

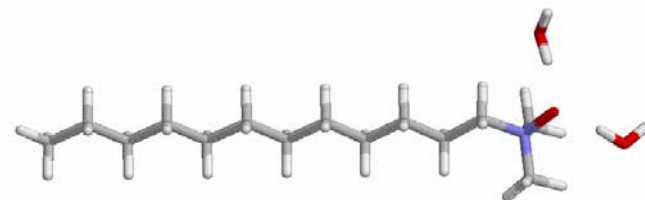
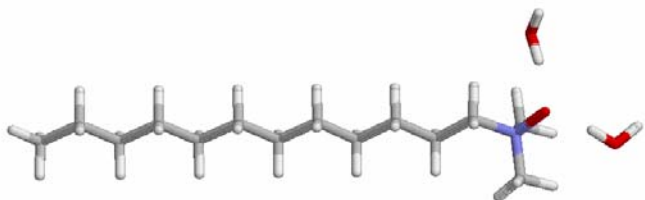
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# Hydration of liquid crystalline phases in the system DDAO-water studied by sorption calorimetry

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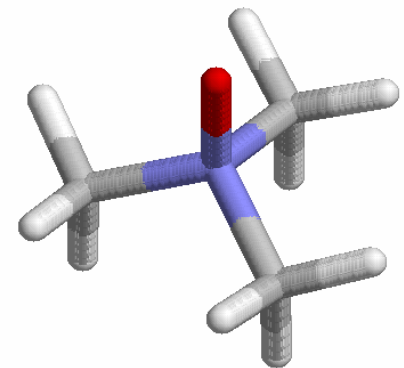
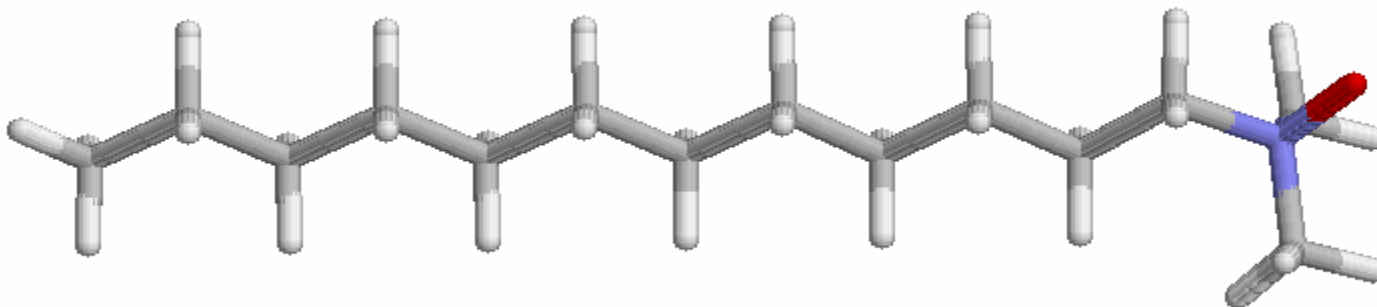
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# DDAO and TMAO

N,N-Dimethyldodecylamine –N-oxide (DDAO) has only one highly polar atom (oxygen) which is able to interact with water (nitrogen atom is obstructed by three carbons and one oxygen). Nevertheless, this surfactant exhibit very hydrophilic properties. It forms direct (normal) liquid crystalline phases and micelles.

The “short” analog of DDAO – Trimethyl amine oxide is used by sharks to keep osmotic pressure of their bodies. Unlike urea (which destabilizes properties), TMAO has stabilizing effect on proteins. This effect is probably due to decrease of the water activity caused by TMAO, which suggests that interactions with water are strong.

In order to understand mechanisms of DDAO – water interactions we have performed sorption calorimetric study of hydration of DDAO.

