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Thermodynamics of inclusion complex formation between 1-alkyl-3-methylimidazolium ionic liquids and cucurbit[7]uril

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The thermodynamics of 1:1 inclusion complex formation between 1-alkyl-3-methylimidazolium type ionic liquids and cucurbit[7]uril was studied by isothermal titration calorimetry in aqueous solution at 298 K. The encapsulation proved to be enthalpy driven for all cations used. The enthalpy change upon binding (ΔH) became more negative when the 1-alkyl moiety of the imidazolium ring was gradually lengthened reaching the most exothermic association with the hexyl derivative. Further increase of the number of carbon atoms in the aliphatic chain led to less negative ΔH values. The much smaller entropy change followed the trend of ΔH. The slope of the linear enthalpy–entropy correlation found in the present work is significantly smaller than that reported previously for cyclodextrin complexes, because the more rigid CB7 macrocycle cannot undergo significant conformational change upon complexation.

Keywords: self-assembly; host-guest complex; isothermal titration calorimetry; entropy; enthalpy

1. Introduction

Due to their unique and widely tunable properties, ionic liquids have diverse applications in chemical synthesis (*1*), catalysis (*2*), electrochemistry (*3*), enzyme reactions (*4*), biomass processing (*5*) and separation techniques (*6*). Several industrial technologies have been using them as beneficial alternatives to conventional organic solvents (*7*). The negligible vapour pressure, high stability and conductivity of ionic liquids were exploited to design durable dye-sensitised solar cells (*8*), but the high viscosity of these electrolytes decreased the light-to-electricity conversion efficiency. In aqueous solutions, ionic liquids can form aggregates, micelles or microemulsion, and can be used to modify the properties of the conventional micelles (*9–11*) in a controlled fashion.

Surface-active 1-alkyl-3-methylimidazolium ($C_n mim^+$)-type ionic liquids formed 1:1 or 2:1 inclusion complexes with β-cyclodextrin depending on the length of their aliphatic chain and concentration (*12*). Such a binding enhances the solubility of both the reactants (*13*). The driving force for the encapsulation of 1-butyl-3-methylimidazolium ($C_4 mim^+$) salts in β-cyclodextrin altered with the anion indicating that the ionic liquid was incorporated as an ion pair (*14*).

The addition of a small amount of cucurbit[7]uril (CB7) or cucurbit[8]uril (CB8), the rigid macrocyclic compounds comprising seven or eight glycoluril units linked by a pair of methylene groups, brought about marked viscosity diminution in the case of 1-butyl-3-methylimidazolium tetrafluorobotate ($C_4 mim^+ BF_4^-$) (*15*). NMR and mass spectrometric studies showed that this effect arises from the encapsulation of $C_4 mim^+$ cation in the pumpkin-shaped cucurbituril macrocycles. Such host–guest complex formations were responsible for the significant solubility enhancement of cucurbiturils in the presence of imidazolium-type ionic liquids (*15*, *16*). In some cases, at least four orders of magnitude increase was observed in the solubility of cucurbit[6]uril (CB6) (*17*). 1,3-Dimethylimidazolium methylsulphonate was utilised to isolate a lid-free and charge-free CB6-diethyl ether inclusion complex (*18*). Complex formation between ionic liquid and CB7 was exploited to isolate CB[7] from a CB[5]/CB[7] mixture (*19*). Sindelar and co-workers (*20*) demonstrated that all 1-alkyl-3-methylimidazolium ions ($C_n mim^+$) produce 1:1 complex with CB6, in which the mode of binding and the electron density distribution of the imidazolium moiety strongly depend on the length of the 1-alkyl substituent.

Despite the importance of the interaction of ionic liquids with macrocyclic compounds, very few systematic studies have been performed to understand how the molecular structure of the constituents affects the strength and thermodynamics of binding. The effects of the cavity size and substituents of cyclodextrins on the equilibrium constant of the complexation of various ionic liquids were revealed by affinity capillary electrophoresis measurements (*21*). The lengthening of the alkyl chain of $C_n mim^+$ diminished the affinity to 4-sulfonatocalix[4]arene, but enhanced the stability of 4-sulfonatocalix[6]arene complexes (*22*). The inclusion of $C_n mim^+$ in CB6 led to

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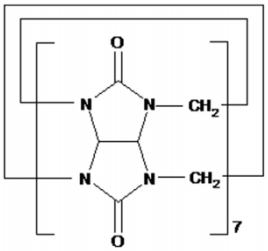
the most stable complex for the pentyl-substituted cation (*17*). Because of the very low solubility of CB6 in water, its host–guest complex formation was studied in the presence of acid or salt, which hampered the measurements of intrinsic binding properties. The larger homologue, CB7, can be used in the absence of any interfering ions.

