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Structural transitions and bilayer formation of CTAB aggregates

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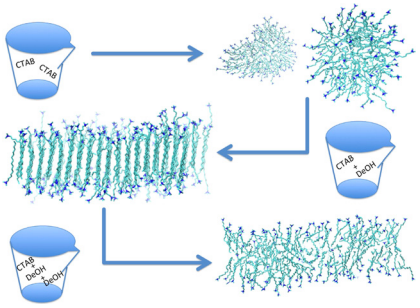
GRAPHICAL ABSTRACT



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ABSTRACT

Controlled CTAB self-assembly is an essential prerequisite for the formation of gold nanorods with tailored shape and monodispersity. In this paper, we exploit the use of salt concentration and co-surfactant decanol for the preparation of CTAB aggregates with different morphologies. To this end we use a model of CTAB recently developed by ourselves, and perform electronic structure calculations in order to improve current point charge parametrization of decanol. Using molecular dynamics simulations with the new models, we find a sequence of structural transitions of CTAB aggregates induced by salt concentration and added cosurfactant. In pure solutions, CTAB aggregates form spherical micelles with a compact ionic shell and a diffuse double layer that can be qualitatively described with Poisson–Boltzmann theory. Addition of decanol as a cosurfactant induces a sequence of dramatic structural transitions at low surfactant concentration and allows the stabilization of compact ordered bilayers in a well defined range of intermediate decanol/CTAB ratios. At low and high decanol/CTAB ratios spherical micelles are transformed into wormlike cylindrical micelles. At intermediate decanol/CTAB ratios, fully formed bilayers are observed, with surfactants exhibiting a compact structure with strong positional and orientational order. We discuss how the controlled self-assembly of compact CTAB bilayers at low global CTAB concentration can pave the way for the selective passivation of gold facets and the controlled formation of monodisperse gold nanorods.

1. Introduction

Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant that is commonly employed as additive in the synthesis of nanoparticles and nanostructured materials, acting either as template [1] or as a colloidal stabilizer and shape directing agent [2]. Our interest on the assembly of CTAB surfactant stems precisely from their use in the synthesis of gold nanorods by the seeded growth method [2–4]. In this

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Marzán, O. Peña-Rodríguez, A. Guerrero-Martínez, Femtosecond laser reshaping yields gold nanorods with ultranarrow surface plasmon resonances, Science 358 (2017) 640–644, https://doi.org/10.1126/science.aan8478.
[5] X. Ye, L. Jin, H. Caglayan, J. Chen, G. Xing, C. Zheng, V. Doan-Nguyen, Y. Kang, N. Engheta, C.R. Kagan, C.B. Murray, Improved size-tunable synthesis of monodisperse gold nanorods through the use of aromatic additives, ACS Nano 6 (2012) 2804–2817, https://doi.org/10.1021/nn300315j.
[6] G. González-Rubio, V. Kumar, P. Llombart, P. Díaz-Núñez, E. Bladt, T. Altantzis, S. Bals, O. Peña-Rodríguez, E.G. Noya, L.G. MacDowell, A. Guerrero-Martínez, L.M. Liz-Marzán, Disconnecting symmetry breaking from seeded growth for reproducible synthesis of high quality gold nanorods, ACS Nano 13 (2019) 4424–4435.
[7] C.J. Murphy, L.B. Thompson, D.J. Chernak, J.A. Yang, S.T. Sivapalan, S.P. Boulos, J. Huang, A.M. Alkilany, P.N. Sisco, Gold nanorod crystal growth: From seed-mediated synthesis to nanoscale sculpting, Curr. Opin. Colloid Interface Sci. 16 (2011) 128–134.
[8] B. Nikoobakht, M.A. El-Sayed, Preparation and growth mechanism of gold nanorods using seed-mediated growth method, Chem. Mater. 15 (2003) 1957–1962, https://doi.org/10.1021/cm020732l.
