

Article

Heterogeneous Interactions During Bubble–Oil Droplet Contact in Water

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Abstract

Oily wastewater is extensively generated during the petroleum extraction and refining processes, as crude oil production water and from the effluent systems in petrochemical enterprises. The discharge standards for such wastewater are stringent, with the Oslo–Paris Convention stipulating that the oil content must be below 30 mg/L for permissible discharge. Flotation, a conventional oil–water separation method, relies on the collision and adhesion of rising bubbles with oil droplets in water to form low-density aggregates that float to the surface for separation. The collision and adhesion mechanisms between bubbles and oil droplets are fundamental to this process. However, systematic studies on their interactions remain scarce. This study employs the extended Derjaguin–Landau–Verwey–Overbeek theory to analyze the three mechanical interactions during the collision–adhesion process theoretically and investigates the heterogeneous interaction dynamics experimentally. Furthermore, given the diverse liquid-phase environments of oily wastewater, the effects of salinity, pH, and surfactant concentration are decoupled and individually explored to clarify their underlying mechanisms. Finally, a solution is proposed to enhance the flotation efficiency fundamentally. This work systematically elucidates the influence of liquid-phase environments on the adhesion behavior for the first time through the unification of theoretical and experimental approaches. The findings provide critical insights for advancing flotation theory and guiding the development of novel coagulants.

Keywords: oil–water separation; extended DLVO theory; heterogeneous interaction; induction time



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1. Introduction

Large volumes of aqueous mixtures containing hazardous liquid-phase chemicals and water are generated during petroleum extraction, refining, storage, and transportation. For instance, the water-to-oil ratio in the water produced during crude oil extraction reaches 3–4:1 [1–3], with even higher ratios reported in extreme cases. Additionally, the wastewater systems in petrochemical parks and oil spills in aquatic environments represent critical targets for oily wastewater treatment. However, the discharge of wastewater must comply with stringent standards. The Oslo–Paris Convention mandates that the oil content in discharge from oil and gas facilities in the Northeast Atlantic must not exceed 30 mg/L [4].

Therefore, the treatment of oily wastewater remains a critical operation in the petrochemical and chemical industries. Various methods are employed, including hydrocyclone

separation [5–7], adsorption [8,9], filtration [10], and membrane separation [11,12]. Among these, flotation technology has been widely adopted due to its operational simplicity [13,14]. This process relies on the collision between the bubbles and oil droplets in water to form low-density aggregates, which enhance the density difference between oil and water. These aggregates rapidly rise to the surface, forming an oil-rich layer that can be efficiently separated [15]. Flotation is thus a prevalent method for oil–water separation.

In the flotation of oily wastewater, the collision and adhesion between bubbles and oil droplets in water represent the critical behaviors in the process, which comprises five sequential phases: the approach phase, the film drainage phase, the spreading phase, the oscillation phase, and the equilibrium phase [16]. In flotation processes, the most critical factor governing oil droplet–bubble adhesion and thus flotation efficiency is the induction time, which corresponds to the film drainage stage [17]. This stage is also governed by bubble–oil droplet interaction forces, commonly referred to as heterogeneous interactions during their contact process. When the separation distance falls within a specific range, the disjoining pressure may transition between repulsive and attractive regimes depending on the bulk liquid conditions. Attractive forces facilitate film drainage, accelerating the formation of stable bubble–oil aggregates.

Crude oil and oily wastewater systems typically contain various impurities, including salts, surfactants, and others introduced during the refining processes (e.g., catalyst residues and lubricant additives). These components have different influences on the bubble–oil droplet interactions during flotation. The classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory describes colloidal stability and interactions through van der Waals (vdW) forces and electrostatic double-layer (EDL) forces [18]. However, subsequent studies revealed that the experimentally observed attractive forces between hydrophobic colloidal surfaces significantly exceed the DLVO predictions, indicating the presence of an additional attraction. To address this, Israelachvili and Pashley proposed an exponential model and termed this force the “hydrophobic interaction (HB) force” [19]. By incorporating this force into the classical DLVO framework, the extended DLVO (EDLVO) theory was established, providing a more comprehensive description of bubble–oil droplet interactions [20]. For instance, Wang et al. [21] applied the EDLVO theory to elucidate the collision–adhesion mechanisms between condensate gas bubbles and crude oil droplets in water. Similarly, Zhang et al. [22] utilized EDLVO to characterize the microscopic interactions during bubble–particle adhesion in particle-laden wastewater. Nevertheless, practical oily wastewater systems exhibit substantial variability in their characteristics. They contain diverse oil fractions (e.g., gasoline, diesel, lubricants) and complex bulk liquid environments with variable salinity, pH, and surfactant concentrations. These variations introduce interfacial energy barriers and adhesion kinetics. However, existing studies have yet to systematically investigate the heterogeneous interactions governing bubble–oil adhesion under such multifaceted conditions.

In this work, the physicochemical properties (e.g., Zeta potential, surface tension) of diverse oil fractions were first measured. Using the EDLVO theory, the interaction forces between bubbles and oil droplets under different liquid environments (e.g., salinity, pH, surfactant concentration) were analyzed. Subsequently, high-speed imaging was employed to capture and quantify the dynamic adhesion process, including film drainage kinetics and aggregate formation, under these conditions. By integrating theoretical and experimental analyses, the adhesion mechanisms between the bubbles and oil droplets were systematically elucidated across various operational scenarios. Furthermore, targeted strategies to enhance flotation efficiency were proposed, such as optimizing liquid-phase parameters to modulate interfacial energy barriers. These findings provide valuable guidance for advancing oily wastewater treatment technologies.

