

The solvation of sodium octanoate micelles in concentrated urea solution studied by means of molecular dynamics simulations

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Introduction

Urea has long been known to decrease the stability of self-assembled and self-organized structures in aqueous solution. For instance, it acts as a protein denaturant and increases the critical micelle concentration of amphiphilic molecules regardless of their chemical nature. The origins of urea's ability to modulate self-assembling processes remain a controversial issue and three mechanisms have been proposed. Two of them focus on the so called hydrophobic effect, suggesting that urea molecules either interact directly with the hydrophobic regions of amphiphilic molecules, thus increasing their solubility in the aqueous environment, or else play the role of a structure breaking solute, that weakens the hydrophobic effect by decreasing the extent¹ of the hydrogen bond network of water molecules. More recently, Dias *et al.* proposed a new mechanism that regards the solvation of the polar and ionic portions of the system as the origins of the observed effects of added urea on self-assembled and self-organized systems.

To the best of our knowledge, there has been no attempt to use a realistic micellar model system to assess the microscopic details regarding the effects of urea on the self-assembling of surfactant molecules. We aim at filling this gap presenting below some results of a 20 ns-long molecular dynamics simulation of the sodium octanoate micellar system in 4.4 mol L⁻¹ urea solution, comparing the solvation features with those obtained previously² for the same micellar system in aqueous solution.

Results and Discussion

We have employed a large model system, comprising three sodium octanoate micelles, surrounded by free octanoate anions and sodium counterions in concentrated aqueous urea solution. Three aggregates were still present at the end of the 20 ns trajectory, along with a few free monomers, but no pre-micellar aggregate was identified during the course of the simulation. This finding differs greatly from previous results obtained for the same micellar system in aqueous solution, which presented a complex size distribution for the aggregates, which ranged from free monomers to larger micelles. The absence of larger aggregates is consistent with the

experimentally observed decrease of the aggregation number in the presence of urea. Another finding that is consistent with experimental observations is the decrease of the association between counterions and micelles in the concentrated urea solution. Both anion-cation and cation-cation pairs are more stable in aqueous solution than in urea solution, supporting the views of Dias *et al.* that micelles are destabilized due to the increased stability of the unpaired ions in aqueous urea solution.

The local concentration of urea around apolar sites in the hydrophobic tails is appreciably larger than its bulk value, indicating that a direct interaction takes place at apolar sites as well.

Our results also support the view that urea disturbs the water structure. Although we have not performed free energy calculations in order to assess entropic informations that could be related to the hydrophobic effect, there is a large excess of urea molecules around water molecules. It should be noted that urea molecules are bulkier than water molecules, so that their presence hinders the approach of other water molecules, thus partly breaking the water hydrogen bond network.

Conclusions

The reported molecular dynamics results support all three mechanisms that try to explain the effects of urea in self-assembled and self-organized systems: the indirect action of urea disrupting the water structure, the direct interaction of urea molecules with the hydrophobic surfactant tails and the stabilization of unpaired ions in urea solution. We do believe that the existence of multiple mechanisms to explain such complex phenomena is quite reasonable.

Acknowledgments

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¹ Dias, L. G.; Florenzano, F. H.; Reed, W. F.; Baptista, M. S.; Souza, S. M. B.; Alvarez, E. B.; Chaimovich, H.; Cuccovia, I. M.; Amaral, C. L. C.; Brasil, C. R.; Romsted, L. S. and Politi, M. J. *Langmuir* **2002**, *18*, 319.

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