Ion Specificity and Micellization of Ionic Surfactants: 
A Monte Carlo Study

Alexandre P. dos Santos,∗,† Wagner Figueiredo,∗,† and Yan Levin∗,‡

Departamento de Física, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, Santa Catarina, Brazil, and Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970, Porto Alegre, RS, Brazil

E-mail: alexandre.pereira@ufg.br; wagfig@fisica.ufsc.br; levin@if.ufrgs.br

Abstract

We develop a simulation method which allows us to calculate the critical micelle concentrations for ionic surfactants in the presence of different salts. The results are in good agreement with the experimental data. The simulations are performed on a simple cubic lattice. The anionic interactions with the alkyl chains are taken into account based on the previously developed theory of the interfacial tensions of hydrophobic interfaces: the kosmotropic anions do not interact with the hydrocarbon tails of ionic surfactants, while chaotropic anions interact with the alkyl chains through a dispersion potential proportional to the anionic polarizability.

Introduction

Micelles are important for various applications such as drug carriers for treatment of tumors,1,2 as detergents and paints in the chemical industry, and emulsifiers in food industry. The process

∗To whom correspondence should be addressed
†Departamento de Física, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, Santa Catarina, Brazil
‡Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970, Porto Alegre, RS, Brazil
of micellization is, therefore, a subject of intense investigation.\textsuperscript{3–7} Similar to many other physico-chemical systems, micellar formation is strongly influenced by the ions present in the solution.\textsuperscript{8–13} Hofmeister\textsuperscript{14} was the first to observe that different salts have a profoundly distinct effect on protein solutions,\textsuperscript{15–18} with anions affecting the stability of proteins more strongly than cations. Hofmeister’s work resulted in the celebrated lyotropic (Hofmeister) series, a list of ions ordered by their ability to precipitate proteins. The series has been observed in many different fields of study such as biophysics,\textsuperscript{19} colloidal science,\textsuperscript{20–24} bacterial growth,\textsuperscript{25} micelle-vesicle transitions,\textsuperscript{26} ionic liquids,\textsuperscript{27,28} surface tensions,\textsuperscript{29–37} peptide bonds,\textsuperscript{38} liquid crystals,\textsuperscript{39,40} microemulsions,\textsuperscript{41} porous interfaces,\textsuperscript{42} etc. Recently, a theory was developed which allowed to accurately calculate surface and interfacial tensions of electrolyte-air\textsuperscript{43–46} and electrolyte-oil\textsuperscript{47} interfaces. The theory showed that, near a hydrophobic surface, kosmotropes remain strongly hydrated and are repelled from the interface. On the other hand, chaotropes can adsorb to the interface by polarizing their electronic cloud and thus gaining hydrophobic cavitation energy.\textsuperscript{48} For the water-oil interface, the theory also showed the fundamental importance of dispersion interactions\textsuperscript{41} between the ions and the hydrocarbons.\textsuperscript{47} The same mechanism was also found to be responsible for the adsorption of hydrophilic cationic polyions to a hydrophobic wall\textsuperscript{49} and for variation of the critical coagulation concentrations (CCCs) of hydrophobic colloidal suspensions in the presence of chaotropic anions.\textsuperscript{22,50} These earlier calculations suggest that the interactions of chaotropic anions with the hydrocarbon tails of ionic surfactants will be predominantly controlled by the dispersion forces and should be proportional to the ionic polarizability. On the other hand, the kosmotropic anions should remain strongly hydrated and should not feel the dispersion interaction with the surfactant tails.

In the present paper we will explore the process of micellization of ionic surfactants in the presence of various Hofmeister electrolytes. Our goal is to develop a simple model which will allow us to calculate the critical micelle concentrations (CMCs) for solutions of ionic surfactants in the presence of different salts. In the next section, we will briefly review a standard lattice model used to study CMCs of neutral surfactant molecules and discuss how this simple model can
be modified to account for the surfactant charged head groups and for salt present in solution.

