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Energetics of interactions of aromatic hydrocarbons with water

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Abstract

The thermodynamics of transfer of aromatic (benzene, toluene) and aliphatic (ethane, propane, butane) hydrocarbons from the gas phase into water in the temperature range 5–125°C have been analyzed in order to determine the net hydration effect of these compounds. In the case of the aromatic hydrocarbons the enthalpic contribution predominates over the entropic contribution to the Gibbs energy of hydration. This results in a negative value of the hydration Gibbs energy of aromatic hydrocarbons, in contrast to the positive Gibbs energy of hydration of aliphatic hydrocarbons. The different sign of the hydration Gibbs energies indicates that the mechanism causing hydrophobicity of aromatic hydrocarbons has different nature than that causing the hydrophobicity of aliphatic hydrocarbons. The comparison of hydration of aliphatic and aromatic hydrocarbons leads to the following thermodynamic parameters for these additional interactions between the benzene ring and water at 25°C: enthalpy −5.4 kJ/mol, entropy 26.8 J/K mol and Gibbs energy −13.4 kJ/mol. The large enthalpic contribution to the Gibbs energy of hydration of aromatic hydrocarbons probably comes from the ability of the aromatic ring to accept hydrogens from water, forming hydrogen bonds.

Key words: Aliphatic hydrocarbons; Aromatic hydrocarbons; Hydration; Hydrophobicity; Energetics; Hydrogen bonding

1. Introduction

The interior of proteins contains many aliphatic and aromatic groups that upon unfolding of the compact native protein structure are exposed to water. It is assumed that their exposure to water is thermodynamically unfavorable. These hydrophobic interactions of non-polar groups attract the greatest attention as they are considered to be the main force maintaining the native protein structure [1,2]. As it was noticed by Kauzmann [1], the transfer from non-polar liquids into water "... is invariably exothermic for the aliphatic compounds, and nearly athermal for the aromatic ones; furthermore, it is invariably accompanied by a very large decrease in entropy." From this observation it was concluded that the positive values of the Gibbs energy for aromatic and aliphatic hydrocarbons are associated mainly with the unfavorable entropic contribution. No further consideration of the origin of the difference in the enthalpic contribution of aromatic and aliphatic hydrocarbons was made and it was always assumed that the interactions of aromatic

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and aliphatic hydrocarbons with water are of the same nature [1]. At the same time it was well known from solution chemistry that aromatic and aliphatic hydrocarbons differ considerably in solubility. In 1948, Durand [3] and then McAuliffe [4] showed that the solubility of *n*-hexane is almost 20 times lower than the solubility of benzene, although these hydrocarbons have similar molecular weight. It was found also that the heat capacity increment upon transfer into aqueous solution, normalized to the water accessible surface area, is smaller for the aromatic hydrocarbons than for the aliphatic ones [5,6]. Correspondingly, the temperature dependencies of the Gibbs energy of transfer of aromatic hydrocarbons into water cluster separate from those of the aliphatic hydrocarbons [7]. Difference in the osmotic second virial coefficient in water for aromatic and aliphatic hydrocarbons was noticed as well [8,9].

In order to clarify the mechanism of interactions of aromatic and aliphatic hydrocarbons with water, we analyze here the thermodynamics of hydration of these compounds. The net hydration effect can be evaluated by studying the transfer of molecules from the gaseous phase, in which they do not interact with each other, into aqueous solution, in which they interact with water molecules. However, in considering transfer of the molecules between phases with different densities one should take into account the volume effects, i.e. the thermal roaming of the molecule in the given phase. These volume effects are significant if one uses mole-fraction scale in considering transfer [7], but they are automatically eliminated if transfer is considered in the molar concentration scale [10–14]. Another significant aspect in the analysis of the thermodynamic data of transfer is that the transfer of non-polar molecules into water is accompanied by a large positive heat capacity increment, which is not constant but decreases with increase of temperature [5,6,15–19]. As a result, the transfer parameters and subsequent conclusions are dependent on temperature. Correspondingly, in discussing transfer we should consider thermodynamic functions and not their values at some arbitrarily chosen temperatures.

