

THERMODYNAMICS OF CATIONIC AND ANIONIC SURFACTANT INTERACTION

POVILAS NORVAIŠAS, VYTAUTAS PETRAUSKAS, AND DAUMANTAS MATULIS

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

E-mails: norvaisas@ibt.lt, v.petrauskas@ibt.lt, matulis@ibt.lt



INTRODUCTION

Isothermal titration calorimetry was used to investigate the interactions between positively and negatively charged linear surfactants. The Gibbs free energies, enthalpies, entropies, and heat capacities of interaction were dissected into hydrophobic and ionic contributions for alkylamine interaction with alkyl sulfates and alkane sulfonates (Norvaišas *et al* (2012), *J Phys Chem B*, 116, 2138).

The reaction between the fully dissolved negatively and positively charged detergents can be divided into two stages:

- ion pair formation $R_1NH_3^+ + R_2SO_3^- \rightleftharpoons R_1NH_3^+ \cdots R_2SO_3^-$, where R_1 and R_2 are linear aliphatic chains of any length ($R_1 + R_2 = m$), and
- precipitation of electrically neutral and highly hydrophobic complex $\nu(R_1NH_3^+ \cdots R_2SO_3^-) \rightleftharpoons (R_1NH_3^+ \cdots R_2SO_3^-)_\nu \downarrow$.

BINDING CONSTANT AS A FUNCTION OF CONCENTRATION

TABLE: The ITC curve fitting parameters of dodecylammonium binding to decane sulfonate.

C (mM)	ΔH^{fit} (kJ/mol)	N^{fit}	K_b^{fit} (M^{-1})	K_b^{mod} (M^{-1})
0.66	-70.9 ± 3.7	1.01 ± 0.03	$(3.5 \pm 0.4) \times 10^5$	5.5×10^5
0.33	-70.5 ± 5.2	0.98 ± 0.05	$(1.9 \pm 0.4) \times 10^5$	2.4×10^5
0.17	-72.7 ± 15.9	0.99 ± 0.03	$(1.1 \pm 0.3) \times 10^5$	1.4×10^5

