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ARTICLE TYPE

Study of Molecular Array Behavior of Laurel Alkanolamide on Oil/Water Interface and the High Interfacial Activity Enhanced by Inherent Synergistic Effect

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5 Interfacial activity of surfactants is an issue attracted a lot of attention, but most of the literature are about pure surfactants, the effect of impurities on activity of surfactants is always thought as an illusive puzzle for clearly understanding of the structure-performance relationship all the time. In this paper, nonionic surfactant Laurel alkanolamide (LAA) synthesized by “one step” method was found to be able to decrease the oil/water interface tension to ultra-low at low concentration without co-surfactants and had surprising oil phase adaptability, which provided a perfect model not only to study the theoretical mechanism achieving ultra-low interface tension but also

10 distinguish the contribution of the molecular interfacial array behavior of surfactants and the concomitants on the interfacial activity. The oil/water interfacial activity of LAA with or without concomitants was investigated experimentally and theoretically using dissipative dynamic simulation (DPD) method. The detailed molecular array behavior of LAA and the concomitants on oil/water interface was investigated by molecular dynamics (MD). It was found that the concomitants coexist at the oil/water interface with LAA and distribute at the different position in the interfacial layer, resulting in the high interfacial activity and oil phase adaptability. The experimental

15 results agree well with the simulation results. We hope our strategy can provide an avenue to understand the structure-performance relationship of surfactants on molecular lever and revealed an effective approach to get ultra-low interfacial tension with different oil phase.

1. Introduction

The systems capable of achieving ultra-low oil/water interfacial tension (ULIT) are of great importance in many fields, such as enhanced oil recovery (EOR)¹ nanometer materials synthesis², etc. In EOR, reducing the oil/water interfacial tension to ultra-low (10^{-3} mN m⁻¹) has been proven to be the most important factor for screening the chemical flooding formula.³

25 In the last 30 years, great efforts have been paid to promote the theoretical mechanism of ultra-low interfacial tension phenomenon,⁴ and a huge amount of research has focused on the development of new surfactants⁵ or synergistic mixtures⁶ with diverse additives to achieve ultra-low interfacial tension, which keeps being one of the hotspots in the region of interface and colloid science. According to the literary reports, formation of fine emulsion or micro-emulsion was thought to have intimate connection with the ultra-low interface tension phenomenon,⁷ and the phase behavior of surfactant/oil/water mixtures⁸ was

utilized to verify if a formula could be adapted to a specific oil phase to decrease the oil-water interfacial tension to ultra-low. Systems that could solubilize almost equal amount of oil and water to form Winsor III type phases would be considered as the optimum formula for achieving ULIT.⁹

The formation of the Winsor III type phases has always been observed at relatively high surfactant concentration and with additives, which induce the impression that the cost to achieve ULIT by formation of emulsion or micro-emulsion could be too expensive¹⁰. Besides, actually the phase behavior of the same surfactants system to various oil phases differed so obviously, though the concept of optimum carbon number of the oil phase was used to describe the dependence of interfacial activity of surfactants on the oil phase composition, the oil adaptability of surfactant was regarded as an insuperable problem.¹¹ Above all, the effect of impurities on the activity of surfactants is always regarded as a puzzle for clearly understanding the micro-mechanisms, which also actually hinders the practical application of surfactants.

Basically, the interfacial activity of a surfactant was determined by its interfacial efficiency and adsorption density,¹² both was affected by the molecular structure and the assembly behavior on the interface, and related to the interactions between oil, water and surfactant molecules. The investigation of the interfacial molecular behavior of surfactants, co-surfactants and other molecules is not only important for deeply understanding the mechanism of ultra-low oil/water interface tension, but also essential in efficiently searching application technologies.¹³

In this paper, nonionic surfactant Laurel alkanolamide (LAA) was synthesized by “one step” method using laurate methyl and diethanol amine as substrates. It was found out that the specific product with determined composition present extra high interfacial activity and surprising oil phase adaptability, which

could be a perfect model system to study the theoretical mechanism achieving ultra-low interface tension. We tried to further purify the product and determine the composition of concomitants with high accuracy, the oil/water interfacial activity of LAA with or without concomitants was investigated experimentally and theoretically using dissipative dynamic simulation (DPD) method. The interfacial activity and molecular array behavior of the pure LAA and the concomitants were investigated by molecular dynamic simulation. The molecular simulation investigations provide a microscopic view on molecular level for better understanding about the structure-performance relationship of interfacial activity of surfactants. The experimental results agree well with the MD simulation prediction.