Model and Monte Carlo Simulations

The Monte Carlo simulations are performed on a three dimensional square lattice, in which each cell represents a charged monomer, a neutral monomer, a water molecule, or an ion. An amphiphilic molecule is modeled as a charged head and three adjacent neutral monomers, representing the tail of the surfactant. The other species are monovalent counterions, cations, and anions. The cells are distributed in a cubic box of side $L$, defined by the concentration of surfactants, $\rho_t$. The typical number of surfactants is around 40, while $L$ should be a multiple of the unit cell length, 4 Å, a typical ionic diameter. We consider periodic boundary conditions and the electrostatic interactions are calculated using the Ewald summation method. In order to model the electrostatic interactions, we consider the water as an uniform dielectric with relative permittivity, $\varepsilon_w = 80$. The Bjerrum length is defined as $\lambda_B = \beta q^2/\varepsilon_w$, where $q$ is the proton charge, $\beta = 1/k_B T$, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. For water at room temperature, the Bjerrum length is 7.2 Å. In order to take into account the hydrophobic interactions, which result in micellar formation, we follow the method developed for polar head surfactants. The interaction energy between two adjacent tail monomers, from different surfactants, is taken to be $-\varepsilon$, while between two adjacent tail monomers and an empty cell (water) is $+\varepsilon$. In order to avoid condensed surfactants, we also consider that each bend in a surfactant molecule costs $+\varepsilon$, and if the head and the last tail monomer are on the adjacent sites, it gives an additional energy penalty $+\varepsilon$. This is a minimal model of micellar formation, with only one adjustable parameter $+\varepsilon$. The model can be elaborated further at a price of introducing more adjustable parameters. Here, however, we are interested to explore if the minimal model is sufficient to quantitatively account for the CMCs of ionic surfactants in solutions containing various electrolytes.

Starting from a random distribution of molecules, we apply the Metropolis algorithm for $1 \times 10^5$ Monte Carlo steps, until the system reaches equilibrium. The movements of ions are simple
Figure 1: A snapshot of a typical salt free equilibrium configuration. The surfactant concentration is $\rho_t = 100$ mM. The small red spheres represent counterions, the larger purple spheres represent the surfactant tail monomers, and the largest spheres represent the charged head groups.

Results

We first consider a salt free solution containing cationic surfactants and negatively charged counterions. A recent experiment\textsuperscript{10} showed that for a cationic surfactant 1-decyl-3-methyl-1H-imidazolium chloride (DMIM), with no added salt, the CMC is around 57.2 mM. Our first goal is to adjust $\varepsilon$ to obtain the correct experimental CMC. Prior to micellar formation, the concentration of free surfactants will increase with the total concentration. However, after the CMC, the new surfactants added to solution will go into micelles, and the concentration of free molecules will decrease. We will, therefore, define the CMC as the concentration $\rho_t^*$ at which $\rho_f$ is at maximum. In Fig[2] we
show that for $\varepsilon = 0.626 \, k_B T$, the maximum of the curve is at $\rho^*_t = 59.2 \, \text{mM}$, very close to the experimental CMC. For $\varepsilon = 0.7 \, k_B T$, the maximum is around 29 mM, while for $\varepsilon = 0.5 \, k_B T$, we cannot find a maximum in the range of the data, see Fig. 2. The precise maximums of all the curves are obtained by interpolating the simulation data, with the cubic spline method. We should note that the CMCs of salt free surfactant solutions depend strongly on the chain length. In particular the alkyl chains of most surfactants have more than 4 monomers used in our lattice model. Nevertheless, it has been shown previously that the properties of formation of micelles are captured quite well with a lattice model containing only 4 monomers and a suitably adjusted parameter $\varepsilon$. We will suppose that the same remains true in the presence of salt.

The experiments also provide us with the values of CMCs for solutions containing various electrolytes, KCl, KBr, KNO$_3$ and KI. Using the same $\varepsilon = 0.626 \, k_B T$, adjusted for the case without salt, we now calculate the CMCs for solutions containing electrolyte at concentration of 50 mM. Consider first the case with added KCl. Following the theory developed in the small alkali metal cations and light halide anions, such as Cl$^-$ and F$^-$, remain hydrated and do not interact with the hydrocarbons. The only interaction between the ions and surfactants is the steric (hardcore) repulsion with the monomers and Coulomb interaction with the head groups. The CMC
Figure 3: Concentration of free surfactants as a function of $\rho_t$, with added 50 mM salts. The dashed lines represent the experimental CMC values for KCl, KNO$_3$ and KI, 42, 28 and 10.5 mM, respectively, in good agreement with the values obtained in simulations, 39.94 mM, 29.93 mM and 11.71 mM, respectively.

obtained from simulations for solution with 50 mM KCl is 39.94 mM, in a good agreement with the experimental value, 42 mM, see Fig. 3. KCl screens the electrostatic repulsion between the head groups, thus lowering the CMC.

