Complementary experimental-simulational study of surfactant micellar phase in the extraction process of metallic ions: Effects of temperature and salt concentration

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A B S T R A C T

The thermoresponsive micellar phase behaviour that exhibits the Triton-X-100 micelles by temperature effect and addition of salt in the extraction process of metallic ions was explored from mesoscopic and experimental points. In the theoretical study, we analyse the formation of Triton-X-100 micelles, load and stabilization of dithizone molecules and metallic ions extraction inside the micellar core at room temperature; finally, a thermal analysis is presented. In the experimental study, the spectrophotometric outcomes confirm the solubility of the copper-dithizone complex in the micellar core, as well as the extraction of metallic ions of aqueous environment via a cloud-point at 332.2 K. The micellar solutions with salt present a low absorbance value compared with the micellar solutions without salt. The decrease in the absorbance value is attributed to a change in the size of hydrophobic region of colloidal micelles. All transitory stages of extraction process are discussed and analysed in this document.

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1. Introduction

The extraction of metallic ions in aqueous environments with selective micelles has attracted great interest in the past two decades because this process involves a green and ecological approach. With this method, the use of organic solvents is discarded completely, which by their chemical nature are pollutants, dangerous and carcinogenic to humans. For example, chloroform is widely used as the solvent in the extraction of metallic ions; however, by its chemical nature, it is highly polluting and quite toxic [1–3]. The use of surfactants for the extraction of metallic ions has broad benefits due to two main reasons: first, the main solvent is water and second, low concentrations are required for the extraction of metal ions [4]. However, we must add that even the use of surfactants is limited in this technique due to its biodegradegrability**. The surfactants most commonly used in metal ion extraction processes in contaminated aqueous environments can be anionic or cationic but are most often nonionic, where polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether

(Triton-X-100) is the most common surfactant due to its structural and chemical characteristics. The Triton-X-100 surfactant is constituted by a poly(ethylene oxide) (PEO) hydrophilic chain (nine to ten repeat units) and a highly hydrophobic segment, where the hydrophilic segment confers high stability to the Triton-X-100 micelles in aqueous environments via the formation of hydrogen bonds with water molecules [5]. Moreover, for this reason, this nonionic surfactant exhibits a low critical micelle concentration (CMC $\approx$ 0.2 mM at 293 K) in aqueous environments; very low concentrations are sufficient to induce micelle formation, and its applications extend to dye and metallic ion extraction [6–8]. A notable aspect of the Triton-X-100 surfactant is that it forms colloidal dispersions with high thermodynamic stability in aqueous environments when a specific micellar concentration is exceeded; when this occurs, the Triton X-100 micelles exhibit a nonpolar core (free of water molecules) constituted by highly insoluble hydrocarbon segments and have the ability to harbour and solubilize insoluble organic compounds in aqueous media [5,9,10,11], such as diphenylthiocarbazone (dithizone). Dithizone molecules are highly insoluble in aqueous environments at acidic pH, but they have the capability to form hydrophobic coordination compounds with metallic ions such as Mg^{+2}, Ca^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2} and Ag^{+1} [5,7,12–18]. In this sense, combination the high

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thermodynamic stability exhibited by the nonionic surfactant micelles and the high compatibility of the hydrophobic core with the dithizone molecules, generates an attractive metallic ions extraction process dissolved in aqueous environment; which as satisfies some principles of green chemistry; this is currently under investigation at the experimental and mesoscopic level. A little known fundamental aspect of this extraction process is the dependence of the stability of the Triton X-100 micelles on the applied temperature and the salinity of the aqueous environment. As the salinity or temperature of the colloidal system is gradually increased, the stability of the surfactant micelles tends to decrease, i.e., above a specific temperature, the micellar corona tends to collapse towards the hydrophobic surface of the micellar core, which leads to the formation of a cloud point and therefore to an extraction process called cloud point extraction [19–21]. The extraction of metallic ions in aqueous environments with nonionic surfactants exhibits a series of possible stages, involving the formation and stabilization of the colloidal dispersion, the charge of the dithizone molecules inside the hydrophobic core, the migration and interaction of the metallic ions with the dithizone molecules inside the micellar core, the effect of the saline environment and finally the extraction at the cloud point by the temperature effect.

The extraction of metallic ions through nonionic surfactants has been extensively investigated experimentally but the detailed stages have not been sufficiently investigated theoretically [22–25]. From a theoretical point of view, mesoscopic simulation methods open a window for exploration via coarse-grained models of each transitory stage of the extraction of metal ions in aqueous environments. The combination of mesoscopic simulations supported by experimental data obtained by spectrophotometric analysis is suitable to expand the knowledge of this physicochemical process. To accomplish the above in the present work, we employed dissipative particle dynamics (DPD) simulations and spectrophotometric analyses to explore in detail the extraction of metallic ions by Triton-X-100 micelles in an aqueous environment at acidic pH (pH = 5). Cu^{+2} metallic ions were employed in this work due to their low toxicity and high reactivity with dithizone molecules [7,18]. Our interest is mainly focused on exploring all transitory stages exhibited in the extraction of metallic ions and the behaviour of micellar phase that exhibits the nonionic surfactant micelles (micellar formation, loading of dithizone molecules in the micellar core, migration of metallic ions towards the hydrophobic core and interaction with dithizone) in aqueous environments, as well as the effect of the saline environment and the detection of the cloud point by a thermal study. Finally, the main goal of our research is to contribute to the understanding of the metallic ion extraction process with nonionic surfactants in aqueous environments and to determine and evaluate the cloud points. This will allow for the identification of analytes and reagents used in this physicochemical process.

