 of them.

Taking into account the originally included or interacting water molecules, the 1:1 complexation reaction of a guest (G) with a cyclodextrin host (H) may be written as follows:

$$G{\cdot}gH_2O + H{\cdot}hH_2O \rightleftarrows H{\cdot}G{\cdot}(g + h - i)H_2O + iH_2O \quad (1)$$

where *g* represents the number of water molecules interacting with the free guest, *h* the number of tightly bound hydration water molecules inside the free cyclodextrin cavity, and *i* the net displacement of water upon complexation. As described above, there is no accurate information available concerning the values of *g*, *h*, and *i* in solution.

Several attempts have been made to separate the contributions of the hydrophobic effect and the hydrogen-bonding interaction from the other terms that contribute to the overall thermodynamic complexation quantities.[10,31] The thermodynamic contribution from the hydrophobic effect may be estimated from increments in the measured values induced by the extension of the methylene chain in a series of aliphatic guests,[8,9,13,33,163−166] while the contribution of hydrogen bonding may be estimated by adding hydroxyl groups to the guest molecule.[10]

As for contribution e, no reliable quantitative information is available for the thermodynamic consequence of conformational changes upon inclusion complexation by cyclodextrins. However, appreciable and different degrees of molecular motions of the cyclodextrin and guest, before and after complexation, have been demonstrated.[167]

V. Inclusion Thermodynamics

All thermodynamic data reported for 1:1 complexation reactions with natural and modified cyclodextrins are presented in Tables 1−3. The data for natural α-, *β*-, and *γ*-cyclodextrins (**1**α, **1***β*, and **1***γ*) are shown in Table 1, while those for cyclodextrin derivatives (**2**−**27**) are listed in Table 2. Heat capacity data ($\Delta C_p°$) for complexation reactions involving **1**α, **1***β*, and **1***γ* are summarized separately in Table 3. The structures of all the cyclodextrins **1**−**27** and some of the rarer guest compounds **28**−**33** are illustrated in Charts 1 and 2. All thermodynamic quantities refer to the standard state. For ionic guest molecules, such as carboxylate and ammonium ions, the counterions are omitted in the tables, since they do not take part in the complexation process as defined in eq 2. It should be noted that the nature and driving forces of cyclodextrin complexation in pure organic solvents[43,168,169] may differ significantly from those in water. However, we have not made a separate table for these data, and have instead included them in Table 1, since there is only a limited amount of thermodynamic data available for organic solvents.

The equilibrium constants for 1:1 complexation reactions listed in these tables are defined by eq 2:

$$K = \gamma_{H{\cdot}G}[H{\cdot}G]/\{\gamma_H[H]\gamma_G[G]\} \cong [H{\cdot}G]/[H][G] \quad (2)$$

where *γ* is activity coefficient of each species. Since most of the cyclodextrins are nonelectrolytes, their activity coefficients will be close to unity at the low concentrations employed in most experimental studies. The same assumption can be applied to guests that are nonelectrolytes. Nonideality corrections are assumed to be negligible for both equilibrium constants and standard molar enthalpies of the reaction in almost all cases. This approximation should be sustainable even when dealing with a charged guest, e.g. naphthalenesulfonates,[14] since the equilibrium is charge symmetrical, and the activity coefficients that occur in the numerator and denominator should largely cancel each other out at low ionic strengths.

For all original data, a comparison between the standard Gibbs energy change ($\Delta G°$) calculated from the reported enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes and that calculated from the equilibrium constant (*K*) in the standard state was made before including them in the tables. If a discrepancy larger than 4 kJ mol^{-1} (or 1 kcal mol^{-1}) was found, all relevant thermodynamic quantities were recalculated, using the raw experimental data in the original paper. In the absence of readily available raw data, the discrepancies are left uncorrected in the tables but are indicated in a footnote.

The general trends of the thermodynamic quantities for the complexation reactions of natural and modified cyclodextrins (Tables 1−3) are consistent with the hydrophobic nature of the host−guest interactions. Obviously, much higher affinities—as defined by $-\Delta G°$—are obtained for neutral compounds compared to those of the corresponding charged species derived from the same original guest molecules. Thus, neutral phenols, acids, and amines give larger *K* values than the corresponding ionized or protonated species. Similarly, the affinity in-

Table 1. Complex Stability Constant (log *K*), Standard Free Energy ($\Delta G°$), Enthalpy ($\Delta H°$), and Entropy Changes ($T\Delta S°$) for 1:1 Inclusion Complexation of Various Guests with Natural α-, *β*-, and *γ*-Cyclodextrins (1α, 1*β*, and 1*γ*)

host	guest	solvent	*T*/K	log *K*	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	acetic acid	H_2O	298	0.96 ± 0.01	−5.5 ± 0.1	−11.2 ± 0.1	−5.6 ± 1.3	pot	172
1α	acetic acid	H_2O	298	3.8 ± 1.2	−21.8 ± 6.7	−5.0 ± 0.4	16.2	cal	192[b]
1α	acetonitrile	H_2O (pH 3.8−4.5)	298	0.75 ± 0.01	−4.3 ± 0.1	−10 ± 1	−6 ± 1	pot	235[c]
1α	acetonitrile	H_2O (0.05 M HCl)	298	0.72	−4.1	−14	−10	uv	236[d]
1α	*N*-acetyl-l-leucinamide	H_2O	298	1.30 ± 0.08	−7.4 ± 0.5	−6.1 ± 0.8	1.3 ± 1.3	cal	201
1α	1-adamantanecarboxylate	H_2O (pH 7.2)	298		−14.2	−14.6	−0.4	cal	21
1α	1-adamantanecarboxylate	H_2O-CH_3CN (98.5:1.5; pH 9.0)	298	3.09 ± 0.03	−17.6	−5.0 ± 1.7	12.5 ± 2.5	kin	125
1α	1-adamantanecarboxylate	H_2O	298	2.15 ± 0.04	−12.2 ± 0.2	−14 ± 3	−2 ± 2	con	133
1α	1-adamantanecarboxylate	H_2O (pH 8.5)	298	2.15	−12.2	−13.4 ± 0.4	−1.2	cal	81
1α	1-adamantanecarboxylate	H_2O	298		−11.6	−14.3	−2.7	cal	188
1α	1-adamantanecarboxylate	H_2O (pH 8.50)	298		−12.3 ± 0.2	−13.5 ± 0.3	−0.4 ± 0.4	cal	237
1α	1-adamantanecarboxylate	H_2O	298	2.16 ± 0.05	−12.3 ± 0.3	−23 ± 3	−11 ± 2	pot	133
1α	1-adamantylammonium	H_2O	298	2.43 ± 0.01	−13.9 ± 0.1	−20.3 ± 1.4	−6.3 ± 1.4	pot	238
1α	1-adamantylammonium	H_2O (pH < 2.5)	298	1.697 ± 0.007	−9.68 ± 0.04	−15.3 ± 0.9	−5.6 ± 0.9	uv	238
1α	adipate (dianion)	H_2O (pH 9.5)	298	2.13 ± 0.01	−12.16 ± 0.04	−15.16 ± 0.04	−3.00 ± 0.06	cal	239
1α	hydrogen adipate (monoanion)	H_2O	298	2.18 ± 0.01	−12.4 ± 0.1	−31.4 ± 1.3	−19.0 ± 1.4	pot	72
1α	adiphenine·HCl	H_2O	298	1.06 ± 0.03	−6.1	−25.5 ± 1.6	−19.5	cal	74
1α	2-aminobenzoic acid	H_2O	298	5.0 ± 1.3	−28.5 ± 7.5	−1.3 ± 0.4	26.2	cal	192
1α	3-aminobenzoic acid	H_2O	298		−9.9	−32.5 ± 0.3	−22.6 ± 0.8	cd	194
1α	4-aminobenzoic acid	H_2O	298		−16.0	−43.6 ± 0.8	−27.6 ± 2.5	cd	194
1α	4-aminobenzoic acid	H_2O	298	2.8 ± 0.1	−15.9 ± 0.4	−49 ± 2	−33	cal	192
1α	6-aminohexanoic acid	H_2O (pH 7.0)	298	1.34	−7.6 ± 0.7	−1.5 ± 0.3	6.0 ± 1.0	cal	35
1α	3-(aminomethyl)proxyl	H_2O	298	0.69 ± 0.10	−3.9 ± 0.6	−33 ± 8	−29 ± 8	esr	114
1α	2-aminooctanoic acid	H_2O (pH 7.8)	298	2.80 ± 0.02	−16.0 ± 0.2	−17.7 ± 0.3	−1.7 ± 0.5	cal	35
1α	8-aminooctanoic acid	H_2O (pH 7.1)	298	1.88 ± 0.02	−10.7 ± 0.1	−14.8 ± 0.4	−4.1 ± 0.5	cal	35
1α	4-aminophenol	H_2O (pH 4.0)	298	1.24 ± 0.02	−7.1 ± 0.3	−20.1 ± 0.5	−13.1 ± 0.6	uv	191
1α	11-aminoundecanoic acid	H_2O (pH 6.7)	298	3.34 ± 0.04	−19.0 ± 0.2	−26.6 ± 0.5	−7.6 ± 0.7	cal	35
1α	*d*-amphetamine	H_2O (pH 11.0)	298	1.38	−7.9	−12.6 ± 2.1	−4.7	uv/cal	202
1α	*l*-amphetamine	H_2O (pH 11.0)	298	1.40	−8.0	−12.6 ± 2.1	−4.6	uv/cal	202
1α	anilinium perchlorate	H_2O	298	1.5 ± 0.2	−8.4 ± 1.3	−52 ± 8	−44	cal	192
1α	8-anilino-1-naphthalene-sulfonate	H_2O (pH 1.95)	298	1.41	−8.0	−10.5	−2.5	fl	240
1α	anthracene	H_2O	298	1.87	−10.7	−79.1	−68.4	lc	241
1α	benz[*a*]anthracene	H_2O	298	1.94	−11.1	−80.3	−69.2	lc	241
1α	benzene	H_2O	298	1.500 ± 0.001	−8.56 ± 0.03	−13.1 ± 0.3	−4.5	vap	29
1α	benzoate	H_2O	298	1.02 ± 0.01	−5.8 ± 0.1	−16.3 ± 1.3	−10.5 ± 1.4	pot	172
1α	benzoic acid	H_2O	298	2.88 ± 0.01	−16.4 ± 0.1	−42.5 ± 0.6	−26.0 ± 0.6	pot	172
1α	benzoic acid	H_2O	298	3.0 ± 0.1	−17.1 ± 0.4	−40.2 ± 0.4	−22.5	cal	192
1α	benzoic acid	H_2O	298		−14.4	−41.8 ± 1.0	−27.4 ± 2.9	cd	194
1α	benzoic acid	H_2O	303	2.96	−17.2 ± 0.2	−33.9 ± 2.0	−16.7 ± 1.5	cal	73
1α	benzoic acid	H_2O	303	2.77	−16.1	−38.2	−22.1	cal	242
1α	benzo[*a*]pyrene	H_2O	298	2.24	−12.8	−46.9	−34.1	lc	241
1α	L-α-*O*-benzylglycerol	H_2O (pH 6.9)	298	1.17 ± 0.07	−6.66 ± 0.48	−14.8 ± 2.2	−8.0 ± 2.4	cal	13
1α	1-benzylimidazole	H_2O (pH 10.0)	298	1.78 ± 0.03	−10.15 ± 0.22	−28.9 ± 1.9	−18.8 ± 2.1	cal	13
1α	4-benzylpiperidine	H_2O (pH 6.9)	298	1.65 ± 0.02	−9.43 ± 0.15	−19.9 ± 0.9	−10.4 ± 0.9	cal	13
1α	1-bicyclo[2.2.1]heptane-carboxylate	H_2O (pH 8.5)	298	1.34	−7.5	−13.0 ± 1.3	−5.2	cal	81
1α	1-bicyclo[2.2.1]hept-2-enecarboxylate	H_2O (pH 8.5)	298	1.38	−8.0	−10.0 ± 1.7	−0.6	cal	81
1α	1-bicyclo[2.2.2]octane-carboxylate	H_2O (pH 8.5)	298	1.48	−8.4	−14.2 ± 1.7	−6.0	cal	81
1α	biebricht scarlet	H_2O (pH 7)	298	3.12	−17.8	−20	−2	kin	87[e]
1α	bromodiphenhydramine·HCl	H_2O	298	3.13 ± 0.03	−17.9	−27.3 ± 0.5	−9.5	cal	74
1α	4-bromophenol	H_2O (pH 4.2)	298	2.85 ± 0.01	−16.3 ± 0.1	−25.6 ± 0.2	−9.2 ± 0.3	cal	39
1α	4-bromophenol	H_2O (pH 4.0)	298	2.84 ± 0.01	−16.2 ± 0.4	−29.8 ± 1.4	−13.7 ± 1.5	uv	191
1α	1,2-butanediol	H_2O	298	1.11 ± 0.01	−6.3 ± 0.1	−7.7 ± 0.1	−1.4 ± 0.2	cal	31
1α	1,3-butanediol	H_2O	298	1.00 ± 0.08	−5.7 ± 0.5	−6.7 ± 1.0	−0.9 ± 1.2	cal	243
1α	1,3-butanediol	H_2O	298		−24.0	−1.3	22.7	cal	244[b]
1α	1,4-butanediol	H_2O	288	0.99 ± 0.03	−5.4 ± 0.2	−9.2 ± 0.5	−3.7 ± 0.6	cal	33
1α	1,4-butanediol	H_2O	298	0.89 ± 0.02	−5.1 ± 0.1	−11.7 ± 0.4	−6.6 ± 0.6	cal	33
1α	1,4-butanediol	H_2O	298	1.08 ± 0.03	−6.1 ± 0.2	−8.0 ± 0.3	−1.8 ± 0.3	cal	243
1α	1,4-butanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	0.95 ± 0.05	−5.4	−13	−7	uv	245
1α	1,4-butanediol	H_2O	298	0.90 ± 0.05	−5.2 ± 0.3	−10.0 ± 1.0	−4.8 ± 0.2	cal	31
1α	1,4-butanediol	H_2O	308	0.81 ± 0.04	−4.8 ± 0.2	−12.4 ± 0.8	−7.7 ± 0.9	cal	33
1α	butanoate	H_2O (pH 11.3)	298	1.93 ± 0.07	−11.0	−0.7 ± 0.1	10.3	cal	246
1α	butanoate	H_2O (pH 6.9)	298	1.10 ± 0.05	−6.3 ± 0.3	−10.6 ± 1.0	−4.3 ± 1.1	cal	9
1α	butanoate	H_2O	298	1.188 ± 0.011	−6.78 ± 0.13	−5.8 ± 0.4	1.0 ± 0.4	pot	71
1α	butanoic acid	H_2O	298	2.130 ± 0.003	−12.15 ± 0.04	−23.2 ± 0.6	−11.0 ± 0.6	pot	71
1α	(*R*)-(−)-2-butanol	H_2O (pH 6.90)	298	1.39 ± 0.02	−7.9 ± 0.2	−11.0 ± 0.5	−3.1 ± 0.5	cal	32
1α	(*S*)-(+)-2-butanol	H_2O (pH 6.90)	298	1.38 ± 0.04	−7.9 ± 0.3	−11.1 ± 0.7	−3.3 ± 0.9	cal	32
1α	(±)-2-butanol	H_2O (pH 6.90)	298	1.44 ± 0.02	−8.2 ± 0.2	−9.9 ± 0.4	−1.7 ± 0.1	cal	32

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	1-butanol	H_2O	298		−10.95 ± 0.03	−10.70 ± 0.05	0.2 ± 0.1	cal	8
1α	1-butanol	H_2O	298	2.00	−11.4	−9.9	1.5	cal	247
1α	1-butanol	H_2O	298	1.95	−11.1	−12.0	−0.6	uv	11
1α	1-butanol	H_2O (pH 6.90)	298	1.90 ± 0.01	−10.9 ± 0.1	−11.6 ± 0.2	−0.9 ± 0.1	cal	32
1α	1-butanol	H_2O	298	1.91	−10.9	−10.2	0.7	cal	18
1α	1-butanol	H_2O (0.05 M HCl)	298	1.92	−10.9	−9	2	uv	236[d]
1α	1-butanol	H_2O	298	1.85 ± 0.06	−10.5 ± 0.4	−9.9 ± 0.4	0.6 ± 0.6	cal	243
1α	1-butanol	H_2O	298	3.96	−22.6	−7.9	14.7	cal	91[b]
1α	2-butanol	H_2O	298	1.45	−8.3	−9.0	−0.7	cal	17, 31, 247
1α	2-butanone	H_2O (0.05 M HCl)	298	1.03	−5.9	−11	−5	uv	236[d]
1α	butylamine	DMF	298	0.67 ± 0.03	−3.8 ± 0.2	−25.1 ± 2.0	−21.2 ± 2.1	cal	168
1α	butylamine	H_2O	298	2.04 ± 0.02	−11.6 ± 0.1	−15.1 ± 0.4	−3.5 ± 0.3	cal	168[f]
1α	butylammonium	H_2O (pH 6.9)	298	1.16 ± 0.03	−6.59 ± 0.16	−9.1 ± 0.4	−2.5 ± 0.5	cal	9
1α	1-butylimidazole	H_2O (pH 10.0)	298	2.24 ± 0.01	−12.77 ± 0.07	−20.4 ± 0.2	−7.6 ± 0.2	cal	13
1α	3-carbamoylproxyl	H_2O	298	0.52 ± 0.16	−3.0 ± 0.9	−22 ± 7	−19 ± 6	esr	114
1α	carbazole−viologen linked compound **28a**	D_2O	303		−19.2 ± 0.4	−54.4 ± 2.1	−34.7 ± 2.0	nmr	248
1α	carbazole−viologen linked compound **28b**	D_2O	303		−24.3 ± 0.4	−54.4 ± 1.7	−29.4 ± 1.4	nmr	248
1α	carbazole−viologen linked compound **28c**	D_2O	303		−27.2 ± 0.4	−56.5 ± 1.3	−29.1 ± 1.2	nmr	248
1α	chlorcyclizine	H_2O	298	2.99 ± 0.01	−17.6	−30.1	−12.5	pot	36
1α	chlorcyclizine·2HCl	H_2O	298	3.05 ± 0.01	−17.4	−23.4 ± 0.9	−6.1	cal	74
1α	chlorcyclizine·HCl	H_2O	298	3.05 ± 0.03	−17.4	−24.4 ± 0.8	−7.0	cal	74
1α	2-chloro-4-[(4-hydroxy-phenyl)azo]benzoate	H_2O	298	4.14 ± 0.06	−23.73	−37.0 ± 0.4	−13.3	cal	43
1α	2-chloro-4-[(4-hydroxy-phenyl)azo]benzoate	DMF	298	3.32 ± 0.18	−18.95	−14.5 ± 1.2	4.4	cal	43
1α	4-chloro-3-[(4-hydroxy-phenyl)azo]benzoate	DMF	298	3.71 ± 0.04	−21.18	−19.3 ± 1.1	1.9	cal	43
1α	4-chlorophenol	H_2O (pH 4.2)	298	2.47 ± 0.01	−14.1 ± 0.1	−20.1 ± 0.2	−6.0 ± 0.3	cal	39
1α	4-chlorophenol	H_2O (pH 4.0)	298	2.43 ± 0.01	−13.8 ± 0.3	−28.4 ± 0.5	−14.6 ± 0.6	uv	191
1α	3-chlorophenyl acetate	H_2O (pH 10)	298	2.38	−13.6	−8	5	kin	126
1α	cinnarizine·2HCl	H_2O	298	1.45 ± 0.01	−8.3	−38.4 ± 0.9	−30.1	cal	74
1α	4-cyanophenol	H_2O (pH 4.0)	298	2.24 ± 0.01	−12.8 ± 0.4	−28.1 ± 0.8	−15.2 ± 0.9	uv	191
1α	4-cyanophenol	H_2O (pH 4.0)	298		−11.3	−19.2	−7.9	cal	193
1α	4-cyanophenolate	H_2O (pH 10.0)	298		−15.9	−25.1	−9.2	cal	193
1α	cyclizine·HCl	H_2O	298	1.68 ± 0.03	−9.6	−20.0 ± 1.0	−10.4	cal	74
1α	cyclobutanol	H_2O (pH 6.9)	298	1.48 ± 0.02	−8.46 ± 0.13	−11.5 ± 0.4	−3.0 ± 0.4	cal	9
1α	cycloheptanol	H_2O (pH 6.9)	298	1.83 ± 0.07	−10.5 ± 0.5	−12.5 ± 1.9	−2.0 ± 2.0	cal	9
1α	cyclohexanecarboxylic acid	H_2O	298	1.701 ± 0.003	−9.74 ± 0.03	−40.6 ± 0.8	−30.9 ± 0.7	pot	71
1α	cyclohexanecarboxylic acid	H_2O	298		−9.7	−39.5	−29.8	pot	177
1α	*cis*-1,2-cyclohexanediol	H_2O (pH 6.90)	298	1.20 ± 0.03	−6.9 ± 0.2	−11.0 ± 0.6	−4.2 ± 0.6	cal	12
1α	*trans*-1,2-cyclohexanediol	H_2O (pH 6.90)	298	1.23 ± 0.05	−7.0 ± 0.3	−11.0 ± 1.0	−3.9 ± 1.2	cal	12
1α	cyclohexanol	H_2O (pH 6.90)	288	1.89 ± 0.02	−10.4 ± 0.1	−10.0 ± 0.2	0.6 ± 0.3	cal	12
1α	cyclohexanol	H_2O (pH 6.90)	294	1.86 ± 0.02	−10.5 ± 0.1	−11.2 ± 0.2	−0.9 ± 0.3	cal	12
1α	cyclohexanol	H_2O (pH 6.90)	298	1.79 ± 0.01	−10.2 ± 0.1	−12.8 ± 0.1	−2.7 ± 0.3	cal	12
1α	cyclohexanol	H_2O	298	1.81	−10.3	−14.0	−4.2	uv	11
1α	cyclohexanol	H_2O (pH 3.8−4.5)	298	1.79 ± 0.01	−10.2 ± 0.1	−13 ± 1	−2 ± 1	pot	23[c]
1α	cyclohexanol	H_2O	298	1.75	−10.0	−12.2	−2.2	cal	18
1α	cyclohexanol	H_2O (pH 6.90)	298	1.76 ± 0.01	−10.1 ± 0.1	−13.3 ± 0.2	−3.3 ± 0.3	cal	12
1α	cyclohexanol	H_2O (pH 6.90)	303	1.76 ± 0.01	−10.2 ± 0.1	−13.8 ± 0.2	−3.6 ± 0.3	cal	12
1α	cyclohexanol	H_2O (pH 6.90)	308	1.70 ± 0.02	−10.0 ± 0.1	−15.4 ± 0.2	−5.2 ± 0.3	cal	12
1α	cyclohexanol	H_2O	298	4.16	−23.8	−7.9	15.9	cal	89[b]
1α	cyclohexanone	H_2O (pH 6.90)	298	1.34 ± 0.06	−7.7 ± 0.4	−11.1 ± 0.9	−3.6 ± 1.2	cal	12
1α	cyclooctanol	H_2O (pH 6.9)	298	2.37 ± 0.30	−14 ± 10	−4 ± 3	10 ± 10	cal	9
1α	cyclopentanol	H_2O (pH 6.9)	298	1.56 ± 0.01	−8.91 ± 0.13	−11.5 ± 0.2	−2.6 ± 0.3	cal	9
1α	decanedioate	D_2O (pD 13)[g]	298		−18.2	−18.2	0.0	nmr	170
1α	decanedioate	H_2O (pH 11.3)	298	3.25 ± 0.02	−18.6 ± 0.1	−16.2 ± 0.1	2.4 ± 0.2	cal	171
1α	decanedioic acid	H_2O (pH 1.3)	298	3.36 ± 0.05	−19.2 ± 0.3	−79.0 ± 1.0	−60.0 ± 1.3	cal	171
1α	1,10-decanediol	H_2O	288	4.05 ± 0.05	−22.4 ± 0.3	−20.3 ± 0.2	2.0 ± 0.6	cal	33
1α	1,10-decanediol	H_2O	298	3.85 ± 0.05	−22.0 ± 0.3	−24.8 ± 0.3	−2.7 ± 0.6	cal	33
1α	1,10-decanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	3.85 ± 0.01	−22.0	−31	−9	uv	245
1α	1,10-decanediol	H_2O	308	3.74 ± 0.02	−22.0 ± 0.1	−28.7 ± 0.2	−6.8 ± 0.3	cal	33
1α	diammine(1,1-cyclobutane-dicarboxylato)platinum(II)	H_2O	298	1.78	−10.1	−25.3	−15.2	cal	249
1α	dibutylamine	DMF	298	0.90 ± 0.03	−5.2 ± 0.2	−12.6 ± 2.0	−7.5 ± 2.1	cal	168
1α	diethylamine	H_2O	298	1.54 ± 0.08	−8.8 ± 0.5	−12.6 ± 0.8	−3.8 ± 0.9	cal	168[f]
1α	(2,5-dimethoxyphenethyl)-ammonium	H_2O (pH 6.9)	298	1.54 ± 0.01	−8.81 ± 0.04	−18.8 ± 0.2	−10.0 ± 0.2	cal	13
1α	(2,5-dimethoxyphenethyl)-ammonium	H_2O (pH 5.0)	298	1.43 ± 0.02	−8.16 ± 0.09	−13.6 ± 0.4	−5.4 ± 0.4	cal	13
1α	(3,4-dimethoxyphenethyl)-ammonium	H_2O (pH 6.9)	298	0.90 ± 0.14	−5.1 ± 1.1	−9.0 ± 2.9	−3.9 ± 3.0	cal	13

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	4-[[4-(*N*,*N*-dimethylamino)-phenyl]azo]naphthalene-1-sulfonate	H_2O (pH 11)	287	3.00	−16.5	−29.7	−13.2	uv	42
1α	2-[[4-(dimethylamino)-phenyl]azo]pyridine	H_2O (pH 6.5−7.5)	298	3.39	−19.4	−29	−10	kin	250
1α	dioxane	H_2O (pH 3.8−4.5)	298	0.64 ± 0.03	−3.7 ± 0.2	−10 ± 1	−6 ± 1	pot	235[c]
1α	diphenhydramine·HCl	H_2O	298	1.65 ± 0.01	−9.4	−16.2 ± 0.2	−6.8	cal	74
1α	diphenidol·HCl	H_2O	298	1.64 ± 0.01	−9.4	−20.4 ± 0.3	−11.1	cal	74
1α	diphenyl phosphate	H_2O (pH 3.4−10)	298	−0.071	0.4	−37	−39	fl	102
1α	diphenylpyraline·HCl	H_2O	298	1.50 ± 0.01	−8.6	−19.8 ± 0.3	−11.3	cal	74
1α	dipropylamine	DMF	298	0.78 ± 0.07	−4.4 ± 0.4	−10.5 ± 2.0	−6.0 ± 2.1	cal	168
1α	di-*tert*-butyl nitroxide	H_2O	298	0.78 ± 0.08	−4.5 ± 0.5	−33 ± 6	−28 ± 5	esr	114
1α	dodecanedioate	D_2O (pD 13)[g]	298		−21.6	−25.7	−4.2	nmr	170
1α	(1*R*,2*S*)-(−)-ephedrine	H_2O (pH 6.9)	298	1.23 ± 0.02	−7.02 ± 0.13	−15.6 ± 0.7	−8.6 ± 0.9	cal	13
1α	(1*R*,2*S*)-(−)-ephedrine	H_2O (pH 5.0)	298	1.07 ± 0.05	−6.10 ± 0.32	−12.0 ± 1.2	−6.0 ± 1.2	cal	13
1α	(1*S*,2*R*)-(+)-ephedrine	H_2O (pH 6.9)	298	1.26 ± 0.02	−7.17 ± 0.13	−15.0 ± 0.6	−7.7 ± 0.6	cal	13
1α	(1*S*,2*R*)-(+)-ephedrine	H_2O (pH 5.0)	298	0.95 ± 0.06	−5.42 ± 0.42	−16.2 ± 2.3	−10.7 ± 2.4	cal	13
1α	ethanol	H_2O	298	0.99	−5.7	−2.4	3.3	cal	18
1α	ethanol	H_2O	298	0.83	−4.7	−2.5	2.2	cal	17, 31, 247
1α	ethanol	H_2O (pH 3.8−4.5)	298	0.61 ± 0.02	−3.5 ± 0.1	−3 ± 2	1 ± 2	pot	235[c]
1α	ethyl decanoate	H_2O-EtOH (85:15; pH 4.3)	293	1.68	−9.4	−35.7	−26.3	gc	115
1α	ferrocenylalkyldimethyl ammonium **29a**	H_2O (0.05 M NaCl)	298	2.32	−13.2 ± 0.4	−15.9 ± 0.4	−2.5 ± 0.8	cal	251
1α	ferrocenylalkyldimethyl ammonium **29b**	H_2O (pH 2.6−6.5)	298	3.08	−17.6 ± 0.4	−18.8 ± 0.8	−1.3 ± 1.3	cal	251
1α	ferrocenylalkyldimethyl ammonium **29c**	H_2O (pH 2.6)	298	3.08	−17.6 ± 0.4	−33.1 ± 0.8	−15.5 ± 1.3	cal	251
1α	ferrocenylalkyldimethyl ammonium **29d**	H_2O (pH 6.5)	298	2.65	−15.1 ± 0.4	−14.6 ± 1.7	0.4 ± 2.1	cal	251
1α	(*R*)-1-ferrocenylethanol	H_2O (pH 11.4)	298	2.02 ± 0.53	−11.5	−20.9	−10.2	lc	252
1α	(*S*)-1-ferrocenylethanol	H_2O (pH 11.4)	298	1.90 ± 0.10	−10.8	−16.7	−6.9	lc	252
1α	4-fluorophenol	H_2O (pH 4.0)	298	1.57 ± 0.02	−8.9 ± 0.5	−15.8 ± 2.4	−6.9 ± 2.4	uv	191
1α	flurbiprofen	H_2O (pH 7.0)	298	1.84	−10.5	−3.7	6.8	cal	253[d]
1α	formic acid	H_2O	298	0.61 ± 0.01	−3.5 ± 0.1	−3.1 ± 0.5	0.4 ± 0.5	pot	172
1α	4-formylphenol	H_2O (pH 4.0)	298	1.98 ± 0.01	−11.3 ± 0.2	−26.4 ± 1.1	−15.2 ± 1.2	uv	191
1α	D-fructose	H_2O	298	1.72	−9.8 ± 1.3	−0.05 ± 0.01	9.8 ± 1.4	cal	37
1α	hydrogen fumarate (monoanion)	H_2O	298	2.170 ± 0.003	−12.4 ± 0.1	−35.8 ± 0.3	−23.8 ± 0.2	pot	72
1α	fumaric acid	H_2O	298	3.24 ± 0.01	−18.5 ± 0.1	−41.7 ± 0.3	−22.8 ± 0.2	pot	72
1α	D-galactose	H_2O	298	1.19	−6.8 ± 1.8	−0.32 ± 0.12	6.5 ± 1.8	cal	37
1α	D-glucose	H_2O	298	1.56	−8.9 ± 1.3	−0.14 ± 0.03	8.8 ± 1.3	cal	37
1α	D-glucose	H_2O	298	2.65 ± 0.14	−15.1 ± 0.8	−46 ± 17	−31	uv/cal	232[b]
1α	hydrogen glutarate (monoanion)	H_2O	298	1.73 ± 0.01	−9.9 ± 0.1	−33.9 ± 0.8	−24.3 ± 0.7	pot	72
1α	glutaric acid	H_2O	298	2.48 ± 0.01	−14.1 ± 0.1	−37.2 ± 0.8	−23.1 ± 0.7	pot	72
1α	heptanedioate (dianion)	H_2O (pH 11.3)	298	1.38 ± 0.02	−7.9 ± 0.1	−10.1 ± 0.3	−2.2 ± 0.4	cal	171
1α	heptanedioate (dianion)	H_2O (pH 9.5)	298	2.69 ± 0.01	−15.36 ± 0.02	−18.74 ± 0.03	−3.38 ± 0.04	cal	239
1α	heptanedioate (dianion)	H_2O	298	1.43 ± 0.01	−8.1 ± 0.1	−14.6 ± 0.4	−6.7 ± 0.5	pot	72
1α	hydrogen heptanedioate (monoanion)	H_2O	298	2.60 ± 0.01	−14.8 ± 0.1	−31.7 ± 0.4	−17.0 ± 0.4	pot	72
1α	heptanedioic acid	H_2O	298	2.87 ± 0.01	−16.4 ± 0.1	−35.1 ± 0.5	−18.7 ± 0.5	pot	72
1α	heptanedioic acid	H_2O (pH 1.3)	298	2.862 ± 0.003	−16.3 ± 0.1	−28.1 ± 0.1	−11.8 ± 0.2	cal	171
1α	1,7-heptanediol	H_2O	288	2.60 ± 0.02	−14.3 ± 0.1	−17.5 ± 0.3	−3.2 ± 0.3	cal	33
1α	1,7-heptanediol	H_2O	298	2.50 ± 0.02	−14.3 ± 0.1	−22.1 ± 0.4	−7.7 ± 0.6	cal	33
1α	1,7-heptanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	2.56 ± 0.02	−14.6	−22	−8	uv	245
1α	1,7-heptanediol	H_2O	308	2.42 ± 0.02	−14.3 ± 0.1	−24.0 ± 0.6	−9.9 ± 0.6	cal	33
1α	heptanoate	H_2O (pH 6.9)	298	2.911 ± 0.009	−16.61 ± 0.05	−17.7 ± 0.1	−1.1 ± 0.1	cal	10
1α	heptanoate	H_2O (pH 6.9)	298	2.93 ± 0.02	−16.7 ± 0.11	−17.5 ± 0.7	−0.8 ± 0.7	cal	9
1α	heptanoate	H_2O (pH 11.3)	298	3.09 ± 0.02	−17.6	−12.2 ± 0.1	5.4	cal	246[h]
1α	(*R*)-(−)-2-heptanol	H_2O (pH 6.90)	298	2.88 ± 0.10	−16.4 ± 0.7	−22.1 ± 2.3	−5.7 ± 2.4	cal	32
1α	(*S*)-(+)-2-heptanol	H_2O (pH 6.90)	298	2.88 ± 0.07	−16.5 ± 0.4	−22.0 ± 1.5	−5.4 ± 1.5	cal	32
1α	1-heptanol	H_2O	298		−17.5 ± 0.3	−22.8 ± 1.1	−5.3 ± 1.1	cal	8
1α	6-heptenoate	H_2O (pH 6.9)	298	2.636 ± 0.005	−15.05 ± 0.03	−18.7 ± 0.2	−3.7 ± 0.2	cal	9
1α	heptylammonium	H_2O (pH 6.9)	298	3.03 ± 0.02	−17.3 ± 0.1	−19.9 ± 0.2	−2.6 ± 0.2	cal	10
1α	heptylammonium	H_2O (pH 6.9)	298	3.033 ± 0.004	−17.31 ± 0.03	−19.5 ± 0.2	−2.2 ± 0.2	cal	9
1α	*trans,trans*-2,4-hexadiene-dioate (dianion)	H_2O	298	1.83 ± 0.01	−10.4 ± 0.1	−18.0 ± 1.7	−7.6 ± 1.9	pot	72
1α	hydrogen *trans,trans*-2,4-hexadienedioate (monoanion)	H_2O	298	2.75 ± 0.01	−15.7 ± 0.1	−28.9 ± 0.8	−13.5 ± 0.7	pot	72
1α	*trans,trans*-2,4-hexadienedioic (muconic) acid	H_2O	298	2.88 ± 0.01	−16.5 ± 0.1	−31.4 ± 1.3	−15.0 ± 1.1	pot	72
1α	hexafluorophosphate	H_2O (0.2 M NaCl)	298	1.60 ± 0.05	−9.1 ± 0.3	−25.4 ± 2.8	−16.4 ± 2.8	cal	254
1α	hexanedioic acid	H_2O	298	2.51 ± 0.01	−14.3 ± 0.1	−34.7 ± 1.3	−20.2 ± 1.0	pot	72

