Thermodynamics of Ion Pair Formation Between Charged Poly(Amino Acid)s and Linear Chain Surfactants

Gediminas Skvarnavičius, Daumantas Matulis, and Vytautas Petrauskas*

*Presenting author. *E-mail:* vytautas.petrauskas@bti.vu.lt

Department of Biothermodynamics and Drug Design, Institute of Biotechnology, Life Sciences Center, Vilnius University, Saulėtekio 7, 10257 Vilnius, Lithuania

Biothermodynamics & Drug Design Dept.
Vilnius University
Institute of Biotechnology

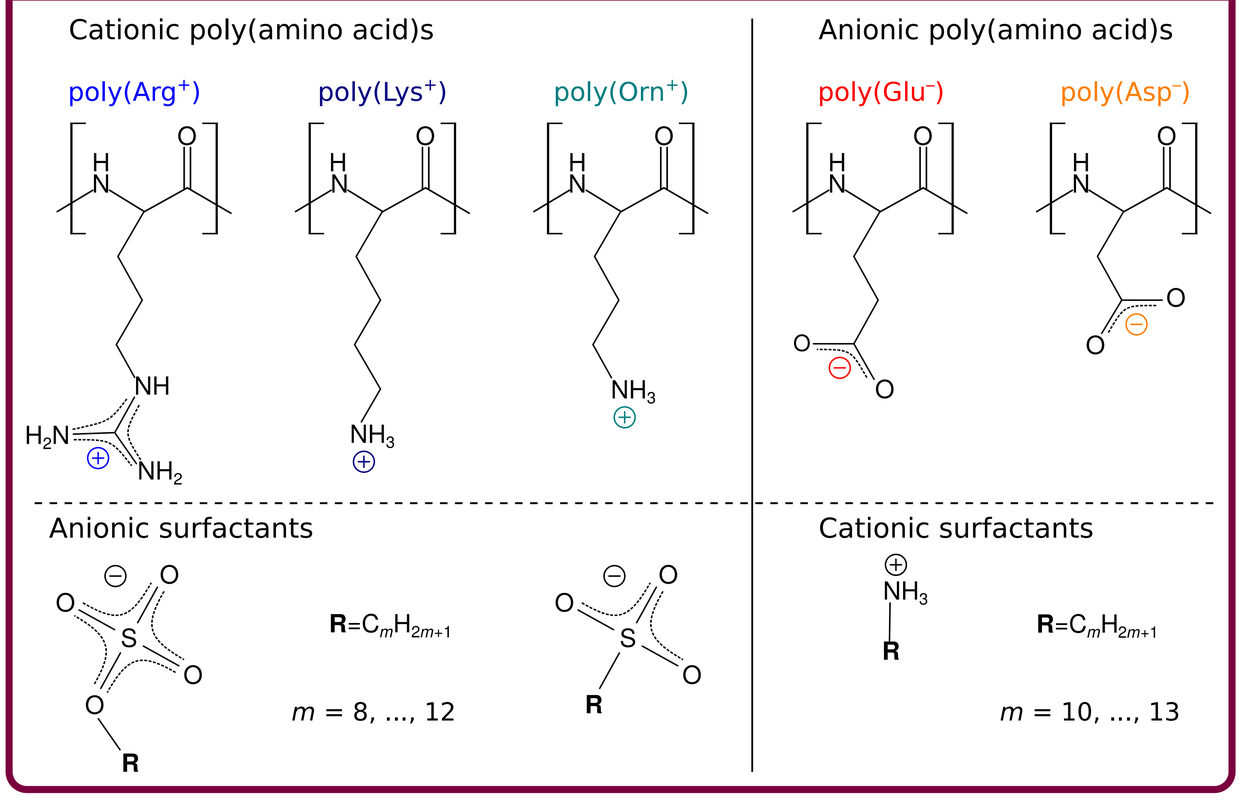
Life Sciences Center

Introduction