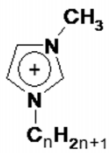
We have previously shown that the equilibrium constant of $C_n mim^+$ confinement in CB7 goes through a maximum as a function of the number of carbon atoms in the alkyl group of the imidazolium ring (*23*). To gain deeper insight into the factors governing the thermodynamics of $C_n mim^+$ inclusion in CB7, now, isothermal titration calorimetry (ITC) measurements were performed. The main objective of the present studies was to explore how the alteration of the molecular structure affects the enthalpy and entropy of $C_n mim^+$–CB7 complex formation. For the rational design of task-specific host–guest complexes, it is important to look for general trends controlling the driving force of encapsulation.

2. Experimental section

Ionic liquids and CB7 were dried in high vacuum at 333 K for 1 day prior to use. CB7 delivered by Aldrich gave identical results to those obtained with the compound synthesised and purified as described by Nau (*24*). The formulas of the investigated substances are given in Scheme 1. 1-Alkyl-3-methylimidazolium bromides ($C_n mim^+Br^-$) were synthesised as described previously (*10*). 1,3-Dimethylimidazolium dimethylphosphate (Aldrich) ($C_1 mim^+(CH_3O)_2PO_2^-$) and 1-ethyl-3-methylimidazolium chloride (Fluka) ($C_2 mim^+Cl^-$) were commercially available. Since a previous study demonstrated that the variation of the ionic liquid anions does not affect the complex stability (*23*), the corresponding bromide derivatives were not prepared. ITC measurements were performed with a MicroCal VP-ITC microcalorimeter in aqueous solutions at 298 K. In direct titrations, 5 μl of concentrated (3–6 mM) ionic liquid solutions were injected from the computer-controlled 295-μl microsyringe at an interval of 180 s into the cell (volume = 1.4569 ml) containing 0.075 mM CB7 solution, while stirring at 450 rpm. The dilution heat was determined by adding the reactant-stock solutions into water using the same number of injections and concentrations as in the titrations. In the competitive binding experiments, $C_1 mim^+(CH_3O)_2PO_2^-$ served as a competitor, whose binding constant was $7.5 \times 10^4\ M^{-1}$. The microcalorimeter cell was filled with a solution of 0.075 mM CB7 and 0.1–0.5 mM $C_1 mim^+(CH_3O)_2PO_2^-$. To this, 0.6–1 mM $C_n mim^+$ salt solutions were added. The experimental data were fitted with the one-site model using Microcal ORIGIN software. The titrations were repeated at least three times, and the deviation of the calculated binding constants and enthalpy changes are less than 6%.



Cucurbit[7]uril (CB7)



1-Alkyl-3-methylimidazolium ($C_n mim^+$)

Scheme 1.

3. Results and discussion

Since large binding constants cannot be determined precisely by direct measurements (*25*), two sets of isothermal calorimetric titration experiments were performed. The enthalpy change was determined both in direct titrations, by adding the solution of $C_n mim^+$ salts into 0.075 mM CB7 in water, and in competitive binding experiments injecting the solution of $C_n mim^+$ salts into the aqueous solution of CB7 and $C_1 mim^+$.

Figure 1(A) and (B) displays a typical result for the titration of CB7 by $C_3 mim^+$. The raw ITC data (Figure 1(A)) show the amount of heat produced per second following each injection of $C_3 mim^+$ stock solution as a function of time. As successive amounts of the ligand are added into the ITC cell, the quantity of released heat is in direct proportion to the amount of binding. The CB7 macrocycle becomes saturated with $C_3 mim^+$, and therefore, the signal diminishes until only the background heat of dilution is observed. The integrated heat evolved per injection, after taking into account heat of dilution, was divided by the mole number of injectant, and the result is presented as a function of $[C_3 mim^+]/[CB7]$ concentration ratio in Figure 1(B). In competitive binding experiments, $C_1 min^+$ was used as a competing ligand with a concentration chosen such as $10^{-6}\ M \times K/K_{ref} < [C_1 min^+] < 10^{-5}\ M \times K/K_{ref}$, where K/K_{ref} denotes the ratio of the equilibrium constants for $C_n mim^+$ and $C_1 min^+$ confinement in CB7. Figure 1(C) and (D) displays a typical result obtained in the titration of CB7/$C_1 min^+$ mixture with $C_6 mim^+$ solution. Nonlinear least-squares analysis of the experimental data gave the apparent binding constants (K_{app}) and enthalpy change (ΔH_{app}). From these, the K and ΔH values, listed in Table 1, were deduced as described by Sigurskjord (*26*). In the calculations, $K_{ref} = 7.5 \times 10^4\ M^{-1}$ and

