Biophysical Chemistry 116 (2005) 137 – 144

Biophysical Chemistry

http://www.elsevier.com/locate/biophyschem

# On the hydration heat capacity change of benzene

Giuseppe Graziano*

*Dipartimento di Scienze Biologiche ed Ambientali, Università del Sannio, Via Port'Arsa 11-82100 Benevento, Italy*

Received 27 December 2004; received in revised form 31 March 2005; accepted 31 March 2005

## 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

---

* Tel.: +39 0824 305133; fax: +39 0824 23013.
*E-mail address:* graziano@unisannio.it.

0301-4622/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.bpc.2005.03.007

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$^{-1}$) | $\Delta H^h$ (kJ mol$^{-1}$) | $\Delta C_p^\bullet$ (J K$^{-1}$mol$^{-1}$) | $\Delta H^h$ (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 $\Delta H^h$ 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]:

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

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

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 $\Delta H^h$ 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:

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

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:

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

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, $\Delta H_b^\circ$ and $\Delta S_b^\circ$, 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 $\Delta H_b^\circ$ and $\Delta S_b^\circ$ 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 $\Delta H_{hs}^\circ$ and $\Delta S_{hs}^\circ$. 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 $\Delta H_{hs}^\circ$ and $\Delta S_{hs}^\circ$ cannot be determined from these equations because the values of $C_{p,hs}$ and $f_{hs}$ are unknown.