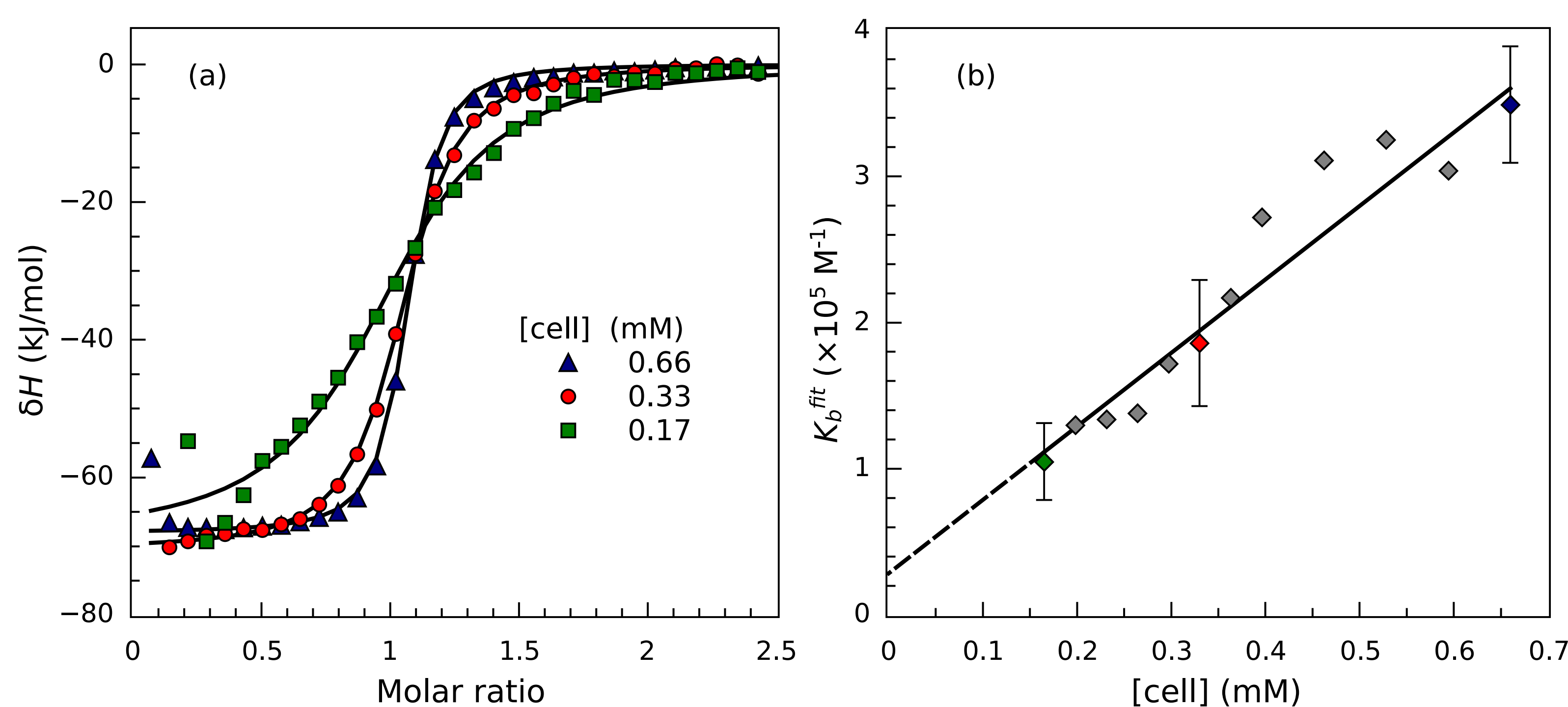


FIGURE: (a) Dodecylammonium binding to decane sulfonate at 25°C, (b) the observed binding constant K_b dependence on decane sulfonate concentration in the cell.

DEPENDENCE ON ALIPHATIC CHAIN LENGTH

TABLE: Thermodynamic parameters of stoichiometric coprecipitate formation between alkane sulfonate and alkylammonium at 25°C as a function of aliphatic chain length m .

m	K_b^{fit} (M^{-1})	K_b^{mod} (M^{-1})	$\Delta_{agg}G$ (kJ/mol)			$\Delta_{agg}H$ (kJ/mol)			$T\Delta_{agg}S$ (kJ/mol)
			fit	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