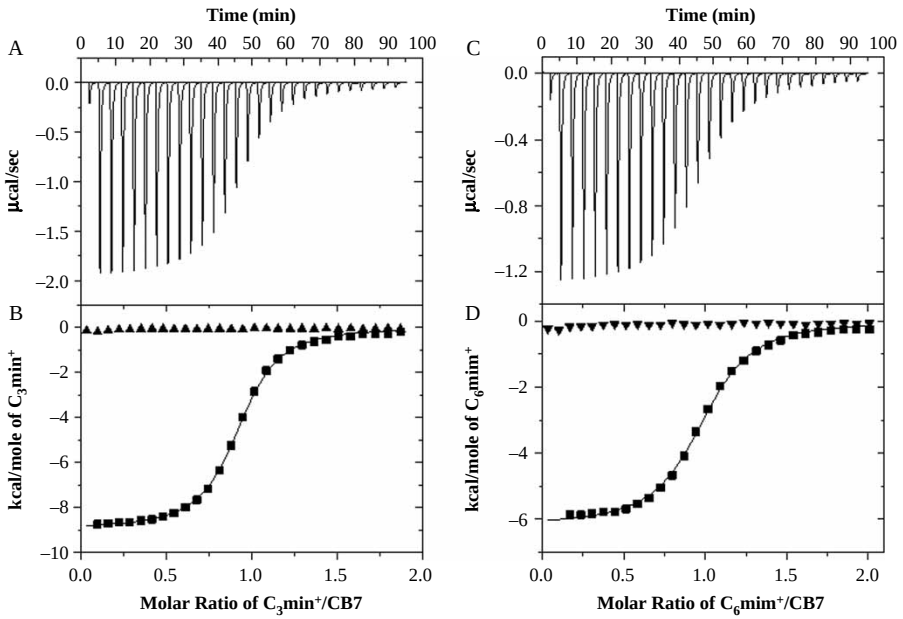


Figure 1. Raw ITC data for the titration of 0.075 mM CB7 solution by 0.68 mM C_3mim^+ solution (A) and for the titration of the mixture CB7 (0.070 mM)/C_1mim^+(0.54 mM) by 0.64 mM C_6mim^+ solution (C). The integrated heat evolved per injection (■) for the titration of CB7 by C_3mim^+ (B) and for the titration of CB7/C_1mim^+ mixture by C_6mim^+ (D). The lines represent the results of the fit of the one-site model, whereas (▲) shows the integrated heat released per injection for ionic liquid addition into water.

Table 1. Stoichiometry of binding, stability constants and thermodynamic parameters for the inclusion complex formation of 1-alkyl-3-methylimidazolium-type ionic liquids with cucurbit[7]uril in aqueous solution at 298 K.

Ionic liquid	n	$K(10^6\ M^{-1})$	ΔG (kJ mol^{-1})	ΔH^a (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
C_1mim^+ $(CH_3O)_2PO_2^-$	0.79[b]	0.075[c]	−27.8	−21.1	22.5
$C_2mim^+Cl^-$	0.94	0.304	−31.3	−28.9 (−33.6)	7.9
$C_3mim^+Br^-$	0.91	2.24	−36.2	−37.5 (−37.6)	−4.2
$C_4mim^+Br^-$	0.94	6.92	−39.0	−40.7 (−40.7)	−5.7
$C_6mim^+Br^-$	0.96	20.4	−41.7	−45.7 (−46.3)	−13.5
$C_8mim^+Br^-$	0.93	11.1	−40.2	−43.8 (−43.4)	−12.0
$C_9mim^+Br^-$	0.89	5.46	−38.4	−41.1 (−42.6)	−9.0
$C_{10}mim^+Br^-$	0.96	2.87	−36.8	−36.9 (−38.4)	−0.3
$C_{12}mim^+Br^-$	0.95	1.43	−35.1	−32.3 (−34.5)	9.4
$C_{14}mim^+Br^-$	1.00	1.22	−34.7	−30.8 (−34.9)	12.3

[a] Values in parenthesis are from competitive binding experiments.
[b] The lower value is due to the somewhat larger experimental uncertainties originating from the very hygroscopic character of this ionic liquid.
[c] From reference (*23*).

