Thermodynamics of cationic and anionic surfactant interaction

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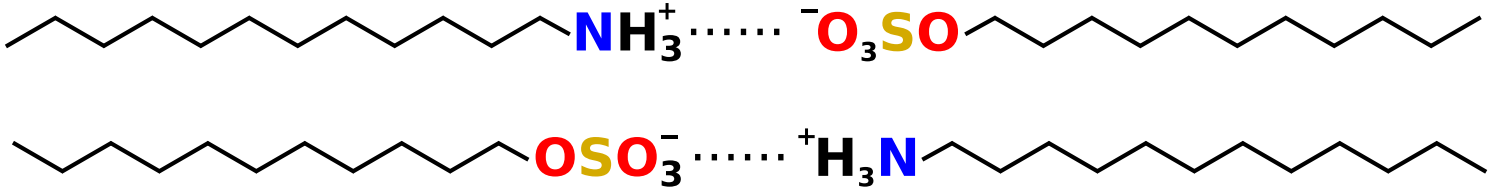
Introduction

Motivation

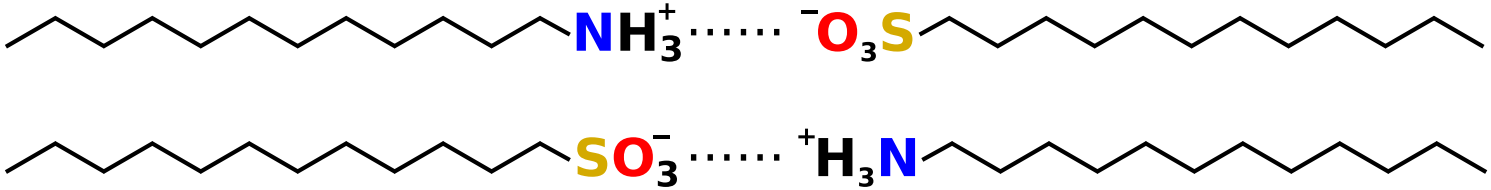
- Fundamental understanding of hydrophobic and ionic forces in lipid membranes and proteins
- Simple model system is the interacting positively and negatively charged linear surfactants
- Dissection of the hydrophobic and ionic contributions to the thermodynamics of surfactant interactions

Alkylamine interactions with alkyl sulfates



and

alkylamine interactions with alkane sulfonates



Model

Reaction between oppositely charged detergents

Reaction between negatively and positively charged detergents can be divided into two arbitrary parts:

1. oppositely charged ions form ion pairs
   $\mathrm{R_1NH_3^+ + R_2SO_3^- \longleftrightarrow R_1NH_3^+ \cdots R_2SO_3^-}$
   and
2. electrically neutral and hydrophobic ion pair complexes form an aggregate of size ν
   $\mathrm{\nu(R_1NH_3^+ \cdots R_2SO_3^-) \longleftrightarrow (R_1NH_3^+ \cdots R_2SO_3^-)_\nu \downarrow}$,
   which precipitates out of aqueous solution.

$\mathrm{R_1}$ and $\mathrm{R_2}$ are linear aliphatic chains of various length.

Isothermal titration calorimetry

Thermogram and binding isotherm of decane sulfonate titration by dodecylammonium

Equipment:

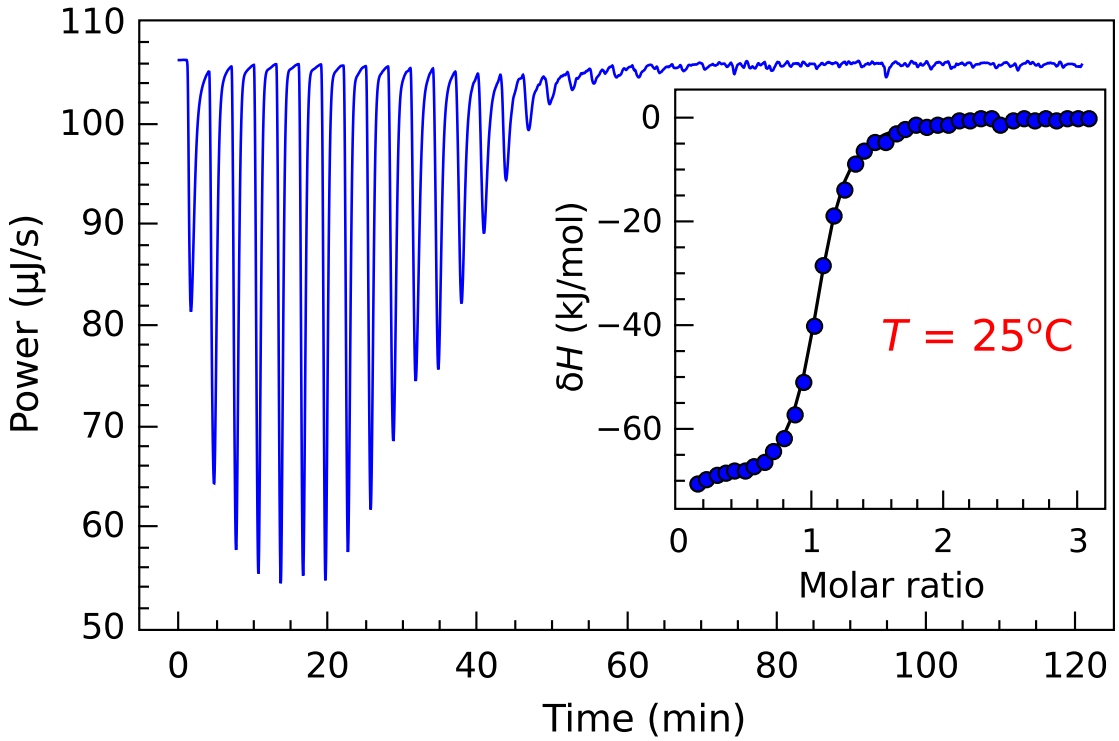
Microcal (Northampton, MA)
Micro Calorimetry System
(MCS)