2. Data analysis

Temperature dependencies of the enthalpy, $\Delta_g^w H(T)$, entropy, $\Delta_g^w S(T)$, and Gibbs energy, $\Delta_g^w G(T)$, changes upon transfer of hydrocarbon from the gaseous phase into water are determined by the heat capacity change upon transfer, $\Delta_g^w C_p(T)$, as

$$\Delta_g^w H(T) = \Delta_g^w H(T_0) + \int_{T_0}^{T} \Delta_g^w C_p(T)\, dT, \qquad (5)$$

$$\Delta_g^w S(T) = \Delta_g^w S(T_0) + \int_{T_0}^{T} \Delta_g^w C_p(T)\, d\ln T, \qquad (6)$$

$$\Delta_g^w G(T) = \Delta_g^w H(T) - T\Delta_g^w S(T). \qquad (7)$$

The values for $\Delta_g^w C_p(T)$, $\Delta_g^w H(25°C)$ and $\Delta_g^w G(25°C)$ reported in the literature are presented in the molality concentration scale. These data can be recalculated into molarity concentration scale (denoted by an asterisk) using the following equations [11]:

$$\Delta_g^w C_p^*(T) = \Delta_g^w C_p(T) + R\left(1 - 2\alpha_w T - \alpha_w' T^2\right), \qquad (1)$$

$$\Delta_g^w H^* = \Delta_g^w H + RT(1 - \alpha_w T), \qquad (2)$$

$$\Delta_g^w S^* = \Delta_g^w S + R\ln(d_w RT/M_w) - R(\alpha_w T - 1), \qquad (3)$$

$$\Delta_g^w G^* = \Delta_g^w H^* - T\Delta_g^w S^*, \qquad (4)$$

were R is a universal gas constant; α_w is the thermal expansion coefficient of water at the temperature, T; α_w', is the temperature derivative of the expansion coefficient; d_w, is density of water; M_w, is molecular weight of water [20].

The thermodynamic parameters of transfer from gaseous phase into water calculated in the molarity concentration scale are actually corrected on the volume difference in these two phases [11]. Therefore in this concentration scale the thermodynamic parameters of transfer $\Delta_g^w G^*(T)$, $\Delta_g^w H^*(T)$, $\Delta_g^w S^*(T)$ and $\Delta_g^w C_p^*(T)$ can be regarded as hydration parameters [13].

The reduced per unit of surface area hydration parameters for a given hydrocarbon were calculated dividing the hydration parameter by the corresponding water accessible surface area

(ASA), computed according to Lee and Richards [21,22].

The data on the thermodynamics of transfer of aliphatic and aromatic hydrocarbons from the gaseous or liquid phases into water in molality concentration scale was obtained from the following sources.

Ethane, propane, butane: $\Delta^w_g C_p(T)$ were taken from refs. [16–18] and extended for the whole temperature range according to Makhatadze and Privalov [6]; $\Delta^w_g H(25°C)$ and $\Delta^w_g G(25°C)$ were taken from Wilhelm et al. [23].

Benzene, Toluene: $\Delta^w_g C_p(T)$ were obtained by Makhatadze and Privalov [19]; $\Delta^w_g H(25°C)$ are from Gill et al. [24]; $\Delta^w_g G(25°C)$ are from Wauchope and Haque [25].

3. Results and discussion

Thermodynamic parameters of hydration in molarity concentration scale (heat capacity increment, $\Delta^w_g C_p^*$, enthalpy, $\Delta^w_g H^*$, entropy, $\Delta^w_g S^*$, and Gibbs energy, $\Delta^w_g G^*$), of the compounds studied are listed in Table 1. Their comparison in terms of reduced hydration parameter (i.e. normalized per square angstrom of water accessible surface area) reveals several interesting features,

Table 1
Temperature dependence of the thermodynamic parameters of hydration for aliphatic and aromatic hydrocarbons