[9] S. Gómez-Graña, F. Hubert, F. Testard, A. Guerrero-Martínez, I. Grillo, L.M. Liz-Marzán, O. Spalla, Surfactant bilayers on gold nanorods, Langmuir 28 (2012) 1453–1459, https://doi.org/10.1021/la203451p.
[10] S.K. Meena, M. Sulpizi, Understanding the microscopic origin of gold nanoparticle anisotropic growth from molecular dynamics simulations, Langmuir 9 (2013) 14954, https://doi.org/10.1021/la403843n.
[11] S.K. Meena, M. Sulpizi, From gold nanoseeds to nanorods: the microscopic origin of the anisotropic growth, Angew. Chem. Int. Ed. 55 (2016) 11960–11964, https://doi.org/10.1002/anie.201604594.
[12] J.A. da Silva, M.R. Meneghetti, New aspects of the gold nanorod formation mechanism via seed-mediated methods revealed by molecular dynamics simulations, Langmuir 34 (2018) 366–375.
[13] P. Ekwall, L. Mandell, P. Solyom, The aqueous cetyl trimethylammonium bromide solution, J. Colloid Interface Sci. 35 (1971) 519–527, https://doi.org/10.1016/0021-9797(71)90210-4.
[14] J. Mata, D. Varade, P. Bahadur, Aggregation behavior of quaternary salt based cationic surfactants, Thermochim. Acta 428 (2005) 147–155, https://doi.org/10.1016/j.tca.2004.11.009.
[15] S.P. Moulik, M.E. Hauqe, P.K. Jana, A.R. Das, Micellar properties of cationic surfactants in pure and mixed states, J. Phys. Chem. 100 (1996) 701–708, https://doi.org/10.1021/jp9506494.
[16] L.M. Bergstr“om, Second CMC in surfactant micellar systems, Curr. Opin. Colloid Interface Sci. 2016 (2016) 46–50 doi:j.cocis.2016.02.008.
[17] F. Quirion, L.J. Magid, Growth and counterion binding of cetyltrimethylammonium bromide aggregates at 25 °C: a neutron and light scattering study, J. Phys. Chem. 90 (1986) 5435–5441, https://doi.org/10.1021/j100412a108.
[18] M. Pisárčik, F. Devínsky, M. Pupák, Determination of micelle aggregation numbers of alkyltrimethylammonium bromide and sodium dodecyl sulfate surfactants using time-resolved fluorescence quenching, Open Chem. 13 (2015) 922–931, https://doi.org/10.1515/chem-2015-0103.
[19] A. Jusufi, A.Z. Panagiotopoulos, Explicit- and implicit-solvent simulations of micellization in surfactant solutions, Langmuir 31 (11) (2015) 3283–3292, https://doi.org/10.1021/la502227v pMID: 25226280.
[20] M. Törnblom, U. Henriksson, M. Ginley, Field dependent ^{2}H nuclear magnetic relaxation study of the aggregation behaviour in micellar solutions of CTAB and SDS, J. Phys. Chem. 98 (1994) 7041–7051, https://doi.org/10.1021/j100079a025.
[21] T. Imae, R. Kamiya, S. Ikeda, Formation of spherical and rod-like micelles of cetyltrimethylammonium bromide in aqueous NaBr solutions, J. Colloid Interface Sci. 108 (1985) 215, https://doi.org/10.1016/0021-9797(85)90253-X.
[22] Y. Wang, D.S.D. Larsson, D. van der Spoel, Encapsulation of myoglobin in a cetyl trimethylammonium bromide micelle in vacuo: a simulation study, Biochemistry 48 (2009) 1006–1015, https://doi.org/10.1021/bi801952f.
[23] N.C. Das, H. Cao, H. Kaiser, G.T. Warren, J.R. Gladden, P.E. Sokol, Shape and size of highly concentrated micelles in CTAB/NaSal solutions by small angle neutron scattering (SANS), Langmuir 28 (2012) 11962–11968, https://doi.org/10.1021/la2022598.
[24] B. Michels, G. Waton, Effect of pentanol and salt on the fusion-scission kinetics for CTAB micelles, J. Phys. Chem. A 107 (2003) 1133–1137, https://doi.org/10.1021/jp025600u.