Temperature range:

(25–65) °C

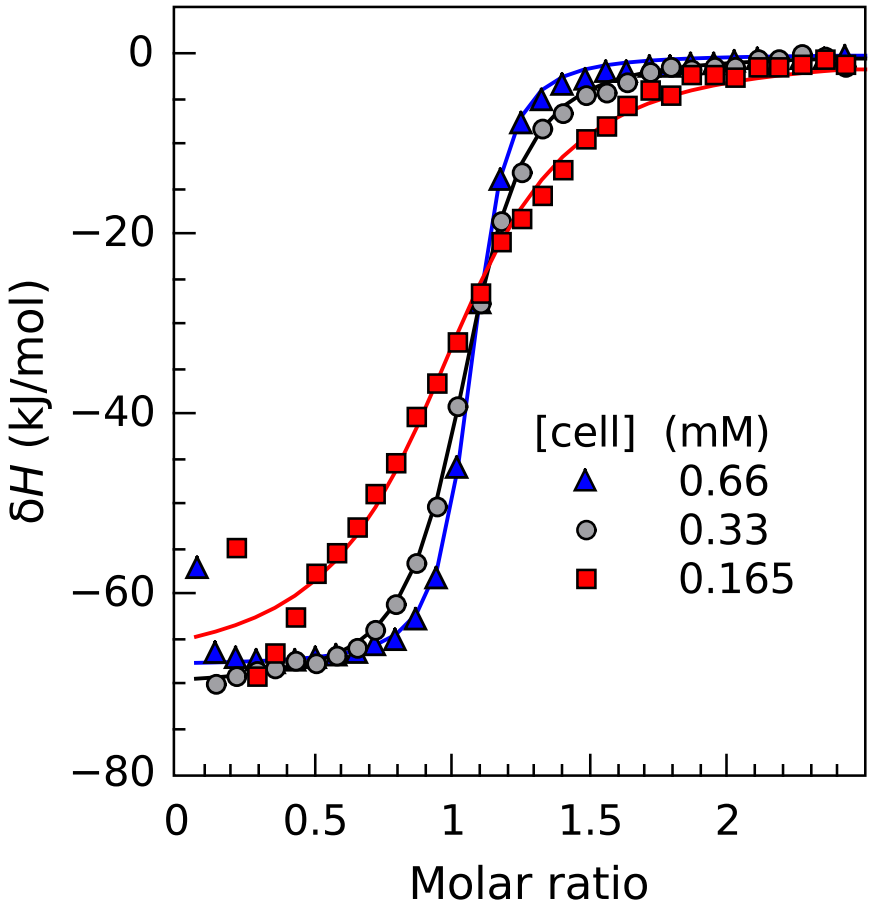
Surfactant concentrations:

Cell – 0.33 mM
Syringe – 5 mM



Observed binding constant dependence on concentration

Example: dodecylammonium binding to decane sulfonate at $T = 25\,℃$



C (mM)	K_b^{obs} (M^{-1})	K_b^{mod} (M^{-1})
0.66	3.5×10^5	5.5×10^5
0.33	1.9×10^5	2.7×10^5
0.165	1.1×10^5	1.4×10^5

$$K_b^{mod} = \frac{[\mathrm{R_1NH_3^+ \cdots R_2SO_3^- \downarrow}]}{[\mathrm{R_1NH_3^+}][\mathrm{R_2SO_3^-}]}$$