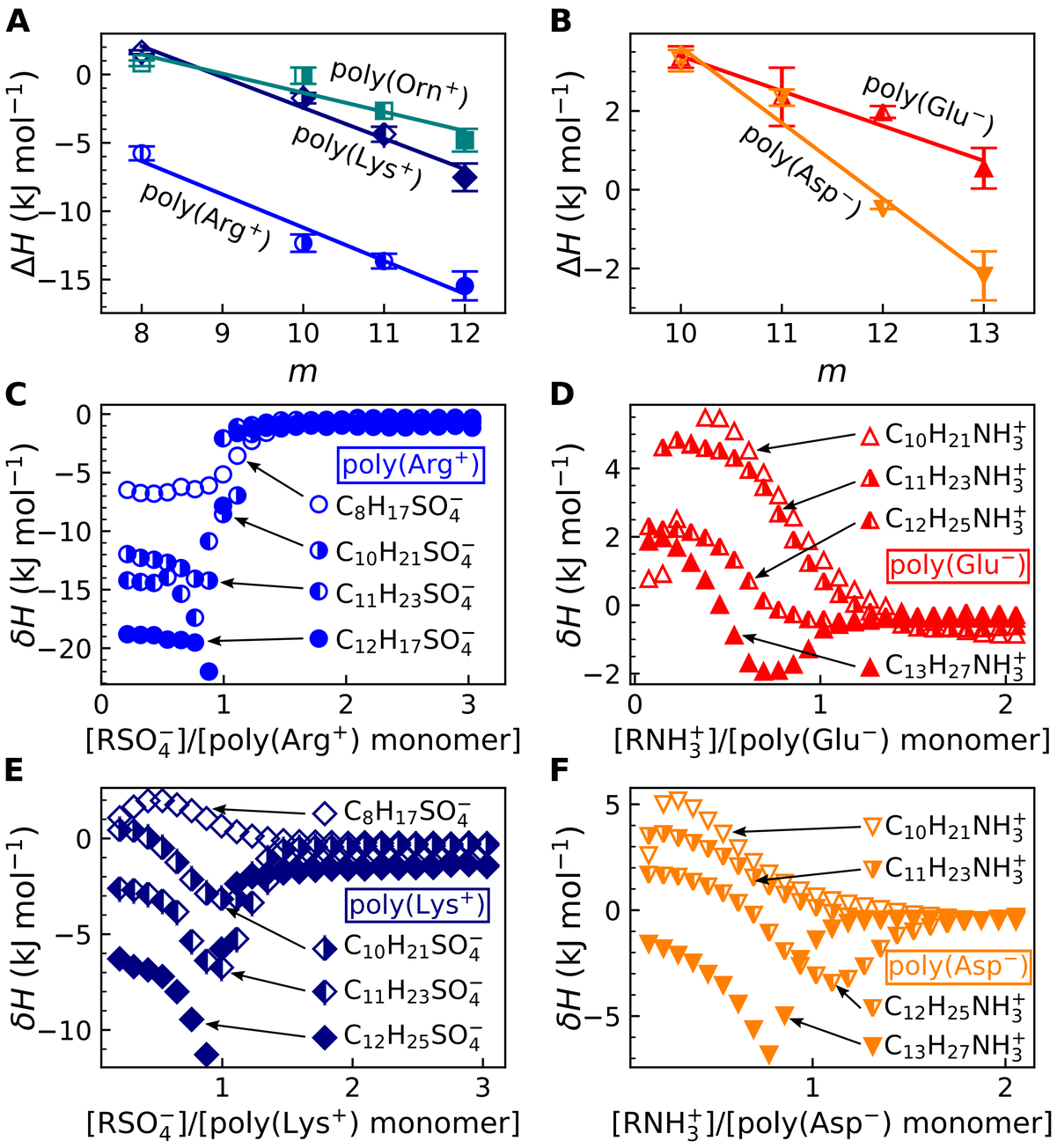
We show by isothermal titration calorimetry that cationic alkylammonium surfactants bind to negatively charged polyaspartate and polyglutamate homopolymers stoichiometrically, one surfactant molecule per one charged amino acid. Similarly, negatively charged alkyl sulfates and alkane sulfonates bind stoichiometrically to positively charged polylysine, polyornithine, and polyarginine homopolymers. In these reactions, the interacting counterparts form ion pairs and the resulting electically neutral complex coprecipitates from solution.