$\Delta H_{ref} = 21.45$ kJ mol^{-1} were used for the equilibrium constant and the enthalpy change of C_1min^+–CB7 complex formation, respectively. The K_{ref} value was obtained from previous work (*23*), whereas ΔH_{ref} is the mean of the results of direct ITC titrations. As seen in Table 1, the ΔH values derived from direct and competitive binding titrations are in good agreement. Similar comparison cannot be made for ΔS and K values because large binding constants cannot be determined by direct measurements. In accordance with previous findings (*23*), calorimetric measurements also confirmed that all C_nmim^+ produced 1:1 host–guest complex with CB7 under our experimental conditions. The reaction stoichiometry (n), determined by nonlinear least-squares analysis of the experimental data, is given in Table 1.

In Figure 2, the equilibrium constants of C_nmim^+–CB7 complex formation obtained by calorimetric method are compared to those found previously using a fluorescent probe (*23*). The results of the two types of measurements agree well. K values go through a maximum when the 1-alkyl group is lengthened reaching the highest value in the case of the hexyl derivative.

The thermodynamic data in Table 1 clearly show that more than two orders of magnitude change of the binding constants arises from the alteration of the reaction enthalpy. The enthalpic (ΔH) and entropic contributions ($T\Delta S$) to the

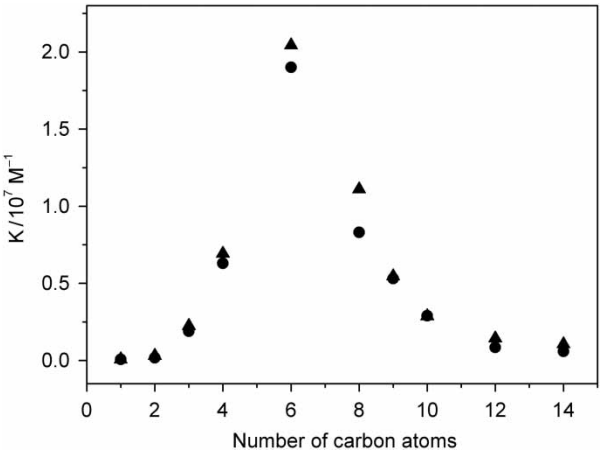


Figure 2. Alteration of the equilibrium constant of $C_n mim^+$ encapsulation in CB7 as a function of the number of carbon atoms in the 1-alkyl chain. Results of calorimetric measurements are represented by (▲). Data determined by fluorescence titrations (*23*) are represented by (●).

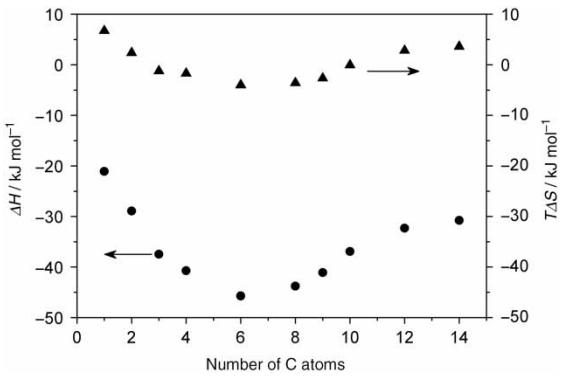


Figure 3. Enthalpic (●) and entropic (▲) contributions to the driving force of $C_n mim^+$ encapsulation in CB7 as a function of the number of carbon atoms in the 1-alkyl chain.