2. Experimental Section

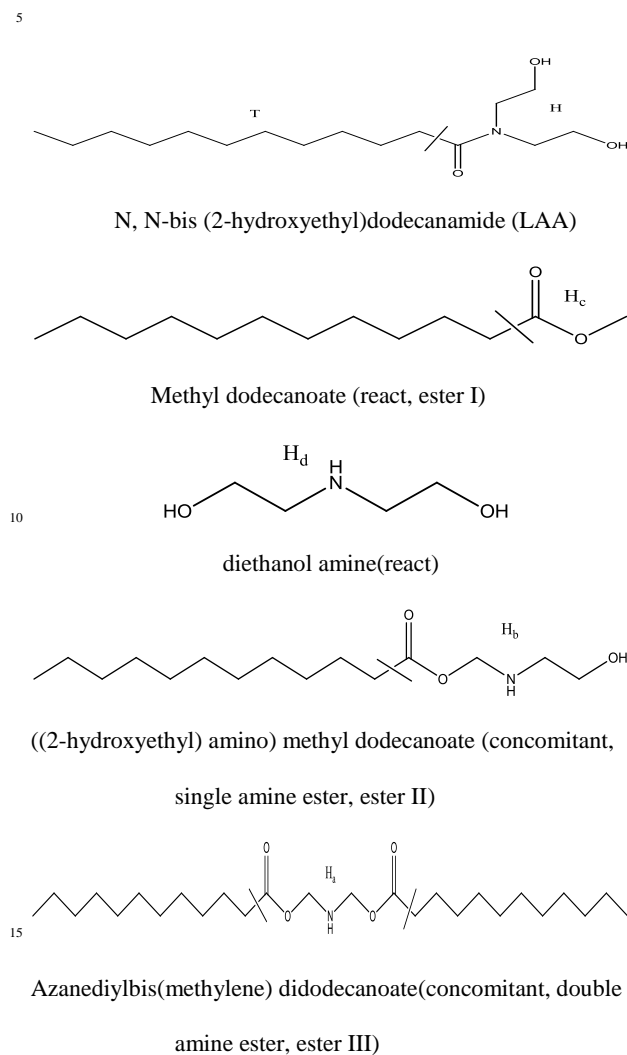
2.1 Materials

Methyl laurate (purity > 98%) was purchased from Hengjia chemicals Corp, China. Diethanol amine (purity > 99%), n-Dodecanese, sodium methylate (CH_3ONa) (> 98.5 %), Sodium chloride (NaCl) (A.R.), petroleum ether were purchased from Saibo chemicals Corp, China. Twice distilled water was used ($5\text{M}\Omega \cdot \text{cm}$). The different kinds of crude oil (I-V) were provided by Shengli Oilfield of SINOPEC and used as given.

2.2 Synthesis and purification of Laurel alkanolamide

Laurel alkanolamide was synthesized according to reference.¹⁴ The amounts of catalyst, reaction ratio, temperature, and time were controlled. The crude product was marked as “LAA-crude”. The crude product was firstly extracted by petroleum ether, then the organic phase was vacuum filtrated, and the solid substance obtained was marked as “LAA-one step purified”. The one step purified sample was solubilized in hot water and got concentrated through evaporation, then was

crystallized by cooling. The procedure was repeated twice, and the precipitated white crystal was marked as “LAA-pure”. The chemical structures of the LAA and several possible concomitants are shown in Scheme 1.



Scheme 1. Some of the model substances investigated in this study and the partition of beads in DPD simulation

20 According to IR and ¹HNMR spectra,¹⁵ all the above substrates coexist in “LAA-crude”, while the esters (I, II, III) were removed via one step purified. Details can be found in the supporting information.