Observed binding constant dependence on concentration

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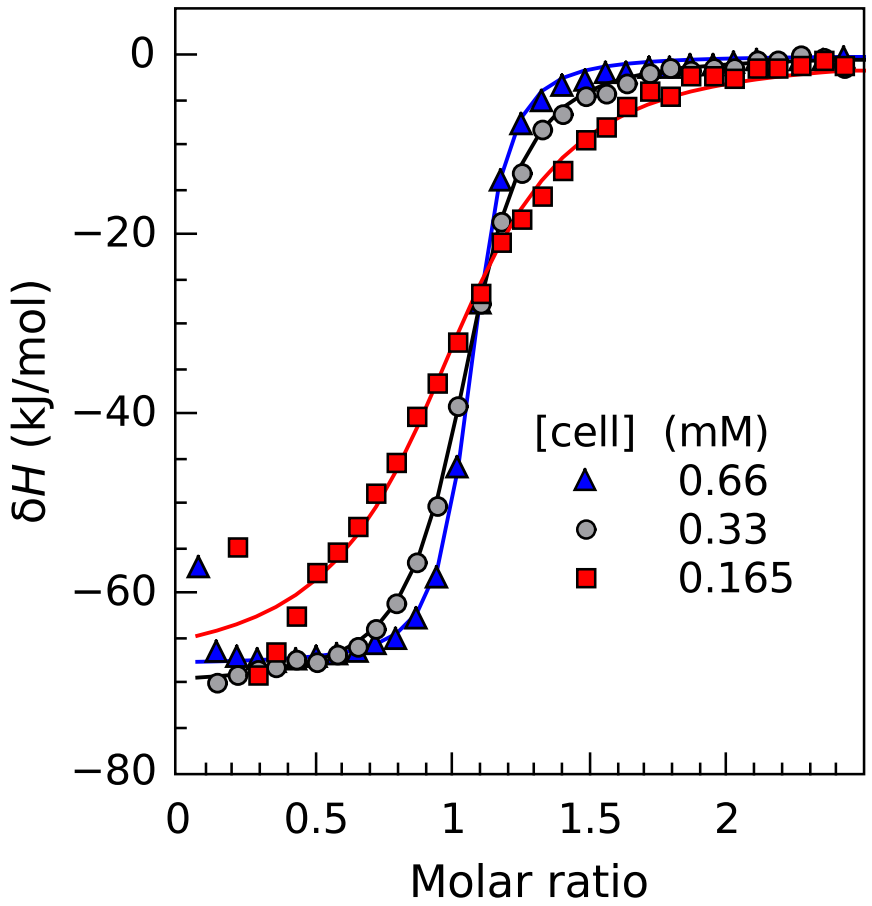
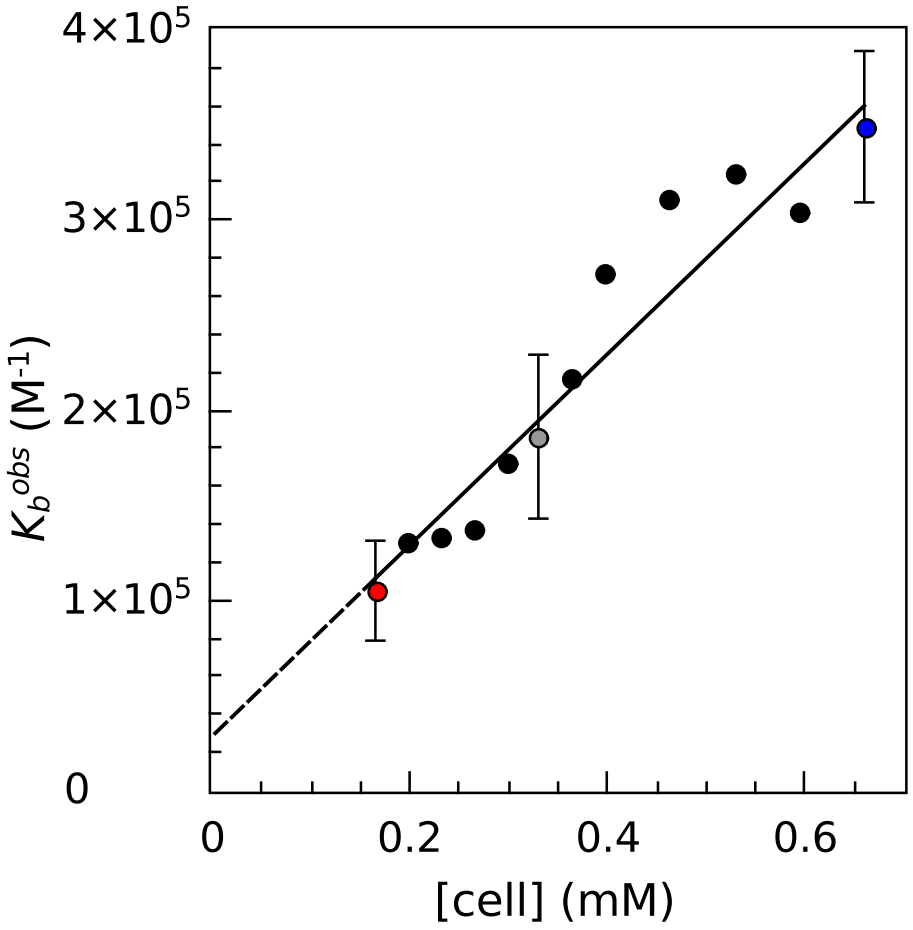


