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DIGITAL SIMULATION AND COMPUTATIONAL MODELLING OF SURFACE-ACTIVE COMPLEXES BASED ON QUATERNIZED ETHYL PIPERAZINE

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ABSTRACT

Modelling and simulation of real-life phenomena in virtual environment is gradually becoming an integral part of science and technology. One crucial benefit of computer modelling in science and engineering is the opportunity to extract useful information about the nature of the subject system that would otherwise be available only through tedious experimental procedures. The other advantage of computer simulation is the ability to analyze the system from a new perspective and identify new information which would not be available via experimental methodologies. Future development and improvement on the accuracy of computer modelling techniques depend on how simulation results are successfully verified against experimental findings. This work presents the outcome of a molecular simulation performed on a novel surface-active complex alongside the relevant experimental findings to verify that the identified simulation methodology is robust enough to predict the behavior of the molecular system under specified real-life conditions.

1. INTRODUCTION

The age of fast digitalization and diminishing resources oversees the rapid development of computational models and simulation techniques in chemistry and chemical engineering. Computational methods are being utilized successfully for prediction of structures and properties of various chemical and biological systems and processes [1]. Simulation of molecular systems in virtual environment using computational tools helps to minimize the usage of resources such as material, energy and time while evaluating various alternatives during chemical product development process. It is predicted that with the future progress of computational methods in chemistry, automated generation of reaction paths will be possible [2]. In addition, application of machine learning to molecular simulations and computational chemistry is another promising idea that can unlock the potential of this field for future product development [3].

However, development of various computational tools depends on their successful benchmarking against experimental data. Several works have been dedicated to linking experimental findings with computer simulations of various molecular systems and processes [4]-[7].

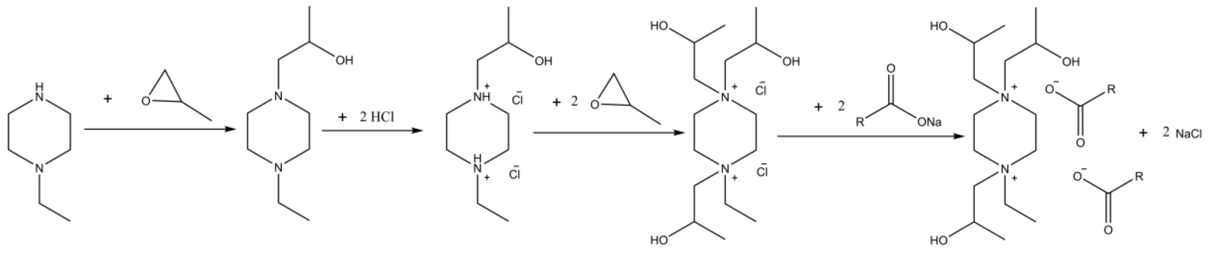
Surface and interfacial science is one of the most important fields in need of progressive computational modelling work for its future development. Combining computational input with novel experimental findings in surface and interfacial science can lead to revolutionary inventions with great application potential. Considering this, our work reports the computer modelling of self-assembly and micellization behavior of a novel surface-active complex. The suggested coarse graining and parametrization scheme can be successfully extrapolated to similar molecular structures.

2. EXPERIMENTAL WORKS

2.1 Synthesis

Synthesis of the surface-active complexes was done as described in Fig. 1 below. In the first step of reaction sequence ethyl piperazine reacted with propylene oxide to produce alkanolamine. In the next step the alkanolamine was protonated with hydrogen chloride to obtain di-ammonium dichloride salt. The third step was the total quaternization of the diammonium salt by reacting it with propylene oxide in 1:2 molar ratio. In the final step surface-active complexes were obtained by mixing the quaternized product with long chain carboxylic acids or their sodium salts.

For the purposes of this study, the surface-active complex with stearic acid fragments (named as [C_{18}-EPPO_3-C_{18} + 2 NaCl]) has been chosen and both experimental and computational evaluation of the product has been performed.