2.3 Oil/Water Interfacial Tension

25 The oil/water interfacial tension was measured using the TX-500C dynamic interfacial tension meter, at 40 ± 0.1 °C, with

a rotating speed of 6000 r/min. The solution was injected into the tube and kept rotated for about 5 minutes to get pre-equilibrium before 0.5 μL oil was injected. If there is no distinct statement, the concentration of surfactant is 0.2 wt % with Sodium chloride (2.0 wt %) as medium at the oil/water interfacial tension measurement.

2.4 Dissipative Particle Dynamics

DPD simulation as a unique tool has been described in detail elsewhere and will be covered here only briefly.¹⁶ In this paper, dissipative particle dynamics simulation (DPD) proposed by Hoogerbrugge and Koelman¹² was used to simulate surfactant/oil/water interfacial system. The quality of beads, distance, time and temperature used DPD units. The weights $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$, and the amplitudes gands of the dissipative and the random forces have to obey equation (2)¹⁷

$$\omega^D(r) = [\omega^R(r)]^2, \sigma^2 = 2\gamma k_B T \quad (2)$$

All three above-mentioned forces incline to 0 when the distance between two particles is larger than the cut-off radii. r_c is the units of length, $k_B T$ (the temperature of the thermostat) is the units of energy, we set the temperature of the system as $k_B T = 1.0$. In these units, γ and σ determine the dissipative, and random forces, respectively, $\sigma = 3.0$ and $\gamma = 4.5$. A surfactant molecule consists of several different beads connected by harmonic springs

$$f_i^{\text{spring}} = \sum_j C r_{ij}$$

50 According to Groot and Rabone¹⁸, this condition is met for spring constant $C = 4$ (in kT units). A linear relation for the repulsion parameters a_{ij} and the Flory – Huggins interaction parameters $\chi_{ij}(T)$ is given¹⁹ in $k_B T$ units:

$$a_{ij} = a_{ii} + \frac{\chi_{ij}(T)}{0.306} = 25 + 3.27 \chi_{ij}(T)$$

Between beads of the same type, the repulsion parameters are taken as $a_{ij} = 75k_B T / \rho = 25 k_B T$ ($\rho = 3$), which is derived from the compressibility of water at room temperature (298K), a_{ij} , determine the amplitude of the conservative.

For studying interfacial properties expediently, a size $20 \times 10 \times 10$ nm ($L_x \times L_y \times L_z$) box containing a total number of 6000 beads is used. We use a coarse-grained approach where one DPD particle represents a group of atoms or a liquid volume. Water beads, oil beads, head groups, and tail groups are denoted by W, O, H, and T, respectively. The head group of ester is denoted by H_a , H_b and H_c and the diethanol amine is H_d . The tail beads are identical to the oil beads and tail beads for ester I, ester II and ester III. While some of the model surfactants investigated are shown in Scheme 1. Periodic boundary conditions are applied in all three directions. The surfactants are inserted in the system by replacing O particles with T particles and W particles with H particles in such a way that the total amount of particles remains constant. The input repulsion parameters are derived from the calculation using the above theories and methods. The DPD simulations run 20,000 steps with a time step of 0.05, simulation was performed through the Gibbs canonical ensemble. Analysis for the simulated properties was done when the state equilibrium is achieved. In DPD simulation, the calculated a_{ij} parameters by the theories and methods are given in table 1 which is determined according to the liner relation with Flory-Huggins parameters χ_{ij} . The χ_{ij} between pairs of particles can be obtained from the calculation of the mixing energy with Blend module. All simulations were carried out by Materials Studio 4.3 from Accelrys in this paper.

Table 1 The interaction parameters a_{ij} of simulation systems (in kT units)

a_{ij}	W	O	H_a	H_b	H_c	d	H	T
W	25.0							
O	82.35	25.0						
H_a	35.75	74.05	25.0					
H_b	23.77	65.68	32.28	25.0				
H_c	29.31	50.86	42.26	22.22	25.0			
d	29.87	58.91	23.27	24.67	22.39	25.0		
H	26.4	80.57	32.29	20.50	29.0	32.62	25.0	
T	78.49	24.28	61.56	56.17	48.41	56.75	78.16	25.0

Note: H represents different head groups, T the tail chain, W the water molecule and O dodecane