We next consider salts with chaotropic anions, KNO$_3$, KI and KBr. The earlier work showed that chaotropic anions, such as NO$_3^-$, I$^-$ and Br$^-$, adsorbs to hydrophobic surfaces mainly due to dispersion interaction between the ions and the hydrocarbons. The dispersion potential is proportional to the ionic polarizability.$^{47,50}$ As the simplest approximation we will, therefore, take the interaction potential between a chaotropic anion and a surfactant monomer to be a simple square well of one lattice spacing (nearest-neighbor interaction) with the depth proportional to the ionic
polarizability $\gamma$,

$$\beta U_c = -\nu \gamma,$$

(1)

where $\nu$ is an adjustable, ion independent, parameter.

Consider first the salt KI (at 50 mM). We will try to adjust the value of the parameter $\nu$ to obtain the correct experimental CMC, 10.5 mM. The same value of $\nu$ will then be used for all other chaotropic anions. The ionic polarizabilities for $I^-$, $Br^-$ and $NO_3^-$, provided in Ref.\textsuperscript{55} are $\gamma = 7.4$, 5.07, and 4.09 Å$^3$, respectively, and are the same as used in the previous theoretical works\textsuperscript{43–47,50} on surface and interfacial tensions. It is difficult to find the exact value of $\nu$ for KI, however with $\nu = 0.155$ Å$^{-3}$ we obtain a CMC of 11.71 mM, in a reasonable agreement with the experimental data, see Fig.\textsuperscript{3} Using the same value of $\nu$, we can now calculate the CMCs for other salts, KNO$_3$ and KBr. For the salt KNO$_3$ the value found from simulations is 29.93 mM, and is very close to the experimental CMC of 28 mM, see Fig.\textsuperscript{3} For the salt KBr we obtain the value 25.48 mM, while the experimental value is 34 mM, see Fig.\textsuperscript{4} The difference in the value of the CMC for NaBr obtained in simulations and experiments is likely due to the overestimate of the ionic polarizability of Br$^-$ anion.\textsuperscript{55} This problem was already noticed in the earlier work on the stability of hydrophobic colloidal suspensions,\textsuperscript{50} and in the recent \textit{ab initio} simulations.\textsuperscript{56}
In Table 1 we summarize the CMCs of DMIM in the presence of various electrolytes at 50 mM concentration.

Table 1: Summary of the calculated and experimental CMCs for DMIM surfactant. The results are for systems without added salt and with salts at 50 mM. The experimental data are from Ref. 10. The $\beta \varepsilon$ and $\nu$ constants are adjusted to 0.626 and 0.155 Å$^{-3}$, respectively.

| Salts (at 50 mM) | simulations (mM) | experiments (mM)$^{10}$ |
|-----------------|------------------|------------------------|
| no salt         | 59.2             | 57.2                   |
| KCl             | 39.94            | 42                     |
| KBr             | 25.48            | 34                     |
| KNO$_3$         | 29.93            | 28                     |
| KI              | 11.71            | 10.5                   |

We next note that the Hamiltonian of the lattice model with monovalent kosmotropic ions is invariant under the charge inversion $+ \leftrightarrow -$ of all the ionic species. This means that the CMCs of anionic surfactants with the same chain length, and a head group of roughly the same size, should be similar to the CMCs of cationic surfactants. Unfortunately, no experimental data for CMCs of anionic surfactants, with the same chain length as DMIM and with added salt, are available. However, for anionic surfactant sodium 9-decenyl sulfate (SDeS) (with the same chain length as DMIM) the salt-free CMC measured experimentally is 61 mM$^{57}$ — very close to the CMC of DMIM,$^{10}$ 57.2 mM, showing that the charge inversion symmetry is indeed closely respected — once again validating our model. For chaotropic anions preferential adsorption to alkyl chains results in an increased net charge of anionic surfactants, while for cationic surfactants anionic adsorption lowers the net charge of the surfactant molecule. This breaks the charge inversion symmetry, resulting in different CMCs of cationic and anionic surfactants (of the same chain length) in solutions containing chaotropic ions. In Table 2 we summarize the predictions of our model for CMCs of anionic surfactant sodium 9-decenyl sulfate (SDeS) in solutions with various salts. Curiously, even though the adsorption of I$^-$ increases the CMC as compared to salt KCl, the CMC of a solution containing KI still remains lower than the CMC of a salt free solution. This shows the dichotomy of electrostatic screening and anion adsorption in solutions containing chaotropic anions.
Table 2: Summary of the calculated CMCs for SDeS anionic surfactant at 50 mM salt concentration. The $\beta \varepsilon$ and $\nu$ parameters are the same as for DMIM.

