



On the superhydrophobicity of tetrafluoromethane

Giuseppe Graziano *

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

ARTICLE INFO

Article history:

Received 12 May 2008

In final form 20 June 2008

Available online 24 June 2008

ABSTRACT

Tetrafluoromethane, CF_4 , is markedly less soluble in water than methane and neopentane around room temperature: it is a superhydrophobic solute. An analysis of the physical origin of this superhydrophobicity is performed, exploiting literature thermodynamic data covering the 5–55 °C temperature range. It results that the CF_4 –water dispersion interactions are markedly weaker in magnitude than those of a 'hypothetical' hydrocarbon having the same size of tetrafluoromethane, providing a smaller counterbalancing effect of the work spent to create the cavity in water. The weakness of the CF_4 –water dispersion interactions is due to the very small polarizability of CF_4 , which, in turn, is caused by the strong electro-negativity of fluorine atoms.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Fluorocarbons are considered to be superhydrophobic because their solubility in water is significantly smaller than that of the corresponding hydrocarbons. For instance, the mole fraction solubility in water, at 25 °C and 1 atm partial pressure of gas, is [1,2]: $x_2 \cdot 10^5 = 0.3802$ for CF_4 , 2.5523 for CH_4 , 1.077 for $\text{C}(\text{CH}_3)_4$, 0.09975 for C_2F_6 , and 3.4043 for C_2H_6 . These mole fraction solubilities give rise to the following values of the Ben-Naim standard [3] (i.e., transfer from a fixed position in the ideal gas phase to a fixed position into water) Gibbs energy of hydration: ΔG° (in kJ mol^{-1}) = 13.1 for CF_4 , 8.3 for CH_4 , 10.5 for $\text{C}(\text{CH}_3)_4$, 16.4 for C_2F_6 , and 7.6 for C_2H_6 . From ligand partitioning between *n*-octanol and water, and from ligand binding it emerged an empirical rule: 1 CF_2 group corresponds to about 1.5 CH_2 groups in terms of hydrophobicity [4]. There is increasing interest in producing and characterizing superhydrophobic materials, and fluorocarbons seem to be good targets [4]. As a consequence, a molecular level explanation of their superhydrophobicity would be a pre-requisite.

In the present Letter, I would like to provide an analysis of the hydration thermodynamics of CF_4 exploiting the data by Wilhelm et al. [5], WBW, covering the 10–55 °C temperature range, the gas solubility measurements of Wen and Muccitelli [6], W&M, covering the 5–30 °C temperature range, and those of Scharlin and Battino [7], S&B, covering the 15–45 °C temperature range. Experimental values of ΔH° , ΔS° , and ΔG° are listed in Table 1. There is good quantitative agreement for the ΔG° values among the three data sets, whereas there is qualitative, but not quantitative, agreement for the ΔH° and ΔS° values. In line with the general features of hydrophobic hydration [8], (a) ΔG° is large and positive, increas-

ing slightly with temperature; (b) ΔH° and ΔS° are large and negative, increasing markedly with temperature. In fact, ΔC_p° is a large and positive quantity, amounting, in $\text{J K}^{-1} \text{mol}^{-1}$ units, to (a) 380 over the 10–55 °C temperature range, on the basis of the ΔH° values of WBW [5]; (b) 433 over the 5–30 °C temperature range, on the basis of the ΔH° values of W&M [6]; (c) 636 over the 15–45 °C temperature range, on the basis of the ΔH° values of S&B [7] (the uncertainty on these ΔC_p° estimates is expected to be large [1]; according to W&M, the uncertainty amounts to 30% of their reported value). It is worth noting that ΔC_p° for the hydration of non-polar solutes is expected to be a decreasing function of temperature on the basis of a large set of experimental data [9]. I preferred to consider ΔC_p° as temperature-independent because the precision of the solubility measurements coupled to the small temperature range investigated did not allow a reliable determination of the temperature dependence of ΔC_p° .