driving force of complexation are displayed in Figure 3. The inclusion in CB7 is always exothermic; the reaction entropy is small and varies only slightly with the structure of the ionic liquid cations. The smallest enthalpy gain is found for the embedment of the most hydrophilic C_1mim^+. However, even in this case, the energy needed for the desolvation of the guest and for the extrusion of water from the macrocycle is significantly overcompensated by the energy gained from the host–guest interactions. The gradual lengthening of the alkyl substituent from methyl to hexyl brings about a substantial ΔH diminution, whereas further extension of the carbon chain reduces the exothermicity of inclusion. Finally, the change levels off for $C_{12}mim^+$ and $C_{14}mim^+$. Two major effects stabilise $C_n mim^+$–CB7 complexes. (i) Because the 1-alkyl group of the cations is preferentially embedded in the apolar interior of CB7, the hydrophobic and van der Waals host–guest interactions are strengthened by the increase of the number of aliphatic carbon atoms until the alkyl chain can be fully confined in the macrocycle. The desolvation energy is low because water is weakly coordinated both to the apolar CB7 cavity and to the 1-alkyl group of the guest, and (ii) on the other hand, the imidazolium ring interacts with the negatively charged carbonyl-rimmed portal of CB7. The fairly negative ΔH even for the embedment of C_1mim^+ indicates the significant contribution of this interaction to the stabilisation of the complex.

When the alkyl chain is lengthened, the position of imidazolium moiety probably changes analogously to that reported for the corresponding CB6 complexes (*20*). Sindelar and co-workers showed that both the ethyl and imidazolium moieties of C_2mim^+ are confined in CB6. In this complex, the electron density in the imidazolium ring is shifted towards the ethyl-substituted nitrogen (N1), whereas the positive charge density is enhanced on the nitrogen bearing the methyl substituent (N3) owing to the ion–dipole interactions with the portal of CB6 (*20*). In the case of C_3mim^+, C_4mim^+ and C_5mim^+, the 1-alkyl group is embedded in the CB6 cavity as a result of hydrophobic effects, while the imidazolium ring remains outside the host. The electron density is shifted from the N1 towards N3 nitrogen due to the interaction with the carbonyls at the rim of the macrocycle, while the positive charge of the imidazolium ring is partially localised on the nitrogen linked to 1-alkyl chain (*20*). Scherman and co-workers (*17*) found that for C_7mim^+ and C_8mim^+ complexes the whole heptyl or octyl group is located inside CB6 because these moieties do not adopt a fully extended conformation. It was also shown that the dodecyl chain of $C_{12}mim^+$ is not fully buried in CB6 (*17*). In the course of the study of dodecyltrimethylammonium–CB7 complex, Kim and co-workers (*27*) observed NMR signal shift only for the methylene protons in the C1–C7 positions, whereas negligible chemical shift change appeared for the terminal part (C8–C12) of the alkyl moiety indicating that the dodecyl chain cannot fold back into the cavity of CB7. Such a U-shaped conformation is produced only in CB8 (*27*).

On the basis of the knowledge available from previous studies, we suggest that the diminution of the exothermicity for $C_n mim^+$ inclusion in CB7 going from hexyl to tetradecyl derivatives is attributed to the conformation alteration of the encapsulated segment of the alkyl moiety, which leads to a less tight fit. An aliphatic chain comprised of more than six carbon atoms cannot be accommodated in CB7 in all-*trans* configuration. To ensure the embedment of a larger part of the alkyl group, conformation rearrangement is likely to occur, leading to somewhat weaker host–guest interaction for $C_n mim^+$ substituted with a longer carbon chain ($n > 6$). When the encapsulated fraction of the alkyl group cannot be increased by conformation change, further extension of the

methylene chain does not affect ΔH, as it is observed for $C_{12}mim^+$ and $C_{14}mim^+$.

The knowledge of the reaction enthalpy (ΔH) and the binding constant (K) enabled the calculation of the standard free enthalpy (ΔG) and entropy changes (ΔS) upon binding (Table 1) according to the equation

$$\Delta G = -RT \ln K = \Delta H - T\Delta S, \quad (1)$$

where R is the gas constant and T is the temperature. The remarkably small entropy change (ΔS) for the formation of all $C_n mim^+$–CB7 complexes (Table 1) indicates that the entropic loss originating from association is balanced by the entropic gain from the desolvation of the reactants. When the alkyl chain is lengthened from methyl to hexyl, the binding entropy slightly decreases from positive to negative. Although a larger guest is able to expel more water from CB7, the thereby achieved entropy advantage is outweighed by the following factors: (i) $C_n mim^+$ comprising a bulkier 1-alkyl group is less solvated, therefore, less water molecules are released from its solvation shell upon encapsulation; and (ii) the larger ion has more degrees of freedom to be limited by inclusion in CB7. The slight dominance of the latter two effects causes ΔS diminution in the series from C_1mim^+ to C_6mim^+. The small increase of ΔS for the derivatives with longer carbon chain is due to the enhanced mobility developed by the weakening of the host–guest interactions.

