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Krassimir D. Danov, Peter A. Kralchevsky, Simeon D. Stoyanov, Joanne L. Cook, Ian P. Stott, Eddie G. Pelan

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Growth of wormlike micelles in nonionic surfactant solutions: Quantitative theory vs. experiment

Krassimir D. Danov [a], Peter A. Kralchevsky [a,*], Simeon D. Stoyanov [b,c,d], Joanne L. Cook [e], Ian P. Stott [e], Eddie G. Pelan [b,f]

[a] *Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, Sofia 1164, Bulgaria*

[b] *Unilever Research & Development Vlaardingen, 3133AT Vlaardingen, The Netherlands*

[c] *Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands*

[d] *Department of Mechanical Engineering, University College London, WC1E 7JE, UK*

[e] *Unilever Research & Development Port Sunlight, Bebington CH63 3JW, UK*

[f] *School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK*

ABSTRACT. Despite the considerable advances of molecular-thermodynamic theory of micelle growth, agreement between theory and experiment has been achieved only in isolated cases. A general theory that can provide self-consistent quantitative description of the growth of wormlike micelles in mixed surfactant solutions, including the experimentally observed high peaks in viscosity and aggregation number, is still missing. As a step toward the creation of such theory, here we consider the simplest system – nonionic wormlike surfactant micelles from polyoxyethylene alkyl ethers, C_iE_j. Our goal is to construct a molecular-thermodynamic model that is in agreement with the available experimental data. For this goal, we systematized data for the micelle mean mass aggregation number, from which the micelle growth parameter was determined at various temperatures. None of the available models can give a quantitative description of these data. We constructed a new model, which is based on theoretical expressions for the interfacial-tension, headgroup-steric and chain-conformation components of micelle free energy, along with appropriate expressions for the parameters of the model, including their temperature and curvature dependencies. Special attention was paid to the surfactant chain-conformation free energy, for which a new more general formula was derived. As a result, relatively simple theoretical expressions are obtained. All parameters that enter these expressions are known, which facilitates the theoretical modeling of micelle growth for various nonionic surfactants in excellent agreement with the experiment. The constructed model can serve as a basis that can be further upgraded to obtain quantitative description of micelle growth in more complicated systems, including binary and ternary mixtures of nonionic, ionic and zwitterionic micelles, which determine the viscosity and stability of various formulations in personal-care and house-hold detergency.

Keywords: Wormlike micelles; Micelle growth; Nonionic surfactants; Micelle free energy; Polyoxyethylene alkyl ethers.

* Corresponding author. Tel.: +359 2 962 5310
E-mail address: pk@lcpe.uni-sofia.bg (P.A. Kralchevsky)