

Thermodynamics of cationic and anionic surfactant interaction

Vytautas Petrauskas

Department of Biothermodynamics and Drug Design
Institute of Biotechnology, Vilnius University

October 16, 2014



Biothermodynamics and Drug Design Department

Vilnius University Institute of Biotechnology

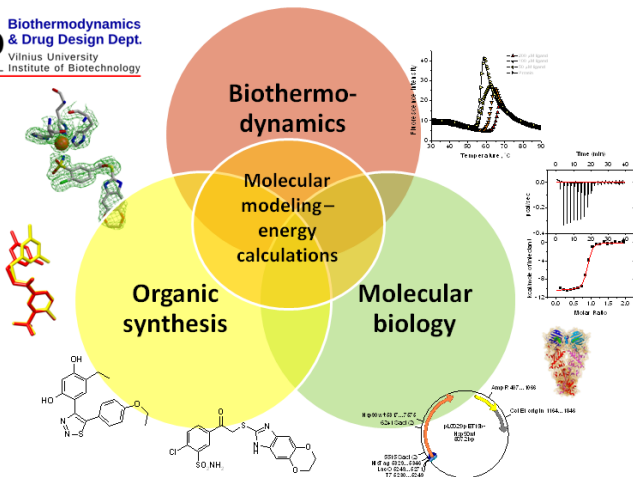
- Head of Department:
Prof. Daumantas Matulis
- Main research direction:
Design of novel chemical
compounds with anticancer
activity



Biothermodynamics and Drug Design Lab, 2013

Biothermodynamics and Drug Design Department

Research activities



Thermodynamic description of protein–ligand interaction
(ΔG , ΔH , ΔS , ΔC_p):

- Thermal shift assay (ThermoFluor®)
- Isothermal titration calorimetry
 - VP-ITC (MicroCal)
 - MCS (MicroCal)
 - Nano ITC (TA Instruments)
 - ITC200 (MicroCal)

Introduction

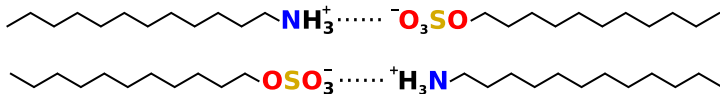
Cationic and anionic surfactant interactions: motivation

- Structure and function of biological macromolecules are governed by a combination of hydrophobic, ionic, and steric interactions at molecular level.
- Fundamental questions of hydrophobic and ionic forces in lipid membranes and proteins
- Simple model systems that mimic the desired properties of proteins and lipid membranes: positively and negatively charged linear surfactants
- Dissection of the hydrophobic and ionic contributions to the thermodynamics of surfactant interactions

Introduction

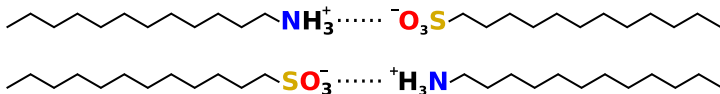
Model system / objects of investigation

Alkylamine interactions with alkyl sulfates



and

Alkylamine interactions with alkane sulfonates



- Equimolar mixtures of the detergents form stoichiometric complexes.
- Concentrations of detergents was several times lower than cmc.

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



and

- 2 electrically neutral and hydrophobic ion pair complexes form an aggregate of size ν



which precipitates out of aqueous solution.

R_1 and R_2 are linear aliphatic chains of various length.

Isothermal titration calorimetry

Thermogram and binding isotherm of decane sulfonate titration by dodecylammonium

Equipment:

MCS, Nano ITC

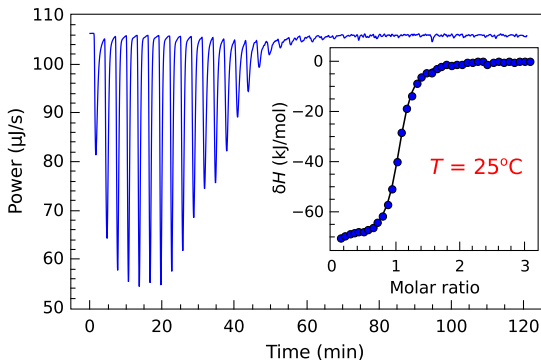
Temperature range:

(25–65) °C

Surfactant concentrations:

Cell – 0.33 mM

Syringe – 5 mM

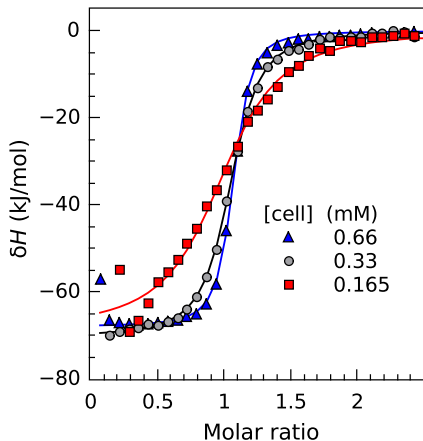


$$\Delta G = -RT \ln K_b$$

$$\Delta G = \Delta H - T\Delta S$$

Observed binding constant dependence on concentration

Example: dodecylammonium binding to decane sulfonate at $T = 25\text{ }^\circ\text{C}$



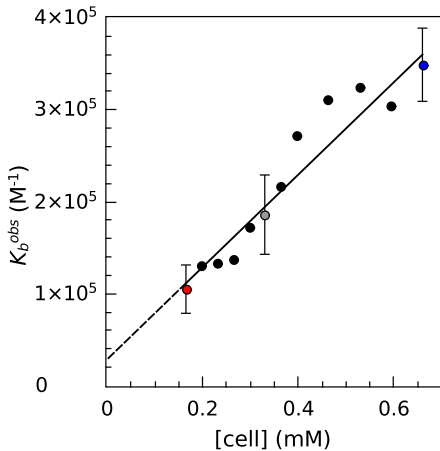
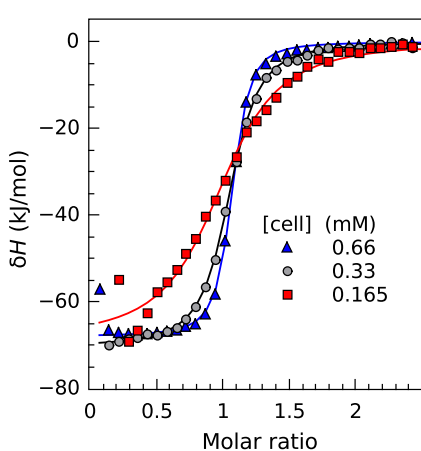
C (mM)	K_b^{obs} (M^{-1})	K_b^{mod} (M^{-1})
0.66	3.5×10^5	5.5×10^5
0.33	1.9×10^5	2.7×10^5
0.165	1.1×10^5	1.4×10^5

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

Apparent binding constant reflects a dissolution–precipitation reaction, which depends on concentration.

Observed binding constant dependence on concentration

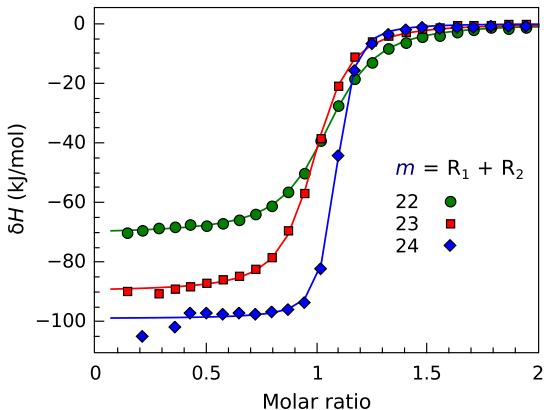
Example: dodecylammonium binding to decane sulfonate at $T = 25\text{ }^{\circ}\text{C}$



Dependence on aliphatic chain length

Example: dodecylammonium binding to alkane sulfonate

Number of carbon atoms $m = R_1 + R_2$ in both R_1 and R_2 linear aliphatic chains.



ΔH and ΔG were increasingly more negative with an increase of m .

Dependence on aliphatic chain length

Alkane sulfonate binding to alkylammonium at 25°C

Table : Thermodynamic parameters of stoichiometric coprecipitate formation at $T = 25^\circ\text{C}$. Gray columns mark experimentally obtained values.

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)
			<i>obs</i>	<i>mod</i>	<i>alk</i>	<i>obs</i>	<i>mod</i>	<i>alk</i>	
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

- Experimental and predicted values of ΔG (K_b) are very similar.
- Model predicts tighter binding (more negative enthalpy) of aliphatic tails.
- Association and aggregation reactions are enthalpy-driven and entropy-opposed.

