

Preparation of Dehydroabietyl Polyethylene Glycol Aldehyde Modified Hydroxyethyl Chitosans and their Physicochemical Properties

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A series of polymeric surfactants based on monodehydroabietyl polyoxyethylene(5) ether (DHA(EO)₅H) and hydroxyethyl chitosan (HEC) were prepared through a three-step process. First, DHA(EO)₅H was oxidized using activated MnO₂ and transformed into dehydroabietyl polyethylene glycol(5) aldehyde (DHA(EO)₄CH₂CHO). Then, the DHA(EO)₄CH₂CHO was reacted with HEC and converted into Schiff-base. Finally, the polymeric surfactant, DHA(EO)₄CH₂CHO modified HEC (DHA(EO)₄CH₂CHO-m-HEC), was obtained by reducing the Schiff-base with sodium borohydride. The grafting degree (DG) of DHA(EO)₄CH₂CHO substitution onto HEC for DHA(EO)₄CH₂CHO-m-HECs was determined using elemental analysis (EA), and the surface activities and foam performance of DHA(EO)₄CH₂CHO-m-HECs in aqueous solution were investigated respectively. The emulsifying capacities of DHA(EO)₄CH₂CHO-m-HECs were evaluated according to the stability times of emulsion composed of water and liquid paraffin. The experimental results showed the DG could have significant influence on the critical micelle concentration (cmc) of DHA(EO)₄CH₂CHO-m-HECs and their surface tensions at cmc (γ_{cmc}), but nearly no effect on their minimum surface tensions (γ_{min}) in aqueous solution. Among the synthetic polymeric surfactants in this investigation, DHA(EO)₄CH₂CHO-m-HEC with DG of 56.95% exhibited the best emulsification and foam properties.

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INTRODUCTION

Polymeric surfactants are soluble macromolecules having both hydrophobic and hydrophilic groups in their molecular structure simultaneously (Afolabi *et al.* 2022). According to the relative distribution of hydrophilic and lipophilic parts, polymeric surfactants are divided into polysoaps and macrosurfactants. Macromolecules constituted by repeating units of intrinsically amphiphilic monomers or oligomers are generally referred to as polysoaps, while polymers in which there is a clear spatial segregation between the hydrophilic groups and hydrophilic groups are called macrosurfactants (Raffa *et al.* 2015).

Compared with the low-molecular weight surfactants, polymeric surfactants possess a much higher structural complexity that results in very different behavior. For example, they show interesting association phenomena in selective solvents and result in peculiar rheological behavior and the formation of self-assembled structures (Farrokhpay 2009). In the last few decades, polymeric surfactants have received increasing attention, especially in agriculture (Yan *et al.* 2017; Zhang *et al.* 2020), coatings (Creutz *et al.* 1998), enhanced oil recovery (Raffa *et al.* 2016; Afolabi *et al.* 2022), nanotechnology (Pirsaeheb *et al.* 2022; Son *et al.* 2022), biotechnology (Sagnella and Mai-Ngam 2005; Mai-ngam 2006), emulsions (Deng *et al.* 2019; Chen *et al.* 2020), and pharmacology (Kirtil *et al.* 2022), *etc.*

Hydroxyethyl chitosan (HEC) is the hydroxyethylation derivative of chitosan (CTS). The presence of hydroxyethyl groups in the sugar chain can weaken the intermolecular forces and endow it with excellent properties, such as water-solubility, moisturizing, and film-forming (Wan *et al.* 2004; Wang *et al.* 2017). These properties can provide the HEC with the ability to be applied as an antioxidant, tissue engineering material, medicine carrier, medical dressing, and others (Liu *et al.* 2007; Dash *et al.* 2011). Meanwhile, HEC has been employed as one of components for preparing amphiphilic chitosan derivatives, and these derivatives have been utilized for the delivery of drugs (Li *et al.* 2010; Huo *et al.* 2012, 2016).