2. Materials and Methods

2.1. Materials

In this study, there were two types of oils, including n-octane and marine fuel. The n-octane was purchased from Sinopharm while the marine fuel was obtained from Sinopec Qingdao Petrochemical. HCl and NaOH were utilized to regulate the pH, while NaCl acted as the salinity-adjusting agent. Cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) acted as the cationic and anionic surfactants, respectively. All the reagents were of analytical purity grade and provided by Sinopharm. Deionized (DI) water (resistivity = 18.2 MΩ/cm) was used in all of the experiments.

2.2. Physical Property Measurements

2.2.1. Zeta Potential Measurements

Based on the principle of electrophoretic mobility, the Zeta potentials of the bubbles and oil droplets were measured with a laser nanoparticle analyzer (Litesizer 500, Anton Paar GmbH, Graz). Firstly, a high-speed shear emulsifier machine stirred different types of oils to form the oil droplet suspension. Then, all the suspensions were left to stand for 0.5 h to allow the separation of the bubbles. Finally, the supernatant was moved to a Ωz cuvette for the follow-up potential measurement. The bubble suspension was produced by a microbubble generator; the measurement was the same as the above process. To ensure the accuracy of the measurement, the average was obtained from three parallel tests.

2.2.2. Surface and Interfacial Tension Measurements

Surface and interfacial tensions were quantified using a tensiometer (DCAT11, Data Physics Instruments GmbH, Stuttgart) via the Wilhelmy plate method. This technique measures the vertical force exerted on a platinum plate as it interacts with air–oil or oil–water interfaces, from which tension values are determined. All measurements were repeated at least three times to ensure statistical reliability, with results averaged to minimize experimental variability.

2.3. Bubble–Oil Droplet Attachment Experiments

To validate the impact of the interaction forces between bubbles and oil droplets on their collision–contact dynamics, a customized bubble–droplet collision experimental platform was established. Monodisperse bubbles and oil droplets were generated using capillary tubes fixed on a three-axis translation stage. The bubble-generating capillary tube was mounted on a precision-controlled actuator to simulate bubble movement during flotation, thereby enabling controlled collisions with stationary oil droplets. The volumetric sizes of the bubbles and droplets were regulated to diameters of $1000 \pm 200 \mu\text{m}$ through the precise adjustment of the displacement volumes based on capillary graduations.

The entire interaction process—including collision, thin-film drainage, rupture, adhesion, and spreading—was recorded using a high-speed camera (FASTCAM MiniWX100, Photron LIMITED, Tokyo) at a resolution of 768×512 pixels and a frame rate of 5000 fps. Diffuse backlighting with tracing paper ensured spatially uniform illumination to enhance imaging clarity for interfacial dynamic quantification. The schematic and photograph of the experimental setup are shown in the Figure 1.

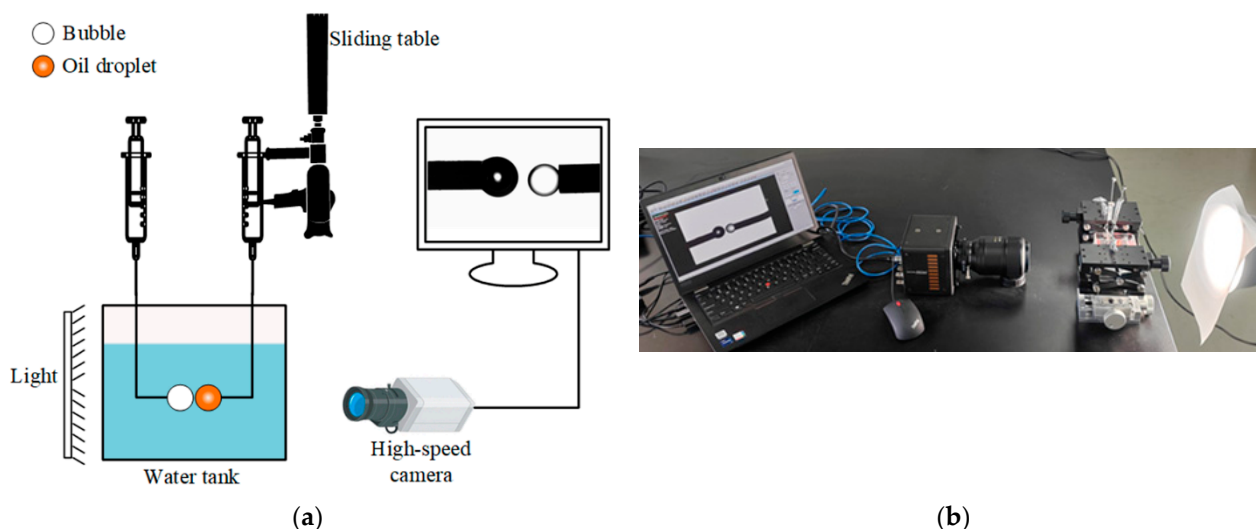


Figure 1. Schematic and photograph of the experimental setup: (a) schematic of oil droplet–bubble adhesion measurement device; (b) photograph of experimental setup.

2.4. Extended DLVO Theory

The classical DLVO theory combines the vdW forces and the EDL repulsive component to describe the forces between colloidal particles. Afterwards, the HB force was added to the above theory, establishing the EDLVO theory. The EDLVO theoretical model is shown in Equation (1) [4,23,24].

$$\Pi_{EDLVO} = \Pi_{vdW} + \Pi_{EDL} + \Pi_{HB} \quad (1)$$

Equation (1) could be used to assess the interaction forces between bubbles and oil droplets. When $\Pi_{EDLVO} > 0$, it indicates repulsive forces between bubbles and droplets. Under such conditions, bubbles and droplets demonstrate significantly inhibited coalescence behavior. When $\Pi_{EDLVO} < 0$, it shows that adhesion more easily occurs. Therefore, this is precisely the optimal condition we require.