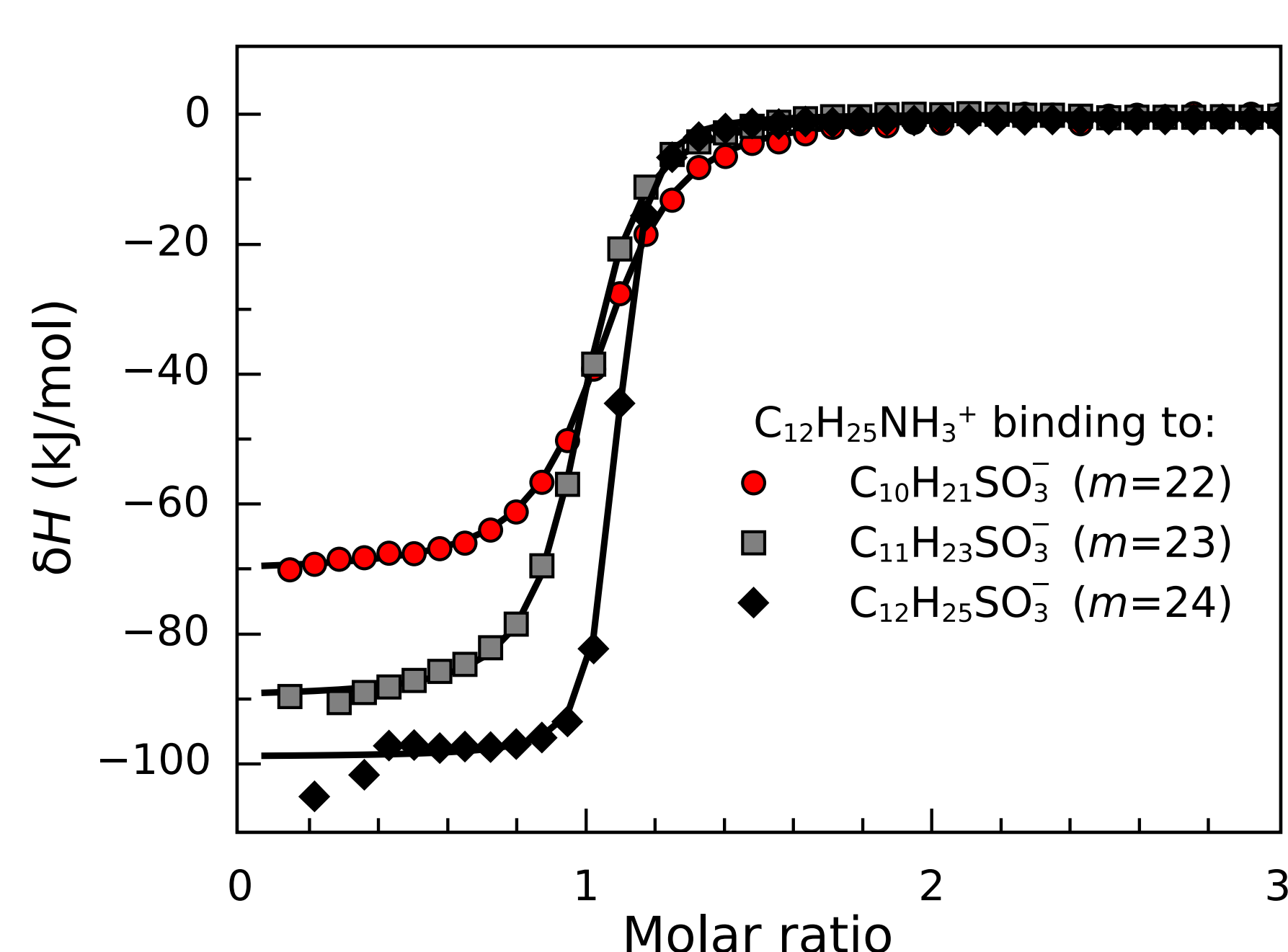


FIGURE: Dodecylammonium binding to alkane sulfonate of varying aliphatic chain length.

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

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

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

C - molar concentration of detergent,
 B - constant factor equal to 4.03×10^{-5} .

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

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

$$\Delta_{agg}G_{alk} = -RT \ln(A_{alk}C)$$

$$\Delta_{agg}H_{alk} = -5.2m + 18.41$$

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.