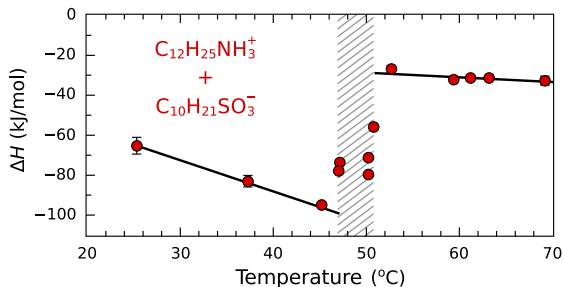
Enthalpy dependence on temperature

Example: decane sulfonate reaction with dodecylammonium

Reaction:



An abrupt change in ΔH at 49°C – solid-to-liquid phase transition



Enthalpy dependence on temperature

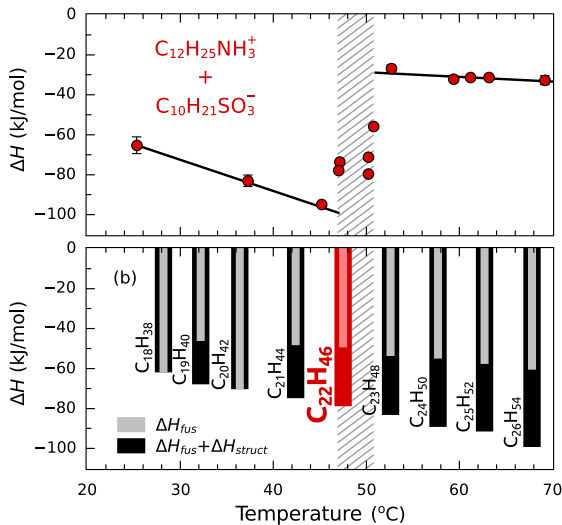
Example: decane sulfonate reaction with dodecylammonium

Reaction:



An abrupt change in ΔH at 49°C – solid-to-liquid phase transition

Fusion enthalpies of alkanes:
Data taken from
CRC Handbook*



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

Dissection of thermodynamic aggregation parameters

Hydrophobic and ionic contributions of dodecylamine binding to dodecane sulfonate

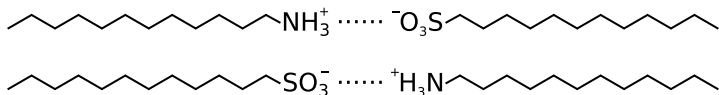


Table : Thermodynamics of aggregation into solid phase (model)

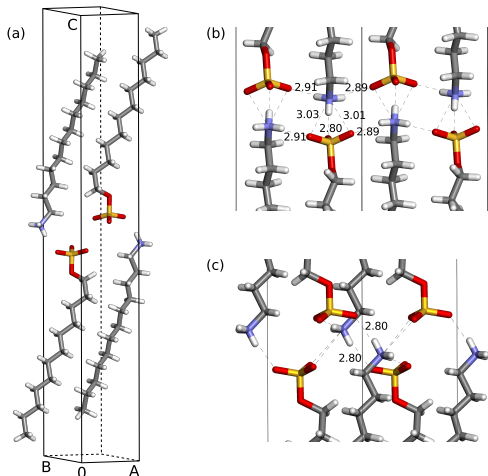
	Hydrophobic	Electrostatic	
$\Delta_b G$ (kJ/mol)	-67	+29	(0.33 mM)
$\Delta_b H$ (kJ/mol)	-106	-7	(any conc.)
$T\Delta_b S$ (kJ/mol)	-39	-36	(0.33 mM)

The dominating enthalpy contribution is due to aliphatic chain packing!

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

- 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.

More detailed information:



P. Norvaišas, V. Petrauskas, and D. Matulis,
Journal of Physical Chemistry B **116** (2012) 2138–2144

Thank you for your attention!

Appendix

$$\Delta_{agg} G^{mod} = \Delta_{agg} G_{ion} + \Delta_{agg} G_{alk} \quad (1)$$

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

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

C – molar concentration of detergent.

$$A_{ion} = B^{-1} \frac{[R_1 NH_3^+ \cdots R_2 SO_3^-]}{[R_1 NH_3^+][R_2 SO_3^-]} \quad (4)$$

$$A_{alk} = C^{-1} \frac{[R_1 NH_3^+ \cdots R_2 SO_3^- \downarrow]}{[R_1 NH_3^+ \cdots R_2 SO_3^-]} \quad (5)$$

$$K_b^{mod} = \frac{[R_1 NH_3^+ \cdots R_2 SO_3^- \downarrow]}{[R_1 NH_3^+][R_2 SO_3^-]} = A_{ion} B A_{alk} C \quad (6)$$

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