2.5 Molecular Dynamic simulation

In the simulation, A reasonable double-layer model was prepared for the simulation of the oil/water interface according to Seung Soon Jang et al.^{12b, 20} The initial configuration of this system was set up by arranging a uniform monolayer of 6 surfactants with the hydroxy (OH) group on an appropriate 2×3 square lattice in the xy plane with the hydrocarbon chains extending perpendicular to this plane with fully extended conformations. The lattice constants were chosen to give the surface area per molecule of 48.71 \AA^2 . The lattice dimension in the xy direction was 7.5 \AA , 25.0 \AA in the z direction. The angle in the zx and zy direction was 90° and 120° for xy direction (see figure 1(a)). Then put kinds of concomitants insert into the surfactants, keep the head at the base level. After that two such Langmuir-type monolayers were placed on opposite sides of the water phase with hydrophilic head groups of surfactants inserted in the xy plane of a roughly 30.70 \AA thick slab of water. The overall system contained 12 surfactants and 300 water molecules. The dimension of the simulation cell in the x was 12.99 \AA and y directions were 22.5 \AA , while the z dimension was kept at 101.95 \AA . Then two 11.61 \AA thick slabs of liquid dodecane were placed

on the two sides of the monolayers in the z direction, The number of oil molecules in the system was determined according to the capacity of grids and the density of the oil molecules is 0.7487g cm^{-3} in molecular dynamic simulation. The overall system contained 12 surfactants, 300 water molecules, and 20 dodecane molecules with 103 \AA final dimension of the cell in the z direction.

The parameters used in the simulation were calculated by COMPASS force field. Ewald summation method was used for non-bond interactions. The Nose-Hoover thermostat with a relaxation time of 0.1 ps was used to control the temperature of 298K .²¹

The layer was first minimized by smart minimize algorithm with 20000 steps to avoid the possible molecule overlaps and make sure the configurations more reasonable. Then a 2 ns NVT dynamics ensemble took place to ensure that the system was equalized and another 1 ns NPT dynamics ensembles followed by, the result of which were used for analysis.

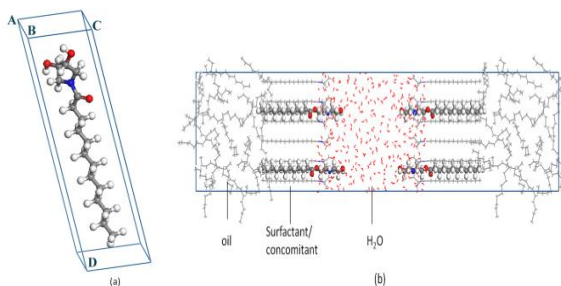


Figure 1. The single alkanolamide molecular in 3D box (a) and initial configuration for alkanolamide with one of the concomitant (b) Note: white for hydrogen, red for oxygen, grey for carbon and blue for nitrogen, the single alkanolamide molecular in figure (a) and concomitant atoms in figure (b) are drawn in stick style and other atoms are drawn in line style.

3. Results and discussion

3.1 Dynamic interfacial tension of the oil/surfactant/water system

3.1.1 Interfacial activity of Laurel alkanolamide and the effect of concomitants

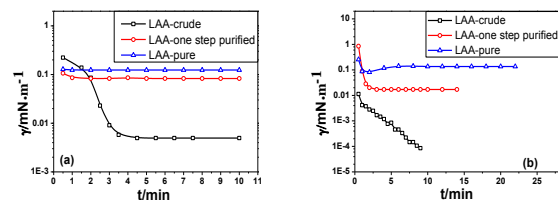


Figure 2. The dynamic interfacial tension between oil phase and aqueous solutions of samples with different purification degree as a function of time. (a) Dodecane was used as the oil phase (b)

Crude oil I was used as the oil phase (\square) $0.2\text{wt}\%$ LAA-crude (\circ) $0.2\text{wt}\%$ LAA-one step purified (\triangle) $0.2\text{wt}\%$ LAA-pure

As it was shown in Figure 2(a), the interfacial activity of the pure and crude LAA varied significantly. For LAA-pure, the dynamic interfacial tension reach the minimum value $1.24 \times 10^{-1}\text{ mN m}^{-1}$ very quickly, and did not change any more afterwards. For sample “LAA-one step purified”, the oil/water interfacial tension decreased as a function of time and reach the equilibrium ($8.27 \times 10^{-2}\text{ mN m}^{-1}$) in two minutes. For the LAA-crude product, the interfacial tension constantly decreased to $4.96 \times 10^{-3}\text{ mN m}^{-1}$ within ten minutes, which was considerably lower than two other samples.

