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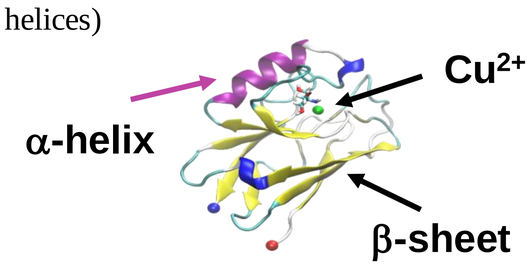
Summary

Azurin is a mixed-structure redox protein involved in bacterial denitrification. Previous studies have shown that azurin is destabilized by imidazolium chloride ionic liquids (ImCl ILs) that can form micelles in aqueous solution, likely by micellar encapsulation. In these ImCl ILs the micelles form from the imidazolium cations. A relatively new class of ionic liquids is fatty acid ionic liquids (FAILs), in which the anion is a fatty acid. In FAILs micelles can form from the fatty acid anions. This presentation presents the results of a thermal unfolding study of azurin in the presence of FAILs in solution**. The FAILs tetramethylguanidinium (TMG) decanoate and choline (Ch) decanoate both strongly destabilize azurin when present above their critical micelle concentrations**, while decanoic acid alone does not affect azurin (at the same concentration). The results point to the special nature of the FAILs and their interactions with the azurin structure and may be related to how the protein is encapsulated by FAIL micelles.

Azurin Structure

Azurin comes from the organism P. Aeruginosa. It is a denitrification redox protein and is a good model for understanding the effects of ILs on mixed structure proteins (i.e. β-sheets and α-helices)



Fatty Acid Ionic Liquids (FAILs)

Have broad potential applications in biotechnology because of their biocompatibility and surfactant properties

These chemicals should form micelles at concentrations above 0.1 M

TMG-Dec in aqueous solution strongly destabilizes Azurin's mixed structure

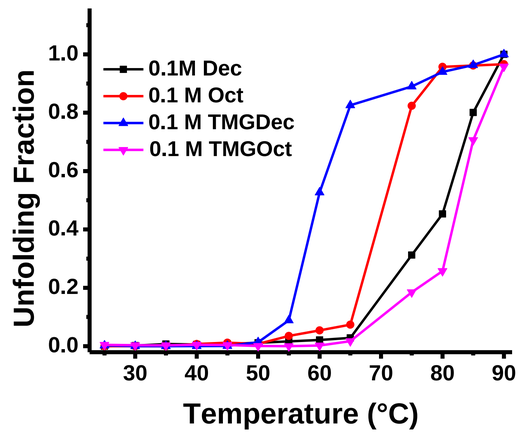


Figure 1. Normalized thermal unfolding curves for azurin in the presence of TMG-FAILs and fatty acids showing strong destabilization of azurin with TMG-Dec

Ch-Dec in aqueous solution strongly destabilizes Azurin's mixed structure

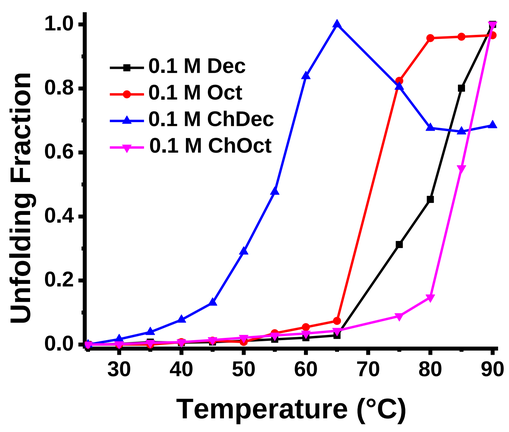


Figure 2. Normalized thermal unfolding curves for azurin in the presence of Ch-FAILs and fatty acids showing strong destabilization of azurin with Ch-Dec