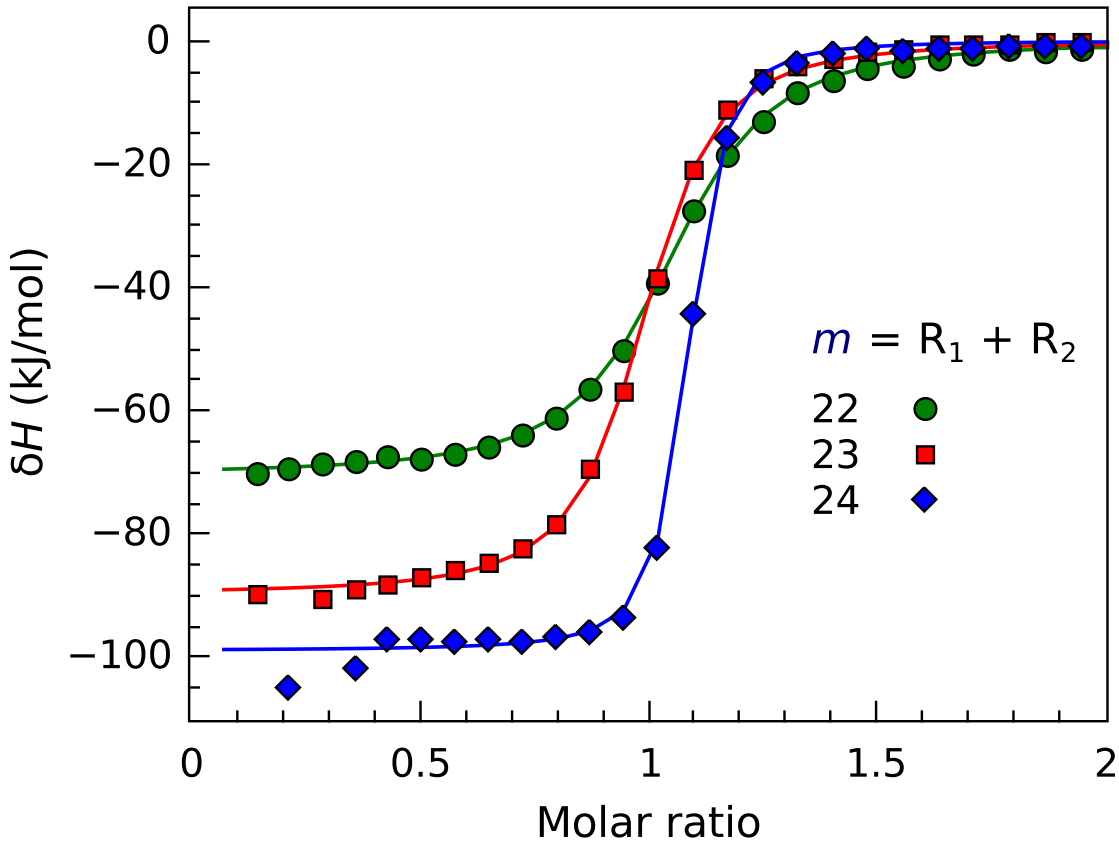


Dependence on aliphatic chain length

Example: dodecylammonium binding to alkane sulfonate

Number of carbon atoms in both R_1 and R_2 linear aliphatic chains:

$$m = R_1 + R_2$$



Dependence on aliphatic chain length

Alkane sulfonate binding to alkylammonium at 25°C

Table: Thermodynamic parameters of stoichiometric coprecipitate formation. Gray columns mark experimentaly obtained values.