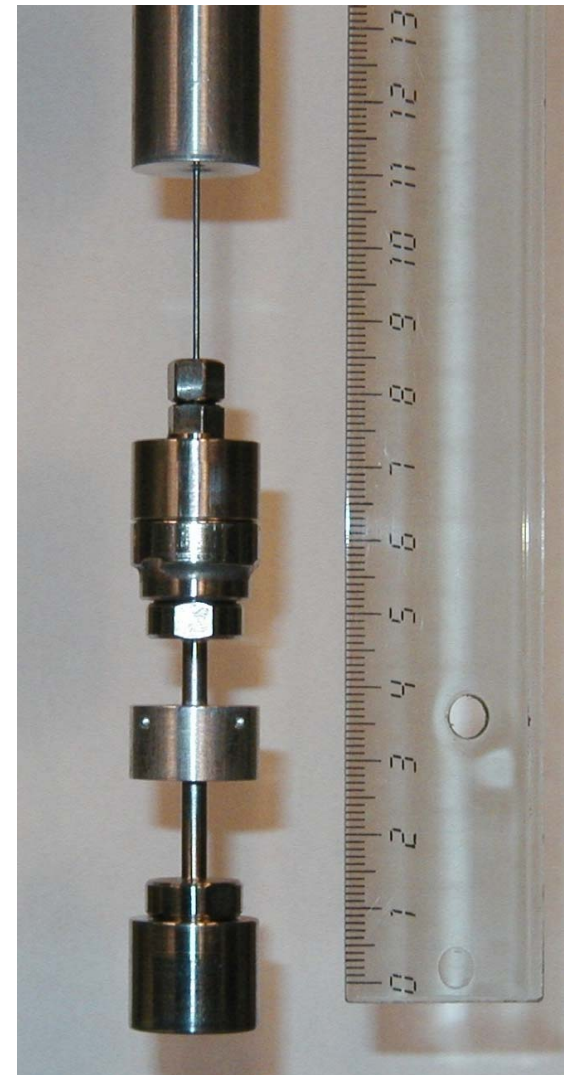
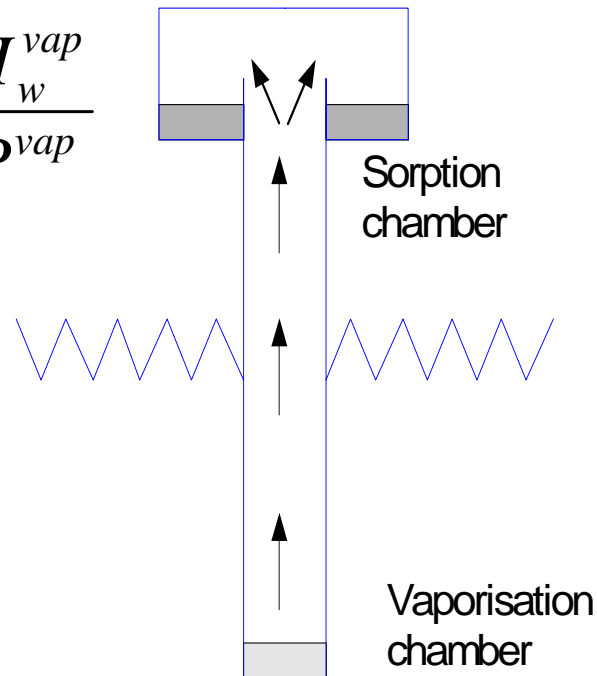


