

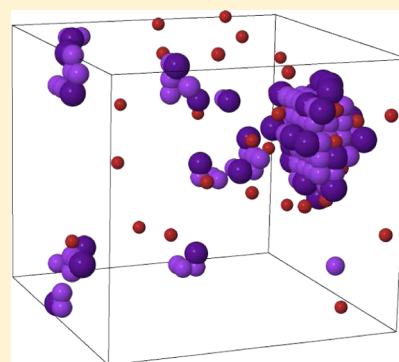
Ion Specificity and Micellization of Ionic Surfactants: A Monte Carlo Study

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ABSTRACT: We developed a simulation method that 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 the treatment of tumors,^{1,2} detergents and paints in the chemical industry, and emulsifiers in the food industry. The process of micellization is, therefore, a subject of intense investigation.^{3–7} Similar to many other physicochemical systems, micellar formation is strongly influenced by the ions present in the solution.^{8–13} Hofmeister¹⁴ was the first to observe that different salts have a profoundly distinct effect on protein solutions,^{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,¹⁹ colloidal science,^{20–24} bacterial growth,²⁵ micelle–vesicle transitions,²⁶ ionic liquids,^{27,28} surface tensions,^{29–37} peptide bonds,³⁸ liquid crystals,^{39,40} microemulsions,⁴¹ porous interfaces,⁴² etc. Recently, a theory was developed that allowed for the accurate calculation of surface and interfacial tensions of electrolyte–air^{43–46} and electrolyte–oil⁴⁷ 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.⁴⁸ For the water–oil interface, the theory also showed the fundamental importance of dispersion interactions⁴¹ between the ions and the hydrocarbons.⁴⁷ The same mechanism was also found to be responsible for the adsorption of hydrophilic cationic polyions to a hydrophobic wall⁴⁹ and variation of the critical coagulation concentrations (CCCs) of hydrophobic colloidal suspensions in the presence of chaotropic anions.^{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 that 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 salt present in solution.

MODEL AND MONTE CARLO SIMULATIONS

The Monte Carlo simulations are performed on a three-dimensional square lattice,⁵¹ 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, ρ . 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

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method.⁵² To model the electrostatic interactions, we consider the water as an uniform dielectric with relative permittivity, $\epsilon_w = 80$. The Bjerrum length is defined as $\lambda_B = \beta q^2 / \epsilon_w$, where q is the proton charge and $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature. For water at room temperature, the Bjerrum length is 7.2 Å. To take into account the hydrophobic interactions, which result in micellar formation, we follow the method developed for polar head surfactants.⁵¹ The interaction energy between two adjacent tail monomers, from different surfactants, is taken to be $-\epsilon$, while between two adjacent tail monomers and an empty cell (water), the interaction energy is taken to be $+\epsilon$. To avoid condensed surfactants,⁵¹ we also consider that each bend in a surfactant molecule costs $+\epsilon$, and if the head and last tail monomer are on the adjacent sites, it gives an additional energy penalty of $+\epsilon$. This is a minimal model of micellar formation, with only one adjustable parameter $+\epsilon$. 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 1×10^5 Monte Carlo steps, until the system reaches equilibrium. The movements of ions are simple one cell translations to a nearest neighbor site, while the surfactants can move by either a reptation or translation to a completely random place on the lattice, with 50–50% probability for either move. After equilibration, we save 1×10^5 uncorrelated states. An uncorrelated state is achieved each 1×10^4 Monte Carlo steps. The data are then analyzed to obtain the concentration of “free” surfactants ρ_f as a function of the total surfactant concentration ρ_t . The free surfactants are defined as molecules that do not have tail monomers of other amphiphiles adjacent to theirs.⁵¹ In Figure 1, we show a snapshot of a typical equilibrium configuration.

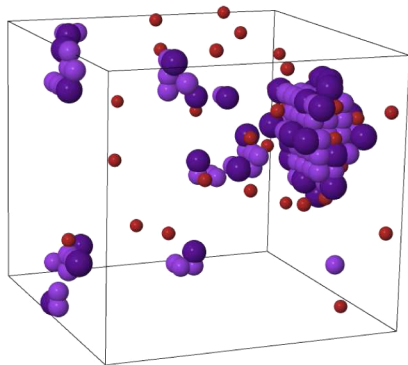


Figure 1. Snapshot of a typical salt-free equilibrium configuration. The surfactant concentration is $\rho_t = 100$ mM. The small red spheres represent counterions; the larger purple spheres represent the surfactant tail monomers; and the largest spheres represent the charged head groups.