R = C_9H_{19}, $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$, CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$, CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$(CH_2)_7$

Fig. 1 Synthesis of the surface-active complexes from ethyl piperazine

2.2 Self-assembly Properties

Critical Micelle Concentration (CMC) of the obtained surface-active complex [C_{18}-EPPO_3-C_{18} + 2 NaCl] has been measured via conductometric method and was recorded as ? mM. Its high surface activity and self-assembly properties were also verified by tensiometric measurements. Fig. 2 and Fig. 3 below present the conductivity and surface tension of aqueous [C_{18}-EPPO_3-C_{18} + 2 NaCl] solutions as a function of their concentration.

The conductometry and tensiometry analyzes indicate that [C_{18}-EPPO_3-C_{18} + 2 NaCl] possess surface activity and is able to form molecule clusters called "micelles" in aqueous solution. The characteristic break point on Fig. 2 corresponds to the minimum concentration that allows formation of micellar clusters and is denoted as CMC point.

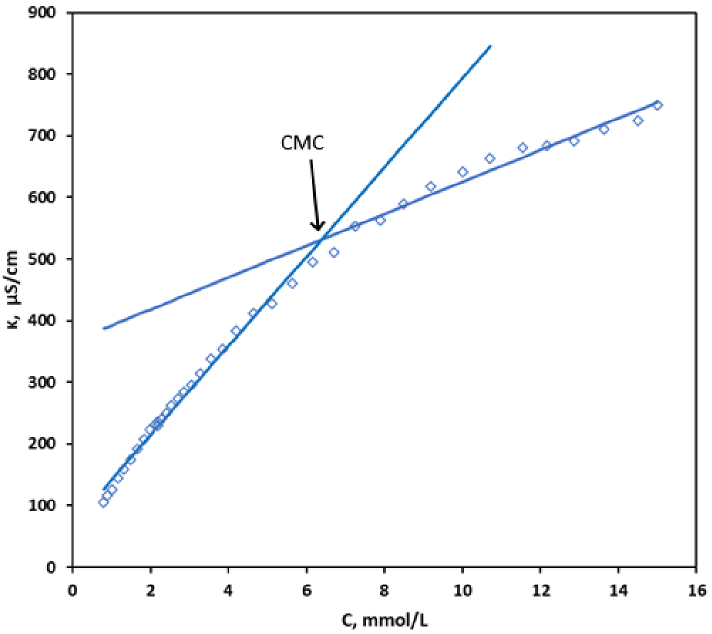


Fig. 2 *Conductivity vs concentration graph of [C_{18}-EPPO$_3$-C_{18}+ 2 NaCl]*

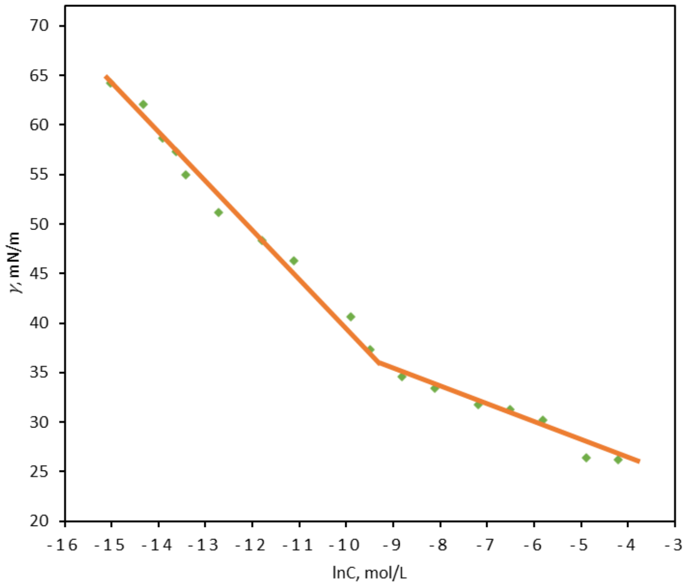


Fig. 3 *Surface tension vs ln of concentration graph of [C_{18}-EPPO$_3$-C_{18}+ 2 NaCl]*

3. DPD METHODOLOGY

Dissipative Particle Dynamics (DPD) technique is a computational scheme designed to simulate the mesoscopic particles' motion in fluid environment by utilizing Newton's classical motion theory [7]. This method is regarded as one of the most useful molecular simulation tools to model and study the behavior of self-assembling systems such as surfactant solutions.