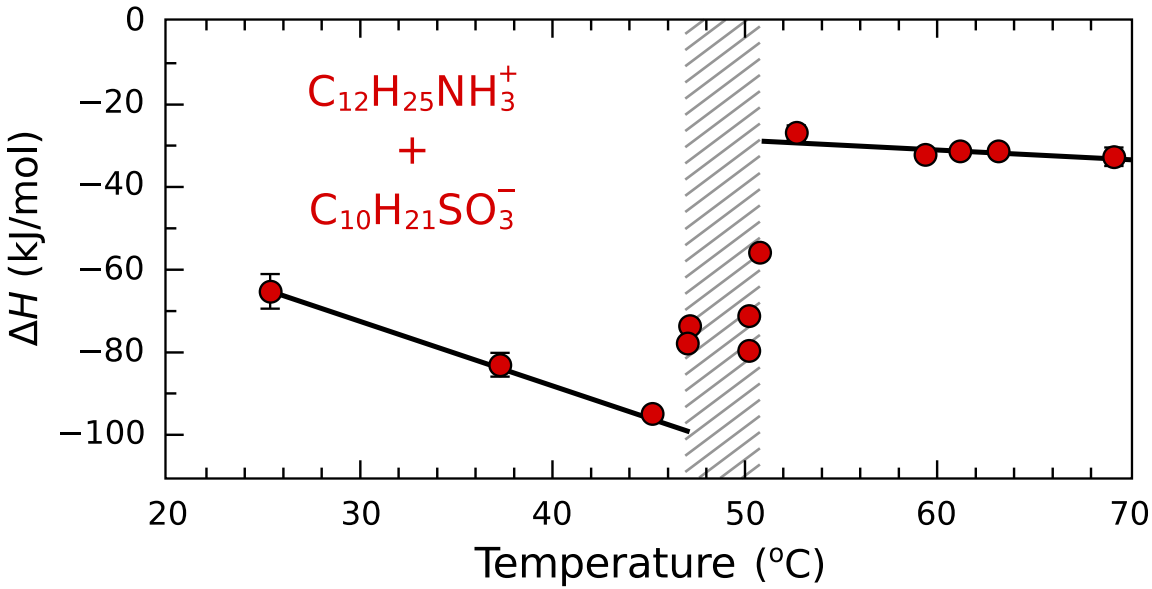
m	K_b^{obs} (M^{-1})	K_b^{mod} (M^{-1})	$\Delta_{agg}G$ (kJ/mol)			$\Delta_{agg}H$ (kJ/mol)		
			obs	*mod*	*alk*	*obs*	*mod*	*alk*
21	3.3×10^4	6.4×10^4	-25.8	-27.5	-56.0	-37.4	-97.4	-90.8
22	1.8×10^5	2.7×10^5	-30.0	-31.0	-59.6	-67.5	-102.6	-96.0
23	2.6×10^5	1.2×10^6	-30.9	-34.6	-63.2	-81.9	-107.8	-101.2
24	1.3×10^6	4.9×10^6	-34.9	-38.2	-66.8	-91.1	-113.0	-106.4

