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# Influence of Temperature and Surfactants on the Solubilization of Hexachlorobutadiene and Hexachloroethane

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ABSTRACT: The solubilization of hexachlorobutadiene (HCBD) and hexachloroethane (HCA) in water as a function of temperature and in the presence of surfactants was investigated in order to predict their fate in groundwater and to increase their recovery. HCBD and HCA solubility data were experimentally determined at five temperatures in the range from (285.15 to 318.15) K. Thermodynamic parameters for dissolution ($\Delta_{sol}G°$, $\Delta_{sol}H°$, and $\Delta_{sol}S°$) have been calculated in order to propose a physical explanation of the minimum solubility observed between 293.15 and 298.15 K for both compounds. The solubilization process appeared to be influenced by the network of water molecules rather than by physical and chemical properties of HCBD or HCA, due to an opposite effect of temperature onto Brownian motion, which increases with temperature, and hydrogen-bond network, which collapses with temperature. Concerning the influence of surfactants, determination of the micelle−water partition coefficients (K_{mw}) and the molar solubilization ratio (MSR) has shown that the solubilization per micelle was more important for nonionic surfactants Triton X-100 and Tween 80 than for anionic SDBS. Also, the increase of solubility was 1 order of magnitude higher for liquid HCBD than for crystalline HCA irrespective of surfactant.
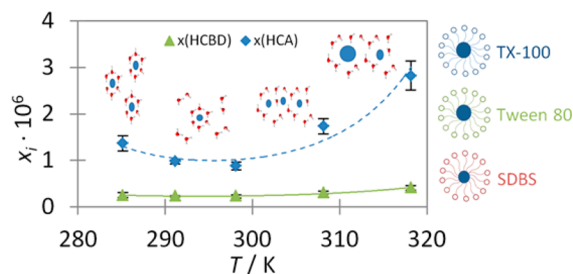
1. INTRODUCTION

Chlorinated organic compounds (COCs) are common contaminants of soil and groundwater, especially in industrial areas. These chlorinated hydrocarbons are known to be toxic for human health and represent a major environmental concern. Among them, hexachlorobutadiene (HCBD) is a byproduct in the manufacture of carbon tetrachloride and tetrachloroethylene (PCE). It has been used as fluid coolant, hydraulic fluid, or solvent for elastomers and rubber compounds.[1,2] HCBD has been added to Annexes A and C of the Stockholm Convention on persistent organic pollutants (POPs) in 2015. Hexachloroethane (HCA) is a solid which exists in three different crystalline phases depending on temperature.[3−5] It is produced by chlorination of ethane and aliphatic chlorinated ethanes, and has been used in smoke-producing devices, as an ignition suppressant, and an explosive inhibitor, or as a component of fungicides.[6]

Their density greater than that of water (d_{HCBD} = 1.66 g·mL^{−1} and d_{HCA} = 2.091 g·mL^{−1}) and their strong hydrophobicity, characterized by their high octanol−water partition coefficient K_{ow} (log K_{ow} > 4), cause their vertical migration and slow release in soils and groundwater, which is responsible for a long-term pollution by these dense nonaqueous phases.[7] Remediation of polluted groundwater is strongly impacted by the presence of dissolved pollutants. An increase in solubility of these compounds will increase the amount of available pollutant in order to enhance in situ remediation techniques.[8,9]

Solubility is thus one of the most important physicochemical parameters. It moreover allows predicting and modeling the fate and transport of the chlorinated solvents in groundwater. It is therefore of a great interest that the solubility be measured and understood in order to further perform and control the remediation processes, especially since literature data has shown (i) discrepancies of both HCA and HCBD solubilities in the range from (293.15 to 298.15) K[10−16] and (ii) a lack regarding the influence of the temperature and the presence of surfactants.

The first main factor affecting the aqueous solubility is temperature. Various studies have highlighted its influence concerning chlorinated methanes, ethanes, ethenes, and benzenes,[17−24] and different observations were made depending on both the physical state and the number of chlorine atoms on the molecule. Generally, aqueous solubility values increase beyond a certain temperature—between 293.15 and 323.15 K depending on the component—except that for the less chlorinated compounds such as chloromethane and chloroethane where a decrease is observed.[12,25] For lower temperature, two different shapes are observed: (i) a continuous increase in solubility as a function of temperature,

Table 1. Source and Purity of the Chemicals

chemical name	source	molar mass (g·mol⁻¹)	solute phase	mass fraction purity	purification method	analysis method
hexachlorobutadiene	Aldrich	260.76	liquid	0.96	none	GC[b]
hexachloroethane	Aldrich	236.74	solid (orthorhombic[a])	0.99	none	GC[b]

[a]According to Atoji et al.[3] [b]Gas chromatography.

Table 2. Properties of the Three Surfactants Used in This Study. CMC Values Are Given for Pure Water at 298.15 K

surfactant	type	M (g·mol⁻¹)	CMC (mM)	CMC (mg·L⁻¹)	HLB
Triton X-100	nonionic	625	0.22−0.24[a]	138−150	13.5[a]
Tween 80	nonionic	1310	0.010−0.012[a]	13−15	15[a]
SDBS	anionic	348.5	1.40[b]−2.28[c]	488−795	

[a]Taken from Hait and Moulik.[78] [b]Taken from Yu et al.[79] [c]Taken from Bakshi et al.[80]

as for hexachlorobenzene,[20] or (ii) an initial decrease followed by an increase, as for PCE, TCE, or carbon tetrachloride.[17−19]

Surfactants can also be used in order to increase aqueous solubility. Due to their amphiphilic structure with hydrophilic heads and hydrophobic tails, surfactants monomers form spontaneously organized structures in water, called micelles, beyond the critical micelle concentration (CMC).[26] This structure provides a hydrophobic core in which COCs can partition as droplets. As surfactant concentration increases, the number of micelles increases, leading to a linear increase in the apparent, or overall, solubility.[9] Some studies have observed this linear evolution for PCE, trichloroethylene (TCE), and hexachlorobenzene (HCB) in the presence of cationic, anionic, or nonionic surfactants at concentrations above their respective CMC.[27−29] Surfactants are classified as anionic, cationic, and nonionic depending on the nature of the headgroup. For subsurface application, anionic surfactants are frequently used due to their low sorption tendency.[30] Nonionic surfactants with a hydrophile−lipophile balance (HLB) between 12 and 15 can also be employed because they have a higher affinity with water than the organic phase at low temperature.[9] However, different factors, especially the increase in temperature, affect HLB value, resulting in higher affinity with the organic phase and the inversion of the microemulsion (progressive change from Winsor Type I to Winsor Type III and Winsor Type II).[9,26,31] Cationic surfactants are less used for subsurface applications as they tend to adsorb on negatively charged soil[32,33] and are more hazardous.[34] Among all surfactants, nonionic surfactants Triton X-100 and Tween 80 as well as anionic surfactant SDBS are widely reported for the solubility enhancement and the enhanced remediation of chlorinated solvents.[27,33,35−37]

The purpose of this study was first to determine experimentally HCBD and HCA solubilities between 285.15 and 318.15 K. It was then to characterize the influence of the temperature on the solubility behavior of the two compounds with the investigation of thermodynamics properties changes ($\Delta_{sol}G°$, $\Delta_{sol}H°$, and $\Delta_{sol}S°$) associated with dissolution reactions to propose a physical explanation of the obtained results. Also, the influence of three surfactants—Triton X-100, Tween 80, and SDBS—at five concentrations has been investigated regarding solubilization under standard ambient temperature (298.15 K).

