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On the hydration heat capacity change of benzene

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Abstract

The heat capacity change associated with the hydration of benzene is a large and positive quantity, but it is significantly smaller than that associated with the hydration of an alkane having the same accessible surface area of benzene, the corresponding alkane. This large difference merits attention and should be rationalized. This task is performed by means of the two-state Muller's model for the reorganization of H-bonds. It results that: (a) the hydration shell of both hydrocarbons consists of H-bonds that are enthalpically stronger but slightly more broken than those in bulk water; (b) the hydration shell of benzene consists, on average, of enthalpically slightly weaker H-bonds with respect to the corresponding alkane. The latter feature, due to the presence of the weak benzene–water H-bonds, is the physical cause of the large difference in the hydration heat capacity change, according to the two-state Muller's model.

Keywords: Hydration heat capacity change; Reorganization of H-bonds; Two-state Muller's model; Accessible surface area

1. Introduction

The hydration thermodynamics of benzene shows a fundamental difference with respect to that of alkanes [1–3]: the Ben-Naim standard Gibbs energy change $\Delta G^{\bullet}$ of benzene is negative over a large temperature range, whereas it is always large and positive for alkanes (note that the Ben-Naim standard refers to the transfer of a solute from a fixed position in the gas phase to a fixed position in water [4]). In other words, under the Ben-Naim standard conditions, the hydration of benzene is a favourable process, whereas the hydration of alkanes is an unfavourable process. This difference can be treated on a quantitative basis by considering a corresponding alkane, a hypothetical alkane having the same accessible surface area (ASA) of benzene, as put forward by Makhatadze and Privalov [1]. I have recently performed an analysis to explain the physical origin of the qualitative difference in $\Delta G^{\bullet}$ values between benzene and the corresponding alkane [5].

A further quantitative difference exists between the hydration thermodynamics of benzene and that of alkanes. The hydration heat capacity change of the latter is significantly larger than that of benzene. Specifically, using always the corresponding alkane for comparison, at 25 °C, $\Delta C_p^{\bullet}$=292 J $K^{-1}mol^{-1}$ for benzene and 384 J $K^{-1}mol^{-1}$ for corresponding alkane [1]. Note that the $\Delta C_p^{\bullet}$ values of the corresponding alkane are reliable because the ratio $\Delta C_p^{\bullet}$/ASA is a constant quantity for alkanes and alkyl chains at the several investigated temperatures [6]. Such a large difference in $\Delta C_p^{\bullet}$, about 30%, holds over the whole temperature range 5–100 °C (see Table 1), and should merit attention.

The large and positive $\Delta C_p^{\bullet}$ associated with the hydration of nonpolar solutes is mainly due to the structural reorganization of water molecules occurring as a response to solute insertion [7–10]. The structural reorganization should correspond to a reorganization of H-bonds among the water molecules constituting the hydration shell. Such H-bond reorganization can be treated by means of the two-state Muller's model [11,12].

In the present study, the Muller's model is used to try to reproduce the $\Delta C_p^{\bullet}$ values of benzene and corresponding alkane over the temperature range 5–100 °C. Since no one

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Table 1
Values of $\Delta C_p^\bullet$ for benzene and corresponding alkane over the range 5–100 °C are listed in the second and fourth columns

T (°C)	Benzene		Corresponding alkane	
	$\Delta C_p^\bullet$ (J K^{-1}mol^{-1})	ΔH^h (kJ mol^{-1})	$\Delta C_p^\bullet$ (J K^{-1}mol^{-1})	ΔH^h (kJ mol^{-1})
5	319	6.9	407	−0.9
25	292	13.0	384	6.8
50	268	20.0	354	16.2
75	248	26.4	331	24.8
100	231	32.4	305	32.8

Estimates of the enthalpy contribution due to H-bond reorganization for benzene and corresponding alkane are listed in the third and fifth columns. The ΔH^h estimates are obtained as $\Delta H^h = \Delta H^\bullet - E_a$, where E_a is considered temperature independent, and $E_a = -42.6$ kJ mol^{-1} for benzene, and −31.0 kJ mol^{-1} for the corresponding alkane (see Refs. [1,5] for further details on the $\Delta H^\bullet$ and E_a values, respectively; note that $\Delta H^\bullet = 1.8$ kJ mol^{-1} at 100 °C for corresponding alkane, and not −23.2 kJ mol^{-1}, as erroneously listed in Table 1 of Ref. [5]).

of the several generated models perfectly reproduces the experimental $\Delta C_p^\bullet$ data, the temperature dependence of $\Delta C_p^\bullet$ is considered to be the right criterion to select the model closer to reality. Application of this criterion leads to the following conclusions: (a) the H-bonds in the hydration shell of both hydrocarbons are enthalpically stronger but slightly more broken than those in bulk water; (b) the H-bonds in the hydration shell of benzene are, on average, enthalpically slightly weaker than those in the hydration shell of corresponding alkane; (c) the latter, according to the two-state Muller's model, is the cause of the quantitative difference in $\Delta C_p^\bullet$ existing between the two hydrocarbons.