Enthalpy dependence on temperature

Example: decane sulfonate reaction with dodecylammonium

Reaction:
$C_{10}H_{21}SO_3^- + C_{12}H_{25}NH_3^+$

Solid-to-liquid phase transition at 49°C



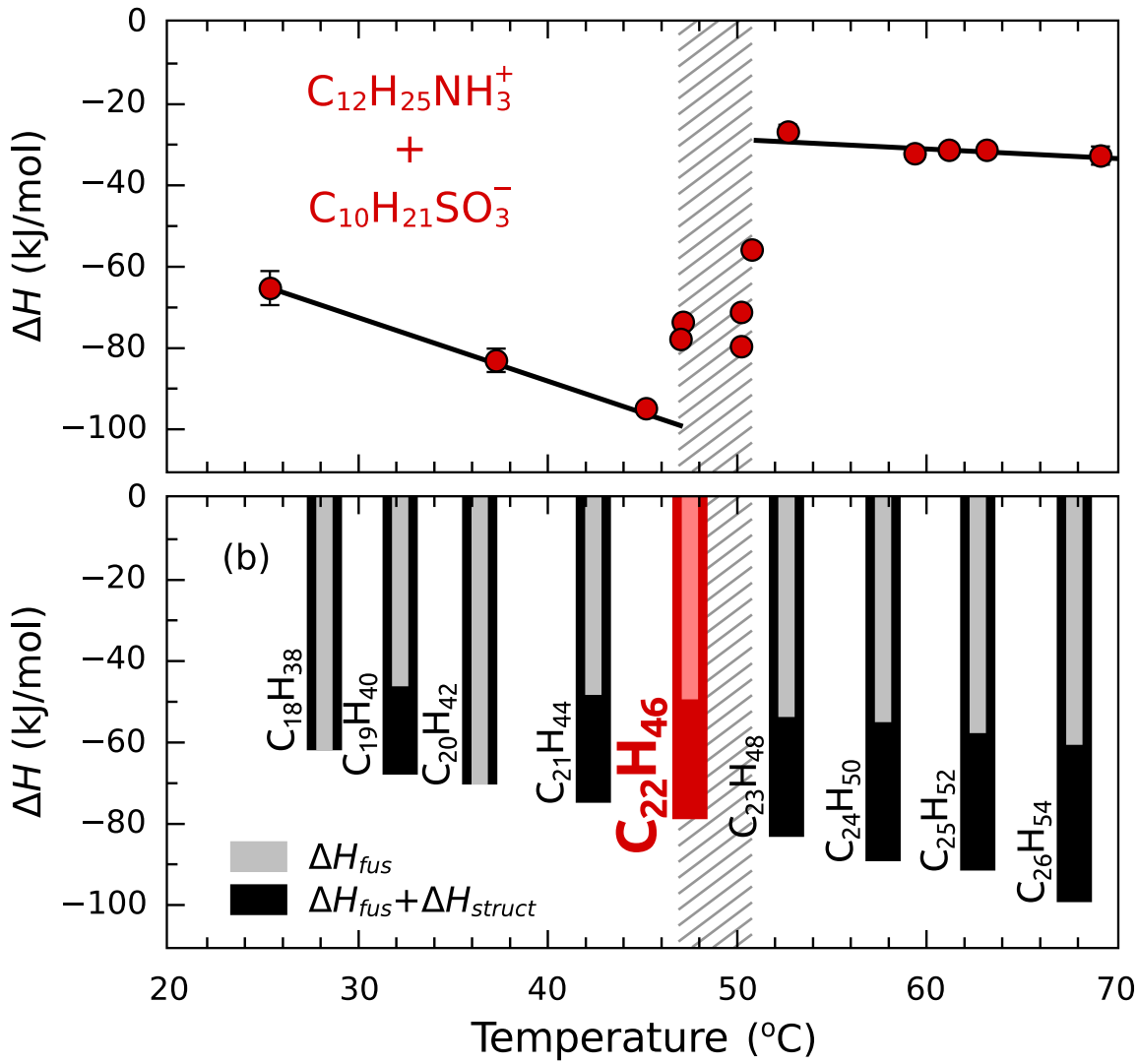
Enthalpy dependence on temperature

Example: decane sulfonate reaction with dodecylammonium

Reaction:
$C_{10}H_{21}SO_3^- + C_{12}H_{25}NH_3^+$

Solid-to-liquid phase transition at 49°C

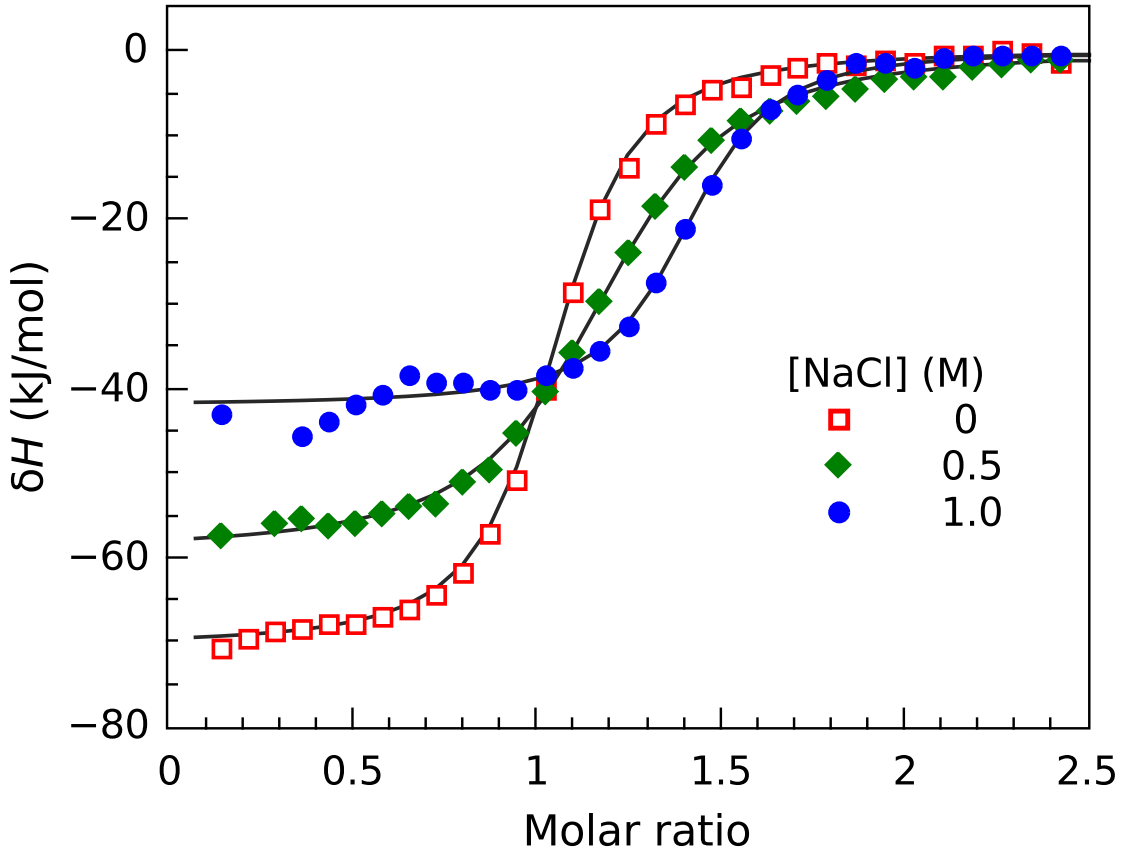
Alkanes:
Data taken from CRC Handbook*