The interfacial tension between crude oil I and different purity samples solution was also determined, as shown in Figure 2(b). The interfacial tension between crude oil I and “crude sample” solution reduced to 10^{-5} mN m^{-1} , while the minimum interfacial tension between the crude oil I and solutions of “one-step purified sample” and “pure sample” could not reach the order of 10^{-3} mN m^{-1} .

According to the above results, it can be concluded that the presence of concomitants affected the interfacial activity of LAA, and some perfect synergistic were presented. To investigate the mechanism of how concomitants affect the behavior of LAA on

oil/water interface, molecular dynamic and dynamic particle simulation methods were used.

3.2. Interfacial behavior and activity of Laurel alkanolamide on oil-water interface

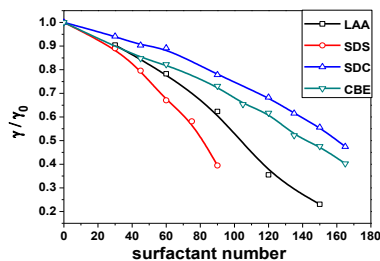


Figure 3. Plot of the relative interfacial tension reduction (γ / γ_0) as a function of surfactant molecule number adsorbed at the interface. (\square) Laurel alkanolamide; (\circ) Sodium dodecyl sulfonate; (Δ) Sodium dodecyl carboxylic; (∇) Betaine. Octane was used as oil phase. Note : here (γ_0) is the interfacial tension of the system without surfactant.

We have calculated the interfacial surface tension (γ) for both the oil/water systems, which is defined by the difference in normal and tangential stress across the interface.

$$\gamma = \frac{1}{2} \int_0^{L_z} \left[P_{zz}(z) - \frac{1}{2} (P_{xx}(z) + P_{yy}(z)) \right] dz \quad (3)$$

Where L_z and P_{zz} denote the dimension of the simulation cell and the component of the pressure tensor in the direction normal to the interface (i.e., along z), respectively, and P_{xx} and P_{yy} are the tangential components of the pressure tensor. The pressure tensors of the systems have been calculated along the simulated trajectories by averaging over the two equivalent interfaces in each of the systems¹⁶.

In experimental studies of surfactant efficiency, the bulk concentration is determined from the total amount of surfactants added, while molecule simulation can give curves of gas a function of interfacial density. It has different indications; the

former reflects efficiency of a surfactant, while the latter reflects efficiency at the interface. In the following sections, the interfacial tension between oil and water solution of LAA was also calculated by DPD. The variation of the interfacial tension as a function of numbers of adsorbed surfactant at oil/water interface, compared with several other common surfactants, such as ionic surfactant sodium dodecyl sulfonate (SDS), sodium dodecyl carboxylic (SDC) and zwitter ionic surfactant betaine (CBE), was shown in Figure 3. The slope of the curve reflects the interfacial efficiency, while the endpoint indicates the maximum interfacial density and the minimum interface tension the system could reach, namely the interfacial effectiveness.^{12a} From Figure 3, the order of the interfacial efficiency of the surfactants is SDS>LAA>CBE> SDC. The order of the maximum interfacial density is SDC \approx CBE>LAA>SDS. And the order of the interfacial effectiveness is LAA>SDS> CBE> SDC. Therefore, LAA has superior interfacial effectiveness compared with the other types of surfactants.

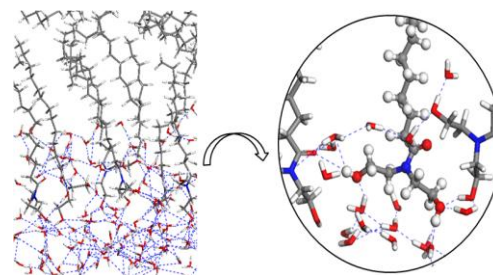


Figure 4. Hydrogen bonds of alkanolamide/dodecane/water interface: white for hydrogen, red for oxygen, grey for carbon and blue for nitrogen, blue dashed line for H-bonds.