2. Theory section

A general theory for the hydration of nonpolar compounds leads to the following expressions for the hydration enthalpy and heat capacity changes [13–18]:

$$\Delta H^\bullet = E_a + \Delta H^h \tag{1}$$

$$\Delta C_p^\bullet = (\partial E_a/\partial T) + \left(\partial \Delta H^h/\partial T\right) \tag{2}$$

where the superscript filled circle denotes the Ben-Naim standard; E_a is the ensemble average value of the direct solute–water interaction energy and ΔH^h is the enthalpy contribution due to the reorganization of H-bonds upon solute insertion into water. By recognizing that the E_a quantity has a small temperature dependence because the density of liquid water decreases by only 4% over the range 0–100 °C [19], Eq. (2) becomes:

$$\Delta C_p^\bullet \cong \left(\partial \Delta H^h/\partial T\right) = \Delta C_p^h \tag{3}$$

which means that the hydration heat capacity change is mainly due to the reorganization of H-bonds. The validity of Eq. (3) is supported by the finding that the transfer heat capacity change, normalized per nonpolar ASA, is a universal quantity, regardless of the chemical compounds and originating phase [8]. Therefore, in order to account for the large and positive $\Delta C_p^\bullet$ values associated with the hydration of nonpolar compounds, one needs a theoretical model to treat the reorganization of H-bonds. The latter can be treated in a simple but reliable manner by means of the model developed by Muller [11,12], who extended a previous approach devised by Angell [20]. The Muller's model was further modified by Lee and Graziano [15]; this version, which has gained attention and reliability [21–24], is spelled out in detail below to avoid ambiguities.

A two-state equilibrium holds for the H-bonds in bulk water:

$$\mathrm{H-bond\ (intact)} \Leftrightarrow \mathrm{H-bond\ (broken)}. \tag{4}$$

Each of these states is considered to be a thermodynamic state with definite enthalpy and entropy values. Liquid water is characterized by the enthalpy and entropy differences between the two states, ΔH_b° and ΔS_b°, respectively; the subscript b refers to the bulk water. The equilibrium between the two states is governed by the constant K_b:

$$K_b = f_b/(1-f_b) = \exp(-\Delta G_b^\circ/RT) \tag{5}$$

where f_b is the fraction of broken H-bonds, $\Delta G_b^\circ \equiv \Delta H_b^\circ - T\Delta S_b^\circ$, and R and T are the gas constant and the absolute temperature, respectively. Assuming that ΔH_b° and ΔS_b° are temperature independent, the two-state equilibrium gives the following contribution to the heat capacity per each H-bond of the system:

$$C_{p,b} = (\Delta H_b^\circ)^2 f_b(1-f_b)/RT^2. \tag{6}$$

Angell [20] found $\Delta H_b^\circ = 7.95$ kJ mol^{-1} and $\Delta S_b^\circ = 20.1$ J K^{-1}mol^{-1}, performing a best-fit of the configurational heat capacity of water, as defined by Eisenberg and Kauzmann [25]. Muller adopted a different procedure and obtained different values [11,12]. Since Silverstein, Haymet and Dill [22] have recently shown that the Angell's parameters for bulk water produce f_b values equal to those derived by a careful analysis of the Raman spectra of liquid water [26], the bulk parameters selected by Angell are used in the present study.

The two-state equilibrium of Eq. (4) holds also for the H-bonds in the hydration shell of a solute, again characterized by the two temperature independent parameters ΔH_{hs}° and ΔS_{hs}°. The corresponding equilibrium constant and heat capacity contributions are:

$$K_{hs} = f_{hs}/(1-f_{hs}) = \exp(-\Delta G_{hs}^\circ/RT) \tag{7}$$

$$C_{p,hs} = (\Delta H_{hs}^\circ)^2 f_{hs}(1-f_{hs})/RT^2 \tag{8}$$

where the subscript hs stands for the hydration shell. However, the values of ΔH_{hs}° and ΔS_{hs}° cannot be determined from these equations because the values of $C_{p,hs}$ and f_{hs} are unknown.