The basis of DPD methodology is computation of two types of forces acting on the particles of interest in the finite simulation volume. The two types of forces are categorized as bonded and non-bonded forces, whereas the particles of interest are generally named as "beads".

3.1 Non-bonded Forces

The non-bonded DPD forces consist of the following:

- The conservative force F_{ij}^{C}
- The dissipative force F_{ij}^{D}
- The random force F_{ij}^{R}
- The electrostatic force F_{ij}^{E}

The conservative force F_{ij}^{C} accounts for the repulsive interactions between bead particles and the soft harmonic form of conservative force (1) is utilized for the simulation:

$$F_{ij}^{C}=\begin{cases} a_{ij}\left(1-\frac{r_{ij}}{r_C}\right) & r_{ij}<r_C \\ 0 & r_{ij}\geq r_C \end{cases} \qquad (1)$$

Where a_{ij} is called the repulsive interaction parameter between beads i and j, r_C is called the cut-off radius and r_{ij} is the distance separating beads i and j. The repulsive interactions take effect only within the cut-off radius r_C.

The frictional forces between the beads in the fluid medium is represented by the dissipative force F_{ij}^{D} (2):

$$F_{ij}^{D}=-\gamma_{ij}\omega^{D}\left(r_{ij}\right)\left(v_{ij}\right) \qquad (2)$$

Where γ_{ij} is the friction coefficient and $\gamma_{ij}=\gamma_{ji}>0$. $v_{ij}=v_i-v_j$ is the velocity difference between the bead particles. ω^{D} is called the distance dependent weight function is calculated by (3):

$$\omega^{D}=\begin{cases} \left(1-\frac{r_{ij}}{r_C}\right)^2 & r_{ij}<r_C \\ 0 & r_{ij}\geq r_C \end{cases} \qquad (3)$$

The random motion of the particles in the fluid medium is represented by the random force F_{ij}^{R} (4):

$$F_{ij}^{R}=\sigma_{ij}\omega^{R}\left(r_{ij}\right)\xi_{ij}\frac{1}{\sqrt{\Delta t}} \qquad (4)$$

Where σ_{ij} is the noise amplitude ($\sigma_{ij}=\sigma_{ji}>0$). $\xi_{ij}=\xi_{ji}>0$ is a randomly fluctuating Gaussian variable with a zero mean and a unit variance, Δt represents the time step utilized in DPD simulations. ω^{R} is the distance dependent weight function (5):

$$\omega^{R}=\begin{cases} 1-\frac{r_{ij}}{r_C} & r_{ij}<r_C \\ 0 & r_{ij}\geq r_C \end{cases} \qquad (5)$$

The noise amplitude σ_{ij} and the friction coefficient γ_{ij} are related:

$$\sigma_{ij}^{2}=2\gamma_{ij}k_BT \qquad (6)$$

In (6) above k_B is the Boltzmann constant ($k_B=1.380649\times10^{-23}\,J\cdot K^{-1}$) and T is the absolute temperature in K (Kelvin).

Finally, the electrostatic force F_{ij}^{E} is represented by the Coulomb's Law (7):

$$F_{ij}^{E}=k_e\frac{q_iq_j}{\varepsilon_r r_{ij}^{2}} \qquad (7)$$

Where k_e is the Coulomb's constant ($k_e=8.99 \times 10^9\ N \cdot m^2 \cdot C^{-2}$), q_i and q_j are the electrostatic charges of the beads *i* and *j*, and ε_r is the relative permittivity.

3.2 Bonded Forces

The spring force F_{ij}^S and the angle force F_{ijk}^A are the bonded forces taking effect when two or more bead particles are sharing a bond in a manner similar to covalent bonds in chemistry.

