Specific Anion Binding to Zwitterionic Micelles and Interfacial Water Concentration: Insights from Chemical Trapping Experiments

Renata S. Mello (PG)[1*], Faruk Nome (PQ)[1], Laurence S. Romsted (PQ)[2]. renata_qmc@hotmail.com

[1]*Departamento de Química, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC;*
[2]*Department of Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, NJ, 08903.*

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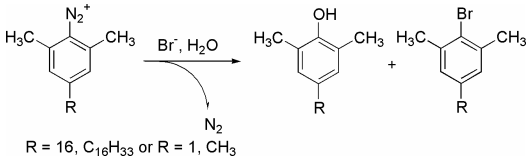
Introduction

Specific anion binding to zwitterionic sulfobetaine micelles has been extensively studied.[1,2] Even at low concentrations, anions enter the micellar interface and interact specifically. The interaction is weak for high charge density, strongly hydrated ions, e.g., OH^-, and increases upon decreasing ion charge density and hydration, consistent with the Hofmeister series and Pearson hard-soft classification.[1] A variety of methods are used to estimate the fractions of anions associated with zwitterionic micelles, but they provide no information on the amount of interfacial H_2O. Chemical trapping experiments provide simultaneous estimates of both the of anion and H_2O molarities in the interfacial regions of association colloids.[3] Here we report how added tetramethylammnonium bromide, TMABr, affects the interfacial anion and water molarities in the interfacial region of 3-(N,N-Dimethylmyristyl-ammonio)propanesulfonate, SB3-14, micelles.

The chemical trapping method is based on the heterolytic chemistry of arenediazonium ions, 16-ArN_2^+. For example, products yields from its reaction with Br^- and H_2O are proportional to their concentrations within the interfacial region (**Scheme 1, Figure 1**). Yields are determined by HPLC.



Scheme 1

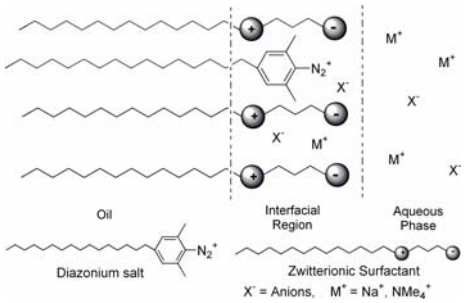


Figure 1. Location of 16-ArN_2^+ in a small section of SB3-14 micelles and the distribution of added salt between the interfacial and aqueous regions.

Results and Discussion

Our initial results (**Figure 2**) show that the $[Br^-]$ in the interfacial region, $[Br^-]_m$, increases continuously with added TMABr and is always higher than in bulk solution, e.g., when at 0.1 M TMABr, $[Br]_m$ is 0.35 M in the interfacial region, consistent with previous work.[4] Intriguingly, as [TMABr] increases, $[H_2O]_m$ initially increases and then decreases gradually, suggesting that site binding of Br^- to the quaternary ammonium group of SB3-14 is accompanied by an increase in hydration followed by a displacement of $[H_2O]_m$ at higher [TMABr]. Results with other, more hydrophobic salts are being gathered, which should help clarify this interpretation.

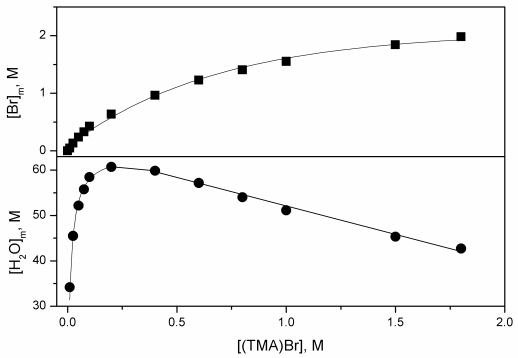


Figure 2. Plots of interfacial bromide ion, Br_m (■), and water, H_2O_m (●) in 0.05 M of SB3-14 solutions in 1 mM HBr at 25 °C.

Conclusions

Chemical trapping experiments provide estimates of interfacial concentrations of both Br^- and H_2O in the interfacial region of zwitterionic SB3-14 micelles. The results are providing new insight into the balance of forces controlling the organization of zwitterionic micelles.

Acknowledgments

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