2. MATERIALS AND METHODS

2.1. Materials. The experimental determination of solubilities was carried out with liquid hexachlorobutadiene (96%, Sigma-Aldrich) and solid hexachloroethane (99%, Sigma-Aldrich), with Milli-Q water (18.2 MΩ·cm of resistivity).

Details information is presented in Table 1. Three surfactants have been selected for solubilization experiments: Triton X-100 (TX-100, nonionic), Tween 80 (T80, nonionic), and sodium dodecylbenzenesulfonate (SDBS, anionic) surfactants, purchased from Sigma-Aldrich.

Dissolution reactions were conducted in 25 mL amber glass vials stirred on a rotating-table shaker. Centrifugation was then performed using a Sigma 3-30 KS centrifuge.

2.2. Solubility Experiments. Isothermal solubility values were measured by the saturation shake-flask method at five constant temperatures in the range from (285.15 to 318.15) K at $P = 0.1$ MPa. An excess amount of HCBD or HCA was introduced in 25 mL zero-headspace vials filled with Milli-Q water and sealed with PTFE-lined septa and aluminum caps. Vials were stirred for at least 24 h until partition equilibrium was reached. The temperature was maintained constant ($T \pm 0.2$ K) during agitation by using a thermostatically controlled enclosure. Vials were then centrifuged at 5000 rpm for 2 h, at constant temperature ($T \pm 0.5$ K), in order to separate the two phases. Finally, an aliquot of the supernatant was collected and sampled for analysis. Up to six replicates were performed for each temperature and for the two compounds.

The same protocol was applied for solubilization experiments in the presence of surfactants. Five concentrations of surfactants have been considered and investigated, according to their respective CMC value (see Table 2), from 0.5·CMC to 10·CMC. All measurements were conducted in triplicate at 298.15 K.

2.3. Analytical Methods. Analysis of samples was performed by gas chromatography (GC) using a Varian CP-3800 equipped with a DB-624 column (30 m × 0.32 mm i.d.) with a 1.80 μm film thickness and a flame ionization detector (FID). Carrier gas was helium, with a flow rate of 1.2 mL·min⁻¹. GC was controlled via Galaxie software from Agilent Technologies.

Samples are preliminarily heated at 353.15 K for 30 min, and 200 μL of the headspace are taken by a gastight syringe and introduced in the injector chamber at 523.15 K (1:25 split ratio). The oven was maintained at 308.15 K for the initial 5 min, and then ramped to 518.15 at 10 K·min⁻¹, with a hold for 10 min at that final temperature. FID temperature was maintained at 573.15 K, with a He makeup at a flow rate of 30 mL·min⁻¹. The combustion of organic compounds is carried out with hydrogen (30 mL·min⁻¹ flow rate) and air (300 mL·min⁻¹ flow rate).

Stock solutions were prepared from hexachlorobutadiene or hexachloroethane in methanol. Seven calibration standards were prepared and analyzed periodically to define the linearity

Table 3. Aqueous Solubilities of HCBD and HCA between 285.15 and 318.15 K under P_{atm} = 0.1 MPa[a]

	hexachlorobutadiene (HCBD)				hexachloroethane (HCA)			
T/K	n	$s/mg \cdot L^{-1}$	$x \cdot 10^7$/mol fraction	$\gamma \cdot 10^{-6}$	n	$s/mg \cdot L^{-1}$	$x \cdot 10^7$/mol fraction	$\gamma \cdot 10^{-4}$
285.15	5	3.66 ± 0.84	2.53 ± 0.58	3.95	4	17.88 ± 2.15	13.6 ± 1.6	3.60
291.15	6	3.31 ± 0.18	2.29 ± 0.13	4.37	5	13.53 ± 1.90	9.65 ± 0.40	5.99
298.15	6	3.25 ± 0.52	2.25 ± 0.36	4.45	5	11.52 ± 1.10	8.79 ± 0.84	7.91
308.15	6	4.41 ± 0.46	3.06 ± 0.32	3.26	4	22.64 ± 2.19	17.3 ± 1.7	5.15
318.15	4	5.84 ± 0.71	4.08 ± 0.49	2.45	4	36.77 ± 4.10	28.3 ± 3.2	3.99

[a]Results are presented in the form mean ± 95% confidence interval. n = number of replicates for each condition. Standard uncertainty u is $u(T)$ = 0.2 K.

of the measurement over a concentration range and to ensure proper quantifications of unknown samples.

2.4. Calculation of Standard Thermodynamic Properties.
Dissolution reactions of HCBD and HCA in water can be written as follows:

$$HCBD_l \leftrightarrows HCBD_{aq} \qquad (1)$$

$$HCA_s \leftrightarrows HCA_{aq} \qquad (2)$$

A correlation with temperature can be carried out with the modified Apelblat equation:

$$\ln x_i = A + B/(T/K) + C \ln(T/K) \qquad (3)$$

where x_i is the mole fraction of the compound in water,

$$x_i = C_i V_w \qquad (4)$$

and V_w is the water molar volume (0.01807 L·mol^{-1} at 298.15 K).

Even if A, B, and C are each not independent of a single thermodynamic property, this simple relation provides a direct representation of the aqueous solubility for a small range of temperature.

Activity coefficient of the saturated aqueous solution γ_i can be calculated for HCBD and HCA. For liquid HCBD, γ_i is the inverse of the mole fraction solubility.[38]

$$\gamma_i = 1/x_i \qquad (5)$$

For crystalline HCA, the free energy of fusion has to be included in the equation, as the solid needs first to be converted in the liquid state.[38]

$$\gamma_i = \frac{1}{x_i} \exp(-\Delta_{fus}G°/RT/K) \qquad (6)$$

where $\Delta_{fus}G°$ is the free energy of fusion (J·mol^{-1}). It can be estimated by the relation:

$$\Delta_{fus}G° \cong (56.5 + 9.2\tau - 19.2 \log \sigma)(T_m/K - T/K) \qquad (7)$$

where τ is the effective number of torsional bonds (0 for HCA), σ is the rotational symmetry number (6 for HCA) and T_m is the melting point temperature in Kelvin (457.15 K for HCA).

