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Scission energies of surfactant wormlike micelles loaded with nonpolar additives

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Abstract

Hypothesis

The previously observed effects of nonpolar additives on the scission energy and rheological properties of surfactant wormlike micelles can be explained in terms of the spatial distribution of the additive within the micelles. The dependence of the scission energy with the molecular organization of the system can be analyzed with a molecular theory capable of describing the thermodynamics and structure of the micelles.

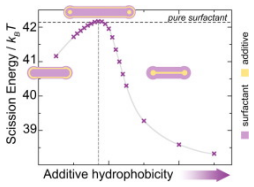
Theory

A new theoretical method to determine the scission energy of surfactant wormlike micelles is introduced. This methodology is based on a molecular theory that explicitly considers molecular details of all components of the micelles, and their inter- and intramolecular interactions without the use of fitting and/or empirical macroscopic parameters.

Findings

The predicted effects of the concentration, molecular structure and hydrophobicity of the additive on the scission energy of cetyltrimethylammonium bromide (CTAB) wormlike micelles are found to be in qualitative agreement with previous experimental observations. In particular, our theory captures the decrease of micellar length with increasing content of highly hydrophobic additives and the non-monotonic dependence of the viscosity with additive hydrophobicity. The latter effect arises because highly and mildly hydrophobic additives affect the scission energy of wormlike micelles *via* markedly different molecular mechanisms.

Graphical abstract



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Introduction

Wormlike micelles are long cylindrical aggregates formed by amphiphilic molecules [1], [2], [3], [4]. Their entanglement imparts high viscosity to the solution [5] and, for this reason, wormlike micelles are commonly used as viscosity modifiers in diverse fields [2], [6], [7], [8], [9], [10], [11], [12]. The rheological response of wormlike micelles is determined by their structural properties, such as length, radius and flexibility [3]. Unlike viscoelastic polymers, wormlike micelles break and rejoin due to thermal fluctuations; hence, they present an equilibrium distribution of lengths. The breaking-rejoining process is controlled by the scission energy, E_{sc}, which is the change in free energy required to cleave a wormlike micelle and generate two hemispherical caps at the point of cleavage (see schemes in Fig. 1a and b) [1], [13]. Cates and coworkers proposed that the average contour length of micelles, $\bar{L}$, grows exponentially with E_{sc} [14], [15]: $\bar{L} \propto \exp(E_{sc}/2k_BT)$

In the original work by Cates and Candau [14], E_{sc} is the only free-energy cost associated with the presence of end caps in wormlike micelles, therefore E_{sc} contains both enthalpic and entropic (*e.g.*, translational entropy from the counterions) contributions and is a free energy [16], [17]. The only entropic contribution that was separately considered in the derivation of Eq. [1], and, therefore, should not be included in E_{sc}, is the translational entropy of the center of mass of the aggregates [14].

The applications of wormlike micelles usually involve contact with substances that affect their rheological properties [17], [18], [19], [20]. For example, hydrophobic molecules such as alkanes shorten the micelles; thus, they decrease the viscosity of the solution [20], [21], [22], [23], [24], [25]. Conversely, less hydrophobic additives, such as aromatic alkenes [20], [24], [25], [26] and alcohols [24], [27], cause the opposite effect, or display complex non-monotonic behaviors. These phenomena remain poorly understood, mainly because experimental determinations of the energy of scission are scarce [18], [28], [29], [30], and present some difficulties that undermine their accuracy. Namely, E_{sc} is generally obtained through Eq. (1) using micelles' length at different temperatures, which implies the incorrect assumption that E_{sc} is independent of the temperature. Furthermore, the length is indirectly determined through rheological measurements [18], [28] or from the model-dependent analysis of light scattering spectra [25], [29].

Recently, computational methods to calculate the free energy of scission have been reported [19], [31], [32], [33]. Most of these methods are based on molecular dynamic (MD) simulations, which provide detailed structural information, but have a large computational cost that hampers their use in systematic studies. The self-assembly and rheological response of wormlike micelles have also been theoretically studied in the past [14], [34], [35], [36], [37], [38], [39], [40]. In a seminal paper, Nagarajan and co-workers theoretically analyzed the wormlike-to-sphere transition triggered by hydrocarbon solubilization [34]. More recently, Danov et al. [32], [41], [42], [43] reported a series of very relevant theoretical works aimed to model neutral and charged micelles. This thermodynamic theory predicted the scission energies of charged micelles in excellent agreement with experiments, although the theory relies on fitting parameters. The effect of additives on the scission energy or the morphology of the micelles was not addressed. These type of analytical theories provide useful thermodynamic information, but they incorporate less molecular details and provide less structural information than MD simulations and usually rely on fitting parameters and/or empirical information (such as the oil–water interfacial tension).

