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Stability of etofenprox in water emulsion induced by block copolymer and surfactant

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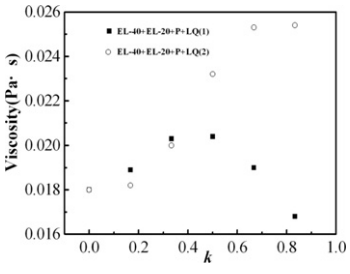
HIGHLIGHTS

- Addition of P and/or LQ enhanced remarkably stability of emulsion systems.
- Droplets dimension and viscosity depended distinctly on P and/or LQ concentrations.
- Droplets dimension and viscosity together affects the freezing temperature.
- EL-40 + EL-20 + P + LQ emulsions had good stability at room and low temperature.

GRAPHICAL ABSTRACT

Effect of block copolymer polyalkoxylated butyl ether (LQ) and anionic surfactant polyoxyethylene styrenated phenol ether phosphonate (P) on the stability of etofenprox in water emulsion was systematically investigated by measuring creaming stability, droplet size, viscosity, and the crystallization temperature. The results indicated that addition of P and/or LQ to EL-40 + EL-20 emulsions exhibits good emulsion stability at room and low temperature, especially EL-40 + EL-20 + P + LQ (2) emulsions show much excellent.



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ABSTRACT

Effect of block copolymer polyalkoxylated butyl ether (LQ) and anionic surfactant polyoxyethylene styrenated phenol ether phosphonate (P) on stability of etofenprox in water emulsion was systematically investigated by measuring creaming stability, droplet size, viscosity, and crystallization temperature. Addition of P (LQ) enhanced markedly stability of emulsions prepared with polyoxyethylene (40) castor oil ether (EL-40) and polyoxyethylene (20) castor oil ether (EL-20). On the basis of it, we prepared the EL-40 + EL-20 + P + LQ (1) and EL-40 + EL-20 + P + LQ (2) emulsions at the fixed concentrations of EL-40 and EL-20, P and EL-20, respectively. The emulsions displayed the excellent stability, observed only a little turbid layer on the surface with time prolong. The distinct trends of droplets size and viscosity in two kinds of emulsions were well analyzed by the structural properties of surfactants (including block copolymer) and the interaction between them. Furthermore, differential scanning calorimetry (DSC) technology was first introduced to study freeze–thaw stability of pesticide emulsions. The data indicated that the freezing point shifted evidently with P and/or LQ concentration, however, the melting point had almost no change. It revealed that the EL-40 + EL-20 + P + LQ emulsions had good stability at low temperature. Combination of droplets size and viscosity measurements with DSC technology can be helpful to examine comprehensively the emulsion stability, and select surfactants and obtain pesticide emulsions with good storage and freeze–thaw stability.

1. Introduction

Emulsions have been described as heterogeneous systems of one immiscible liquid dispersed in another in the form of droplets,

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which are extensively used in many fields such as petrochemicals, cosmetics, paints, pharmaceuticals, food and agricultural products. However, they are thermodynamically unstable systems that tend to break down over time due to a variety of physicochemical mechanisms, e.g., gravitational separation, creaming, flocculation and Ostwald ripening. Therefore, emulsifiers and/or polymers are often added to emulsion to achieve the kinetic stability. Emulsifiers are mainly surfactants that can adsorb to the droplet surfaces by lowering the interfacial tension and preventing the droplets from coming close enough together to aggregate. Polymers can be separated into adsorbing and non-adsorbing polymers according to their adsorbing properties. Non-adsorbing polymers (such as xanthan gum [1]) are often used to prepare kinetically stable emulsions by increasing the viscosity of the continuous phase, thereby slowing down the rate of creaming or flocculation. Adsorbing polymers can improve emulsion stability by providing steric stabilization via a surface layer and opposing close contact between the droplets. Adsorbing polymers include proteins [2–4], block copolymers [5–7], and hydrophobically modified polysaccharides [8–11], etc., wherein polysaccharides are also used as the thickening agent to improve emulsion stability via viscosity enhancement or gelation in the aqueous continuous phase.

Pesticide in water emulsion is a kind of water based formulation, which is widely viewed as one of the green and environmentally friendly formulations. However, the destabilization of emulsion restricts severely its quick development. The pesticide emulsions can be stabilized by addition of the small molecular surfactants [12–14]. However, these surfactants are often not particularly well suited for providing long-term stability. Polymers such as block copolymers containing aromatic hydrophobic (benzyl methacrylate) and ethylene oxide hydrophilic units (methoxy hexa(ethylene glycol) methacrylate) have been used to stabilize the diazinon emulsions [15]. In addition, our previous study [16] has shown that surfactants and polysaccharide used together can improve pesticide emulsions stability. Etofenprox is an insecticide used widely in a variety of crops, fruit trees and vegetables in China, which becomes presently one of the most important pesticides for controlling rice planthopper, cabbage caterpillar and cotton bollworm. As far as we know, the systematic study on stabilization of etofenprox emulsion made with emulsifiers and block copolymers has been little reported up to now.

