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The influence of agricultural emulsifiable concentrate on the formation of aqueous phase foam

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Abstract:

Foam pollution in water bodies is increasing year by year, while agricultural emulsifiable concentrate, a common formulation used in agricultural production, is often discharged into various water bodies after use. An analysis of references revealed that surfactants and organic solvents in agricultural emulsifiable concentrates have a significant impact on water phase foam. Among them, anionic and nonionic surfactants mostly promote foam formation by changing the surface tension of the liquid and the strength of the liquid film. For example, alkylbenzene sulfonate has strong foaming ability and high stability, while sodium diester succinate sulfonate has weak foaming ability and low stability. In terms of organic solvents, aromatic hydrocarbons, alcohols and lipids increase foam production, while ketones and solvent oils have less effect. In view of this, improvements such as adjusting the HLB value of surfactants and introducing ethanol or n-butanol as defoamers are proposed to reduce water foam pollution caused by agricultural emulsifiable oils, providing a reference for the field of environmental prevention and control.

Keywords: Agricultural emulsifiable concentrate, Water phase foam, Surfactant, Defoaming

1 Introduction

Foam is a gas/liquid dispersion system in which gas is dispersed in a liquid in the form of micrometer to millimeter-sized bubbles, with the liquid as the continuous phase and the gas as the dispersed phase[1-3]. It is well known that oil has a significant influence[4-9] on the formation and stability of foam. Recent studies have shown that the oil phase can be retained in the liquid film of the foam to produce foam[10] that is beneficial for structural stability. In agricultural production, a large amount of agricultural production waste[11] such as fertilizer and pesticide packaging bags, agricultural films, and crop straw is produced. Agricultural emulsifiable oils, as common formulations, often enter various water bodies through runoff, soil infiltration, etc. after application. In aqueous foam, agricultural emulsifiable oils usu-

ally exist in the form of oil droplets, and the oil droplets exhibit the following four configurations at the interface of aqueous foam: 1) The oil droplets are relatively far from the bubble interface, and the oil droplets maintain a regular spherical shape; 2) The oil droplets are close to the bubble interface, and the oil droplets are deformed due to compression, and the oil droplets are separated from the bubble by a pseudo-emulsion film; 3) The fake emulsion film breaks, and the oil droplet enters the bubble interface, forming an oil lens; 4) The oil phase spreads at the bubble interface, forming an oil film, and the foam breaks. There are many factors that affect the formation and stability of oil-water mixed foam, such as the type of oil phase, the content of the oil phase and the structure[12-15] of the surfactant. Therefore, when studying the mechanism by which oil affects the formation of water-phase foam, due to the complex composition of agricultural emulsifiable concentrates, it is crucial to understand which components in agricultural emulsifiable concentrates have a stabilizing effect on oil-water phase foam.

2 The effect of surfactants in agricultural emulsifiable concentrates on foam

Research shows that foam in the aqueous phase is a thermodynamically unstable system. Surfactant molecules can effectively reduce the surface energy between the two phases through adsorption, making the gas-liquid dispersion system easier to form. The foaming performance and foam stability of surfactants are affected by the structure of surfactant molecules and when two or more surfactants are used in combination, there is a certain synerg[16]istic effect on foam performance. Nguyen[17] et al. compared the foaming power and foam stability of anionic and cationic surfactants. For example, the hydrophilic head group of sodium dodecyl sulfate (SDS) can form hydrogen bond associations with surrounding water molecules, which is stronger than the dipole interaction between dodecyl trimethylammonium bromide (DTAB) and water. This enables SDS to form a denser adsorption layer at the interface.

Agricultural emulsifiable concentrate systems also contain anionic surfactants and nonionic surfactants. The main difference between ionic surfactants and nonionic surfactants is that ionic surfactants can stabilize the foam film at a lower surface coverage/higher surface fluidity. This is because there is a strong electrostatic repulsive force between the charged film surfaces of surfactant molecules. In contrast, nonionic surfactants require very high surface coverage and high dynamic Gibbs elasticity to ensure the low surface fluidity and stereostability[18-19] of foam films. In agricultural emulsifiable concentrate systems, anionic surfactants include four typical types of anionic surfactants: alkylbenzene sulfonate, lignobenzene sulfonate, alkyl naphthalene sulfonate and sodium diester sulfonate of succinate. Nonionic surfactants include fatty alcohol polyoxyethylene ethers, alkylphenol polyoxyethylene ethers, polystyrene phenol polyoxyethylene ethers, castor oil polyoxyethylene ethers and polyoxyethylene polyoxypropylene block polyethers.

2.1 Anionic surfactants

1) Alkylbenzene sulfonates are mainly used in emulsifiable concentrates (EC), wettable powders (WP), suspensions (SC), etc. They are commonly used anionic surfactants in agricultural emulsifiable concentrates, and their molecules consist of hydrophobic alkyl chains, benzene rings and hydrophilic sulfonic acid groups. The molecules are closely arranged, the adsorption film has high elasticity, and the foaming time and adsorption rate in the dynamic surface tension parameters increase with the growth of the alkyl chain, resulting in a decrease in surface tension, and the bubble film carries a negative charge during the ionization process of the sulfonic acid group charge repulsion inhibits bubble coalescence. Meanwhile, the critical micelle concentration (CMC) of LAS is relatively low. The excess surfactant forms a bimolecular film, enhancing the mechanical strength of the liquid film, resulting in strong foaming ability and high foam stability.