The detailed molecular array behavior of LAA at oil/water interface was described by MD, the snapshot of one system was shown in Figure 4. It was demonstrated that intricate H-bonds existed between alkanolamide molecules and water molecules. At least five H-bonds could be formed between one alkanolamide molecule and five water molecules nearby, and a huge H-bond

network was formed in the oil/water interface layer. This phenomenon clearly states the theoretical source of the high interfacial density and high interfacial efficiency of LAA at oil/water interface.

3.3. The interfacial array behavior of LAA and the concomitant

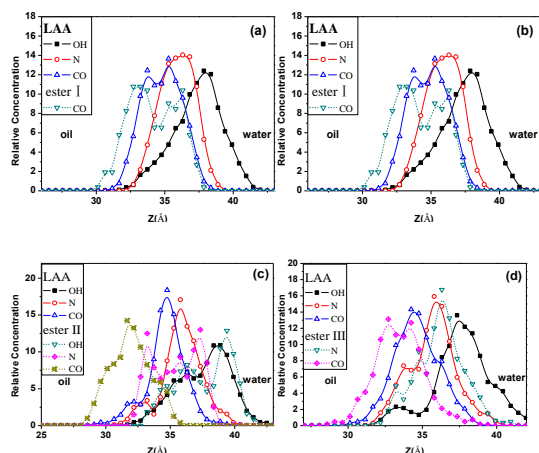


Figure 5. The relative concentration of groups of LAA and several concomitants as a function of distance on the Z axis. (a) LAA and ester I coexisted system. The distribution of hydroxyl, amide nitrogen (signed by N atom), the carbonyl group of LAA and ester based carbonyl of ester I was showed; (b) LAA and diethanol amine coexisted system. The distribution of hydroxyl, amide nitrogen, carbonyl for LAA and the alcohol amine (signed by nitrogen atom), the two different hydroxyl groups of diethanol amine; (c) LAA and ester II coexisted system. The relative concentration of hydroxyl, amide nitrogen, carbonyl of LAA and the hydroxyl, hydroxyl, carbonyl of ester II was shown; (d) LAA and ester III coexisting system. The relative concentration of hydroxyl, amide nitrogen, carbonyl of LAA and the amide nitrogen, carbonyl of ester III was shown.

The detailed array behavior of LAA and the several concomitants at oil/water interface was further investigated by MD, and was shown in figure 5. According to Figure 5 (a - d), the concomitants could co-adsorb with LAA molecules at the

oil/water interface, though the different components located at different relative positions, because of their difference hydrophilicity. React ester I prefer to exist at the side of oil phase compared with LAA, while the other react diethanol amine stayed at the side of water phase. The two concomitants ester II and ester III both exist at the similar position at the oil/water interface with LAA molecules.

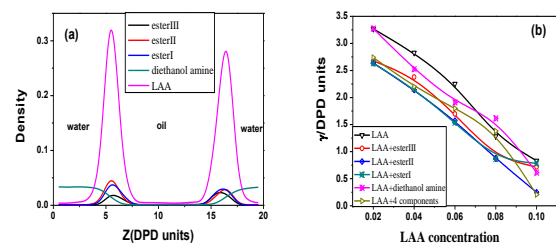


Figure 6. The interfacial density (a) and interfacial tension (b) of different molecules coexist with LAA

Figure 6 (a) showed the variation of molecule density as a function of distance at the Z axis, obtained by DPD, which represented the distribution of different components in interfacial layer. The peak values are 3.37, 5.50, 5.55, 5.65 and 5.80 for diethanol amine, LAA, ester II, ester I and ester III, respectively. The distribution of components in the interface layer described by DPD was coincided with MD shown in Figure 5. Figure 6(b) shows how the interfacial tension is reduced with increasing surfactant concentration with different concomitant at the interface calculated by DPD, the concentration of concomitants are kept for 0.02 all the time. It was found that when LAA exists individually at the oil/water interface, the minimum interfacial tension γ (the endpoint of the curve) for dodecane/water is higher than any other systems that containing at least one kind of concomitants, these components can increase the interfacial activity of LAA at the oil/water interface to a certain extent, in sequence as : the four components coexisting > ester II>diethanol amine> ester III>

ester I. The system LAA coexisted with four components possess the lowest interfacial tension, which was consistent with experiment results listed in figure 2. The different kinds of the concomitants absorb at different position at the oil/water interface LAA molecules on oil/water interface, which resulting in higher interfacial density of the system and higher interfacial effectiveness.

