A Cosolvent Surfactant Mechanism Affects Polymer Collapse in Miscible Good Solvents

Project Manager
Dr. Swaminath Bharadwaj

Principal Investigator
Prof. Dr. Nico van der Vegt

Project Term
2019 - 2020

Clusters
Lichtenberg Cluster Darmstadt

Software
GROMACS

Additional Software
PLUMED

Institute
Physikalische Chemie

University
Technische Universität Darmstadt

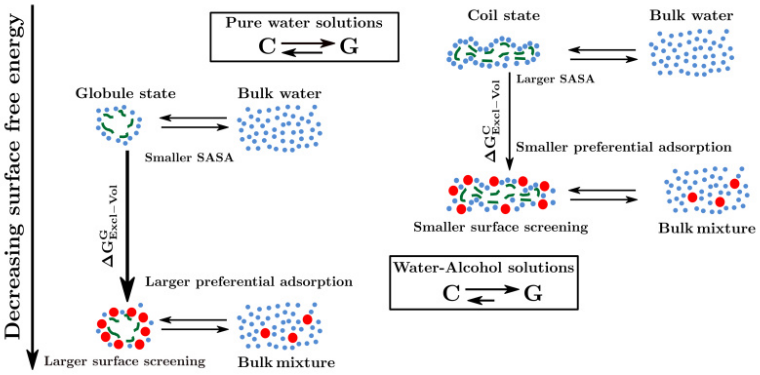

Figure 1: The data has been reproduced from: S. Bharadwaj, D. Nayar, C. Dalgicdir, N. F. A van der Vegt, Communications Chemistry, 3, 165, 2020; licensed under a Creative Commons Attribution 4.0 International License.

Introduction

The coil-globule transition of aqueous polymers is of profound significance in understanding the structure and function of responsive soft matter. In particular, the remarkable effect of amphiphilic cosolvents (e.g. alcohols, which preferentially adsorb on the polymer surface) that leads to both swelling and collapse of stimuli responsive polymers has been hotly debated in the literature, often with contradictory mechanisms proposed. The predominant focus has been on the attractive polymer-(co)solvent interactions and the role of solvent-excluded volume interactions has been largely neglected. The solvent-excluded volume contribution to the solvation free energy of a macromolecular solute corresponds to the formation of a repulsive polymersolvent interface and is related to the surface tension of the (mixed) solvent. The aim of this project is to understand the role of solvent-excluded-volume interactions in the coil-to-globule transitions of polymers in water-cosolvent (amphiphilic) mixtures.

Methods

We employ a generic hydrophobic polymer model consisting of 32 uncharged Lennard-Jones beads which exhibits a two-state conformational equilibrium between coil and globule states. Investigating the coil-to-globule transitions for such a polymer model circumvents the sampling bottlenecks associated with atomistic models of real polymer systems such as of Poly(Nisopropylacrylamide). A combination of free energy techniques such as umbrella sampling and thermodynamic integration were employed to calculate the polymer collapse free energy and the reversible work of creating a repulsive polymer-solvent interface.

Results

Our work show that polymer collapse, which occurs in conjunction with preferential adsorption of amphiphilic alcohol molecules (methanol and ethanol), can be driven by changes in the interface formation free energy originating from repulsive polymer-(co)solvent interactions (solvent-excluded-volume interactions). We demonstrate that alcohols, added to the solution at low concentration, reduce the interface formation free energy of extended coil-like chains and compact globular chains at different rates, corresponding to faster alcohol saturation and a faster lowering of the free energy of globular chains. This role of interfacial solvation thermodynamics corresponds to a surfactant mechanism driving polymer collapse. It also rationalizes experimentally observed changes in lower critical solution temperature (LCST) behavior of higher molecular weight polymers and changes in LCST behavior in aqueous solutions with higher alcohols.

Discussion

Polymer collapse, which occurs in conjunction with preferential adsorption of amphiphilic cosolvents, can also be driven by changes in the interface formation free energy originating from repulsive polymer-(co)solvent interactions (solvent-excluded-volume interactions) via a surfactant-like mechanism. We observe that the free energy corresponding to the formation of both coil- ($\Delta G^{C}_{\mathrm{Excl-Vol}}$) and globule-sized cavities ($\Delta G^{G}_{\mathrm{Excl-Vol}}$) (repulsive polymer-solvent interface) monotonically decreases with increase in the alcohol concentration with a faster decrease for the globule-size cavity. This is due to the surfactant-like behavior of amphiphilic cosolvents such as alcohols which screen the hydrophobic polymer-water interface and reduce the unfavorable polymer-water interactions by preferentially adsorbing on the polymer surface. These results correlate with the trends in the surface tension of water-alcohol solutions, indicating that a macroscopic thermodynamic description applies in macromolecular solvation. The extent of preferential adsorption of the cosolvent is dependent on the interplay between the extent of screening and the loss of cosolvent translational entropy in the bulk (due to preferential accumulation). At low alcohol concentrations, the cosolvent can screen the surface of the globule state more effectively than the coil state due to the compact shape and smaller solvent accessible surface area (SASA) of the former. This leads to a higher preferential adsorption of the cosolvent on the globule state in comparison to the coil state which in turn causes $\Delta G^{G}_{\mathrm{Excl-Vol}}$ to decrease faster than $\Delta G^{C}_{\mathrm{Excl-Vol}}$ thereby shifting the coil-globule equilibrium towards the globule state. Our results also show that both $\Delta G^{G}_{\mathrm{Excl-Vol}}$ and $\Delta G^{C}_{\mathrm{Excl-Vol}}$ decrease faster with alcohol concentration in water-ethanol solutions in comparison to water-methanol solutions. This occurs because, at the same alcohol concentration, ethanol screens the hydrophobic polymer interface more effectively than methanol due to its larger size.

These trends correlate with the observation that the surface tension of alcohol-water mixtures decreases at a higher rate for higher alcohols. This surfactant-like mechanism is able to rationalize the experimentally observed changes in lower critical solution temperature (LCST) behavior of higher molecular weight polymers and changes in LCST behavior in aqueous solutions with higher alcohols. Given that this mechanism is not dependent on the specific attractive interactions, it is generic and applicable to wide variety of macromolecular systems.

Publications

Bharadwaj, S.; Nayar, D., Dalgicdir; C.; Van der Vegt, N. F. A.: A cosolvent surfactant mechanism affects polymer collapse in miscible good solvents. Communications Chemistry 3, 165, 2020
https://doi.org/10.1038/s42004-020-00405-x

Last Update: 2022-04-11 10:11