Assuming the activity coefficients for water in water phase and for the organic component in the organic phase are equal to 1, the standard Gibbs energy $\Delta_{sol}G°$ (J·mol^{-1}) of both reactions at constant temperature is written as

$$\Delta_{sol}G° = -RT \ln x_i \qquad (8)$$

Enthalpy of dissolution $\Delta_{sol}H°$ (J·mol^{-1}) can be calculated by using eq 9.

$$\Delta_{sol}H° \cong RT^2 \partial \ln x_i / \partial (T/K) \qquad (9)$$

Entropy of dissolution $\Delta_{sol}S°$ (J·mol^{-1}·K^{-1}) can be calculated by the definition of $\Delta_{sol}G°$.

$$\Delta_{sol}S° = (\Delta_{sol}H° - \Delta_{sol}G°)/(T/K) \qquad (10)$$

Heat capacity of solution $\Delta_{sol}Cp°$ (J·mol^{-1}) can be calculated with eq 11.

$$\Delta_{sol}Cp° = \partial \Delta_{sol}H°/\partial(T/K) \qquad (11)$$

As proposed by Clarke and Glew (1966),[39] a weighted multiple linear regression (eq 12) can be used to provide the best estimate for the thermodynamic functions by the association of a different weight for each data point (here, the 95% confidence interval for the mole fraction).

$$R \ln x_i = \sum_{i=0}^{n} b_i u_i \qquad (12)$$

where b_i is related to the thermodynamics functions and is the partial regression coefficients of $R \ln x_i$ on the n temperature variables u_i, with

$$u_i = y^i \sum_{n=1}^{\infty} \frac{n}{n + i - 1}(-y)^{n-1} \qquad (13)$$

where $y = (T - \theta)/\theta$, and T and θ, the reference temperature at which the thermodynamic properties are calculated, are in Kelvin. Only the first two variables u_1 and u_2 have been calculated in order to obtain the best regression provided by analysis of variance (ANOVA).

$$R \ln x_i = b_0 + b_1 u_1 + b_2 u_2 \qquad (14)$$

The regression coefficients b_0, b_1, and b_2 are expressed as

$$b_0 = -\Delta_{sol}G°_{(\theta)}/(\theta/K) \qquad (15)$$

$$b_1 = \Delta_{sol}H°_{(\theta)}/(\theta/K) \qquad (16)$$

$$b_2 = \Delta_{sol}C°_{p(\theta)} \qquad (17)$$

Change in entropy can then be calculated by combining eqs 15 and 16:

$$\Delta_{sol}S°_{(\theta)} = (\Delta_{sol}H°_{(\theta)} - \Delta_{sol}G°_{(\theta)})/(\theta/K) = (15) + (16) \qquad (18)$$

3. RESULTS AND DISCUSSION

3.1. Influence of Temperature.
Solubility values s and activity coefficients γ of HCBD and HCA between 285.15 and 318.15 K are presented in Table 3. A comparison with literature data shows that the solubility value for HCBD at 298.15 K is in good agreement with the 3.23 mg·L^{-1} value obtained by Banerjee et al. (1980)[10] and close to the 2.00 mg·L^{-1} value

obtained by Pearson and McConnell (1975)[11] at 293.15 K. Concerning HCA, the value obtained in this study is lower than previous experiments, 50 mg·L^{-1} at 295.15 K,[12−14] 27.2 mg·L^{-1} at 298.15 K,[15] and 77·1 mg·L^{-1} at 293.15 K,[16] or a little higher than the 7.7 mg·L^{-1} at 293.15 K value proposed by the GESTIS Substance Database.

Results in the temperature range (285.15 to 318.15) K showed an initial small decrease of solubility, followed by a greater increase after reaching a minimum solubility for the two compounds. The solubility of HCBD decreased from 3.66 mg·L^{-1} at 285.15 K to 3.25 mg·L^{-1} at 298.15 K, and increased then to 5.84 mg·L^{-1} at 318.15 K. The solubility of HCA decreased from 17.88 mg·L^{-1} at 285.15 K to 11.52 mg·L^{-1} at 298.15 K, and then increased to 36.77 mg·L^{-1} at 318.15 K.

Results obtained by the weighted multiple linear regression of eq 3 are presented in Figure 1 and Table 4. Similar shapes
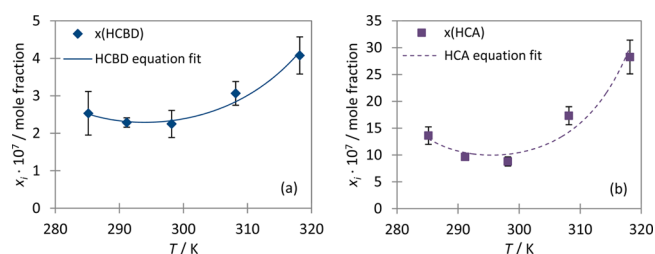

Figure 1. Measured solubility data in mole fraction for (a) HCBD and (b) HCA in the temperature range from T = (285.15 to 318.15) K, with fitted values obtained by eq 3 regression. Errors bars represent the 95% confidence interval. ◆ = HCBD, ■ = HCA.

Table 4. Aqueous Solubility versus Temperature Regression eq 3 Parameters ($\ln x_i = A + B/(T/K) + C \ln(T/K)$). The 95% Confidence Intervals Are Extracted from the Regression Interpretation

cmpd	A	B	C	R^2
HCBD	−1.33 (±0.27) 10^3	5.78 (±1.20) 10^4	1.96 (±0.40) 10^2	0.9999
HCA	−2.79 (±0.87) 10^3	1.23 (±0.39) 10^5	4.15 (±1.29) 10^2	0.9998

have already been observed by other authors for other chlorinated organic compounds, such as PCE, TCE, cis-1,2-DCE and different chlorinated ethanes and methanes.[12,17,18,23,25,40] Thus, this study supports *a minima* the fact that a minimum solubility is obtained for perchlorinated aliphatic compounds versus temperature.

Results obtained for thermodynamic functions calculation by regression of eq 14 are presented in Table 5 and Figure 2.

Gibbs free energy change is positive over the entire temperature range, indicating that solubilization is a nonspontaneous process (reaction shifts toward the reactants), and its equilibrium constant is lower than 1. Because of the hydrogen bonds network between water molecules, hydrophobic molecules tend to agglomerate in order to minimize contact with water molecules, as no hydrogen bonds can be formed between water and nonpolar chlorinated hydrocarbons. It is characterized by the low solubilities in water.

A linear variation of standard enthalpy of solution as a function of temperature is observed for the two compounds, with a sign change observed in this temperature range. Dissolution, which is exothermic at low temperature, becomes endothermic when temperature increases. In exothermic

Table 5. Changes of the Thermodynamic Properties Resulting from Modeling for the Dissolution of HCBD and HCA in Milli-Q Water between 285.15 and 318.15 K[a]

T	$\Delta_{sol}G°$	$\Delta_{sol}H°$	$\Delta_{sol}S°$	$\Delta_{sol}C_p°$
K	kJ·mol^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	kJ·mol^{-1}
		HCBD		
285.15	36.0 ± 0.1	−14.4 ± 5.3	−177 ± 18	1.6 ± 0.3
291.15	37.0 ± 0.1	−4.6 ± 3.4	−143 ± 12	
298.15	37.9 ± 0.1	6.9 ± 1.7	−104 ± 6	
308.15	38.6 ± 0.1	23.2 ± 3.1	−50 ± 10	
318.15	38.9 ± 0.2	39.6 ± 6.3	2 ± 20	
		HCA		
285.15	32.1 ± 0.4	−35.7 ± 17.5	−238 ± 61	3.4 ± 1.1
291.15	33.3 ± 0.3	−15.0 ± 11.5	−166 ± 40	
298.15	34.2 ± 0.3	9.1 ± 5.8	−84 ± 19	
308.15	34.5 ± 0.3	43.6 ± 9.3	30 ± 30	
318.15	33.6 ± 0.4	78.1 ± 19.2	140 ± 60	

[a]The 95% confidence intervals are derived from the regression interpretation. Standard uncertainty u is $u(T)$ = 0.2 K.