Disproportionated rosin consists of derivatives of gum rosin, a natural product obtained by heating pine oleoresin, and with dehydroabietic acid (DHAA) as main component (Sacripante *et al.* 2015). Dehydroabietinol (DHA) is a derivative of DHAA and can be prepared from methyl dehydroabietate or DHAA through reduction reaction (Fieser and Campbell 1939; Popova *et al.* 2013). Because of its hydrogenated phenanthrene nucleus, which can endow the DHA and DHAA with lipophilicity and rigidity (Lei *et al.* 2017), the DHA and DHAA have been utilized as a basic material for preparing green surfactants, such as monodehydroabietyl polyethylene glycol(n) ether (DHA(EO)_nH) (Roloff *et al.* 2008) and poly(oxyethylene) dehydroabietate (Persson *et al.* 1980), 2-hydroxy-3-dehydroabietyloxypropyl chitoooligosaccharides (Cai *et al.* 2017), and others. DHA and DHA(EO)_nH can be converted into dehydroabietyl glycidyl ether (DAGE) and dehydroabietyl polyoxyethylene(n) glycidyl ether (DHA(EO)_nGE) by reacting with epichlorohydrin respectively, and the epoxy group existed in the DAGE and DHA(EO)_nGE can endow them with the capability to react with the compounds containing hydroxyl or amino group, thus introducing the hydrophobic phenanthrene nucleus into these compounds. Meanwhile, the primary alcohol structure existed in DHA and DHA(EO)_nH can also be converted into aldehyde group by oxidation, and the formation of aldehyde can endow the oxidative product with the ability to react with amino group and form Schiff base.

In previous works, a series of water-soluble amphiphilic polymers with HEC, hydroxypropyl chitosan (HPC), DAGE, and DHA(EO)₁₀GE as basic materials were synthesized, and their physicochemical properties in aqueous solution were investigated (Wang *et al.* 2019; Guo *et al.* 2020; Huang *et al.* 2022). This study reports the synthesis of a novel polymeric surfactant, dehydroabietyl polyethylene glycol(5) aldehyde modified HEC (DHA(EO)₄CH₂CHO-m-HEC) with mono dehydroabietyl polyethylene glycol(5) ether (DHA(EO)₅H) and HEC as basic materials. These were studied relative to their surface activities, foam performance, and emulsifying capacities. The detailed procedure for preparing DHA(EO)₄CH₂CHO-m-HECs is shown in Fig. 1.