2.4.1. Van Der Waals Forces

The vdW forces between two spherical colloidal particles can be expressed by the following equation:

$$\Pi_{vdW} = \frac{A_{132}}{6\pi h^3} \quad (2)$$

where A_{132} is the Hamaker constant for a bubble and an oil droplet in a water medium; h represents the distance between the bubble and the droplet, which is also the film thickness. In this study, the range of h was on the nanoscale, being significantly smaller than the diameters of the bubbles and oil droplets. Thus, the Stefan–Reynolds flat-film drainage model was employed to describe the film drainage process [16].

From Equation (2), it can be seen that A_{132} exerts a significant influence on this force. It depends fundamentally on the intrinsic properties of the material. To determine A_{132} , the following formula must be applied [24,25]:

$$A_{132} = \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right) \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right) \quad (3)$$

There exists no comprehensive handbook that exhaustively tabulates the Hamaker constants for all materials, particularly for the complex components used in this study. While the Hamaker constant of pure n-octane in a vacuum is well documented as 4.5×10^{-20} J, marine fuel, as a heterogeneous mixture, lacks experimentally measured values. For ma-

rine fuel, the Hamaker constant was approximated as 8.3×10^{-20} J through a literature review and compositional analysis, assuming additive contributions from its dominant hydrocarbon constituents [26,27]. Notably, while the Hamaker constant manifests intrinsic material dependence, it exhibits negligible sensitivity to environmental parameters such as pH and salinity in the surrounding medium.

2.4.2. Electrical Double-Layer Forces

Electric double layer (EDL) forces arise from the electric double layers surrounding colloidal particle surfaces. Typically, both the bubbles and oil droplets in water carry negative surface charges. When their charge layers overlap, the EDL forces manifest and influence interfacial interactions. The electrostatic interaction force for a bubble and an oil droplet is given in the following equation [28]:

$$\Pi_{EDL} = 64KT\rho_{\infty}\tanh\left(\frac{Ze\psi_o}{4KT}\right)\tanh\left(\frac{Ze\psi_b}{4KT}\right)\exp(\kappa h) \quad (4)$$

where h represents the distance between the bubble and the droplet; K is the Boltzmann constant, 1.38×10^{-23} J/K; T is the absolute temperature; ρ_{∞} is the density of ions in aqueous solution; Z is the valence of the ions in water; e is the charge of the electron, 1.602×10^{-19} C. ψ_b and ψ_o are the surface potentials of bubbles and oil droplets in water, respectively. Their values can be approximated by the Zeta potentials. κ^{-1} is the Debye length, reflecting the thickness of the electric double layer, which is given by Equation (6) [24,29]. In Equation (5), the reciprocal of the Debye length (κ^{-1}) is used.

$$\kappa^{-1} = \sqrt{\frac{\epsilon KT}{2000N_A e^2 C Z^2}} \quad (5)$$

where N_A is the Avogadro constant, 6.02×10^{23} ; C is the concentration of the electrolyte; $\epsilon = \epsilon_r \epsilon_0$ is the dielectric constant of the medium; ϵ_r is the relative permittivity of the solution (for water, $\epsilon_r = 78.5$); ϵ_0 is the vacuum permittivity ($\epsilon_0 = 8.854 \times 10^{-12}$ F/m). It is noteworthy that Equations (4) and (5) are valid for symmetric electrolytes.

2.4.3. Hydrophobic Forces

Hydrophobic interactions primarily arise from the tendency of nonpolar molecules or groups in aqueous environments to aggregate together due to their thermodynamic aversion to water. The hydrophobic interaction model adopts an exponential functional form, which was proposed by Israelachvili and Pashley in 1982 [19].

$$\Pi_{HB} = -\frac{S}{\lambda} \exp\left(-\frac{h}{\lambda}\right) \quad (6)$$

The constant S is the thermodynamic spreading coefficient: $S = \sigma_{w-b} - \sigma_{w-o} - \sigma_{o-b}$. σ_{w-b} , σ_{w-o} , σ_{o-b} denote the interfacial tensions between water and bubbles, water and oil, oil and bubbles, respectively. In addition, it intrinsically correlates with another key parameter, λ , which is referred as the decay length of the HB force.

The decay length of the HB force is a key parameter of the HB force. It has been found that the decay length is between 0.35 and 1.6 nm [28]. In general, nonpolar molecules like octane have a longer decay length than polar ones. Marine fuel molecules have a shorter decay length due to impurities. However, the decay length is independent of the surfactant concentration in the bulk liquid phase [30].

3. Results and Discussion

3.1. Material Property Analysis

3.1.1. Zeta Potential Analysis

The Zeta potentials of the bubbles and oil droplets measured under different liquid-phase conditions (e.g., salinity, pH, surfactant concentration) using a Zeta potential analyzer are shown in Figure 2.