|       | CMCs(mM) |
|-------|----------|
| no salt | 59.2     |
| KI     | 52.1     |
| KNO$_3$ | 48.04    |
| KBr    | 46.92    |
| KCl    | 39.94    |

To account for large hydration radii of small kosmotropic ions such as Na$^+$ and F$^-$, we can slightly increase the size of the unit cell of the lattice model, from 4 Å to 5 Å. The value of $\varepsilon$ then must also be recalculated. In the case of DMIM surfactant this leads $\varepsilon = 0.552 k_B T$. If we replace 50 mM KCl by 50 mM NaF, we calculate that the CMC of DMIM will increase from 39.94 mM to 46 mM. The larger ionic radius hinders the electrostatic screening, resulting in higher CMC in the presence of strongly hydrated kosmotropic ions.

Finally we consider an anionic surfactant sodium dodecyl sulphate (SDS). We find that $\varepsilon = 0.76 k_B T$ results in a CMC of 7.76 mM, very close to the experimental value of 7.8 mM for a salt free solution of SDS.$^{58}$ When 15 mM of NaCl is added to solution, we calculate that the CMC for SDS will drop down to 4.35 mM, very close to the experimental$^{58}$ value, 4.2 mM. Unfortunately there is no experimental data for SDS with chaotropic salts to compare with our simulation predictions.

**Conclusions**

We have investigated the effect of various salts on the CMCs of ionic surfactants. The Monte Carlo simulations of a minimal lattice model were employed to quantitatively predict the CMCs of various ionic surfactants in different electrolyte solutions. The specific interactions between the hydrophobic tails of surfactants and ions were explored based on the insights gained from the earlier theoretical studies of the interfacial tensions$^{43-47}$ and the CCCs of hydrophobic colloidal suspensions.$^{50}$ We find that the kosmotropic anions do not interact with the ionic surfactants, ex-
cept through steric repulsion and the Coulomb force, while the chaotropic anions interact with the
surfactant alkyl tails by the dispersion potential proportional to the ionic polarizability. This is also
consistent with the recent experiments which show that strongly hydrated ions are repelled from
the hydrophobic groups, while iodide ions are observed next to them.\(^5\) The results of simulations
are in a good agreement with the available experimental data for cationic surfactants. Using the
same model, we are also able to predict the CMCs for anionic surfactants. Unfortunately, at the
moment, there is only a very limited experimental data available for these systems to compare with
our predictions.

Acknowledgments

This work was partially supported by the CNPq, FAPERGS, FAPESC, INCT-FCx, and by the
US-AFOSR under the grant FA9550-12-1-0438.

References

(1) Trivedi, R.; Kompella, U. B. Nanomicellar formulations for sustained drug delivery: strate-
gies and underlying principles. *Nanomedicine (Lond)* **2010**, *5*, 485–505.

(2) Wei, T.; Liu, J.; Ma, H.; Cheng, Q.; Huang, Y.; Huo, J. Z. S.; Xue, X.; Liang, Z.; Liang, X. J.
Functionalized Nanoscale Micelles Improve Drug Delivery for Cancer Therapy in Vitro and
in Vivo. *Nano Lett.* **2013**, *13*, 2528–2534.

(3) Gunnarsson, G.; Jönsson, B.; Wennerström, H. Surfactant association into micelles. An elec-
etrostatic approach. *J. Phys. Chem.* **1980**, *84*, 3114–3121.

(4) Bales, B. L. A Definition of the Degree of Ionization of a Micelle Based on Its Aggregation
Number. *J. Phys. Chem. B* **2001**, *105*, 6798–6804.

(5) Girardi, M.; Henriques, V. B.; Figueiredo, W. Amphiphilic aggregation in hydrogen bonding
liquids: Dynamic and equilibrium properties. *J. Chem. Phys.* **2006**, *328*, 139–146.
(6) Heinzelmann, G.; Figueiredo, W.; Girardi, M. Monte Carlo simulations for amphiphilic aggregation near a water phase transition. *J. Chem. Phys.* **2009**, *131*, 144901.