The thermodynamic values reported in Table 1 indicate that, around room temperature, the superhydrophobicity of CF_4 is entropy-dominated, even though a significant enthalpy–entropy compensation occurs. By applying a general statistical mechanical theory of hydration [10,11], it emerges that the superhydrophobicity of CF_4 is mainly because the work spent for cavity creation is to a little extent counterbalanced by the work gained on turning on the CF_4 –water attractive interactions. The latter are weak due to the low molecular polarizability of tetrafluoromethane, reflecting the strength of C–F bonds and the strong electronegativity of fluorine atoms.

2. Calculation procedure

The theory has already been presented in detail [10,11], and only the main points are summarized to provide a correct perspective. The Ben-Naim standard Gibbs energy change for the transfer

* Fax: +39 0824 23013.

E-mail address: graziano@unisannio.it

Table 1

Experimental values of the Ben-Naim standard thermodynamic functions for the hydration of CF₄, determined from solubility measurements, over the 10–55 °C temperature range by WBW [5] (part A), over the 5–30 °C temperature range by W&M [6] (part B), and over the 15–45 °C temperature range by S&B [7] (part C)

	<i>T</i> (°C)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	$-T\Delta S^\circ$ (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)
A	10	-18.5	-106.3	30.1	11.6
	25	-12.8	-86.9	25.9	13.1
	40	-7.1	-68.0	21.3	14.2
	55	-1.4	-50.3	16.5	15.1
B	5	-22.0	-118.6	33.0	11.0
	15	-17.8	-104.1	30.0	12.2
	25	-13.4	-88.9	26.5	13.1
	30	-11.2	-81.8	24.8	13.6
C	15	-18.6	-106.5	30.7	12.1
	25	-12.2	-84.9	25.3	13.1
	35	-5.9	-63.9	19.7	13.8
	45	0.5	-43.7	13.9	14.4

of a solute molecule from a fixed position in the ideal gas phase to a fixed position in water at constant temperature and pressure is

$$\Delta G^\circ = \Delta G_c + \Delta G_a \quad (1)$$

where the first term is the reversible work to create a cavity suitable to host the solute molecule in water; the second term represents the reversible work to turn on the attractive potential between the solute molecule inserted in the cavity and the surrounding water molecules. The latter can be expressed as [11]:

$$\Delta G_a \approx \langle \psi_a \rangle_c - [\langle \kappa^2 \rangle_c / 2RT] \quad (2)$$

where ψ_a is the attractive solute–water potential energy and $\kappa = \psi_a - \langle \psi_a \rangle_c$. Note that: (a) $\langle \psi_a \rangle_c$ is the attractive energy between the solute molecule inserted in the cavity and the surrounding water molecules that have not yet reorganized in response to switching on the ψ_a attractive potential [11] (i.e., in this statistical ensemble the ψ_a potential acts as a ghost); (b) this implies that $\langle \psi_a \rangle_c \equiv E_a$ accounts for the solute–water dispersion attractions and a fraction of dipole-induced dipole attractions, because in this ensemble the dipoles of water molecules will rarely possess the orientation to attractively interact with the nonpolar solute in the cavity [11,12]. When the attractive solute–water potential is weak in comparison to water–water H-bonds, the fluctuations in the value of $\langle \psi_a \rangle_c$ are small, and the second term on the right-hand side of Eq. (2) can be neglected [11]. The condition of small fluctuations in the value of $\langle \psi_a \rangle_c$ is verified for nonpolar compounds in water [11,12], and ΔG_a is simply given by the average solute–water interaction energy:

$$\Delta G_a \approx \langle \psi_a \rangle_c \equiv E_a \quad (3)$$

The Gibbs energy cost to create a cavity is calculated by means of the formula provided by scaled particle theory, SPT [13]. According to the above theoretical approach, ΔG_c is the work to create the cavity in the real liquid, and the pressure to be used in SPT formula is the experimental one, 1 atm, the hydrostatic pressure over water [13].

The cavity size is defined as the diameter of the spherical region from which any part of any solvent molecules is excluded (i.e., it corresponds to the size of the solute molecule). It is well known that SPT results are sensitive to the σ values selected for the solvent and solute molecules [14]. For water, I selected $\sigma = 2.80$ Å [15], which is close to the location of the first peak in the oxygen–oxygen pair correlation function of water [16], and allows a satisfactory description of the cavity size distribution function of water by means of SPT. The 2.80 Å effective diameter has been considered to be temperature-independent. The experimental values of water density over the 5–55 °C temperature range have been used in SPT calculations [17].