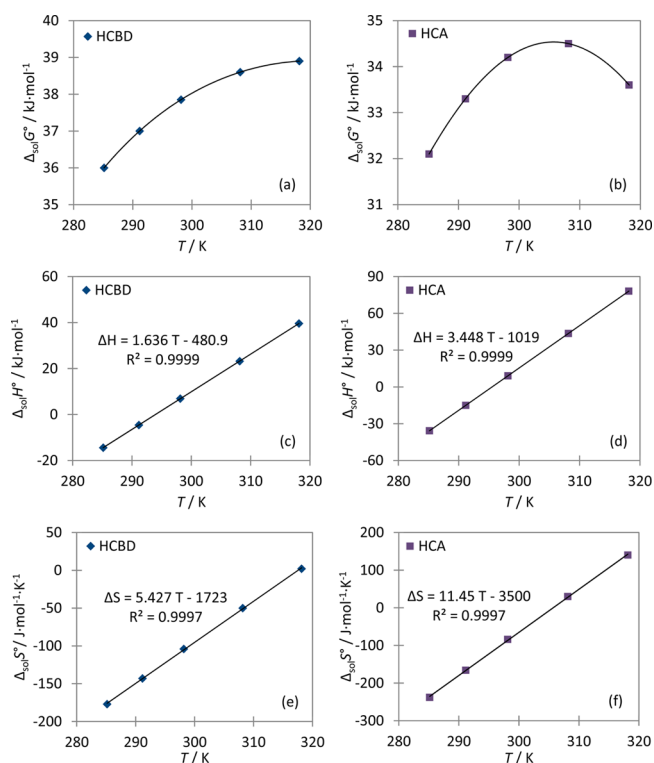**Figure 2.** Changes in standard thermodynamic parameters for HCBD and HCA dissolution reactions in the temperature range from T = (285.15 to 318.15) K obtained by eq 14 regression. (a and b) $\Delta_{sol}G°$/kJ·mol^{-1}; (c and d) $\Delta_{sol}H°$/kJ·mol^{-1}; and (e and f) $\Delta_{sol}S°$/J·mol^{-1}·K^{-1}. ◆ = HCBD, ■ = HCA.

reactions, an increase of temperature decreases the equilibrium constant of dissolution; conversely, in endothermic reactions, an increase of temperature increases the equilibrium constant.[41] Hence, solubility values decrease with an increase of temperature in an exothermic reaction, and increase with an increase of temperature in an endothermic reaction (Le Chatelier's principle), in accordance with experimental observations. The minimum solubility is observed in the absence of heat exchange with the surroundings (athermic reaction), that is, for a zero enthalpy of solution.[25] The minimum solubility is observed at a

Table 6. Influence of Surfactants on the Solubilization of HCBD and HCA in Mole Fraction at 298.15 K under P = 0.1 MPa[a]

| surfactant | hexachlorobutadiene | | hexachloroethane | |
	surfactant concentration (μmol·kg^{-1})	apparent solubility (x·10^7)	surfactant concentration (μmol·kg^{-1})	apparent solubility (x·10^7)
no surfactant	0	2.25 ± 0.36	0	8.79 ± 0.84
Triton X-100	83.2	2.15 ± 1.63	89.6	10.5 ± 4.23
	174	2.19 ± 0.67	202	13.6 ± 1.2
	395	3.39 ± 1.52	336	14.5 ± 2.9
	880	131 ± 2	813	24.0 ± 6.9
	1729	302 ± 10	1717	39.8 ± 1.5
Tween 80	13.4	4.41 ± 2.65	13.5	12.8 ± 2.65
	26.7	6.28 ± 3.34	27.1	13.7 ± 2.5
	53.4	10.7 ± 2.2	54.2	14.5 ± 3.5
	135	16.3 ± 3.1	135	15.0 ± 5.7
	267	34.9 ± 6.0	267	20.4 ± 3.8
SDBS	760	9.00 ± 2.34	748	11.4 ± 2.1
	1600	6.91 ± 3.08	1600	12.8 ± 4.2
	3049	20.9 ± 4.9	3049	22.2 ± 2.7
	7378	134 ± 2	7602	53.6 ± 3.7
	14 375	286 ± 2	14 375	101 ± 3

[a]Standard uncertainties u are $u(T)$ = 0.2 K.

temperature accessible using the linear equations shown in Figure 2c and 2d. The calculated minimum solubility is 3.31 mg·L^{-1} at 294.05 K for HCBD and 13.08 mg·L^{-1} at 295.55 K for HCA.

Dissolution reactions involve multiple consecutive steps. The first steps are the separation of chlorinated organic molecules to enable the transfer of a single molecule of HCBD or HCA within the cavities formed by the partial separation of water molecules. These solute−solute and solvent−solvent interactions are endothermic reactions of dispersion. Then, exothermic reactions of attraction between solute and solvent will take place. The enthalpy of solution is the result of the contribution of enthalpy of vaporization ($\Delta_{vap}H°$, endothermic process) and enthalpy of hydration ($\Delta_{hyd}H°$), which is the result of the enthalpy of cavitation ($\Delta_{cav}H°$, endothermic process), and the enthalpy of attractive interactions ($\Delta_{attrac}H°$, exothermic process).[42]

$$\Delta_{sol}H°_{(\theta)} = \Delta_{vap}H°_{(\theta)} + \Delta_{cav}H°_{(\theta)} + \Delta_{attract}H°_{(\theta)} \quad (19)$$

In this study, attractive interactions energy is more important than dispersive interactions at low temperature, while the opposite is observed at high temperature. At low temperature, chlorinated hydrocarbons can fit in the pre-existing small cavities in the low-density water clusters and will gain van der Waals interactions, resulting in a negative enthalpy of solution.

A linear variation of standard entropy of solution with temperature is also observed. Change in entropy is negative at low temperatures and becomes positive when the temperature increases. Frank and Evans (1945) proposed first that the decrease of entropy could be explained by the formation of an ice-like clathrate compound in the hydration shell of the hydrophobic compound, with the proposition of the so-called iceberg model.[43] This model was subsequently criticized by some authors, and others models, such as Muller or Mercedes-Benz models, were later proposed,[44−52] and no evidence of such ice-like structure has been detected by neutron-scattering analysis.[53] More recent studies indicate that a loss of entropy can be explained by an enhanced tetrahedral water structure in the first hydration shell around a hydrophobic compound, that was observed by Raman-MCR[54] and molecular simulation.[55]

This structure is however different than the first conception of an ice-like structure in the "iceberg" model, but reflects the gain of order in the surrounding of hydrophobic molecules.[56] These water clusters are characterized by a depletion of weak hydrogen bonds[54,57] and slower orientational dynamics,[58] probably due to the presence of low-density water.[59]

However, water cavities are small and can accommodate only a few molecules. This can partly explain the difference of solubility between HCBD and HCA; as the molecular diameter of HCBD is more important than the one of HCA. In comparison with literature data for other perchlorinated compounds such as PCE and carbon tetrachloride,[18,19,40] the difference in the order of magnitude of solubility values can be attributed to the size of the molecules; the smaller the molecules, the easier it is to fit into a water cavity.