(7) Jusufi, A.; LeBard, D. N.; Levine, B. G.; Klein, M. L. Surfactant Concentration Effects on Micellar Properties. *J. Phys. Chem. B* **2012**, *116*, 987–991.

(8) Jiang, N.; Li, P.; Wang, Y.; Wang, J.; Yan, H.; Thomas, R. K. Micellization of Cationic Gemini Surfactants with Various Counterions and Their Interaction with DNA in Aqueous Solution. *J. Phys. Chem. B* **2004**, *108*, 15385–15391.

(9) Romsted, L. S. Do amphiphile aggregate morphologies and interfacial compositions depend primarily on interfacial hydration and ion-specific interactions? The evidence from chemical trapping. *Langmuir* **2007**, *23*, 414–424.

(10) Luczak, J.; Markiewicz, M.; Thöming, J.; Hupka, J.; Jungnickel, C. Influence of the Hofmeister anions on self-organization of 1-decyl-3-methylimidazolium chloride in aqueous solutions. *J. Colloid Interface Sci.* **2011**, *362*, 415–422.

(11) Murgia, S.; Monduzzi, M.; Palazzo, G. Quantification of Specific Anion Binding to Non-Ionic Triton X-100 Micelles. *Langmuir* **2012**, *28*, 1283–1289.

(12) Müller, W.; Déjugnat, C.; Zemb, T.; Dufrêche, J. F.; Diat, O. How Do Anions Affect Self-Assembly and Solubility of Cetylpyridinium Surfactants in Water. *J. Phys. Chem. B* **2013**, *117*, 1345–1356.

(13) Manet, S.; Karpichev, Y.; Dedovets, D.; Oda, R. Effect of Hofmeister and Alkylcarboxylate Anionic Counterions on the Krafft Temperature and Melting Temperature of Cationic Gemini Surfactants. *Langmuir* **2013**, *29*, 3518–3526.

(14) Hofmeister, F. Zur Lehre von der Wirkung der Salze. *Arch. Exp. Pathol. Pharmakol.* **1888**, *24*, 247–260.
(15) Record, M. T.; Zhang, W. T.; Anderson, C. F. Analysis of effects of salts and uncharged solutes on protein and nucleic acid equilibria and processes: A practical guide to recognizing and interpreting polyelectrolyte effects, Hofmeister effects, and osmotic effects of salts. *Adv. Protein Chem.* **1998**, *51*, 281–353.

(16) Medda, L.; Barse, B.; Cugia, F.; Bostrom, M.; Parsons, D. F.; Ninham, B. W.; Monduzzi, M.; Salis, A. Hofmeister Challenges: Ion Binding and Charge of the BSA Protein as Explicit Examples. *Langmuir* **2012**, *28*, 16355–16363.

(17) Rembert, K. B.; Paterova, J.; Heyda, J.; Hilty, C.; Jungwirth, P.; Cremer, P. S. Molecular Mechanisms of Ion-Specific Effects on Proteins. *J. Am. Chem. Soc.* **2012**, *134*, 10039–10046.

(18) Record, M. T.; Guinn, E.; Pegram, L.; Capp, M. Introductory lecture: interpreting and predicting Hofmeister salt ion and solute effects on biopolymer and model processes using the solute partitioning model. *Faraday Discuss.* **2013**, *160*, 9–44.

(19) Collins, K. D. Charge density-dependent strength of hydration and biological structure. *Biophys. J.* **1997**, *72*, 65–76.

(20) Lopez-Leon, T.; Jodar-Reyes, A. B.; Bastos-Gonzalez, D.; Ortega-Vinuesa, J. L. Hofmeister Effects in the Stability and Electrophoretic Mobility of Polystyrene Latex Particles. *J. Phys. Chem. B* **2003**, *107*, 5696–5708.

(21) Lopez-Leon, T.; Santander-Ortega, M. J.; Ortega-Vinuesa, J. L.; Bastos-Gonzalez, D. Hofmeister Effects in Colloidal Systems: Influence of the Surface Nature. *J. Phys. Chem. C* **2008**, *112*, 16060–16069.