2) Lignosulfonate is widely used in suspensions (SC), water dispersions (WDG), dry suspensions (DF), etc. It is a natural macromolecular surfactant produced by sulfonation modification of lignin, and its structure contains a polyphenyl ring skeleton and functional groups such as sulfonic acid groups and hydroxyl groups. The macromolecular size and dispersed benzene ring framework enhance the continuity of the adsorption film, forming a uniform and dense liquid film structure. Hydroxyl and alkoxy groups enhance the elasticity of the film through hydrogen bonding, suppress the drainage process, thereby extending the life of the foam, which is generally beneficial for foam formation. Due to the synergistic effect, such as the combination with sodium dodecylbenzene sulfonate to reduce the system reflectance, the amount of foam will be appropriately reduced through steric hindrance, with moderate foaming capacity and high foam stability.

3) Alkyl naphthalene sulfonates are commonly found in suspensions (SC), water dispersions (WDG), and wettable powders (WP), with naphthalene rings as the core, and the synergistic effect of sulfonic acid groups and alkyl chains gives them special interfacial properties. Naphthalene

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rings have better hydrophobicity than benzene rings, higher efficiency in reducing surface tension, and the planar rigid structure of naphthalene rings makes the adsorption film arrangement tighter, enhances film elasticity, overall foaming ability, and foam stability higher.

4) Sodium diester sulfonate for emulsifiers (EC) and microemulsions (ME) has a unique structure of diester and sulfonic acid groups, and the balance of short-chain hydrophobic groups (such as octyls) and polar ester groups makes it highly reactive, with a compact molecular configuration and low adsorption film strength.It has a low foamy tendency. At the same time, as an auxiliary surfactant, it can accelerate drainage by destroying the Marangoni effect (a surface tension gradient-driven repair mechanism) of the bubble film, inhibit foam formation, and overall has weak foaming ability and low foam stability.

2.2 Nonionic surfactants

1) Fatty alcohol polyoxyethylene ethers are used in emulsifiers (EC), water emulsions (EW), and microemulsions (ME), where the hydrophobic chain of fatty alcohol and the hydrophilic polyoxyethylene (EO) chain are linked by ether bonds. When the number of EO increases, the hydrophilicity increases, the ability to reduce surface tension increases, and the foam height shows a "first increase then decrease" trend. It exhibits optimal foaming near the critical micelle concentration (CMC). At the same time, the tight arrangement of fatty alcohol hydrophobic chains forms a highly elastic adsorption film, which inhibits drainage through the Gibbs Marangoni effect, delays bubble rupture, and is conducive to foam formation.

2) Alkylphenol polyoxyethylene ethers are used in water emulsions (EW), microemulsions (ME), and suspensions (SC), with nonylphenol or octylphenol as the hydrophobic base. The rigid hydrophobic core of the benzene ring enhances the interfacial adsorption efficiency. The CMC is 30%-50% lower than AEO, and the dynamic surface tension equilibrium time is short, which can quickly form a dense foam layer. The synergy between the flexibility of the EO chain and the planar structure of the benzene ring is poor, the mechanical strength of the adsorption film is lower than that of AEO, there is a lack of strong hydrogen bonds between molecules, the liquid film drainage rate is high, the foaming ability is strong but the stability is poor.

3) Polystyrene phenol in polyoxyethylene ether, polystyrene phenol is a hydrophobic core with 3-4 benzene rings. The polystyrene ring skeleton provides rigid support. The EO chains form a three-dimensional network structure at the interface, which inhibits bubble coalesces through steric hindrance effect. The high EO number enhances the thickness of the hydrated layer, reduces van der Waals attraction, and delays Ostwald ripening. Under shear force, its shear thickening behavior can briefly increase the viscosity of the liquid film.It ADAPTS to dynamic foaming requirements, with moderate foaming ability and extremely high foam stability.

4) Castor oil polyoxyethylene ether for emulsifiers and suspensions, with castor oil as the hydrophobic base, grafted with EO chains, with ester groups, hydroxyl groups and ether bonds. The highly branched castor oil structure hinders the tight arrangement of molecules at the interface, the adsorption film has defects, the elastic modulus of the liquid film is low, and the polar interaction between hydroxyl and ester groups promotes the detachment of some molecules from the interface, forming a "self-defoaming" effect. At the same time, it is temperature-sensitive and stabilizes the foam at low temperatures, but dehydration at high temperatures causes the foam to collapse rapidly, resulting in weak overall foaming ability and moderate foam stability.