ITC DATA

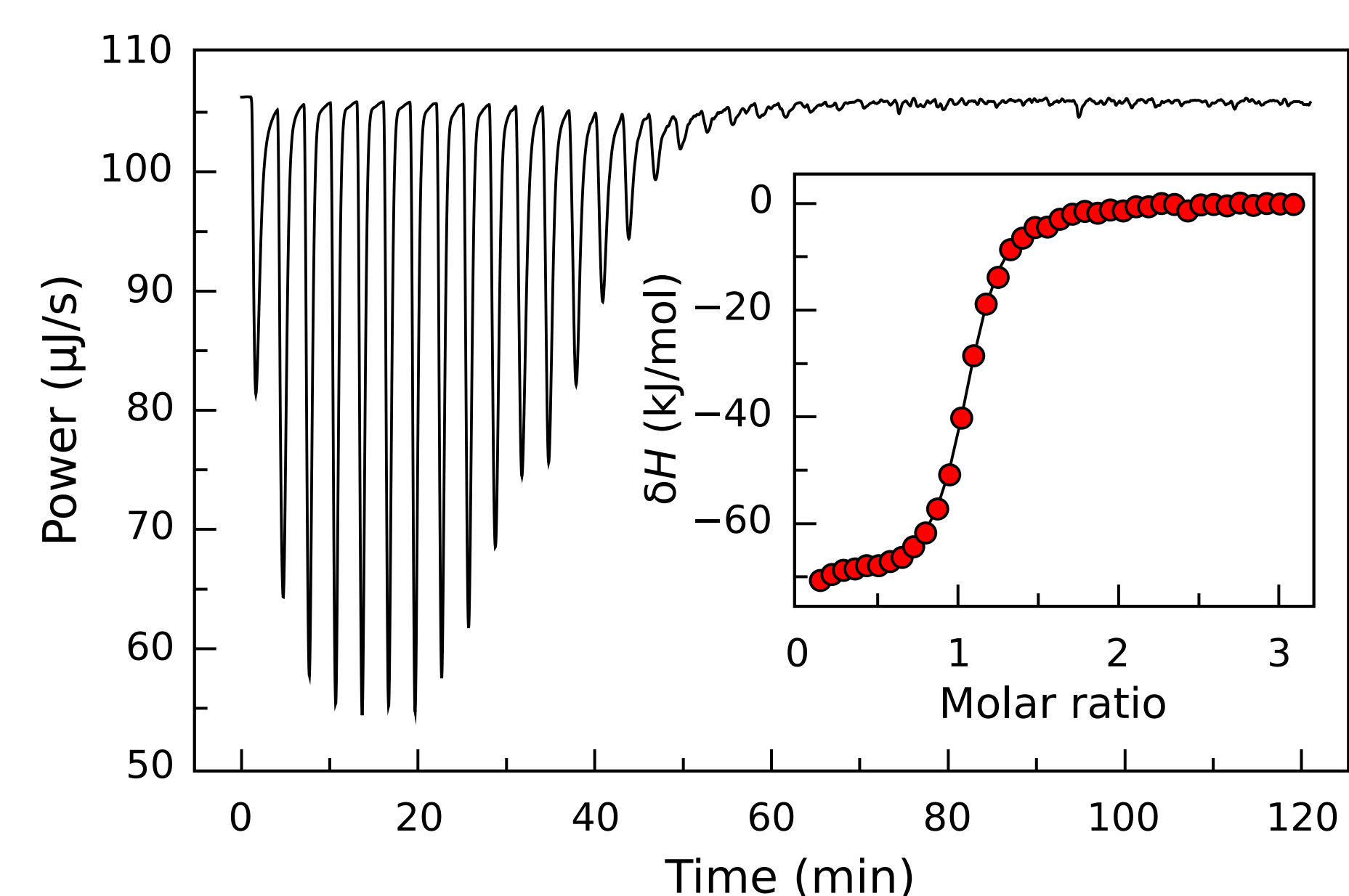


FIGURE: Raw ITC data of decane sulfonate (0.33 mM in the cell) titration by dodecylammonium (5 mM in the syringe) at 25°C.

HYDROPHOBIC-ELECTROSTATIC

	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)