As the temperature increases, the size of water molecule clusters decreases due to the breaking of hydrogen-bonds,[60] resulting in a collapsed structure and smaller free volumes in the structure, but global free volumes can expand due to kinetic energy.[61] For small increases in temperature, the decrease of the number of pre-existing cavities is not compensated by the increase of thermal motion, resulting in a decrease of aqueous solubility. At higher temperature, there is a predominance of collapsed clusters or isolated molecule fragments, and cavities formation requires energy to accommodate the solute, resulting in a high enthalpy of cavitation. However, these cavities will be larger than the cavities in the enhanced-structure cluster and can accommodate more solute molecules, which can explain the increase of aqueous solubility with temperature.

Studies focused on the influence on temperature on water reorientation in the hydration shells indicated that slower reorientation were observed at low temperature, and that the ordered structure vanished when the temperature increases.[54,62,63] The large negative value of entropy can mostly be attributed to the water-excluded volume to the creation of cavities in water.[52,64−66] Kim et al. (2015) explained that the hydration entropy magnitude increased with the solute size and decreased with temperature.[67] The slower orientational dynamics have been attributed to a slower hydrogen-bond exchange.[68] Also, more hydrophobic interactions will occur in order to minimize the surface contact between water and

hydrophobic molecules. Because of the size difference, more water molecules are impacted than hydrophobic molecules in these interactions, which can explain the positive values of entropy changes at high temperature.

Results obtained for the heat capacity are $\Delta_{sol}C_p^\circ = 1.6$ kJ·mol^{-1}·K^{-1} for HCBD and $\Delta_{sol}C_p^\circ = 3.4$ kJ·mol^{-1}·K^{-1} for HCA. Such large values have been, for example, observed in processes involving proteins[48,69,70] and can be attributed to the hydrophobic effect.

The evolution curve of solubility is related to the variation of $\Delta_{sol}H^\circ$ and $\Delta_{sol}S^\circ$ in the hydration shell, which have shown a linear variation with a sign change versus temperature. This result can be explained by the opposite effect of temperature onto Brownian motion, which increases with temperature, and the hydrogen-bond network, which collapses with temperature. The whole results have indicated that the global process is less impacted by physical and chemical properties of the hydrophobic compounds but rather by water molecules network. It can also be pointed out that the entropic contribution ($T\Delta_{sol}S^\circ$) is greater than the enthalpic contribution ($\Delta_{sol}H^\circ$), so both dissolution reactions are entropy-driven processes.

3.2. Influence of Surfactants. To increase the solubility of both COCs, the influence of the presence of three surfactants was investigated under standard ambient temperature (298.15 K). Results presented in Table 6 and Figure 3 have shown that a linear evolution of apparent solubility is observed when surfactants concentrations are higher than their respective CMC. Previous studies have already observed this linear evolution for other chlorinated organic compounds such as
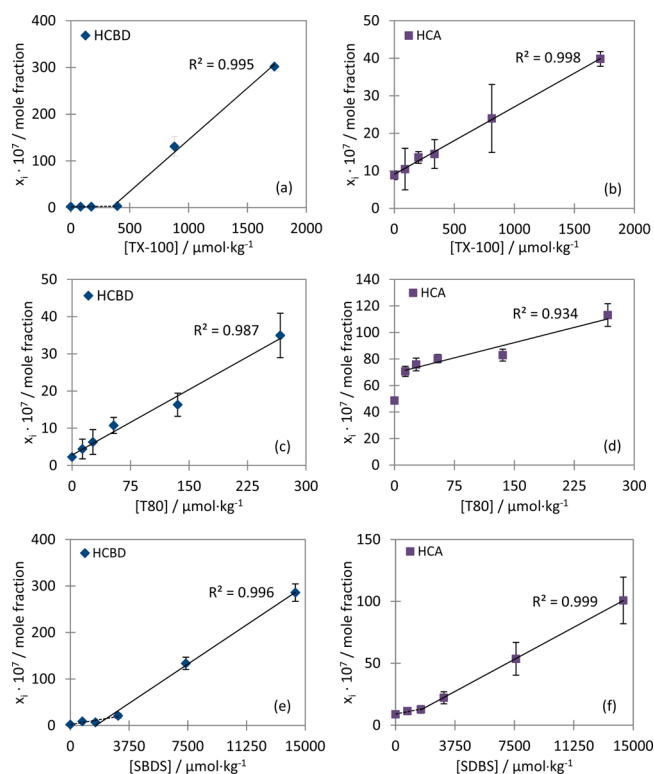
PCE, TCE, and HCB.[27−29] The whole results are in good agreement with the fact that the creation of micelles, which can partition the droplets of hydrophobic compounds, leads to an enhancement of the apparent solubility; the higher the number of micelle, the higher the apparent solubility.

As shown in Figure 3, it can be pointed out that CMC values are different in the presence of HCBD or HCA compared to the values reported for pure water (Table 2). The presence of each organic compound affects therefore CMC values,[26] probably due to the hydrophobic effect.[71] In the presence of HCBD, CMC values are about 0.37 mM for Triton X-100 and 2.30 mM for SDBS, whereas a linear evolution is observed for all concentrations for Tween 80. In the presence of HCA, CMC values are about 0.013 mM for Tween 80 and 1.7 mM for SDBS, whereas a linear evolution is observed for all concentrations for Triton X-100.

A weight solubilization ratio (WSR) which represents the ratio of the number of moles of solubilized COCs to the number of moles of surfactants in the micellar form can be calculated with eq 20.[72,73]

$$\text{WSR} = (C_o - C_{o,CMC})/(C_S - \text{CMC}) \qquad (20)$$

where C_o is the apparent solubility of HCBD or HCA at the concentration C_S of surfactants, and $C_{o,CMC}$ is the aqueous solubility at the measured CMC of the surfactant. WSR represents the slope of the relationship between apparent solubility of HCBD and HCA and surfactant concentration above CMC, when the linear evolution is observed. The calculation of WSR is restricted within the investigated range as linearity may no longer be observed for high concentrations in each compound. For HCBD, WSR values are 0.51 for Triton X-100, 0.13 for Tween 80, and 0.093 for SDBS. For HCA, WSR values are 0.038 for Triton X-100, 0.028 for Tween 80, and 0.026 for SDBS.