# Sorption calorimetry

$$H_w^{mix} = H_w^{vap} + P^{sorp} \frac{H_w^{vap}}{P^{vap}}$$

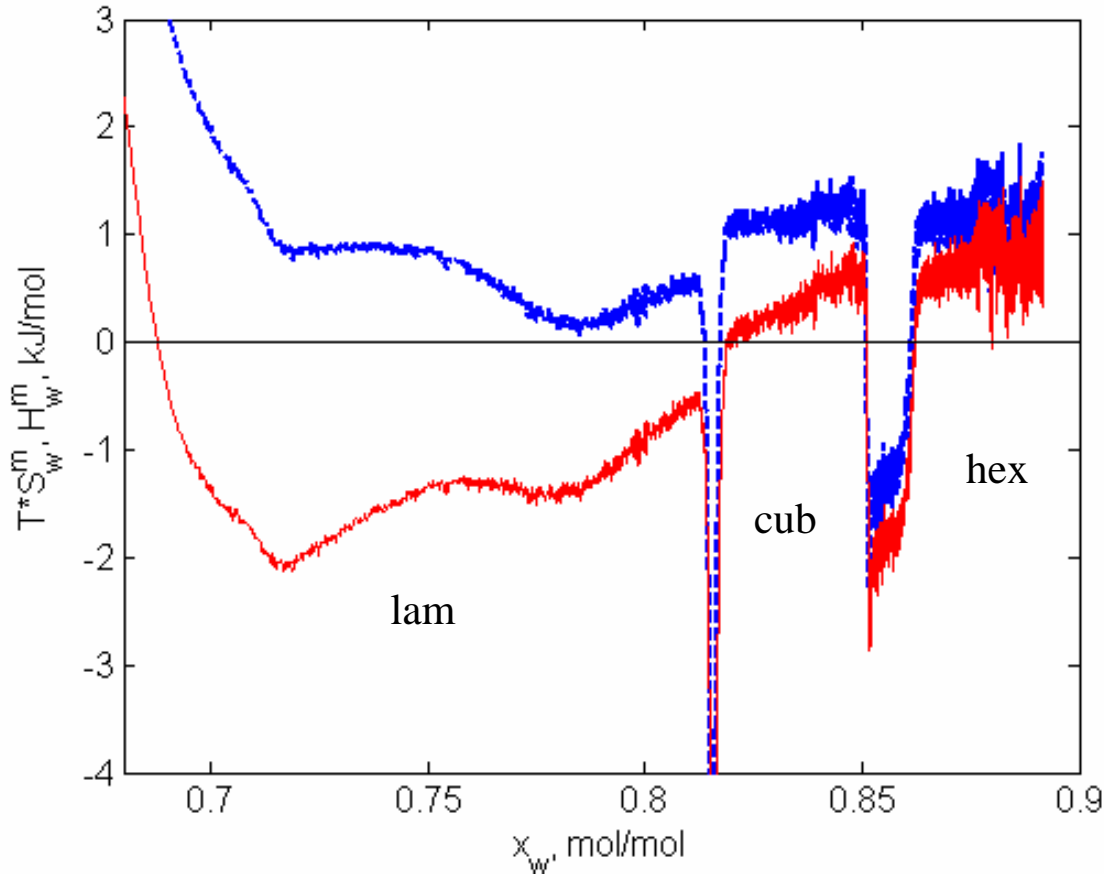
$$a_w = 1 - \frac{P^{vap}}{P_{max}^{vap}}$$

$$m_w = \frac{\int P^{vap} dt}{H_w^{vap}}$$



Ref: V. Kocherbitov and L. Wadsö. *A Desorption Calorimetric Method for Use at High Water Activities*. *Thermochimica Acta*, 2004. **411**(1): p. 31-36.  
 L. Wadsö and N. Markova. *A method to simultaneously determine sorption isotherms and sorption enthalpies with a double twin microcalorimeter*.  
*Review of Scientific Instruments*, 2002. **73**(7): p. 2743-2754.