* *CRC Handbook of Chemistry and Physics*, 90th ed.; CRC Press: Boca Raton, FL, 2009

Enthalpy dependence on salt concentration

Dodecylammonium binding to alkane sulfonate at various salt concentrations



Dissection of thermodynamic aggregation parameters

Hydrophobic and ionic contributions of dodecylamine binding to dodecane sulfonate

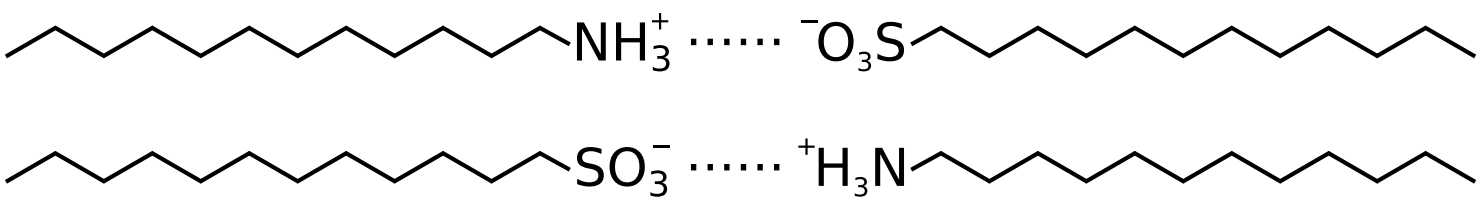


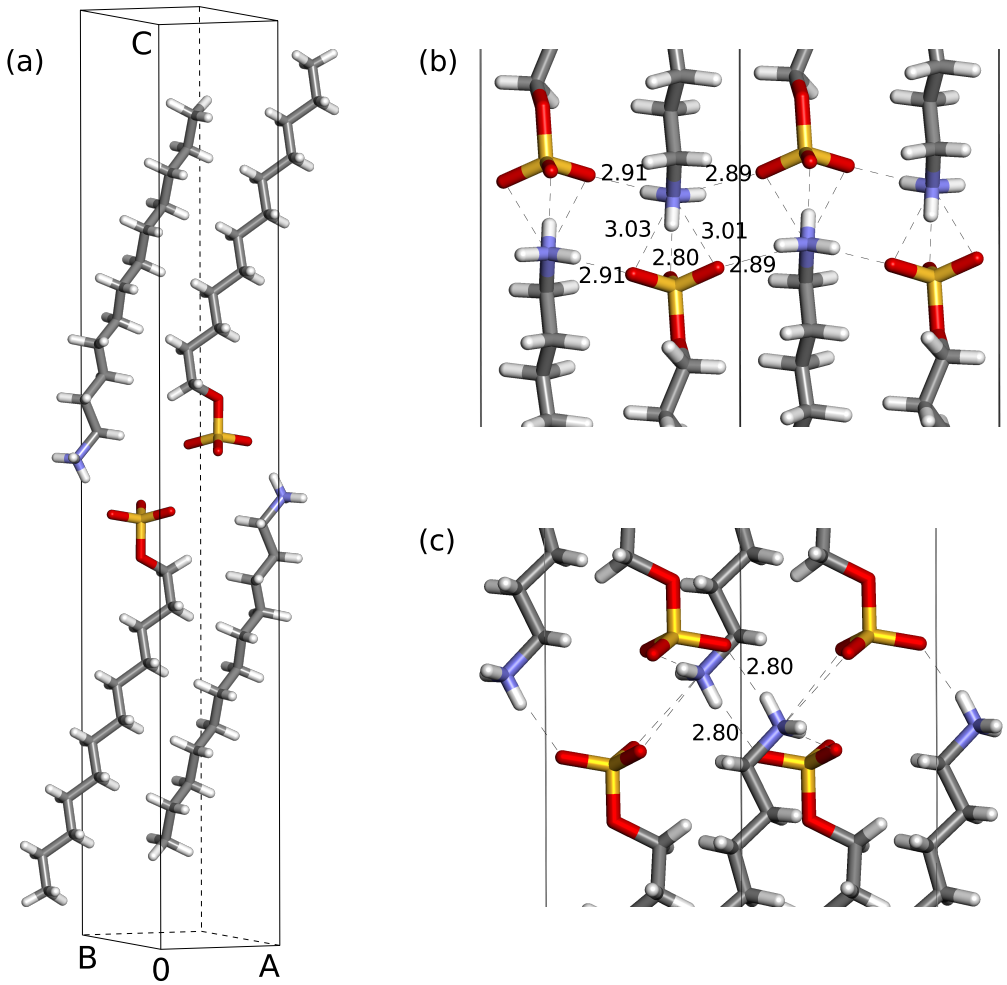
Table: Thermodynamics of aggregation into solid phase (model)