A micelle−water partition coefficient K_{mw} which represents the ratio of pollutant solubilized within the micelles to the pollutant solubilized in water is calculated with eq 21.[72]

$$K_{mw} = X_m/X_w \qquad (21)$$

where X_m is the mole fraction of organic in the micellar phase ($X_m = \text{MSR}/(1+\text{MSR})$, with MSR being the molar solubilization ratio) and $X_w = C_S V_w$, where V_w is the molar volume of water.[9]

Hence, K_{mw} can be expressed as

$$K_{mw} = \text{MSR}/(C_S V_w(1 + \text{MSR})) \qquad (22)$$

MSR and K_{mw} values at 298.15 K are reported in Table 7. For all studied surfactants, K_{mw} values are at least 1 order of magnitude greater for HCBD than for HCA; as HCA is a crystalline solid while pure HCBD is a liquid, the difference can be attributed to the latent heat of fusion[26] and the conversion of the solid in the liquid state.[38] Solubilization enhancement per

Figure 3. Evolution of the apparent solubility of HCBD and HCA in mole fraction as a function of surfactant concentration: (a and b) apparent solubility in the presence of Triton X-100; (c and d) apparent solubility in the presence of Tween 80; and (e and f) apparent solubility in the presence of SDBS. Errors bars represent the standard error obtained with three replicates. ◆ = HCBD, ■ = HCA.

Table 7. MSR and log K_{mw} Values for HCBD and HCA with Triton X-100, Tween 80, and SDBS at 298.15 K under $P = 0.1$ MPa

	hexachlorobutadiene		hexachloroethane	
surfactant	MSR	log K_{mw}	MSR	log K_{mw}
Triton X-100	1.22	3.39	0.10	2.01
Tween 80	0.65	3.24	0.15	2.17
SDBS	0.12	2.68	0.038	1.64

micelle for HCBD and HCA is higher for Triton X-100 and Tween 80, respectively, while anionic surfactant SDBS has shown the lowest efficiency. This result is in agreement with literature, which has shown that anionic surfactants can solubilize less organic compounds than the nonionic ones.[74,75] Nevertheless, for *in situ* application, adsorption of nonionic surfactants into soils results in large losses of surfactant, whereas anionic surfactants are less impacted due to the repulsive forces between negative charges of the surfactant head and soil surfaces.[26,76] It is therefore important to define the best compromise between surfactant efficiency and losses for each specific soil. For this reason, some studies have been performed with a mixture of nonionic and anionic surfactants, resulting in a synergetic effect with higher solubility enhancement and partition losses reduction.[76,77]

4. CONCLUSION

This study aimed to investigate the influence of the temperature in the range from (285.15 to 318.15) K and the presence of surfactants at 298.15 K on the solubility behavior of HCBD and HCA.

The influence of temperature on the solubility of the two chlorinated compounds showed a minimum solubility between 293.15 and 298.15 K for both compounds. For a better insight, a nonlinear Van't Hoff equation was used to calculate the thermodynamic properties changes of dissolution. The variation of $\Delta_{sol}H°$ and $\Delta_{sol}S°$ in the hydration shell showed a linear variation with a sign change versus temperature. This result was explained by the opposite effect of temperature onto Brownian motion, which increases with temperature, and the hydrogen-bond network, which collapses with temperature. The results as a whole indicated that the solubilization process is less impacted by the physical and chemical properties of HCBD or HCA but rather by the water molecules' network changes with temperature.

Concerning the influence of nonionic or anionic surfactants, the presence of Triton X-100, Tween 80, and SDBS at concentrations above their respective CMC linearly enhanced the apparent solubility of HCBD and HCA, in agreement with the increase number of micelles in which they can partition. For both compounds, nonionic surfactants Triton X-100 and Tween 80 showed similar performances regarding the micelle concentration in solution, higher than those obtained by using SDBS.

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■ REFERENCES

(1) Verschueren, K. *Handbook of Environmental Data on Organic Chemicals*, 2nd ed.; Van Nostrand Reinhold: New York, NY, USA, 1983.
(2) *Environmental Health Criteria 156: Hexachlorobutadiene*; WHO: Geneva, Switzerland, 1994.
(3) Atoji, M.; Oda, T.; Watanabé, T. On the Crystal Structure of Cubic Hexachloroethane. *Acta Crystallogr.* **1953**, *6*, 868−868.
(4) Sasada, Y.; Atoji, M. Crystal Structure and Lattice Energy of Orthorhombic Hexachloroethane. *J. Chem. Phys.* **1953**, *21*, 145−152.
(5) Woost, B.; Bougeard, D. Vibrational Spectra and Phase Transitions of Crystalline Hexachloroethane. *J. Chem. Phys.* **1986**, *84*, 4810−4817.
(6) Budavari, S. *The Merck Index, Print Version*, 12th ed.; CRC Press: Whitehouse Station, NJ, USA, 1996.
(7) Johnson, R. L.; Pankow, J. F. Dissolution of Dense Chlorinated Solvents into Groundwater. 2. Source Functions for Pools of Solvent. *Environ. Sci. Technol.* **1992**, *26*, 896−901.
(8) Kingston, J. L. T.; Johnson, P. C.; Kueper, B. H.; Mumford, K. G. In Situ Thermal Treatment of Chlorinated Solvent Source Zones. In *Chlorinated Solvent Source Zone Remediation*; Kueper, B. H., Stroo, H. F., Vogel, C. M., Ward, C. H., Eds.; Springer: New York, NY, 2014; pp 509−557.
(9) Pennell, K. D.; Cápiro, N. L.; Walker, D. I. Surfactant and Cosolvent Flushing. In *Chlorinated Solvent Source Zone Remediation*; Kueper, B. H., Stroo, H. F., Vogel, C. M., Ward, C. H., Eds.; Springer: New York, NY, USA, 2014; pp 353−394.
(10) Banerjee, S.; Yalkowsky, S. H.; Valvani, C. Water Solubility and Octanol/Water Partition Coefficients of Organics. Limitations of the Solubility-Partition Coefficient Correlation. *Environ. Sci. Technol.* **1980**, *14*, 1227−1229.
(11) Pearson, C. R.; McConnell, G.; Cain, R. B. Chlorinated C1 and C2 Hydrocarbons in the Marine Environment. *Proc. R. Soc. London, Ser. B* **1975**, *189*, 305−332.
(12) Horvath, A. L. *Halogenated Hydrocarbons: Solubility-Miscibility with Water*; Marcel Dekker: New York, NY, USA, 1982.
(13) McGovern, E. W. Chlorohydrocarbon Solvents. *Ind. Eng. Chem.* **1943**, *35*, 1230−1239.
(14) Van Arkel, A. E.; Vles, S. E. Löslichkeit von Organischen Verbindungen in Wasser. *Recl. des Trav. Chim. des Pays-Bas* **1936**, *55*, 407−411.
(15) Veith, G.; Macek, K.; Petrocelli, S.; Carroll, J. *Aquatic Toxicology*; Eaton, J., Parrish, P., Hendricks, A., Eds.; ASTM International: West Conshohocken, PA, USA, 1980.
(16) Munz, C.; Roberts, P. V. Effects of Solute Concentration and Cosolvents on the Aqueous Activity Coefficient of Halogenated Hydrocarbons. *Environ. Sci. Technol.* **1986**, *20*, 830−836.
(17) Heron, G.; Christensen, T. H.; Enfield, C. G. Henry's Law Constant for Trichloroethylene between 10 and 95 °C. *Environ. Sci. Technol.* **1998**, *32*, 1433−1437.
(18) Knauss, K. G.; Dibley, M. J.; Leif, R. N.; Mew, D. A.; Aines, R. D. The Aqueous Solubility of Trichloroethene (TCE) and Tetrachloroethene (PCE) as a Function of Temperature. *Appl. Geochem.* **2000**, *15*, 501−512.
(19) Chen, F.; Freedman, D. L.; Falta, R. W.; Murdoch, L. C. Henry's Law Constants of Chlorinated Solvents at Elevated Temperatures. *Chemosphere* **2012**, *86*, 156−165.
(20) Oleszek-Kudlak, S.; Shibata, E.; Nakamura, T. The Effects of Temperature and Inorganic Salts on the Aqueous Solubility of Selected Chlorobenzenes. *J. Chem. Eng. Data* **2004**, *49*, 570−575.
(21) Shiu, W.-Y.; Ma, K.-C. Temperature Dependence of Physical−Chemical Properties of Selected Chemicals of Environmental Interest. II. Chlorobenzenes, Polychlorinated Biphenyls, Polychlorinated