The differences in the H-bonding states between the bulk and the hydration shell water will contribute to the hydration heat capacity, enthalpy and entropy changes, which are experimentally measurable quantities. Three additional parameters are needed to compute these contributions: one is n^h, the number of H-bonds in the hydration shell; the other two are ΔH_U and ΔS_U, the enthalpy and entropy, respectively, of the upper state in the hydration shell relative to that in the bulk. Thus, one obtains [15]:

$$\Delta C_p^h = n^h\left[C_{p,hs} - C_{p,b}\right] \tag{9}$$

$$\Delta H^h = n^h[\Delta H_U - (1-f_{hs})\Delta H_{hs}^\circ + (1-f_b)\Delta H_b^\circ] \tag{10}$$

$$\Delta S^h = n^h[\Delta S_U - (1-f_{hs})\Delta S_{hs}^\circ + (1-f_b)\Delta S_b^\circ - R\Delta F] \tag{11}$$

where the superscript h indicates the H-bonding contribution. In Eq. (11), $\Delta F = F_{hs} - F_b$, with $F_b = f_b \ln f_b + (1-f_b)\ln(1-f_b)$, and F_{hs} similarly defined for the hydration shell. Clearly, according to Eq. (9), the molecular mechanism producing a large and positive heat capacity change upon hydration of nonpolar molecules is a reorganization of H-bonds between two H-bonded networks, the bulk water and the hydration shell, in complete agreement with the ideas put forward by Cooper [27].

Muller determined n^h assuming that each water molecule in the hydration shell points in three tetrahedral directions tangentially to the nonpolar surface and the last one radially to the bulk [11,12]. Therefore, the number of H-bonds in the hydration shell $n^h = 3 \cdot N_{H_2O}/2$, where N_{H_2O} is the number of water molecules in the hydration shell. The latter can be estimated from: (a) the ratio of the ASA of the solute to the surface of a water molecule; (b) Monte Carlo or molecular dynamics, MD, computer simulations. Using the first route, Privalov and Gill obtained $N_{H_2O} = 26.7$ for benzene [28], in agreement with the value determined by Linse [29], from MD simulations of benzene in TIP4P water [30]. In the present study, it is used $N_{H_2O} = 26.7$ for both benzene and corresponding alkane.

The Muller's model, as modified by Lee and Graziano [15], has seven parameters: the values of ΔH_b° and ΔS_b° are fixed; n^h is known for a given solute; the remaining four parameters, ΔH_{hs}°, ΔS_{hs}°, ΔH_U and ΔS_U, are related to each other by three equations, Eqs. (9)–(11). Since the model is underdetermined, a set of models will be generated, each corresponding to a particular value of a selected parameter, which is ΔH_U. On the other hand, ΔS_U is obtained using Eq. (11) and the compensation relation:

$$\Delta H^h = T \cdot \Delta S^h \tag{12}$$

which means that the reorganization of H-bonds is a perfectly compensating process at all temperatures [31–35]. To satisfy Eq. (12), ΔS_U has to depend on temperature [36–38].

Once the seven parameters are determined at 25 °C, the values for ΔC_p^h, ΔH^h and ΔS^h at any other temperature can be obtained from the temperature dependence of f_b and f_{hs} according to Eqs. (5), (7) and (9–12). The fundamental quantity is ΔC_p^h because it represents the temperature dependence of ΔH^h, and the latter function determines ΔS^h via Eq. (12). For this reason, and to improve the clarity of the results, I have reported solely the values of ΔC_p^h and f_{hs} for each of the generated models.

3. Results and discussion

The values, at 25 °C, of $\Delta C_p^\bullet$ (in J K^{-1}mol^{-1}) = 292 and 384, and ΔH^h (in kJ mol^{-1}) = 13.0 and 6.8 for benzene and the corresponding alkane, respectively, together with $n^h = 3 \cdot 26.7/2$, are the starting point to determine the hydration shell parameters ΔH_{hs}° and ΔS_{hs}°. The parameter values obtained by varying ΔH_U (in kJ mol^{-1}) over the range −0.5–2.0 are listed in Table 2 for benzene, and Table 5 for the corresponding alkane. Such ΔH_{hs}° and ΔS_{hs}° values are then used to calculate the ΔC_p^h and f_{hs} functions over the range 5–100 °C. The calculated numbers are reported in Tables 3 and 4 for benzene, and in Tables 6 and 7 for the corresponding alkane. Inspection of such tables indicates that no one of the several models is able to reproduce with accuracy the experimental $\Delta C_p^\bullet$ values for both benzene and corresponding alkane over the whole temperature range 5–100 °C. This failure is not unexpected in view of the simplicity of the Muller's model, and the fundamental assumption that all the parameters, except ΔS_U, are temperature independent quantities.