[25] V. Patel, N. Dharaiya, D. Ray, V.K. Aswal, P. Bahadur, ph controlled size/shape in CTAB micelles with solubilized polar additives: a viscometry, scattering and spectral evaluation, Colloids Surf. A 455 (2014) 67–75, https://doi.org/10.1016/j.colsurfa.2014.04.025.
[26] J. Karayil, S. Kumar, P.A. Hassan, Y. Talmon, L. Sreejith, Microstructural transition of aqueous CTAB micelles in the presence of long chain alcohols, RSC Adv. 5 (2015) 12434–12441, https://doi.org/10.1039/C4RA10052B.
[27] T. Schmutzler, T. Schindler, M. Schmiele, M.-S. Appavou, S.L. abd, A. Kriele, R. Gilles, T. Unruh, The influence of n-hexanol on the morphology and composition of CTAB micelles, Colloids Surf. A 5 (2018) 12434–12441, https://doi.org/10.1016/j.colsurfa.2017.12.039.
[28] X. Jia, J. Chen, B. Wang, W. Lu, J. Hao, Molecular dynamics simulation of shape and structure evolution of preassembled cylindrical cetyltrimethylammonium bromide micells induced by octanol, Colloids Surf. A 457 (2014) 152–159, https://doi.org/10.1016/j.colsurfa.2014.05.028.
[29] X. Jia, S. Yu, Y. Ma, X. Li, W. Xu, J. Liu, Model of cylindrical micelles with different endcaps, J. Dispers. Sci. Technol. 457 (2017) 621–625, https://doi.org/10.1080/01932691.2016.1185016.
[30] L. Sreejith, S. Parathakkat, S.M. Nair, S. Kumar, G. Varma, P.A. Hassan, Y. Talmon, Octanol-triggered self-assemblies of the CTAB/KBr system: a microstructural study, J. Phys. Chem. B 115 (2011) 464–470, https://doi.org/10.1021/jp1043255.
[31] A.B. Cortes, M. Valiente, E. Rodenas, Properties of the l and lyotropic phases in CTAB/glycerol/water and CTAB/glyceraldehyde/water systems, Langmuir 118 (1999) 6658–6663, https://doi.org/10.1021/la9817516.
[32] A.J. Mills, J. Wilkie, M.M. Britton, NMR and molecular dynamics study of the size, shape and composition of reverse micelles in a cetyltrimethylammonium bromide (CTAB)/n-hexane/pentanol/water microemulsion, J. Phys. Chem. B 118 (2014) 10767–10775, https://doi.org/10.1021/jp504585k.
[33] M. Jorge, Structure of cationic surfactant micelles from molecular simulations of self-assembly, J. Mol. Struct.: THEOCHEM 946 (1) (2010) 88–93, https://doi.org/10.1016/j.theochem.2009.09.054 achievements and Challenges of Computational Chemistry in Portugal.
[34] G.F. Catá, H.C. Rojas, A.P. Gramatges, C.M. Zicovich-Wilson, L. Alvarez, C. Searle, Initial structure of cetyltrimethylammonium bromide micelles in aqueous solution from molecular dynamics simulations, Soft Matter 7 (2011) 8508, https://doi.org/10.1039/C1SM05127J.
[35] S. Storm, S. Jakobtorweihen, I. Smirnova, A.Z. Panagiotopoulos, Molecular dynamics simulations of SDS and CTAB micellization and prediction of partition equilibria with COSMOmic, Langmuir 29 (2013) 11582, https://doi.org/10.1021/la402415b.
[36] S. Illa-Tuset, D.C. Malaspina, J. Faraudo, Coarse-grained molecular dynamics simulation of interface behaviour and self-assembly of CTAB cationic surfactant, Phys. Chem. Chem. Phys. 20 (2018) 26422–26430, https://doi.org/10.1039/C8CP04505D.