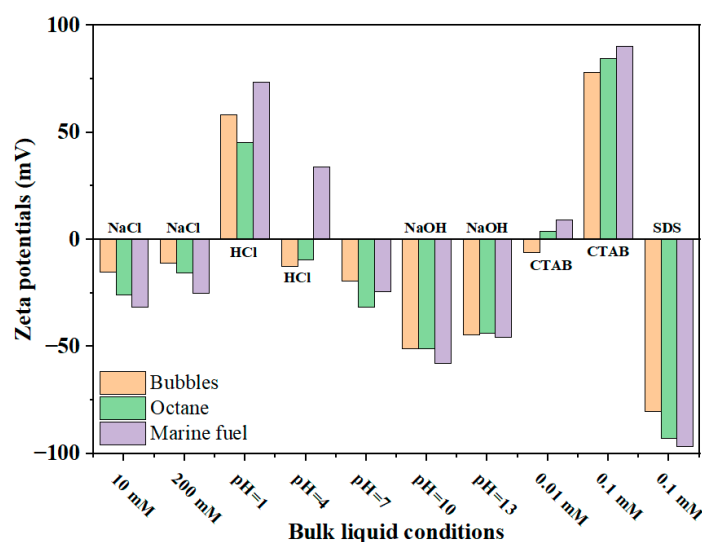


Figure 2. Zeta potentials of bubble and oil droplets in different solutions.

The Zeta potentials of the colloidal particles (bubbles and oil droplets) in aqueous systems are intrinsically linked to their physicochemical properties and liquid-phase environments. In neutral solutions ($\text{pH} = 7$), the preferential adsorption of hydroxide ions (OH^-) imparts a negative surface charge. Under alkaline conditions ($\text{pH} > 10$), the enrichment of OH^- further intensifies surface electronegativity, resulting in a more negative Zeta potential. Conversely, in acidic environments ($\text{pH} < 4$), surface protonation progressively neutralizes the negative charge, causing the Zeta potential to transition from negative to positive. For instance, in surfactant-free systems, the isoelectric point (IEP) of bubbles typically occurs at $\text{pH} 2\text{--}4$. Elevated salinity compresses the electrical double layer via charge screening, significantly reducing the effective range of surface charges and thereby diminishing the absolute Zeta potential.

Surfactants in aqueous solutions, owing to their amphiphilic nature, are adsorbed onto bubble or oil droplet surfaces via their hydrophobic tail. When cationic surfactants (e.g., CTAB) are adsorbed, their positively charged headgroups ($-\text{N}(\text{CH}_3)_3^+$) neutralize the inherent negative surface charge. The resultant Zeta potentials of the bubbles/oil droplets become concentration-dependent. At 0.01 mM CTAB, the cationic headgroups reduce the negative Zeta potential of the bubble surface compared to pure water. Conversely, the oil droplet's Zeta potential reverses to positive values due to the stronger hydrophobic affinity between CTAB tails and the oil phase. At 0.1 mM CTAB, both bubbles and oil droplets exhibit net positive surface charges. In contrast, anionic surfactants like SDS enhance surface electronegativity through the adsorption of negatively charged headgroups ($-\text{SO}_4^-$). Thus, at elevated surfactant concentrations ($>$ critical micelle concentration), the Zeta potentials of bubbles/oil droplets are predominantly governed by the surfactant type. Cationic surfactants (e.g., CTAB) induce positive surface charges on bubbles and oil droplets through hydrophobic tail adsorption, whereas anionic surfactants (e.g., SDS) generate negative charges via analogous adsorption mechanisms. This charge inversion

mechanism highlights the dominance of surfactant headgroup chemistry over intrinsic surface properties under saturation conditions.

3.1.2. Surface and Interfacial Tension

This study investigated the influence of the surfactant concentration in the bulk liquid phase on the EDLVO forces. Within the experimental concentration range, the surfactant levels remained far below the critical micelle concentration, resulting in the limited adsorption of surfactant molecules on the oil droplet surfaces. Consequently, the interfacial tensions at the water–bubble (σ_{w-b}) and oil–bubble (σ_{o-b}) interfaces exhibited minimal changes, while the water–oil interfacial tension (σ_{w-o}) was predominantly affected. The σ_{w-o} values under all tested conditions are summarized in Table 1.

Table 1. Interfacial tension for water–oil.

Interfacial Tension, σ_{w-o}	No Surfactant	0.01 M CTAB	0.1 M CTAB	0.1 M SDS
$\sigma_{w-octane}$, mN/m	43.2	37.2	25.8	37.7
$\sigma_{w-marine\ fuel}$, mN/m	27.4	21.4	12.5	22.2

3.2. Surface Forces in the Attachment Process of Bubbles and Oil Droplets

3.2.1. Van Der Waals Interaction Force Analysis

The vdW force interaction formula reveals that its magnitude is intricately linked to both the Hamaker constant and the separation distance between bubbles and oil droplets.

As shown in Figure 3, the vdW forces between bubbles and various oil droplets exhibit positive values, indicating repulsive interactions throughout their contact process [22]. These forces become significant only at separation distances below 10 nm. Owing to its inverse cubic dependence on separation distance ($\Pi_{vdW} \propto h^{-3}$), the repulsive vdW force escalates rapidly as the distance decreases, particularly within the critical range of $h < 5$ nm. At equivalent distances, the magnitude of the vdW forces varies with the Hamaker constants (A) of the oil-phase properties, resulting in the following hierarchy: $\Pi_{vdW-Octane} > \Pi_{vdW-Marine\ fuel}$.