ENTHALPY DEPENDENCE ON TEMPERATURE

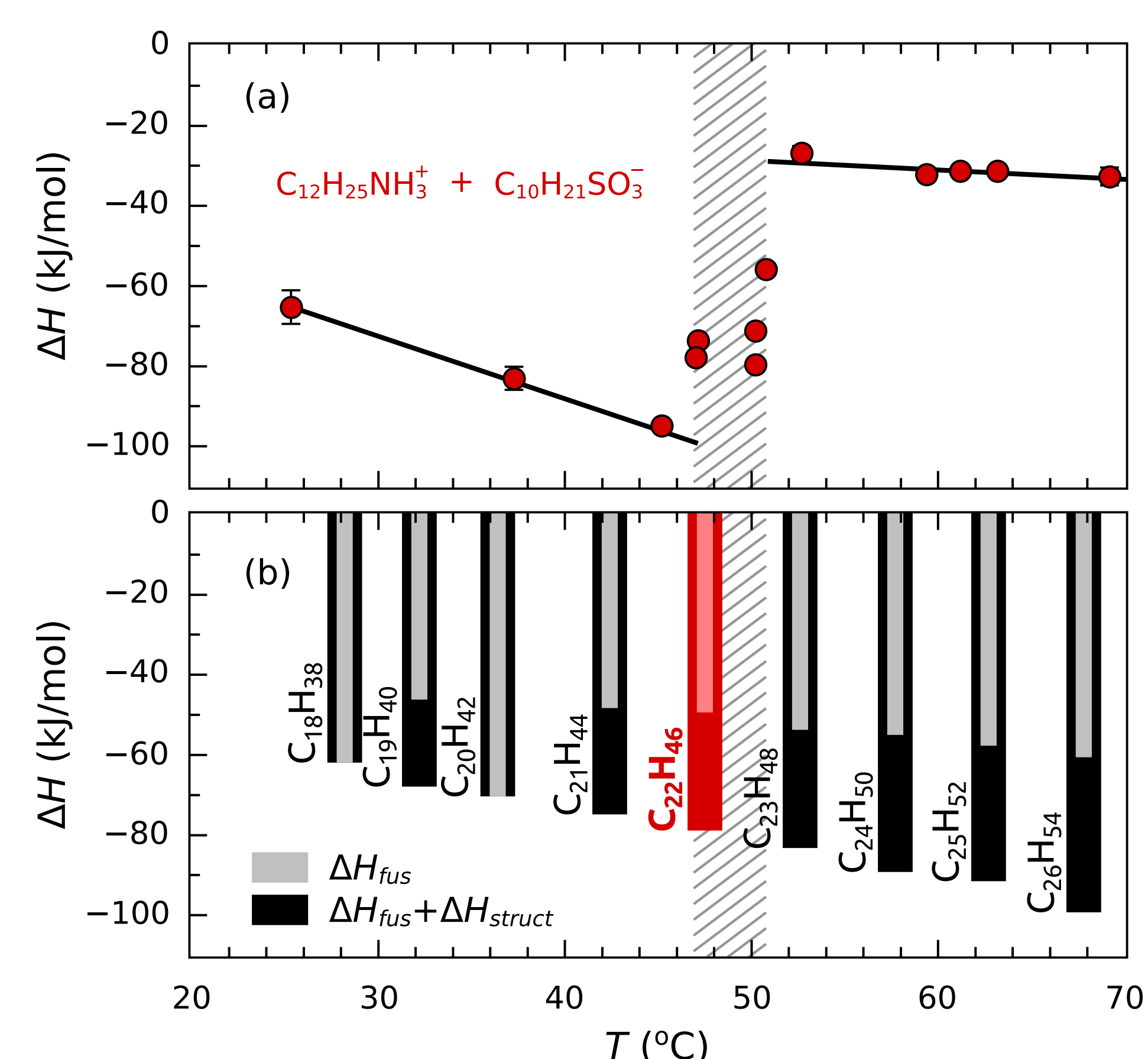


FIGURE: (a) Enthalpy dependence on temperature for decane sulfonate reaction with dodecylammonium, (b) enthalpies of phase transitions of alkanes containing various number of carbon atoms.