The strength of bonds connecting the bead particles is simulated by the spring force F_{ij}^S. The spring force F_{ij}^S (8) and its potential U^S (9) are:

$$F_{ij}^S=-\frac{\delta U^S}{\delta r_{ij}} \qquad (8)$$

$$U^S=\sum_j \frac{1}{2} C^b \left(r_{ij}-r_0\right)^2 \qquad (9)$$

Where C^b is the spring constant and r_0 is the equilibrium length of the bond connecting beads *i* and *j*.

The stiffness of the angle between two bonds is simulated by the angle force F_{ijk}^A. The cosine harmonic functional form the angle force F_{ijk}^A is used as expressed by (10) and (11):

$$F_{ijk}^A=-\frac{\delta U^A}{\delta r_{ij}} \qquad (10)$$

$$U^A=\sum_j \frac{1}{2} C^a \left(cos\theta_{ijk}-cos\theta_0\right)^2 \qquad (11)$$

Where C^a is the angle constant, θ_{ijk} is the actual bond angle, θ_0 is the equilibrium bond angle between *i-j* and *j-k* bonds.

4. SIMULATION SET-UP

The simulation was performed using Materials Studio v23 molecular modelling software. The simulation was performed in a box with dimensions of 200 Å × 200 Å × 200 Å with NVT ensemble for 100000 time steps.

4.1 Coarse Graining

Coarse graining in molecular simulation is the process of modelling the actual molecular structure for computational process via the specified scheme. Water molecules and molecules of surface-active complex [C_{18}-EPPO_3-C_{18} + 2 NaCl] have been coarse grained in accordance with the schematic described in Fig. 4 below.

4.2 Parametrization

The repulsive interaction parameters a_{ij} used in Materials Studio v23 are presented in Table 1 below.

In addition, all other DPD parameters from (1) to (11) that are required by the software to converge are defined below:

- The cut-off radius r_C=6.46 Å
- The friction coefficient $\gamma_{ij}=4.5$

- Time step $\Delta t=0.05$
- The bond spring constant $C^b=150$
- The bond angle constant $C^a=5$
- The equilibrium bond angle $\theta_0=180°$

For electrostatic effects the charges of +1, +1 and -1 were assigned to NH, eNH and CO beads, respectively. The relative permittivity ε_r of water at 25°C ($\varepsilon_r=78.2$) was selected to simulate aqueous environment.

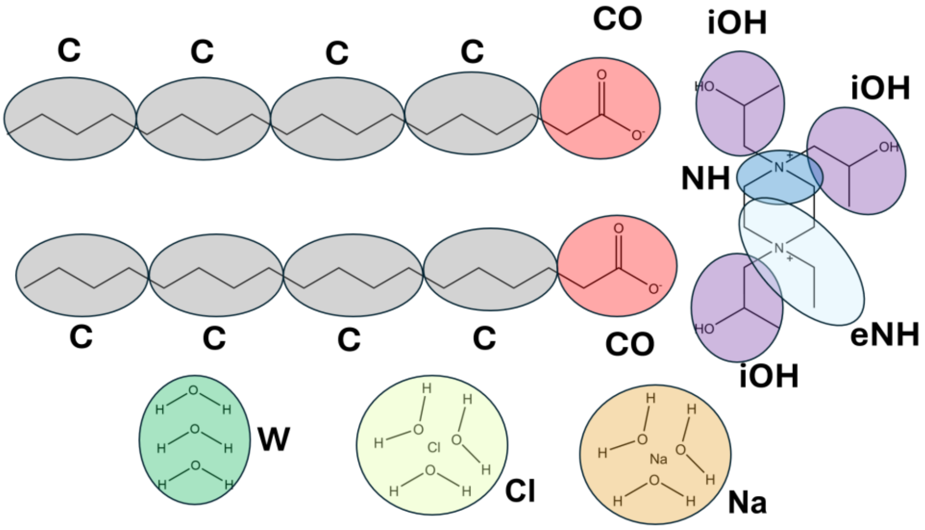


Fig. 4 Coarse graining schematic of $[C_{18}\text{-EPPO}_3\text{-}C_{18} + 2\,NaCl]$