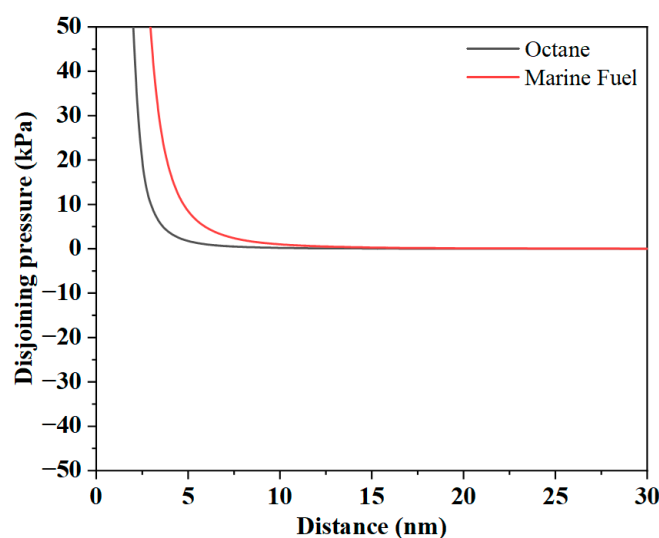


Figure 3. Van der Waals forces for bubbles–oil droplets.

3.2.2. Electrical Double-Layer Interaction Force Analysis

The relationship between EDL forces and the physicochemical properties of interacting substances (e.g., surface charge, ionic strength) is inherently complex, as these forces may

transition between repulsive and attractive regimes. Based on Equation (4), the distance-dependent EDL forces between bubbles and oil droplets (n-octane vs. marine fuel) under varying salinity conditions are plotted in Figure 4.

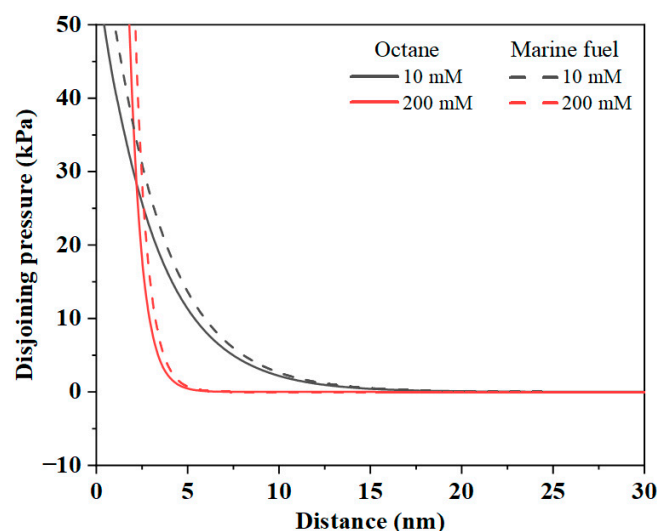


Figure 4. Electrical double-layer forces for bubbles–oil droplets at different salinities.

During the interaction between bubbles and oil droplets, EDL forces remain positive under saline conditions, indicating repulsive interactions. The magnitude of these forces depends on the Zeta potentials of the bubble and oil droplet surfaces, as well as the Debye length of the liquid phase. At a salinity of 10 mM, the EDL repulsion becomes significant at a separation distance of 15 nm. However, at 200 mM salinity, this critical distance decreases to 3 nm due to the compression of the double layer by the high salt concentration. Specifically, the Debye length is 3.04 nm at 10 mM but reduces to 0.68 nm at 200 mM. Although the Debye length defines the theoretical thickness of the double layer, practical EDL interactions initiate at distances up to five times this thickness (e.g., 15 nm at 10 mM) and intensify exponentially as the separation decreases below twice the Debye length. This exponential growth explains why repulsive forces dominate strongly at smaller separations, particularly in high-salinity environments.

In the range of 3–15 nm, the EDL repulsion in low-salinity environments is significantly stronger than that in high-salinity conditions. However, at separations below 3 nm, the EDL forces between bubbles and oil droplets become greater in high-salinity solutions. This dual behavior arises from the interplay between the Debye length and the ion concentration. Under low salinity, a larger Debye length leads to a greater overlap of the diffuse layers between bubbles and oil droplets at the same separation distance. This overlap enhances ionic interactions, resulting in stronger repulsive forces dominated by the extended double-layer thickness. In contrast, under high salinity, although the Debye length is shorter, the high ion concentration drives a steeper exponential increase in repulsion as the separation distance decreases. Here, the ion concentration governs the interaction strength. Furthermore, for different oil droplets, the magnitude of the EDL repulsion with bubbles correlates positively with the absolute value of their surface Zeta potentials. A higher Zeta potential amplifies the repulsive forces, regardless of salinity conditions.

Figure 5 illustrates the distance-dependent variations in the EDL forces between bubbles and oil droplets within a 1 mM NaCl solution under varying pH conditions.

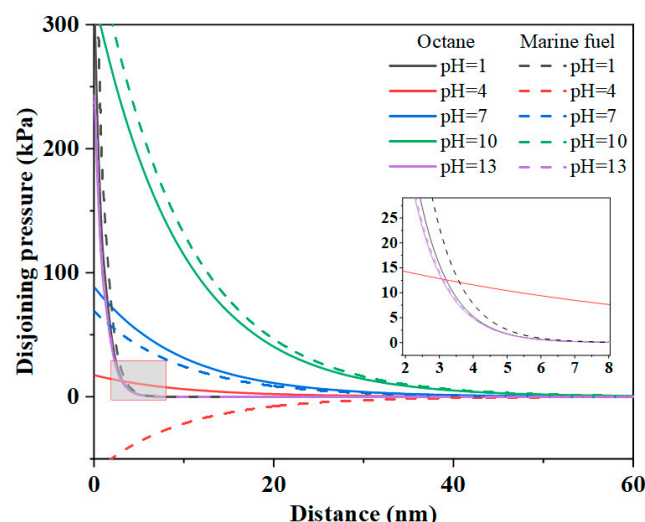


Figure 5. Electrical double-layer forces for bubbles–oil droplets at different pH values.