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	hexanedioic acid	H_2O (pH 1.3)	298	2.45 ± 0.01	−14.0 ± 0.1	−26.8 ± 0.2	−12.8 ± 0.3	cal	171
1α	1,2-hexanediol	H_2O	298	2.27 ± 0.09	−12.9 ± 0.6	−14.0 ± 0.4	−1.1 ± 1.0	cal	31
1α	1,5-hexanediol	H_2O	298	1.54 ± 0.06	−8.8 ± 0.4	−13.0 ± 1.0	−4.2 ± 1.4	cal	31
1α	1,6-hexanediol	H_2O	288	2.13 ± 0.01	−11.74 ± 0.05	−13.8 ± 0.2	−2.0 ± 0.3	cal	33
1α	1,6-hexanediol	H_2O	298	2.01 ± 0.02	−11.4 ± 0.1	−17.9 ± 0.3	−6.0 ± 0.3	cal	33
1α	1,6-hexanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	2.04 ± 0.02	−11.7	−20	−9	uv	245
1α	1,6-hexanediol	H_2O	298	1.97 ± 0.03	−11.3 ± 0.2	−16.1 ± 0.4	−4.8 ± 0.6	cal	31
1α	1,6-hexanediol	H_2O	308	1.90 ± 0.02	−11.2 ± 0.1	−20.5 ± 0.4	−9.2 ± 0.6	cal	33
1α	2,5-hexanediol	H_2O	298	1.41 ± 0.10	−8.1 ± 0.7	−2.1 ± 0.4	6.0 ± 1.1	cal	31
1α	1-hexanesulfonate	H_2O	298	2.057 ± 0.008	−11.73 ± 0.04	−22.7 ± 0.2	−11.0	cal	255
1α	hexanoate	H_2O (pH 6.9)	298	2.46 ± 0.01	−14.1 ± 0.1	−14.5 ± 0.2	−0.4 ± 0.2	cal	10
1α	hexanoate	H_2O (pH 11.3)	298	2.71 ± 0.04	−15.5	−6.1 ± 0.1	9.4	cal	246
1α	hexanoate	H_2O (pH 6.9)	298	2.48 ± 0.01	−14.14 ± 0.04	−14.2 ± 0.1	−0.1 ± 0.2	cal	9
1α	hexanoate	H_2O	298	2.324 ± 0.024	−13.26 ± 0.27	−14.2 ± 0.8	−0.9 ± 0.7	pot	71
1α	hexanoic acid	H_2O	298	2.908 ± 0.021	−16.59 ± 0.24	−32.2 ± 1.3	−15.1 ± 1.3	pot	71
1α	(*R*)-(−)-2-hexanol	H_2O (pH 6.90)	298	2.54 ± 0.02	−14.5 ± 0.2	−17.2 ± 0.4	−2.7 ± 0.4	cal	32
1α	(*S*)-(+)-2-hexanol	H_2O (pH 6.90)	298	2.54 ± 0.01	−14.5 ± 0.1	−16.9 ± 0.3	−2.4 ± 0.3	cal	32
1α	1-hexanol	H_2O (pH 6.90)	294	2.96 ± 0.02	−16.7 ± 0.1	−17.6 ± 0.3	−0.9 ± 0.3	cal	12
1α	1-hexanol	H_2O	298		−16.25 ± 0.06	−18.2 ± 0.1	−1.9 ± 0.1	cal	8
1α	1-hexanol	H_2O	298	2.95	−16.8	−19.0	−2.4	uv	11
1α	1-hexanol	H_2O	298	2.90	−16.6	−17.2	−0.6	cal	18
1α	1-hexanol	H_2O	298	2.77 ± 0.04	−15.8 ± 0.2	−15.6 ± 0.1	0.2 ± 0.2	cal	243
1α	1-hexanol	H_2O	298	2.58 ± 0.05	−14.7 ± 0.3	−17.5 ± 0.8	−2.8 ± 1.1	cal	31
1α	1-hexanol	H_2O (pH 6.90)	298	2.94 ± 0.02	−16.8 ± 0.2	−18.5 ± 0.4	−1.8 ± 0.6	cal	12
1α	1-hexanol	H_2O (pH 6.90)	303	2.84 ± 0.02	−16.5 ± 0.1	−20.8 ± 0.4	−4.2 ± 0.6	cal	12
1α	1-hexanol	H_2O (pH 6.90)	308	2.77 ± 0.02	−16.3 ± 0.2	−23.8 ± 0.6	−7.4 ± 0.6	cal	12
1α	1-hexanol	H_2O	298		−22.2	−29.1	−6.9	cal	256[b]
1α	2-hexanol	H_2O	298	2.45 ± 0.02	−14.0 ± 0.2	−15.5 ± 0.2	−1.5 ± 0.3	cal	31
1α	2-hexanol	H_2O	298	2.23 ± 0.03	−12.7 ± 0.2	−15.0 ± 0.2	−2.4 ± 0.3	cal	243
1α	3-hexanol	H_2O	298	2.19 ± 0.06	−12.5 ± 0.4	−13.8 ± 0.6	−1.3 ± 1.0	cal	31
1α	*trans*-2-hexenoate	H_2O (pH 6.9)	298	2.45 ± 0.01	−13.99 ± 0.08	−17.2 ± 0.5	−3.2 ± 0.5	cal	9
1α	*trans*-3-hexenoate	H_2O (pH 6.9)	298	2.21 ± 0.01	−12.6 ± 0.08	−14.1 ± 0.4	−1.5 ± 0.4	cal	9
1α	hexylamine	DMF	298	0.90 ± 0.05	−5.2 ± 0.3	−21.3 ± 0.4	−16.1 ± 0.6	cal	168
1α	hexylammonium	H_2O (pH 6.9)	298	2.583 ± 0.006	−14.74 ± 0.03	−17.6 ± 0.1	−2.9 ± 0.1	cal	10
1α	hexylammonium	H_2O (pH 6.9)	298	2.590 ± 0.004	−14.78 ± 0.03	−17.5 ± 0.2	−2.8 ± 0.2	cal	9
1α	hexyl-β-D-glucopyranoside	H_2O (pH 6.9)	298	2.92 ± 0.02	−16.69 ± 0.11	−18.5 ± 0.3	−1.8 ± 0.3	cal	13
1α	hexyltrimethylammonium	H_2O	298	2.428 ± 0.003	−13.85 ± 0.02	−16.1 ± 0.02	−2.4	cal	255
1α	L-histidine	H_2O (pH 11.3)	298	1.08 ± 0.03	−6.2 ± 0.2	−3.2 ± 0.3	3.0 ± 0.5	cal	35
1α	L-histidine	H_2O	298	0.95 ± 0.16	−5.4 ± 1.0	−14 ± 6	−9 ± 7	cal	35
1α	hydroquinone	H_2O (pH 4.2)	298	1.38 ± 0.08	−7.9 ± 0.5	−10 ± 2	−2 ± 2	cal	39
1α	hydroquinone	H_2O	298	0.92	−5.3	−16.2	−10.8	cal	242
1α	3-hydroxybenzoic acid	H_2O	298		−15.3	−48.1	−32.8	pot	177
1α	3-hydroxybenzoic acid	H_2O	298		−13.9	−47.4 ± 0.8	−33.6 ± 2.5	cd	194
1α	4-hydroxybenzoic acid	H_2O	298		−15.1	−40.7 ± 0.9	−25.7 ± 2.9	cd	194
1α	4-hydroxybenzoic acid	H_2O (pH 4.0)	298	3.09 ± 0.01	−17.6 ± 0.4	−56.9 ± 0.6	−39.3 ± 0.6	uv	191
1α	4-[(4-hydroxy-3-chlorophenyl)-azo]naphthalene-1-sulfonate (dianion)	H_2O (pH 11.1)	298	2.66	−15.1	−27.0	−11.8	kin	231
1α	*trans*-3-hydroxycinnamate	H_2O (pH 8.2)	298	1.95	−11.2	−29.7	−18.8	uv	257
1α	*trans*-4-hydroxycinnamate	H_2O (pH 8.2)	298	2.04	−11.6	−27.2	−15.5	uv	257
1α	*trans*-2-hydroxycinnamic acid	H_2O (pH 1.6)	298	3.05	−17.4	−31.4	−14.0	uv	257
1α	*trans*-3-hydroxycinnamic acid	H_2O (pH 1.6)	298	3.12	−17.8	−31.8	−14.3	uv	257
1α	*trans*-4-hydroxycinnamic acid	H_2O (pH 1.6)	298	3.30	−18.8	−30.1	−10.9	uv	257
1α	4-[(4-hydroxy-3,5-diisopropyl-phenyl)azo]benzenesulfonate	H_2O (pH 4.6)	298		−16.4	−19.6	−3.2	kin	44
1α	4-[(4-hydroxy-3,5-diisopropyl-phenyl)azo]benzenesulfonate (dianion)	H_2O	298		−16.6	−21.9	−5.3	kin	44
1α	4-[(4-hydroxy-3-ethylphenyl)-azo]naphthalene-1-sulfonate	H_2O (pH 3.5)	287	2.66	−14.6	−27.2	−12.6	uv	42
1α	5-[(4-hydroxy-3-ethylphenyl)-azo]naphthalene-1-sulfonate	H_2O (pH 4.6)	298	2.34	−11.3	−24.6	−13.7	kin	231, 258
1α	4-[(4-hydroxy-3-ethylphenyl)-azo]naphthalene-1-sulfonate (dianion)	H_2O (pH 11.5)	287	2.46	−13.5	−32.2	−18.7	uv	42
1α	5-[(4-hydroxy-3-ethylphenyl)-azo]naphthalene-1-sulfonate (dianion)	H_2O (pH 11.1)	298	2.86	−13.1	−18.8	−5.8	kin	231, 258
1α	4-[(4-hydroxy-3-methylphenyl)-azo]naphthalene-1-sulfonate	H_2O (pH 3.5)	287	2.62	−14.4	−26.8	−12.4	uv	42
1α	4-[(4-hydroxy-3-methylphenyl)-azo]naphthalene-1-sulfonate (dianion)	H_2O (pH 11)	287	2.68	−14.7	−24.3	−9.6	uv	42
1α	4-[(4-hydroxy-3-methylphenyl)-azo]naphthalene-1-sulfonate (dianion)	H_2O (pH 11.1)	298	2.26	−12.7	−44.5	−31.9	kin	231

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	8-hydroxy-5-[(4-nitrophenyl)-azo]naphthalene-1-sulfonate (dianion)	H_2O (pH 11)	287	2.49	−13.7	−26.4	−12.7	uv	42
1α	4-(hydroxyphenethyl)ammonium	H_2O (pH 6.9)	298	0.97 ± 0.03	−5.55 ± 0.19	−21.5 ± 1.3	−16.1 ± 1.5	cal	13
1α	4-(hydroxyphenethyl)ammonium	H_2O (pH 5.0)	298	0.87 ± 0.05	−4.96 ± 0.32	−18.4 ± 2.0	−13.4 ± 2.1	cal	13
1α	2-[(4-hydroxyphenyl)azo]benzoate	DMF	298	3.20 ± 0.04	−18.27	−9.29 ± 0.08	9.0	cal	43
1α	3-[(4-hydroxyphenyl)azo]benzoate	H_2O	298	3.72 ± 0.03	−21.23	−33.4 ± 1.9	−12.1	cal	43
1α	3-[(4-hydroxyphenyl)azo]benzoate	DMF	298	3.47 ± 0.03	−19.81	−21.4 ± 0.2	−1.6	cal	43
1α	4-[(4-hydroxyphenyl)azo]benzoate	H_2O	298	3.63 ± 0.04	−20.72	−29.1 ± 0.4	−8.4	cal	43, 259
1α	4-[(4-hydroxyphenyl)azo]benzoate	DMF	298	3.77 ± 0.12	−21.52	−15.5 ± 0.9	6.2	cal	43, 259
1α	4-[(4-hydroxyphenyl)azo]-naphthalene-1-sulfonate	H_2O (pH 3.5)	287	2.43	−13.4	−29.3	−15.9	uv	42
1α	4-[(4-hydroxyphenyl)azo]-naphthalene-1-sulfonate (dianion)	H_2O (pH 11)	287	2.81	−15.4	−26.4	−11.0	uv	42
1α	4-[(4-hydroxy-3-propylphenyl)-azo]benzenesulfonate	H_2O (pH 4.6)	298	−22.5		−33.3	−10.7	kin	44
1α	4-[(4-hydroxy-3-propylphenyl)-azo]benzenesulfonate	H_2O (pH 4.6; 0.1 M NaCl)	298	−24.2		−42.1	−17.6	uv	41[e]
1α	4-[(4-hydroxy-3-propylphenyl)-azo]benzenesulfonate (dianion)	H_2O (pH 12; 0.1 M NaCl)	298	−25.7		−42.7	−17.2	uv	41[e]
1α	4-[(4-hydroxy-3-propylphenyl)-azo]benzenesulfonate (dianion)	H_2O	298	−22.2		−31.8	−9.5	kin	44
1α	5-[(4-hydroxy-3-propylphenyl)-azo]naphthalene-1-sulfonate	H_2O (pH 4.6)	298	2.36	−13.5	−20.4	−6.9	kin	231, 258
1α	5-[(4-hydroxy-3-propylphenyl)-azo]naphthalene-1-sulfonate (dianion)	H_2O (pH 11.1)	298	2.51	−14.4	−17.9	−3.5	kin	231, 258
1α	hydroxyzine·2HCl	H_2O	298	3.06 ± 0.01	−17.5	−21.1 ± 0.6	−3.7	cal	74
1α	hydroxyzine·HCl	H_2O	298	3.06 ± 0.02	−17.5	−22.0 ± 1.1	−4.5	cal	74
1α	imidazole	H_2O (pH 9.5; 0.5 M Na_2SO_4)	298	1.23 ± 0.01	−7.0 ± 0.1	−22.9 ± 0.5	−15.9	cal	260
1α	imidazole	H_2O (pH 9.5; 0.5 M NaOAc)	298	1.15 ± 0.02	−6.5 ± 0.1	−22.6 ± 0.5	−16.1	cal	260
1α	imidazole	H_2O (pH 9.5)	298	1.08 ± 0.01	−6.2 ± 0.1	−21.7 ± 0.5	−15.5	cal	260
1α	indole	H_2O	298	7.8 ± 0.1[i]	−44.3 ± 0.4	−3.3 ± 0.4	41.2	cal	192
1α	iodide	H_2O	298	1.279 ± 0.007	−7.29 ± 0.04	−24.7 ± 0.8	−17.1 ± 0.7	pot	261
1α	4-iodoaniline	H_2O	298	3.45 ± 0.03	−19.7 ± 0.2	−34.3 ± 2.1	−15.1 ± 2.2	pot	262
1α	4-iodoanilinium	H_2O	298	3.04 ± 0.04	−17.3 ± 0.2	−26.4 ± 2.9	−9.5 ± 2.7	pot	262
1α	4-iodophenol	H_2O (pH 4.0)	298	3.31 ± 0.01	−18.9 ± 0.5	−32.4 ± 0.8	−13.4 ± 0.9	uv	191
1α	4-iodophenol	H_2O	298		−16.8	−26.3	−9.5	cal	188
1α	4-iodophenolate	H_2O	298		−19.1	−36.5	−17.3	cal	188
1α	hydrogen maleate (monoanion)	H_2O	298	1.83 ± 0.01	−10.4 ± 0.1	−33.1 ± 1.7	−22.8 ± 1.6	pot	72
1α	maleic acid	H_2O	298	1.40 ± 0.02	−8.0 ± 0.1	−29 ± 4	−21 ± 4	pot	72
1α	hydrogen malonate (monoanion)	H_2O	298	1.51 ± 0.01	−8.6 ± 0.1	−26.8 ± 0.4	−18.2 ± 0.6	pot	72
1α	malonic acid	H_2O	298	1.19 ± 0.03	−6.8 ± 0.2	−23.6 ± 0.2	−16.8 ± 0.2	pot	72
1α	*d*-mandelate	H_2O (pH 11.0)	298	0.89	−5.1	−13.0 ± 2.5	−7.9	uv/cal	202
1α	*l*-mandelate	H_2O (pH 11.0)	298	0.9	−5.2	−14.2 ± 2.1	−9.0	uv/cal	202
1α	*l*-mandelic acid	H_2O	298	2.3 ± 1.4	−13.0 ± 7.9	−21 ± 11	−8	cal	192
1α	D-mannose	H_2O	298	1.77	−10.1 ± 1.0	−0.11 ± 0.01	10.0 ± 1.0	cal	37
1α	meclizine·2HCl	H_2O	298	2.94 ± 0.01	−16.8	−22.7 ± 0.1	−5.9	cal	74
1α	methapyriline·HCl	H_2O (pH 7.0)	298	1.85	−10.6	−16.0	−5.4	cal	263[d]
1α	L-methionine	H_2O	298	0.95 ± 0.09	−5.4 ± 0.6	−14 ± 3	−9 ± 4	cal	201
1α	(2-methoxyphenethyl)ammonium	H_2O (pH 5.0)	298	1.14 ± 0.03	−6.52 ± 0.17	−15.8 ± 0.8	−9.2 ± 0.9	cal	13
1α	(3-methoxyphenethyl)ammonium	H_2O (pH 6.9)	298	1.35 ± 0.01	−7.73 ± 0.08	−19.0 ± 0.4	−11.3 ± 0.4	cal	13
1α	(3-methoxyphenethyl)ammonium	H_2O (pH 5.0)	298	1.23 ± 0.01	−7.04 ± 0.07	−14.6 ± 0.3	−7.6 ± 0.3	cal	13
1α	(4-methoxyphenethyl)ammonium	H_2O (pH 6.9)	298	1.645 ± 0.004	−9.39 ± 0.02	−19.8 ± 0.2	−10.4 ± 0.2	cal	13
1α	(4-methoxyphenethyl)ammonium	H_2O (pH 5.0)	298	1.48 ± 0.01	−8.44 ± 0.05	−15.0 ± 0.2	−6.6 ± 0.2	cal	13
1α	4-methoxyphenol	H_2O (pH 4.0)	298	1.76 ± 0.03	−10.0 ± 0.7	−19.5 ± 2.3	−9.5 ± 2.4	uv	191
1α	methyl orange (acid form)	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	2.93 ± 0.03	−16.7	−25	−9	uv	245
1α	methyl orange (acid form)	H_2O (0.05 M HCl)	298	2.85	−16.3	−28	−12	uv	236[d]
1α	methyl orange (acid form)	H_2O (pH 1.1)	298		−16.2	−22.3 ± 0.8	−6.1 ± 0.8	uv	264
1α	methyl orange (anion)	H_2O (pH 7.5)	298		−22.6	−36.0	−13.7	uv	265
1α	methyl red (anion)	H_2O (pH 9.5)	298	3.96 ± 0.01	−22.7 ± 2.4	−20.9 ± 1.2	1.8 ± 1.2	uv	266
1α	methyl red (cation, protonated)	H_2O (pH 1.0)	298	3.61 ± 0.01	−20.6 ± 0.6	−27.3 ± 0.3	−6.7 ± 0.3	uv	266
1α	3-methylbenzoic acid	H_2O	298	2.4 ± 0.1	−13.8 ± 0.4	−49 ± 4	−35	cal	192
1α	4-methylbenzoic acid	H_2O (pH 2.0)	298	2.91	−16.6	−34.8	−8.1	uv	208[j]
1α	(+)-α-methylbenzylamine	H_2O (pH 11.0)	298	1.41	−8.1	−15.1 ± 3.3	−7.0	uv/cal	202
1α	(−)-α-methylbenzylamine	H_2O (pH 11.0)	298	1.53	−8.7	−15.5 ± 1.3	−6.8	uv/cal	202
1α	(±)-2-methylbutanoate	H_2O (pH 6.9)	298	1.37 ± 0.02	−7.83 ± 0.11	−12.5 ± 0.4	−4.7 ± 0.4	cal	9
1α	3-methyl-1-butanol	H_2O−EtOH (85:15; pH 4.3)	293	1.36	−7.6	−52.0	−44.3	gc	115
1α	3-methyl-1-butanol	H_2O	298	2.17 ± 0.04	−12.4 ± 0.2	−7.6 ± 0.1	4.8 ± 0.2	cal	243
1α	3-methylbutyl acetate	H_2O−EtOH (85:15; pH 4.3)	293	1.70	−9.5	−39.4	−29.9	gc	115
1α	*N*-methylbutylamine	DMF	298	0.78 ± 0.07	−4.4 ± 0.4	−18.8 ± 1.7	−14.3 ± 1.8	cal	168

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	(1-methylbutyl)ammonium	H_2O (pH 6.9)	298	1.29 ± 0.03	−7.38 ± 0.17	−11.2 ± 0.6	−3.8 ± 0.6	cal	9
1α	*N*-methylbutylammonium	H_2O (pH 6.9)	298	1.24 ± 0.02	−7.05 ± 0.15	−10.7 ± 0.5	−3.7 ± 0.5	cal	9
1α	*trans*-3-methylcinnamate	H_2O (pH 8.2)	298	2.12	−12.1	−21.8	−9.7	uv	257
1α	*trans*-4-methylcinnamate	H_2O (pH 8.2)	298	2.55	−14.5	−40.2	−25.1	uv	257
1α	*trans*-2-methylcinnamic acid	H_2O (pH 1.6)	298	2.44	−13.9	−21.8	−8.4	uv	257
1α	*trans*-3-methylcinnamic acid	H_2O (pH 1.6)	298	3.49	−19.9	−29.7	−10.2	uv	257
1α	*trans*-4-methylcinnamic acid	H_2O (pH 1.6)	298	4.13	−23.6	−52.3	−28.7	uv	257
1α	2-methylcyclohexanone	H_2O (pH 6.90)	298	1.48 ± 0.07	−8.4 ± 0.5	−8.9 ± 1.1	−0.6 ± 1.2	cal	12
1α	4-*O*-methyldopamine	H_2O (pH 6.9)	298	0.72 ± 0.23	−4.1 ± 2.9	−10 ± 6	−6 ± 7	cal	13
1α	(1-methylheptyl)ammonium	H_2O (pH 6.9)	298	3.053 ± 0.005	−17.43 ± 0.03	−19.8 ± 0.2	−2.4 ± 0.2	cal	9, 10
1α	(1-methylheptyl)ammonium	H_2O (pH 6.9)	298	3.053 ± 0.006	−17.42 ± 0.04	−19.8 ± 0.1	−2.4 ± 0.1	cal	10
1α	(1-methylhexyl)ammonium	H_2O (pH 6.9)	288	2.735 ± 0.006	−15.05 ± 0.03	−13.8 ± 0.1	1.3 ± 0.1	cal	10
1α	(1-methylhexyl)ammonium	H_2O (pH 6.9)	298	2.642 ± 0.005	−15.08 ± 0.03	−17.9 ± 0.2	−2.8 ± 0.2	cal	9, 10
1α	(1-methylhexyl)ammonium	H_2O (pH 6.9)	318	2.48 ± 0.02	−15.1 ± 0.1	−23.6 ± 0.5	−8.5 ± 0.5	cal	10
1α	*N*-methylhexylammonium	H_2O (pH 6.9)	288	2.668 ± 0.010	−14.69 ± 0.06	−14.0 ± 0.1	0.7 ± 0.1	cal	10
1α	*N*-methylhexylammonium	H_2O (pH 6.9)	298	2.577 ± 0.005	−14.7 ± 0.03	−17.6 ± 0.1	−2.9 ± 0.1	cal	9, 10
1α	*N*-methylhexylammonium	H_2O (pH 6.9)	318	2.37 ± 0.02	−14.4 ± 0.1	−23.3 ± 0.5	−8.8 ± 0.5	cal	10
1α	(4-methylphenethyl)ammonium	H_2O (pH 6.9)	298	1.78 ± 0.01	−10.17 ± 0.06	−16.5 ± 0.3	−6.3 ± 0.3	cal	13
1α	(4-methylphenethyl)ammonium	H_2O (pH 5.0)	298	1.65 ± 0.01	−9.44 ± 0.07	−13.9 ± 0.3	−4.5 ± 0.3	cal	13
1α	*N*-methylphenethylammonium	H_2O (pH 5.0)	298	1.14 ± 0.03	−6.52 ± 0.19	−11.8 ± 0.7	−5.4 ± 0.6	cal	13
1α	*N*-methylphenethylammonium	H_2O (pH 6.9)	298	1.13 ± 0.05	−6.47 ± 0.35	−14.8 ± 1.7	−8.3 ± 1.8	cal	13
1α	4-methylphenol	H_2O (pH 4.0)	298	1.75 ± 0.01	−10.0 ± 0.3	−16.8 ± 0.7	−6.9 ± 0.6	uv	191
1α	4-methylphenol	H_2O (pH 4.2)	298	1.57 ± 0.03	−8.9 ± 0.2	−17.7 ± 0.7	−8.6 ± 0.6	cal	39
1α	3-methylphenyl acetate	H_2O (pH 10)	298	1.77	−10.1	−18	−9	kin	126
1α	4-methylphenyl acetate	H_2O (pH 10)	298	1.96	−11.2	−23	−11	kin	126
1α	2-methyl-1-propanol	H_2O	298	1.79 ± 0.01	−10.2 ± 0.1	−5.1 ± 0.1	5.0 ± 0.1	cal	243
1α	2-methyl-1-propanol	H_2O	298	1.34	−7.7	−9.4	−1.7	cal	17, 247
1α	2-methyl-2-propanol	H_2O	298	1.47	−8.4	−12.0	−3.6	uv	11
1α	2-methyl-2-propanol	H_2O (pH 3.8−4.5)	298	0.61 ± 0.02	−3.5 ± 0.1	2 ± 1	6 ± 1	pot	235[c]
1α	2-methylpropyl acetate	H_2O−EtOH (85:15; pH 4.3)	293	0.50	−2.8	−69.8	−67.0	gc	115
1α	2-methylpropylamine	H_2O	298	2.01 ± 0.02	−11.5 ± 0.1	−11.7 ± 0.4	−0.2 ± 0.3	cal	168
1α	5-methylresorcinol	H_2O	303	1.19	−6.7	−13.7	−6.8	cal	242
1α	modant yellow 7	H_2O (pH 7)	298	3.39	−19.3	−36	−17	kin	87, *e*
1α	monobutylurea	H_2O	298	2.10	−12.0	−13.0	−1.0	cal	178
1α	monoethylurea	H_2O	298	0.45	−2.6	−7.4	−4.8	cal	178
1α	monopropylurea	H_2O	298	1.11	−6.3	−11.2	−4.9	cal	178
1α	1-naphthaleneacetate	H_2O (pH 7.2)	298	2.94 ± 0.04	−16.8 ± 0.2	−3.1 ± 0.1	13.7	cal	14
1α	2,7-naphthalenedisulfonate	H_2O (pH 7.2)	298	0.98 ± 0.06	−5.6 ± 0.3	−25.1 ± 0.2	−19.4	cal	14
1α	2-naphthalenesulfonate	H_2O (pH 7.2)	298	2.56 ± 0.01	−14.6 ± 0.1	−3.3 ± 0.3	11.3	cal	14
1α	3-nitroaniline	H_2O	298		−10.7	−28.8 ± 0.3	−18.2 ± 0.8	cd	194
1α	4-nitroaniline	H_2O	298		−15.2	−42.3 ± 0.3	−27.1 ± 0.8	cd	194
1α	4-nitrobenzoate	H_2O (pH 5.5)	298		−9.2	−20.1	−10.9	cal	193
1α	4-nitrobenzoic acid	H_2O (pH 2.0)	298		−13.0	−38.5	−25.5	cal	193
1α	4-nitrobenzoic acid	H_2O	298		−13.3	−33.9	−20.6	pot	177
1α	2-nitrophenol	H_2O	298	3.7 ± 1.1	−20.9 ± 6.3	−2.1 ± 0.4	18.7	cal	192
1α	3-nitrophenol	H_2O	298	2.09 ± 0.02	−12.0 ± 0.1	−28.4 ± 0.7	−16.4 ± 0.6	cal	39
1α	3-nitrophenol	H_2O	298		−12.4	−30 ± 1	−17 ± 1	cd	267
1α	3-nitrophenol	H_2O	298		−12.1	−35.3 ± 0.4	−23.2 ± 1.3	cd	194
1α	4-nitrophenol	H_2O (pH 3.5)	287	2.59	−14.2	−17.6	−3.4	uv	42
1α	4-nitrophenol	H_2O (pH 4.0, 1 M NaCl)	298		−14.4	−19.2	−4.8	cal	193
1α	4-nitrophenol	H_2O	298	2.34 ± 0.04	−13.4 ± 0.2	−25.8 ± 0.4	−12.5 ± 0.6	cal	39
1α	4-nitrophenol	H_2O (pH 4.0)	298	2.34 ± 0.01	−13.3 ± 0.2	−29.7 ± 1.1	−16.4 ± 1.2	uv	191
1α	4-nitrophenol	H_2O (pH 4.2)	298	2.30 ± 0.02	−13.1 ± 0.1	−27.1 ± 0.2	−14.0 ± 0.3	cal	39
1α	4-nitrophenol	H_2O	298		−13.0	−30.5 ± 1.3	−17.5 ± 1.2	uv	268
1α	4-nitrophenol	H_2O (pH 4.3)	298	2.25	−12.8	−24.7	−11.9	uv	118
1α	4-nitrophenol	H_2O (pH 3.0)	298		−12.6	−19.2	−6.6	cal	193
1α	4-nitrophenol	H_2O	298		−11.5	−23.0	−11.5	cal	188
1α	4-nitrophenol	H_2O	298		−13.2	−33 ± 1	−21 ± 1	cd	267
1α	4-nitrophenol	H_2O	298	2.31	−13.2	−31.9 ± 0.6	−18.7 ± 0.5	cd	210
1α	4-nitrophenol	H_2O	298	2.1 ± 0.3	−12.1 ± 1.7	−31 ± 6	−19	cal	192
1α	3-nitrophenolate	H_2O (pH 11.1)	298	2.31 ± 0.01	−13.2 ± 0.1	−32 ± 0.3	−18.8 ± 0.3	cal	39
1α	4-nitrophenolate	H_2O (pH 11)	287	3.57	−19.6	−30.1	−10.5	uv	42
1α	4-nitrophenolate	H_2O (pH 9.5)	298		−17.6	−38.9	−21.0	cal	21
1α	4-nitrophenolate	H_2O (pH 10)	298	3.55	−20.3	−56.1	−35.8	uv	118
1α	4-nitrophenolate	H_2O	298		−19.5	−46.9 ± 1.7	−27.4 ± 1.2	uv	268
1α	4-nitrophenolate	H_2O (pH 11.0)	298		−19.2	−37.8	−18.7	cal/uv	269
1α	4-nitrophenolate	H_2O	298		−18.7	−42.8	−24.1	cal	188
1α	4-nitrophenolate	H_2O (pH 11)	298	3.30	−18.7 ± 0.1	−37.9 ± 0.3	−19.6 ± 0.2	uv	211
1α	4-nitrophenolate	H_2O (pH 11.1)	298	3.26 ± 0.07	−18.6 ± 0.4	−40.9 ± 0.9	−22.4 ± 0.9	cal	39
1α	4-nitrophenolate	H_2O (pH 10.0, 1 M NaCl)	298		−18.6	−40.2	−21.6	cal	193
1α	4-nitrophenolate	H_2O (pH 9.5)	298		−18.2	−38.9	−20.7	cal	193
1α	4-nitrophenolate	H_2O (1 M NaOH)	298	2.13 ± 0.03	−12.2 ± 0.2	−20.2 ± 0.8	−8.0 ± 0.9	cal	39

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	3-nitrophenyl acetate	H_2O (pH 10.6)	298	1.72	−9.8	−16	−6	kin	126
1α	4-nitrophenyl acetate	H_2O (pH 10.6)	298	1.92	−10.9	−22	−11	kin	126
1α	4-nitrophenylacetate	H_2O (pH 7.0)	298		−10.5	−20.9	−10.4	cal	193
1α	4-nitrophenylacetic acid	H_2O (pH 2.0)	298		−9.6	−40.2	−30.6	cal	193
1α	4-nitrophenyl-β-D-galactoside	H_2O	298	1.88	−10.7	−22.6 ± 0.3	−11.8 ± 0.2	cd	210
1α	4-nitrophenyl-β-D-glucosamide	H_2O	298	2.06	−11.8	−24.2 ± 0.3	−12.5 ± 0.2	cd	210
1α	4-nitrophenyl-β-D-glucoside	H_2O	298	1.87	−10.7	−24.4 ± 0.4	−13.7 ± 0.4	cd	210
1α	4-nitrophenyl-β-D-xyloside	H_2O	298	2.04	−11.6	−25.4 ± 0.3	−13.7 ± 0.2	cd	210
1α	nonanedioate	D_2O (pD 13)[g]	298		−16.2	−22.6	−6.3	nmr	170
1α	nonanedioate	H_2O (pH 11.3)	298	2.80 ± 0.01	−16.0 ± 0.1	−14.0 ± 0.1	2.0 ± 0.2	cal	171
1α	nonanedioic acid	H_2O (pH 1.3)	298	2.64 ± 0.01	−15.0 ± 0.1	−70.7 ± 0.5	−55.6 ± 0.6	cal	171
1α	1,9-nonanediol	H_2O	288	3.64 ± 0.05	−20.0 ± 0.3	−19.0 ± 0.3	0.9 ± 0.6	cal	33
1α	1,9-nonanediol	H_2O	298	3.55 ± 0.05	−20.3 ± 0.3	−22.8 ± 0.4	−2.4 ± 0.6	cal	33
1α	1,9-nonanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	3.46 ± 0.06	−19.8	−27	−8	uv	245
1α	1,9-nonanediol	H_2O	308	3.41 ± 0.05	−20.1 ± 0.3	−26.5 ± 0.4	−6.5 ± 0.6	cal	33
1α	2-norbornaneacetate	H_2O (pH 8.5)	298	2.00	−11.3	−14.2 ± 1.3	−2.9	cal	81
1α	D-norleucine	H_2O	298	1.66 ± 0.06	−9.5 ± 0.3	−9.3 ± 0.8	0.2 ± 1.1	cal	201
1α	L-norleucine	H_2O	298	1.66 ± 0.02	−9.5 ± 0.1	−8.9 ± 0.3	0.6 ± 0.4	cal	201
1α	(±)-norphenylephrine	H_2O (pH 6.9)	298	0.85 ± 0.11	−4.8 ± 0.9	−16 ± 4	−11 ± 4	cal	13
1α	(±)-norphenylephrine	H_2O (pH 5.0)	298	0.65 ± 0.15	−3.7 ± 1.4	−17 ± 7	−13 ± 7	cal	13
1α	D-norvaline	H_2O	298	1.08 ± 0.15	−6.2 ± 1.1	−3 ± 1	3 ± 2	cal	201
1α	L-norvaline	H_2O	298	1.08 ± 0.20	−6.2 ± 1.6	−2 ± 1	4 ± 3	cal	201
1α	octanedioate (dianion)	H_2O (pH 9.5)	298	3.18 ± 0.01	−18.15 ± 0.04	−20.87 ± 0.06	−2.71 ± 0.07	cal	239
1α	octanedioate (dianion)	H_2O	298	2.21 ± 0.01	−12.6 ± 0.1	−16.7 ± 1.3	−4.1 ± 1.2	pot	72
1α	octanedioate (dianion)	H_2O (pH 11.3)	298	1.97 ± 0.01	−11.2 ± 0.1	−11.8 ± 0.1	−0.6 ± 0.2	cal	171
1α	octanedioate (dianion)	D_2O (pD 13)[g]	298		−14.5	−14.9	−0.3	nmr	170
1α	hydrogen octanedioate (monoanion)	H_2O	298	2.99 ± 0.01	−17.1 ± 0.1	−33.1 ± 1.3	−16.1 ± 1.4	pot	72
1α	octanedioic acid	H_2O	298	3.15 ± 0.01	−18.0 ± 0.1	−34.7 ± 1.3	−16.7 ± 1.1	pot	72
1α	octanedioic acid	H_2O (pH 1.3)	298	2.46 ± 0.01	−14.1 ± 0.1	−54.6 ± 0.7	−40.5 ± 0.8	cal	171
1α	1,8-octanediol	H_2O	288	3.20 ± 0.07	−17.7 ± 0.4	−18.2 ± 0.3	−0.6 ± 0.6	cal	33
1α	1,8-octanediol	H_2O	298	3.08 ± 0.03	−17.6 ± 0.2	−22.4 ± 0.2	−4.8 ± 0.3	cal	33
1α	1,8-octanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	3.11 ± 0.09	−17.8	−25	−7	uv	245
1α	1,8-octanediol	H_2O	308	2.95 ± 0.02	−17.4 ± 0.1	−25.3 ± 0.1	−7.9 ± 0.2	cal	33
1α	octanoate	H_2O (pH 6.9)	298	3.39 ± 0.02	−19.34 ± 0.14	−20.5 ± 0.3	−1.1 ± 0.3	cal	9
1α	octanoate	H_2O	298	2.96	−16.9	−46.9 ± 0.4	−30.0 ± 0.2	pot	71
1α	octanoic acid	H_2O	298	3.26	−18.6	−46.9 ± 0.8	−28.3 ± 1.0	pot	71
1α	(±)-octopamine	H_2O (pH 6.9)	298	1.09 ± 0.02	−6.22 ± 0.12	−28.1 ± 1.2	−21.8 ± 1.2	cal	13
1α	(±)-octopamine	H_2O (pH 5.0)	298	0.95 ± 0.03	−5.45 ± 0.17	−23.1 ± 1.3	−17.6 ± 1.2	cal	13
1α	octylammonium	H_2O (pH 6.9)	298	3.37 ± 0.04	−19.2 ± 0.2	−22.0 ± 0.5	−2.9 ± 2.6	cal	10
1α	octylammonium	H_2O (pH 6.9)	298	3.38 ± 0.01	−19.27 ± 0.06	−22.9 ± 0.2	−3.6 ± 0.3	cal	9
1α	orphenadrine·HCl	H_2O	298	1.55 ± 0.01	−8.8	−21.0 ± 0.3	−12.1	cal	74
1α	hydrogen oxalate (monoanion)	H_2O	298	0.38 ± 0.05	−2.2 ± 0.3	1 ± 4	4 ± 4	pot	72
1α	oxalic acid	H_2O	298	1.40 ± 0.05	−8.0 ± 0.3	−29 ± 3	−20 ± 3	pot	72
1α	pentakis(ethyleneglycol) monohexyl ether	H_2O	298	2.26 ± 0.03	−12.9 ± 0.1	−16.9 ± 0.6	−4.2	cal	255
1α	pentanedioic acid	H_2O (pH 1.3)	298	2.41 ± 0.02	−13.8 ± 0.1	−25.4 ± 0.6	−11.6 ± 0.7	cal	171
1α	1,2-pentanediol	H_2O	298	1.89 ± 0.03	−10.8 ± 0.2	−11.5 ± 0.2	−0.7 ± 0.4	cal	31
1α	1,5-pentanediol	H_2O	288	1.54 ± 0.01	−8.53 ± 0.07	−14.2 ± 0.2	−5.6 ± 0.2	cal	33
1α	1,5-pentanediol	H_2O	298	1.45 ± 0.01	−8.29 ± 0.05	−17.4 ± 0.2	−9.1 ± 0.2	cal	33
1α	1,5-pentanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	1.49 ± 0.05	−8.5	−18	−9	uv	245
1α	1,5-pentanediol	H_2O	298	1.49 ± 0.01	−8.5 ± 0.1	−14.3 ± 0.3	−5.8 ± 0.4	cal	31
1α	1,5-pentanediol	H_2O	308	1.38 ± 0.02	−8.1 ± 0.1	−19.1 ± 0.4	−11.1 ± 0.6	cal	33
1α	pentanoate	H_2O (pH 11.3)	298	2.16 ± 0.02	−12.3	−4.5 ± 0.1	7.8	cal	246
1α	pentanoate	H_2O (pH 6.9)	298	1.90 ± 0.01	−10.86 ± 0.04	−11.5 ± 0.1	−0.7 ± 0.2	cal	9
1α	pentanoate	H_2O	298	1.880 ± 0.003	−10.72 ± 0.04	−10.1 ± 0.2	0.6 ± 0.2	pot	71
1α	pentanoic acid	H_2O	298	2.727 ± 0.002	−15.56 ± 0.02	−29.8 ± 0.4	−14.2 ± 0.4	pot	71
1α	(*R*)-(−)-2-pentanol	H_2O (pH 6.90)	298	2.10 ± 0.01	−12.0 ± 0.1	−15.4 ± 0.3	−3.4 ± 0.3	cal	32
1α	(*S*)-(+)-2-pentanol	H_2O (pH 6.90)	298	2.10 ± 0.01	−12.0 ± 0.1	−15.2 ± 0.2	−3.2 ± 0.2	cal	32
1α	1-pentanol	H_2O	298		−13.64 ± 0.05	−14.92 ± 0.07	−1.3 ± 0.1	cal	8
1α	1-pentanol	H_2O	298	2.51	−14.4	−14.8	−0.4	cal	18
1α	1-pentanol	H_2O	298	2.51	−14.3	−16.0	−1.5	uv	11
1α	1-pentanol	H_2O	298	2.44 ± 0.02	−13.9 ± 0.2	−11.8 ± 0.2	2.1 ± 0.4	cal	31
1α	1-pentanol	H_2O	298	2.41 ± 0.01	−13.8 ± 0.1	−14.3 ± 0.1	−0.5 ± 0.1	cal	243
1α	1-pentanol	H_2O	298	4.265	−24.4	−13.9	10.4	cal	89, 270[b]
1α	2-pentanol	H_2O	298	2.21 ± 0.03	−12.6 ± 0.2	−11.2 ± 0.1	1.4 ± 0.2	cal	243
1α	2-pentanol	H_2O	298	2.00 ± 0.03	−11.4 ± 0.2	−13.4 ± 0.4	−2.0 ± 0.6	cal	31
1α	3-pentanol	H_2O	298	1.85 ± 0.02	−10.5 ± 0.2	−12.8 ± 0.3	−2.3 ± 0.5	cal	31
1α	pentylamine	DMF	298	0.74 ± 0.04	−4.2 ± 0.2	−23.8 ± 1.3	−19.7 ± 1.2	cal	168
1α	pentylamine	H_2O	298	2.67 ± 0.04	−15.2 ± 0.2	−15.9 ± 0.4	−0.7 ± 0.6	cal	168[f]
1α	pentylammonium	H_2O (pH 6.9)	298	1.968 ± 0.009	−11.23 ± 0.05	−13.6 ± 0.2	−2.4 ± 0.2	cal	10
1α	pentylammonium	H_2O (pH 6.9)	298	1.994 ± 0.004	−11.38 ± 0.03	−13.7 ± 0.1	−2.4 ± 0.2	cal	9