	Hydrophobic	Electrostatic	
$\Delta_b G$ (kJ/mol)	-67	+29	(0.33 mM)
$\Delta_b H$ (kJ/mol)	-106	-7	(any conc.)
$T\Delta_b S$ (kJ/mol)	-39	-36	(0.33 mM)

Packing model

Packing diagram of dodecylamine complex with dodecyl sulfate

- Crystallographic data of most similar O-lauroylethanolamine – dodecylsulfate structure was used*.
- O-lauroylethanolamine was substituted with dodecylamine.
- Resulting structure was optimized using the semiempirical quantum chemistry program MOPAC.



*Tarafdar et al. *J. Phys. Chem. B* **114** (2010) 13710

Conclusions

- Association and aggregation reactions between long-chain aliphatic surfactants at temperatures below the fusion temperature are enthalpy-driven and entropy-opposed.
- The dominating enthalpy contribution is primarily due to aliphatic chain packing.

Acknowledgment

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Daumantas Matulis,
Povilas Norvaišas

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Appendix

Dodecylammonium binding to decane sulfonate

ITC fitting parameters at three different concentrations in the cell

Table: Binding constants K_b^{fit} obtained from experimental data fits are compared to binding constants K_b^{mod} obtained from the model

C (mM)	ΔH^{obs} (kJ/mol)	N^{obs}	K_b^{obs} (M^{-1})	K_b^{mod} (M^{-1})
0.66	-70.9 $\pm$ 3.7	1.01 ± 0.03	$(3.5 \pm 0.4) \times 10^5$	5.5×10^5
0.33	-70.5 $\pm$ 5.2	0.98 ± 0.05	$(1.9 \pm 0.4) \times 10^5$	2.4×10^5
0.165	-72.7 $\pm$ 15.9	0.99 ± 0.03	$(1.1 \pm 0.3) \times 10^5$	1.4×10^5

Thermodynamic parameters of coprecipitate formation

Alkane sulfonate binding to alkylammonium at 25°C

m	K_b^{obs} (M^{-1})	K_b^{mod} (M^{-1})	$\Delta_{agg}G$ (kJ/mol)			$\Delta_{agg}H$ (kJ/mol)			$T\Delta_{agg}S$ (kJ/mol)
			obs	*mod*	*alk*	*obs*	*mod*	*alk*	
21	3.3×10^4	6.4×10^4	-25.8	-27.5	-56.0	-37.4	-97.4	-90.8	-11.6
22	1.8×10^5	2.7×10^5	-30.0	-31.0	-59.6	-67.5	-102.6	-96.0	-37.4
23	2.6×10^5	1.2×10^6	-30.9	-34.6	-63.2	-81.9	-107.8	-101.2	-51.0
24	1.3×10^6	4.9×10^6	-34.9	-38.2	-66.8	-91.1	-113.0	-106.4	-56.3

Model formulae

$$\Delta_{agg} G^{mod} = \Delta_{agg} G_{ion} + \Delta_{agg} G_{alk} \tag{1}$$

$$\Delta_{agg} G_{ion} = -RT \ln(A_{ion} C) \tag{2}$$

$$\Delta_{agg} G_{alk} = -RT \ln(A_{alk} C) = -RT(m \ln(\Delta w) + \ln(w_0) + \ln(C)) \tag{3}$$

C – molar concentration of detergent.

$$A_{ion} = B^{-1} \frac{[\mathrm{R_1NH_3^+ \cdots R_2SO_3^-}]}{[\mathrm{R_1NH_3^+}][\mathrm{R_2SO_3^-}]} \tag{4}$$

$$A_{alk} = C^{-1} \frac{[\mathrm{R_1NH_3^+ \cdots R_2SO_3^-} \downarrow]}{[\mathrm{R_1NH_3^+ \cdots R_2SO_3^-}]} \tag{5}$$

$$K_b^{mod} = \frac{[\mathrm{R_1NH_3^+ \cdots R_2SO_3^-} \downarrow]}{[\mathrm{R_1NH_3^+}][\mathrm{R_2SO_3^-}]} = A_{ion} B A_{alk} C \tag{6}$$

B – constant factor equal to 4.03×10^{-5}.