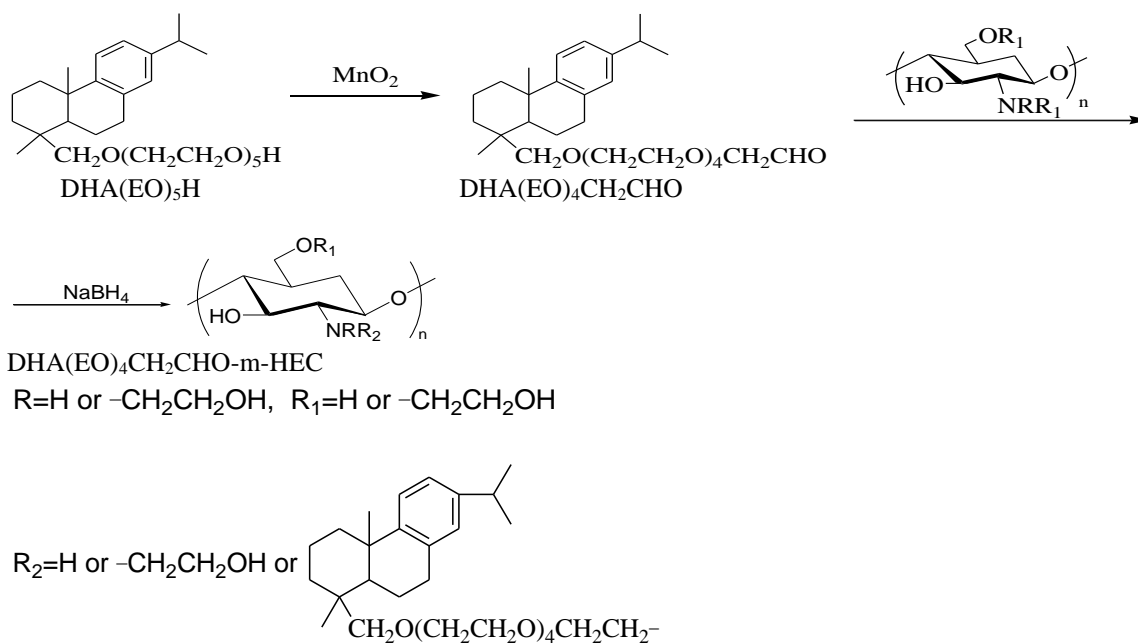


Fig. 1. Procedure for preparing DHA(EO)₄CH₂CHO-m-HECs

EXPERIMENTAL

Materials

The monodehydroabietyl polyethylene glycol(5) ether (DHA(EO)₅H) was prepared as described previously (Huang *et al.* 2022), except that the molar ratio of oxirane versus DHA was changed from 10.0 to 5.0. Activated MnO₂ was prepared according to Li *et al.* (1996). The HEC was prepared according to literature (Wang *et al.* 2019), and its degree of substitution (DS) was 112.4% (determined by elemental analysis). The sodium borohydride (NaBH₄), liquid paraffin and ethyl acetate were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). The dialysis bag (MW cut-off =3000 Da) was purchased from Biosharp Co. (Beijing, China). All other chemicals were of reagent grade and used without purification as received.

Instruments and Equipment

The Fourier transform infrared (FTIR) spectra were recorded with potassium bromide (KBr) pellets on a Nicolet Nexux 670 spectrometer (Thermo Fischer Scientific, Waltham, MA, USA). The DHA(EO)₅H and its oxidized product were referenced against KBr pellets, while the HEC and its modified products were referenced against air. The ¹H NMR pattern was obtained at 500.13 MHz with a Bruker DRX-500 spectrometer (Billerica, MA, USA) at 30 ± 0.5 °C, and the sample was dissolved in a 5 mm diameter tube at a concentration of approximately 20 mg/mL with D₂O as solvent. The measurement of surface tension (γ) of aqueous solution was carried out with a JYM-200D automatic tensiometer (Shipeng Testing Equipment Co., Ltd of Chengde, P. R. China) at 25.0 °C. Elemental analysis (C, H, and N) were performed on a FLASH 2000 Vario micro elemental analyzer (THERMO Inc., Waltham, MA, USA). The ultraviolet-visible (UV-Vis) spectra were measured on a TU-1810 PC ultraviolet visible spectrophotometer (Persee General Co., Ltd. of Beijing, P. R. China).

Preparation of Dehydroabietyl Polyethylene Glycol(5) Aldehyde (DHA(EO)₄CH₂CHO)

The DHA(EO)₄CH₂CHO was prepared by oxidizing the DHA(EO)₅H with active MnO₂ as oxidant. Briefly, the DHA(EO)₅H (56.66 g, 0.10 mol) was added into ethyl acetate (200 mL) at room temperature (RT) with continuous stirring until it dissolved completely, followed by adding 86.94 g of active MnO₂ (1.0 mol) in batches at RT. After the MnO₂ was added into totally, the temperature of reaction mixture was raised to 80 °C and stirred at this temperature for 4.0 h. Then, the solids in the reaction mixture were separated by filtration and washed using ethyl acetate 3 times, followed by collecting the organic phase and drying it using anhydrous sodium sulfate. Finally, the DHA(EO)₄CH₂CHO, an oil-like liquid with light yellow, was obtained by recovering ethyl acetate through vacuum distillation.

Synthesis of DHA(EO)₄CH₂CHO-m-HECs

The DHA(EO)₄CH₂CHO-m-HECs were synthesized through nucleophilic addition condensation reaction between DHA(EO)₄CH₂CHO and HEC, and reduction reaction between NaBH₄ and Schiff-base. Briefly, dried HEC (2.16 g, 10 mmol sugar unit) was dissolved by *ca.* 100 mL of distilled water at RT. Then, metrological DHA(EO)₄CH₂CHO, which was dissolved in *ca.* 50 mL of ethanol previously, was added into the reactant, and the mixture was stirred at RT for forming Schiff-base. After 8.0 h, metrological NaBH₄, which was dissolved in *ca.* 100 mL of distilled water previously, was added dropwisely into the reactant and reacted at RT for 12.0 h, followed by removing the water and ethanol from the reaction mixture using vacuum distillation. The distillation residue was extracted with ethanol 3 times, and then was dispersed in *ca.* 200 mL of distilled water before transferring into dialysis bag and dialyzing against deionized water for 48.0 h. Finally, DHA(EO)₄CH₂CHO-m-HECs were obtained by concentrating the dialyzed aqueous solution using vacuum distillation and lyophilizing the concentrated solution under vacuum.