The $E_a \equiv \langle \psi_a \rangle_c$ term is estimated using the simple formula devised by Pierotti [13], in the assumption that the solute–solvent dispersion interactions are represented by the Lennard-Jones 6–12 potential, and that the solvent density around the solute is uniform and equal to that of pure solvent. For CF₄ in water, E_a should consist of dispersion attractions and a fraction of the dipole-induced dipole attractions. I assume that the latter can be absorbed into the parameterization of the dispersion contribution because both terms depend on the inverse sixth power of distance. On this basis the ϵ/k value of water is increased from 85 K to 120 K [18], considering that the dipole moment of water in the liquid phase is markedly larger than that in the gas phase. For CF₄, I selected the Lennard-Jones parameters reported by Reid and Sherwood [19], $\sigma = 4.66$ Å and $\epsilon/k = 134$ K. By considering the van der Waals surface or volume of the CF₄ molecule [1], the diameter of the corresponding sphere is 4.84 Å or 4.51 Å; the average value, $\sigma = 4.68$ Å, is in line with that of Reid and Sherwood. In addition, the selected σ value for CF₄ agrees with the location of the first peak in the carbon–carbon radial distribution function of liquid CF₄ determined by means of both neutron scattering measurements and computer simulations [20,21]. Clearly, the Lennard-Jones parameters of Reid and Sherwood cannot be directly compared to the van der Waals diameters and ϵ/k values assigned to fluorine and carbon atoms in all-atom force fields [21].

The E_a magnitude depends on temperature mainly because the liquid density decreases with temperature. Since the water density decreases by less than 1.5% over the 5–55 °C temperature range [17], the E_a quantity has been considered to be temperature-independent. A similar calculation procedure was used by both W&M [6], and S&B [7]; however, without the framework provided by the statistical mechanical theory of hydration [10–12], the numerical results would not be so transparent.

3. Results and discussion

3.1. Gibbs energy change

The calculated values of ΔG_c and E_a are listed in the third and fourth columns, respectively, of Table 2. Notwithstanding the simplicity of the used formulae, the present values are in line with those calculated by means of direct computer simulations in different water models. At 25 °C and 1 atm, ΔG_c (in kJ mol⁻¹) = 33.6 from SPT formula; 35.4 in SPC water by means of a thermodynamic integration procedure [22]; 33.8 in TIP3 P water by means of the test particle insertion method [23]; 35.3 in SPC/E water by means of both the test particle insertion method and perturbation theory [24]. On the same line, E_a (in kJ mol⁻¹) = -20.4 from Pierotti's formula; $-(22.6 \pm 2.5)$ for a poly-atomic model of CF₄, and

Table 2

Values of the work of cavity creation calculated by means of SPT, assuming $\sigma(\text{H}_2\text{O}) = 2.80$ Å over the whole temperature range; values of the CF₄–water interaction energy, calculated by means of Pierotti's formula, and considered to be temperature-independent; comparison between the calculated $\Delta G_c + E_a$ numbers and the experimental ΔG° values (i.e., those from the data of S&B [7], except the value at 5 °C that comes from the data of W&M [6], and that at 55 °C that comes from the data of WBW [5]; see Table 1)

<i>T</i> (°C)	ξ	ΔG_c (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)	$\Delta G_c + E_a$ (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)
5	0.384	31.5	-20.4	11.1	11.0
15	0.384	32.6	-20.4	12.2	12.1
25	0.383	33.6	-20.4	13.2	13.1
35	0.382	34.5	-20.4	14.1	13.8
45	0.380	35.3	-20.4	14.9	14.4
55	0.379	36.0	-20.4	15.6	15.1

For CF₄, I selected $\sigma = 4.66$ Å and $\epsilon/k = 134$ K, while for water $\epsilon/k = 120$ K.

Download English Version:

<https://daneshyari.com/en/article/5387486>

Download Persian Version:

<https://daneshyari.com/article/5387486>

[Daneshyari.com](https://daneshyari.com)