To select the model that is closer to reality, one can use a qualitative feature of the experimental data: the $\Delta C_p^\bullet$ values of both benzene and corresponding alkane decrease in a continuous and monotonous manner over the range 5–100 °C [1]. This is a general feature of the heat capacity change associated with hydrophobic hydration [39–43]. Using this criterion to select the model which is closer to reality, one finds that a model characterized by $0.5 < \Delta H_U$ (in kJ mol^{-1}) < 1.0 could be a reasonable choice for both benzene and corresponding alkane, even though the ΔC_p^h values

Table 2
Parameter values of the Muller's model for benzene calculated as a function of ΔH_U, by assuming for bulk water the parameters determined by Angell (i.e., $\Delta H_b^\circ = 7.95$ kJ mol^{-1} and $\Delta S_b^\circ = 20.1$ J K^{-1}mol^{-1}); $n^h = 3 \cdot N_{H2O}/2 = 1.5 \cdot 26.7$, and, at 25 °C, $\Delta C_p^h = \Delta C_p^\bullet = 292$ J K^{-1}mol^{-1}, $\Delta H^h = \Delta H^\bullet - E_a = -29.6 - (-42.6) = 13$ kJ mol^{-1} and $\Delta S^h = \Delta H^h/T$

ΔH_U (kJ mol^{-1})	f_{hs} at 25 °C (%)	ΔH_{hs}° (kJ mol^{-1})	ΔS_{hs}° (J K^{-1}mol^{-1})	ΔS_U at 25 °C (J K^{-1}mol^{-1})
−0.5	46.8	8.73	28.20	1.7
0	41.8	8.83	26.85	2.4
0.5	37.3	9.00	25.89	3.2
1.0	33.4	9.23	25.23	3.9
1.5	30.1	9.50	24.83	4.7
2.0	27.1	9.80	24.63	5.5

Table 3
Estimates of ΔC_p^h for benzene calculated using the parameter values for the hydration shell listed in Table 2; $\Delta C_p^h[0.5]$ means the values of ΔC_p^h for ΔH_U=0.5 kJ mol^{-1}

T (°C)	$\Delta C_p^\bullet$	ΔC_p^h [−0.5]	ΔC_p^h [0]	ΔC_p^h [0.5]	ΔC_p^h [1.0]	ΔC_p^h [1.5]	ΔC_p^h [2.0]
5	319	377	348	**321**	297	275	254
25	292	292	292	**292**	**292**	292	292
50	268	196	220	244	**266**	288	309
75	248	119	157	194	**230**	**266**	301
100	231	63	106	150	192	**235**	279

The values of $\Delta C_p^\bullet$ are reported for comparison purposes. All the heat capacity values are in J K^{-1}mol^{-1} units; those in bold give rise to the "combined" ΔC_p^h function.

decrease too rapidly with temperature compared to the experimental ones. In this respect, it is worth noting that a nonlinear regression of experimental $\Delta C_p^\bullet$ data with respect to Eq. (9) does not produce a good fit, for both benzene and corresponding alkane. In particular, the best-fit ΔC_p^h function does not decrease in a continuous and monotonous manner over the range 5–100 °C (results not shown). Nevertheless, I would like to show that it is possible to gain a physico-chemical interpretation from the application of the Muller's model.

By considering together the three models characterized by ΔH_U (in kJ mol^{-1})=0.5, 1.0 and 1.5, one can construct a "combined" ΔC_p^h function which is in satisfactory agreement with the experimental $\Delta C_p^\bullet$ data over the whole range 5–100 °C for both benzene (see Fig. 1), and corresponding alkane (see Fig. 2). In both cases, one can use $\Delta C_p^h[0.5]$ over 5–25 °C, $\Delta C_p^h[1.0]$ over 25–75 °C and $\Delta C_p^h[1.5]$ over 75–100 °C (note that $\Delta C_p^h[0.5]$ means the ΔC_p^h values calculated with the model characterized by ΔH_U=0.5 kJ mol^{-1}). All the three models, in the respective temperature ranges where each is able to reproduce the $\Delta C_p^\bullet$ data, are characterized by $f_{hs}>f_b$ (see Tables 4 and 7). The H-bonds in the hydration shell of both benzene and corresponding alkane are enthalpically stronger but slightly more broken than those in bulk water (see Tables 2–7). This result is in line with (a) the original finding by Muller [11,12]; and (b) the analysis performed on the hydration thermodynamics of noble gases, alkanes and n-alcohols using the Muller's parameters for bulk water [15,36–38]. The finding that the H-bonds in the hydration shell are slightly more broken than

Table 4
Percentage values of f_{hs} calculated using the parameter values listed in Table 2 for benzene; those in bold correspond to the scenario produced by the "combined" ΔC_p^h function; $f_{hs}[0.5]$ means the values of f_{hs} for ΔH_U=0.5 kJ mol^{-1}

T (°C)	f_b	f_{hs} [−0.5]	f_{hs} [0]	f_{hs} [0.5]	f_{hs} [1.0]	f_{hs} [1.5]	f_{hs} [2.0]
5	26.5	40.6	35.7	**31.4**	27.8	24.6	21.9
25	31.2	46.8	41.8	**37.3**	**33.4**	30.1	27.1
50	36.8	53.6	48.6	44.1	**40.1**	36.6	33.5
75	41.9	59.3	54.5	50.1	**46.2**	**42.7**	39.6
100	46.4	64.1	59.5	55.3	51.5	**48.1**	45.1

The percentage values of f_b are reported for comparison purposes.