Dibenzo-P-Dioxins, and Dibenzofurans. *J. Phys. Chem. Ref. Data* **2000**, *29*, 387−462.

(22) Sleep, B. E.; Ma, Y. Thermal Variation of Organic Fluid Properties and Impact on Thermal Remediation Feasibility. *Soil Sediment Contam.* **1997**, *6*, 281−306.

(23) Stephenson, R. M. Mutual Solubilities: Water-Ketones, Water-Ethers, and Water-Gasoline-Alcohols. *J. Chem. Eng. Data* **1992**, *37*, 80−95.

(24) Ma, J. H. Y.; Hung, H.; Shiu, W.-Y.; Mackay, D. Temperature Dependence of the Aqueous Solubility of Selected Chlorobenzenes and Chlorotoluenes. *J. Chem. Eng. Data* **2001**, *46*, 619−622.

(25) Mackay, D.; Shiu, W.-Y.; Ma, K.-C.; Lee, S. C. *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2006.

(26) Rosen, M. J.; Kunjappu, J. T. *Surfactants and Interfacial Phenomena*, 4th ed.; Wiley-Blackwell: Hoboken, NJ, USA, 2012.

(27) Harendra, S.; Vipulanandan, C. Effects of Surfactants on Solubilization of Perchloroethylene (PCE) and Trichloroethylene (TCE). *Ind. Eng. Chem. Res.* **2011**, *50*, 5831−5837.

(28) Jafvert, C. T. Solubilization of Non-Polar Compounds by Non-Ionic Surfactant Micelles. *Water Res.* **1994**, *28*, 1009−1017.

(29) Kommalapati, R. R.; Valsaraj, K. T.; Constant, W. D.; Roy, D. Aqueous Solubility Enhancement and Desorption of Hexachloroben-zene from Soil Using a Plant-Based Surfactant. *Water Res.* **1997**, *31*, 2161−2170.

(30) Taylor, T.; Pennell, K.; Abriola, L.; Dane, J. Surfactant Enhanced Recovery of Tetrachloroethylene from a Porous Medium Containing Low Permeability Lenses. 1. Experimental Studies. *J. Contam. Hydrol.* **2001**, *48*, 325−350.

(31) Schick, M. J. *Nonionic Surfactants: Physical Chemistry*; CRC Press: Boca Raton, FL, USA, 1987.

(32) Wagner, J.; Chen, H.; Brownawell, B. J.; Westall, J. C. Use of Cationic Surfactants to Modify Soil Surfaces to Promote Sorption and Retard Migration of Hydrophobic Organic Compounds. *Environ. Sci. Technol.* **1994**, *28*, 231−237.

(33) Mao, X.; Jiang, R.; Xiao, W.; Yu, J. Use of Surfactants for the Remediation of Contaminated Soils: A Review. *J. Hazard. Mater.* **2015**, *285*, 419−435.

(34) Ivanković, T.; Hrenović, J. Surfactants in the Environment. *Arh. Hig. Rada Toksikol.* **2010**, *61*, 95−110.

(35) Cho, H.-H.; Park, J.-W. Sorption and Reduction of Tetrachloro-ethylene with Zero Valent Iron and Amphiphilic Molecules. *Chemosphere* **2006**, *64*, 1047−1052.

(36) Zhang, M.; He, F.; Zhao, D.; Hao, X. Degradation of Soil-Sorbed Trichloroethylene by Stabilized Zero Valent Iron Nano-particles: Effects of Sorption, Surfactants, and Natural Organic Matter. *Water Res.* **2011**, *45*, 2401−2414.

(37) Nie, X.; Liu, J.; Zeng, X. Effect of Surfactant on HCB Dechlorination by Ag/Fe Bimetal in Polluted Soil Eluent. *Procedia Environ. Sci.* **2012**, *16*, 320−326.

(38) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. Activity Coefficient and Solubility in Water. In *Environmental Organic Chemistry*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2005; pp 133−180.

(39) Clarke, E. C. W.; Glew, D. N. Evaluation of Thermodynamic Functions from Equilibrium Constants. *Trans. Faraday Soc.* **1966**, *62*, 539−547.

(40) Imhoff, P. T.; Frizzell, A.; Miller, C. T. Evaluation of Thermal Effects on the Dissolution of a Nonaqueous Phase Liquid in Porous Media. *Environ. Sci. Technol.* **1997**, *31*, 1615−1622.

(41) Gordus, A. A. Chemical Equilibrium: I. The Thermodynamic Equilibrium Constant. *J. Chem. Educ.* **1991**, *68*, 138−140.

(42) Freire, M. G.; Razzouk, A.; Mokbel, I.; Jose, J.; Marrucho, I. M.; Coutinho, J. A. P. Solubility of Hexafluorobenzene in Aqueous Salt Solutions from (280 to 340) K. *J. Chem. Eng. Data* **2005**, *50*, 237−242.

(43) Frank, H. S.; Evans, M. W. Free Volume and Entropy in Condensed Systems III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes. *J. Chem. Phys.* **1945**, *13*, 507−532.

(44) Muller, N. Search for a Realistic View of Hydrophobic Effects. *Acc. Chem. Res.* **1990**, *23*, 23−28.

(45) Gill, S. J.; Dec, S. F.; Olofsson, G.; Wadso, I. Anomalous Heat Capacity of Hydrophobic Solvation. *J. Phys. Chem.* **1985**, *89*, 3758−3761.

(46) Lee, B.; Graziano, G. A Two-State Model of Hydrophobic Hydration That Produces Compensating Enthalpy and Entropy Changes. *J. Am. Chem. Soc.* **1996**, *118*, 5163−5168.

(47) Southall, N. T.; Dill, K. A. The Mechanism of Hydrophobic Solvation Depends on Solute Radius. *J. Phys. Chem. B* **2000**, *104*, 1326−1331.