Table 1. DPD repulsive interaction parameters

Bead type	C	CO	iOH	NH	eNH	W	Na	Cl
C	78.33							
CO	134.22	78.33						
iOH	89.25	93.35	78.33					
NH	82.32	80.68	73.97	78.33				
eNH	79.38	77.98	74.75	78.18	78.33			
W	118.79	80.77	75.50	74.24	72.69	78.33		
Na	118.79	80.77	75.50	74.24	72.69	78.33	78.33	
Cl	118.79	80.77	75.50	74.24	72.69	78.33	78.33	78.33

4.3 Simulation Outcomes

The molecular simulation converged successfully, and the equilibrated simulation trajectories were obtained (see Fig. 5). Water molecules have been hidden in the final simulation box frames to clearly indicate the structure of surface-active molecules. The final state of the simulation box shows distinctive clustering of the surfactant molecules. The ionic moieties, on the other hand, are randomly distributed within solution phase. These findings agree with the experimental findings, indicating self-assembly and micellization tendencies of [C_{18}-$EPPO_3$-C_{18} + 2 NaCl].

Therefore, it is established that DPD simulation performed in Materials Studio could successfully predict system behavior provided that correct parametrization is done.

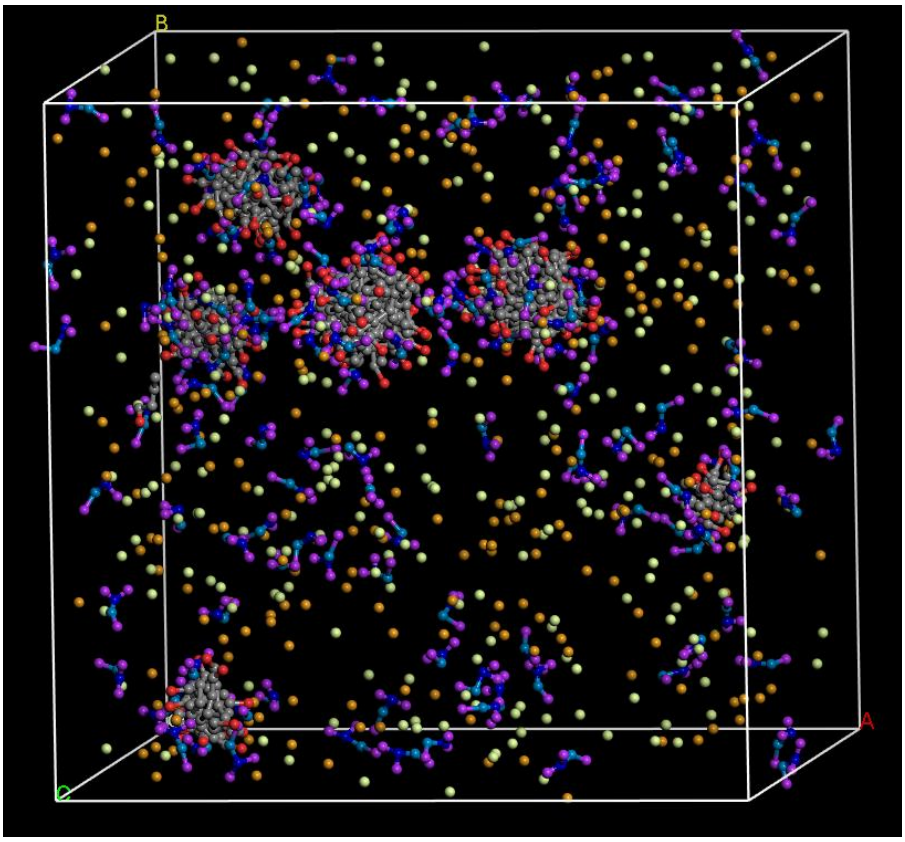


Fig. 5 Equilibrated simulation box depicting micelle formation

5. CONCLUSION

The synthesis of a completely new surface-active complex and its successful computer modelling have been done. The simulation results agree with the experimental findings. The methodology utilized for computational modelling of the novel surface-active complexes can be further applied to similarly constructed molecular systems for deeper and more rigorous study of self-assembly and micellization behavior.

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