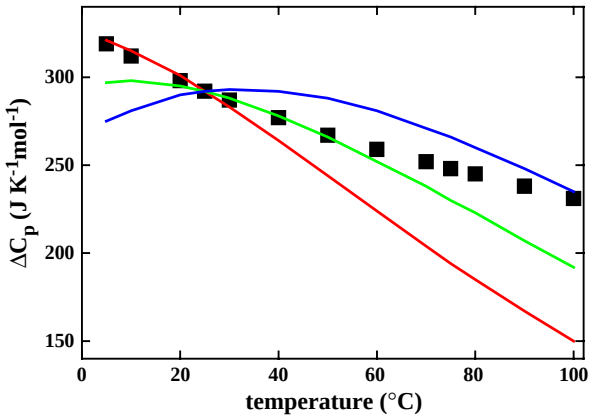

Fig. 1. Comparison between the experimental hydration heat capacity change of benzene over the temperature range 5–100 °C (filled squares) and the ΔC_p^h functions calculated with the Muller's model for ΔH_U (in kJ mol^{-1})=0.5 (red line), 1.0 (green line) and 1.5 (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

those in the bulk is in line with: (a) the structural information provided by neutron scattering and X-ray absorption spectroscopy measurements that found the hydration shell of nonpolar moieties slightly more disordered than the bulk water [44–47]; (b) the results emerged from computer simulation studies of nonpolar solutes dissolved in detailed models of water [48–50].

On this basis, one can try to explain the origin of the large difference in $\Delta C_p^\bullet$ existing between benzene and the corresponding alkane. When $0.5 \le \Delta H_U$ (in kJ mol^{-1}) ≤ 1.5, the models are characterized by: (a) for benzene, $9.00 \le \Delta H_{hs}^\circ$ (in kJ mol^{-1}) ≤ 9.50, and $24.83 \le \Delta S_{hs}^\circ$ (in J K^{-1}mol^{-1}) ≤ 25.89; (b) for the corresponding alkane, $9.36 \le \Delta H_{hs}^\circ$ (in kJ mol^{-1}) ≤ 9.84, and $26.30 \le \Delta S_{hs}^\circ$ (in J K^{-1}mol^{-1}) ≤ 27.35. With these parameters, the H-bonds in the hydration shell of benzene are only slightly less broken than those in the hydration shell of the corresponding alkane

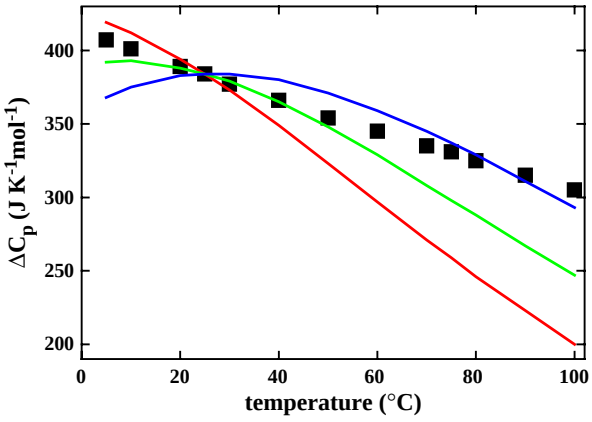

Fig. 2. Comparison between the experimental hydration heat capacity change of corresponding alkane over the temperature range 5–100 °C (filled squares) and the ΔC_p^h functions calculated with the Muller's model for ΔH_U (in kJ mol^{-1})=0.5 (red line), 1.0 (green line) and 1.5 (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5
Parameter values of the Muller's model for the corresponding alkane calculated as a function of ΔH_U, by assuming for bulk water the parameters determined by Angell (i.e., ΔH°_b=7.95 kJ mol^{-1} and ΔS°_b=20.1 J K^{-1}mol^{-1}); n^h=3·N_{H2O}/2=1.5·26.7, and, at 25 °C, ΔC^h_p=$\Delta C^\bullet_p$=384 J K^{-1}mol^{-1}, ΔH^h=$\Delta H^\bullet$−E_a=−24.2−(−31.0)=6.8 kJ mol^{-1} and ΔS^h=ΔH^h/T

ΔH_U (kJ mol^{-1})	f_{hs} at 25 °C (%)	ΔH°_{hs} (kJ mol^{-1})	ΔS°_{hs} (J K^{-1}mol^{-1})	ΔS_U at 25 °C (J K^{-1}mol^{-1})
−0.5	47.3	9.10	29.63	1.8
0	42.4	9.20	28.30	2.5
0.5	38.1	9.36	27.35	3.3
1.0	34.2	9.58	26.70	4.1
1.5	30.9	9.84	26.30	4.9
2.0	28.0	10.13	26.10	5.8

(see Tables 4 and 7). This result agrees with MD simulation data of Raschke and Levitt characterizing the hydration shell of benzene and cyclohexane [51]. Therefore, according to Eq. (9), the difference in $\Delta C^\bullet_p \cong \Delta C^h_p$ is due to the fact that ΔH°_{hs} is smaller for benzene with respect to the corresponding alkane by about 0.3 kJ mol^{-1}. Since ΔH°_{hs} is squared in the $C_{p,hs}$ formula, Eq. (8), and n^h is a large multiplicative factor in the ΔC^h_p formula, Eq. (9), even small differences in ΔH°_{hs} produce a large effect [15]. The finding that ΔH°_{hs} is smaller for benzene with respect to the corresponding alkane may be rationalized.