(48) Southall, N. T.; Dill, K. A.; Haymet, A. D. J. A View of the Hydrophobic Effect. *J. Phys. Chem. B* **2001**, *106*, 521−533.

(49) Silverstein, K. A. T.; Haymet, A. D. J.; Dill, K. A. A Simple Model of Water and the Hydrophobic Effect. *J. Am. Chem. Soc.* **1998**, *120*, 3166−3175.

(50) Ben-Naim, A. Statistical Mechanical Study of Hydrophobic Interaction. II. Interaction among a Set of M Identical, Spherical, and Nonpolar Solute Particles. *J. Chem. Phys.* **1971**, *54*, 3696.

(51) Chalikian, T. V. Structural Thermodynamics of Hydration. *J. Phys. Chem. B* **2001**, *105*, 12566−12578.

(52) Lee, B. Solvent Reorganization Contribution to the Transfer Thermodynamics of Small Nonpolar Molecules. *Biopolymers* **1991**, *31*, 993−1008.

(53) Buchanan, P.; Aldiwan, N.; Soper, A. K.; Creek, J. L.; Koh, C. A. Decreased Structure on Dissolving Methane in Water. *Chem. Phys. Lett.* **2005**, *415*, 89−93.

(54) Davis, J. G.; Gierszal, K. P.; Wang, P.; Ben-Amotz, D. Water Structural Transformation at Molecular Hydrophobic Interfaces. *Nature* **2012**, *491*, 582−585.

(55) Galamba, N. Water's Structure around Hydrophobic Solutes and the Iceberg Model. *J. Phys. Chem. B* **2013**, *117*, 2153−2159.

(56) Galamba, N. Reply to "Comment on 'Water's Structure around Hydrophobic Solutes and the Iceberg Model. *J. Phys. Chem. B* **2014**, *118*, 2600−2603.

(57) Ahmed, M.; Singh, A. K.; Mondal, J. A. Hydrogen-Bonding and Vibrational Coupling of Water in a Hydrophobic Hydration Shell as Observed by Raman-MCR and Isotopic Dilution Spectroscopy. *Phys. Chem. Chem. Phys.* **2016**, *18*, 2767−2775.

(58) Rezus, Y. L. A.; Bakker, H. J. Observation of Immobilized Water Molecules around Hydrophobic Groups. *Phys. Rev. Lett.* **2007**, *99*, 148301.

(59) Titantah, J. T.; Karttunen, M. Hydrophobicity: Effect of Density and Order on Water's Rotational Slowing Down. *Soft Matter* **2015**, *11*, 7977−7985.

(60) Swiatla-Wojcik, D.; Pabis, A.; Szala, J. Density and Temperature Effect on Hydrogen-Bonded Clusters in Water - MD Simulation Study. *Open Chem.* **2008**, *6*, 555−561.

(61) Sun, D.-W. *Handbook of Frozen Food Processing and Packaging*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2012.

(62) Petersen, C.; Tielrooij, K.-J. K.-J.; Bakker, H. J. Strong Temperature Dependence of Water Reorientation in Hydrophobic Hydration Shells. *J. Chem. Phys.* **2009**, *130*, 214511.

(63) Bakker, H. J. Physical Chemistry: Water's Response to the Fear of Water. *Nature* **2012**, *491*, 533−535.

(64) Graziano, G. Comment on "The Hydrophobic Effect" by B. Widom, P. Bhimalapuram and K. Koga, Phys. Chem. Chem. Phys., 2003, 5, 3085. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4527−4528.

(65) Graziano, G. Cavity Thermodynamics and Hydrophobicity. *J. Phys. Soc. Jpn.* **2000**, *69*, 1566−1569.

(66) Chandler, D. Interfaces and the Driving Force of Hydrophobic Assembly. *Nature* **2005**, *437*, 640−647.

(67) Kim, J.; Tian, Y.; Wu, J. Thermodynamic and Structural Evidence for Reduced Hydrogen Bonding among Water Molecules near Small Hydrophobic Solutes. *J. Phys. Chem. B* **2015**, *119*, 12108−12116.

(68) Laage, D.; Stirnemann, G.; Hynes, J. T. Why Water Reorientation Slows without Iceberg Formation around Hydrophobic Solutes. *J. Phys. Chem. B* **2009**, *113*, 2428−2435.

(69) Hawkes, R.; Grutter, M. G.; Schellman, J. Thermodynamic Stability and Point Mutations of Bacteriophage T4 Lysozyme. *J. Mol. Biol.* **1984**, *175*, 195−212.

(70) Sturtevant, J. M. Heat Capacity and Entropy Changes in Processes Involving Proteins. *Proc. Natl. Acad. Sci. U. S. A.* **1977**, *74*, 2236−2240.

(71) Kronberg, B.; Castas, M.; Silvestonti, R. Understanding the Hydrophobic Effect. *J. Dispersion Sci. Technol.* **1994**, *15*, 333−351.

(72) Edwards, D. A.; Luthy, R. G.; Liu, Z. Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant Solutions. *Environ. Sci. Technol.* **1991**, *25*, 127−133.

(73) Irvine, R. L.; Sikdar, S. K. *Bioremediation: Principles and Practice. Vol. I: Fundamentals and Applications*; CRC Press: Lancaster, PA, USA, 1997.

(74) Kile, D. E.; Chiou, C. T. Water Solubility Enhancements of DDT and Trichlorobenzene by Some Surfactants below and above the Critical Micelle Concentration. *Environ. Sci. Technol.* **1989**, *23*, 832−838.

(75) Zhou, M.; Rhue, R. D. Screening Commercial Surfactants Suitable for Remediating DNAPL Source Zones by Solubilization. *Environ. Sci. Technol.* **2000**, *34*, 1985−1990.

(76) Zhao, B.; Zhu, L.; Yang, K. Solubilization of DNAPLs by Mixed Surfactant: Reduction in Partitioning Losses of Nonionic Surfactant. *Chemosphere* **2006**, *62*, 772−779.

(77) Yang, K.; Zhu, L.; Zhao, B. Minimizing Losses of Nonionic and Anionic Surfactants to a Montmorillonite Saturated with Calcium Using Their Mixtures. *J. Colloid Interface Sci.* **2005**, *291*, 59−66.

(78) Hait, S. K.; Moulik, S. P. Determination of Critical Micelle Concentration (CMC) of Nonionic Surfactants by Donor-Acceptor Interaction with Lodine and Correlation of CMC with Hydrophile-Lipophile Balance and Other Parameters of the Surfactants. *J. Surfactants Deterg.* **2001**, *4*, 303−309.

(79) Yu, D.; Huang, F.; Xu, H. Determination of Critical Concentrations by Synchronous Fluorescence Spectrometry. *Anal. Methods* **2012**, *4*, 47−49.

(80) Bakshi, M.; Sachar, S.; Mahajan, N.; Kaur, I.; Kaur, G.; Singh, N.; Sehgal, P.; Doe, H. Mixed-Micelle Formation by Strongly Interacting Surfactant Binary Mixtures: Effect of Head-Group Modification. *Colloid Polym. Sci.* **2002**, *280*, 990−1000.