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	perchlorate	H_2O (0.2 M NaCl)	298	1.82 ± 0.03	−10.4 ± 0.2	−15.8 ± 1.0	−5.4 ± 1.0	cal	254
1α	perchlorate	H_2O	298	1.661 ± 0.008	−9.47 ± 0.05	−26.4 ± 0.8	−16.8 ± 1.0	pot	261
1α	perchlorate	H_2O	298	1.3 ± 0.1	−7.5 ± 0.4	−41 ± 5	−29	cal	192[j]
1α	perchloric acid	H_2O	298	1.6 ± 0.1	−9.2 ± 0.4	−31 ± 4	−21	cal	192
1α	phenethylammonium	H_2O (pH 6.9)	298	1.12 ± 0.04	−6.40 ± 0.24	−13.3 ± 0.9	−6.9 ± 0.9	cal	13
1α	phenethylammonium	H_2O (pH 5.0)	298	1.06 ± 0.04	−6.03 ± 0.23	−13.2 ± 1.0	−7.2 ± 0.9	cal	13
1α	pheniramine maleate	H_2O (pH 7.0)	298	1.83	−10.4	−9.7	0.7	cal	263[d]
1α	phenol	H_2O (pH 4.2)	298	1.57 ± 0.04	−8.9 ± 0.3	−10.2 ± 0.8	−0.6 ± 0.6	cal	39
1α	phenol	H_2O (pH 4.0)	298	1.46 ± 0.02	−8.3 ± 0.4	−19.7 ± 0.7	−11.3 ± 0.6	uv	191
1α	phenol	H_2O (pH 3.8−4.5)	298	1.32 ± 0.01	−7.5 ± 0.1	−13 ± 2	−5 ± 2	pot	235[c]
1α	phenol	H_2O	298	4.2 ± 1.3	−23.9 ± 7.5	−7.5 ± 0.8	16.2	cal	192
1α	D-phenylalanine	H_2O (pH 11.0)	298	1.29	−7.3	−16.3 ± 0.8	−9	uv/cal	202
1α	D-phenylalanine	H_2O (pH 5.01)	298	0.90 ± 0.24	−5.2 ± 3.4	−15 ± 11	−10 ± 2	cal	32
1α	L-phenylalanine	H_2O (pH 7.4)	298	1.63	−9.3	−1.2	8.1	cal	271[d]
1α	L-phenylalanine	H_2O (pH 11.3)	298	1.40 ± 0.02	−8.0 ± 0.1	−13.0 ± 0.4	−5.0 ± 0.5	cal	35
1α	L-phenylalanine	H_2O (pH 11.0)	298	1.20	−6.8	−15.5 ± 0.4	−8.7	uv/cal	202
1α	L-phenylalanine	H_2O	298	1.18 ± 0.03	−6.7 ± 0.2	−7.0 ± 0.4	−0.3 ± 0.6	cal	35
1α	L-phenylalanine	H_2O	298	1.13 ± 0.03	−6.5 ± 0.2	−7.7	−1.2	cal	272
1α	L-phenylalanine	H_2O (pH 5.01)	298	0.90 ± 0.21	−5.2 ± 2.4	−12 ± 7	−7 ± 8	cal	32
1α	L-phenylalanine	H_2O (pH 13.6)	298	0.90 ± 0.14	−5.0 ± 1.0	−2.1 ± 0.6	3.0 ± 1.6	cal	35
1α	L-phenylalanine	H_2O	298	4.1 ± 1.4	−23.4 ± 7.9	−4.6 ± 1.3	18.7	cal	192
1α	L-phenylalanineamide	H_2O (pH 10.02)	298	1.27 ± 0.05	−7.2 ± 0.3	−18.2 ± 1.9	−11.0 ± 2.1	cal	32
1α	L-phenylalanineamide	H_2O (pH 5.01)	298	1.08 ± 0.04	−6.2 ± 0.3	−14.3 ± 1.1	−8.0 ± 1.0	cal	32
1α	(*R*)-(−)-phenylephrine	H_2O (pH 6.9)	298	0.61 ± 0.14	−3.5 ± 1.2	−34 ± 12	−30 ± 12	cal	13
1α	(*R*)-(−)-phenylephrine	H_2O (pH 5.0)	298	0.56 ± 0.12	−3.2 ± 1.0	−25 ± 8	−22 ± 8	cal	13
1α	phenyl-β-d-glucopyranoside	H_2O (pH 6.9)	298	0.98 ± 0.26	−5.6 ± 4.0	−21 ± 15	−16 ± 16	cal	13
1α	1-phenylimidazole	H_2O (pH 10.0)	298	1.57 ± 0.12	−9.0 ± 1.0	−20 ± 6	−11 ± 6	cal	13
1α	3-phenylpropionate	H_2O (pH 6.9)	298	1.50 ± 0.01	−8.54 ± 0.05	−15.5 ± 0.2	−6.9 ± 0.2	cal	13
1α	3-phenylpropionic acid	H_2O	298	3.1 ± 0.1	−17.6 ± 0.4	−31.4 ± 0.4	−13.7	cal	192
1α	1-phenyltrifluoroethanol	H_2O (pH 11.0)	298	1.73	−9.9	−12.6 ± 2.9	−2.7	uv/cal	202
1α	*d*-phenyltrifluoroethanol	H_2O (pH 11.0)	298	1.67	−9.5	−14.6 ± 2.1	−5.1	uv/cal	202
1α	(3-phenylpropyl)ammonium	H_2O (pH 6.9)	298	1.37 ± 0.01	−7.85 ± 0.08	−16.8 ± 0.4	−8.9 ± 0.4	cal	13
1α	(3-phenylpropyl)ammonium	H_2O (pH 5.0)	298	1.34 ± 0.01	−7.63 ± 0.08	−15.9 ± 0.4	−8.3 ± 0.4	cal	13
1α	phosphorofluoridate	H_2O (pH 10.0)	298	0.68	−4.3	−30.5 ± 2.9	−26.2	kin	127
1α	piroxicam	H_2O (pH 7.0)	298	1.68	−9.6	−15.7	−6.1	cal	263[d]
1α	proadifen·HCl	H_2O	298	2.27 ± 0.02	−12.9	−20.8 ± 0.5	−7.9	cal	74
1α	1,2-propanediol	H_2O	298	0.48 ± 0.22	−2.7 ± 2.0	−2 ± 1	1 ± 3	cal	31
1α	1,3-propanediol	H_2O	298	1.04 ± 0.07	−5.9 ± 0.4	−6.5 ± 0.5	−0.3 ± 0.6	cal	243
1α	1,3-propanediol	H_2O	298	0.63 ± 0.04	−3.6 ± 0.2	−6.7 ± 0.5	−3.1 ± 0.7	cal	31
1α	1,3-propanediol	H_2O	298	0.34 ± 0.04	−1.9 ± 0.2	−13 ± 1	−11 ± 1	cal	33
1α	1-propanol	H_2O	298		−7.75 ± 0.04	−6.81 ± 0.06	1.0 ± 0.1	cal	8
1α	1-propanol	H_2O	298	1.46	−8.4	−6.1	2.3	cal	18
1α	1-propanol	H_2O	298	1.43	−8.2	−6.1	2.1	cal	17, 31, 247
1α	1-propanol	H_2O (0.05 M HCl)	298	1.38	−7.9	−11	−4	uv	236[d]
1α	1-propanol	H_2O	298	3.124	−17.8	−6.6	11.2	cal	89, 270[b]
1α	2-propanol	H_2O (pH 6.90)	298	0.99 ± 0.12	−5.6 ± 1.0	−1.2 ± 0.3	4.5 ± 0.9	cal	32
1α	2-propanol	H_2O (0.05 M HCl)	298	0.68	−3.9	−12	−8	uv	236[d]
1α	2-propanol	H_2O (pH 3.8−4.5)	298	0.66 ± 0.02	−3.8 ± 0.1	−2 ± 2	2 ± 1	pot	235[c]
1α	2-propanol	H_2O	298		−19.2	−0.4	18.8	cal	89[b]
1α	propionic acid	H_2O	298		−8.4	−17.3	−8.9	pot	177[d]
1α	propylamine	DMF	298	0.66 ± 0.01	−3.8 ± 0.1	−23.4 ± 0.4	−19.7 ± 0.3	cal	168
1α	propylamine	H_2O	298	1.66 ± 0.02	−9.5 ± 0.1	−14.6 ± 0.4	−5.1 ± 0.3	cal	168[f]
1α	(1*R*,2*R*)-(−)-pseudoephedrine	H_2O (pH 6.9)	298	1.27 ± 0.01	−7.25 ± 0.08	−17.8 ± 0.4	−10.5 ± 0.4	cal	13
1α	(1*S*,2*S*)-(+)-pseudoephedrine	H_2O (pH 6.9)	298	1.30 ± 0.01	−7.41 ± 0.07	−18.4 ± 0.4	−11.0 ± 0.4	cal	13
1α	(1*S*,2*S*)-(+)-pseudoephedrine	H_2O (pH 5.0)	298	1.17 ± 0.03	−6.66 ± 0.16	−13.7 ± 0.7	−7.2 ± 0.6	cal	13
1α	pyrene	H_2O	298	2.17	−12.4	−13.4	−1.0	lc	241
1α	pyridine	H_2O	298	2.2 ± 1.4	−12.6 ± 7.9	−11 ± 4	3	cal	192
1α	pyrilammonium maleate	H_2O (pH 7.0)	298	2.07	−11.8	−19.1	−7.3	cal	263[d]
1α	resorcinol	H_2O	298	1.21	−6.9	−10.7	−4.0	cal	242
1α	resorcinol	H_2O	303	1.22	−7.1	−10.2	−3.1	cal	242
1α	(*E*)-stilbene derivative (*E*)-**30**	H_2O	298	3.10 ± 0.10	−18.0	−26.8 ± 0.4	−8.8	cal	78
1α	(*Z*)-stilbene derivative (*Z*)-**30**	H_2O	298	2.56 ± 0.11	−14.6	−7.9 ± 6.3	6.7	cal	78
1α	hydrogen succinate (monoanion)	H_2O	298	1.25 ± 0.01	−7.1 ± 0.1	−29.3 ± 0.4	−22.3 ± 0.4	pot	72
1α	succinic acid	H_2O	298	2.01 ± 0.01	−11.4 ± 0.1	−33.1 ± 0.8	−21.6 ± 0.7	pot	72
1α	terfenadine·HCl	H_2O	298	1.72 ± 0.01	−9.8	−49.4 ± 0.8	−39.6	cal	74
1α	thenyldiamine·HCl	H_2O (pH 7.0)	298	2.02	−11.5	−13.9	−2.4	cal	263[d]
1α	thiocyanate	H_2O	298	1.539 ± 0.005	−8.78 ± 0.03	−28.5 ± 1.3	−19.8 ± 1.4	pot	261
1α	6-(*p*-toluidinyl)-2-naphthalene-sulfonate	H_2O (pH 1.95)	298	1.92	−10.6	−5.4	5.4	fl	240
1α	6-(*p*-toluidinyl)-2-naphthalene-sulfonate	H_2O (pH 5.2)	298		−1.3	6.7	7.7	fl	138
1α	triethylamine	H_2O	298	1.74 ± 0.10	−9.9 ± 0.6	−14.2 ± 1.0	−4.3 ± 1.2	cal	168[f]
1α	trifluoromethanesulfonate	H_2O (0.2 M NaCl)	298	1.58 ± 0.10	−9.0 ± 0.6	−8.1 ± 2.2	0.9 ± 2.2	cal	254
1α	triiodide (I_3^-)	H_2O (pH 11.0)	298		−30.5	−49.4	−19.0	cal/uv	269
1α	trimethylacetic acid	H_2O	298		−6.9	−19.7	−12.8	pot	177

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1α	triprolidine·HCl	H_2O (pH 7.0)	298	1.75	−10.0	−14.3	−4.3	cal	263[d]
1α	L-tryprophan	H_2O	298	1.5 ± 0.1	−8.4 ± 0.4	−7.5 ± 0.4	1.3	cal	192
1α	L-tryptophan	H_2O (pH 11.3)	298	1.45 ± 0.02	−8.3 ± 0.1	−8.0 ± 0.2	0.3 ± 0.3	cal	35
1α	L-tryptophan	H_2O	298	1.28 ± 0.08	−7.3 ± 0.6	−9.0 ± 1.0	−1.7 ± 1.6	cal	35
1α	L-tryptophan	H_2O (pH 7.4)	298	1.33	−7.6	−1.0	6.6	cal	271[d]
1α	Tyr-Gly-Gly-Phe-Leu	H_2O (pH 7.0)	298		−7.2	−25 ± 2	−18 ± 2	fl	36
1α	Tyr-Gly-Gly-Phe-Leu	H_2O (pH 10.0)	298		−6.2	−21 ± 3	−14 ± 3	fl	36[d]
1α	Tyr-Ile-Gly-Ser-Arg	H_2O (pH 7.0)	298		−6.9	−33 ± 4	−24 ± 5	fl	36
1α	Tyr-Ile-Gly-Ser-Arg	H_2O (pH 10.0)	298		−6.8	−26 ± 2	−19 ± 4	fl	36[d]
1α	L-tyrosine	H_2O (pH 7.0)	298		−7.3	−26 ± 3	−19 ± 3	fl	36
1α	L-tyrosine	H_2O	298	2.9 ± 0.6	−16.7 ± 3.3	−4 ± 4	13	cal	192
1α	L-tyrosine	H_2O (pH 7.4)	298	1.44	−8.2	−2.1	6.1	cal	271[d]
1α	L-tyrosine	H_2O (pH 10.0)	298		−7.5	−20 ± 3	−12 ± 3	fl	36[d]
1α	undecanedioate	H_2O (pH 11.3)	298	3.20 ± 0.07	−18.3 ± 0.4	−22.7 ± 0.6	−4.4 ± 1.0	cal	171
1α	undecanedioate	D_2O (pD 13)[g]	298		−18.4	−25.1	−6.6	nmr	170
1α	δ-valerolactam	H_2O (pH 6.90)	298	0.70 ± 0.20	−4.0 ± 2.3	−12 ± 5	−8 ± 6	cal	12
1α	D-xylose	H_2O	298	1.57	−9.0 ± 1.4	−0.09 ± 0.01	8.9 ± 0.6	cal	37
1α	DL-xylose	H_2O	298	1.42	−8.1 ± 0.7	−0.11 ± 0.01	8.0 ± 0.7	cal	37
1α	L-xylose	H_2O	298	2.07	−11.8 ± 2.1	−0.12 ± 0.01	11.7 ± 2.1	cal	37
1β	acenocoumarin	H_2O (pH 7.4)	298	2.58 ± 0.04	−14.7	−15.5 ± 0.7	−0.7 ± 0.1	cal	273
1β	*N*-acetyl-1-aminonaphthalene	H_2O	298	2.12	−12.1	−11.5	0.6	fl	140, 198
1β	1-adamantaneacetate	H_2O (pH 9.94)	298		−28.7	−33.1 ± 1.7	−4.4 ± 1.5	uv	206
1β	1-adamantaneammonium	H_2O (pH 7.2)	298	3.92 ± 0.02	−22.4 ± 0.1	−22.1 ± 0.2	0.3	cal	84
1β	1-adamantanecarboxylate	H_2O (pH 7.2)	298		−24.9	−23.0	1.9	cal	21
1β	1-adamantanecarboxylate	H_2O (pH 9.94)	298		−26.1	−25.5 ± 0.8	0.6 ± 0.7	uv	206
1β	1-adamantanecarboxylate	H_2O (pH 8.50)	298	4.51 ± 0.03	−25.74 ± 0.2	−21.48 ± 0.04	4.26 ± 0.09	cal	75
1β	1-adamantanecarboxylate	H_2O	298		−24.5	−21.6	2.9	cal	188
1β	1-adamantanecarboxylate	H_2O (pH 8.5)	298	4.26	−24.3	−20.3 ± 0.9	3.9	cal	81
1β	1-adamantanecarboxylate	H_2O (pH 7.2; 6 M urea)	298		−23.8	−32.2	−8.4	cal	21
1β	1-adamantanecarboxylate	H_2O (pH 8.6)	298	4.02 ± 0.05	−22.9 ± 0.3	−22.8 ± 0.3	0.2 ± 0.5	cal	209
1β	1-adamantanecarboxylate	H_2O (pH 8.6, 8 M urea)	298	3.41 ± 0.05	−19.5 ± 0.3	−27.8 ± 0.8	−8.3 ± 1.0	cal	209
1β	1-adamantanecarboxylate	H_2O−CH_3CN (98.5:1.5; pH 9.0)	298	3.22 ± 0.04	−18.4	−20 ± 3	−1 ± 4	kin	125
1β	1-adamantanecarboxylate	H_2O (pH 8.50)	298		−24.5 ± 0.2	−20.3 ± 0.1	4.2 ± 0.2	cal	237
1β	1-adamantanecarboxylate	H_2O (pH 7.2)	298	4.51 ± 0.02	−25.7 ± 0.1	−23.9 ± 0.1	1.8	cal	84
1β	1-adamantanecarboxylate	H_2O (pH 7.0)	298	4.60 ± 0.02	−26.2	−21.8 ± 0.2	4.4	cal	54
1β	1-adamantanecarboxylic acid	H_2O	298		−32.4	−42.1	−9.7	cal	188
1β	1-adamantylammonium	H_2O	298	5.04	−28.7	−29.0 ± 0.8	0.1 ± 0.7	pot	238
1β	1-adamantylammonium	H_2O (pH 2.5)	298	3.95 ± 0.05	−22.5 ± 0.3	−24.7 ± 2.1	−2.2 ± 1.9	uv	205
1β	1-adamantylammonium	H_2O (pH < 2.5)	298	3.926 ± 0.010	−22.4 ± 0.1	−27.8 ± 1.3	−5.5 ± 1.4	uv	238
1β	1-adamantylammonium	H_2O (pH 4.0)	298		−22.2	−20.1	2.1	cal	21
1β	2-adamantylammonium	H_2O (pH 2.5)	298	3.87 ± 0.05	−22.1 ± 0.3	−21.8 ± 0.8	0.2 ± 0.7	uv	205
1β	1-adamantylmethylammonium	H_2O (pH 2.5)	298	4.48 ± 0.08	−25.5 ± 0.5	−17.2 ± 2.9	8.6 ± 2.7	uv	205
1β	1-adamantyltrimethyl-ammonium	H_2O (pH 8.6)	298	3.59 ± 0.02	−20.5 ± 0.1	−24.5 ± 0.2	−4.0 ± 0.3	cal	209
1β	1-adamantyltrimethyl-ammonium	H_2O (pH 8.6, 8 M urea)	298	3.06 ± 0.07	−17.5 ± 0.4	−18.7 ± 1.0	−1.2 ± 1.3	cal	209
1β	adiphenine·HCl	H_2O	298	3.44 ± 0.03	−19.6	−31.9 ± 0.8	−12.3	cal	74
1β	aflatoxin B1	H_2O−MeOH (60:40)	298	2.41	−13.8	−0.9	13.0	lc	116
1β	aflatoxin B2	H_2O−MeOH (60:40)	298	2.33	−13.3	−1.0	14.3	lc	116
1β	aflatoxin G1	H_2O−MeOH (60:40)	298	2.52	−14.4	−0.7	13.1	lc	116
1β	aflatoxin G2	H_2O−MeOH (60:40)	298	2.42	−13.8	−0.5	14.3	lc	116
1β	3-aminobenzoic acid	H_2O	298		−10.3	−8.7 ± 0.3	1.6 ± 1.3	cd	194
1β	4-aminobenzoic acid	H_2O	298		−15.4	−23.4 ± 0.4	−8.0 ± 1.3	cd	194
1β	4-amino-*N*-methylphthalimide	H_2O	298		−11.8	−6.3 ± 0.8	5.5 ± 0.5	fl*	106
1β	1-aminonaphthalene	H_2O	298	2.47	−14.1	−20.3	−6.2	fl	140, 198
1β	4-amino-1-naphthalene-sulfonate	H_2O	298	1.70 ± 0.03	−9.7 ± 0.2	−10.0 ± 0.2	0.3	cal	14
1β	8-anilino-1-naphthalene-sulfonate	D_2O	298	1.85	−10.6	−8.0	2.6	nmr	142
1β	[2-(4-aminophenyl)ethyl]-ammonium	H_2O (pH 6.9)	298	1.50 ± 0.03	−8.54 ± 0.16	−8.7 ± 0.4	−0.2 ± 0.4	cal	13
1β	amitriptylin	H_2O	298	4.38	−25.0	−32.4 ± 0.3	−7.3 ± 0.3	pot	123
1β	amobarbital	H_2O (pH 5.0)	298	3.08	−17.5	−26.4	−7.8	uv	179
1β	amobarbital	H_2O (pH 5.0)	298	3.10	−17.7	−17.8	−0.1	cal	52
1β	6-anilino-2-naphthalene-sulfonate	H_2O (1.0 M NaCl)	298		−19.8	−18.3 ± 0.4	1.5 ± 0.4	fl	274
1β	6-anilino-2-naphthalene-sulfonate	H_2O (0.5 M NaCl)	298		−19.2	−21.0 ± 1.0	−1.8 ± 1.0	fl	274
1β	6-anilino-2-naphthalene-sulfonate	H_2O (0.3 M Na_2SO_4)	298		−18.9	−19.1 ± 0.5	−0.2 ± 0.4	fl	274
1β	6-anilino-2-naphthalene-sulfonate	H_2O (0.2 M NaCl)	298		−18.8	−19.3 ± 0.9	−0.5 ± 0.8	fl	274

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1β	6-anilino-2-naphthalene-sulfonate	H_2O	298		−18.6	−19.1 ± 1.4	−0.5 ± 1.4	fl	274
1β	8-anilino-1-naphthalene-sulfonate	H_2O (pH 1.95)	298	2.06	−11.3	−7.5	3.9	fl	240
1β	(±)-anisodamine	H_2O (pH 5.8)	298	2.19 ± 0.02	−12.5	−17.2 ± 0.4	−4.7	cal	275
1β	(−)-anisodamine	H_2O (pH 5.8)	298	2.33 ± 0.01	−13.3	−17.6 ± 0.2	−4.3	cal	275
1β	(−)-anisodamine·HBr	H_2O (pH 5.8)	298	2.31 ± 0.01	−13.2	−18.0 ± 0.4	−4.8	cal	275
1β	(−)-anisodine·HBr	H_2O (pH 5.8)	298	1.85 ± 0.01	−10.6	−11.6 ± 0.1	−1.0	cal	275
1β	anthracene	H_2O	298	3.31	−18.9	−17.6	1.3	lc	241
1β	D-arabinose	H_2O	298	1.21	−6.9 ± 1.8	−0.4 ± 0.2	6.5 ± 1.8	cal	37
1β	aspartame	H_2O (pH 4.0)	298	2.11 ± 0.07	−12.0 ± 0.4	−11.7 ± 0.7	0.3	cal	276
1β	(±)-atropine·H_2SO_4	H_2O (pH 5.8)	298	2.56 ± 0.01	−14.6	−19.5 ± 0.3	−4.9	cal	275
1β	barbital	H_2O (pH 5.0)	298	2.44	−13.9	−11.5	2.4	cal	52
1β	benz[*a*]anthracene	H_2O	298	3.54	−20.2	−13.4	6.8	lc	241
1β	benzene	H_2O	298	2.228 ± 0.003	−12.72 ± 0.02	−1.9 ± 0.3	10.8	vap	29
1β	benzene	H_2O	298	2.03 ± 0.11	−11.6 ± 0.8	−3.5 ± 0.6	8.1 ± 1.0	cal	152
1β	benzoate	H_2O (pH 6.9)	298	1.20 ± 0.03	−6.86 ± 0.20	−10.5 ± 0.7	−3.6 ± 0.8	cal	9
1β	benzoate	H_2O	298	1.559 ± 0.005	−8.89 ± 0.05	−4.6 ± 1.7	4.2 ± 2.9	pot	71
1β	benzoate	H_2O	303	1.00 ± 0.01	−5.8 ± 0.3	−15.0 ± 1.5	−8.8 ± 3.0	cal	277
1β	benzoic acid	H_2O	298	2.1 ± 0.4	−12 ± 2	−32 ± 11	−20	cal	192
1β	benzoic acid	H_2O	298	3.26	−18.6	−6.2	12.5	cal	52
1β	benzoic acid	H_2O	298	2.737 ± 0.002	−15.62 ± 0.02	−17.2 ± 1.3	−1.3 ± 1.1	pot	71
1β	benzoic acid	H_2O	298		−14.4	−22.3 ± 0.3	−7.8 ± 0.8	cd	194
1β	benzoic acid	H_2O	303	2.57	−14.9 ± 0.2	−15.0 ± 1.0	0	cal	277
1β	benzoic acid	H_2O	303	2.56	−14.8	−18.0	−3.2	cal	242
1β	benzoic acid	H_2O	323	2.40	−14.8 ± 0.2	−19.0 ± 1.4	−4 ± 2	cal	277
1β	benzo[*a*]pyrene	H_2O	298	4.81	−27.5	−28.9	−1.4	lc	241
1β	benzo[*a*]pyrene	H_2O	298	3.34	−19.1	−31.0	−11.9	lc	241
1β	benzoylacetic acid	H_2O	323	2.01 ± 0.03	−11.5 ± 0.2	−24 ± 5	−12 ± 5	kin	278
1β	benzyl alcohol	H_2O	303	1.32	−7.7	−13.8	−6.2	cal	242
1β	L-α-*O*-benzylglycerol	H_2O (pH 6.9)	298	2.11 ± 0.01	−12.03 ± 0.06	−9.2 ± 0.1	2.8 ± 0.1	cal	13
1β	1-benzylimidazole	H_2O (pH 10.0)	298	2.61 ± 0.01	−14.92 ± 0.08	−15.9 ± 0.2	−1.0 ± 0.2	cal	13
1β	4-benzylpiperidine	H_2O (pH 6.9)	298	3.30 ± 0.05	−18.83 ± 0.29	−13.8 ± 0.4	5.1 ± 0.6	cal	13
1β	1-bicyclo[2.2.1]heptane-carboxylate	H_2O (pH 8.5)	298	2.92	−16.7	−8.0 ± 0.8	8.8	cal	81
1β	1-bicyclo[2.2.1]hept-2-ene-carboxylate	H_2O (pH 8.5)	298	2.75	−15.7	−7.5 ± 0.8	8.1	cal	81
1β	1-bicyclo[2.2.2]octane-carboxylate	H_2O (pH 8.5)	298	3.85	−21.9	−15.9 ± 0.8	5.9	cal	81
1β	(4*Z*,15*Z*)-bilirubin-IXa	H_2O (pH 10.8)	298	1.36	−7.8	−27 ± 2	−20 ± 2	cd	97
1β	(4*Z*,15*Z*)-bilirubin-IXa + cyclooctanol	H_2O (pH 10.8)	298	1.71	−9.7	−40 ± 3	−29 ± 3	cd	97
1β	(*R*)-1,1′-binaphthyl-2,2′-diyl phosphate	D_2O (pD 5.5)	298	2.42 ± 0.04	−13.8 ± 0.2	−22.0 ± 0.8	−7.7 ± 0.7	nmr	203
1β	(*S*)-1,1′-binaphthyl-2,2′-diyl phosphate	D_2O (pD 5.5)	298	2.54 ± 0.04	−14.5 ± 0.2	−21.1 ± 0.6	−5.9 ± 0.2	nmr	203
1β	bromodiphenhydramine·HCl	H_2O	298	3.33 ± 0.05	−19.0	−25.4 ± 1.0	−6.4	cal	74
1β	1-bromomethylnaphthalene	H_2O	298	2.84	−16.6	−68.4	−51.8	fl	140, 198
1β	4-bromophenol	H_2O (pH 4.2)	298	2.93 ± 0.07	−16.7 ± 0.4	−12.2 ± 0.3	4.5 ± 0.6	cal	39
1β	butabarbital	H_2O (pH 5.0)	298	2.95	−16.9	−33.2	−16.4	cal	52
1β	1,3-butanediol	H_2O	298	4.08	−23.3	−1.4	21.9	cal	244[b]
1β	1,4-butanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	0.59 ± 0.10	−3.4	−10	−7	uv	245
1β	butanoic acid	H_2O	298	1.511 ± 0.013	−8.62 ± 0.15	−13.1 ± 0.1	−4.5 ± 0.1	pot	71
1β	(*R*)-(−)-2-butanol	H_2O (pH 6.90)	298	1.11 ± 0.12	−6.4 ± 0.9	4.9 ± 1.3	11.3 ± 1.5	cal	32
1β	(*S*)-(+)-2-butanol	H_2O (pH 6.90)	298	1.30 ± 0.10	−7.4 ± 0.7	3.2 ± 0.6	10.7 ± 0.9	cal	32
1β	(±)-2-butanol	H_2O (pH 6.90)	298	1.11 ± 0.12	−6.4 ± 0.9	4.9 ± 1.1	11.3 ± 0.6	cal	32
1β	1-butanol	H_2O	298	1.22	−7.0	2.9	9.8	uv	11
1β	1-butanol	H_2O (pH 6.90)	298	1.20 ± 0.05	−6.9 ± 0.5	4.3 ± 0.4	11.2 ± 0.2	cal	32
1β	1-butanol	H_2O	298		−18.0	3.0	21.0	cal	91[b]
1β	butethal	H_2O (pH 5.0)	298	2.94	−16.8	−9.8	7.0	cal	52
1β	butylbarbituric acid	H_2O (pH 5.0)	298	2.59	−14.8	−15.8	−1.0	uv	179
1β	1-butylimidazole	H_2O (pH 10.0)	298	2.19 ± 0.02	−12.5 ± 0.13	−10.7 ± 0.3	1.8 ± 0.3	cal	13
1β	6-[(4-*tert*-butylphenyl)-amino]-2-naphthalene-sulfonate	H_2O (pH 7.0)	298	4.75 ± 0.02	−27.1	−25.3 ± 0.3	1.8	cal	54
1β	butylthiobarbituric acid	H_2O (pH 5.0)	298	2.88	−16.4	−20.4	−3.9	uv	179
1β	chloramine-T	H_2O (pH 7.5)	298	3.18	−18.1	−29.8	−12.0	pot	124
1β	chlorcyclizine	H_2O	298	3.62 ± 0.01	−21.0	−22.0	−1.0	pot	36
1β	chlorcyclizine·2HCl	H_2O	298	3.38 ± 0.02	−19.4	−22.8 ± 1.0	−3.4	cal	74
1β	chlorcyclizine·HCl	H_2O	298	3.39 ± 0.06	−19.4	−24.1 ± 1.3	−4.7	cal	74
1β	3-chlorobenzoylacetic acid	H_2O	323	2.22 ± 0.01	−12.7 ± 0.1	−22 ± 5	−8 ± 4	kin	278
1β	(10-chloro-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-decyl)trimethylammonium	H_2O	308	4.50	−26.4 ± 0.3	−7.1 ± 2.1	19.3 ± 2.5	sur	134