Determination of Substitution Degrees of DHA(EO)₄CH₂CHO-m-HECs

The grafting degree (DG) of DHA(EO)₄CH₂CHO into the sugar unit of HEC for DHA(EO)₄CH₂CHO-m-HECs was determined according to the results of elemental analysis (EA) and calculated using Eq. 1,

$$DG = \frac{7 \times C/N - 48 + 12DD - 12DS_{HE}}{180} \times 100\% \quad (1)$$

where DS_{HE} is the substitution degree of hydroxyethylation of HEC (112.4%), DG is the grafting degree of DHA(EO)₄CH₂CHO onto HEC of DHA(EO)₄CH₂CHO-m-HEC, DD is the degree of deacetylation of CTS (88.0%, result of chemical titration analysis), and C/N is the mass ratio of carbon versus nitrogen of samples.

Evaluation of Critical Micelle Concentration (*cmc*), Surface Tension at *cmc* (γ_{cmc}) and Minimum Surface Tension (γ_{min})

The *cmc*, γ_{cmc} and γ_{min} of DHA(EO)₄CH₂CHO-m-HECs in aqueous solution were determined according to the relation between the surface tension (γ) and their concentration (C) in aqueous solution, and the temperature for measuring the γ of aqueous solution was maintained at 25.0 °C. A concentrated stock solution was prepared by direct dissolving quantitative DHA(EO)₄CH₂CHO-m-HECs in double distilled water. The stock solution was well soluble and aged at 25.0 °C for 12.0 h to reach equilibrium, and then diluted using

double diluting method. The diluted solutions were equilibrated in a thermostatic bath at 25.0 °C over 12.0 h before measurement. The γ of double distilled water was confirmed as being in the range of 72.0±0.20 mN/m at 25.0 °C prior to measurements. For each concentration, the γ was measured three times with an average deviation was less than 0.20 mN/m.

The curves reflecting the relation between γ and logC were well structured, and the concentration and surface tension at inflexion were regarded as the cmc and γ_{cmc} respectively. The γ_{min} of solution was determined according to final various trend of surface tension with the increase of DHA(EO)₄CH₂CHO-m-HECs in aqueous solution.

Foam Performance of DHA(EO)₄CH₂CHO-m-HECs

Firstly, 40 mL of DHA(EO)₄CH₂CHO-m-HECs aqueous solution, its concentration was of 0.10% (w/w), was transferred into a 100 mL stoppered cylinder, then shaken up and down 25 times vigorously, and the foam height at 0 min (H_0) and that at 5.0 min (H_5) were recorded respectively. The ratio of the foam height at 5.0 min to that at 0 min was taken as the foam retention of the surfactant. The above operation was repeated three times and the average value was utilized for evaluating the foam performance of the DHA(EO)₄CH₂CHO-m-HECs.

Evaluation of Emulsifying Property

The emulsifying property of DHA(EO)₄CH₂CHO-m-HECs was evaluated according to their emulsifying capacity. Briefly, the sample of DHA(EO)₄CH₂CHO-m-HECs (0.10 g) was dissolved in double distilled water (99.90 g), and the aqueous solution, in which the mass concentration of DHA(EO)₄CH₂CHO-m-HECs was 0.10 % (w/w), was obtained. 40.0 mL of the above aqueous solution was added into 100 mL of a measuring cylinder with stopper and mixed with 40.0 mL of liquid paraffin. The mixture was surged up and down five times drastically. After standing for 1.0 min, the mixture was surged up and down another five times drastically. This operation was repeated five times, and the interval between initial stage and that for separating 10.0 mL of aqueous solution from the emulsion after the last vibration was recorded. The experiments were conducted at 25.0 °C in triplicate, and the times required for this interval were averaged and defined as stability time of emulsion. The stability time could be regarded as the relative emulsifying capacity of DHA(EO)₄CH₂CHO-m-HECs.