In this report, we introduce a method to calculate the energy of scission based on a thermodynamical statistical tool known as molecular theory [44], [45], [46], [47], [48]. The MOLT provides both structural details and thermodynamic properties, enabling a systematic exploration of the system, while retaining a molecular level of description. This description explicitly includes the chemical structures, conformations, volume and charge distributions and inter and intramolecular interactions of all components in the system. The MOLT incorporates the interactions between components in terms of coarse-grain particle–particle interactions and, unlike other thermodynamic approaches, it does not require fitting parameters or the use of empirical data.

In a recent work, we used the MOLT to study the structure of wormlike and spherical micelles of co-assembled cetyltrimethylammonium bromide (CTAB) and nonpolar additives [49]. We introduce here a novel methodology to determine free energies of scission from MOLT calculations and apply it to the same system. Our predicted scission energies for pure CTAB micelles in solution of varying ionic strength are in good agreement with experimental measurements. Moreover, the predicted trends of the effects of additive hydrophobicity and content on the scission energy are also consistent with available experimental observations. Using our theoretical tool, we propose molecular mechanisms to explain the puzzling non-monotonic dependence of the scission energy with the hydrophobicity of the additive.

Section snippets

Molecular theory for surfactant self-assembly.

We used a theoretical approach known as molecular theory, which was originally developed by Szleifer and coworkers [44], [45], [46], and adapted by us to study the morphology of multicomponent micelles of ionic surfactants [48], [49]. The theory is briefly outlined here and the reader is referred to the Supporting Information (SI) for additional details.

Our theory considers a wormlike co-aggregate of N_S surfactants (CTAB) and N_{NP} nonpolar additives in an aqueous electrolyte solution. The …

Typical structure of CTAB/additive wormlike micelles

Hereafter, all the results will refer to an additive formed by four CG beads except in Section 3.4 where we will address how the length of the additive affects the behavior of the system. Fig. 2 shows the structure of a wormlike micelle formed by CTAB and an additive with $\epsilon_{NP\text{-}NP}$=7.0 k_BT (alkane-like hydrophobicity) and a mole fraction of x_{NP}=0.01. The caps are approximately hemispherical and their radii are larger than that of the cylindrical body. The swollen, hemispherical end-caps seem …

Comparison with experiments

Our predicted energies of scission for pure CTAB micelles are 42.1 and 53.7 k_BT for salt concentrations of 0.1 and 0.3 M, respectively. These values agree very well with the values of 39 k_BT (0.1 M $NaNO_3$) and 52 k_BT (0.3 M $NaNO_3$) obtained from rheological measurements for the same system by Helgeson et al. [18] (E_{sc} values calculated from the average micelle lengths in Table 4 of Ref. [18] using eq. [1]). We note that smaller values of E_{sc} (from 18.5 k_BT for a 0.1 M salt concentration to 24.7 k_B …

Conclusions

This work introduces a novel methodology to calculate the scission energy of wormlike micelles (E_{sc}, the free-energy cost of cleaving the micelle and forming two hemispherical caps at the point of cleavage) using a molecular theory (MOLT). The MOLT, unlike previous analytical theories [32], [34], [40], [41], [42], [43], [63], [64], provides both detailed structural and thermodynamic information of the system. In a recent work [49], we used the MOLT to study infinitely long CTAB wormlike …

CRediT authorship contribution statement

Gervasio Zaldivar: Conceptualization, Methodology, Formal analysis, Software, Writing - original draft. **Martin Conda-Sheridan:** Conceptualization, Writing - original draft, Resources, Supervision. **Mario Tagliazucchi:** Conceptualization, Methodology, Formal analysis, Software, Writing - original draft, Resources, Supervision. …

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. …

Acknowledgements

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Citation Excerpt :
…As a result, a continuous exchange of surfactant monomers between micelles at equilibrium is always present. That is, WLMs are in thermal equilibrium with their unimer species, experiencing breaking and re-formation, and their contour length is thus a thermodynamic quantity [23–25]. Consequently, the rheological properties of WLM fluids are significantly impressionable to the variation of circumambient environment, such as temperature [7,8,26,27].…

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