RESULTS

We first consider a salt-free solution containing cationic surfactants and negatively charged counterions. A recent experiment¹⁰ showed that, for a cationic surfactant 1-decyl-3-methyl-1*H*-imidazolium chloride (DMIM), with no added salt, the CMC is around 57.2 mM. Our first goal is to adjust ϵ 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 ρ_t^* , at which ρ_f is at a maximum. In Figure 2, we show that, for $\epsilon = 0.626k_B T$,

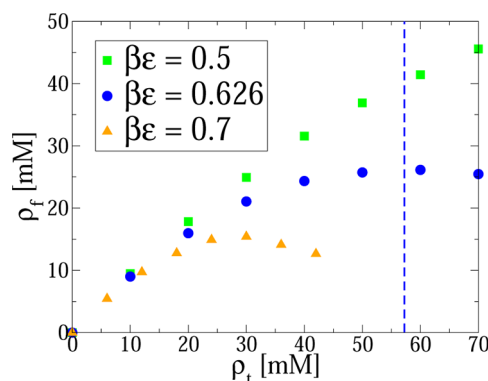


Figure 2. Concentration of free surfactants as a function of the total surfactant concentration. The vertical dashed line represents the experimental¹⁰ CMC, at 57.2 mM. We observe that it passes very near the maximum of the simulation curve, with $\beta\epsilon = 0.626$, at 59.2 mM. This value of $\beta\epsilon$ will then be used to model DMIM.

the maximum of the curve is at $\rho_t^* = 59.2$ mM, very close to the experimental CMC. For $\epsilon = 0.7k_B T$, the maximum is around 29 mM, while for $\epsilon = 0.5k_B T$, we cannot find a maximum in the range of the data (see Figure 2). The precise maxima of all of 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 strongly depend upon the chain length.⁵³ In particular, the alkyl chains of most surfactants have more than four monomers used in our lattice model. Nevertheless, it has been shown previously that the properties of the formation of micelles are captured quite well with a lattice model containing only four monomers and a suitably adjusted parameter⁵⁴ ϵ . 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,¹⁰ KCl, KBr, KNO₃, and KI. Using the same $\epsilon = 0.626k_B T$, adjusted for the case without salt, we now calculate the CMCs for solutions containing electrolyte at a concentration of 50 mM. We consider first the case with added KCl. Following the theory developed in refs 43–47 and 50, 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 the Coulomb interaction with the head groups. The CMC obtained from simulations for solution with 50 mM KCl is 39.94 mM, in good agreement with the experimental value, at 42 mM (see Figure 3). KCl screens the electrostatic repulsion between the head groups, thus lowering the CMC.

We next consider salts with chaotropic anions, KNO₃, KI, and KBr. The earlier work showed that chaotropic anions, such as NO₃[−], I[−], and Br[−], adsorb to hydrophobic surfaces mainly because of the dispersion interaction between the ions and 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, γ

$$\beta U_c = -\nu\gamma \quad (1)$$

where ν is an adjustable, ion-independent parameter.