The ΔH alteration as a function of aliphatic chain length in the case of $C_n mim^+$–CB7 complex qualitatively resembles that reported for the inclusion of alkylammonium ($C_nNH_3^+$) guests in CB6 (*28*, *29*), or in its water-soluble derivative, cyclohexanocucurbit[6]uril (*30*). Since the encapsulation in CB6 was studied in the presence of inorganic salt to enhance the solubility, the thermodynamics of $C_nNH_3^+$–CB6 complex formation significantly differed from that found for $C_n mim^+$–CB7 in the present work due to the competitive binding of inorganic cations to CB6. The association with cyclohexanocucurbit[6]uril was examined without such an interference (*30*), and the most exothermic reaction was found with $C_4NH_3^+$ and $C_5NH_3^+$. In these cases, ΔH is about 4 kJ mol^{-1} more negative compared to that of C_6mim^+–CB7 formation because of the tighter embedment in the smaller macrocycle. Despite the same height of cyclohexanocucurbit[6]uril and CB7, the larger space inside the latter compound allows more deviation from the fully extended conformation for the guest facilitating inclusion of longer aliphatic chain. This explains why the length of the carbon chain differs for the most stable $C_nNH_3^+$–cyclohexanocucurbit[6]uril and $C_n mim^+$–CB7 complexes.

Enthalpy–entropy compensation has been observed for a wide variety of binding phenomena (*31*) because a strong interaction characterised by a large enthalpic benefit usually limits the movement of the reactants

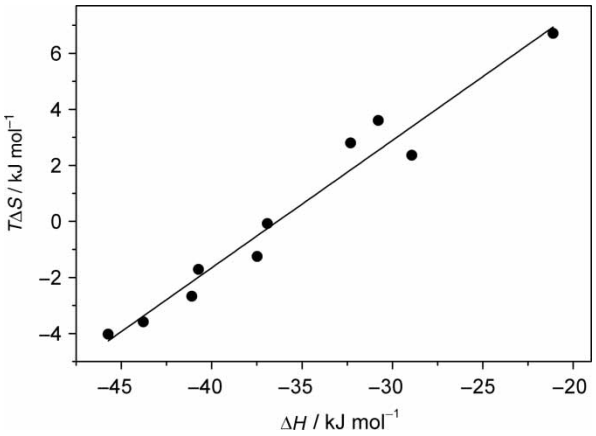


Figure 4. Enthalpy–entropy compensation plot for $C_n mim^+$ inclusion in CB7 in aqueous solution at 298 K.

leading to a substantial loss of entropy. In contrast to the lack of enthalpy–entropy compensation for the formation of $C_nNH_3^+$–cyclohexanocucurbit[6]uril and $C_nNH_3^+$–CB6 inclusion complexes (*28*, *30*), a good linear correlation appears between the enthalpy and entropy terms obtained in this study (Figure 4):

$$T\Delta S = \alpha \Delta H + T\Delta S_0. \quad (2)$$

The slope (α) of the plot reflects to what extent the enthalpy change induced by the alteration of the aliphatic chain length is cancelled by the accompanying entropic loss (*30*). The positive intercept ($T\Delta S_0$) indicates that the complex is stabilised even in the absence of enthalpic contribution to the driving force. The $T\Delta S_0$ value of 16.5 kJ mol^{-1}, calculated by a linear least-squares fit of the experimental data, is attributed primarily to the entropy gain from the release of water molecules from the CB7 cavity and the solvation shell of the reactants. It is noteworthy that almost the same $T\Delta S_0$ value (15 kJ mol^{-1}) was found in the analysis of the thermodynamic parameters of γ-cyclodextrin complexes (*33*). When the ring size was decreased, $T\Delta S_0$ values of 11 and 8 kJ mol^{-1} were obtained for β- and α-cyclodextrin complexes, respectively, implying that less water molecules can be expelled from a smaller cavity upon inclusion of a guest. For the slope of ΔH vs. $T\Delta S$ correlation, α values of 0.97, 0.80 and 0.79 were reported in the case of γ-, β-, and α-cyclodextrin complexes, respectively (*33*). These α values are much larger than that found for $C_n mim^+$–CB7 complexes ($\alpha = 0.45$) in the present study (Figure 4). This difference arises from the rigidity of CB7 macrocycle, which hinders any significant conformational change of the host upon complexation. In contrast, the large α values for cyclodextrin complexes indicate considerable reorganisation of the original hydrogen-bond network upon inclusion of a guest (*32*). A recent computational study of host–guest complexation also found different trends for