5) Polyoxyethylene polyoxypropylene block polyether has hydrophilic PEO chains at both ends and hydrophobic PPO chains in the middle. The strong hydrophobicity of its PPO chains causes it to preferentially adsorb at the gas-liquid interface, but the "U-shaped" folding of the molecular conformation leads to discontinuity of the adsorption film. The hydrated layer of the PEO chain is susceptible to temperature, and dehydration at high temperatures causes molecular aggregation, which disrupts the foam structure through reverse micelles. Studies have shown that low HLB value models can act as defoamers to suppress foam by reducing membrane elasticity and enhancing drainage.While high HLB models stabilize foam at low temperatures and have variable effects on foam.

3 Effects of organic solvents in agricultural emulsifiable concentrates on foam

The influence of organic solvents on water phase foam formation is a multidisciplinary research topic, and the mechanisms by which organic solvents affect foam formation include reducing surface tension, changing solution viscosity and interacting with surfactants, etc. Domestic studies have focused on the effects of organic solvents in wastewater on foam formation in biochemical systems, finding that some hard-to-degrade organic solvents can be transformed into surface-active substances under the action of microorganisms, promoting foam formation. Meanwhile, some scholars abroad have studied the adsorption behavior of different organic solvents at the

water-air interface and their effects on foam performance through experiments and theoretical simulations, and found that some organic solvents with special molecular structures can form stable adsorption layers at the interface, improving the foam's resistance to rupture. It is not difficult to find from a large amount of literature that most organic solvents promote the formation of foam in water.

In agricultural emulsifiable concentrate systems, organic solvents are often used as carriers of active ingredients, and their active ingredients include aromatic hydrocarbons, alcohols, ketones, lipids and solvent oils. The effects of organic solvents in agricultural emulsifiable concentrates on the formation of foam in the aqueous phase are multifaceted, involving changes in physical properties such as surface tension, interfacial properties, interaction with surfactants, and viscosity of the aqueous phase. Different types of organic solvents, due to differences in their chemical structure and physical properties, have different mechanisms and degrees of influence on foam formation.

1)Aromatic hydrocarbons such as xylene and toluene are commonly used organic solvents in agricultural emulsifiable concentrates. These solvents have strong solubility and can effectively dissolve the active ingredients of pesticides, allowing them to be evenly dispersed in the emulsifiable concentrate system. When aromatic hydrocarbon organic solvents are present, they reduce the surface tension at the gas-liquid interface, making it easier for the gas to disperse in water to form bubbles and promoting the initial formation of foam.

2) Alcohol-based organic solvents include methanol, ethanol, isopropanol, etc. Alcohols have a certain degree of miscibility with water and contain hydrophilic hydroxyl groups in their molecules. Alcohols form hydrogen bonds with water molecules, destroying the original structure of water and reducing its surface tension. When subjected to external forces such as stirring, the gas is more likely to enter the water phase and form bubbles, which in turn form foams.

3) Ketones and lipids work in a similar way to change interfacial surface tension, but they interact with surfactants, which can affect the adsorption and arrangement of surfactants at the gas-liquid interface, thereby affecting the strength and stability of the foam liquid film.

4) Solvent oil is a mixture of hydrocarbons obtained from the fractionation of petroleum, with a more complex composition, containing alkanes, cycloalkanes, etc. with different carbon numbers. Its influence on the formation of water phase foam mainly comes from its physical properties and has no significant effect on foam formation.

4 Improve defoaming

In the demonstration analysis of the effects of each component in agricultural emulsifiable concentrate on water phase foam, it is not difficult to see that it as a whole in water promotes foam formation, thus making it one of the causes of water foam pollution. In response to the foam pollution caused by pesticide discharge, I will propose reasonable improvement suggestions from two aspects: adjusting surfactants and adding appropriate defoamers to reduce foam pollution without destroying the original efficacy.

Adjust surfactants: Select surfactants with similar HLB values based on the polarity of organic solvents in agricultural emulsifiable concentrates (such as aromatic hydrocarbons, lipids) to avoid interface instability and increased foam due to mismatch of HLB values; Add appropriate defoamers: Introducing ethanol and n-butanol into agricultural emulsifiable oil systems, whose hydrophobic ends can be inserted between the hydrophobic chains of surfactants, disrupts the tight arrangement of the original adsorption film, reduces the elastic modulus of the interfacial film, weakens the self-healing ability of the foam liquid film, and also has the ability to dynamically adjust the HLB value, improve low-temperature stability, adapt to a variety of surfactant systems and be low-toxic and easily degradable. It also has the advantage of reducing environmental residues.

5 Summary and outlook

Agricultural emulsifiers contain both anionic and nonionic types of surfactants, which mostly promote the formation of foam in water by influencing the size of the liquid surface tension and the strength of the liquid film; In organic solvents, aromatic hydrocarbons, alcohols, and lipids tend to increase foam formation based on their own structural and property characteristics, while ketones and solvent oils have little effect on foam formation; Agricultural emulsifiable concentrate discharge in water bodies can increase the formation of foam pollution, explaining one of the causes of foam in water bodies, and proposing improvements such as the selection of surfactants with similar HLB values and the introduction of ethanol or n-butanol defoamers, hoping to provide some reference in the field of environmental protection prevention and control.

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