In addition, freezing storage is one of the most important preservation methods for maintaining the microbiological and chemical stability, and extending the shelf life of food [17] and pharmaceutical products [18,19]. Oil-in-water (o/w) emulsions that can be frozen and then thawed prior to use have the potential applications in refrigerated and frozen food or pharmaceutical products. When an o/w emulsion is cooled, a variety of physicochemical processes may occur including oil phase crystallization, ice formation, freeze-concentration, interfacial phase transitions and biopolymer conformational changes [19]. The differential scanning calorimetry (DSC) technique has been employed to study effectively the crystallization behavior of emulsions. The freezing points of different emulsions have depended closely on the amount of dispersed water [20]. The higher the water content in the emulsion, the higher was the freezing point due to the larger droplet size of highly concentrated emulsions. A large number of studies have shown that fat crystallization affected emulsion stability by an amount that depended on emulsifier type [21–25]. In addition, the crystallization temperature depends on droplet size [23,26], presence of impurities [27] and emulsifier type [23,28]. Researchers can obtain quickly the information on the major factors that promote emulsion freeze–thaw stability through DSC technique, which will be helpful in taking effective strategies to improve stability of emulsion products during processing and storage. Therefore, in this work, DSC technique is first introduced to study freeze–thaw stability of pesticide emulsions.

In continuation of our previous study [16], the aim is to investigate systematically stability of etofenprox in water emulsion induced by block copolymer and surfactant by measuring creaming stability, droplet size, viscosity, and crystallization behavior. It is further attempted to gain an insight on the stability mechanism of o/w emulsion. Furthermore, the present work combines effectively thermal characteristics with the composition of emulsions, which better tests the applicability of DSC technique in pesticide emulsion.

2. Materials and methods

2.1. Materials

The pesticide etofenprox, $w = 96.1\%$, was obtained from Shanxi LvHai Agochemical Co., Ltd. Technical grade surfactants polyoxyethylene (40) castor oil ether (EL-40), polyoxyethylene (20) castor oil ether (EL-20), and anionic surfactant polyoxyethylene styrenated phenol ether phosphonate (P) with about 20 EO units were supplied by Xingtai Lantian Jingxi Chemical Co. Ltd. EO/PO block copolymer polyalkoxylated butyl ether (LQ) was obtained as a gift from AkzoNobel Corp., and used as received. Its pH value is in the range of 6.5–7.5, the molecular weight is 5000, and HLB is 14. Xylene, butanol and propylene glycol, of A.R. grade, were purchased from Tianjin Medicine Co., Ltd. All water used was deionized water or fresh doubly distilled water.

2.2. Methods

2.2.1. Emulsion preparation

The pesticide etofenprox was dissolved in the mixture of xylene and butanol (m(xylene)/m(butanol) = 7.80), and the mass percentage of etofenprox in mixed solvents was 26.4%. The mixture surfactants of EL-40, EL-20, P and /or LQ in different ratio were added to the pesticide solution, which was as oil phase. Propylene glycol was mixed with deionized water, which was as water phase. The emulsion systems were denoted by EL-40 + EL-20 + P, EL-40 + EL-20 + LQ, EL-40 + EL-20 + P + LQ (1) and EL-40 + EL-20 + P + LQ (2), respectively. EL-40 + EL-20 + P (LQ) represented the emulsion prepared with the fixed EL-20 concentration; EL-40 + EL-20 + P + LQ (1) and EL-40 + EL-20 + P + LQ (2) represented the emulsion prepared with the fixed concentrations of EL-40 and EL-20, P and EL-20, respectively. The emulsion was then prepared by adding slowly the oil phase to the water phase, and after the premix, the mixture was emulsified at 5500 rpm for 20 min at room temperature. The mass percentages of etofenprox, EL-20, total surfactants (including block copolymer), and propylene glycol in pesticide in water emulsion were 10.0, 3.0, 6.0, and 5.0%, respectively.

2.2.2. Stability measurement

Approximately 20 mL of freshly prepared emulsion was transferred into a glass tube, then sealed and stored at room temperature. The emulsion volume was read at different times to monitor stability to creaming and coalescence throughout the storage time. The emulsion stability with time was assessed by monitoring the variation of the emulsion volume.

2.2.3. Droplets size measurement

The droplets size were measured using Zeta PALS+BI-90plus (Brookhaven Co.,USA) fitted with a 30 mW laser, operating at 659 nm, and placing the sample tube in the thermostated chamber. All measurements were taken at 90°. Emulsion was prepared and stored at room temperature for 24 h prior to analysis. 0.5 mL