PACKING MODEL

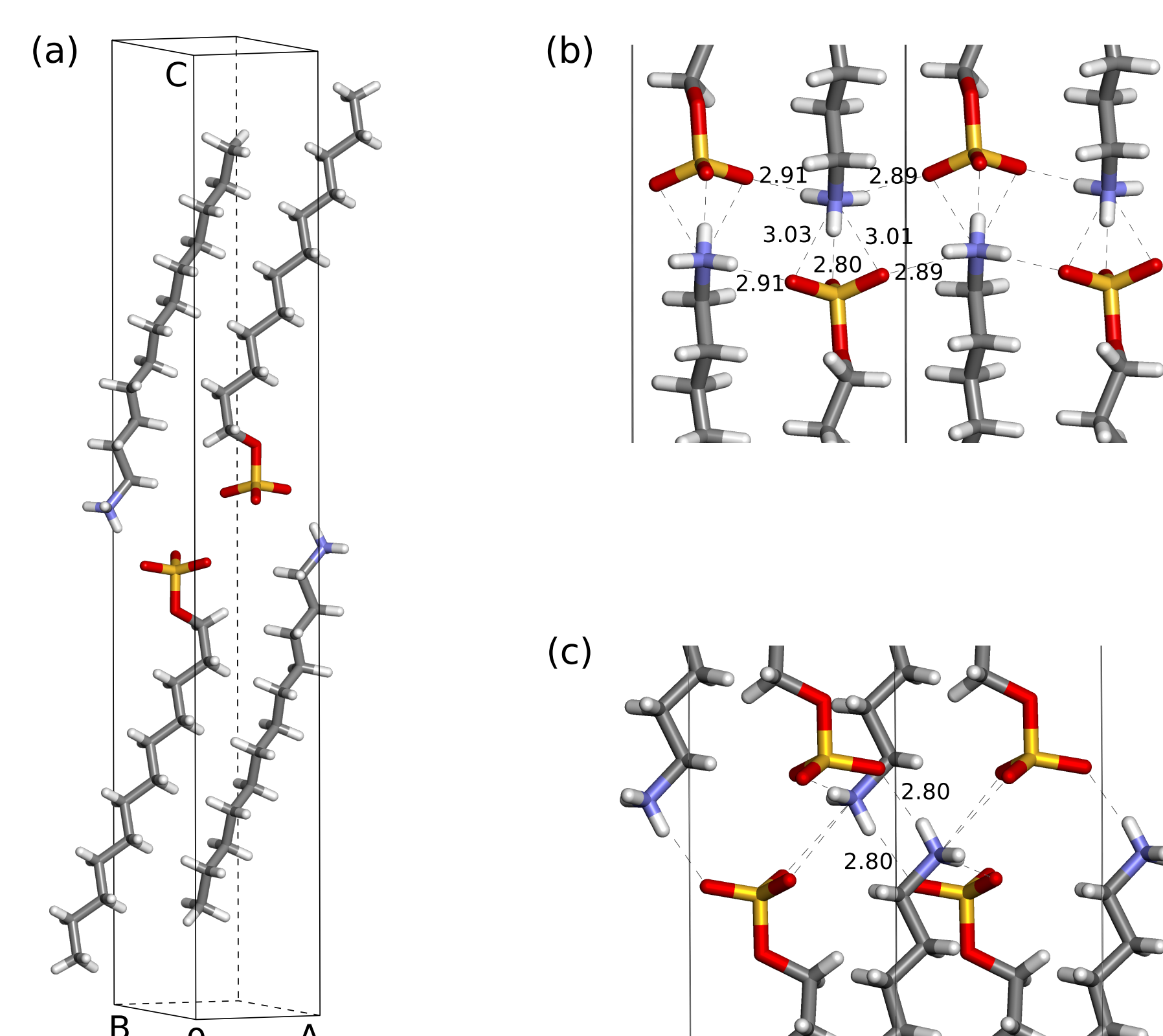


FIGURE: Packing diagrams of dodecylamine complex with dodecyl sulfate: (a) crystalline lattice unit cell, (b) and (c) - orthogonal enlarged views of the hydrogen bonding network with the distances between ionic headgroups.