	Temperature (°C)					
	5	25	50	75	100	125
$\Delta^w_g C_p^*$ (kJ K^{-1} mol^{-1})						
ethane	290.6	274.1	254.3	236.2	218.2	196.8
propane	340.1	320.5	297.0	275.5	254.1	228.6
butane	407.1	384.5	357.4	332.6	307.9	278.5
benzene	318.8	291.6	268.1	247.7	231	200.8
toluene	385.7	360.5	333.3	307.1	283	259.8
$\Delta^w_g H^*$ (kJ mol^{-1})						
ethane	−23.12	−17.47	−10.87	−4.74	0.94	6.13
propane	−26.82	−20.21	−12.49	−5.33	1.29	7.32
butane	−31.60	−23.68	−14.41	−5.79	2.22	9.55
benzene	−35.71	−29.60	−22.61	−16.16	−10.18	−4.78
toluene	−41.35	−33.89	−25.22	−17.22	−9.84	−3.06
$\Delta^w_g S^*$ (J K^{-1} mol^{-1})						
ethane	−104.0	−84.4	−63.1	−44.8	−29.0	−15.5
propane	−118.3	−95.3	−70.4	−49.0	−30.6	−14.9
butane	−136.2	−108.7	−78.8	−53.0	−30.7	−11.6
benzene	−108.43	−87.2	−64.6	−45.3	−28.7	−14.7
toluene	−127.4	−101.4	−73.4	−49.5	−29.0	−11.4
$\Delta^w_g G^*$ (kJ mol^{-1})						
ethane	5.81	7.69	9.52	10.86	11.76	12.30
propane	6.09	8.20	10.26	11.73	12.71	13.25
butane	6.28	8.73	11.05	12.66	13.68	14.17
benzene	−5.56	−3.60	−1.73	−0.39	0.53	1.07
toluene	−5.91	−3.66	−1.50	0.01	0.98	1.48
reduced hydration parameters for aliphatic hydrocarbons [a]						
$\Delta\hat{h}$	−0.140	−0.106	−0.065	−0.027	0.008	0.040
$\Delta\hat{s}$	−0.62	−0.50	−0.37	−0.26	−0.16	−0.07
$\Delta\hat{g}$	0.032	0.043	0.055	0.064	0.068	0.068

[a] Reduced hydration parameters are averaged among ethane, propane and butane, values. $\Delta\hat{h}$ and $\Delta\hat{g}$ are in kJ mol^{-1} Å^{-2} and $\Delta\hat{s}$ in kJ mol^{-1} K^{-1} Å^{-2}. Estimated error of the data is less than 10 percent.

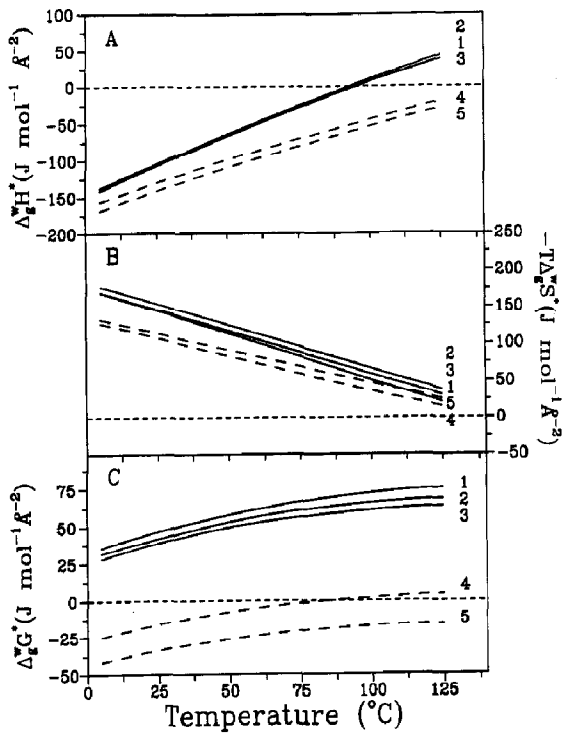

Fig. 1. Temperature dependencies of the reduced hydration parameters for aliphatic (solid lines) and aromatic (dashed lines) hydrocarbons. Panel (a) enthalpy of hydration, panel (b) entropy of hydration and panel (c) Gibbs energy of hydration for ethane (1), propane (2), butane (3), benzene (4) and toluene (5). Reduced hydration parameters are obtained from the data listed in Table 1, using the following ASA [25]: ethane 163 Å^2; propane 194 Å^2; butane 224 Å^2; benzene 228 Å^2; toluene 256 Å^2.

reflecting the difference in the thermodynamics of hydration for aromatic and aliphatic hydrocarbons (Fig. 1).