The pH of the bulk liquid phase significantly influences the EDL forces between bubbles and oil droplets. In a neutral solution (pH = 7), both bubbles and oil droplets (n-octane and marine fuel) exhibit negative Zeta potentials. Since the Zeta potentials of n-octane and marine fuel are similar under these conditions, their EDL forces are nearly identical. The limited ions from the dissolved NaCl adsorb onto the bubble and oil droplet surfaces, resulting in a relatively large Debye length (9.6 nm) and thus an extended EDL interaction range. However, the sparse ion distribution in the diffuse layer leads to weak EDL repulsion. At pH = 10, the OH^- -rich environment increases the absolute Zeta potentials of the bubbles and oil droplets, amplifying EDL repulsion. Within distances smaller than the Debye length, the repulsive force rises sharply as separation decreases. The isoelectric points of bubbles and n-octane droplets lie between pH 2 and 4. At pH = 4, both surfaces remain negatively charged, but the Zeta potential of n-octane droplets drops to -9.4 mV, reducing the EDL force to near-zero levels. In contrast, marine fuel droplets acquire a positive Zeta potential due to the protonation of nitrogen-containing compounds, leading to attractive EDL forces with bubbles. For oil–water separation via flotation, this attraction transitions from a hindrance to a driving force. At extreme pH values (pH 1 or 13), the ionic strength of the solution reaches 0.1 M, compressing the Debye length to 0.96 nm. Here, the EDL force–distance profiles resemble those in high-salinity environments: rapid exponential force escalation occurs once the double layers overlap, dominated by the high ion concentration.

The EDL interactions between bubbles and oil droplets in different surfactant solutions are plotted in Figure 6.

Surfactants are effective at extremely low concentrations. In solutions containing only surfactants (e.g., 0.1 mM in the experiments), a large Debye length (30.4 nm) results in an extended electrostatic double-layer thickness, leading to long-range interactions. However, at higher surfactant concentrations, both anionic and cationic surfactants induce similar surface charges on bubbles and oil droplets (both negative or both positive), generating repulsive EDL forces that hinder flotation efficiency. Attractive EDL forces become dominant only when one surface (bubble or oil droplet) undergoes charge reversal. For instance, in a 0.01 mM CTAB (cationic surfactant) solution, the hydrophobic affinity between CTAB tails and oil droplets drives the oil droplets to adopt a positive surface charge, while the bubbles retain a negative charge but with reduced Zeta potential magnitudes. As shown in Figure 6, this charge asymmetry reverses the EDL force to net attraction. However, the persistently large Debye length (due to the low ionic strength) limits the ion density in the diffuse

layer, resulting in weak attractive forces. The addition of salts (e.g., NaCl) compresses the double layer by reducing the Debye length and increasing the counterion concentration, thereby significantly amplifying the attractive EDL forces to levels practical for enhancing bubble–oil adhesion in flotation processes.

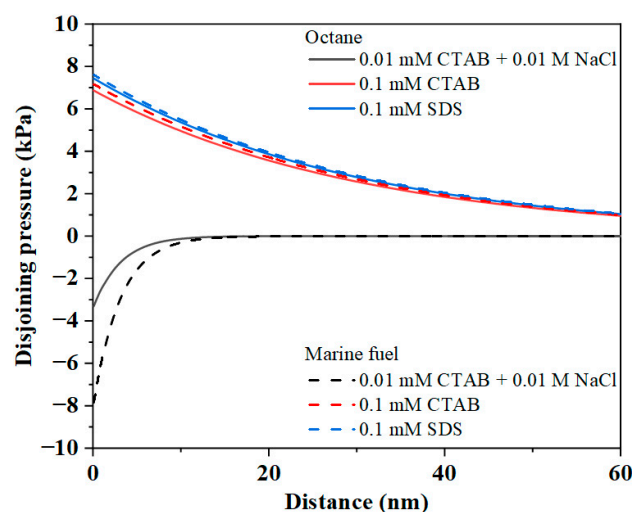


Figure 6. Electrical double-layer forces for bubbles–oil droplets at different surfactants.

3.2.3. Hydrophobic Interaction Force Analysis

Under varying pH and salinity conditions, the surface tensions of oil and water, as well as their interfacial tension, exhibit minimal changes. Since HB forces are closely linked to interfacial tensions, the hydrophobic attraction between bubbles and oil droplets remains relatively constant under these conditions. However, the introduction of a surfactants alters the hydrophobic interactions. HB forces are inherently attractive, with the force magnitude escalating exponentially as the separation distance decreases. Figure 7 illustrates the distance-dependent HB forces between bubbles and oil droplets under three scenarios: in the absence of surfactants, with CTAB (cationic surfactant), and with SDS (anionic surfactant).

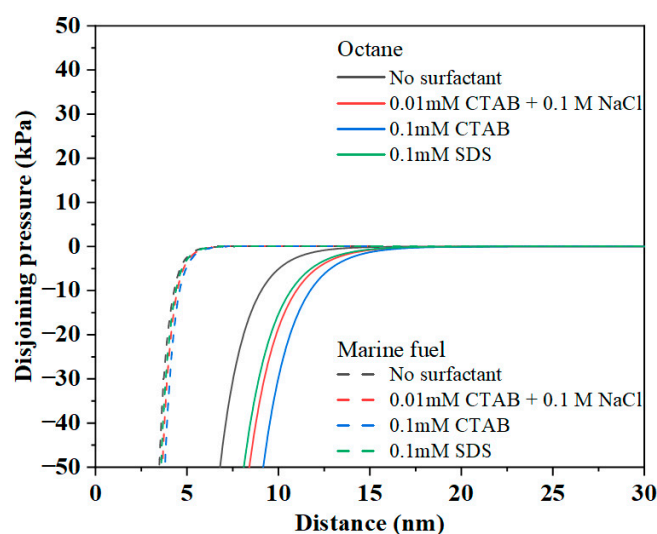


Figure 7. Hydrophobic forces for bubbles–oil droplets.