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1β	2-chloro-4-[(4-hydroxyphenyl)-azo]benzoate	DMF	298	3.64 ± 0.05	−20.78	−12.9 ± 0.4	7.8	cal	43
1β	4-chloro-3-[(4-hydroxyphenyl)-azo]benzoate	DMF	298	3.51 ± 0.14	−20.04	−20.1 ± 0.6	0.0	cal	43
1β	1-chloronaphthalene	H_2O	298	3.08	−17.6	−71.7	−54.1	fl	140, 198
1β	2-chlorophenol	H_2O	298	2.30 ± 0.06	−13.1 ± 0.3	−19 ± 4	−6 ± 3	uv	169
1β	3-chlorophenol	H_2O	298	2.30 ± 0.02	−13.1 ± 0.1	−19 ± 2	−5 ± 2	uv	169
1β	4-chlorophenol	H_2O (pH 4.2)	298	2.61 ± 0.06	−14.9 ± 0.3	−11.9 ± 0.4	3.0 ± 0.6	cal	39
1β	4-chlorophenol	H_2O	298	2.40 ± 0.02	−13.7 ± 0.1	−16 ± 2	−2 ± 2	uv	169
1β	3-chlorophenyl acetate	H_2O (pH 10.6)	298	2.46 ± 0.13	−14 ± 4	−4 ± 4	10 ± 4	kin	212
1β	chlorpromazine	H_2O (0.02 M Na_2SO_4)	298	4.10	−23.4	−41.1	−17.7	pot	124
1β	chlorpromazine	H_2O (pH 5.0)	298	3.92	−22.4	−26.8	−4.5	cal	52
1β	chlorpromazine·HCl	H_2O	298	4.04	−23.1	−27.6	−4.6	pot	279[d]
1β	cinnarizine·2HCl	H_2O	298	3.46 ± 0.03	−19.8	−17.3 ± 0.4	2.4	cal	74
1β	L-cocaine·HCl	H_2O	298		−15.1	−12.1	2.7	cd	280
1β	1-cyanonaphthalene	H_2O	298	2.40	−13.7	−29.3	−15.7	fl	140, 198
1β	cyclizine·HCl	H_2O	298	3.08 ± 0.03	−17.6	−28.8 ± 1.5	−11.2	cal	74
1β	cyclobarbital	H_2O (pH 5.0)	298	3.15	−17.9	−20.2	−4.8	uv	179
1β	cyclobutanol	H_2O (pH 6.9)	298	1.15 ± 0.15	−6.5 ± 1.4	3.7 ± 1.4	10.2 ± 2.0	cal	9
1β	cycloheptanol	H_2O (pH 6.9)	298	3.34 ± 0.01	−19.08 ± 0.09	−12.37 ± 0.12	6.7 ± 0.2	cal	9
1β	cyclohexanecarboxylate	H_2O	298	2.42	−13.8	−4.6 ± 1.7	9.2 ± 1.5	pot	71
1β	cyclohexanecarboxylic acid	H_2O	298	3.61	−20.6	−23.0 ± 1.7	−2.4 ± 1.5	pot	71
1β	*cis*-1,2-cyclohexanediol	H_2O (pH 6.90)	298	2.43 ± 0.04	−13.9 ± 0.3	−9.8 ± 0.4	4.2 ± 0.6	cal	12
1β	*trans*-1,2-cyclohexanediol	H_2O (pH 6.90)	298	2.00 ± 0.04	−11.4 ± 0.3	−4.4 ± 0.2	7.2 ± 0.6	cal	12
1β	cyclohexanol	H_2O (pH 6.90)	293	2.89 ± 0.02	−16.2 ± 0.1	−4.9 ± 0.1	11.1 ± 0.3	cal	12
1β	cyclohexanol	H_2O (pH 6.9)	298	2.838 ± 0.007	−16.19 ± 0.04	−6.5 ± 0.1	9.7 ± 0.1	cal	10
1β	cyclohexanol	H_2O	298	2.70	−15.3	−10.0	5.1	uv	11
1β	cyclohexanol	H_2O (pH 6.90)	298	2.85 ± 0.01	−16.3 ± 0.1	−6.6 ± 0.1	9.8 ± 0.3	cal	12
1β	cyclohexanol	H_2O (pH 6.90)	303	2.84 ± 0.02	−16.5 ± 0.1	−8.2 ± 0.1	8.5 ± 0.3	cal	12
1β	cyclohexanol	H_2O (pH 6.90)	308	2.78 ± 0.02	−16.4 ± 0.2	−9.9 ± 0.2	6.8 ± 0.3	cal	12
1β	cyclohexanol	H_2O	298	4.36	−24.9	−7.0	17.9	cal	89[b]
1β	cyclohexanone	H_2O (pH 6.90)	298	2.71 ± 0.07	−15.5 ± 0.5	−11.7 ± 0.7	3.9 ± 0.9	cal	12
1β	cyclooctanol	H_2O (pH 6.9)	298	3.64 ± 0.05	−20.8 ± 0.3	−16.4 ± 0.5	4.4 ± 0.6	cal	9
1β	cyclopentanol	H_2O (pH 6.9)	298	2.24 ± 0.01	−12.76 ± 0.08	−4.56 ± 0.05	8.2 ± 0.1	cal	9
1β	dansylalanine	H_2O	298	2.28	−13.0	−7.1	6.7	fl	34
1β	dansyl-L-arginine	H_2O	298	2.04	−11.3	−8.8	2.7	fl	34
1β	dansyl-L-asparagine	H_2O	298	2.04	−11.7	−5.9	5.7	fl	34
1β	dansyl-L-aspartic acid	H_2O	298	2.15	−12.1	−13.0	−0.9	fl	34
1β	dansyl-L-cysteic acid	H_2O	298	2.18	−12.1	−10.0	2.4	fl	34
1β	dansyl-L-glutamine	H_2O	298	2.11	−12.1	−6.7	5.5	fl	34
1β	dansyl-L-glutamine	H_2O	298	2.00	−11.3	−4.2	8.4	fl	34
1β	dansyl-L-histidine	H_2O	298	2.20	−12.6	−7.5	4.7	fl	34
1β	dansyl-L-hydroxyplorine	H_2O	298	2.11	−11.7	−10.0	1.9	fl	34
1β	dansyl-L-isoleucine	H_2O	298	2.28	−13.0	−10.0	2.7	fl	34
1β	dansyl-L-leucine	H_2O	298	2.30	−13.0	−15.5	−2.5	fl	34
1β	ϵ-dansyl-L-lysine	H_2O	298	2.40	−13.4	−10.9	2.6	fl	34
1β	dansyl-L-phenylalanine	H_2O	298	1.95	−10.9	−23.4	−12.5	fl	34
1β	dansyl-L-proline	H_2O	298	2.34	−13.4	−9.2	4.0	fl	34
1β	dansyl-L-serine	H_2O	298	2.20	−12.6	−3.8	8.7	fl	34
1β	dansyl-L-threonine	H_2O	298	2.26	−12.6	−8.4	4.4	fl	34
1β	*O*-dansyl-L-threonine	H_2O	298	2.04	−11.3	−5.4	6.0	fl	34
1β	dansyl-L-tryptophan	H_2O	298	2.62	−14.6	−14.2	0.6	fl	34
1β	dansyl-L-valine	H_2O	298	2.30	−12.6	−13.0	0.2	fl	34
1β	1,10-decanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	3.35 ± 0.08	−19.1	−26.0	−7.0	uv	245
1β	decanoate	H_2O	298	3.82	−21.8	−20.5 ± 1.7	1.3 ± 1.8	pot	71
1β	decanoic acid	H_2O	298	4.01	−22.9	−25.1 ± 1.3	−2.2 ± 1.3	pot	71
1β	di-2-(1-adamantyl)ethyl hydrogen phosphate	H_2O (pH 7.0)	298	5.35 ± 0.09	−30.5	−29.3 ± 0.4	1.3	cal	54[k]
1β	di-2-(1-adamantyl)ethyl hydrogen phosphate	H_2O (pH 7.0)	298	3.64 ± 0.04	−20.8	−16.1 ± 0.5	4.7	cal	54[l]
1β	diazepam (anion)	H_2O (pH 6)	298		−23.9	−18.4 ± 0.4	5.5 ± 0.4	sol	49
1β	dibucaine·HCl	H_2O	298	2.82 ± 0.04	−16.1 ± 0.2	−13.3	2.6	pot	279[d]
1β	dicumarol	H_2O (pH 8.4)	298	3.60 ± 0.04	−20.5	−40.4 ± 2.0	−20.0 ± 2.1	cal	273
1β	didansyl-l-lysine	H_2O	298	2.28	−13.0	−17.6	−4.6	fl	34
1β	4,4′-dihydroxybiphenyl	H_2O−MeOH (50:50)	298		−4.2	−1.3	2.9	lc	117
1β	(3,4-dihydroxyphenethyl)-ammonium	H_2O (pH 6.9)	298	1.50 ± 0.01	−8.58 ± 0.04	−16.52 ± 0.17	−7.9 ± 0.2	cal	13
1β	(3,4-dihydroxyphenethyl)-ammonium	H_2O (pH 5.0)	298	1.48 ± 0.01	−8.46 ± 0.03	−18.3 ± 0.2	−9.8 ± 0.2	cal	13
1β	(2,5-dimethoxyphenethyl)-ammonium	H_2O (pH 6.9)	298	1.59 ± 0.01	−9.08 ± 0.07	−9.39 ± 0.17	−0.3 ± 0.2	cal	13
1β	(2,5-dimethoxyphenethyl)-ammonium	H_2O (pH 5.0)	298	1.57 ± 0.01	−8.94 ± 0.07	−10.2 ± 0.2	−1.3 ± 0.2	cal	13

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1β	(3,4-dimethoxyphenethyl)-ammonium	H_2O (pH 6.9)	298	1.14 ± 0.16	−6.52 ± 1.4	−2.0 ± 0.7	4.5 ± 1.5	cal	13
1β	5-(dimethylamino)-1-naphthalenesulfonate	H_2O	298	2.15	−12.1	−3.3	9.0	fl	34
1β	2-(dimethylamino)-6-propionyl-naphthalene	H_2O	298		−18.8	−16.3 ± 0.4	2.5 ± 0.2	fl*	106
1β	2,2-dimethyl-1-propanol	H_2O	298	2.76	−15.5	−8.8	6.3	uv	11
1β	diphenhydramine·HCl	H_2O	298	3.06 ± 0.01	−17.5	−29.4 ± 1.0	−11.9	cal	74
1β	diphenidol·HCl	H_2O	298	2.97 ± 0.04	−17.0	−33.7 ± 1.1	−16.7	cal	74
1β	diphenyl phosphate	H_2O (pH 3.4−10)	298	2.30	−13.1	−8.0	4.5	fl	102
1β	diphenylpyraline	H_2O	298	3.53 ± 0.04	−20.4	−15.0	5.4	pot	36
1β	diphenylpyraline·HCl	H_2O	298	3.36 ± 0.02	−19.1	−27.8 ± 0.6	−8.7	cal	74
1β	doxepin	H_2O	298	4.12	−23.5	−37.9 ± 0.9	−14.3 ± 1.0	pot	123
1β	(1*R*,2*S*)-(−)-ephedrine	H_2O (pH 6.9)	298	1.90 ± 0.01	−10.84 ± 0.05	−9.7 ± 0.1	1.1 ± 0.1	cal	13
1β	(1*R*,2*S*)-(−)-ephedrine	H_2O (pH 5.0)	298	1.77 ± 0.01	−10.12 ± 0.06	−9.31 ± 0.12	0.8 ± 0.1	cal	13
1β	(1*S*,2*R*)-(+)-ephedrine	H_2O (pH 6.9)	298	1.85 ± 0.01	−10.58 ± 0.05	−8.71 ± 0.09	1.9 ± 0.1	cal	13
1β	(1*S*,2*R*)-(+)-ephedrine	H_2O (pH 5.0)	298	1.74 ± 0.01	−9.95 ± 0.07	−8.79 ± 0.13	1.2 ± 0.1	cal	13
1β	estradiol	H_2O−MeOH (55:45)	298		−15.6	−37.2	−21.6	lc	281
1β	estradiol	H_2O−CH_3CN (70:30)	298		−13.3	−25.1	−11.8	lc	281
1β	estriol	H_2O−MeOH (55:45)	298		−14.5	−33.1	−18.6	lc	281
1β	estriol	H_2O−CH_3CN (70:30)	298		−12.7	−23.8	−11.1	lc	281
1β	estrone	H_2O−MeOH (55:45)	298		−14.4	−33.5	−19.1	lc	281
1β	estrone	H_2O−CH_3CN (70:30)	298		−12.2	−21.8	−9.6	lc	281
1β	ethinyloestradiol	H_2O−MeOH (55:45)	298		−15.4	−35.6	−20.2	lc	281
1β	ethinyloestradiol	H_2O−CH_3CN (70:30)	298		−12.4	−21.8	−9.4	lc	281
1β	ethyl decanoate	H_2O−EtOH (85:15; pH 4.3)	293	2.03	−11.4	−20.0	−8.6	gc	115
1β	ethyl 1-naphthalenecarboxylate	H_2O	298	2.66	−15.2	−32.3	−17.0	fl	140, 198
1β	ethylbis(coumacetate)	H_2O (pH 7.4)	298	3.57 ± 0.04	−20.4	−37.5 ± 1.8	−17.3 ± 1.8	cal	273
1β	3-ethylphenyl acetate	H_2O (pH 10.0)	298	2.66 ± 0.08	−15 ± 3	−19 ± 3	−4 ± 2	kin	212
1β	ethylthiobarbituic acid	H_2O (pH 5.0)	298	2.46	−14.0	−15.5	−0.3	uv	179
1β	ferrocenecarboxylate	H_2O (pH 8.6)	298	3.33 ± 0.05	−19.0 ± 0.3	−15.3 ± 0.4	3.7 ± 0.7	cal	209
1β	ferrocenecarboxylate	H_2O (pH 8.6, 8 M urea)	298	2.85 ± 0.06	−16.2 ± 0.3	−11.1 ± 0.6	5.1 ± 1.0	cal	209
1β	ferrocenylalkyldimethyl-ammonium **28a**	H_2O (0.05 M NaCl)	298	3.46	−19.7 ± 0.4	−28.5 ± 0.8	−8.8 ± 1.3	cal	251
1β	ferrocenylalkyldimethyl-ammonium **28a**	H_2O (0.1 M NaCl; 2 M urea)	298	3.20 ± 0.07	−18.3 ± 0.4	−25.5 ± 2.5	−7.1 ± 2.9	cal	251
1β	ferrocenylalkyldimethyl-ammonium **28a**	H_2O (0.1 M NaCl; 4 M urea)	298	3.14 ± 0.06	−17.9 ± 0.4	−24.3 ± 2.1	−6.3 ± 2.5	cal	251
1β	ferrocenylalkyldimethyl-ammonium **28a**	H_2O (0.1 M NaCl; 6 M urea)	298	3.00 ± 0.07	−17.1 ± 0.4	−21.3 ± 2.5	−4.2 ± 2.9	cal	251
1β	ferrocenylalkyldimethyl-ammonium **28a**	H_2O (0.1 M NaCl; 8 M urea)	298	2.85 ± 0.06	−16.3 ± 0.4	−20.5 ± 2.9	−4.2 ± 3.3	cal	251
1β	ferrocenylalkyldimethyl-ammonium **28b**	H_2O (pH 2.6−6.5)	298	3.40	−19.4 ± 0.4	−23.8 ± 0.4	−4.6 ± 0.8	cal	251
1β	ferrocenylalkyldimethyl-ammonium **28c**	H_2O (pH 2.6)	298	3.68	−21.0 ± 0.4	−23.0 ± 0.4	−2.1 ± 0.8	cal	251
1β	ferrocenylalkyldimethyl-ammonium **28d**	H_2O (pH 6.5)	298	3.40	−19.4 ± 0.4	−25.5 ± 0.4	−6.3 ± 0.8	cal	251
1β	flufenamic acid	H_2O (pH 7.0)	298	3.17	−18.1	−11.4	6.7	cal	52
1β	flufenamic acid	H_2O (pH 7.0)	298	3.10	−17.7	−14.6	3.0	cd	230
1β	flurbiprofen	H_2O	298	3.65	−20.8	−14.9	5.9	cal	253[d]
1β	flurbiprofen	H_2O (pH 7.0)	298	3.29	−18.8	−23.3	−4.5	cal	253[d]
1β	D-glucose	H_2O (pH 7.0)	298	−0.22	1.3 ± 0.9	1.6 ± 1.5	0.3	fl/cal	141
1β	D-glucose	H_2O	298	2.62 ± 0.11	−15.0 ± 0.6	−63 ± 21	−48	uv/cal	232[b]
1β	1,7-heptanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	2.12 ± 0.02	−12.1	−20	−8	uv	245
1β	heptanoate	H_2O (pH 6.9)	298	2.48 ± 0.16	−14.2 ± 1.5	1.8 ± 0.3	15.9 ± 1.5	cal	9
1β	heptylbarbituric acid	H_2O (pH 5.0)	298	3.47	−19.8	−32.0	−12.2	uv	179
1β	hexafluorophosphate	H_2O (0.2 M NaCl)	298	1.93 ± 0.02	−11.0 ± 0.1	−22.2 ± 0.9	−11.2 ± 0.9	cal	254
1β	1,6-hexanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	1.59 ± 0.03	−9.1	−19	−10	uv	245
1β	hexanoate	H_2O (pH 6.9)	298	1.67 ± 0.04	−9.54 ± 0.25	5.5 ± 0.3	15.0 ± 0.4	cal	9
1β	hexanoate	H_2O	298	1.830 ± 0.011	−10.44 ± 0.13	2 ± 3	12 ± 4	pot	71
1β	hexanoic acid	H_2O	298	2.467 ± 0.007	−14.07 ± 0.08	−7.9 ± 1.3	5.9 ± 1.5	pot	71
1β	(*R*)-(−)-2-hexanol	H_2O (pH 6.90)	298	2.07 ± 0.18	−11.8 ± 1.8	1.9 ± 0.6	13.7 ± 1.8	cal	32
1β	1-hexanol	H_2O	298	2.34	−13.3	0.4	13.7	uv	11
1β	1-hexanol	H_2O	298		−21.5	0.6	22.1	cal	256[b]
1β	hexobarbital	H_2O (pH 5.0)	298	3.11	−17.7	−23.5	−5.9	uv	179
1β	hexobarbital	H_2O (pH 5.0)	298	2.86	−16.4	−24.5	−8.2	cal	52
1β	hexylammonium	H_2O (pH 6.9)	298	1.81 ± 0.10	−10.4 ± 0.7	2.5 ± 0.4	12.9 ± 0.8	cal	9
1β	hexylbarbituric acid	H_2O (pH 5.0)	298	3.33	−19.2	−25.9	−6.8	uv	179
1β	hexylthiobarbituric acid	H_2O (pH 5.0)	298	3.50	−20.0	−29.6	−10.2	uv	179
1β	hydrochlorothiazide	H_2O (pH 5)	298		−58.5	−40.2 ± 1.7	18.3 ± 1.7	sol	49
1β	hydroquinone	H_2O (pH 4.2)	298	2.05 ± 0.02	−11.7 ± 0.1	−17.1 ± 0.5	−5.4 ± 0.6	cal	39

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1β	3-hydroxybenzoic acid	H_2O	298		−14.0	−27.6 ± 0.3	−13.6 ± 1.3	cd	194
1β	4-hydroxybenzoic acid	H_2O	298		−15.5	−25.6 ± 0.4	−10.1 ± 1.3	cd	194
1β	2-hydroxybiphenyl	H_2O−MeOH (50:50)	298		−3.5	−0.3	3.2	lc	117
1β	3-hydroxybiphenyl	H_2O−MeOH (50:50)	298		−4.0	−1.2	2.8	lc	117
1β	4-hydroxybiphenyl	H_2O−MeOH (50:50)	298		−4.1	−1.3	2.8	lc	117
1β	*trans*-3-hydroxycinnamate	H_2O (pH 8.2)	298	2.37	−13.5	−21.3	−8.0	uv	257
1β	*trans*-4-hydroxycinnamate	H_2O (pH 8.2)	298	2.61	−14.9	−20.5	−5.6	uv	257
1β	*trans*-2-hydroxycinnamic acid	H_2O (pH 1.6)	298	2.58	−14.7	−23.0	−8.9	uv	257
1β	*trans*-3-hydroxycinnamic acid	H_2O (pH 1.6)	298	2.63	−15.0	−19.2	−4.6	uv	257
1β	*trans*-4-hydroxycinnamic acid	H_2O (pH 1.6)	298	2.76	−15.7	−21.8	−5.6	uv	257
1β	4-hydroxycoumarin	H_2O (pH 7.4)	298	2.30 ± 0.08	−13.1	−12.0 ± 0.6	1.1 ± 0.1	cal	273
1β	(1-hydroxymethyl)naphthalene	H_2O	298	2.90	−14.7	−43.6	−28.9	fl	140, 198
1β	4-[(4-hydroxy-1-naphthyl)azo]-naphthalene-1-sulfonate	H_2O (pH 10.5)	298		−4.6	−16.3	−11.7	uv	282
1β	(4-hydroxyphenethyl)ammonium	H_2O (pH 6.9)	298	1.845 ± 0.012	−10.53 ± 0.07	−13.8 ± 0.2	−3.4 ± 0.1	cal	10
1β	(4-hydroxyphenethyl)ammonium	H_2O (pH 6.9)	298	1.853 ± 0.004	−10.58 ± 0.03	−13.8 ± 0.2	−3.2 ± 0.2	cal	13
1β	(4-hydroxyphenethyl)ammonium	H_2O (pH 5.0)	298	1.799 ± 0.005	−10.27 ± 0.03	−13.79 ± 0.14	−3.5 ± 0.1	cal	13
1β	3-[(4-hydroxyphenyl)azo]benzoate	DMF	298	4.01 ± 0.03	−22.89	−17.47 ± 0.03	5.4	cal	43
1β	4-[(4-hydroxyphenyl)azo]benzoate	DMF	298	4.04 ± 0.09	−23.06	−17.2 ± 0.8	5.9	cal	43, 259
1β	3-(4-hydroxyphenyl)-1-propanol	H_2O	298	2.98	−17.0	−9.6	7.6	fl	137
1β	3-(2-hydroxyphenyl)propionate	H_2O (pH 6.9)	298	1.908 ± 0.011	−10.89 ± 0.06	−15.1 ± 0.2	−4.2 ± 0.2	cal	10
1β	3-(4-hydroxyphenyl)propionate	H_2O (pH 6.9)	298	2.473 ± 0.006	−14.11 ± 0.03	−14.2 ± 0.1	−0.1 ± 0.1	cal	10
1β	hydroxyzine·HCl	H_2O	298	3.36 ± 0.02	−19.2	−24.2 ± 0.4	−5.0	cal	74
1β	ibuprofen	H_2O (pH 2)	298	−33.3	−28.9 ± 1.3	4.4 ± 1.2	sol	49	
1β	imidazole	H_2O (pH 9.5; 0.5 M NaOAc)	298	0.41 ± 0.05	−2.4 ± 0.3	−15	−13	cal	260
1β	imidazole	H_2O (pH 9.5)	298	0.28 ± 0.12	−1.6 ± 0.7	−16 ± 4	−14	cal	260
1β	imipramin	H_2O	298	3.94	−22.5	−30 ± 3	−7 ± 3	pot	123
1β	4-iodophenol	H_2O	298		−17.0	−16.1	0.9	cal	188
1β	4-iodophenolate	H_2O	298		−17.1	−12.7	4.5	cal	188
1β	ketoprofen	H_2O (pH 2.0)	298	2.85	−16.3	−12.6	3.2	sol	48
1β	maprotilin	H_2O	298	3.68	−21.0	−24.6 ± 2.1	−3.5 ± 2.1	pot	123
1β	meclizine·2HCl	H_2O	298	3.35 ± 0.05	−19.1	−22.6 ± 0.9	−3.4	cal	74
1β	meclofenamic acid	H_2O (pH 7.0)	298	2.69	−15.3	−41.8	−26.8	cd	230
1β	mefenamic acid	H_2O (pH 7.0)	298	2.79	−15.9	−24.1	−8.3	cd	230
1β	mephobarbital	H_2O	298	3.21	−18.3	−33.9	−15.8	pot	50
1β	mephobarbital	H_2O (pH 5.0)	298	3.18	−18.1	−39.7	−21.6	uv	179
1β	mephobarbital (anion)	H_2O	298	2.57	−14.7	−48.6	−34.3	pot	50[d]
1β	methapyriline·HCl	H_2O (pH 7.0)	298	2.55	−14.5	−15.5	−1.0	cal	263[d]
1β	1-methoxynaphthalene	H_2O	298	3.14	−17.9	−17.6	0.3	fl	140, 198
1β	(2-methoxyphenethyl)ammonium	H_2O (pH 5.0)	298	0.90 ± 0.05	−5.15 ± 0.33	−13.5 ± 1.6	−8.3 ± 1.8	cal	13
1β	(3-methoxyphenethyl)ammonium	H_2O (pH 6.9)	298	1.88 ± 0.01	−10.74 ± 0.04	−11.7 ± 0.1	−1.0 ± 0.1	cal	13
1β	(3-methoxyphenethyl)ammonium	H_2O (pH 5.0)	298	1.82 ± 0.01	−10.39 ± 0.04	−13.32 ± 0.13	−2.9 ± 0.1	cal	13
1β	(4-methoxyphenethyl)ammonium	H_2O (pH 6.9)	298	1.97 ± 0.01	−11.23 ± 0.04	−8.08 ± 0.08	3.2 ± 0.1	cal	13
1β	(4-methoxyphenethyl)ammonium	H_2O (pH 5.0)	298	1.89 ± 0.01	−10.78 ± 0.05	−8.21 ± 0.08	2.6 ± 0.1	cal	13
1β	3-methoxyphenylacetate	H_2O (pH 6.9)	298	1.58 ± 0.01	−9.02 ± 0.08	−12.3 ± 0.2	−3.2 ± 0.3	cal	9
1β	4-methoxyphenylacetate	H_2O (pH 6.9)	298	1.84 ± 0.01	−10.51 ± 0.06	−8.22 ± 0.11	2.3 ± 0.2	cal	9
1β	methyl orange (acid form)	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	3.51 ± 0.02	−20.0	−33	−13	uv	245
1β	methyl orange (acid form)	H_2O	298	2.36 ± 0.07	−13.5 ± 0.4	−7.9 ± 2.9	3.7 ± 2.5	uv	205
1β	methyl orange (acid form)	H_2O (pH 1.1)	298		−14.0	−10.7 ± 1.0	3.2 ± 1.0	uv	264
1β	methyl orange (anion)	H_2O	298	3.65 ± 0.04	−20.8 ± 0.2	−19.7 ± 1.7	1.5 ± 1.5	uv	205
1β	methyl orange (anion)	H_2O (pH 7.5)	298		−18.8	−15.9	3.1	uv	265
1β	methyl red (anion)	H_2O (pH 9.5)	298	3.58 ± 0.01	−20.5 ± 2.0	−19.6 ± 1.0	0.9 ± 1.0	uv	266
1β	methyl red (cation, protonated)	H_2O (pH 1.0)	298	3.50 ± 0.03	−20.0 ± 0.4	−18.9 ± 0.2	1.1 ± 0.2	uv	266
1β	*N*-methyl-1-aminonaphthalene	H_2O	298	2.61	−14.9	−28.4	−13.5	fl	140, 198
1β	3-methylbenzoic acid	H_2O	298	7.1 ± 0.1[m]	−40.2 ± 0.4	−49 ± 5	−9	cal	192
1β	4-methylbenzoylacetic acid	H_2O	323	2.33 ± 0.03	−13.3 ± 0.2	−28 ± 2	−13 ± 1	kin	278
1β	3-methyl-1-butanol	H_2O−EtOH (85:15; pH 4.3)	293	2.19	−12.3	−49.9	−37.6	gc	115
1β	3-methylbutyl acetate	H_2O−EtOH (85:15; pH 4.3)	293	2.31	−13.0	−28.5	−15.6	gc	115
1β	*trans*-3-methylcinnamate	H_2O (pH 8.2)	298	2.53	−14.4	−18.8	−4.6	uv	257
1β	*trans*-4-methylcinnamate	H_2O (pH 8.2)	298	2.67	−15.2	−17.6	−1.9	uv	257
1β	*trans*-2-methylcinnamic acid	H_2O (pH 1.6)	298	2.62	−14.9	−12.1	3.5	uv	257
1β	*trans*-3-methylcinnamic acid	H_2O (pH 1.6)	298	2.98	−17.0	−25.1	−8.4	uv	257
1β	*trans*-4-methylcinnamic acid	H_2O (pH 1.6)	298	2.64	−15.1	−49.8	−34.7	uv	257
1β	(±)-*cis*-2-methylcyclohexanol	H_2O (pH 6.9)	298	2.99 ± 0.01	−17.08 ± 0.06	−9.9 ± 0.2	7.2 ± 0.2	cal	9
1β	(±)-*trans*-2-methylcyclohexanol	H_2O (pH 6.9)	298	2.87 ± 0.01	−16.38 ± 0.04	−8.66 ± 0.09	7.72 ± 0.10	cal	9
1β	1-methylcyclohexanol	H_2O (pH 6.9)	298	3.06 ± 0.01	−17.47 ± 0.08	−9.6 ± 0.3	7.9 ± 0.3	cal	9
1β	3-methylcyclohexanol	H_2O (pH 6.9)	298	2.92 ± 0.01	−16.66 ± 0.05	−8.74 ± 0.09	7.93 ± 0.10	cal	9
1β	*cis*-4-methylcyclohexanol	H_2O (pH 6.9)	298	3.17 ± 0.01	−18.1 ± 0.1	−9.6 ± 0.1	8.5 ± 0.1	cal	10
1β	*cis*-4-methylcyclohexanol	H_2O (pH 6.9)	298	3.16 ± 0.01	−18.07 ± 0.05	−9.50 ± 0.10	8.55 ± 0.10	cal	9
1β	*trans*-4-methylcyclohexanol	H_2O (pH 6.9)	298	3.33 ± 0.01	−19.00 ± 0.07	−9.1 ± 0.2	9.9 ± 0.2	cal	9
1β	2-methylcyclohexanone	H_2O (pH 6.90)	298	2.74 ± 0.02	−15.7 ± 0.1	−13.7 ± 0.2	2.1 ± 0.3	cal	12
1β	3-*O*-methyldopamine	H_2O (pH 6.9)	298	1.03 ± 0.13	−5.9 ± 1.1	−5.7 ± 1.8	0.3 ± 2.1	cal	13

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1β	3-*O*-methyldopamine	H_2O (pH 5.0)	298	0.63 ± 0.15	−3.6 ± 1.3	−13.4 ± 5.5	−9.8 ± 5.7	cal	13
1β	4-*O*-methyldopamine	H_2O (pH 6.9)	298	1.781 ± 0.004	−10.71 ± 0.07	−13.41 ± 0.07	−3.2 ± 0.1	cal	13
1β	4-*O*-methyldopamine	H_2O (pH 5.0)	298	1.71 ± 0.01	−9.78 ± 0.07	−15.3 ± 0.3	−5.5 ± 0.3	cal	13
1β	(1-methylhexyl)ammonium	H_2O (pH 6.9)	298	1.88 ± 0.08	−10.7 ± 0.6	2.0 ± 0.2	12.7 ± 0.8	cal	9
1β	1-methylnaphthalene	H_2O	298	2.84	−16.2	−8.4	7.8	fl	140, 198
1β	(4-methylphenethyl)ammonium	H_2O (pH 6.9)	298	1.95 ± 0.01	−11.11 ± 0.09	−6.84 ± 0.14	4.3 ± 0.2	cal	13
1β	(4-methylphenethyl)ammonium	H_2O (pH 5.0)	298	1.87 ± 0.02	−10.7 ± 0.1	−7.23 ± 0.14	3.5 ± 0.2	cal	13
1β	*N*-methylphenethylammonium	H_2O (pH 6.9)	298	1.45 ± 0.04	−8.3 ± 0.3	−6.3 ± 0.5	2.0 ± 0.5	cal	13
1β	*N*-methylphenethylammonium	H_2O (pH 5.0)	298	1.33 ± 0.02	−7.59 ± 0.14	−7.3 ± 0.3	0.3 ± 0.3	cal	13
1β	4-methylphenol	H_2O (pH 4.2)	298	2.40 ± 0.02	−13.7 ± 0.1	−12.5 ± 0.2	1.2 ± 0.3	cal	39
1β	(3-methylphenyl)acetate	H_2O (pH 6.9)	298	1.08 ± 0.05	−6.1 ± 0.3	−11.5 ± 1.1	−5.4 ± 1.2	cal	9
1β	(4-methylphenyl)acetate	H_2O (pH 6.9)	298	1.61 ± 0.02	−9.17 ± 0.11	−12.1 ± 0.4	−2.9 ± 0.4	cal	9
1β	(2-methylpropyl)acetate	H_2O−EtOH (85:15; pH 4.3)	293	1.89	−10.5	−36.6	−26.0	gc	115
1β	5-methylresorcinol	H_2O	298	1.68	−9.8	−21.2	−11.2	cal	242
1β	5-methylresorcinol	H_2O	303	1.96	−11.4	−20.8	−9.5	cal	
1β	naphthalene	H_2O	298	2.83	−16.2	−11.4	4.7	fl	140, 198
1β	1-naphthaleneacetate	H_2O	298	4.35 ± 0.05	−24.8 ± 0.3	−4.6 ± 0.3	20.2	cal	14
1β	1-naphthalenecarboxamide	H_2O	298	2.63	−15.0	−79.1	−64.0	fl	140, 198
1β	2-naphthalenecarboxylate	H_2O (pH 8.6, 9 M urea)	298	3.60 ± 0.11	−20.5 ± 2.1	−1.7 ± 0.1	18.9 ± 2.2	cal	209
1β	2-naphthalenecarboxylate	H_2O (pH 8.6)	298	2.51 ± 0.03	−14.3 ± 0.2	−19.2 ± 0.8	−5.0 ± 1.0	cal	209
1β	1-naphthalenecarboxylic acid	H_2O (pH 1.5)	298	2.54	−14.5	−11.2	3.3	fl	140, 198
1β	2,6-naphthalenedisulfonate	H_2O	298	3.29 ± 0.05	−18.8 ± 0.03	−11.7 ± 0.3	7.1	cal	14
1β	2,7-naphthalenedisulfonate	H_2O	298	2.44 ± 0.02	−13.9 ± 0.1	−28.2 ± 0.3	−14.3	cal	14
1β	1-naphthalenesulfonate	H_2O	298	3.40 ± 0.06	−19.4 ± 0.3	−6.2 ± 0.2	13.2	cal	14
1β	2-naphthalenesulfonate	H_2O (pH 7.20)	298	5.37 ± 0.07	−30.7 ± 0.4	−29.3 ± 0.3	1.3	cal	14
1β	2-naphthalenesulfonate derivative **31**	H_2O (pH 7.0)	298	4.91 ± 0.02	−28.0	−18.5 ± 1.7	9.5	cal	54[j]
1β	2-naphthalenesulfonate derivative **31**	H_2O (pH 7.0)	298	3.37 ± 0.04	−19.2	−16.2 ± 0.1	3.0	cal	54[l]
1β	2,3,6-naphthalenetrisulfonate	H_2O	298	2.22 ± 0.03	−12.7 ± 0.2	−12.9 ± 0.6	−0.3	cal	14
1β	2-naphthoate	H_2O	298	2.57 ± 0.04	−14.6 ± 0.2	−25.5 ± 0.8	−11.0 ± 0.6	cd	98
1β	1-naphthol	H_2O	298	3.09	−17.6	−11.3	6.3	fl	140, 198
1β	1-naphthol	H_2O-MeOH (1:1)	298		−3.6	−0.5	3.1	lc	117
1β	2-naphthol	H_2O	298	2.70 ± 0.04	−15.4 ± 0.3	−26.8 ± 0.9	−11.3 ± 0.9	cd	98
1β	2-naphthol	H_2O-MeOH (1:1)	298		−3.6	−0.3	3.3	lc	117
1β	1-naphthyl acetate	H_2O	298	2.19	−12.5	−14.7	−2.2	fl	140, 198
1β	2-naphthyl acetate	H_2O	298	2.51 ± 0.03	−14.3 ± 0.2	−23.0 ± 0.6	−8.6 ± 0.6	cd	98
1β	1-naphthylaldehyde	H_2O	298	2.60	−14.8	−42.5	−27.7	fl	140, 198
1β	(2-naphthyloxy)acetic acid	H_2O	298	2.57 ± 0.02	−14.6 ± 0.1	−22.2 ± 0.5	−7.2 ± 0.6	cd	98
1β	naproxen	H_2O (pH 2.0)	298	3.17	−18.1	−12.8	5.1	sol	48
1β	naproxenate	H_2O (pH 9.0)	298	2.83	−16.1	−26.2	−10.1	pot	124
1β	niflumic acid	H_2O (pH 7.0)	298	2.72	−15.5	−19.0	−3.5	cal	263, *d*
1β	3-nitroaniline	H_2O	298		−9.1	−11.1 ± 0.6	−2.0 ± 1.7	cd	194
1β	4-nitroaniline	H_2O	298		−14.3	−19.6 ± 0.3	−5.4 ± 1.3	cd	194
1β	2-nitrophenol	H_2O (pH 3.57)	298		−8.1	−17.6	−9.5	lc	80
1β	3-nitrophenol	H_2O	298	2.44 ± 0.04	−13.9 ± 0.2	−12.1 ± 0.5	1.8 ± 0.6	cal	39
1β	3-nitrophenol	H_2O	298		−11.4	−17.2 ± 0.3	−5.9 ± 0.8	cd	194
1β	3-nitrophenol	H_2O (pH 3.57)	298		−8.7	−21.3	−12.6	lc	80
1β	4-nitrophenol	H_2O	298	3.0 ± 1.7	−17 ± 10	−44 ± 10	−26	cal	192
1β	4-nitrophenol	H_2O	298	2.54 ± 0.06	−14.5 ± 0.4	−12.0 ± 0.6	2.4 ± 0.6	cal	39
1β	4-nitrophenol	H_2O	298		−14.2	−10.2	3.9	cal	188
1β	4-nitrophenol	H_2O (pH 4.3)	298	2.48	−14.1	−14.6	−0.4	uv	118
1β	4-nitrophenol	H_2O (pH 4.2)	298	2.41 ± 0.05	−13.8 ± 0.3	−13.4 ± 0.6	0.3 ± 0.6	cal	39
1β	4-nitrophenol	H_2O	298	2.28	−13.0	−15.9 ± 0.6	−3.0 ± 0.5	cd	210
1β	4-nitrophenol	H_2O (pH 3.57)	298		−10.0	−21.8	−11.8	lc	80
1β	3-nitrophenolate	H_2O (pH 11.1)	298	2.07 ± 0.07	−11.8 ± 0.4	−6.7 ± 0.6	5.1 ± 0.6	cal	39
1β	4-nitrophenolate	H_2O (pH 9.5)	298		−14.6	−16.7	−2.1	cal	21
1β	4-nitrophenolate	H_2O (pH 9.0)	298	3.25	−18.5	−32.3	−14.0	pot	124
1β	4-nitrophenolate	H_2O (pH 10)	298	2.97	−17.0	−10	7	uv	118
1β	4-nitrophenolate	H_2O (pH 11)	298	2.80	−16.0 ± 0.1	−15.9 ± 0.3	0.1 ± 0.2	uv	211
1β	4-nitrophenolate	H_2O (pH 11.0)	298		−15.7	−14.2	1.5	cal/uv	269
1β	4-nitrophenolate	H_2O (pH 11.1)	298	2.76 ± 0.02	−15.7 ± 0.1	−15.5 ± 0.2	0.3 ± 0.3	cal	39
1β	4-nitrophenolate	H_2O	298		−15.0	−16.1	−1.1	cal	188
1β	4-nitrophenyl-β-D-galactoside	H_2O	298	1.77	−10.1	−16.9 ± 0.3	−6.7 ± 0.2	cd	210
1β	4-nitrophenyl-β-D-glucosamide	H_2O	298	1.90	−10.8	−18.5 ± 0.3	−7.7 ± 0.2	cd	210
1β	4-nitrophenyl-β-D-glucoside	H_2O	298	1.57	−8.8	−15.4 ± 0.4	−6.4 ± 0.4	cd	210
1β	4-nitrophenyl-β-D-xyloside	H_2O	298	1.78	−10.1	−17.3 ± 0.5	−7.1 ± 0.5	cd	210
1β	*d*-nitroxide **32a**	DMSO−H_2O (1:1)	298	1.32	−7.5	−36 ± 6	−28 ± 4	esr	113
1β	*l*-nitroxide **32b**	DMSO−H_2O (1:1)	298	0.95	−5.4	−21 ± 4	−14 ± 4	esr	113
1β	1,9-nonanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	2.98 ± 0.13	−17.0	−25	−8	uv	245
1β	3-noradamantanecarboxylate	H_2O (pH 8.5)	298	3.70	−21.1	−15.7 ± 1.1	5.4	cal	81
1β	2-norbornaneacetate	H_2O (pH 8.6)	298	3.65 ± 0.04	−20.8 ± 0.3	−10.7 ± 0.2	10.2 ± 0.4	cal	209