All three panels on Fig. 1 show that aromatic and aliphatic hydrocarbons have different temperature dependencies of the reduced thermodynamic parameters of hydration caused by the difference in the hydration heat capacity increments. Reduced hydration heat capacity increment is larger for the aliphatic hydrocarbons than for aromatic. Bearing in mind that large positive $\Delta_g^w C_p^*$ is specific for the non-polar surface and negative $\Delta_g^w C_p^*$ is specific for the polar surface [6], one can conclude that the aromatic molecule behaves as less non-polar than the aliphatic. The reduced enthalpy of hydration for aromatic hydrocarbons is larger than the aliphatic ones (Fig. 1a). The reduced entropy of hydration for the aromatic surface is smaller than that for the aliphatic surface (Fig. 1b). This results in a negative value of the Gibbs energy of hydration of aromatic groups for almost the whole range of temperature (Fig. 1c). In contrast, the Gibbs energy of hydration of aliphatic groups is positive at all temperatures studied.

This finding immediately raises several questions:

(a) *Why is the solubility of aromatic liquid low if their interactions with water are favorable?*

Solubility, which is expressed by the equilibrium constant, k, of transfer of solute into aqueous phase, depends on the energy balance of the interactions of the solute molecule in both phases, in its pure liquid phase and in its aqueous solution, $k = \exp(-\Delta_l^w G/RT)$. To analyze the cause of the low solubility of aromatic hydrocarbons with water, we can divide the process of transfer from the liquid state into water in two steps: transfer from the liquid state into gaseous state and then transfer from the gaseous state into water $\Delta_l^w G^* = \Delta_l^g G^* + \Delta_g^w G^*$ (see e.g. refs. [7,26]). The transfer from the liquid state to the gaseous state (Table 2) is nothing but vaporization, $\Delta_l^g G^*$, and its Gibbs energy is always positive [11]. The second step is hydration of the solute molecule, $\Delta_g^w G^*$. In the case of aliphatic hydrocarbons, both Gibbs energies, i.e. the Gibbs energy of transfer from the liquid to gaseous phase, $\Delta_l^g G^*$, and the Gibbs energy of transfer from the gaseous phase to water, $\Delta_g^w G^*$, are positive so the Gibbs energy of transfer from

Table 2
Thermodynamic parameters of the transfer of hydrocarbons between liquid (l), gaseous (g) and aqueous (w) phases at 25°C

	Ethane	Propane	Butane	Benzene	Toluene
$\Delta_l^w G^*$	13.14 [a]	16.14 [a]	20.04 [a]	15.46 [b]	17.95 [b]
$\Delta_l^g G^*$	5.45 [b]	7.94 [b]	11.31 [b]	19.06 [c]	21.61 [c]
$\Delta_g^w G^*$	7.69	8.20	8.73	−3.60	−3.66

[a] $\Delta_l^w G^*$ transfer from the liquid phase into water [25].
[b] Calculated using the relation, $\Delta_g^w G^* = \Delta_l^g G^* + \Delta_l^w G^*$.
[c] $\Delta_l^g G^*$ transfer from the liquid phase into gaseous phase [11]. All ΔG values are in kJ/mol.

liquid phase into water, $\Delta^{w}_{l}G^{*}$, is positive and the solubility is low. For polar compounds, the Gibbs energy of hydration, $\Delta^{w}_{g}G^{*}$, is negative and larger in absolute value than the Gibbs energy of transfer from the liquid to gaseous state, $\Delta^{g}_{l}G^{*}$. The resultant Gibbs energy is negative and the solubility is high. For aromatic hydrocarbons the hydration Gibbs energy, $\Delta^{w}_{g}G^{*}$, is also negative, but smaller in absolute value than the Gibbs energy of the liquid to gaseous state transfer, $\Delta^{g}_{l}G^{*}$. It is also notable that the latter term, $\Delta^{g}_{l}G^{*}$, is significantly larger by absolute value for aromatic hydrocarbons than for the aliphatic hydrocarbons (Table 2), i.e. the interactions between aromatic molecules are much stronger than the interactions between aliphatic ones. Therefore, although the interactions of aromatic compounds with water are favorable they are not large enough to overcome the interactions between these molecules in the pure liquid phase, causing low solubility, i. e. hydrophobicity, of aromatic hydrocarbons.