The HB forces between bubbles and oil droplets exhibit distinct activation distances depending on the oil type. For n-octane droplets, hydrophobic attraction initiates at a

separation of 17 nm, whereas for marine fuel droplets, this threshold decreases to 5 nm. This disparity arises from the differences in the HB force decay length, with marine fuel having a shorter decay length, which causes rapid force attenuation. Below the critical micelle concentration, increasing the surfactant concentration reduces the surface tension of water but more significantly lowers the oil–water interfacial tension. According to Equation (6), this interfacial tension reduction amplifies the hydrophobic attraction between bubbles and oil droplets. Notably, the HB force magnitude depends solely on surface/interfacial tensions and is independent of surfactant type (anionic or cationic).

3.2.4. Total EDLVO Interaction Forces

The overall EDLVO interaction forces between bubbles and oil droplets in aqueous solutions, calculated as a function of separation distance using Equation (1), are plotted in Figure 8.

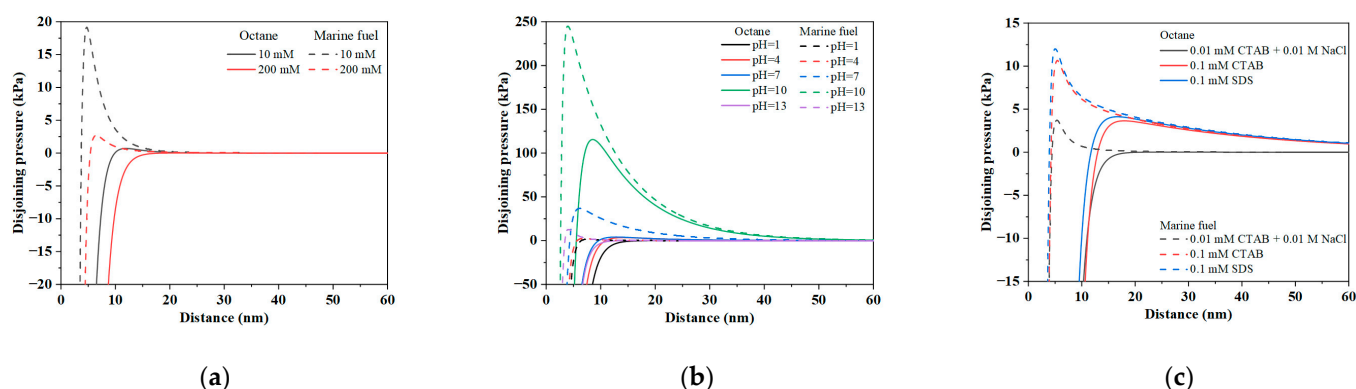


Figure 8. Total interaction forces for bubbles–oil droplets: (a) total EDLVO force for different liquid salinities; (b) total EDLVO force for different pH values; (c) total EDLVO force for different surfactant concentrations.

As shown in Figure 8, the overall interaction forces between bubbles and n-octane droplets exhibit a weak repulsive barrier upon initial contact under varying salinity, pH, and surfactant conditions. At pH = 10, the maximum repulsive pressure reaches 116 kPa at a separation distance of 8 nm. In the other conditions, the peak repulsion is limited to 4.5 kPa, followed by an exponential rise in attraction as the separation decreases, favoring bubble–octane aggregate formation. In contrast, for bubble–marine fuel systems, the interaction forces display a much stronger repulsive barrier during approach compared to n-octane. At pH = 10, the maximum repulsive pressure surges to 250 kPa, significantly hindering the flotation efficiency for marine fuel. Within the experimental range, increasing the salinity and reducing the cationic surfactant concentration both significantly decrease the total repulsive force between bubbles and marine fuel droplets.

To enhance marine fuel flotation efficiency, two theoretical strategies targeting EDL repulsion reduction are proposed. One is liquid-phase modulation, which involves co-optimizing the cationic surfactant (e.g., CTAB) and salinity to reverse the Zeta potential of marine fuel droplets while maintaining bubble negativity. This converts EDL repulsion to attraction. However, the limited Zeta potential magnitudes of both surfaces restrict attractive force strength. The other is bubble pre-modification, which involves generating positively charged microbubbles (e.g., via pressurized dissolution with cationic modifiers) prior to flotation. Positively charged bubbles interact with negatively charged oil droplets, sustaining strong EDL attraction throughout separation.

3.3. Induction Time Analysis Between Bubbles and Oil Droplets

In flotation processes, the collision between bubbles and oil droplets leads to the rupture of the thin liquid film separating them. Successful adhesion and aggregate formation occur only if the induction time is shorter than the contact time between the surfaces [31]. Thus, induction time plays a critically important role in determining flotation efficiency.