The enthalpies and heat capacities were determined for various pairs of ionic surfactants and charged amino acid homopolymers. The results here dissect the energetic contributions of several ionic surfactant binding to polyamino acids and show the additivity of ionic and hydrophobic interactions.

Poly(amino acid)–surfactant systems

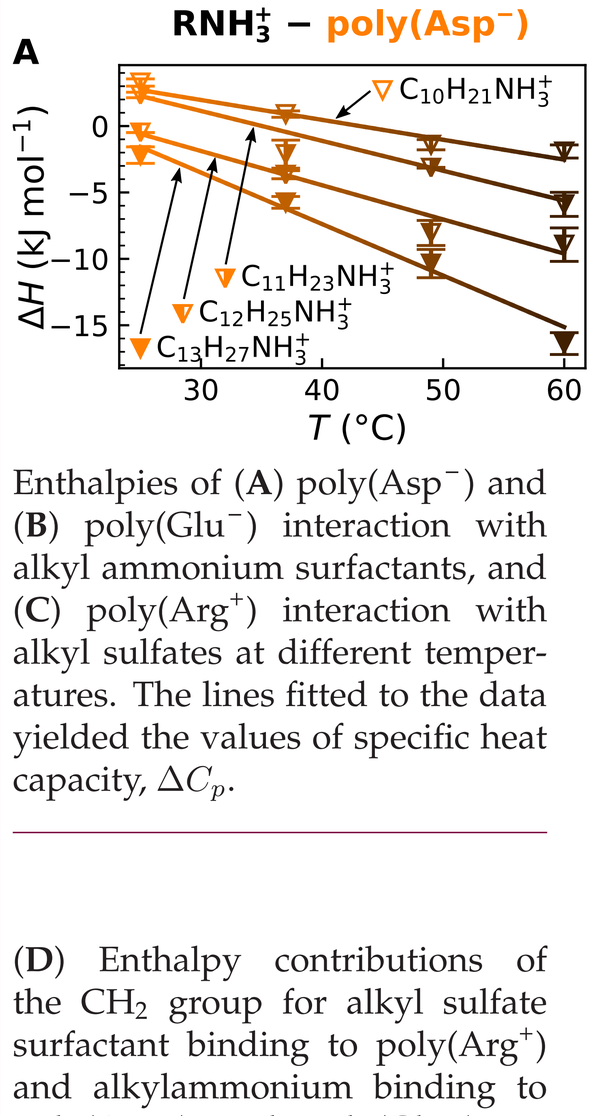


Binding enthalpy *vs* aliphatic chain length

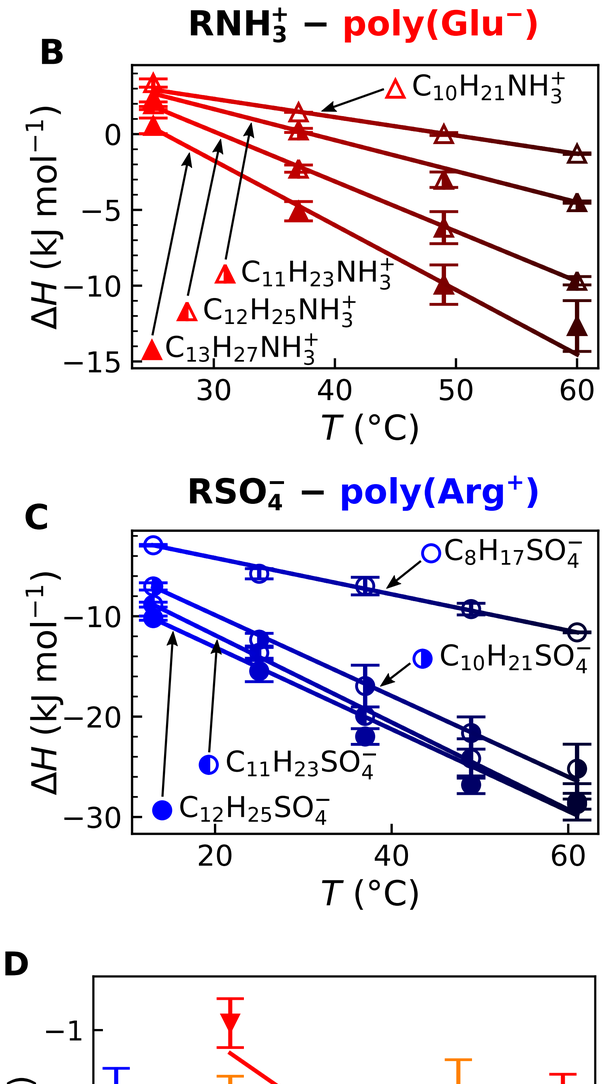


Enthalpies of surfactant–poly(amino acid) interaction as a function of the aliphatic chain length, m, at 25 °C. Linear alkyl sulfates and alkylamines were used to measure their binding enthalpies to (**A**) positively and (**B**) negatively charged poly(amino acid)s, respectively. Panels **C** and **E** show isotherms of RSO_4^- binding to poly(Arg^+) and poly(Lys^+), panels **C** and **E** – RNH_3^+ binding to poly(Glu^-) and poly(Asp^-), respectively.

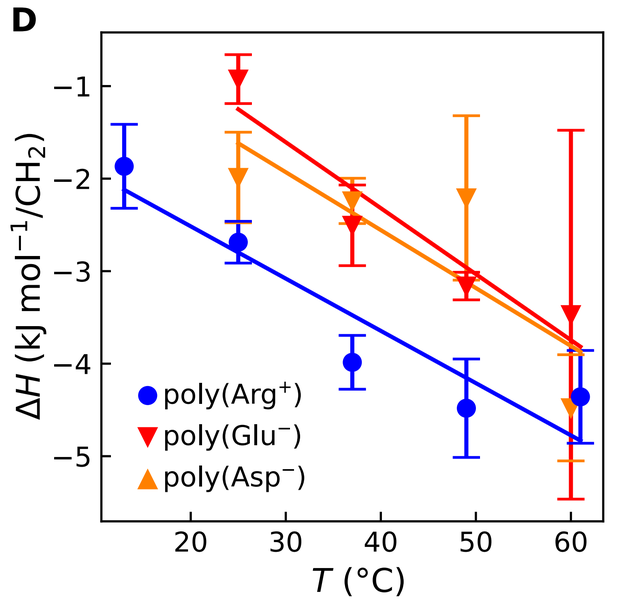
Binding enthalpy *vs* temperature



Enthalpies of (**A**) poly(Asp^-) and (**B**) poly(Glu^-) interaction with alkyl ammonium surfactants, and (**C**) poly(Arg^+) interaction with alkyl sulfates at different temperatures. The lines fitted to the data yielded the values of specific heat capacity, ΔC_p.



(**D**) Enthalpy contributions of the CH_2 group for alkyl sulfate surfactant binding to poly(Arg^+) and alkylammonium binding to poly(Asp^-) and poly(Glu^-), at different temperatures. The slopes yielded approximate ΔC_p values for the CH_2 group equal to: $-0.056\,\mathrm{kJ/mol/K}$ for poly(Arg^+), $-0.062\,\mathrm{kJ/mol/K}$ for poly(Asp^-), $-0.071\,\mathrm{kJ/mol/K}$ for poly(Glu^-). The average value of ΔC_p was $-0.064\pm0.006\,\mathrm{kJ/mol/K}$ per CH_2 group.



Conclusions

- Stoichiometry of charged surfactant binding to the oppositely charged linear poly(amino acid)s is one molecule of surfactant per one amino acid moiety of a polymer.
- The increased length of surfactant's aliphatic chain results in a more favorable interaction enthalpy.
- The observed enthalpy gain per CH_2 group of longer aliphatic chain is similar in various surfactant–poly(amino acid) systems.

Acknowledgement

This research was funded by the European Social Fund under the No 09.3.3-LMT-K-712 "Development of Competences of Scientists, other Researchers and Students through Practical Research Activities" measure.