# Driving forces of hydration of liquid crystalline phases in DDAO - water system

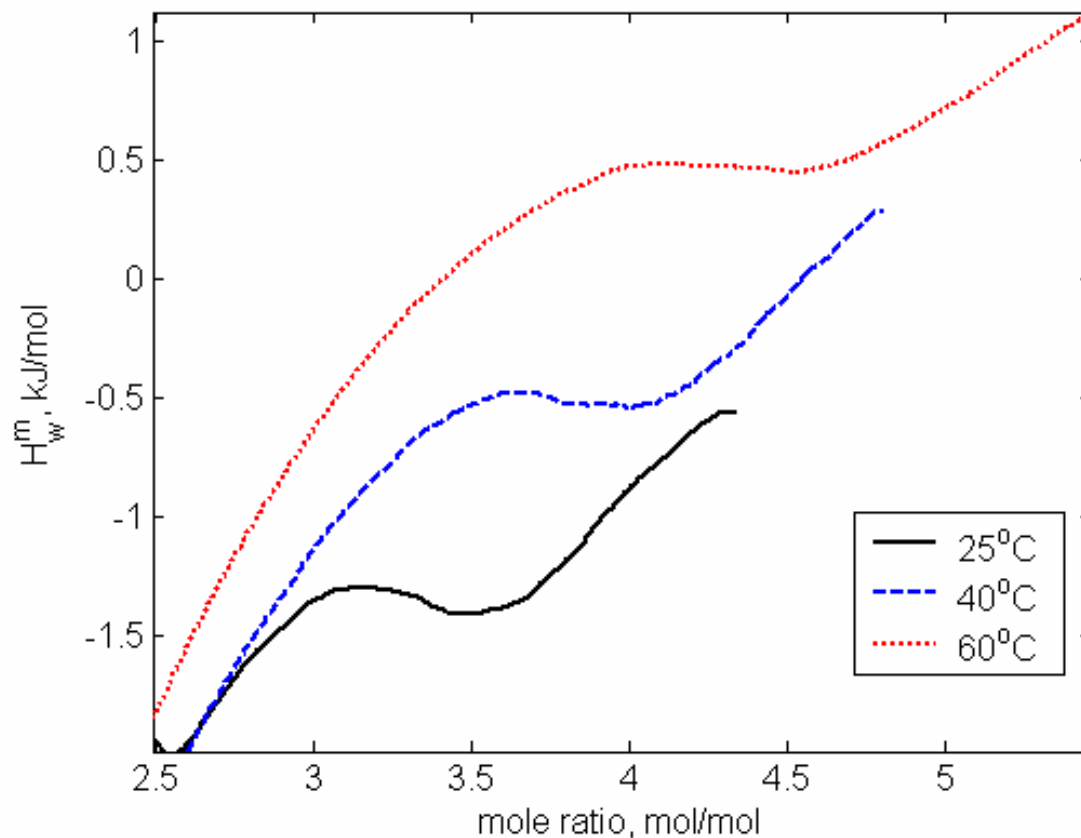


Data for 25 °C

Phase	Sign of $H_w^m$	Sign of $S_w^m$	Driving force
Lamellar	-	+	S and H
Cubic	+	+	Only S
Hexagonal	+	+	Only S

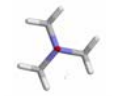
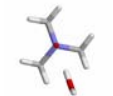
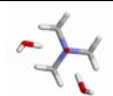
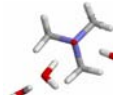
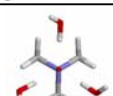
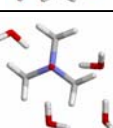
The hydration of the lamellar phase is driven by enthalpy and entropy. Hydration of the cubic and the hexagonal phases is driven only by entropy at 25 °C

# Hydration of the lamellar phase



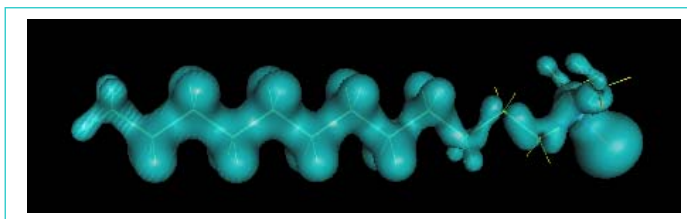
The exothermic enthalpy of hydration of the lamellar phase is not the only parameter that differs hydration of DDAO from that of other surfactants. Another interesting feature is the shape of curve in the concentration region of the lamellar phase. The enthalpy curves obtained during hydration of lamellar phases in other surfactant systems were featureless horizontal lines [5, 6, 17]. In case of DDAO the enthalpy of hydration of the lamellar phase significantly increases with water content and has a shallow maximum followed by a minimum (see figure). Interestingly, the difference in the compositions of the maxima and the minima at all studied temperatures is 0.5 water molecules per DDAO molecule. Moreover, all the shallow peaks appear approximately at half-integer values. These facts show that the interactions of DDAO molecule with water molecules are strong (stronger than in other studied non-ionic surfactant systems).