Figure 9a,b depict the attachment processes of n-octane and marine fuel droplets with bubbles under different pH conditions. During collision, the water film between the bubble and oil droplet is compressed, initiating outward drainage. Subsequently, as the water film ruptures, a liquid bridge forms. The negative pressure within this liquid bridge drives the spreading of oil droplets across the bubble surface, ultimately resulting in the formation of bubble–oil droplet aggregates [32,33]. However, the drainage time varies depending on the bulk liquid-phase environment and the distance-dependent interaction forces. The maximum induction times for both oil types occur at pH 10, where the diluted liquid phase maximizes the total EDLVO repulsion between bubbles and oil droplets, resulting in induction times of 536.8 ms for n-octane and 300.6 ms for marine fuel. N-octane, with its lower viscosity, undergoes greater deformation during collision, reducing the squeezing pressure on the liquid film and prolonging the induction time. Conversely, the higher viscosity of marine fuel limits deformation, leading to faster film drainage (shorter induction time). Despite this, the deformability of n-octane allows the complete encapsulation of bubbles, forming stable aggregates, whereas marine fuel droplets only partially coat the bubbles, resulting in unstable semi-wrapped aggregates. Consequently, flotation-based separation is more effective for low-viscosity oils like n-octane. The challenges in separating high-viscosity marine fuel highlight the need for process optimization, such as modifying bubble surfaces or incorporating viscosity-reducing agents.

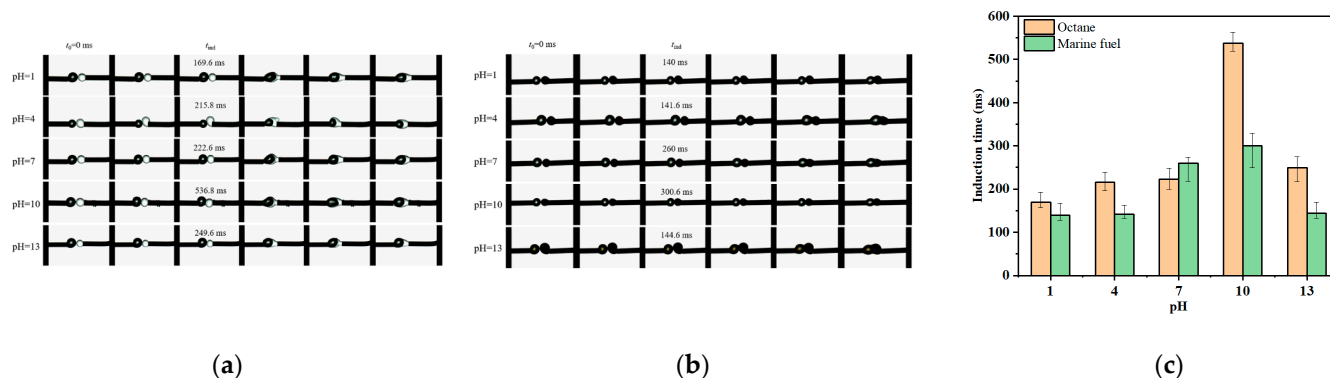


Figure 9. Attachment process of bubbles and oil droplets at different pH values: (a) attachment of bubbles and octane droplets; (b) attachment of bubbles and marine fuel droplets; (c) induction time of bubbles and oil droplets at different pH values.

For the bubble–octane droplet system, the total EDLVO forces are predominantly attractive across all separation distances, with induction times varying minimally (169.6–249.6 ms) under different pH conditions. In contrast, for the bubble–marine fuel system, significant repulsive forces persist even at pH = 7, yielding the second-longest induction time (140–144.6 ms for the other pH conditions). These results demonstrate strong alignment between the theoretical analyses of bubble–oil interaction forces and the experimental observations of collision–adhesion dynamics, validating the EDLVO framework for predicting flotation behavior in complex oily wastewater systems.

4. Conclusions

This study employed both theoretical analysis and experimental investigation to comprehensively explore the heterogeneous interactions between bubbles and oil droplets during flotation. Utilizing the extended DLVO theory, we examined the vdW forces, EDL forces, HB forces, and total EDLVO forces under varying liquid-phase conditions (salinity, pH, surfactant). The theoretical results revealed that vdW forces act repulsively across all separation distances, while HB forces remain consistently attractive. The nature of EDL forces, however, depends on the liquid-phase environment. When bubbles and oil droplets exhibit opposite surface charges (e.g., via pH or surfactant modulation), EDL forces transition to attraction, thereby enhancing aggregate formation. Experimentally, the longest induction time for bubble–oil adhesion was observed at pH = 10, coinciding with the peak repulsive force predicted by the EDLVO theory. This correlation confirms that induction time—critical for flotation efficiency—is intrinsically tied to the magnitude and polarity of interfacial forces. Shorter induction times, driven by dominant attractive forces, significantly improve separation performance. Based on these insights, two practical strategies were proposed to optimize flotation-based oil–water separation: first, maintaining optimal cationic surfactant concentrations and salinity in the liquid phase to induce charge asymmetry, and, second, pre-modifying the surface potential of the bubbles (e.g., generating positively charged microbubbles) prior to their introduction into the flotation system. These approaches aim to maximize interfacial attraction and minimize energy barriers, thereby advancing the efficiency of oily wastewater treatment technologies.

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Conflicts of Interest: Author Tao Yang, Hao Xiao, Chunyu Jiang, Ming Ma, Guangwen Zhang, Chun Wang, Yi Zheng and Xiangdi Zhao were employed by the company SINOPEC Research Institute of Safety Engineering Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

DLVO	Derjaguin–Landau–Verwey–Overbeek
EDLVO	extended DLVO
vdW	van der Waals
EDL	electric double layer
HB	hydrophobic interaction
CTAB	cetyltrimethylammonium bromide
SDS	sodium dodecyl sulfate

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