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1β	2-norbornaneacetate	H_2O (pH 8.6, 8 M urea)	298	3.27 ± 0.07	−18.7 ± 0.4	−18.0 ± 0.8	0.8 ± 1.3	cal	209
1β	norbornaneacetate	H_2O (pH 8.5)	298	3.79	−21.6	−8.2 ± 0.4	13.3	cal	81
1β	(±)-norphenylephrine	H_2O (pH 6.9)	298	1.59 ± 0.01	−9.06 ± 0.04	−18.2 ± 0.2	−9.1 ± 0.2	cal	13
1β	(±)-norphenylephrine	H_2O (pH 5.0)	298	1.51 ± 0.01	−8.65 ± 0.05	−20.7 ± 0.3	−12.0 ± 0.3	cal	13
1β	nortriptylin	H_2O	298	4.43	−25.3	−33 ± 3	−9 ± 3	pot	123
1β	1,8-octanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	2.61 ± 0.02	−14.9	−23	−8	uv	245
1β	octanoate	H_2O	298	3.10	−17.7	−12 ± 3	6 ± 3	pot	71
1β	octanoic acid	H_2O	298	2.75	−15.7	−5 ± 4	10 ± 4	pot	71
1β	(±)-octopamine	H_2O (pH 6.9)	298	1.72 ± 0.01	−9.83 ± 0.03	−13.68 ± 0.14	−3.8 ± 0.1	cal	13
1β	(±)-octopamine	H_2O (pH 5.0)	298	1.65 ± 0.01	−9.4 ± 0.04	−15.86 ± 0.17	−6.5 ± 0.2	cal	13
1β	octylammonium	H_2O (pH 6.9)	298	2.62 ± 0.12	−15.0 ± 1.0	−2.0 ± 0.3	13.0 ± 1.0	cal	9
1β	orphenadrine·HCl	H_2O	298	3.11 ± 0.03	−17.7	−31.3 ± 0.8	−13.5	cal	74
1β	1,5-pentanediol	H_2O (0.1 M H_2SO_4 + 0.5 M Na_2SO_4)	298	1.06 ± 0.07	−6.0	−15	−9	uv	245
1β	pentanoate	H_2O (pH 6.9)	298	0.92 ± 0.22	−5.3 ± 2.7	8 ± 4	13 ± 5	cal	9
1β	pentanoic acid	H_2O	298	1.956 ± 0.010	−11.16 ± 0.12	−15.1 ± 1.3	−4.0 ± 1.3	pot	71
1β	(*R*)-(−)-2-pentanol	H_2O (pH 6.90)	298	1.52 ± 0.13	−8.7 ± 1.1	3.7 ± 1.0	12.5 ± 1.5	cal	32
1β	(*S*)-(+)-2-pentanol	H_2O (pH 6.90)	298	1.51 ± 0.13	−8.6 ± 1.0	4.1 ± 1.1	12.8 ± 1.5	cal	32
1β	1-pentanol	H_2O	298	1.80	−10.3	4.6	14.9	uv	11
1β	1-pentanol	H_2O	298	3.964	−22.6	2.2	24.8	cal	89, 283, 270[b]
1β	pentobarbital	H_2O (pH 5.0)	298	3.02	−17.2	−20.3	−3.0	uv	179
1β	pentobarbital	H_2O (pH 5.0)	298	3.16	−18.0	−23.2	−5.2	cal	52
1β	pentylbarbituric acid	H_2O (pH 5.0)	298	3.08	−17.6	−21.0	−3.6	uv	179
1β	pentylthiobarbituric acid	H_2O (pH 5.0)	298	3.38	−19.2	−23.6	−6.7	uv	179
1β	perchlorate	H_2O (0.2 M NaCl)	298	1.08 ± 0.03	−6.3 ± 0.2	−16.5 ± 0.6	−10.3 ± 0.6	cal	254
1β	phenethylammonium	H_2O (pH 6.9)	298	1.38 ± 0.03	−7.9 ± 0.2	−6.4 ± 0.4	1.5 ± 0.4	cal	10, 13
1β	phenethylammonium	H_2O (pH 5.0)	298	1.30 ± 0.04	−7.43 ± 0.25	−6.9 ± 0.5	0.6 ± 0.6	cal	13
1β	pheniramine maleate	H_2O (pH 7.0)	298	2.49	−14.2	−14.6	−0.4	cal	263[d]
1β	phenobarbital	H_2O (pH 5.0)	298	3.22	−18.4	−43.1	−24.8	uv	179
1β	phenobarbital	H_2O (pH 5.0)	298	3.20	−18.3	−31.2	−12.9	cal	52
1β	phenobarbital (anion)	H_2O	298	2.28	−13.0	−27.6	−15.1	pot	50
1β	phenol	H_2O	298	3.4 ± 1.0	−19 ± 6	−11 ± 1	9	cal	192
1β	phenol	H_2O (pH 4.2)	298	1.97 ± 0.01	−11.3 ± 0.1	−12.2 ± 0.2	−1.2 ± 0.3	cal	39
1β	phenolphthalein	H_2O (pH 9.94)	298		−26.8	−45.2 ± 0.8	−18.4 ± 0.9	uv	206
1β	phenolphthalein	H_2O (pH 10.5)	298		−6.1	−58.2	−52.09	uv	282
1β	phenprocoumon	H_2O (pH 7.4)	298	2.83 ± 0.04	−16.2	−13.6 ± 0.6	2.6 ± 0.3	cal	273
1β	phenylacetate	H_2O (pH 6.9)	298	1.24 ± 0.06	−7.1 ± 0.4	−7.5 ± 0.9	−0.4 ± 1.0	cal	9
1β	L-phenylalanine	H_2O (pH 11.3)	298	2.03 ± 0.05	−11.6 ± 0.3	−5.2 ± 0.3	6.4 ± 0.6	cal	35
1β	L-phenylalanine	H_2O	298	1.26 ± 0.07	−7.2 ± 0.4	−9.0 ± 1.0	−1.8 ± 1.4	cal	35
1β	L-phenylalanine	H_2O (pH 5.01)	298	0.48 ± 0.52	−3 ± 3	−12 ± 22	−9 ± 22.4	cal	32
1β	L-phenylalanineamide	H_2O (pH 10.02)	298	2.03 ± 0.01	−11.6 ± 0.1	−11.9 ± 0.2	−0.3 ± 0.2	cal	32
1β	L-phenylalanineamide	H_2O (pH 5.01)	298	1.34 ± 0.04	−7.7 ± 0.3	−9 ± 0.5	−1.3 ± 0.6	cal	32
1β	*N*-phenylanthranilic acid	H_2O (pH 7.0)	298	2.90	−16.5	−8.7	7.8	cd	230
1β	3-phenylbutanoate	H_2O (pH 6.9)	298	2.588 ± 0.007	−14.76 ± 0.04	−9.2 ± 0.1	5.6 ± 0.1	cal	10
1β	3-phenylbutanoate	H_2O (pH 6.9)	298	2.58 ± 0.01	−14.72 ± 0.06	−9.41 ± 0.1	5.3 ± 0.1	cal	9
1β	4-phenylbutanoate	H_2O (pH 6.9)	298	2.64 ± 0.03	−15.06 ± 0.15	−11.78 ± 0.12	3.3 ± 0.2	cal	9
1β	(*R*)-(−)-phenylephrine	H_2O (pH 6.9)	298	1.668 ± 0.005	−9.52 ± 0.03	−19.44 ± 0.13	−9.9 ± 0.1	cal	13
1β	(*R*)-(−)-phenylephrine	H_2O (pH 5.0)	298	1.594 ± 0.004	−9.1 ± 0.03	−21.9 ± 0.22	−12.8 ± 0.2	cal	13
1β	1-phenylimidazole	H_2O (pH 10.0)	298	1.40 ± 0.19	−8 ± 2	−39 ± 19	−31 ± 19	cal	13
1β	3-phenylpropionate	H_2O (pH 6.9)	298	2.173 ± 0.012	−12.4 ± 0.07	−7.3 ± 0.1	5.1 ± 0.1	cal	10
1β	3-phenylpropionate	H_2O (pH 6.9)	298	2.15 ± 0.01	−12.27 ± 0.06	−7.6 ± 0.1	4.7 ± 0.1	cal	13
1β	(3-phenylpropyl)ammonium	H_2O (pH 6.9)	298	2.03 ± 0.01	−11.61 ± 0.07	−9.2 ± 0.1	2.4 ± 0.1	cal	13
1β	(3-phenylpropyl)ammonium	H_2O (pH 5.0)	298	1.98 ± 0.01	−11.29 ± 0.08	−9.44 ± 0.15	1.8 ± 0.2	cal	13
1β	phenytoin	H_2O (pH 5)	293	2.928	−16.43	−38.1	−19.6	sol	284
1β	phenytoin	H_2O (pH 5.0)	298		−27.6	−40.7 ± 0.4	−13.1 ± 0.4	sol	82
1β	phenytoin (anion)	H_2O (pH 10.0)	293		−10.8	−23	−12	sol	284
1β	phenytoin (anion)	H_2O (pH 10.0)	298		−22	−38 ± 5	−16 ± 5	sol	82
1β	piroxicam	H_2O (pH 7.0)	298	1.97	−11.2	−10.5	0.7	cal	263, *d*
1β	proadifen·HCl	H_2O	298	2.96 ± 0.02	−16.9	−29.5 ± 1.2	−12.6	cal	74
1β	procaine·HCl	H_2O	298	2.52 ± 0.07	−14.4 ± 0.4	−14.2	0.1	pot	279, *d*
1β	1-propanol	H_2O (pH 6.90)	298	0.65 ± 0.14	−3.7 ± 1.2	6.0 ± 2.0	9.8 ± 2.4	cal	32
1β	1-propanol	H_2O	298	3.059	−17.5	1.9	19.4	cal	89, 283, 270[b]
1β	2-propanol	H_2O (pH 6.90)	298	0.41 ± 0.08	−2.4 ± 0.5	11.1 ± 1.8	13.4 ± 1.8	cal	32
1β	2-propanol	H_2O	298		−19.7	1.2	20.9	cal	89[b]
1β	propanolol	H_2O	298	2.14 ± 0.02	−12.7	−25.3	−12.4	pot	36
1β	propylbarbituric acid	H_2O (pH 5.0)	298	2.26	−12.8	−11.6	1.3	uv	179
1β	propylthiobarbituric acid	H_2O (pH 5.0)	298	2.48	−14.1	−16.4	−2.2	uv	179
1β	prostaglandin E2	H_2O	298	3.27	−18.7	−19.3	−0.6	cal	52
1β	protriptylin	H_2O	298	4.26	−24.3	−29.1 ± 0.8	−4.9 ± 0.8	pot	123
1β	(1*R*,2*R*)-(−)-pseudoephedrine	H_2O (pH 6.9)	298	1.84 ± 0.01	−10.49 ± 0.03	−9.99 ± 0.10	0.5 ± 0.1	cal	13
1β	(1*S*,2*S*)-(+)-pseudoephedrine	H_2O (pH 6.9)	298	1.985 ± 0.004	−11.33 ± 0.03	−12.54 ± 0.13	−1.2 ± 0.1	cal	13
1β	(1*S*,2*S*)-(+)-pseudoephedrine	H_2O (pH 5.0)	298	1.893 ± 0.004	−10.8 ± 0.03	−12.23 ± 0.13	−1.4 ± 0.1	cal	13
1β	pyrene	H_2O	298	2.69	−15.4	−29.3	−13.9	lc	241

Table 1 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1β	pyrene	H_2O−*t*-BuOH (9:1)	298		−23	−34	−11	fl*	104[d]
1β	pyrene	H_2O (0.02 M Na hexanesulfate)	298		−17.1	−50.2	−33.1	fl*	105
1β	pyrene	H_2O	298		−9.1	−28.4	−19.3	fl*	105
1β	pyrilamine maleate	H_2O (pH 7.0)	298	2.86	−16.3	−15.3	1.0	cal	263[d]
1β	resorcinol	H_2O	303	2.00	−11.6	−18.2	−6.5	cal	242
1β	(*E*)-stilbene derivative (*E*)-**30**	H2O	298	2.85 ± 0.01	−16.3	−11.3 ± 0.4	5.0	cal	78
1β	(*Z*)-stilbene derivative (*Z*)-**30**	H2O	298	2.73 ± 0.13	−15.5	−41 ± 35	−25	cal	78
1β	(−)-scopolamine·HBr	H_2O (pH 5.8)	298	2.27 ± 0.01	−12.9	−17.9 ± 0.2	−5.0	cal	275
1β	secobarbital	H_2O (pH 5.0)	298	3.26	−18.6	−25.4	−6.7	cal	52
1β	sulfadiazine	H_2O	298	2.75	−15.70	−24.0 ± 1.0	−8.3	cal	53
1β	sulfadimethoxine	H_2O	298	2.79	−15.92	−19.1 ± 1.0	−3.2	cal	53
1β	sulfadimethoxine	H_2O	298	−12.5	−18.0	−5.5	sol	51	
1β	sulfaethidole	H_2O (pH 7.0)	298	3.16	−18.0	−14.6	3.5	cal	52
1β	sulfaguanidine	H_2O	298		−14.6	−46.0	−31.4	sol	51
1β	sulfamerazine	H_2O	298	2.53	−14.44	−16.5 ± 0.4	−2.1	cal	53
1β	sulfamerazine	H_2O	298		−11.8	−29.3	−17.3	sol	51
1β	sulfamethazine	H_2O	298		−11.8	−27.6	−15.7	sol	51
1β	sulfamethizole	H_2O	298	3.10	−17.7	−27.6 ± 0.9	−9.9	cal	53
1β	sulfamethizole	H_2O	298		−16.8	−27.2	−10.5	sol	51
1β	sulfamethoxazole	H_2O	298	2.77	−15.81	−22.5 ± 0.3	−6.7	cal	53
1β	sulfamonomethoxine	H_2O	298		−14.5	−31.0	−16.5	sol	51
1β	sulfapyridine	H_2O	298	2.83	−16.15	−19.3 ± 0.7	−3.2	cal	53
1β	sulfasnilamide	H_2O	298		−11.4	−39.3	−27.9	sol	51
1β	sulfathiazole	H_2O	298	3.37	−19.24	−29.8 ± 0.6	−10.5	cal	53
1β	sulfathidole	H_2O (pH 7.0)	298	3.18	−18.1	−35.4	−17.3	cal	52
1β	sulfisomidine	H_2O	298		−11.7	−13.8	−2.0	sol	51
1β	sulfisoxazole	H_2O	298	2.79	−15.95	−28.0 ± 1.0	−12.0	cal	53
1β	sulfisoxazole	H_2O	298		−15.6	−18.4	−2.9	sol	51
1β	sulfoisomidine	H_2O	298	2.25	−12.84	−15.6 ± 0.6	−2.8	cal	53
1β	sulfapyridine	H_2O (pH 7.0)	298	2.66	−15.2	−33.9	−18.7	cal	263[d]
1β	terfenadine·HCl	H_2O	298	4.27 ± 0.04	−24.4	−20.0 ± 0.3	4.4	cal	74
1β	tetracaine·HCl	H_2O	298	3.04 ± 0.02	−17.3 ± 0.1	−14.1	3.2	pot	279[d]
1β	thenyldiamine	H_2O (pH 7.0)	298	2.31	−13.2	−14.8	−1.6	cal	263[d]
1β	thiopental	H_2O (pH 5.0)	298	3.43	−19.6	−25.7	−6.3	uv	179
1β	thiophenobarbital	H_2O (pH 5.0)	298	3.60	−20.5	−34.4	−14.0	uv	179
1β	6-(*p*-toluidinyl)-2-naphthalenesufonate	H_2O	298	3.10 ± 0.01	−17.7 ± 0.1	−3 ± 1	25 ± 2	con	76[j]
1β	6-(*p*-toluidinyl)-2-naphthalenesulfonate	H_2O (pH 1.95)	298	3.45	−19.7	−6.3	13.3	fl	240
1β	6-(*p*-toluidinyl)-2-naphthalenesulfonate	H_2O (pH 5.2)	298		−13.4	−8.8	4.6	fl	138
1β	6-(*p*-toluidinyl)-2-naphthalenesulfonate	H_2O	298	3.20	−18.3	−3 ± 1	15	con	76[d]
1β	trifluoromethanesulfonate	H_2O (0.2 M NaCl)	298	1.76 ± 0.01	−10.0 ± 0.1	−20.2 ± 0.8	−10.2 ± 0.8	cal	254
1β	triiodide (I_3^-)	H_2O (pH 11.0)	298		−19.1	−23.9	−4.7	cal/uv	269
1β	α-(2,4,6-trimethoxyphenyl)benzyl *tert*-butyl nitroxide	H_2O (2 M KCl)	293	2.93	−16.3	−25.1	−8.8	esr	85[e]
1β	α-(2,4,6-trimethoxyphenyl)benzyl *tert*-butyl nitroxide	H_2O	293	2.72	−15.1	−19.2	−3.8	esr	85[e]
1β	3,4,5-trimethylphenyl acetate	H_2O (pH 10.0)	298	2.32 ± 0.06	−13 ± 4	−10 ± 4	2 ± 4	kin	212
1β	triprolidine·HCl	H_2O (pH 7.0)	298	2.42	−13.8	−13.8	0.0	cal	263[d]
1β	tropicamide	H_2O (pH 7.0)	298	2.63	−15.0	−25.0	−10.0	cal	263[d]
1β	D-tryptophan	H_2O (pH 8.9)	298	1.11 ± 0.21	−6.3 ± 1.3	1± 5	8 ± 6	fl	139
1β	L-tryptophan	H_2O (pH 7.4)	298	2.33	−13.3	−0.8	12.5	cal	271[d]
1β	Tyr-Gly-Gly-Phe-Leu	H_2O (pH 7.0)	298		−11.4	−36 ± 4	−25 ± 7	fl	36[d]
1β	Tyr-Ile-Gly-Ser-Arg	H_2O (pH 7.0)	298		−13.2	−15 ± 2	−2 ± 1	fl	36[d]
1β	L-tyrosine	H_2O (pH 11.3)	298	2.17 ± 0.02	−12.04 ± 0.1	−6.7 ± 0.2	5.7 ± 0.3	cal	35
1β	L-tyrosine	H_2O (pH 7.4)	298	1.52	−8.7	−3.8	4.9	cal	271[d]
1β	δ-valerolactam	H_2O (pH 6.90)	298	1.40 ± 0.06	−8.0 ± 0.5	−3.7 ± 0.4	4.2 ± 0.6	cal	12
1β	valethamate bromide	H_2O	298	4.20 ± 0.01	−24.0 ± 0.1	−34.6	−10.5	pot	279[d]
1β	warfarin	H_2O (pH 7.4)	298	2.86 ± 0.04	−16.3	−11.6 ± 0.5	4.8 ± 0.6	cal	273
1β	D-xylose	H_2O	298	1.22	−7.0 ± 0.6	−0.62 ± 0.06	6.3 ± 0.3	cal	37
1β	DL-xylose	H_2O	298	1.06	−6.1 ± 0.4	−1.12 ± 0.18	4.9 ± 0.4	cal	37
1β	L-xylose	H_2O	298	1.32	−7.5 ± 0.7	−0.87 ± 0.12	6.6 ± 0.7	cal	37
1γ	1-adamantaneacetate	H_2O (pH 9.94)	298		−17.4	7.5 ± 0.8	24.9 ± 1.0	uv	206
1γ	1-adamantanecarboxylate	H_2O (pH 8.50)	298		−20.1 ± 0.2	5.0 ± 0.2	25.2 ± 0.4	cal	237
1γ	1-adamantanecarboxylate	H_2O (pH 9.94)	298		−13.9	8.8 ± 1.3	22.7 ± 1.3	uv	206
1γ	adiphenine·HCl	H_2O	298	2.61 ± 0.01	−14.9	−5.10 ± 0.04	9.8	cal	74
1γ	4-amino-1-naphthalenesulfonate	H_2O	298	1.31 ± 0.08	−7.5 ± 0.5	−28.0 ± 0.5	−20.5	cal	14
1γ	anthracene	H_2O	298	2.35	−13.4	−23.0	−9.6	lc	241
1γ	benz[*a*]anthracene	H_2O	298	2.78	−15.9	−17.2	−1.3	lc	241
1γ	benzene	H_2O	298	0.96 ± 0.01	−5.47 ± 0.03	14.2 ± 0.8	19.7	vap	29
1γ	benzoic acid	H_2O	303	2.10	−12.1 ± 0.2	−4.5 ± 0.2	7.6 ± 0.6	cal	73
1γ	bromodiphenhydramine·HCl	H_2O	298	3.39 ± 0.01	−19.3	−10.0 ± 0.1	9.3	cal	74
1γ	[10-(4-bromonaphthoyl)decyl]trimethyl-ammonium bromide	H_2O	298		−24.3	−37.7	−13.7	ph*	86[e]
1γ	chlorcyclizine·2HCl	H_2O	298	3.04 ± 0.01	−17.4	−7.2 ± 0.1	10.2	cal	74
1γ	chlorcyclizine·HCl	H_2O	298	3.11 ± 0.02	−17.8	−8.2 ± 0.1	9.6	cal	74

Table 1 (Continued)

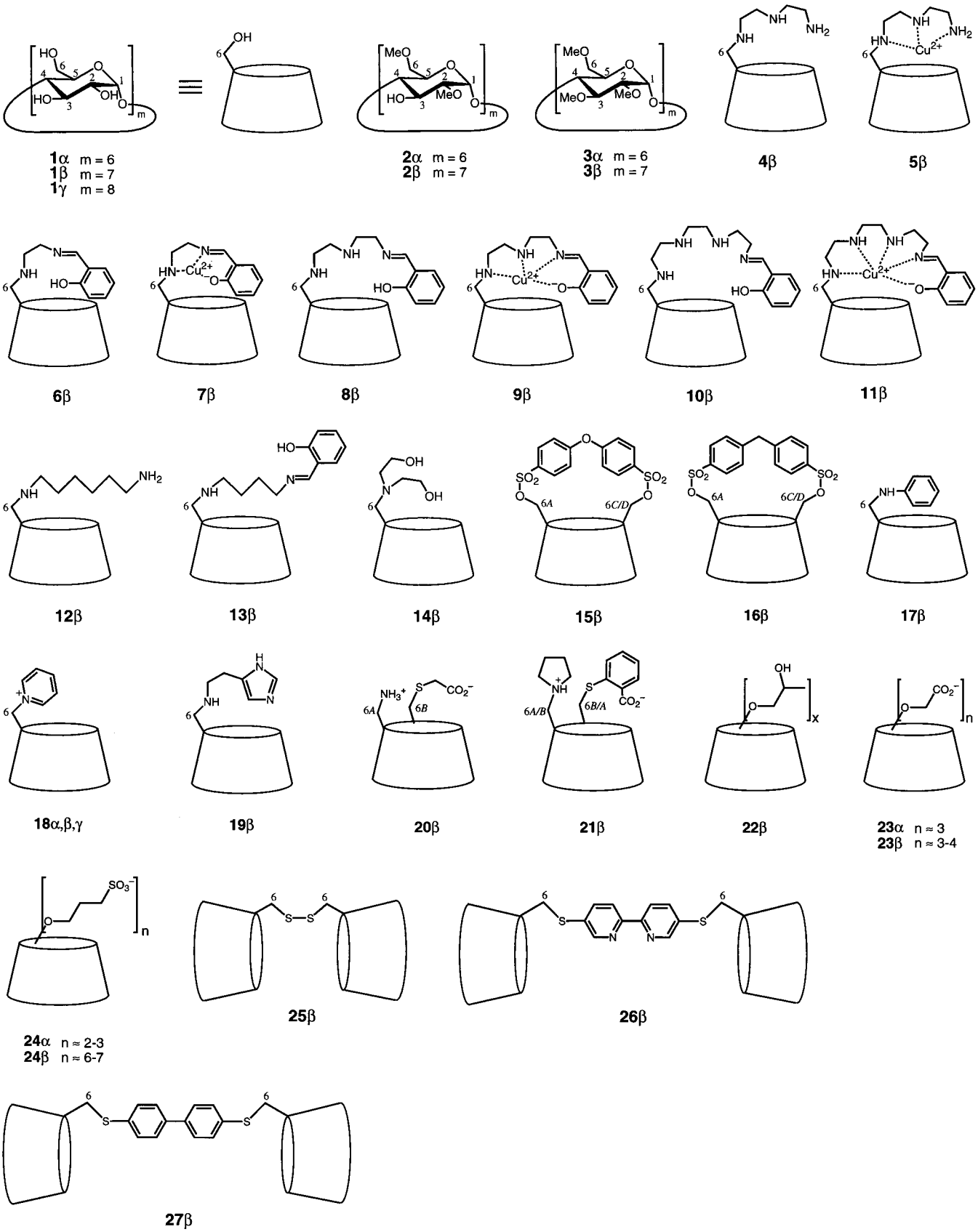
host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
1γ	2-chloro-4-[(4-hydroxyphenyl)azo]benzoate	H_2O	298	4.30 ± 0.17	−24.55	−28.0 ± 0.8	−3.5	cal	43
1γ	2-chloro-4-[(4-hydroxyphenyl)azo]benzoate	DMF	298	3.63 ± 0.07	−20.72	−14.8 ± 0.5	5.9	cal	43
1γ	4-chloro-3-[(4-hydroxyphenyl)azo]benzoate	H_2O	298	4.16 ± 0.02	−23.75	−34.8 ± 1.2	−11.1	cal	43
1γ	4-chloro-3-[(4-hydroxyphenyl)azo]benzoate	DMF	298	3.88 ± 0.02	−22.15	−18.7 ± 0.5	3.4	cal	43
1γ	cinnarizine·2HCl	H_2O	298	1.89 ± 0.01	−10.8	−20.3 ± 0.3	−9.5	cal	74
1γ	cyclizine·HCl	H_2O	298	2.86 ± 0.01	−16.4	−4.11 ± 0.03	12.3	cal	74
1γ	diphenidol·HCl	H_2O	298	2.57 ± 0.01	−14.7	−2.39 ± 0.03	12.3	cal	74
1γ	diphenylpyraline·HCl	H_2O	298	2.89 ± 0.01	−16.5	−2.84 ± 0.02	13.7	cal	74
1γ	estradiol	H_2O−MeOH (55:45)	298		−17.2	−26.4	−9.2	lc	281
1γ	estradiol	H_2O−CH_3CN (70:30)	298		−15.1	−17.6	−2.5	lc	281
1γ	estriol	H_2O−MeOH (55:45)	298		−16.0	−26.8	−10.8	lc	281
1γ	estriol	H_2O−CH_3CN (70:30)	298		−14.4	−18.8	−4.4	lc	281
1γ	estrone	H_2O−MeOH (55:45)	298		−15.0	−27.2	−12.2	lc	281
1γ	estrone	H_2O−CH_3CN (70:30)	298		−13.4	−17.6	−4.2	lc	281
1γ	ethinyloestradiol	H_2O−MeOH (55:45)	298		−17.8	−31.0	−13.2	lc	281
1γ	ethinyloestradiol	H_2O−CH_3CN (70:30)	298		−15.2	−17.6	−2.4	lc	281
1γ	ethyl decanoate	H_2O−EtOH (85:15; pH 4.3)	293	1.39	−7.7	−16.3	−8.5	gc	115
1γ	flurbiprofen	H_2O (pH 7.0)	298	3.48	−19.9	−10.1	9.8	cal	253[d]
1γ	2-[(4-hydroxyphenyl)azo]benzoate	DMF	298	3.28 ± 0.06	−18.72	−10.2 ± 0.7	8.5	cal	43
1γ	3-[(4-hydroxyphenyl)azo]benzoate	H_2O	298	3.94 ± 0.05	−22.49	−25.2 ± 0.3	−2.7	cal	43
1γ	3-[(4-hydroxyphenyl)azo]benzoate	DMF	298	4.04 ± 0.01	−23.06	−22.1 ± 0.2	1.0	cal	43
1γ	4-[(4-hydroxyphenyl)azo]benzoate	H_2O	298	4.13 ± 0.09	−23.57	−20.4 ± 0.1	3.1	cal	43, 259
1γ	4-([(4-hydroxyphenyl)azo]benzoate	DMF	298	4.15 ± 0.05	−23.69	−15.6 ± 2.2	8.1	cal	43, 259
1γ	hydroxyzine·2HCl	H_2O	298	3.12 ± 0.03	−17.8	−6.7 ± 0.3	11.1	cal	74
1γ	hydroxyzine·HCl	H_2O	298	3.08 ± 0.02	−17.6	−8.7 ± 1.2	8.8	cal	74
1γ	meclizine·2HCl	H_2O	298	2.93 ± 0.01	−16.7	−9.4 ± 0.2	7.3	cal	74
1γ	methyl orange (anion)	H_2O (pH 7.5)	298		−41.4	−50.2	−10.1	uv	265
1γ	3-methyl-1-butanol	H_2O−EtOH (85:15; pH 4.3)	293	1.33	−7.4	−25.5	−18.0	gc	115
1γ	3-methylbutyl acetate	H_2O−EtOH (85:15; pH 4.3)	293	1.47	−8.2	−21.8	−13.5	gc	115
1γ	2-methylpropyl acetate	H_2O−EtOH (85:15; pH 4.3)	293	1.00	−5.6	−37.4	−31.8	gc	115
1γ	5-methylresorcinol	H_2O	303	0.73	−4.3	−28.2	−23.9	cal	242
1γ	2,7-naphthalenedisulfonate	H_2O	298	2.58 ± 0.02	−14.7 ± 0.1	−3.6 ± 0.1	11.1	cal	14
1γ	2-naphthalenesulfonate	H_2O	298	1.58 ± 0.03	−6.6 ± 0.1	−17.5 ± 0.3	−10.9	cal	14
1γ	niflumic acid	H_2O (pH 7.0)	298	2.44	−13.9	−6.4	7.5	cal	263[d]
1γ	4-nitrophenol	H_2O (pH 4.3)	298	1.79	−10.2	−43.6	−33.4	uv	118
1γ	4-nitrophenolate	H_2O (pH 10)	298	2.08	−11.8	−21.8	−10.0	uv	118
1γ	orphenadrine·HCl	H_2O	298	2.98 ± 0.05	−17.0	−2.9 ± 0.1	14.1	cal	74
1γ	phenolphthalein	H_2O (pH 9.94)	298		−20.1	−29.3 ± 1.3	−9.2 ± 1.3	uv	206
1γ	piroxicam	H_2O (pH 7.0)	298	1.72	−9.8	−14.3	−4.5	cal	263[d]
1γ	proadifen·HCl	H_2O	298	3.05 ± 0.02	−17.4	−14.5 ± 0.4	3.0	cal	74
1γ	pyrene	H_2O	298	3.05	−17.4	−42.7	−25.3	lc	241
1γ	pyrene	H_2O−*t*-BuOH (9:1)	298		−19	−53	−34	fl*	104[d]
1γ	4-(1-pyrenyl)butanoate	H_2O (0.5 M NaOH)	298	3.11	−17.7	−18.4	−0.5	fl*	103
1γ	resorcinol	H_2O	298	1.33	−7.7	−4.7	3.0	cal	242
1γ	(*E*)-stilbene derivative (*E*)-**30**	H2O	298	2.59 ± 0.01	−14.6	−4.6 ± 1.3	10.0	cal	78
1γ	*cis*-1,2,3,4-tetraphenylcyclobutane derivative *cis*-**33**	H2O	298	2.72 ± 0.35	−15.5	23 ± 46	38	cal	78
1γ	*trans*-1,2,3,4-tetraphenylcyclobutane derivative *trans*-**33**	H2O	298	4.26 ± 0.13	−24.3	−29.7	−5.4	cal	78
1γ	α-(2,4,6-trimethoxyphenyl)benzyl *tert*-butyl nitroxide	H_2O (2 M KCl)	293	2.93	−16.3	−29.3	−13.0	esr	85[e]
1γ	α-(2,4,6-trimethoxyphenyl)benzyl *tert*-butyl nitroxide	H_2O	293	2.30	−13.0	−21.3	−8.4	esr	85[e]

[a] Method employed: cal, calorimetry; con, conductometry; fl, fluorimetry; fl*, fluorescence lifetime measurement; gc, gas chromatography; kin, kinetics (competitive rate constant determination or stopped flow); lc, high-performance liquid chromatography; ph, phosphorometry; ph*, phosphorescence lifetime measurement; pot, potentiometry; sol, solubility measurement; sur, surface tension measurement; uv, spectrophotometry; vap, vapor pressure measurement. [b] Controversial data which seriously deviate from the relevant data. [c] Poor correlation in the van't Hoff plot; less reliable data. [d] $\Delta G°$, $\Delta H°$, and/or $\Delta S°$ were recalculated from the data presented in the original paper. [e] There are thermodynamic data reported for metastable complex(es), but the data for the most stable complex are cited. [f] No correction for protonation of amine in unbuffered aqueous solution was made. [g] At this pD, cyclodextrin is partially ionized. [h] Data for octanoate to dodecanoate were also reported but not cited here because of sudden decreases in K; probably micelle formation occurs at the concetrations emplyed. [i] Precision limit given; accuracy, however, is on the order of ±3 units because of possible systematic errors in the calculations at values of log $K > 5$. [j] $\Delta G° \neq \Delta H° - T\Delta S°$ (|error| > 4 kJ/mol). [k] Binding by the first host molecule. [l] Binding by the second host molecule. [m] Precision limit given; accuracy, however, is on the order of ±2 units because of possible systematic errors in the calculations at values of log $K > 5$.

creases with increasing ionic strength or concentration of the salt in aqueous solution.