# Ab initio calculations

N waters	structure	DDAO			TMAO		
		-Energy, a.u	H-bond Energy, kJ/mol	same/N, kJ/mol	-Energy, a.u	H-bond Energy, kJ/mol	same/N, kJ/mol
0		682.08554861	0	0	249.65436549	0	0
1		758.56146248	57.76	57.76	326.13001433	57.07	57.07
2		835.03479625	108.76	54.37	402.60312808	107.48	53.74
3 non-simm		911.50637579	155.14	51.71	No data	-	-
3 simm		911.5063.....	~155	~51	479.0744.....	~153	~51
4 (5 hydr. bonds)		No data	-	-	555.54600799	199.52	49.88 (39.9 per bond)

Ab Initio quantum mechanics calculations were done using the B3LYP procedure. Atomic natural orbital (ANO) basis set was used. The hydrogen bond energy was calculated as the difference between the energies of the hydrogen bonded complex and the sum of energies of isolated molecules in vacuum.

The results show that the hydrogen bonds in the complexes of DDAO (and TMAO) with water are stronger than between water molecules in pure water. (The energy of hydrogen bonds in water was calculated using similar procedure and it was about 20 kJ/mol)

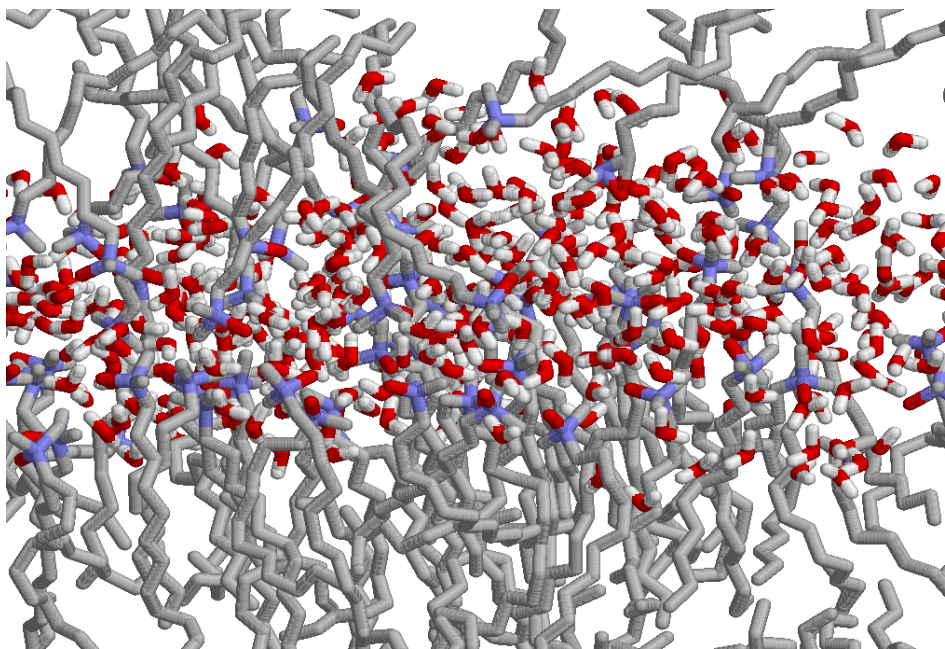




# Molecular dynamics simulations

Ab initio calculations give information that is related to 0 K.

In order to get detailed molecular – level information of structure of lamellar phase of DDAO at temperatures of the calorimetric experiments, one has to perform molecular dynamics simulations. The potentials for MD simulations should be adjusted using the results of ab initio calculations. The experimental fact that the minimum on enthalpy curve shifts to higher water contents at higher temperatures is probably due to expansion of the hydrophobic layer because of the thermal movement of the tails. The expansion of the layer makes the complexes with higher water contents be the most stable at higher temperatures. This suggestion will be tested using MD simulations. In the figure is a snapshot of a MD simulation for DDAO-water mixture with mole ratio 1:3.5



## • Conclusions

- The entropy of hydration in all liquid crystalline phases of DDAO – water system is positive, i.e. the hydration is driven by entropy
- The enthalpy of hydration in the lamellar phase is negative, while in other phases it is positive
- The specific shape of H and S curves at low water content indicate strong interactions between DDAO and water, including formation of DDAO – water complexes
- Ab initio calculations show that hydrogen bonds in complexes of water with DDAO and with TMAO are stronger than in pure water, which explains negative values of enthalpy of hydration in the lamellar phase
- More studies are needed to obtain more exact structures of DDAO – water mixtures at different temperatures

## Acknowledgement

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