[37] D.N. LeBard, B.G. Levine, P. Mertmann, S.A. Barr, A. Jusufi, S. Sanders, M.L. Klein, A.Z. Panagiotopoulos, Self-assembly of coarse-grained ionic surfactants accelerated by graphics processing units, Soft Matter 8 (2012) 2385, https://doi.org/10.1039/C1SM06787G.
[38] C. Oostenbrick, A. Villa, A.E. Mark, W.F. van Gunsteren, A biomolecular force field based on the free enthalpy of hydration and solvation: the GROMOS force-field parameter sets 53A5 and 53A6, J. Comput. Chem. 25 (2004) 1656–1676, https://doi.org/10.1002/jcc.20090.
[39] B. Hess, C. Kutzner, D. van der Spoel, E. Lindahl, GROMACS 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation, J. Chem. Theory Comput. 4 (2008) 435, https://doi.org/10.1021/ct700301q.
[40] G. Bussi, D. Donadio, M. Parrinello, Canonical sampling through velocity rescaling, J. Chem. Phys. 126 (2007) 014101, https://doi.org/10.1063/1.2408420.
[41] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, Molecular-dynamics with coupling to an external bath, J. Chem. Phys. 81 (1984) 3684, https://doi.org/10.1063/1.448118.
[42] L. Martínez, R. Andrade, E.G. Birgin, J.M. Martínez, PACKMOL: A package for building initial configurations for molecular dynamics simulations, J. Comp. Chem. 30 (2009) 2157–2164, https://doi.org/10.1002/jcc.21224.
[43] S. Bogusz, R.M. Venable, R.W. Pastor, Molecular dynamics simulations of octyl glucoside micelles: structural properties, J. Phys. Chem. B 104 (2000) 5462, https://doi.org/10.1021/jp000159y.
[44] S. Salaniwal, S. Cui, H.D. Cochran, P.T. Cummings, Molecular simulations of a dichain surfactant/water/carbon dioxide system. 1. Structural properties of aggregates, Langmuir 17 (2001) 1773–1783, https://doi.org/10.1021/la000554f.
[45] C.J. Fennell, L. Li, K.A. Dill, Simple liquid models with corrected dielectric constants, J. Phys. Chem. B 116 (2012) 6936–6944, https://doi.org/10.1021/jp3002383.
[46] I. Boruhhov, Charge renormalization of cylinders and spheres: ion size effects, J. Polym. Sci. B: Polym. Phys. 42 (2004) 3598–3615, https://doi.org/10.1002/polb.20204.
[47] W.R. Inc, Mathematica, Version 11.3, (2018) Champaign, IL.
[48] G. Hertel, H. Hoffmann, Lyotropic nematic phases of double chain surfactants, Trends Colloid Interf. Sci. II (2007) 123–131, https://doi.org/10.1007/BFb0114182.
[49] J.N. Israelachvili, D.J. Mitchell, B.W. Ninham, Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers, J. Chem. Soc. Faraday Trans. 72 (1976) 1525.
[50] E. Sloutskin, Z. Sapir, C.D. Bain, Q. Lei, K.M. Wilkinson, L. Tamam, M. Deutsch, B.M. Ocko, Wetting, mixing, and phase transitions in Langmuir-Gibbs films, Phys. Rev. Lett. 99 (2007) 136102, https://doi.org/10.1103/PhysRevLett.99.136102.
[51] J. Benet, L.G. MacDowell, E. Sanz, Computer simulation study of surface wave dynamics at the crystal-melt interface, J. Chem. Phys. 141 (2014) 034701.
[52] J. Benet, L.G. MacDowell, E. Sanz, A study of the ice-water interface using the TIP4P/2005 water model, Phys. Chem. Chem. Phys. 16 (2014) 22159–22166, https://doi.org/10.1039/C4CP03398A.
[53] J. Benet, P. Llombart, E. Sanz, L.G. MacDowell, Premelting-induced smoothening of the ice-vapor interface, Phys. Rev. Lett. 117 (2016) 096101, https://doi.org/10.1103/PhysRevLett.117.096101.
[54] R. Nagarajan, Molecular packing parameter and surfactant self-assembly: the neglected role of the surfactant tail, Langmuir 18 (2002) 31.