One can find analogous tendencies in the effects of organic solvents upon $\Delta G°$; for example, the complexation of aliphatic amines with α-cyclodextrin in *N*,*N*-dimethylformamide (DMF) gives less negative $\Delta G°$ values than those obtained in water.[168] However, the interactions of aromatic guests with cyclo-

Chart 1. Natural and Modified Cyclodextrins



dextrins cannot readily be accounted for in terms of typical hydrophobic interactions. For instance, ((4-hydroxyphenyl)azo)benzoates exhibit almost comparable affinities toward α- and γ-cyclodextrins in water and in DMF.[43] Chlorophenols show even higher affinities to heptakis(2,3,6-tri-*O*-methyl)-*β*-cyclodextrin (**3***β*) in organic solvents, such as cyclohexane, than in water.[169]

The inaccuracy of thermodynamic data is often too large to reveal solvent isotope effects upon switching

Table 2. Complex Stability Constant (log *K*), Standard Free Energy ($\Delta G°$), Enthalpy ($\Delta H°$), and Entropy Changes ($T\Delta S°$) for 1:1 Inclusion Complexation of Various Guests with Modified α-, *β*-, and *γ*-Cyclodextrins (2−27)

host	guest	solvent	*T*/K	log *K*	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
2α	4-nitrophenolate	H_2O (pH 11)	298	3.90	−21.1 ± 0.2	−42.1 ± 0.3	−20.9 ± 0.4	uv	211
2*β*	1-adamantylammonium	H_2O (pH 2.5)	298	3.90 ± 0.02	−22.3 ± 0.1	−12.6 ± 0.8	9.6 ± 0.6	uv	205
2*β*	2-adamantylammonium	H_2O (pH 2.5)	298	3.88 ± 0.02	−22.1 ± 0.1	−11.7 ± 1.3	10.5 ± 1.2	uv	205
2*β*	1-adamantylmethylammonium	H_2O (pH 2.5)	298	4.55 ± 0.02	−25.9 ± 0.1	−13.8 ± 1.7	11.8 ± 1.5	uv	205
2*β*	8-anilino-1-naphthalenesulfonate	H_2O (pH 7.4)	298	1.80	−10.3	−13.4 ± 1.3	−3.2 ± 0.4	fl	142
2*β*	4-*tert*-butylbenzoate	H_2O (pH 7.2)	298	4.45	−25.4	−20.1	5.3	cal	285
2*β*	3-(4-hydroxyphenyl)-1-propanol	H_2O	298	3.13	−17.9	−6.1	11.9	fl	137
2*β*	methyl orange (acid form)	H_2O	298	2.98 ± 0.04	−17.0 ± 0.2	−5.0 ± 1.3	11.8 ± 1.2	uv	205
2*β*	methyl orange (anion)	H_2O	298	4.57 ± 0.02	−26.1 ± 0.1	−17.2 ± 1.7	8.5 ± 1.6	uv	205
2*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	2.94 ± 0.03	−16.8	−12.1 ± 0.3	4.7	cal	55
2*β*	3-nitrophenol	H_2O	298	2.48 ± 0.04	−14.1 ± 0.3	−11.0 ± 0.6	3.0 ± 0.6	cal	39
2*β*	4-nitrophenol	H_2O	298	2.58 ± 0.05	−14.7 ± 0.3	−10.5 ± 0.5	4.2 ± 0.6	cal	39
2*β*	4-nitrophenol	H_2O	298	2.11 ± 0.01	−12.0 ± 0.5	−13.0 ± 0.9	−0.9 ± 0.9	cal	39
2*β*	4-nitrophenolate	H_2O (pH 11)	298	2.91	−16.7 ± 0.2	−13.8 ± 0.3	2.9 ± 0.4	uv	211
3α	benzoic acid	H_2O	298		−15.6	−68.6	−53.6	cd	207
3α	3-hydroxybenzoic acid	H_2O	298		−17.5	−72.4	−54.9	cd	207
3α	4-hydroxybenzoic acid	H_2O	298		−17.0	−60.2	−42.4	cd	207
3α	2-methylbenzoic acid	H_2O (pH 2.0)	298	2.43	−13.9	−11.5	2.4	uv	208
3α	4-methylbenzoic acid	H_2O (pH 2.0)	298	3.25	−18.5	−7.1	11.4	uv	208
3α	3-nitroaniline	H_2O	298		−17.4	−48.1	−33.7	cd	207
3α	4-nitroaniline	H_2O	298		−19.8	−60.2	−41.2	cd	207
3α	3-nitrophenol	H_2O	298		−16.1	−42.7	−26.2	cd	207
3α	4-nitrophenol	H_2O	298		−16.4	−62.3	−46.1	cd	207
3*β*	1-adamantaneacetate	H_2O (pH 9.94)	298		−25.6	−36.8 ± 1.7	−11.2 ± 1.8	uv	206
3*β*	1-adamantanecarboxylate	H_2O (pH 9.94)	298		−23.2	−21.3 ± 1.3	1.9 ± 1.3	uv	206
3*β*	1-adamantylammonium	H_2O (pH 2.5)	298	1.76 ± 0.04	−10.0 ± 0.2	−8.4 ± 2.1	1.7 ± 1.9	uv	205
3*β*	2-adamantylammonium	H_2O (pH 2.5)	298	1.92 ± 0.03	−11.0 ± 0.2	−10.0 ± 1.3	0.7 ± 1.2	uv	205
3*β*	1-adamantylmethylammonium	H_2O (pH 2.5)	298	2.57 ± 0.02	−14.6 ± 0.1	−10.0 ± 2.1	4.2 ± 2.0	uv	205
3*β*	(*R*)-1,1′-binaphthyl-2,2′-dicarboxylic acid	D_2O (pD 2.0)	298	2.84 ± 0.03	−16.2 ± 0.1	−12.7 ± 0.3	3.6 ± 0.4	nmr	203, 204
3*β*	(*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid	D_2O (pD 2.0)	298	2.06 ± 0.01	−11.7 ± 0.1	−22.7 ± 1.1	−10.5 ± 0.7	nmr	203, 204
3*β*	(*R*)-1,1′-binaphthyl-2,2′-diyl phosphate	D_2O (pD 5.5)	298	1.91 ± 0.02	−10.9 ± 0.1	−12.9 ± 0.4	−2.1 ± 0.1	nmr	203, 204
3*β*	(*S*)-1,1′-binaphthyl-2,2′-diyl phosphate	D_2O (pD 5.5)	298	2.60 ± 0.04	−14.8 ± 0.2	−11.9 ± 0.2	3.0 ± 0.1	nmr	203, 204
3*β*	2-chlorophenol	H_2O	298	1.93 ± 0.02	−11.0 ± 0.1	−23 ± 3	−13 ± 3	uv	169
3*β*	3-chlorophenol	methylcyclohexane	298	3.41 ± 0.03	−19.5 ± 0.2	−71 ± 4	−51 ± 3	uv	169
3*β*	3-chlorophenol	cyclohexane	298	3.40 ± 0.03	−19.4 ± 0.2	−53 ± 6	−33 ± 6	uv	169
3*β*	3-chlorophenol	H_2O	298	2.08 ± 0.01	−11.9 ± 0.1	−17 ± 1	−6 ± 1	uv	169
3*β*	4-chlorophenol	methylcyclohexane	298	3.15 ± 0.03	−17.9 ± 0.2	−68 ± 11	−51 ± 30	uv	169
3*β*	4-chlorophenol	cyclohexane	298	3.00 ± 0.04	−17.1 ± 0.2	−51 ± 4	−33 ± 3	uv	169
3*β*	4-chlorophenol	H_2O	298	2.00 ± 0.03	−11.4 ± 0.1	−18 ± 1	−6 ± 1	uv	169
3*β*	3-(4-hydroxyphenyl)-1-propanol	H_2O	298	2.03	−11.6	−21.2	−9.9	fl	137
3*β*	methyl orange (anion)	H_2O	298	3.71 ± 0.02	−21.2 ± 0.1	−24.3 ± 1.7	−3.0 ± 1.7	uv	205
3*β*	3-nitrophenolate	H_2O (pH 11.1)	298	1.93 ± 0.07	−11.0 ± 0.4	−11 ± 2	0 ± 2	cal	39
3*β*	4-nitrophenolate	H_2O (pH 11.1)	298	3.03 ± 0.05	−17.3 ± 0.3	−17.1 ± 0.3	0.3 ± 0.3	cal	39
3*β*	4-nitrophenolate	H_2O (pH 11.1)	298	2.45 ± 0.02	−14.0 ± 0.1	−30.9 ± 0.5	−17.0 ± 0.6	cal	39
3*β*	phenolphthalein	H_2O (pH 9.94)	298		−23.8	−60.2 ± 0.8	−36.4 ± 0.7	uv	206
4*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.13 ± 0.02	−17.9	−57.5 ± 0.4	−39.7	cal	55
5*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	2.50 ± 0.03	−14.3	−43.1 ± 0.4	−28.8	cal	55
6*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.13 ± 0.10	−17.9	−30.1 ± 0.3	−12.2	cal	55
7*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.42 ± 0.02	−19.5	−16.7 ± 0.4	2.8	cal	55
8*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.21 ± 0.03	−18.3	−33.5 ± 0.3	−15.2	cal	55
9*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.81 ± 0.06	−21.8	−13.8 ± 0.2	8.0	cal	55
10*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.93 ± 0.05	−22.4	−27.7 ± 0.2	−5.3	cal	55
11*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	2.95 ± 0.02	−16.8	−28.2 ± 0.2	−11.4	cal	55
12*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.58 ± 0.05	−20.4	−45.6 ± 0.2	−25.2	cal	55
13*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.62 ± 0.02	−20.7	−44.8 ± 0.2	−24.2	cal	55
14*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	1.85 ± 0.04	−10.5	−85.3 ± 1.0	−74.8	cal	55
15*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	3.94 ± 0.02	−22.5	−12.5 ± 0.3	10.0	cal	55
16*β*	2-naphthalenesulfonate	H_2O (pH 7.20)	298	2.74 ± 0.06	−15.6	−16.2 ± 0.3	−0.6	cal	55
17*β*	D-alanine	H_2O (pH 7.20)	298	3.52	−20.1	−30.5	−10.5	uv	56
17*β*	L-alanine	H_2O (pH 7.20)	298	3.62	−20.6	33.5	54.4	uv	56
17*β*	L-aspartic acid	H_2O (pH 7.20)	298	4.04	−22.9	−30.1	−7.1	uv	56
17*β*	L-cysteine	H_2O (pH 7.20)	298	2.65	−15.1	−66.1	−50.6	uv	56
17*β*	L-glutamine	H_2O (pH 7.20)	298	4.17	−23.8	−71.5	−47.3	uv	56
17*β*	L-isoleucine	H_2O (pH 7.20)	298	3.79	−21.6	−47.7	−25.9	uv	56
17*β*	D-leucine	H_2O (pH 7.20)	298	3.67	−21.0	−13.4	7.5	uv	56
17*β*	L-leucine	H_2O (pH 7.20)	298	3.70	−21.1	30.1	51.0	uv	56
17*β*	L-lysine	H_2O (pH 7.20)	298	2.57	−14.6	30.1	44.8	uv	56
17*β*	L-proline	H_2O (pH 7.20)	298	3.64	−20.8	−16.7	4.0	uv	56
17*β*	D-serine	H_2O (pH 7.20)	298	3.43	−19.5	21.3	41.8	uv	56
17*β*	L-serine	H_2O (pH 7.20)	298	3.49	−19.8	26.4	46.0	uv	56
17*β*	L-valine	H_2O (pH 7.20)	298	3.82	−21.8	−40.2	−18.4	uv	56
18α	D-alanine	H_2O (pH 7.20)	298	3.186	−18.19	−16.4	1.8	uv	57
18α	L-alanine	H_2O (pH 7.20)	298	3.373	−19.25	−24.6	−5.4	uv	57
18α	L-aspartic acid	H_2O (pH 7.20)	298	3.646	−20.81	5.2	26.0	uv	57

Table 2 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	method[a]	ref
18α	L-cysteine	H_2O (pH 7.20)	298	2.989	−17.06	−30.5	−13.3	uv	57
18α	L-isoleucine	H_2O (pH 7.20)	298	3.722	−21.24	−73.3	−51.8	uv	57
18α	D-leucine	H_2O (pH 7.20)	298	3.352	−19.13	−37.0	−17.8	uv	57
18α	L-leucine	H_2O (pH 7.20)	298	3.597	−20.53	−5.4	15.2	uv	57
18α	L-proline	H_2O (pH 7.20)	298	3.336	−19.04	12.9	31.9	uv	57
18α	D-serine	H_2O (pH 7.20)	298	2.920	−16.67	−27.7	−11.0	uv	57
18α	L-serine	H_2O (pH 7.20)	298	3.154	−18.0	−25.4	−7.3	uv	57
18α	D-valine	H_2O (pH 7.20)	298	3.325	−18.98	−10.1	8.9	uv	57
18α	L-valine	H_2O (pH 7.20)	298	3.564	−20.34	17.7	38.0	uv	57
18β	D-alanine	H_2O (pH 7.20)	298	3.06	−17.4	−20.5	−3.0	uv	56
18β	L-alanine	H_2O (pH 7.20)	298	3.14	−17.9	−35.6	−17.6	uv	56
18β	L-aspartic acid	H_2O (pH 7.20)	298	3.61	−20.6	9.2	32.2	uv	56
18β	L-cysteine	H_2O (pH 7.20)	298	2.43	−13.8	9.6	23.4	uv	56
18β	L-glutamine	H_2O (pH 7.20)	298	2.88	−16.4	13.4	29.7	uv	56
18β	L-isoleucine	H_2O (pH 7.20)	298	3.90	−22.3	−6.3	15.5	uv	56
18β	D-leucine	H_2O (pH 7.20)	298	3.46	−19.7	20.9	40.6	uv	56
18β	L-leucine	H_2O (pH 7.20)	298	3.69	−21.0	−7.1	14.2	uv	56
18β	L-lysine	H_2O (pH 7.20)	298	2.31	−13.2	20.5	33.5	uv	56
18β	L-methionine	H_2O (pH 7.20)	298	2.52	−15.9	39.7	55.2	uv	56
18β	L-proline	H_2O (pH 7.20)	298	3.08	−17.5	5.0	22.2	uv	56
18β	D-serine	H_2O (pH 7.20)	298	2.82	−16.1	−53.1	−34.7	uv	56
18β	L-serine	H_2O (pH 7.20)	298	3.07	−17.5	−39.3	−21.8	uv	56
18β	D-valine	H_2O (pH 7.20)	298	3.34	−19.1	42.7	61.9	uv	56
18β	L-valine	H_2O (pH 7.20)	298	3.65	−20.9	−3.8	17.2	uv	56
18γ	D-alanine	H_2O (pH 7.20)	298	2.958	−16.88	−14.5	2.4	uv	57
18γ	L-alanine	H_2O (pH 7.20)	298	3.025	−17.27	−43.9	−26.0	uv	57
18γ	L-aspartic acid	H_2O (pH 7.20)	298	3.583	−20.45	11.0	31.5	uv	57
18γ	L-cysteine	H_2O (pH 7.20)	298	2.694	−15.37	18.9	34.3	uv	57
18γ	L-isoleucine	H_2O (pH 7.20)	298	3.647	−20.82	15.7	36.5	uv	57
18γ	D-leucine	H_2O (pH 7.20)	298	3.222	−18.39	−16.1	2.4	uv	57
18γ	L-leucine	H_2O (pH 7.20)	298	3.496	−19.95	−7.7	12.2	uv	57
18γ	L-proline	H_2O (pH 7.20)	298	3.060	−17.47	29.3	46.8	uv	57
18γ	D-serine	H_2O (pH 7.20)	298	2.772	−15.82	−20.4	−4.6	uv	57
18γ	L-serine	H_2O (pH 7.20)	298	3.000	−17.12	−23.4	−6.3	uv	57
18γ	L-valine	H_2O (pH 7.20)	298	3.458	−19.74	−17.8	1.8	uv	57
19β	Cu^{2+}	H_2O (0.1 M KNO_3)	298	7.26	−41.4	−41.1	0.2	cal	77
19β·H^+	Cu^{2+}	H_2O (0.1 M KNO_3)	298	2.94	−16.8	−18.4	−1.2	cal	77
20β	D-tryptophan	H_2O (pH 8.9)	298	1.18 ± 0.22	−6.7 ± 1.7	−3 ± 5	4 ± 5	fl	139
21β	D-tryptophan	H_2O (pH 8.9)	298	1.73 ± 0.06	−9.6 ± 0.4	−18 ± 8	−8 ± 8	fl	139
22β	adiphenine·HCl	H_2O	298	2.81 ± 0.03	−16.0	−23.0 ± 0.8	−7.0	cal	286
22β	bromodiphenhydramine·HCl	H_2O	298	2.74 ± 0.03	−15.7	−10.6 ± 0.6	5.0	cal	286
22β	chlorcyclizine·2HCl	H_2O	298	2.61 ± 0.07	−14.9	−10.6 ± 0.3	4.3	cal	286
22β	chlorcyclizine·HCl	H_2O	298	2.63 ± 0.04	−15.0	−10.1 ± 1.1	4.9	cal	286
22β	cyclizine·HCl	H_2O	298	2.42 ± 0.02	−13.8	−14.2 ± 0.7	−0.4	cal	286
22β	2′,3′-dideoxyadenosine	H_2O (pH 8.95)	298	1.68	−9.6	−17.4	−7.9	uv	94[b]
22β	2′,3′-dideoxyadenosine·H^+	H_2O	298	1.09	−6.2	−10.5	−4.4	pot	94
22β	diphenidol·HCl	H_2O	298	2.20 ± 0.02	−12.5	−21.0 ± 0.7	−8.4	cal	286
22β	diphenyhydramine·HCl	H_2O	298	2.39 ± 0.03	−13.6	−14.1 ± 0.9	−0.5	cal	286
22β	diphenylpyraline·HCl	H_2O	298	2.55 ± 0.02	−14.6	−14.1 ± 0.5	0.5	cal	286
22β	hydroxyzine·2HCl	H_2O	298	2.58 ± 0.04	−14.7	−8.9 ± 0.7	5.8	cal	286
22β	hydroxyzine·HCl	H_2O	298	2.59 ± 0.02	−14.8	−10.1 ± 1.8	4.7	cal	286
22β	meclizine·2HCl	H_2O	298	2.54 ± 0.03	−14.5	−9.5 ± 0.3	5.0	cal	286
22β	orphenadrine·HCl	H_2O	298	2.375 ± 0.007	−13.55	−14.7 ± 1.3	−1.1	cal	286
22β	proadifen·HCl	H_2O	298	2.743 ± 0.002	−15.66	−16.2 ± 0.6	−0.5	cal	286
22β	terfenadine·HCl	H_2O	298	4.49 ± 0.03	−25.6	−7.33 ± 0.03	18.3	cal	286
23α	2,3-dimethylbutane	H_2O	298		4.6	−40 ± 7	−44 ± 6	sol	83, 287[c]
23α	hexane	H_2O	298		1.3	−44 ± 3	−44 ± 3	sol	83, 287[c]
23β	2,3-dimethylbutane	H_2O	298		−1.5	−31 ± 5	−29 ± 4	sol	83, 287[c]
23β	hexane	H_2O	298		1.9	−28 ± 4	−29 ± 4	sol	83, 287[c]
24α	2,3-dimethylbutane	H_2O	298		2.6	−44 ± 3	−46 ± 3	sol	83, 287[c]
24α	hexane	H_2O	298		−1.5	−47 ± 2	−46 ± 2	sol	83, 287[c]
24β	2,3-dimethylbutane	H_2O	298		−2.2	−27 ± 4	−25 ± 3	sol	83, 287[c]
24β	hexane	H_2O	298		1.2	−25 ± 1	−26 ± 1	sol	83, 287[c]
25β	bis(2-(1-adamantyl)ethyl) hydrogen phosphate	H_2O (pH 7.0)	298	7.25 ± 0.06	−41.4	−68 ± 4	−26	cal	54
25β	6-[(4-*tert*-butylphenyl)amino]-2-naphthalenesulfonate	H_2O (pH 7.0)	298	6.56 ± 0.15	−37.4	−65.5 ± 2.1	−28.1	cal	54
26β	bis(2-(1-adamantyl)ethyl) hydrogen phosphate	H_2O (pH 7.0)	298	7.05 ± 0.04	−40.3	−61 ± 4	−20	cal	54
26β	2-naphthalenesulfonate derivative **31**	H_2O (pH 7.0)	298	7.54 ± 0.01	−43.1	−90 ± 5	−47	cal	54
27β	bis(2-(1-adamantyl)ethyl) hydrogen phosphate	H_2O (pH 7.0)	298	6.33 ± 0.03	−36.1	−62 ± 5	−26	cal	54

[a] See footnote *a* of Table 1 for method. [b] Due to serious deviation in the van't Hoff plot, recalculation was made, excluding the data at 5 °C. [c] $\Delta G°$ at 298 K was obtained by interpolating the data at 293 and 303 K.

Table 3. Complex Stability Constant (log *K*), Free Energy ($\Delta G°$), Enthalpy ($\Delta H°$), and Entropy Changes ($T\Delta S°$), and Heat Capacity ($\Delta C_p°$) at Various Temperatures for 1:1 Inclusion Complexation of Various Guests with Natural α-, *β*-, and *γ*-Cyclodextrins (1α, 1*β*, and 1*γ*)

host	guest	solvent	*T*/K	log *K*	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	$\Delta C_p°$/ J mol^{-1} K^{-1}	method[a]	ref
1α	1-adamantanecarboxylate	H_2O (pH 7.2)	298		−14.2	−14.6	−0.4	−440	cal	21
1α	adipate (dianion)	H_2O (pH 9.5)	288	2.19 ± 0.01	−12.08 ± 0.03	−12.34 ± 0.03	−0.26 ± 0.04	−279 ± 2	cal	239
1α	adipate (dianion)	H_2O (pH 9.5)	298	2.13 ± 0.01	−12.16 ± 0.04	−15.16 ± 0.04	−3.00 ± 0.06	−279 ± 2	cal	239
1α	adipate (dianion)	H_2O (pH 9.5)	308	2.037 ± 0.004	−12.02 ± 0.02	−17.91 ± 0.03	−5.89 ± 0.04	−279 ± 2	cal	239
1α	benzene	H_2O	298	1.500 ± 0.001	−8.56 ± 0.03	−13.1 ± 0.3	−4.5	−272 ± 8	vap	29
1α	1,4-butanediol	H_2O	298	0.89 ± 0.02	−5.1 ± 0.1	−11.7 ± 0.4	−6.6 ± 0.6	−160 ± 47	cal	33
1α	1-butanol	H_2O	288		−11.25 ± 0.03	−7.18 ± 0.03	4.1 ± 0.1	−348 ± 9	cal	8
1α	1-butanol	H_2O	298		−10.95 ± 0.03	−10.70 ± 0.05	0.2 ± 0.1	−348 ± 9	cal	8
1α	1-butanol	H_2O	308		−10.50 ± 0.04	−14.13 ± 0.09	−3.6 ± 0.1	−348 ± 9	cal	8
1α	cyclohexane	H_2O	323	2.31	−14.3	−27.6	−13.3	−372	vap	28
1α	cyclohexane	H_2O	313	2.44	−14.6	−24.3	−9.7	−347	vap	28
1α	cyclohexane	H_2O	303	2.57	−14.9	−20.9	−6.0	−318	vap	28
1α	cyclohexane	H_2O	293	2.68	−15.1	−17.6	−2.5	−289	vap	28
1α	cyclohexane	H_2O	283	2.79	−15.1	−15.1	0.0	−264	vap	28
1α	cyclohexane	H_2O	273	2.88	−15.0	−12.6	2.4	−243	vap	28
1α	1,10-decanediol	H_2O	298	3.85 ± 0.05	−22.0 ± 0.3	−24.8 ± 0.3	−2.7 ± 0.6	−424 ± 40	cal	33
1α	heptane	H_2O	323	3.39	−20.9	−35.1	−14.2	−607	vap	28
1α	heptane	H_2O	303	3.70	−21.5	−23.8	−2.3	−515	vap	28
1α	heptane	H_2O	293	3.82	−21.4	−18.8	2.6	−469	vap	28
1α	heptane	H_2O	273	4.01	−21.0	−10.5	10.5	−385	vap	28
1α	heptane	H_2O	283	3.93	−21.3	−14.6	6.7	−427	vap	28
1α	heptane	H_2O	313	3.55	−21.3	−29.3	−8.0	−561	vap	28
1α	heptanedioate (dianion)	H_2O (pH 9.5)	288	2.77 ± 0.01	−15.29 ± 0.04	−15.02 ± 0.04	0.27 ± 0.06	−317 ± 4	cal	239
1α	heptanedioate (dianion)	H_2O (pH 9.5)	298	2.69 ± 0.01	−15.36 ± 0.02	−18.74 ± 0.03	−3.38 ± 0.04	−317 ± 4	cal	239
1α	heptanedioate (dianion)	H_2O (pH 9.5)	308	2.65 ± 0.01	−15.63 ± 0.02	−21.36 ± 0.04	−5.72 ± 0.05	−317 ± 4	cal	239
1α	1,7-heptanediol	H_2O	298	2.50 ± 0.02	−14.3 ± 0.1	−22.1 ± 0.4	−7.7 ± 0.6	−326 ± 34	cal	33
1α	heptanoate	H_2O (pH 6.9)	288	3.017 ± 0.008	−16.60 ± 0.05	−14.0 ± 0.1	2.6 ± 0.1	−84 ± 2	cal	10
1α	heptanoate	H_2O (pH 6.9)	298	2.911 ± 0.009	−16.61 ± 0.05	−17.7 ± 0.1	−1.1 ± 0.1	−84 ± 2	cal	10
1α	heptanoate	H_2O (pH 6.9)	308	2.818 ± 0.009	−16.61 ± 0.05	−20.9 ± 0.2	−4.3 ± 0.1	−84 ± 2	cal	10
1α	heptanoate	H_2O (pH 6.9)	318	2.701 ± 0.009	−16.44 ± 0.05	−24.7 ± 0.2	−8.2 ± 0.2	−84 ± 2	cal	10
1α	1-heptanol	H_2O	288		−17.5 ± 0.4	−16.2 ± 1.1	1.3 ± 1.2	−604 ± 90	cal	8
1α	1-heptanol	H_2O	298		−17.5 ± 0.3	−22.8 ± 1.1	−5.3 ± 1.1	−604 ± 90	cal	8
1α	1-heptanol	H_2O	308		−17.1 ± 0.4	−27.5 ± 1.7	−10.4 ± 1.7	−604 ± 90	cal	8
1α	heptylammonium	H_2O (pH 6.9)	288	3.137 ± 0.006	−17.26 ± 0.03	−15.5 ± 0.1	1.8 ± 0.1	−92 ± 4	cal	10
1α	heptylammonium	H_2O (pH 6.9)	298	3.03 ± 0.02	−17.3 ± 0.1	−19.9 ± 0.2	−2.6 ± 0.2	−92 ± 4	cal	10
1α	heptylammonium	H_2O (pH 6.9)	308	2.898 ± 0.014	−17.08 ± 0.08	−23.6 ± 0.3	−6.6 ± 0.2	−92 ± 4	cal	10
1α	heptylammonium	H_2O (pH 6.9)	318	2.772 ± 0.014	−16.88 ± 0.08	−27.3 ± 0.3	−10.4 ± 0.4	−92 ± 4	cal	10
1α	1,6-hexanediol	H_2O	298	2.01 ± 0.02	−11.4 ± 0.1	−17.9 ± 0.3	−6.0 ± 0.3	−337 ± 23	cal	33
1α	hexanoate	H_2O (pH 6.9)	288	2.554 ± 0.007	−14.06 ± 0.04	−11.0 ± 0.1	3.1 ± 0.1	−74 ± 2	cal	10
1α	hexanoate	H_2O (pH 6.9)	298	2.46 ± 0.01	−14.1 ± 0.1	−14.5 ± 0.2	−0.4 ± 0.2	−74 ± 2	cal	10
1α	hexanoate	H_2O (pH 6.9)	308	2.396 ± 0.014	−14.13 ± 0.08	−17.0 ± 0.3	−3.0 ± 0.2	−74 ± 2	cal	10
1α	hexanoate	H_2O (pH 6.9)	318	2.310 ± 0.004	−14.06 ± 0.03	−20.5 ± 0.2	−6.4 ± 0.2	−74 ± 2	cal	10
1α	1-hexanol	H_2O	288		−16.33 ± 0.07	−12.9 ± 0.1	3.4 ± 0.2	−561 ± 18	cal	8
1α	1-hexanol	H_2O	298		−16.25 ± 0.06	−18.2 ± 0.1	−1.9 ± 0.1	−561 ± 18	cal	8
1α	1-hexanol	H_2O	308		−15.36 ± 0.07	−24.1 ± 0.2	−8.9 ± 0.2	−561 ± 18	cal	8
1α	hexylammonium	H_2O (pH 6.9)	288	2.685 ± 0.006	−14.78 ± 0.03	−13.9 ± 0.1	0.8 ± 0.1	−78 ± 4	cal	10
1α	hexylammonium	H_2O (pH 6.9)	298	2.583 ± 0.006	−14.74 ± 0.03	−17.6 ± 0.1	−2.9 ± 0.1	−78 ± 4	cal	10
1α	hexylammonium	H_2O (pH 6.9)	308	2.479 ± 0.011	−14.61 ± 0.07	−20.9 ± 0.3	−6.3 ± 0.2	−78 ± 4	cal	10
1α	hexylammonium	H_2O (pH 6.9)	318	2.356 ± 0.013	−14.34 ± 0.08	−23.9 ± 0.3	−9.6 ± 0.4	−78 ± 4	cal	10
1α	4-nitrophenolate	H_2O (pH 9.5)	298		−17.6	−38.9	−21.0	−110	cal	21
1α	1,9-nonanediol	H_2O	298	3.55 ± 0.05	−20.3 ± 0.3	−22.8 ± 0.4	−2.4 ± 0.6	−374 ± 25	cal	33
1α	octanedioate (dianion)	H_2O (pH 9.5)	288	3.20 ± 0.01	−17.68 ± 0.05	−17.66 ± 0.07	0.01 ± 0.09	−327 ± 3	cal	239
1α	octanedioate (dianion)	H_2O (pH 9.5)	298	3.18 ± 0.01	−18.15 ± 0.04	−20.87 ± 0.06	−2.71 ± 0.07	−327 ± 3	cal	239
1α	octanedioate (dianion)	H_2O (pH 9.5)	308	3.10 ± 0.01	−18.29 ± 0.03	−24.21 ± 0.06	−5.91 ± 0.07	−327 ± 3	cal	239
1α	1,8-octanediol	H_2O	298	3.08 ± 0.03	−17.6 ± 0.2	−22.4 ± 0.2	−4.8 ± 0.3	−354 ± 60	cal	33
1α	octylammonium	H_2O (pH 6.9)	288	3.49 ± 0.03	−19.2 ± 0.1	−17.5 ± 0.3	1.7 ± 1.0	−108 ± 6	cal	10
1α	octylammonium	H_2O (pH 6.9)	298	3.37 ± 0.04	−19.2 ± 0.2	−22.0 ± 0.5	−2.9 ± 2.6	−108 ± 6	cal	10
1α	octylammonium	H_2O (pH 6.9)	308	3.20 ± 0.03	−18.8 ± 0.2	−27.1 ± 0.6	−8.3 ± 2.6	−108 ± 6	cal	10
1α	octylammonium	H_2O (pH 6.9)	318	3.06 ± 0.02	−18.7 ± 0.1	−31.1 ± 0.5	−12.4 ± 2.1	−108 ± 6	cal	10
1α	1,5-pentanediol	H_2O	298	1.45 ± 0.01	−8.29 ± 0.05	−17.4 ± 0.2	−9.1 ± 0.2	−238 ± 23	cal	33
1α	1-pentanol	H_2O	288		−14.19 ± 0.08	−10.49 ± 0.08	3.7 ± 0.2	−432 ± 12	cal	8
1α	1-pentanol	H_2O	298		−13.64 ± 0.05	−14.92 ± 0.07	−1.3 ± 0.1	−432 ± 12	cal	8
1α	1-pentanol	H_2O	308		−13.5 ± 0.05	−19.12 ± 0.10	−4.7 ± 0.1	−432 ± 12	cal	8
1α	pentylammonium	H_2O (pH 6.9)	288	2.045 ± 0.012	−11.26 ± 0.06	−10.8 ± 0.2	0.5 ± 0.1	−65 ± 5	cal	10
1α	pentylammonium	H_2O (pH 6.9)	298	1.968 ± 0.009	−11.23 ± 0.05	−13.6 ± 0.2	−2.4 ± 0.2	−65 ± 5	cal	10
1α	pentylammonium	H_2O (pH 6.9)	308	1.914 ± 0.016	−11.28 ± 0.09	−16.0 ± 0.4	−4.8 ± 0.4	−65 ± 5	cal	10
1α	pentylammonium	H_2O (pH 6.9)	318	1.778 ± 0.014	−10.82 ± 0.09	−19.2 ± 0.4	−8.4 ± 0.4	−65 ± 5	cal	10
1α	1-propanol	H_2O	288		−8.17 ± 0.08	−4.33 ± 0.07	3.8 ± 0.1	−240 ± 13	cal	8
1α	1-propanol	H_2O	298		−7.75 ± 0.04	−6.81 ± 0.06	1.0 ± 0.1	−240 ± 13	cal	8
1α	1-propanol	H_2O	308		−7.27 ± 0.06	−9.13 ± 0.11	−1.8 ± 0.2	−240 ± 13	cal	8
1*β*	1-adamantanecarboxylate	H_2O (pH 7.2)	298		−24.9	−23.0	1.9	−400	cal	21
1*β*	benzene	H_2O	298	2.228 ± 0.003	−12.72 ± 0.02	−1.9 ± 0.3	10.8	−498 ± 42	vap	29
1*β*	benzene	H_2O	291	1.81 ± 0.18	−10.1 ± 0.9	−1.7 ± 0.6	8.3 ± 1.1	−268 ± 12	cal	152

Table 3 (Continued)

host	guest	solvent	T/K	log K	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$T\Delta S°$/ kJ mol^{-1}	$\Delta C_p°$/ J mol^{-1} K^{-1}	method[a]	ref
1β	benzene	H_2O	298	2.03 ± 0.11	−11.6 ± 0.8	−3.5 ± 0.6	8.1 ± 1.0	−268 ± 12	cal	152
1β	benzene	H_2O	308	2.06 ± 0.12	−12.2 ± 1.0	−6.3 ± 1.3	5.9 ± 1.6	−268 ± 12	cal	152
1β	cyclohexane	H_2O	323	3.59	−22.2	−14.2	8.0	−389	vap	28
1β	cyclohexane	H_2O	313	3.65	−21.9	−10.5	11.4	−360	vap	28
1β	cyclohexane	H_2O	303	3.70	−21.5	−7.1	14.4	−331	vap	28
1β	cyclohexane	H_2O	293	3.73	−20.9	−3.8	17.1	−301	vap	28
1β	cyclohexane	H_2O	283	3.74	−20.3	−0.8	19.5	−276	vap	28
1β	cyclohexane	H_2O	273	3.74	−19.6	1.7	21.3	−247	vap	28
1β	cyclohexanol	H_2O (pH 6.9)	288	2.93 ± 0.02	−16.1 ± 0.1	−2.8 ± 0.1	13.2 ± 0.1	−79 ± 2	cal	10
1β	cyclohexanol	H_2O (pH 6.9)	298	2.838 ± 0.007	−16.19 ± 0.04	−6.5 ± 0.1	9.7 ± 0.1	−79 ± 2	cal	10
1β	cyclohexanol	H_2O (pH 6.9)	308	2.773 ± 0.008	−16.35 ± 0.05	−9.8 ± 0.1	6.6 ± 0.1	−79 ± 2	cal	10
1β	cyclohexanol	H_2O (pH 6.9)	318	2.712 ± 0.010	−16.51 ± 0.06	−13.0 ± 0.1	3.6 ± 0.1	−79 ± 2	cal	10
1β	heptane	H_2O	323	3.37	−20.8	−8.8	12.0	−377	vap	28
1β	heptane	H_2O	303	3.42	−19.8	−2.1	17.7	−318	vap	28
1β	heptane	H_2O	293	3.42	−19.2	0.8	20.0	−293	vap	28
1β	heptane	H_2O	273	3.38	−17.6	6.3	23.9	−243	vap	28
1β	heptane	H_2O	283	3.41	−18.5	3.8	22.3	−268	vap	28
1β	heptane	H_2O	313	3.40	−20.4	−5.4	15.0	−347	vap	28
1β	(4-hydroxyphenethyl)ammonium	H_2O (pH 6.9)	288	1.919 ± 0.005	−10.56 ± 0.03	−12.3 ± 0.1	−1.8 ± 0.1	−36 ± 3	cal	10
1β	(4-hydroxyphenethyl)ammonium	H_2O (pH 6.9)	298	1.845 ± 0.012	−10.53 ± 0.07	−13.8 ± 0.2	−3.4 ± 0.1	−36 ± 3	cal	10
1β	(4-hydroxyphenethyl)ammonium	H_2O (pH 6.9)	308	1.778 ± 0.014	−10.48 ± 0.08	−15.2 ± 0.3	−4.8 ± 0.2	−36 ± 3	cal	10
1β	(4-hydroxyphenethyl)ammonium	H_2O (pH 6.9)	318	1.690 ± 0.009	−10.29 ± 0.05	−16.9 ± 0.2	−6.6 ± 0.2	−36 ± 3	cal	10
1β	3-(2-hydroxyphenyl)propionate	H_2O (pH 6.9)	288	1.97 ± 0.02	−10.8 ± 0.1	−13.6 ± 0.3	−2.8 ± 0.2	−44 ± 6	cal	10
1β	3-(2-hydroxyphenyl)propionate	H_2O (pH 6.9)	298	1.908 ± 0.011	−10.89 ± 0.06	−15.1 ± 0.2	−4.2 ± 0.2	−44 ± 6	cal	10
1β	3-(2-hydroxyphenyl)propionate	H_2O (pH 6.9)	308	1.83 ± 0.02	−10.8 ± 0.1	−17.6 ± 0.5	−6.8 ± 0.5	−44 ± 6	cal	10
1β	3-(2-hydroxyphenyl)propionate	H_2O (pH 6.9)	318	1.76 ± 0.01	−10.7 ± 0.1	−19.0 ± 0.4	−8.2 ± 0.4	−44 ± 6	cal	10
1β	3-(4-hydroxyphenyl)propionate	H_2O (pH 6.9)	288	2.550 ± 0.002	−14.04 ± 0.01	−12.6 ± 0.1	1.4 ± 0.1	−45 ± 4	cal	10
1β	3-(4-hydroxyphenyl)propionate	H_2O (pH 6.9)	298	2.473 ± 0.006	−14.11 ± 0.03	−14.2 ± 0.1	−0.1 ± 0.1	−45 ± 4	cal	10
1β	3-(4-hydroxyphenyl)propionate	H_2O (pH 6.9)	308	2.386 ± 0.007	−14.07 ± 0.04	−16.4 ± 0.1	−2.3 ± 0.1	−45 ± 4	cal	10
1β	3-(4-hydroxyphenyl)propionate	H_2O (pH 6.9)	318	2.305 ± 0.006	−14.03 ± 0.04	−18.2 ± 0.1	−4.1 ± 0.1	−45 ± 4	cal	10
1β	*cis*-4-methylcyclohexanol	H_2O (pH 6.9)	288	3.23 ± 0.02	−17.8 ± 0.1	−5.6 ± 0.1	12.2 ± 0.1	−87 ± 1	cal	10
1β	*cis*-4-methylcyclohexanol	H_2O (pH 6.9)	298	3.17 ± 0.01	−18.1 ± 0.1	−9.6 ± 0.1	8.5 ± 0.1	−87 ± 1	cal	10
1β	*cis*-4-methylcyclohexanol	H_2O (pH 6.9)	308	3.12 ± 0.02	−18.4 ± 0.1	−13.1 ± 0.1	5.4 ± 0.1	−87 ± 1	cal	10
1β	*cis*-4-methylcyclohexanol	H_2O (pH 6.9)	318	3.03 ± 0.02	−18.5 ± 0.1	−16.8 ± 0.1	1.7 ± 0.1	−87 ± 1	cal	10
1β	4-nitrophenolate	H_2O (pH 9.5)	298		−14.6	−16.7	−2.1	−250	cal	21
1β	phenethylammonium	H_2O (pH 6.9)	298	1.38 ± 0.03	−7.9 ± 0.2	−6.4 ± 0.4	1.5 ± 0.4	−58 ± 1	cal	10, 13
1β	phenethylammonium	H_2O (pH 6.9)	308	1.41 ± 0.03	−8.3 ± 0.2	−8.8 ± 0.4	−0.5 ± 0.4	−58 ± 1	cal	10
1β	phenethylammonium	H_2O (pH 6.9)	318	1.41 ± 0.02	−8.6 ± 0.1	−11.3 ± 0.3	−2.8 ± 0.2	−58 ± 1	cal	10
1β	3-phenylbutanoate	H_2O (pH 6.9)	298	2.588 ± 0.007	−14.76 ± 0.04	−9.2 ± 0.1	5.6 ± 0.1	−69 ± 1	cal	10
1β	3-phenylbutanoate	H_2O (pH 6.9)	288	2.597 ± 0.013	−14.29 ± 0.07	−6.1 ± 0.1	8.2 ± 0.1	−69 ± 1	cal	10
1β	3-phenylbutanoate	H_2O (pH 6.9)	308	2.561 ± 0.005	−15.1 ± 0.03	−12.0 ± 0.1	3.2 ± 0.1	−69 ± 1	cal	10
1β	3-phenylbutanoate	H_2O (pH 6.9)	318	2.509 ± 0.013	−15.27 ± 0.08	−14.9 ± 0.1	0.4 ± 0.1	−69 ± 1	cal	10
1β	3-phenylpropionate	H_2O (pH 6.9)	298	2.173 ± 0.012	−12.4 ± 0.07	−7.3 ± 0.1	5.1 ± 0.1	−61 ± 1	cal	10
1β	3-phenylpropionate	H_2O (pH 6.9)	288	2.12 ± 0.02	−11.7 ± 0.1	−4.8 ± 0.1	6.8 ± 0.1	−61 ± 1	cal	10
1β	3-phenylpropionate	H_2O (pH 6.9)	288	2.121 ± 0.016	−11.67 ± 0.09	−4.8 ± 0.1	6.8 ± 0.1	−61 ± 1	cal	10
1β	3-phenylpropionate	H_2O (pH 6.9)	308	2.158 ± 0.012	−12.73 ± 0.07	−9.9 ± 0.2	2.8 ± 0.1	−61 ± 1	cal	10
1β	3-phenylpropionate	H_2O (pH 6.9)	318	2.137 ± 0.012	−13.01 ± 0.08	−12.5 ± 0.2	0.5 ± 0.1	−61 ± 1	cal	10
1γ	benzene	H_2O	298	0.96 ± 0.01	−5.47 ± 0.03	14.2 ± 0.8	19.7	−1340 ± 130	vap	29