The hydration shell of benzene contains the weak H-bonds between the delocalised π-electron cloud of the aromatic ring and the hydrogen atoms of two water molecules, each located over one of the two faces of the ring [3,5,29,52,53]. The energetic strength of a benzene–water H-bond would amount to about 9 kJ mol^{-1}, whereas that of a water–water H-bond would amount to about 27 kJ mol^{-1} [29,54]. The weak benzene–water H-bonds have a significant structural freedom according to quantum mechanical calculations [53–55], and so they should be characterized by small ΔH°_{hs} values. This fact should render smaller the ΔH°_{hs} quantity when averaged over the whole hydration shell with respect to the situation existing around the corresponding alkane. Nevertheless, the existence of such weak benzene–water H-bonds is fundamental, from the geometric point of view, for the formation of a good network of water–water H-bonds around the flat surface of benzene [3] (i.e., computer simulations emphasized that water molecules close to an extended planar surface are not able to form all the potential H-bonds for simple geometric reasons [56]). As a consequence, the H-bonds in the hydration shell of benzene are not more broken than those in the hydration shell of the corresponding alkane, even though the latter are enthalpically slightly stronger. It can be tested, by keeping fixed the $\Delta C^\bullet_p$ value at 25 °C, that all the above results are more-than-qualitatively robust to large changes of ΔH^h at 25 °C (data not shown).

Table 6
Estimates of ΔC^h_p for the corresponding alkane calculated using the parameter values for the hydration shell listed in Table 5

T (°C)	$\Delta C^\bullet_p$	ΔC^h_p [−0.5]	ΔC^h_p [0]	ΔC^h_p [0.5]	ΔC^h_p [1.0]	ΔC^h_p [1.5]	ΔC^h_p [2.0]
5	407	480	448	**419**	392	368	345
25	384	384	384	**384**	**384**	384	384
50	354	270	297	323	**348**	371	395
75	331	177	218	259	**298**	**337**	376
100	305	106	154	200	247	**293**	340

The values of $\Delta C^\bullet_p$ are reported for comparison purposes. All the heat capacity values are in J K^{-1}mol^{-1} units; those in bold give rise to the "combined" ΔC^h_p function.

Table 7
Percentage values of f_{hs} calculated using the parameter values listed in Table 5 for the corresponding alkane; those in bold correspond to the scenario produced by the "combined" ΔC^h_p function

T °C	f_b	f_{hs} [−0.5]	f_{hs} [0]	f_{hs} [0.5]	f_{hs} [1.0]	f_{hs} [1.5]	f_{hs} [2.0]
5	26.5	40.8	36.0	**31.9**	28.3	25.2	22.4
25	31.2	47.3	42.4	**38.1**	**34.3**	30.9	28.0
50	36.8	54.4	49.5	45.2	**41.3**	37.8	34.7
75	41.9	60.3	55.6	51.4	**47.6**	**44.1**	41.1
100	46.4	65.2	60.8	56.8	53.1	**49.8**	46.9

The percentage values of f_b are reported for comparison purposes.

The application of the Muller's model with the aim to obtain a ΔC^h_p function that decreases in a continuous and monotonous manner over the temperature range 5–100 °C, which is a general qualitative feature of hydrophobic hydration, leads to the following scenario: the H-bonds in the hydration shell of a nonpolar solute are slightly more broken than those in the bulk. This scenario of the hydration shell contrasts with the traditional iceberg, flickering-cluster or clathrate models of Frank and co-workers [57–59], but it is supported by the results of both neutron scattering and X-ray absorption spectroscopy measurements [44–47], and computer simulations [48–50]. It agrees also with an important observation by Cooper [27]: in general, the heat capacity increases on passing from a well-ordered H-bonded network to a less-ordered H-bonded one (i.e., the heat capacity markedly increases upon melting ice to water).

The temperature dependence of E_a has entirely been neglected in the present analysis. If the Pierotti's formula [60] were used for E_a, its temperature dependence could readily be estimated because $(\partial E_a/\partial T) = -\alpha \cdot E_a$, where α is the thermal expansion coefficient of the liquid. By using the E_a values reported in the legend of Table 1 for benzene and corresponding alkane, and the experimental values of α for liquid water [61], one obtains that $(\partial E_a/\partial T)$ is always small in comparison to $\Delta C^\bullet_p$, amounting, at most, to about 30 J K^{-1}mol^{-1} around 100 °C. The latter number confirms the validity of Eq. (3).