(22) Peula-Garcia, J. M.; Ortega-Vinuesa, J. L.; Bastos-Gonzalez, D. Inversion of Hofmeister Series by Changing the Surface of Colloidal Particles from Hydrophobic to Hydrophilic. *J. Phys. Chem. C* **2010**, *114*, 11133–11139.
(23) Calero, C.; Faraudo, J.; Bastos-Gonzalez, D. Interaction of Monovalent Ions with Hydrophobic and Hydrophilic Colloids: Charge Inversion and Ionic Specificity. *J. Am. Chem. Soc.* **2011**, *133*, 15025–15035.

(24) Schwierz, N.; Netz, R. R. Effective Interaction between Two Ion-Adsorbing Plates: Hofmeister Series and Salting-In/Salting-Out Phase Diagrams from a Global Mean-Field Analysis. *Langmuir* **2012**, *28*, 3881–3886.

(25) Lo Nostro, P.; Ninham, B. W.; Pesavento, A. L. G.; Fratoni, L.; Baglioni, P. Specific ion effects on the growth rates of *Staphylococcus aureus* and *Pseudomonas aeruginosa*. *Phys. Biol.* **2005**, *2*, 1–7.

(26) Renoncourt, A.; Vlachy, N.; Bauduin, P.; Drechsler, M.; Touraud, D.; Verbavatz, J. M.; Dubois, M.; Kunz, W.; Ninham, B. W. Specific Alkali Cation Effects in the Transition from Micelles to Vesicles through Salt Addition. *Langmuir* **2007**, *23*, 2376–2381.

(27) Ao, M.; Kim, D. Aggregation Behavior of Aqueous Solutions of 1-Dodecyl-3-methylimidazolium Salts with Different Halide Anions. *J. Chem. Eng. Data* **2013**, *58*, 1529–1534.

(28) Wang, W.; Sung, W.; Ao, M.; Anderson, N. A.; Vaknin, D.; Kim, D. Halide Ions Effects on Surface Excess of Long Chain Ionic Liquids Water Solutions. *J. Phys. Chem. B* **2013**, *117*, 13884–13892.

(29) Aveyard, R.; Saleem, S. M. Interfacial Tensions at Alkane-Aqueous Electrolyte Interfaces. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1609–1617.

(30) Collins, K. D.; Washabaugh, M. W. The Hofmeister effect and the behaviour of water at interfaces. *Q. Rev. Biophys.* **1985**, *18*, 323–422.

(31) Weissenborn, P. K.; Pugh, R. J. Surface Tension of Aqueous Solutions of Electrolytes: Rela-
tionship with Ion Hydration, Oxygen Solubility, and Bubble Coalescence. *J. Colloid Interface Sci.* 1996, 184, 550–563.

(32) Matubayasi, N.; Tsunetomo, K.; Sato, I.; Akizuki, R.; Morishita, T.; Matuzawa, A.; Nat-sukari, Y. Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions: IV. Sodium Halides, Anion Mixtures, and Sea Water. *J. Colloid Interface Sci.* 2001, 243, 444–456.

(33) Jungwirth, P.; Tobias, D. J. Specific Ion Effects at the Air/Water Interface. *Chem. Rev.* 2006, 106, 1259–1281.

(34) Pegram, L. M.; Record, M. T. Hofmeister salt effects on surface tension arise from partition-
ing of anions and cations between bulk water and the air-water interface. *J. Phys. Chem. B* 2007, 111, 5411–5417.

(35) Baer, M. D.; Mundy, C. J. Toward an Understanding of the Specific Ion Effect Using Density Functional Theory. *J. Phys. Chem. Lett.* 2011, 2, 1088–1093.

(36) Tobias, D. J.; Stern, A. C.; Baer, M. D.; Levin, Y.; Mundy, C. J. Simulation and Theory of Ions at Atmospherically Relevant Aqueous Liquid-Air Interfaces. *Annu. Rev. Phys. Chem.* 2013, 64, 339–359.

(37) Lima, E. R. A.; de Melo, B. M.; Baptista, L. T.; Paredes, M. L. L. Specific ion effects on the interfacial tension of water/hydrocarbon systems. *Braz. J. Chem. Eng.* 2013, 30, 55–62.

(38) Heyda, J.; Vincent, J. C.; Tobias, D. J.; Dzubiella, J.; Jungwirth, P. Ion Specificity at the Peptide Bond: Molecular Dynamics Simulations of N-Methylacetamide in Aqueous Salt Solutions. *J. Phys. Chem. B* 2010, 114, 1213–1220.