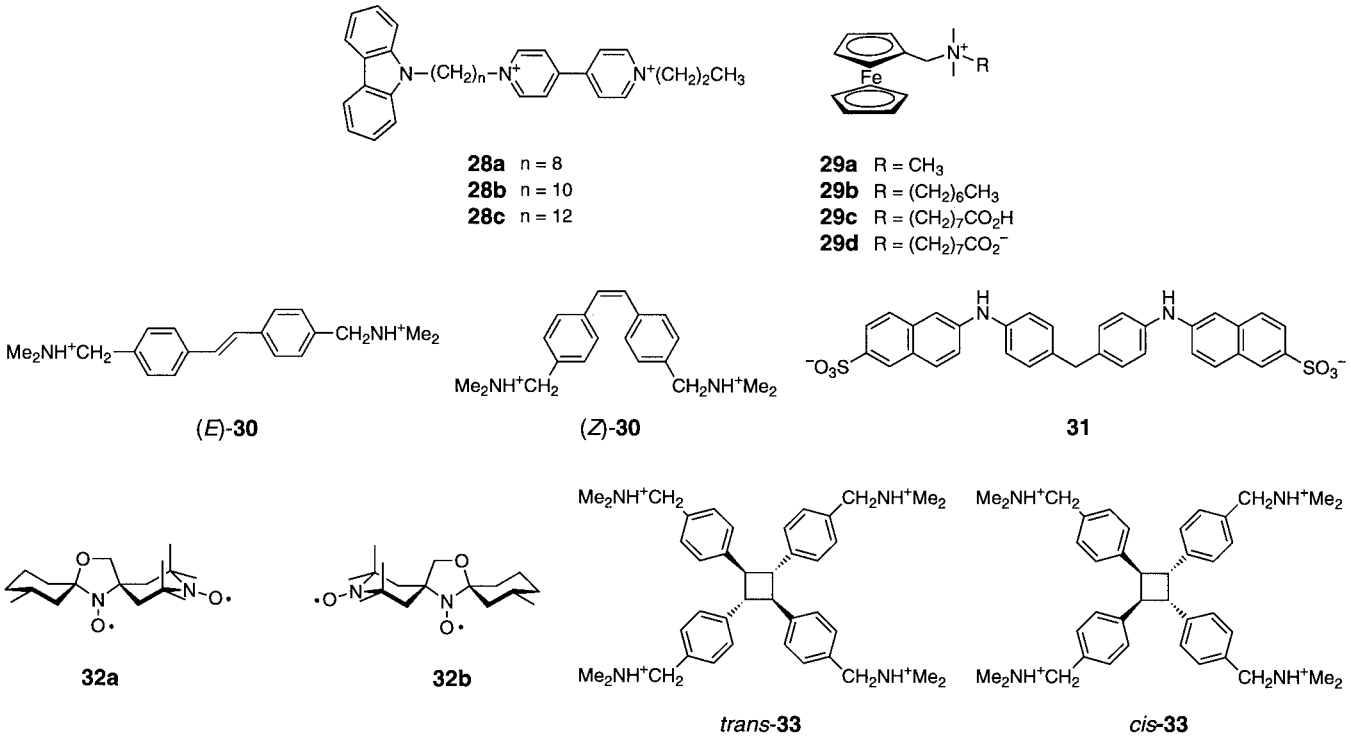
[a] See footnote *a* of Table 1 for method.

from H_2O to D_2O. An example of this is shown when we compare the results of an NMR study carried out in D_2O[170] and a calorimetric study in H_2O,[171] where the $\Delta G°$ values for the complexation of nonanedioate and decanedioate with α-cyclodextrin are comparable, yet the results afforded for octanedioate in H_2O[171] and D_2O[170] substantially disagree with each other. The differences in the ΔH values reported for these three dicarboxylates in H_2O[171] or D_2O[170] are inconsistent across the series, varying from 2 to 8 kJ mol^{-1} from one study to the next.

There is a general lack of experimental data on the effect of different buffers upon the thermodynamics of cyclodextrin complexation reactions. However, recently a comparison of acetate and phosphate buffers has been made,[13] in which it was found that acetate buffer interacted with both α- and β-cyclodextrins but that phosphate buffer was free from such unwanted interactions. It should be emphasized that almost all of the neutral components of organic buffers (with some exceptions such as glycine buffer)[239] can interact with cyclodextrins. Even the simplest organic acid (formic acid), which has an extremely limited ability to form hydrophobic interactions, shows an appreciable affinity to α-cyclodextrin.[172]

Because the details of experimental procedures, calculation of uncertainties for thermodynamic quantities, and/or characterization of the materials used are not usually fully presented in most of the papers cited in Tables 1−3, it is quite difficult to choose the "best" thermodynamic values or to pick one set of thermodynamic data as "best" when more than two papers deal with the same host−guest combinations under comparable conditions. In such an instance, the only criterion for selecting specific thermodynamic quantities, which are used in the following discussion and in the figures, is an agreement of the results for the same complexation reaction in two or more papers.

Chart 2. Less-Common Guests



It should be noted that, although we have cited many thermodynamic data for a wide variety of pharmaceuticals and other complicated organic compounds of great industrial and scientific importance in Tables 1−3, we will not discuss those data in detail, since the chemical structures presented to us are so diverse in nature that a meaningful systematic interpretation would appear difficult to make in most instances. The immediate goal of the discussion is to find regularities and generalities in the thermodynamic quantities for each homologous series of the organic guests. We also wish to understand the factors that govern the host−guest interactions in cyclodextrin complexes from the thermodynamic point of view.

A. Natural Cyclodextrins

The thermodynamic data for a very wide variety of homologous aliphatic and aromatic guest compounds which are compiled in Table 1 permit us to examine how the structural and electronic features of the guests affect their complexation behavior with natural cyclodextrins. However, we will focus our discussion on the most crucial structural and electronic features that lead to significant alterations of the complexation thermodynamics. The factors examined include the position and number of additional methyl or methylene, hydroxyl, and other functional group(s) in aliphatic and/or aromatic guest homologues, as well as the flexibility and the chirality of organic guest molecules. These are the governing factors that determine the thermodynamic quantities of the complexation of cyclodextrins with various organic guests. From such a discussion, we will elucidate the nature of the complexation behavior of cyclodextrins. Studies that deal with the influence of the other structural features such as the location of sulfonyl group(s) on a naphthalene ring[14] and the location of various functional groups on phenol have already been published.[39]

In the following discussion, quite detailed examinations are made to elucidate the relationships between the complexation thermodynamic quantities and the structural and electronic features of various guests. We should note that these comparisons neglect contributions arising from the solvation of all the species involved, as well as the influence of different buffers upon the thermodynamic quantities of cyclodextrin complexation. Nevertheless, a reasonably consistent picture of the trends can be drawn in several cases.

It should be emphasized that almost all of the thermodynamic relationships elucidated below refer to the standard temperature 298.15 K. Since the heat capacities of cyclodextrin complexation reactions are large (see Heat Capacity), the magnitude and even the sign of thermodynamic parameters may vary at different temperatures.

In a very general sense, the size-fit concept, which predicts the highest complex stabilities for the best size-matched host−guest pairs, may explain the global trends of the thermodynamic quantities for complexation of natural cyclodextrins. For instance, because the cavity diameter of α-cyclodextrin (ca. 4.9 Å) is much smaller than that of β-cyclodextrin (ca. 6.2 Å) and because van der Waals forces are critically dependent on the distance of separation, one can expect that the forces induced upon complexation of straight-chain guests will be larger (more negative $\Delta H°$) for α-cyclodextrin than for β-cyclodextrin, while the same forces will be larger for the complexation of adamantyl guests with β-cyclodextrin than with α-cyclodextrin.

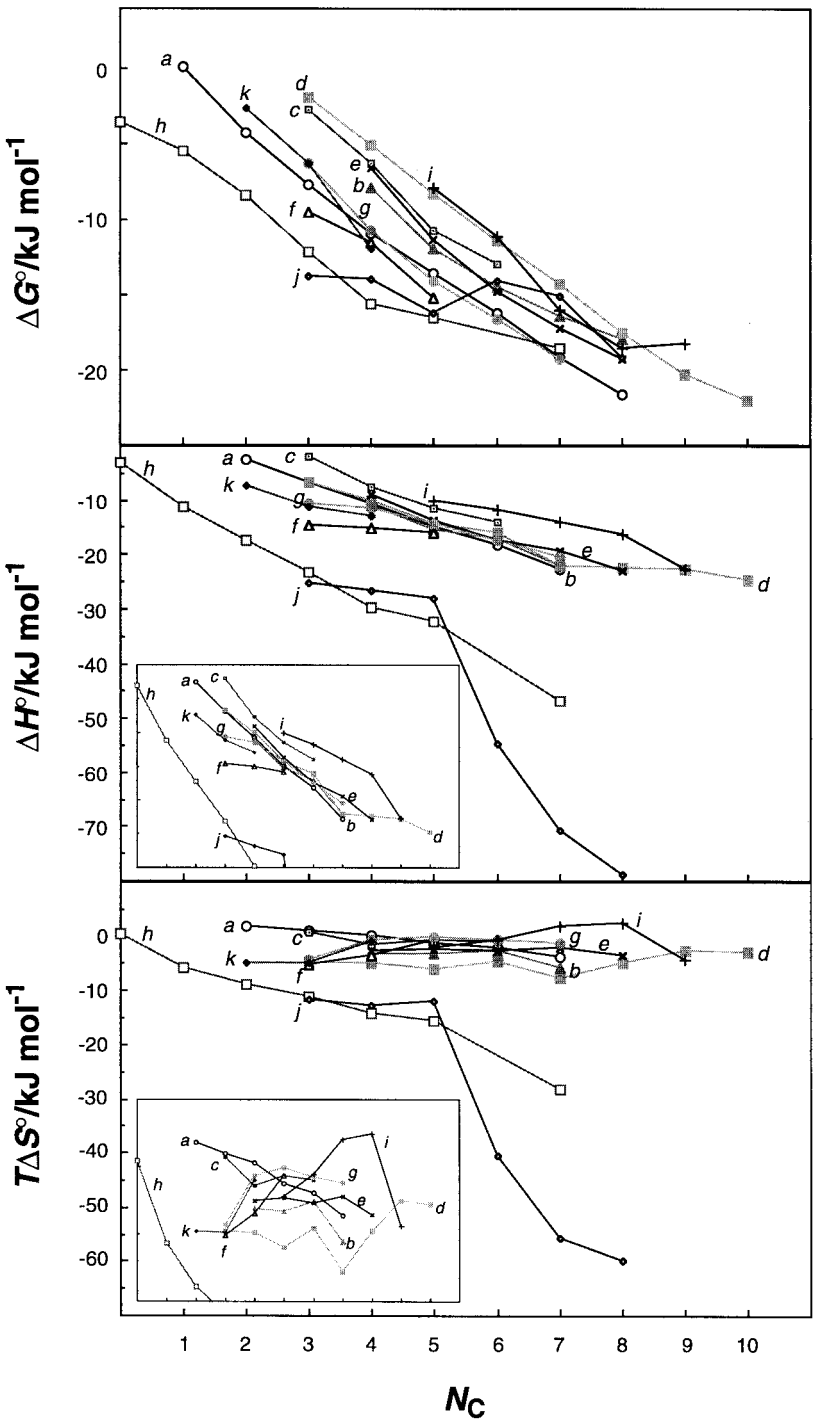


Figure 1. Thermodynamic quantities ($\Delta G°$, $\Delta H°$, and $T\Delta S°$ at 298 K) for the complexation of various classes of guests with α-cyclodextrin as a function of the number of methylenes (N_C) in guest molecules, the carboxyl carbons being not counted): (a) 1-alkanol (○), (b) *sec*-alkanol (▲), (c) 1,2-alkanediol (⊡), (d) α,ω-alkanediol (■), (e) alkylammonium (×), (f) alkylamine (△), (g) alkanoate (●), (h) alkanoic acid (□), (i) alkanedioate (+), (j) alkanedioic acid (◇), (k) alkylurea (◆). Insets are partial enlargements.

Certainly, the van der Waals interactions will be highly dependent not only on the size but also on the shape of the guest molecule. When the guest molecule cannot be completely accommodated within the cyclodextrin cavity, steric effects may play a dominant role. A typical example of this is the steric hindrance caused by the ortho derivatization of aromatic guests upon complexation with β-cyclodextrin. While the concepts based on the size- or shape-matching between guests and hosts are not new,[39,81,146,159,173−176] it will be demonstrated in the following discussion that these rather straightforward ideas provide us with a useful qualitative framework to account for most of the thermodynamic data.

1. Effects of Adding a Methylene Group to the Guest

In Figure 1, the $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the complexation reactions of α-cyclodextrin with 1-alkanols, *sec*-alkanols, 1,2-alkanediols, α,ω-alkanediols, neutral alkylamines, alkylammonium ions, neutral alkanoic acids, alkanoate ions, neutral alkanedioic

acids, alkanedioate ions, and monoalkylureas are plotted as a function of the number of aliphatic carbon atoms (N_C) present in the guest. Only the number of aliphatic carbon atoms possessing hydrogen(s) are counted in the calculation of N_C, so the carbon of a carboxyl group does not contribute toward N_C. It should be noted that aliphatic CH groups and aromatic CH groups make considerably different contributions to the overall molecular hydrophobicity, which is evaluated by Hansch's π parameter.[160] The complexation quantities, listed in Table 1, also depend strongly upon the nature of the CH group added to guest molecule. For these reasons, we have decided not to include aromatic carbon atoms in the calculation of N_C.

The sources of the $\Delta G°$ data used in Figure 1 (top) are 1-alkanols ($N_C = 1$, 2, 7, and 8[11] and $N_C = 3-6$[8]), *sec*-alkanols ($N_C = 4-7$[32] and $N_C = 8$[11]), 1,2-alkanediols,[31] α,ω-alkanediols,[33] neutral alkylamines,[168] alkylammonium ions,[9] neutral alkanoic acids ($N_C = 0-2$[172,177] and $N_C = 3-5$ and 7[71]), alkanoate ions,[9] neutral alkanedioic acids,[171] alkanedioate ions,[171,239] and monoalkylureas.[178] The sources of the $\Delta H°$ data used in Figure 1 (middle) are 1-alkanols ($N_C = 2$[31] and $N_C = 3-7$[8]), *sec*-alkanols,[32] 1,2-alkanediols,[31] α,ω-alkanediols ($N_C = 3-6$[31] and $N_C = 7-10$[33]), neutral alkylamines,[168] alkylammonium ions,[9] neutral alkanoic acids ($N_C = 0-2$[172,177] and $N_C = 3-5$ and 7[71]), alkanoate ions,[9] neutral alkanedioic acids,[171] alkanedioate ions,[171,239] and monoalkylureas.[178] Values of $\Delta S°$, plotted in Figure 1 (bottom), were calculated from the $\Delta G°$ and $\Delta H°$ values used above.

In Figure 2, the $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the complexation reactions of β-cyclodextrin with 1-alkanols, *sec*-alkanols, alkylammonium ions, cycloalkanols, alkanoic acids, alkanoate ions, alkylbarbituric acids (pH 5.0), alkylthiobarbituric acids (pH 5.0), ω-phenylalkylamine (phenethylamine and 3-phenylpropylamine), and ω-phenylalkanoate ions (phenylacetate, 3-phenylpropanoate and 4-phenylbutanoate) are plotted as functions of N_C. The same counting convention of the carbon atoms in a guest is applied to both α-cyclodextrin (Figure 1) and β-cyclodextrin (Figure 2) systems.

The sources of the $\Delta G°$ values used in Figure 2 (top) are 1-alkanols,[11] *sec*-alkanols,[11] alkylammonium ions,[9] cycloalkanols ($N_C = 4$, 5, 7, and 8[9] and $N_C = 6$[12]), alkanoic acids,[71] alkanoates ($N_C = 4-6$[9] and $N_C = 7$ and 9[71]), alkylbarbituric acids (pH 5.0),[179] alkylthiobarbituric acids (pH 5.0),[179] phenethylamine,[13] 3-phenylpropylamine,[13] phenylacetate,[9] 3-phenylpropanoate,[13] and 4-phenylbutanoate.[9] The sources of the $\Delta H°$ data used in Figure 2 (middle) are 1-alkanols ($N_C = 3$ and 4[32] and $N_C = 5$ and 6[11]), *sec*-alkanols,[32] alkylammonium ions,[9] cycloalkanols ($N_C = 4$, 5, 7, and 8[9] and $N_C = 6$[12]), alkanoic acids,[71] alkanoates ($N_C = 4-6$[9] and $N_C = 7$ and 9[71]), alkylbarbituric acids (pH 5.0),[179] alkylthiobarbituric acids (pH 5.0),[179] phenethylamine,[13] 3-phenylpropylamine,[13] phenylacetate,[9] 3-phenylpropanoate,[13] and 4-phenylbutanoate.[9] Values of $\Delta S°$, plotted in Figure 2 (bottom), were calculated from the $\Delta G°$ and $\Delta H°$ values used above.

We note that the $\Delta G°$ and $\Delta H°$ values become more negative with increasing N_C for all combinations of hosts and guests. The contribution of increasing N_C to the complex stability can be quantitatively evaluated from the slope of the plot, or the unit increment, $d\Delta G°/dN_C$.

Somewhat surprisingly, the slope remains almost constant up to $N_C = 10$, where the length of the guest is significantly longer than the formal depth (7.9 Å) of cyclodextrin's geometrical cavity. This behavior is consistent with the idea of the so-called "expanded hydrophobic cavity".[8,3,11,19,20] It is estimated that alkyl chains with a maximum of five or six carbon atoms can be accommodated in the α-cyclodextrin cavity.[3,11,19,20] Hence, one would expect that, for aliphatic guests of $N_C \geq 7$, at least one methylene group is forced to stay outside the hydrophobic cavity and will not be able to form effective van der Waals contacts with the cyclodextrin's inner wall.

One possible rationalization for this is that the properties of the water inside the cavity as well as in close proximity to the cavity are quite different from those of the bulk water.[8,3,11,19,20] The effect of the cavity on the bulk water may be comparable to that of a charged functional group, such as the carboxylate or ammonium ion. As with charged groups that create an electric field around themselves, the hydrophobic cavity and the incompletely embedded methylene groups of included guest may create an "expanded hydrophobic sphere" by rearranging the original structure of the water molecules around themselves. The release of water molecules from the cyclodextrin cavity and from its close proximity (contribution d) to the bulk water and the rearrangement of nearby water molecules appear to play the decisive role that determines the overall complexation thermodynamics.

Values obtained for $d\Delta G°/dN_C$ and $d\Delta H°/dN_C$ are summarized in Table 4. The $d\Delta G°/dN_C$ values range from -0.8 kJ mol^{-1} obtained for the complexation of neutral alkanedioic acids with α-cyclodextrin to -4.7 kJ mol^{-1} for the complexation of alkylureas with α-cyclodextrin. The $d\Delta G°/dN_C$ values for the remaining classes of guests occur over the relatively narrow range of -1.7 to -4.0 kJ mol^{-1}. The $d\Delta G°/dN_C$ values for both α- and β-cyclodextrins are quite similar to the corresponding values reported for the transfer of one methylene group from water to a nonpolar organic solvent such as hexane ($\Delta G°_{transfer}/CH_2 = -3$ to -4 kJ mol^{-1}), which is considered to be a representative hydrophobic interaction process.[159]

The crucial role of size-matching between host and guest is further demonstrated by examining the unit increment ($d\Delta G°/dN_C$) for the complexation of cycloalkanols with α-cyclodextrin. Although the data are not included in Figure 1 or Table 4, because cycloalkanols are not fully accommodated within the cavity and are not therefore appropriate for direct comparison with the other guests, an attempted calculation gives the unusually small $d\Delta G°/dN_C$ value of -0.74 kJ mol^{-1} for these oversized guests. This clearly indicates that cycloalkanols cannot be fully embedded in the small cavity and therefore the addition of a methylene group contributes to the complex stability in only a very limited way.

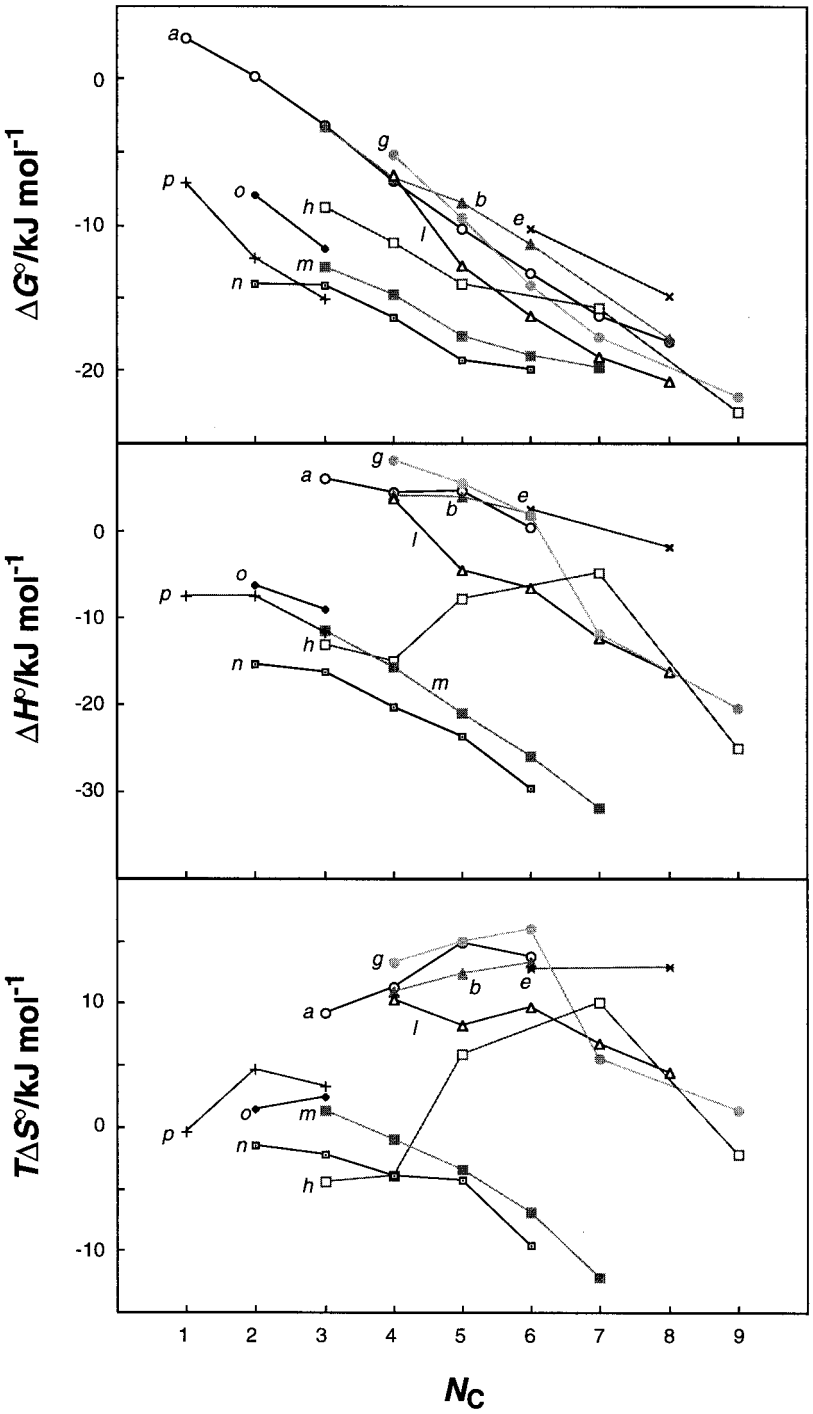


Figure 2. Thermodynamic quantities ($\Delta G°$, $\Delta H°$, and $T\Delta S°$ at 298 K) for the complexation of various classes of guests with β-cyclodextrin as a function of the number of methylenes (N_C) in guest molecules, the carboxyl carbons being not counted): (a) 1-alkanol (○), (b) *sec*-alkanol (▲), (e) alkylammonium (×), (g) alkanoate (X), (●) alkanoic acid (□), (l) cycloalkanol (△), (m) alkylbarbituric acid (■), (n) alkylthiobarbituric acid (⊡), (o) ω-phenlyalkylamine (◆), and (p) ω-phenylalkanoate (+).

Similar, but somewhat reduced, regularities can be found in the changing profile of $\Delta H°$ for complexation with both α- and β-cyclodextrins. The $d\Delta H°/dN_C$ values obtained from the linear fits of $\Delta H°$ against N_C are scattered over a range of -0.65 kJ mol^{-1} for the complexation of neutral alkylamines with α-cyclodextrin to -12.2 kJ mol^{-1} for the complexation of neutral alkanedioic acids with α-cyclodextrin. The $d\Delta H°/dN_C$ for the remaining classes of guests fall within a range of -1.1 to -6.2 kJ mol^{-1}.

The global treatment of these data led us to an interesting conclusion. For complexation with α-cyclodextrin, the average values of $d\Delta G°/dN_C$ and $d\Delta H°/dN_C$ are -3.1 and -3.3 kJ mol^{-1}, respectively. In the case of β-cyclodextrin, the average values of $d\Delta G°/dN_C$ and $d\Delta H°/dN_C$ are -2.8 and -3.3 kJ mol^{-1}, respectively. A major conclusion which can be derived from the above calculations is that the inclusion of methylene groups into both α- and β-cyclodextrin cavities is an almost completely enthalpy-driven

Table 4. Unit Increments of $\Delta G°$ and $\Delta H°$ Per Methylene ($d\Delta G°/dN_C$ and $d\Delta H°/dN_C$) for Various Classes of Guests upon Complexaton with Natural α- and β-Cyclodextrins

		α-cyclodextrin		β-cyclodextrin	
guest	entry[a]	$d\Delta G°/dN_C$[b]	$d\Delta H°/dN_C$[b]	$d\Delta G°/dN_C$[b]	$d\Delta H°/dN_C$[b]
1-alkanol	a	−3.0	−4.0	−3.1	−1.7
sec-alkanol	b	−2.5	−3.5	−2.8	−1.1
1,2-alkanediol	c	−3.5	−4.0		
α,ω-alkanediol	d	−2.9	−2.6		
alkylammonium	e	−3.1	−3.3	−2.3	−2.3
alkylamine	f	−2.8	−0.7		
alkanoate	g	−3.2	−2.6	−3.3	−6.2
alkanoic acid	h	−2.3	−6.0	−2.2	(−1.3)[c]
alkanedioate	i	−2.8	−3.0		
alkanedioic acid	j	(−0.8)[c]	(−12.2)[c]		
alkylurea	k	−4.7	−2.8		
cycloalkanol	l			−3.5	−4.8
alkylbarbituric acid	m			−1.8	−5.1
alkylthiobarbituric acid	n			−1.7	−3.5
ω-phenylalkylamine	o			−3.7	−2.8
ω-phenylalkanoate	p			−4.0	−2.1
mean		-3.1 ± 0.6[d]	-3.3 ± 1.3[d]	-2.8 ± 0.8[d]	-3.3 ± 1.6[d]

[a] Guest entry code corresponds to that shown in Figures 1 and 2. [b] In kJ mol^{-1}. [c] Poor correlation; not included in the calculation of mean value. [d] Standard deviation.

process. The averaged unit increments in $\Delta G°$ (3.1 and 2.8 kJ mol^{-1} for α- and β-cyclodextrin, respectively) are very similar to the averaged unit enthalpic gains (3.3 kJ mol^{-1} for both α- and β-cyclodextrin). However, a closer examination of the values obtained for each host−guest combination reveals that the unit enthalpic gain obtained may be canceled by entropic loss or enhanced by entropic gain. The degree to which the enthalpic gain is altered is critically dependent upon the nature of the guest. In other words, *the complexation itself is obviously driven by enthalpy at the standard temperature (298.15 K), but the entropic term controls the complex's ultimate stability*.

It should be noted that the $d\Delta H°/dN_C$ values for both α- and β-cyclodextrin are more negative than the corresponding values for the transfer of organic molecules from water to nonpolar solvents ($\Delta H°_{sol}/CH_2 \geq -1.5$ kJ mol^{-1}), which are derived from the enthalpy of solution for a series of organic compounds.[163−166]

As can be seen from Figure 2, the $\Delta G°$ and $\Delta H°$ values for complexation with β-cyclodextrin are more negative for aromatic guests than for aliphatic guests with the same N_C simply because we have not taken into account the aromatic carbons in the calculation of N_C. However, even for these aryl guests, the $d\Delta G°/dN_C$ and $d\Delta H°/dN_C$ values are very close to those found for the corresponding alkyl guests.

The introduction of a methyl substituent at the 4-position of the phenyl group in aromatic guests such as phenethylamine leads to an increase in $\Delta G°$ which is comparable to the $d\Delta G°/dN_C$ value obtained in the complexation of aliphatic guests with α- and β-cyclodextrin. Insertion of an extra methylene group in the methylene chain connecting the phenyl moiety and the terminal hydrophilic group, as exemplified by switching to 3-phenylpropylamine from phenethylamine, also leads to almost the same unit increment for the complexation with β-cyclodextrin. In contrast, a much smaller unit increment is obtained for the complexation of the same guests with α-cyclodextrin. The reduced increment for α-cyclodextrin complexes may be rationalized by the steric effect imposed by the phenyl group, since this group is only able to perch on the top of α-cyclodextrin's small cavity, and this does not permit the full accommodation of the lipophilic methylene chain. Thus, only small additional hydrophobic and/or van der Waals interactions are found upon the addition of a methylene group to these systems.

It should be emphasized, however, that the introduction of an extra methylene in a guest molecule does not always enhance the complex stability and sometimes leads to no appreciable effects, depending on the position at which the methylene group is introduced. When an extra methyl group is introduced in close proximity to the hydrophilic terminal group which is thought to remain in the bulk solution even after complexation,[2,5] quite similar $\Delta G°$, $\Delta H°$, and $\Delta S°$ values are obtained for the original and methylated guests. In fact, only negligible changes in the thermodynamic quantities are seen for several sets of homologous guest molecules including hexyl-, (1-methylhexyl)-, and *N*-methylhexylammonium ions, phenethyl- and *N*-methylphenethylammonium ions, 1-alkanols (N_C) and *sec*-alkanols ($N_C + 1$), and 1-alkanols (N_C) and 1,2-alkanediols ($N_C + 1$).

In summary, the thermodynamic quantities for the cyclodextrin complexations compiled in Table 1 cannot be entirely explained in terms of the formal number of carbon atoms in the guest molecule, for which the conventional solute−solvent interaction has been well-accounted. Instead, the thermodynamics of the host−guest complexation with cyclodextrins should be correlated to the extent in which the guest penetrates into the cyclodextrin cavity. These findings lead us to the important conclusions that (1) any differences in solute−solvent interactions of the free guest prior to inclusion complexation do not contribute measurably to the complexation thermodynamics and (2) only those parts of a guest

molecule that experience any changes in their environment upon complexation contribute to the thermodynamic quantities.

The fact that the thermodynamic quantities correlate directly with the extent in which the guest has penetrated into the cyclodextrin cavity enables us to gain a better understanding of some structural features of cyclodextrin complexes. As can be seen from Figure 1, the $\Delta G°$, as well as the $\Delta H°$, values for the complexation of α-cyclodextrin with 1-alkanols (plot a) and alkanoates (plot g) which share the same N_C values are very close to one another. This result may indicate that both the alkanol's hydroxyl group and the alkanoate's carboxylate moiety remain in the bulk water even after inclusion complexation and that only the alkyl groups interact with the cyclodextrin cavity. Interestingly, the $\Delta G°$ values for the complexation of 1-alkanols (plot a) of N_C with α-cyclodextrin are quite similar to those for alkylammonium ions (plot e) of $N_C + 1$ (see Figure 1). From this, we can deduce that the charged ammonium group is located in the bulk water far away from the cavity opening and the methylene group adjacent to the ammonium is completely prevented from direct interaction with the cyclodextrin. Likewise, many additional valuable structural estimations for the other host−guest combinations can be derived using the data presented in Table 1 and Figures 1 and 2.

2. Effect of Guest Hydroxyl Group

We note that only a limited number of studies on the thermodynamics of hydrogen-bond formation using simple model compounds in aqueous solution exist. Particular attention has been paid to amide hydrogen bonding as a result of its importance in protein structure. A nonideality of aqueous urea solutions has been analyzed in terms of the indefinite association model, giving a value of $K = 0.041$ M^{-1} at 25 °C for the dimeric association of urea.[180] The enthalpic change of ca. −6 kJ mol^{-1} was estimated for the association of urea, although this value is a compromise based upon the possibility of forming both linear and cyclic dimers.[180,181] Other thermodynamic studies of model hydrogen-bonding associations include the dimerization of *N*-methylacetamide,[182] lactams,[183,184] carboxylic acids,[185] the dissolving of diketopiperazine,[186] and other cyclic dipeptides which bear amino acid side chains.[187] Although these investigations are certainly informative, the systems described above usually have additional factors that contribute to the thermodynamics, such as hydrophobic effects arising from the organic side chains and, in the solid-state studies, the enforcement of the crystal lattice; these factors serve only to complicate the issue.

Recently, a study to evaluate the contribution of hydrogen bonding to the complexation thermodynamics of cyclodextrin has been performed, using several pairs of structurally related aromatic guest molecules, either with or without a phenolic hydroxyl group.[10] Comparison of the complexation thermodynamics of structurally related guests such as these should provide us with a good measure of the thermodynamic properties associated with the formation of an O−H···O hydrogen bond, the existence of which has been proven spectroscopically.[10] For the phenolic O−H···O hydrogen bond, the increments in $\Delta H°$ that can be attributed to the hydrogen-bonding interaction for several pairs of guests occur over a range of −6.9 to −7.8 kJ mol^{-1}.[10] The increments in $\Delta G°$ due to the formation of one phenolic hydrogen bond vary from −1.5 to −2.5 kJ mol^{-1} for several guest pairs such as 4-hydroxyphenethylamine (tyramine) and phenethylamine, 3-(4-hydroxyphenyl)propionate and 3-phenylpropionate, and 3-(2-hydroxyphenyl)propionate and 3-phenylpropionate (see Table 1).