Melting temperatures of azurin with FAILs and fatty acids

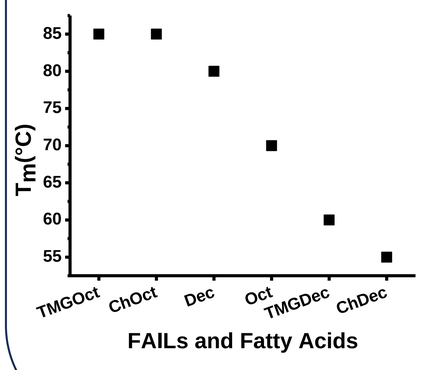
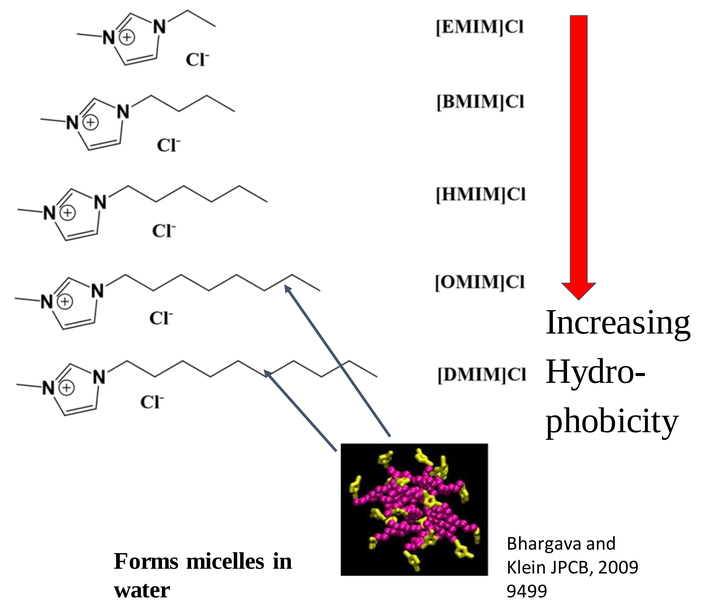


Figure 3. Melting temperatures affecting different FAILs and fatty acids showing that TMGDec and ChDec strongly destabilize azurin.

For comparison: Imidazolium chloride ionic liquids



Unfolding curves of imidazolium chloride ionic liquids

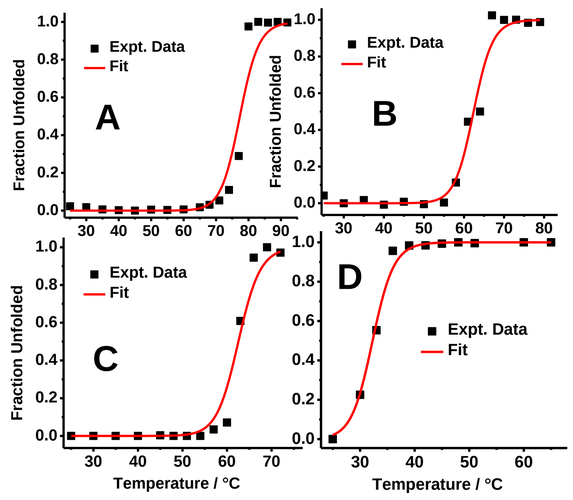


Figure 4. Normalized thermal unfolding curves for azurin in the presence of ImCl ILs where A is no IL, B is [BMIM]Cl, C is [HMIM]Cl, and D is [OMIM]Cl, all at 1.0 M, showing strong destabilization of azurin with [OMIM]Cl (*from J. Phys. Chem. B 2019, 123, 32, 6933–6945*)

Conclusion

- We can conclude that TMG-Dec and Ch-Dec have a strong destabilizing effect on the protein azurin.
- FAILs are biocompatible ILs that can be used as biomaterial having a cationic polar head and an anionic fatty acid tail.
- Unlike the ImCl ILs, only the FAILs that had decanoate showed a destabilizing effect.
- FAILs with decanoate showed a destabilizing effect but decanoic acid itself has no observable effect.

Acknowledgements

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