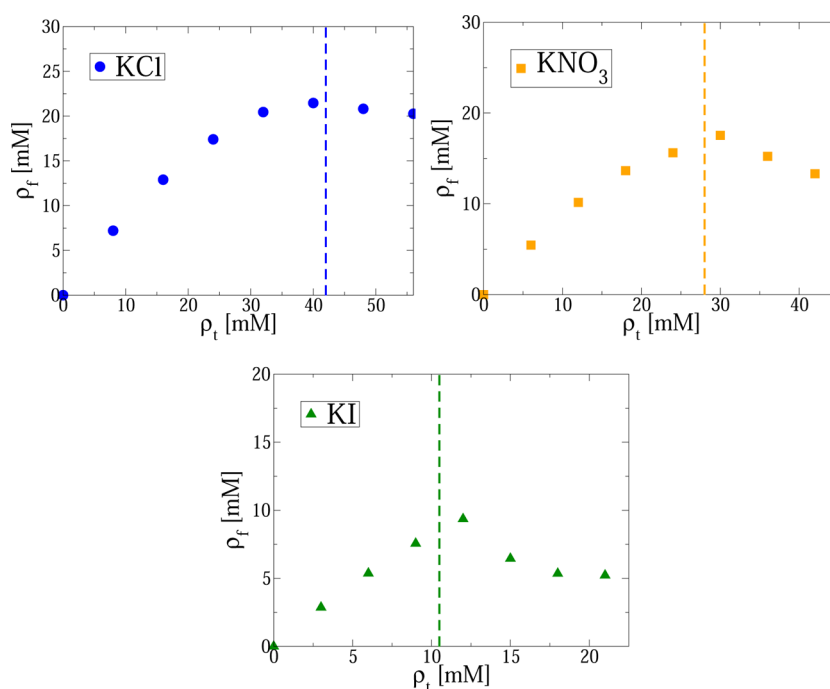


Figure 3. Concentration of free surfactants as a function of ρ_t with added 50 mM salts. The dashed lines represent the experimental¹⁰ CMC values for KCl, KNO₃, and KI, at 42, 28, and 10.5 mM, respectively, in good agreement with the values obtained in simulations, at 39.94, 29.93, and 11.71 mM, respectively.

Consider first the salt KI (at 50 mM). We will try to adjust the value of the parameter ν to obtain the correct experimental CMC, at 10.5 mM. The same value of ν will then be used for all other chaotropic anions. The ionic polarizabilities for I[−], Br[−], and NO₃[−], provided in ref 55, are $\gamma = 7.4$, 5.07, and 4.09 Å³, respectively, and are the same as used in the previous theoretical studies^{43–47,50} on surface and interfacial tensions. It is difficult to find the exact value of ν 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 Figure 3). Using the same value of ν , we can now calculate the CMCs for other salts, KNO₃ and KBr. For the salt KNO₃, the value found from simulations is 29.93 mM and is very close to the experimental CMC of 28 mM (see Figure 3). For the salt KBr, we obtain the value 25.48 mM, while the experimental value is 34 mM (see Figure 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 the Br[−] anion.⁵⁵ This

problem was already noticed in the earlier work on the stability of hydrophobic colloidal suspensions⁵⁰ and in the recent *ab initio* simulations.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^a

	simulations (mM)	experiments (mM) ¹⁰
no salt	59.2	57.2
salts (at 50 mM)		
KCl	39.94	42
KBr	25.48	34
KNO ₃	29.93	28
KI	11.71	10.5

^aThe results are for systems without added salt and with salts at 50 mM. The experimental data are from ref 10. The βe and ν constants are adjusted to 0.626 and 0.155 Å^{−3}, respectively.

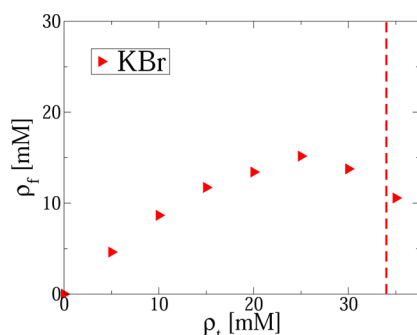


Figure 4. Concentration of free surfactants as a function of the total surfactant concentration for 50 mM KBr. The dashed line represents the experimental¹⁰ CMC value for KBr, at 34 mM. The CMC found in simulation is 25.48 mM.

We next note that the Hamiltonian of the lattice model with monovalent kosmotropic ions is invariant under the charge inversion $+ \rightleftharpoons -$ of all of the ionic species. This means that the CMCs of anionic surfactants with the same chain length and a headgroup 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-decyl 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 at 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

Table 2. Summary of the Calculated CMCs for SDeS Anionic Surfactant at 50 mM Salt Concentration^a

	CMCs (mM)
no salt	59.2
KI	52.1
KNO ₃	48.04
KBr	46.92
KCl	39.94

^aThe $\beta\epsilon$ and ν parameters are the same as for DMIM.

our model for CMCs of anionic surfactant SDeS in solutions with various salts. Curiously, even though the adsorption of I^- increases the CMC 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.

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 to 5 Å. The value of ϵ then must also be recalculated. In the case of DMIM surfactant, this leads to $\epsilon = 0.552k_B T$. If we replace 50 mM KCl with 50 mM NaF, we calculate that the CMC of DMIM will increase from 39.94 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 sulfate (SDS). We find that $\epsilon = 0.76k_B T$ 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 NaCl is added to solution, we calculate that the CMC for SDS will drop down to 4.35 mM, very close to the experimental⁵⁸ value, at 4.2 mM. Unfortunately, there is no experimental data for SDS with chaotropic salts to compare to our simulation predictions.

CONCLUSION

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 on the basis of 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, except 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 that show that strongly hydrated ions are repelled from the hydrophobic groups, while iodide ions are observed next to them.⁵⁹ The results of simulations are in 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 very limited experimental data available for these systems to compare to our predictions.

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Notes

The authors declare no competing financial interest.

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