This document is organized as follows. In Section 2, we briefly present the theoretical and experimental aspects. In the theoretical section (Section 2.1), we describe the DPD simulation method, mesoscopic (coarse-grained) models, interparticle interactions and simulation details. In the experimental section (Section 2.2), we detail the employed materials and the general methodology to explore the extraction of metallic ions in aqueous and saline environments (pH = 5) with Triton-X-100 micelles. Section 3 contains our main results and a discussion of the extraction of copper ions by dithizone in the Triton-X-100 micelles in an aqueous environment. This section is divided into two parts. In the first part, we present the theoretical outcomes and predictions of the mesoscopic simulations and the mesoscopic thermal study. In the second part, we discuss our experimental findings regarding the extraction of metallic ions by nonionic surfactant micelles loaded with dithizone and the sodium chloride effect, and finally, we

analyse the micellar stability as a function of temperature (cloud point). In section 4, we offer our general conclusions.

2. Methodology

2.1. Theoretical aspects

2.1.1. DPD model

To explore in detail the behaviour of micellar phase that exhibits the nonionic surfactant micelles as well as main stages in the extraction of metallic ions in an aqueous environment, we employed the dissipative particle dynamics (DPD) method [26–31]. This innovative scheme provides a unique numeric algorithm to describe the dynamic behaviour of mesoscale models (coarse-grained) constituted by particles or beads that represent atoms or real molecules. In the DPD simulations, the beads obey Newton's equations of motion [29–31].To simplify the numeric calculus, the mass of each DPD particle is assigned a value equal to unity. In this way, each particle is subject to soft interactions by means of three specific forces (conservative F_{ij}^C, dissipative F_{ij}^D and random F_{ij}^R) via the following relationship [30,31]:

$$\mathbf{F}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R) \tag{1}$$

The full summation is made over all neighbouring particles within a certain cut-off of $r_c = 1$. The conservative force F_{ij}^C focuses on the pairwise interaction between particles and principally includes contributions from bonded particles, which is described by:

$$\mathbf{F}_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij})\hat{\mathbf{r}}_{ij}| & (r_{ij} < 1) \\ 0,| & (r_{ij} \geqslant 1) \end{cases} \tag{2}$$

where a_{ij} is the DPD repulsion parameter between particle i and particle j, $r_{ij} = |\vec{r}_i - \vec{r}_j|$, and $\hat{r} = \vec{r}_{ij}/r_j$. The dissipative F_{ij}^D and random forces F_{ij}^R in the DPD scheme function as a thermostat, and both forces describe the viscous drag on a particle due to the surrounding fluid molecules represented by the particle and the random interaction between a particle i and its neighbouring particle j. $\mathbf{F}_{ij}^C$ and $\mathbf{F}_{ij}^D$ are given by [29]:

$$\mathbf{F}_{ij}^D = -\gamma \omega^D(r_{ij})(\upsilon_{ij}.\hat{\mathbf{r}}_{ij})\hat{\mathbf{r}}_{ij} \text{ and } \mathbf{F}_{ij}^R = \sigma \omega^R(r_{ij})\theta_{ij}\hat{\mathbf{r}}_{ij} \tag{3}$$

where $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ are the weighting functions of $\mathbf{F}_{ij}^D$ and $\mathbf{F}_{ij}^R$ respectively and are dependent on the distance between particles i and j, γ is a coefficient that controls the strength of the dissipative force between particles, $\upsilon_{ij} = \upsilon_i - \upsilon_j$, θ_{ij} is a randomly fluctuating parameter that satisfies Gaussian statistics and σ is the amplitude of the random force [29–31]; in DPD scheme the balance temperature is given by $k_BT = \sigma^2/\gamma$, in this way k_BT is usually defined as the reduced unity of energy. The DPD multiparticle scheme is solved by employing the modified velocity Verlet algorithm [30–32] described by the following relationship:

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{1}{2}\Delta t^2 \mathbf{f}_i(t),$$

$$\tilde{\mathbf{v}}_i(t + \Delta t) = \mathbf{v}_i(t) + \lambda \Delta t \mathbf{f}_i(t),$$

$$\mathbf{f}_i(t + \Delta t) = \mathbf{f}_i(\mathbf{r}(t + \Delta t), \tilde{\mathbf{v}}_i(t + \Delta t)), \tag{4}$$

$$\upsilon(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2}\Delta t(\mathbf{f}_i(t) + \mathbf{f}_i(t + \Delta t))$$

In this last equation, $\tilde{v}_i$ describes the velocity of a particle at time $t + \Delta t$ [32]. The evaluation of the positions and velocities of each DPD particle by this modified algorithm allows for the