It is apparent that additional hydrogen-bond formation does not necessarily lead to an enhanced stability of the complex, as demonstrated by the data for 3-phenylpropionate ($\Delta G° = -12.4$ kJ mol^{-1}) and 3-(2-hydroxyphenyl)propionate ($\Delta G° = -10.9$ kJ mol^{-1}). In this particular case, even though the formation of a hydrogen bond was proven spectroscopically and supported by a typical increment in $\Delta H°$, a weaker complex was obtained with β-cyclodextrin as compared to the parent compound. This destabilization arises as a result of an unfavorable entropy change associated with the substitution of the 2-position of the aromatic ring. It does not depend on the chemical nature of the substituent, only on the position at which the hydroxyl group is introduced.

As discussed above, the data in Table 1 are totally consistent with the assumption that the charged and hydrophilic groups of the guests, with the exception of the phenolic hydroxyl group, remain in the bulk solution before and after association with cyclodextrin. This is further confirmed by the comparison of the thermodynamic quantities for the complexations of 1-*O*-hexyl-β-D-glucopyranoside[13] and of 1-hexanol[13] with α-cyclodextrin. The thermodynamic quantities for these hexane derivatives which bear completely different types of hydrophilic groups are almost identical within the range of experimental error, i.e. $K = 839 \pm 35$ M^{-1} and $\Delta H° = -18.5 \pm 0.3$ kJ mol^{-1} for hexyl glucopyranoside and $K = 871 \pm 46$ M^{-1} and $\Delta H° = -18.5 \pm 0.4$ kJ mol^{-1} for 1-hexanol. These results are consistent with the view that only the hexyl group of these substances is included in the α-cyclodextrin cavity, while the glucopyranose moiety of hexyl glucopyranoside as well as the hydroxyl group of 1-hexanol are both excluded from the α-cyclodextrin cavity due to their hydrophilic nature. It may be further deduced that none of the hydroxyl or ether groups in the glucopyranose moiety appear to form hydrogen bonds to the cyclodextrin's hydroxyl groups. However, such similarities are rarely found in the complexation thermodynamics of the guests with functional groups that are hydrophilic to some extent but are also capable of interacting with the cyclodextrin cavity; this important difference in the complexation behavior of 1-butanol and 1-butylimidazole should be noted.

Another example of differences in hydrogen-bonding interactions may be found in the complexations of ephedrines and pseudoephedrines with α- and β-cyclodextrins.[13] These molecules contain two dif-

ferent hydrophilic groups, these being a hydroxyl and an aminomethyl group. From the thermodynamic point of view, molecules of ephedrines and pseudoephedrines differ from phenethylamine only by the presence of an additional hydroxyl group (as the *N*-methyl group is not involved in the binding process[10,13]), and this structural difference endows them with somewhat increased affinities and more negative enthalpy changes upon complexation. This can be attributed to the weak hydrogen-bond formation between the host and guest. This example probably indicates that even aliphatic hydroxyl groups can form a hydrogen bond to the cyclodextrin's peripheral hydroxyls, although these interactions are not as strong as those formed by phenolic hydroxyl groups.

3. Effect of Guest Ring Size and Substitution

The affinity of guest molecules toward cyclodextrins depends on a conformity between the guest molecule and the cyclodextrin cavity. In the case of the cycloalkanol series, only cyclobutanol, which is the smallest cycloalkanol studied, can fit into the α-cyclodextrin cavity better than the *β*-cyclodextrin cavity. In general, cyclic aliphatic compounds fit better into *β*-cyclodextrin, while acyclic guests prefer α-cyclodextrin (see Table 1 and Figures 1 and 2). Typically, the plots of $\Delta G°$ for the complexation of 1-alkanols with α-cyclodextrin (Figure 1) and with *β*-cyclodextrin (Figure 2) give almost parallel lines, which are shifted by ca. 4 kJ mol^{-1}. Similarly, the $\Delta G°$ plots for 1-alkanols (plot a) and cycloalkanols (plot l) with *β*-cyclodextrin, shown in Figure 2, are shifted by ca. 3 kJ mol^{-1}, which is comparable to the addition of one methylene unit, except for the cyclobutanol example.

It is interesting to note that the $\Delta G°$ and $\Delta H°$ values for the complexation of cyclobutanol with *β*-cyclodextrin are very close to those reported for the complexation of 1-butanol with *β*-cyclodextrin. This coincidence may imply that the compact structure of the constrained cyclobutanol cannot fully experience van der Waals interactions within the relatively large *β*-cyclodextrin cavity. It should be noted that the overall complexation thermodynamics of cyclobutanol and 1-butanol with the smaller α-cyclodextrin are, in contrast, quite different from one another.

Methylations of cyclohexane derivatives at different positions lead to considerable, but varying degrees of enhancement in their affinity to *β*-cyclodextrin (for example, see the data for 1-, 2-, 3-, and 4-methylcyclohexanols shown in Table 1). The *β*-cyclodextrin cavity is capable of accommodating even larger cycloalkane derivatives, and one of the "best" guest moieties that fits almost perfectly into the *β*-cyclodextrin cavity is the adamantyl group. The equilibrium constants for complexations of various adamantane derivatives with *β*-cyclodextrin can often exceed 10 000 or even 100 000 M^{-1}, whereas the corresponding values for α-cyclodextrin are more than 100 times smaller.

Imidazole, which comprises a five-membered ring, is the only aromatic ring that fits better into the α-cyclodextrin cavity than the *β*-cyclodextrin cavity. Usually, guest molecules carrying a phenyl moiety exhibit stronger affinities to *β*-cyclodextrin than α-cyclodextrin (for instance, see the data concerning phenethylamine, 3-phenylpropanoate, and 3-phenylpropylamine). A methyl group added to the 3- or 4-position of a phenyl group may penetrate into the cavities of both α-cyclodextrin and *β*-cyclodextrin. One extra methyl group introduced at the para position of phenethylamine causes a 4-fold increase in its affinity to both α- and *β*-cyclodextrins, an increase in $\Delta G°$ of 3.5 kJ mol^{-1}. The insertion of a methylene into the aliphatic chain of phenethylamine, giving 3-phenylpropylamine, leads to a similar enhancement in affinity toward to *β*-cyclodextrin, but the affinity increase is much smaller when α-cyclodextrin is the host, since the extra methylene added is believed to stay outside the α-cyclodextrin cavity.

Phenethylamine and 2-methoxyphenethylamine exhibit similar affinities toward α-cyclodextrin. However, phenethylamine gives a much higher equilibrium constant for complexation with *β*-cyclodextrin than 2-methoxyphenethylamine. A plausible explanation for this contrasting result is that the benzene ring cannot penetrate deeply into the α-cyclodextrin cavity and the 2-methoxy group is left outside, even after complexation, and in this position, it is incapable of significantly affecting the overall complexation thermodynamics. When the system is switched to the larger *β*-cyclodextrin, the cavity may permit a deeper penetration of the benzene ring, ironically resulting in a considerable decrease in complex stability owing to the severe steric hindrance caused by the 2-methoxy group. This again leads to the conclusion that the α-cyclodextrin cavity is too small to accommodate the benzene ring in its entirety.

As we have already mentioned earlier in this section, the interactions of aromatic guests with cyclodextrins cannot be understood simply as a typical hydrophobic effect, even though this is the case for aliphatic guests. Indeed, the affinity of aromatic guests toward cyclodextrins is sometimes comparable or even higher in organic solvents than in water.[43,169] Another feature that makes the complexation of aromatic guests with cyclodextrins distinctly different from that of aliphatic guests is that there is a higher affinity for the charged species than for the corresponding neutral species among certain aromatic guests such as nitrophenols.[39,188] This is inconsistent with the idea of typical hydrophobic interactions but may be accounted for in terms of the dipole−dipole interaction between host and guest.

The examination of the substituent's electronic effects has been carried out using Hammett parameters. This has been a limited success, as exemplified by the complexation of α-cyclodextrin with para-substituted benzoic acid[189] and 1,4-disubstituted benzenes.[190] However, similar analyses of the complexation thermodynamic quantities for a series of phenethylamine derivatives[9,13] do not necessarily afford satisfactory results. For instance, the order of complex stability, or $-\Delta G°$, of para-substituted phenethylamine derivatives does not appear to correlate with the Hammett σ value, i.e. $CH_3 > OCH_3 > H > OH > NH_2$ for α-cyclodextrin and $OCH_3 >$

$CH_3 > OH > NH_2 > H$ for β-cyclodextrin, while the order of the $-\Delta H°$ value is $OH > OCH_3 > CH_3 > H$ for α-cyclodextrin and $OH > NH_2 > OCH_3 > CH_3 \approx H$ for β-cyclodextrin. More comprehensive comparisons between several electron-donating and electron-withdrawing substituents can be made for the complexation behavior of 4-substituted phenols with α-cyclodextrin,[39,191] for which the order of the complex stability is $I > COOH > Br > Cl > NO_2 > CN > CHO > CH_3 > OCH_3 > CH_3 > F > H > NH_2$, whereas the order of the $-\Delta H°$ values is completely different. The thermodynamic quantities for the complexation reactions of a series of substituted benzoates with α-cyclodextrin[192−194] and β-cyclodextrin[194] have also been reported. From these simple comparisons, it may be concluded that the electronic effect, as measured by the Hammett parameter, fails to rationalize the complexation thermodynamics of cyclodextrins.

In this context, the correlation analysis with multiple factors seems more reasonable and indeed offers a better fit in many cases. In these analyses[140,195−199] the complex stabilities (log K or $\Delta G°$) are correlated with some of the empirical parameters of the substituent that has been introduced. Frequently employed parameters are the molar refractivity (R_m) as a measure of substituent's volume, the Hammett σ value as a measure of guest's dipole (rather than electron density), the charge as a measure of hydrophilicity, and the Hansch π parameter[160] as a measure of hydrophobicity. The log K values for the complexations of monosubstituted and 1,4-disubstituted benzenes with α-cyclodextrin[195] and of 4-substituted aryl alkyl sulfides, sulfoxides, and sulfones with α-cyclodextrin[196] can be expressed by linear combinations of these empirical parameters. Similarly, multiregression analyses using artificial neural networks of the log K values for the complexations of various mono- and disubstituted benzenes[197,199,200] and 1-substituted naphthalenes[140,198] with β-cyclodextrin demonstrate that the log K values correlate to some extent with the R_m, σ, and π parameters, enabling one to predict the complex stability from these parameters.

4. Effect of Guest Flexibility

The introduction of a double bond into the aliphatic chain reduces the flexibility of the molecule. Thus, unsaturated compounds have lower conformational degrees of freedom than the analogous saturated compounds. The equilibrium constants for the complexation of *trans*-3-hexenoate and 6-heptenoate with α-cyclodextrin are approximately half those corresponding to hexanoate and heptanoate.[9] Comparison of the relevant $\Delta H°$ and $\Delta S°$ values for these reactions indicates that this effect is entropic in origin.[9]

Another example of drastic changes in the entropy and enthalpy terms caused by increasing molecular flexibility as a result of the addition of an extra methylene group can be seen in the comparison of the complexations of 1-phenylimidazole and 1-benzylimidazole, where the affinity toward β-cyclodextrin is 15 times greater for 1-benzylimidazole than for 1-phenylimidazole.[13] The difference in $\Delta G°$ of −6.9 kJ mol^{-1} is much greater than the typical unit increment (3 kJ mol^{-1}) for a methylene group, so the major part of the increased affinity for benzylimidazole may be attributed to the increased freedom. This is also the case for the complexations of 1-phenylimidazole and 1-benzylimidazole with α-cyclodextrin.[13] The main source of the large increments in $\Delta G°$ for the complexation of 1-benzylimidazole with both α- and β-cyclodextrin is a highly favorable $\Delta S°$, which is partly annulled by an unfavorable $\Delta H°$.[13]

These examples clearly demonstrate the decisive role of guest's flexibility in the stability of cyclodextrin complexes. Thus, increasing flexibility or degrees of freedom in a guest molecule leads to a more favorable complexation entropy, since more of the possible "conformers" can fit properly into the cavity. Unfortunately, at the present time, the concept of using entropic control for cyclodextrin complexation has not been developed to the same level as manipulations based on the available knowledge concerning the influence of the introduction and position of methyl(ene) groups, charged or hydrophilic groups, hydrogen-bonding groups, the attachment of functional groups to aromatic rings, or the role of steric hindrance.

5. Chiral Discrimination

Since most enantiomeric pairs of guests give only small differences in thermodynamic quantities upon complexation with cyclodextrins, it is essential that we compare thermodynamic data determined under exactly the same physicochemical conditions.

No appreciable differences are found in the thermodynamic quantities for the complexation of α- and β-cyclodextrin with the enantiomeric pairs of *sec*-alkanols,[32] norvaline and norleucine,[201] or carbohydrates.[37] Among several enantiomeric pairs of aromatic guests such as phenylalanine, α-methylbenzylamine, mandelate, phenylfluoroethanol, and amphetamine, only α-methylbenzylamine gives significantly different thermodynamic quantities for its enantiomeric pair upon complexation with α-cyclodextrin.[202] It seems, therefore, quite exceptional to find significant chiral discriminations in the complexation thermodynamics of enantiomeric guests with natural cyclodextrins, probably because most of the guest molecules are included only through nonorientating van der Waals and hydrophobic interactions and are not rigorously fixed either conformationally or rotationally in the cavity.

Small differences in $\Delta G°$ (typically less than 1 kJ mol^{-1}) are reported for the complexation of enantiomeric pairs of some amino acids with mono(6-anilino-6-deoxy)-β-cyclodextrin (**17**β),[56,57] and also for enantiomeric ephedrines and pseudoephedrines—which possess two asymmetric carbons—upon complexation with both α- and β-cyclodextrins.[13]

Some of the largest differences in thermodynamic quantities for enantiomeric pairs have been reported for complexation reactions of atropisomeric (*R*)- and (*S*)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate with β-cyclodextrin.[203,204] The log K value for the (*S*)-isomer is 1.3 times larger than that for the (*R*)-isomer, and the difference in $\Delta G°$ ($\Delta\Delta G° = 0.7$ kJ

mol^{-1}) arises mostly from the entropic gain ($T\Delta\Delta S°$ = 1.8 kJ mol^{-1}). The chiral discrimination of the same atropisomeric pair and of 1,1′-binaphthyl-2,2′-dicarboxylic acid is greatly enhanced by up to 4.9 and 6.1 times, respectively, by the use of methylated β-cyclodextrin **3**β as the host.[203,204] The increased stabilities ($\Delta\Delta G$ = 3.9 and 4.5 kJ mol^{-1}) again originate from the large entropic gains ($T\Delta\Delta S°$ = 5.1 and 14.1 kJ mol^{-1}) in both cases, which completely cancel the accompanying enthalpic losses ($\Delta\Delta H$ = −1.0 and −10.0 kJ mol^{-1}). It may be concluded therefore that, as judged from the more positive $\Delta S°$ value for the preferred enantiomer, conformational freedom and extensive desolvation are the decisive factors determining the enantioselectivity upon complexation with cyclodextrins.

B. Modified Cyclodextrins

Careful microcalorimetric study has been performed with the ditopic bis(β-cyclodextrin)s **25**β−**27**β, in which two cyclodextrin moieties are connected via several different cross-linking chains.[54] Extraordinarily high association constants of up to 4×10^7 are reported.[54] The enthalpic gain ($-\Delta H°$) which may be as high as 61−90 kJ mol^{-1} is obviously the dominant driving force for this kind of very strong complexation, although a substantial part of the enthalpic gain is canceled by a similarly large entropy change ($T\Delta S$) of between −20 and −47 kJ mol^{-1}. To obtain such high affinities, Zheng and Breslow employed the synergetic effects of the ditopic cyclodextrins, along with ditopic guest molecules containing either two adamantyl or naphthyl units. In these cases, the successive complexation of two linked guest moieties with the ditopic host is greatly enhanced by the favorable (much less negative) entropic contribution that arises from the reduced freedom of both the host and guest molecules prior to complexation.

Simpler guest molecules carrying adamantyl or naphthyl moieties have also been used in the complexation thermodynamic studies of a wide variety of cyclodextrin derivatives **2**−**24**.[55,84,205,206] In the complexations of 2-naphthalenesulfonate with a variety of β-cyclodextrin derivatives **2**β−**16**β,[55] the complex stabilities obtained are lower in most cases than those which are obtained for natural β-cyclodextrin as a result of less favorable entropy changes.

Typical adamantane derivatives[142,205,206] and phenol derivatives[39,137,207] afford stronger complexes with heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (**2**β) than with natural β-cyclodextrin, but weaker complexes with heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (**3**β) as a result of very unfavorable entropy changes for these reactions.

Benzene, adamantane, and naphthalene are too large to be accommodated in the α-cyclodextrin cavity. For oversized guest molecules such as 4-methylbenzoic acid,[208] 3- and 4-nitrophenols,[39,207,209−211] and nitroanilines,[209,212] the extended hydrophilic cavities of hexakis(2,6-di-*O*-methyl)-α-cyclodextrin (**2**α) and hexakis(2,3,6-tri-*O*-methyl)-α-cyclodextrin (**3**α) offer some assistance toward guest accommodation.

It is interesting to note that the affinity toward amino acids is much higher for mono(6-anilino-6-deoxy)-β-cyclodextrin (**17**β)[56,57] and for a mixture of 6*A*-amino-6*B*-carboxy- and 6*B*-amino-6*A*-carboxy-β-cyclodextrins (**20**β and **21**β)[139] than for natural β-cyclodextrin, probably as a result of the electrostatic interactions formed between the host and guest, which are zwitterionic in nature.

C. Heat Capacity

Heat capacity data ($\Delta C_p°$) derived from precise microcalorimetric studies[8,10] allow a more detailed comparison between the transfer of hydrophobic groups from water to a pure organic solvent like hexane and the transfer from water to a cyclodextrin cavity. Large, negative $\Delta C_p°$ values of −50 to −60 J mol^{-1} K^{-1} per methylene unit have been reported for the transfer of alkyl groups from water to nonaqueous hydrophobic environments.[163−166,213] Recently, a unit increment of $\Delta C_p°$ = −56 J mol^{-1} K^{-1} per methylene group has also been reported in the microcalorimetric study of α-cyclodextrin complexation with alkylammonium (N_C = 5−8) and alkanotes (N_C = 5 and 6) at different temperatures.[10] This $\Delta C_p°$ value is identical to that found for the transfer of a methylene group from water to nonpolar environment.

However, some $\Delta C_p°$ values have been reported that are in conflict with the above results; the unit increment of $\Delta C_p°$ per methylene group observed for the complexation of 1-alkanols with α-cyclodextrin is much more negative, amounting to ca. −100 J mol^{-1} K^{-1}.[8] We are unable to explain these distinct differences in the $\Delta C_p°$ values obtained for alkanols[8] and with alkylammonium and alkanoate ions.[10]

In the complexation with β-cyclodextrin, the average unit increment in $\Delta C_p°$ reported for the methyl substitution of aromatic guests is −33 J mol^{-1} K^{-1}. This is considerably smaller than the corresponding values given above for methylene insertion into α-cyclodextrin, either because the methyl substituent is more exposed to the bulk water or because it is less efficiently buried in the hydrophobic environment in the larger β-cyclodextrin cavity.[10]

Attempts to estimate the $\Delta C_p°$ value for hydrogen-bond formation in bulk water were made for the first time in an analysis of the temperature dependence of $\Delta H°$ observed for the dimerization of urea in water.[180,181] However, the authors do not report the $\Delta C_p°$ value and instead describe that a small positive trend in $\Delta H°$ is observed over the temperature range 0−40 °C, which is within the limits of experimental error (±0.2 kJ mol^{-1}).

In a recent study on the hydrogen-bonding interactions of β-cyclodextrin with some guest pairs either with or without an additional phenolic hydroxyl group,[10] a positive $\Delta C_p°$ value of 75 J mol^{-1} K^{-1} is reported for the formation of a hydrogen bond. The most important conclusion of this study is that the stability of the hydrogen bond decreases with increasing temperature, whereas the contribution from the hydrophobic interaction of methylene groups remains essentially unchanged. This result also suggests that, although the major forces that maintain biological supramolecular systems are hydrogen-bonding and hydrophobic interactions, the disinte-

gration or dissociation of such biosystems at elevated temperatures is driven primarily by breaking the hydrogen bonds.

As clearly demonstrated earlier in this section, only that part of a guest molecule that experiences appreciable changes in its environment upon association makes a contribution to the complexation thermodynamics. Therefore, the substantial differences between carboxylate and ammonium ions in solute−solvent interaction are not expected to significantly affect the complexation thermodynamics because upon complexation the charged terminal groups are located away from the major binding site of the cyclodextrin complex and usually do not experience any great effect in their solvation. Thus, the $\Delta C_p°$ values around −60 J K^{-1} mol^{-1} for phenethylammonium and 3-phenylpropionate ions[10] should primarily reflect the interaction of the identical aromatic part of these two guests with β-cyclodextrin. This may be considered as yet another thermodynamic confirmation of the inability of most hydrophilic groups to penetrate into the cyclodextrin cavity.

VI. Enthalpy–Entropy Compensation

In principle, no explicit relationship between the enthalpy change and the entropy change can logically be derived from fundamental thermodynamics. Nevertheless, the compensatory enthalpy−entropy relationship has often been observed empirically in both activation and thermodynamic quantities determined for a very wide variety of reactions and equilibria. This extrathermodynamic relationship between ΔH and ΔS was first extensively analyzed and proposed as an empirical rule by Leffler.[214] Further exemplification and more thorough and critical analyses have been carried out by Leffler and Grunwald,[215a] Grunwald and Steel,[215b] Exner,[216] Chen,[217] Danil de Namor et al.,[53] and Linert et al.[68]

In chemical reactions and equilibria, both the rate constant (k) and the equilibrium constant (K) are critically varied by changing substituent, solvent, and other such internal and external factors. However, the change in k or K ($\Delta\Delta G^{‡}$ or $\Delta\Delta G°$) caused by such alterations is generally much smaller than that expected from the induced enthalpic change alone ($\Delta\Delta H^{‡}$ or $\Delta\Delta H°$), since the relevant entropy term ($\Delta\Delta S^{‡}$ or $\Delta\Delta S°$) often compensates to cancel out a substantial part of the enthalpic change. Qualitatively, this is the source of the $\Delta H-\Delta S$ compensation effect.

The linear $\Delta H-\Delta S$ relationship observed experimentally leads to eq 3, where the proportional coefficient β has the same dimension as temperature.[214,215] From eq 3 and the differential form of the Gibbs−Helmholtz eq 4, we obtain eq 5:

$$\Delta H° = \beta\Delta\Delta S° \tag{3}$$

$$\Delta G° = \Delta\Delta H° - T\Delta\Delta S° \tag{?}$$

$$\Delta G° = (1 - T/\beta)\Delta\Delta H° \tag{5}$$

Equation 5 clearly indicates that, at the critical point, or so-called isokinetic or isoequilibrium temperature (β), the rate or equilibrium constant is entirely independent of the enthalpic change caused by any alterations in substituent, solvent, and so on. It is interesting that such phenomena have been abundantly observed for a wide variety of reactions.[214−217]

However, much debate has been devoted to the basis of this extrathermodynamic relationship,[68,218−225] since the enthalpy and entropy changes are not independent of one another in their determination—especially using the van't Hoff or Arrhenius equations.[68] Therefore, even a minute error in either term may propagate to the other and lead to an apparent enthalpy−entropy compensation effect. Hence, the accuracy in experiments and data treatments as well as the quality of the correlation coefficient for the enthalpy−entropy plot could be a criteria for the significance of such a correlation. It should also be emphasized that, while using a greater number of data sets is preferable for more global analysis of such a correlation, integration of all the data available from various sources with different levels of accuracy inevitably leads to more or less scattered plots, affording low-quality correlation coefficients. However, this does not immediately rule out the correlation itself, since such correlations often show high levels of significance. Recently, some experimental and theoretical support for the validity of the enthalpy−entropy compensation has also been reported.[157]

More recently, several somewhat different quantitative correlation analyses of compensatory enthalpy−entropy relationships were performed, using the thermodynamic quantities reported for a wide variety of molecular recognition systems in chemistry and biology.[14,55,158,227−229] In these analyses, the $T\Delta S°$ value was linearly correlated with the $\Delta H°$ value to give eq 6. When integrated, this gives us eq 7 and subsequent combination with eq 4 affords eq 8:

$$T\Delta\Delta S° = \alpha\Delta\Delta H° \tag{6}$$

$$T\Delta S° = \alpha\Delta H° + T\Delta S_0° \tag{7}$$

$$\Delta G° = (1 - \alpha)\Delta\Delta H° \tag{8}$$

Thus, the slope (α) of the $T\Delta S°$-vs-$\Delta H°$ plot (eq 7) indicates to what extent the enthalpic gain ($\Delta\Delta H°$) induced by any alterations in host, guest, and/or solvent is canceled by the accompanying entropic loss ($\Delta\Delta S°$). In other words, only a fraction ($1 - \alpha$) of the enthalpic gain can contribute to the enhancement of complex stability. On the other hand, the intercept ($T\Delta S_0°$) represents the inherent complex stability ($\Delta G°$) obtained at $\Delta H° = 0$, which means that the complex is stabilized even in the absence of enthalpic stabilization, if the $T\Delta S_0°$ term is positive.[227,228] From comparative analyses of the thermodynamic data for cation binding by three types of ionophores (glymes, crown ethers, and cryptands) with different topologies or dimensionalities, the slope (α) and the intercept ($T\Delta S_0°$) of the regression line were related to the degree of conformational change and to the extent of desolvation upon complexation, respectively.[227,228] Using the slope (α) and intercept ($T\Delta S_0°$) as quantitative measures for changes in conformation and desolvation of both host and guest, respectively,

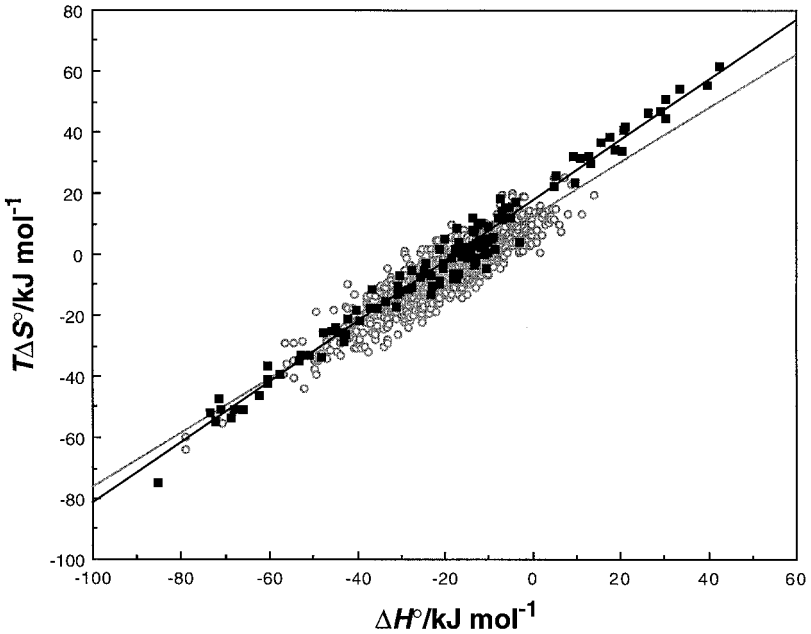


Figure 3. Enthalpy−entropy compensation plots for natural (○) and modified cyclodextrins (■). The gentle and steep regression lines correspond to natural and modified cyclodextrins, respectively.

diverse chemical and biological supramolecular systems have been analyzed consistently, although it should be noted that the weak interactions involved are quite different in each supramolecular system.[14,55,158,226−229]

In the case of natural cyclodextrins, a linear $\Delta H°-\Delta S°$ relationship has been reported in several studies.[140,198,209,230−232] A recent comprehensive study[14] has revealed that the complexation thermodynamic quantities for natural cyclodextrin afford a large slope of 0.90, which indicates that only 10% of the enthalpic gain or loss ($\Delta\Delta H°$) induced by system alterations is reflected in the net increase of the complex stability ($\Delta\Delta G°$). This is a result of the accompanying canceling entropic effect ($\Delta\Delta S°$). A lower value might be expected for the slope in view of the apparently rigid structure of cyclodextrins. However, a rearrangement of the peripheral hydrogen-bond network and the accompanying skeletal conformational changes[3,233] were considered to be responsible for such a large slope.[14] Although the results obtained for cyclodextrins may not be directly compared with those for ionophores as a result of the different species and weak interactions involved, the intercept obtained for cyclodextrin ($T\Delta S_0° = 13$ kJ mol^{-1}) is comparable to that found for crown ethers (12 kJ mol^{-1}). Thus, the entropic gain that arises from desolvation upon guest inclusion is quite significant. The release of water molecules that were originally residing within the cavity and the induced dehydration from the peripheral hydroxyl groups of cyclodextrin and the guest molecule appear to be jointly responsible for such a large intrinsic entropic gain.

The thermodynamic quantities for some cyclodextrin derivatives (**2**−**16**),[55] which generally possess flexible hydrophilic substituents, were similarly analyzed and afforded an even larger slope and intercept ($\alpha = 1.07$ and $T\Delta S_0° = 21$ kJ mol^{-1}). Although only a limited number of data sets were available in this particular case, the large slope and intercept obtained were attributed to the increased conformational changes and extensive desolvation as compared to the natural cyclodextrins.[55]

Table 5. Enthalpy−Entropy Compensation Analyses: Slopes (α) and Intercepts ($T\Delta S_0°$) of the $\Delta H°-T\Delta S°$ Plots as Quantitative Measures of the Conformational Changes and the Extent of Desolvation upon Complexation with Natural and Modified Cyclodextrins

host	α	$T\Delta S_0°$/ kJ mol^{-1}	n^a	r^b
natural cyclodextrins[c]	0.88	12	1070	0.92
α-cyclodextrin	0.79	8	524	0.90)[d]
β-cyclodextrin	0.80	11	488	0.89)[d]
γ-cyclodextrin	0.97	15	58	0.93)[d]
modified cyclodextrins[e]	0.99	17	128	0.99

[a] Number of data sets used. [b] Correlation coefficient. [c] All α-, β-, and γ-cyclodextrins included. [d] Tentative values. [e] Mostly β-cyclodextrin derivatives.

To examine the validity of the above extrathermodynamic analyses involving cyclodextrins, we plotted the complexation data accumulated in this review for natural cyclodextrins and cyclodextrin derivatives (except for some less reliable and/or inapplicable data which are marked as such—along with our reasoning—in Tables 1 and 2). As can be seen from Figure 3, both plots, which comprise more than 1000 and 100 data sets, respectively, give good to excellent linear relationships between the ΔH and $T\Delta S$ values. The slopes and intercepts calculated are distinctly different from each other, with natural cyclodextrins affording a slope α of 0.88 and an intercept $T\Delta S_0°$ of 12 kJ mol^{-1}, while modified cyclodextrins possessing flexible hydrophilic sidearm(s) give the much larger values of $\alpha = 0.99$ and $T\Delta S_0° = 17$ kJ mol^{-1} (see Table 5). These values confirm the previous conclusions made by using more limited data sets.[14,55]

As can be seen from the individual plots shown in Figure 4 and the tentatively calculated slopes and

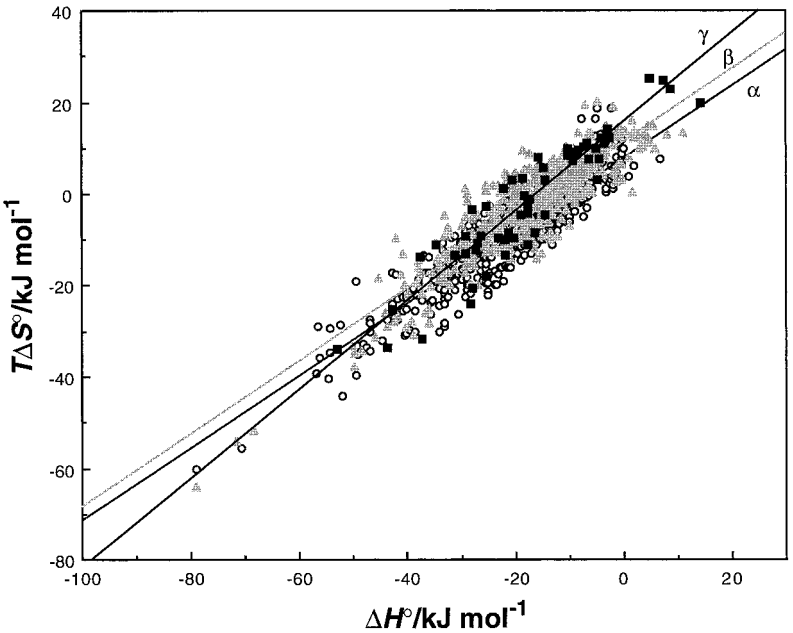


Figure 4. Individual enthalpy−entropy compensation plots for natural α- (○), β- (▲), and γ-cyclodextrins (■).

intercepts in Table 5, a more detailed analysis of the specific data for each of the α-, β-, and γ-cyclodextrins reveals interesting features concerning the conformational changes and desolvation induced by complexation with various guests. For α-, β-, and γ-cyclodextrins, the slope α increases gradually from 0.79 to 0.80 and then to 0.97 and the intercept $T\Delta S_0°$ also increases from 8 to 11 and then to 15 kJ mol^{-1} with expanding cyclodextrin ring size. These trends are consistent with a greater ring flexibility and a larger number of associated water molecules in and around the cavity of the cyclodextrin as the ring size increases. These results suggest that this extrathermodynamic relationship between $\Delta H°$ and $T\Delta S°$ may be applied globally as a conventional tool to aid our understanding of the complexation behavior of natural and modified cyclodextrins, as well as for a wide variety of ionophores,[227,228] cyclophanes/calixarenes,[55] porphyrin derivatives,[55] and other biological supramolecular systems.[158,229]

VII. Conclusions

The complexation thermodynamics of cyclodextrins have been studied using many different experimental approaches with an enormous number of guest molecules. In many cases, particularly for small organic guest molecules with simple chemical structures, reproducibility and reliability of the thermodynamic data have been confirmed by several experimental studies using various techniques. Nevertheless, the reliability of a considerable part of the thermodynamic data available still needs verification.

The global trends of the relationship between the thermodynamic quantities ($\Delta G°$, $\Delta H°$, and $\Delta S°$) for 1:1 complexation reactions, and the structural and electronic features of the guest molecules can be rationalized in terms of hydrophobicity (as measured by the number of methylene groups or Hansch's hydrophobicity constant π), the shape-matching and steric effects upon host−guest interaction, the hydrogen-bonding ability of an aromatic hydroxyl group, the position of a substituent in aromatic or aliphatic guests, and the flexibility of the guest molecule. Only that part of the guest molecule which "senses" any changes in environment such as hydrophobicity or solvation upon penetration into cyclodextrin cavity contributes appreciably to the overall complexation thermodynamics. This does not mean that the influence and interaction of the cavity and the included guest are immediately limited within the geometrical cavity. Rather, it suggests the presence of some "expanded cavity", the nature of which depends on the charged and hydrophilic groups located near the outer edges of the cavity before and after complexation, but these groups have been demonstrated not to affect the complexation thermodynamics at all.

Chiral discrimination upon complexation with cyclodextrins which are inherently chiral has also been investigated with the enantiomeric pairs of several chiral guests such as amino acids. However, appreciable differences in the thermodynamic quantities are observed with only a limited number of chiral guests. The use of modified cyclodextrins and atropisomeric guests appears to enhance the chiral discrimination.

Heat capacity data ($\Delta C_p°$) show a direct correlation between the inclusion complexation of cyclodextrin and the transfer of organic molecules from water to nonpolar organic phases that are usually considered as being "typical" hydrophobic processes. These heat capacity data are also consistent with the idea that only the part of the guest molecule undergoing appreciable desolvation makes a contribution to the overall complexation thermodynamics.

The validity of the compensatory enthalpy−entropy relationship has been examined for cyclodextrin complexation and has been shown to afford good to excellent linear plots for natural and modified cyclodextrins. The large slope (α = 0.83−0.99) and moderate intercept ($T\Delta S_0°$ = 8−17 kJ mol^{-1}) of the

$\Delta H°-T\Delta S°$ plots indicate that natural cyclodextrins and, more importantly, modified cyclodextrins undergo substantial conformational changes and that both host and guest are desolvated. The gradually increasing tendencies of the slope and intercept in these plots as the ring size and flexibility of the host increase are consistent with well-established structural features and dynamics of natural and modified cyclodextrins.

Further progress in the study of complexation thermodynamics of cyclodextrins should certainly be directed toward an expansion of the scope of reliable thermodynamic data available (particularly $\Delta C_p°$), which in turn promotes a better understanding of the nature of host−guest interactions and also of the relationship between thermodynamic quantities and structural and electronic features of guest molecules and cyclodextrins. For us, a unified picture of the diverse supramolecular molecular recognition phenomena in chemistry and biology, which includes cyclodextrin complexation, will be drawn together not only by the close examination of existing thermodynamic quantities but also through their global treatment using the extrathermodynamic relationship,[228,229] since the entropy factor and the enthalpy factor play equally crucial roles in the supramolecular interactions where the cooperative effect of several weak interactions governs the association processes.[234]

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