(39) Dawin, U. C.; Lagerwall, J. P. F.; Giesselmann, F. Electrolyte Effects on the Stability of Ne-
matic and Lamellar Lyotropic Liquid Crystal Phases: Colligative and Ion-Specific Aspects. *J. Phys. Chem. B* 2009, 113, 11414–11420.
(40) Carlton, R. J.; Ma, C. D.; Gupta, J. K.; Abbott, N. L. Influence of Specific Anions on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces. *Langmuir* **2012**, *28*, 12796–12805.

(41) Murgia, S.; Monduzzi, M.; Ninham, B. W. Hofmeister effects in cationic microemulsions. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 102–106.

(42) Cecchi, T.; Marcotulli, F. Chromatography and the hundred year mystery of inorganic ions at aqueous interfaces: Adsorption of inorganic ions at the Porous Graphitic Carbon Aqueous Interface follows the Hofmeister series. *J. Chromatogr. A* **2013**, *1314*, 106–114.

(43) Levin, Y.; dos Santos, A. P.; Diehl, A. Ions at the Air-Water Interface: An End to a Hundred-Year-Old Mystery? *Phys. Rev. Lett.* **2009**, *103*, 257802.

(44) dos Santos, A. P.; Diehl, A.; Levin, Y. Surface Tensions, Surface Potentials, and the Hofmeister Series of Electrolyte Solutions. *Langmuir* **2010**, *26*, 10778–10783.

(45) dos Santos, A. P.; Levin, Y. Surface tensions and surface potentials of acid solutions. *J. Chem. Phys.* **2010**, *133*, 154107.

(46) dos Santos, A. P.; Levin, Y. Surface and interfacial tensions of Hofmeister electrolytes. *Faraday Discuss.* **2013**, *160*, 75–87.

(47) dos Santos, A. P.; Levin, Y. Ions at the Water-Oil Interface: Interfacial Tension of Electrolyte Solutions. *Langmuir* **2012**, *28*, 1304–1308.

(48) Levin, Y. Polarizable Ions at Interfaces. *Phys. Rev. Lett.* **2009**, *102*, 147803.

(49) dos Santos, A. P.; Levin, Y. Adsorption of cationic polyions onto a hydrophobic surface in the presence of Hofmeister salts. *Soft Matter* **2013**, *9*, 10545–10549.

(50) dos Santos, A. P.; Levin, Y. Ion Specificity and the Theory of Stability of Colloidal Suspensions. *Phys. Rev. Lett.* **2011**, *106*, 167801.
(51) Girardi, M.; Figueiredo, W. Transition in three-dimensional micellar systems. *J. Chem. Phys.* **2000**, *112*, 4833–4835.

(52) Allen, M. P. and Tildesley, D. J., *Computer Simulations of Liquids*; Oxford: Oxford University Press: New York, 1987.

(53) Jungnickel, C.; Luczak, J.; Ranke, J.; Fernández, J. F.; Müller, A.; Thöming, J. Micelle formation of imidazolium ionic liquids in aqueous solution. *Colloids Surf., A* **2008**, *316*, 278–284.

(54) Brindle, D.; Care, C. M. Phase diagram for the lattice model of amphiphile and solvent mixtures by Monte Carlo simulation. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2163–2166.

(55) Pyper, N. C.; Pike, C. G.; Edwards, P. P. The polarizabilities of species present in ionic solutions. *Mol. Phys.* **1992**, *76*, 353–372.

(56) Bauer, B. A.; Lucas, T. R.; Krishtal, A.; Van Alsenoy, C.; Patel, S. Variation of Ion Polarizability from Vacuum to Hydration: Insights from Hirshfeld Partitioning. *J. Phys. Chem. A* **2010**, *114*, 8984–8992.

(57) Akbay, C.; Shamsi, S. A. Polymeric sulfated surfactants with varied hydrocarbon tail: I. Synthesis, characterization, and application in micellar electrokinetic chromatography. *Electrophoresis* **2004**, *25*, 622–634.

(58) Dutkiewicz, E.; Jakubowska, A. Effect of electrolytes on the physicochemical behaviour of sodium dodecyl sulphate micelles. *Colloid Polym. Sci.* **2002**, *280*, 1009–1014.

(59) Rankin, B. M.; Ben-Amotz, D. Expulsion of Ions from Hydrophobic Hydration Shells. *J. Am. Chem. Soc.* **2013**, *135*, 8818–8821.