(b) *Why is the Gibbs energy of hydration of aromatic hydrocarbons negative?*

It is clear that there are some additional interactions between the aromatic ring and water which are not present in the interactions of aliphatic hydrocarbons with water. In order to calculate the energetics of these additional interactions between the aromatic ring and water it is necessary to compare the transfer thermodynamics of, for example, benzene with the aliphatic hydrocarbon having the same water accessible surface area. The water accessible surface area for benzene is 228 Å^2 [22]. The hydration parameters for aliphatic hydrocarbon with ASA = 228 Å^2 can be calculated as: $\Delta^{w}_{g}H^{*}_{alp} = ASA \cdot \Delta\hat{h}$; $\Delta^{w}_{g}S^{*}_{alp} = ASA \cdot \Delta\hat{s}$; $\Delta^{w}_{g}G^{*}_{alp} = ASA \cdot \Delta\hat{g}$, where $\Delta\hat{h}$, $\Delta\hat{s}$, $\Delta\hat{g}$ are aliphatic reduced hydration parameters (Table 1). It comes out that the aliphatic hydrocarbon of this ASA should have the following hydration parameters at 25°C: $\Delta^{w}_{g}H^{*} = -24.2$ kJ/mol, $\Delta^{w}_{g}S^{*} = -114$ J/K mol, $\Delta^{w}_{g}G^{*} = 9.8$ kJ/mol. Hydration parameters for benzene at the same temperature are (Table 1): $\Delta^{w}_{g}H^{*} = -29.6$ kJ/mol, $\Delta^{w}_{g}S^{*} = -87.2$ J/K mol, $\Delta^{w}_{g}G^{*} = -3.6$ kJ/mol. Their difference might be assigned to the energetics of the additional interactions between the aromatic ring of benzene and water. At 25°C this gives the Gibbs energy of −13.4 kJ/mol with enthalpic contribution −5.4 kJ/mol and entropic contribution ($-T\Delta S$) −8.0 kJ/mol.

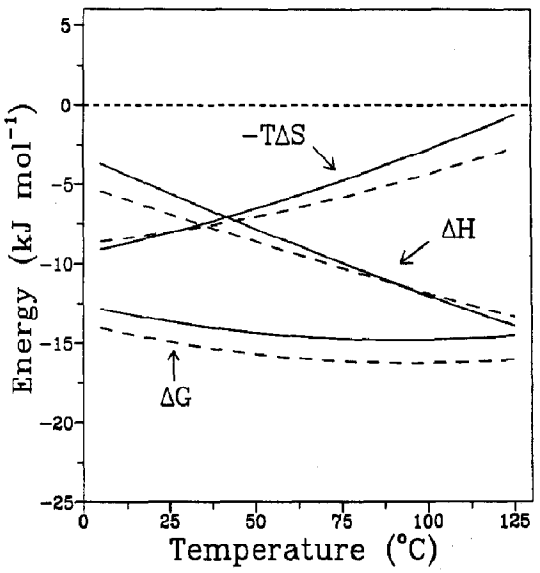

Fig. 2. Energetics of the additional interactions of aromatic ring with water. Solid lines benzene, dashed lines: toluene.

Similar type analysis can be done for toluene. The Gibbs energy of the additional interactions of the aromatic ring of toluene and water appears to be about −14.7 kJ/mol. The enthalpic, −6.8 kJ/mol, and entropic ($-T\Delta S$), −7.9 kJ/mol, terms of the Gibbs energy of these additional interactions between the aromatic ring of toluene and water are close to that of benzene. The deviations from the values, obtained for benzene are within the accuracy of analysis, which estimated to be better than 10 percent. The temperature dependencies of energetics of these additional interactions between aromatic ring and water are presented in Fig. 2.

(c) *Which forces might contribute to the additional interactions of aromatic hydrocarbons with water?*

The ability of the aromatic ring to act as hydrogen bond acceptor has been discussed in the literature for a long time. This idea was proposed from theoretical considerations [27–32] and indirectly followed from the spectroscopic studies [33–37] as well as from the X-ray crystallography

of biopolymers [38–42]. Direct evidence for this phenomenon was reported recently [43]. By using ground-state microwave spectra of jet-cooled C_6H_6–H_2O, Suzuki et al. [43] showed that benzene is nucleophillic and accepts hydrogen from water, forming hydrogen bonds. Thus one can suppose that the additional interactions between aromatic ring and water might be provided by hydrogen bonding.

4. Conclusions

The hydrophobicity of aromatic hydrocarbons derives from interactions different in nature than those found in aliphatic hydrocarbons. The low solubility of aromatic hydrocarbons results not from thermodynamically unfavorable interactions with water, but from their more favorable interactions with each other. It appears that the same situation occurs in proteins [39,40,44–49]: the aromatic side chains of the amino acid residues are buried in the interior of the protein because their interactions with other groups are stronger than their interactions with water.

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