3.4. Oil phase adaptability of LAA-crude

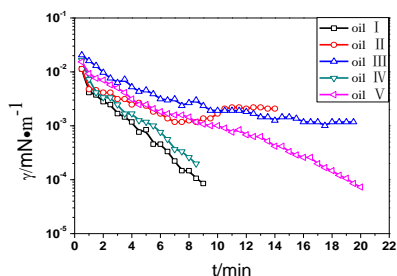


Figure 7. The dynamic interfacial tension between crude oil I~V and LAA-crude solution

Under normal conditions, oil can insert into the interface layer, and it was well known that the oil/water interfacial activity of a specific surfactant as always related with the oil phase components,^{5c, 22} the oil adaptability of surfactant is inherently limited.

The dynamic interfacial tension between crude oil I~V (ShengliOilfield of SINOPEC) and solutions of the LAA-crude sample was illustrated in figure 7. The result was showed that interfacial tension between the crude oil I~V and solution of LAA-crude sample all reduced to ultra-low within 30min, without using any other accessory ingredient. The IFT even decreased to 10^{-4} mN m⁻¹ for crude oil I, III and IV, which demonstrated that the favorable oil phase adaptability of crude LAA.

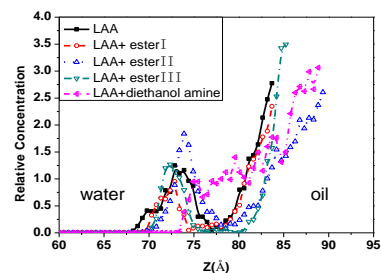


Figure 8. The distribution of the interfacial density of dodecane as a function of distance in the Z direction perpendicular to the interface.

The distribution of the interfacial density of dodecane as a function of distance in the Z direction perpendicular to the interface of the systems shown was calculated, the results were shown in figure 8. The amount of the dodecane molecules in the oil/water interface layer decreased with concomitants existing. Thus the concomitants in LAA crude products could not only increase the interfacial activity of the system, but also hinder the oil phase from inserting into the interface layer, which guaranteed the oil phase adaptability.

4. Conclusion

Laurel alkanolamide (LAA) was synthesized by "one step" method using Laurate methyl and diethanol amine as substrates could decrease the oil/water interfacial tension to ultra-low at low concentration which has a widely used in EOR. It is found by analysis that the concomitants play an important role in lowering the interfacial tension between oil and water for the system. The molecular simulations results showed that high interfacial density of LAA at oil/water interface induced by the hydrogen bond interaction between the hydrophilic head groups of alkanolamide laid the foundation for its high interfacial density and high interfacial effectiveness. The interlaced co-array of the concomitants coexist at the oil/water interface and distribute in the different position in interfacial layer, resulting in higher

interfacial activity and oil phase adaptability. The simulation results agreed well with the experimental results. In this way, we can pay more attention to the concomitants introduced by synthesis for surfactant system except for alkanolamide, if the perfect component of system is definite, we can control the synthesis and purification condition to get the specific composition of the system thus obtain product with high interfacial activity and oil adaptation.

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Notes and references

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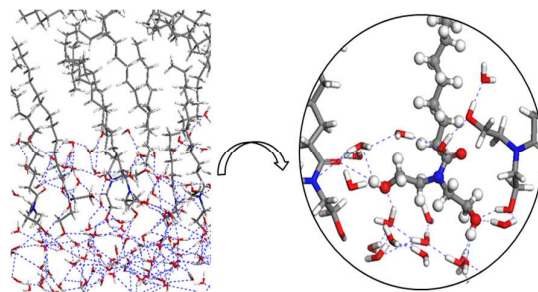
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The intricate H-bonds existed between alkanolamide molecules and water molecules and formed a huge H-bond network in the oil/water interface layer. This provide a basis for residued reactants and the concomitants coexist with alkanolamide molecules at the oil/water interface and absorb at different position, resulting in the inherent synergistic effect, which clearly states the theoretical source of the high interfacial density and high interfacial efficiency of alkanolamide at oil/water interface.