4. Relationship with the approach by Gallagher and Sharp

Gallagher and Sharp [62], G&S, recently proposed a new approach to calculate $\Delta C^\bullet_p$, using structural information

extracted from water configurations around a solute generated with computer simulations. By means of Monte Carlo simulations in TIP4P water [30] at room temperature, G&S determined the joint radial/angular distribution function $p(r,\theta)$ representing the probability that a pair of water molecules is characterized by a separation r and an angle θ, which is the smallest O···O–H angle formed by two neighbouring water molecules. In water, the joint radial/angular distribution is bimodal with a first peak at r=2.8 Å and $\langle\theta\rangle$=16° and a second broad peak centred at r=4.5 Å and $\langle\theta\rangle$=40°. The meaning of such distance/angle values is grasped by comparison with the coordination shells in tetrahedral ice: the central molecule is H-bonded to 4 waters and the latter are H-bonded to other 12 waters in the second coordination shell of the central one. In water, the two peaks of $p(r,\theta)$ correspond to waters in the first and second coordination shell, respectively.

In the case of solutes, G&S partitioned the water molecules in each simulation snapshot into three regions: (a) first shell, (b) second shell and (c) bulk water. Then they computed the joint radial/angular configuration for each pair of waters whose oxygen atoms lay within 4.9 Å of each other. The bimodal character of $p(r,\theta)$ was found also for the waters in the first shell of the investigated solutes, regardless of polarity and charge, but with quantitative differences with respect to pure water. For the waters in the second shell, the function $p(r,\theta)$ was indistinguishable from that of pure water.

For this reason, G&S focused their attention on $p(r,\theta)$ of the first shell waters and called: N_I the number of water pairs in the first peak characterized by r<3.1 Å and θ<38°; and N_{II} the number of water pairs in the second peak characterized by 3.1 Å<r<4.5 Å and θ>38°. Thus, there are low-angle/short-distance H-bonds and high-angle/large-distance H-bonds, always within the first hydration shell of a solute. Specifically, G&S found: (a) for pure water, N_I=3.8, N_{II}=10.1 and $N_{tot}=N_I+N_{II}$=13.9, so that f_I=27% and f_{II}=73%; (b) for argon in water, N_I=18.1, N_{II}=28.3 and N_{tot}=46.4, so that f_I=39% and f_{II}=61%; (c) for benzene in water, N_I=41.2, N_{II}=68.9 and N_{tot}=110.1, so that f_I=37.4% and f_{II}=62.6%. On this basis, G&S stated that there is an increase of low-angle/short-distance H-bonds on inserting nonpolar solutes in water. They defined an excess of low-angle/short-distance H-bonds in the first hydration shell of a solute with respect to the bulk water by means of the following formula:

$$\Delta N = \left[f_I(\text{solute hydration shell}) - f_I(\text{bulk water})\right]\cdot N_{tot}(\text{solute}) \quad (13)$$

where N_{tot}(solute) is the total number of water pairs in the first hydration shell of the solute with a separation smaller than 4.5 Å.

Then G&S found a linear correlation between the ΔN estimates and the experimental $\Delta C_p^\bullet$ values for several solutes. Accordingly, they attributed great significance to the ΔN quantity and inferred that the energy fluctuations between water pairs must increase on decreasing their angle and/or their separation (i.e., energy fluctuations are the microscopic physical origin of $\Delta C_p^\bullet$). From the Monte Carlo simulations, G&S determined that closer water pairs with more linear θ angles are characterized by: (a) stronger (more negative) average interaction energies; (b) larger fluctuations in the interaction energy.

Using the average values of the mean squared energy fluctuation characterizing peak I and peak II of $p(r,\theta)$, G&S calculated the contribution to $\Delta C_p^\bullet$ of a water pair that passes from the high-angle/large-distance geometry to the low-angle/short-distance geometry (i.e., this is the mechanism producing the heat capacity change according to G&S). In this manner, they obtained estimates of $\Delta C_p^\bullet$ for the considered solutes and they wrote that such calculated values are too large by about 50% with respect to the experimental data. Actually, for several noncharged solutes, the error is more than 100%, as can be readily verified from the numbers reported in Table 8 [39–43,63–67]. This finding suggests that something is not entirely correct in the G&S approach.