β-cyclodextrin and CB7 complexes and suggested that the comparatively flexible former host loses more internal entropy on binding, while the rigid CB7 leads to a greater loss of rotational and translational entropy on binding (*34*).

The ΔH value of C_8mim^+ insertion into CB7 ($-43.8\,kJ\ mol^{-1}$) is very close to that reported for L-phenylalanine–CB7 complex formation ($-43.4\,kJ\ mol^{-1}$) (*35*), but $T\Delta S$ values differ by a factor 1.8 (values of -4.3 and $-7.7\,kJ\ mol^{-1}$ in the former and latter cases, respectively). The smaller entropy loss for C_8mim^+ confinement is probably ascribed to the more substantial desolvation of the CB7 portal promoted by the more hydrophobic and bulkier methylimidazolium head group.

It is worth comparing the thermodynamic quantities of C_6mim^+–CB7 and 1,6-hexanediammonium–CB7 complexes. The formation of the latter species is associated with large enthalpy and entropy gains ($\Delta H = -32.9\,kJ\ mol^{-1}$ and $T\Delta S = 20.3\,kJ\ mol^{-1}$) at 298 K (*35*). Interestingly, the formation of the less stable complex, C_6mim^+–CB7, is more exothermic ($\Delta H = -45.7\,kJ\ mol^{-1}$) but accompanied by a slight entropy diminution ($T\Delta S = -4.2\,kJ\ mol^{-1}$). These data demonstrate that the *ca*. 2 orders of magnitude larger stability constant of 1,6-hexanediammonium–CB7 complex is due to the substantial entropy increase, which probably results from the release of water molecules from the hydrate shell of the ammonium moieties. Such a process is much less important for C_6mim^+ because of the more hydrophobic character of methylimidazolium group. The less negative ΔH value of 1,6-hexanediammonium–CB7 formation compared to that of C_6mim^+–CB7 may partly arise from the larger energy needed for the desolvation of the ammonium moieties. On the other hand, the position of the polarisable imidazolium ring within C_6mim^+–CB7 complex is not so crucial for strong interaction with the carbonyl-rimmed portals. In contrast, the charge localised on nitrogen of the ammonium moiety should be situated in close vicinity and right orientation to a carbonyl group of the macrocycle for strong 1,6-hexanediammonium–CB7 binding. It is difficult to reach the optimal ion–dipole distance for both ammoniums simultaneously with the maximal hydrophobic interactions between the methylene chain and the inner wall of the host.

4. Conclusions

The results of ITC measurement demonstrated that the inclusion of C_nmim^+ in CB7 is enthalpically driven and the entropy change is close to zero. Both ΔH and ΔS of the process go through a minimum as a function of the number of carbon atoms in the aliphatic chain of the guest reaching the smallest values for the hexyl derivative. On the basis of these results, CB7 is expected to decrease the viscosity most efficiently in the case of ionic liquids comprised of C_6mim^+ cation. The interaction of the head group with the carbonyl-fringed portal of the macrocycle and the hydrophobic interaction of the methylene chain with the inner wall of the cavity have comparable contribution to the enthalpy change in the formation of C_6mim^+–CB7 complex.

The extent of enthalpy–entropy compensation is smaller for C_nmim^+–CB7 than for cyclodextrin complexes because the more rigid CB7 macrocycle cannot undergo significant conformational change upon binding of a guest. The inflexibility of CB7 allows limited structural rearrangement in the course of complex formation. Therefore, stronger binding of a guest does not lead to considerable entropy penalty. This may explain why even uncharged guests produce more stable complexes with cucurbiturils than with cyclodextrins, whose complexation is accompanied by substantial reorganisation of the original hydrogen-bond network.

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