A serious concern might be related to the choice of the reference to quantify the structural features of the H-bonds in the hydration shell of the several solutes. G&S considered that the fraction of H-bonds in peak I of water, f_I(bulk water), is the correct quantity. However, f_I(bulk water) is calculated in a different way with respect to f_I(solute hydration shell). In water, the two peaks of $p(r,\theta)$ account

Table 8
Water pairs in peak I and peak II of the joint radial/angular distribution as determined by Gallagher and Sharp from the first hydration shell of several noncharged solutes

	N_I	N_{II}	ΔN	$\Delta C_p^\bullet$ (calc) [J K^{-1}mol^{-1}]	$\Delta C_p^\bullet$ (exp) [J K^{-1}mol^{-1}]
Ar	18.1	28.3	5.6	325	195[a]
CH_4	21.4	32.1	7.0	407	209[b]
C_2H_6	30.8	50.6	8.8	512	273[c]
C_3H_8	38.8	66.2	10.5	611	319[c]
n-C_4H_{10}	41.2	68.9	11.5	669	383[d]
c-C_6H_{12}	35.8	50.6	12.5	728	400[e]
C_6H_6	41.0	69.6	11.0	646	292[f]
Ethanol	29.2	49.2	8.0	466	197[g]
NMA	37.3	65.7	9.5	553	162[h]
Urea	19.5	39.4	3.6	209	31[i]
TMAO	38.1	66.2	9.9	576	214[j]

The ΔN values, obtained from Eq. (13), allow the calculation of $\Delta C_p^\bullet$ at 25 °C, using the following estimate by Gallagher and Sharp: $\Delta C_p^\bullet/\Delta N$=58.2 J K^{-1}mol^{-1} per water pair.

[a] Ref. [39].
[b] Ref. [41].
[c] Ref. [42].
[d] Ref. [43].
[e] Ref. [63].
[f] Ref. [1].
[g] Ref. [64].
[h] Refs. [65,66].
[i] Ref. [67].
[j] Calculated using the group contributions listed in Ref. [67].

for waters in the first and second coordination shells of a central water molecule. In the case of a solute, the two peaks account for the geometric relationships between waters all in the first hydration shell of the solute molecule. Therefore, this procedure does not appear entirely consistent, and should be the cause of the finding that the fraction of low-angle/short-distance H-bonds is larger in the hydration shell of nonpolar solutes than in bulk water.

A significant result obtained by G&S is the finding of larger energy fluctuations associated with low-angle/short-distance H-bonds with respect to those associated with high-angle/large-distance H-bonds. Large energy fluctuations indicate that the shorter and more linear H-bonds are not always formed so that only a fraction of them is intact. This seems to be in line with the results obtained by the application of the Muller's model to the analysis of the hydration thermodynamics of nonpolar compounds: the H-bonds in the hydration shell of nonpolar solutes are enthalpically stronger but slightly more broken than those in bulk water [15,36–38]. In addition, according to the numbers listed in Table 8, there is a clear relationship between the number of short and linear H-bonds in the hydration shell, N_I, and $\Delta C_p^\bullet$ for the nonpolar solutes, as claimed in the two-state Muller's model.

Finally, G&S calculated solely the values of $\Delta C_p^\bullet$ at 25 °C, but entirely neglected the temperature dependence of the hydration heat capacity change. This point is very important and needs to be considered. As unequivocally pointed out by the Muller's model calculations, the temperature dependence of ΔC_p^h is the fundamental feature to select the model closer to reality. Many different models can reproduce the $\Delta C_p^\bullet$ values at 25 °C, but very few of them show the qualitatively correct temperature dependence of the heat capacity change. This implies that the temperature dependence of the calculated $\Delta C_p^\bullet$ function is a necessary test to verify the performance of the G&S approach. Similar criticism should be raised against the two-state hydration model developed by Chalikian [68], because such a model tries to describe thermodynamic data only at 25 °C. Therefore, even though the G&S approach is surely a step-forward to arrive at a theoretical calculation of $\Delta C_p^\bullet$ starting from structural data on water configurations, it cannot be considered of general validity for the moment.

5. Conclusions

The aim of the present study is to provide an explanation of the large quantitative difference in $\Delta C_p^\bullet$ existing between benzene and the corresponding alkane (i.e., an alkane having the same ASA of benzene) using the two-state Muller's model. Even though no one of the several generated models is able to perfectly reproduce the $\Delta C_p^\bullet$ data, the following general results have emerged: (a) the H-bonds in the hydration shell of both hydrocarbons are slightly more broken than those in bulk water; (b) the H-bonds in the hydration shell of benzene are enthalpically slightly weaker than those in the hydration shell of the corresponding alkane, but no more broken; (c) the latter features readily account for the difference in $\Delta C_p^\bullet$ on the basis of the Muller's model. Point (a) is in line with both the structural information provided by neutron scattering and X-ray absorption spectroscopy measurements [44–47], and the results of detailed computer simulations [48–50]. Point (b) is in line with the earlier suggestion that the weak benzene–water H-bonds are to be considered in the hydration shell of benzene [3,5]. Point (c) is a simple consequence of the mathematical formulas characterizing a two-state model.

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