RESULTS AND DISCUSSION

Results of the Grafting Degree (DG) of the DHA(EO)₄CH₂CHO-m-HECs

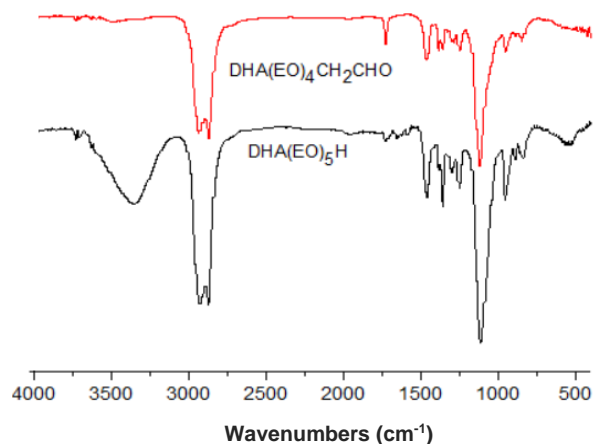
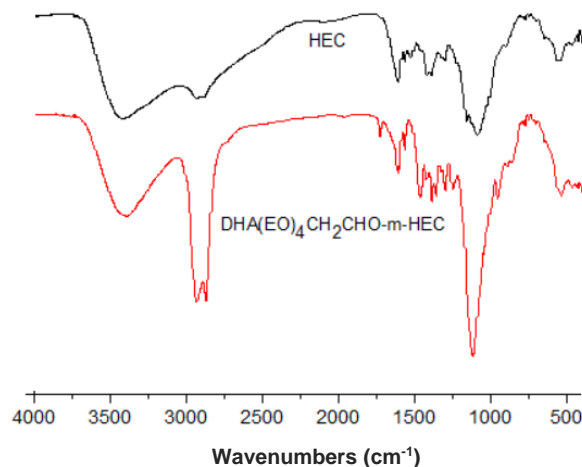
Five kinds of DHA(EO)₄CH₂CHO-m-HECs were obtained with different mass ratios of DHA(EO)₄CH₂CHO *versus* sugar unit of HEC, and the results concerned with their EA and calculated DG are shown in Table 1. The increase of the mass ratio of DHA(EO)₄CH₂CHO *versus* sugar unit of HEC could result in the increase of DG of DHA(EO)₄CH₂CHO-m-HECs. The increase of DHA(EO)₄CH₂CHO in the reactant could provide much more opportunity for the reaction between DHA(EO)₄CH₂CHO and HEC, and it was favorable for much more DHA(EO)₄CH₂CHO to react with the amino group existing in the sugar chain.

Table 1. Results of EA of the DHA(EO)₄CH₂CHO-m-HECs and their DG Values

Sample	n(DHA(EO) ₄ CH ₂ CHO): n(sugar unit)	C Content (w, %)	N Content (w, %)	DG%
DHA(EO) ₄ CH ₂ CHO-m-HEC1	0.50	57.49	3.99	27.74
DHA(EO) ₄ CH ₂ CHO-m-HEC2	1.0	61.08	3.11	48.04
DHA(EO) ₄ CH ₂ CHO-m-HEC3	1.5	62.19	2.84	56.95
DHA(EO) ₄ CH ₂ CHO-m-HEC4	2.0	62.59	2.74	60.57
DHA(EO) ₄ CH ₂ CHO-m-HEC5	3.0	63.09	2.62	65.44

Results of FTIR, UV, and ¹H NMR Analysis and Their Ascription

The FTIR spectra of DHA(EO)₅H and DHA(EO)₄CH₂CHO are shown in Fig. 2, and that of HEC and DHA(EO)₄CH₂CHO-m-HEC3 are shown in Fig. 3. In the FTIR spectrum of DHA(EO)₅H, the peak at 3352 cm⁻¹ was ascribed to ν_{O-H} of hydroxyl, the peaks at 2924 and 2864 cm⁻¹ were ascribed to ν_{C-H} of methyl and methylene respectively, and the peak at 1105 cm⁻¹ was ascribed to the ν_{C-O} of ether bond. Compared with the FTIR spectrum of DHA(EO)₅H, a new peak appeared at 1725 cm⁻¹, which could be ascribed to the ν_{C=O} of aldehyde, and the peak at 3352 cm⁻¹ had almost disappeared in the FTIR spectrum of DHA(EO)₅CH₂CHO. All of these indicated the DHA(EO)₅H had been transformed into DHA(EO)₄CH₂CHO.

**Fig. 2.** FTIR spectra of DHA(EO)₅H and DHA(EO)₄CH₂CHO**Fig. 3.** FTIR spectra of HEC and DHA(EO)₄CH₂CHO-m-HEC3

Compared the FTIR spectrum of DHA(EO)₄CH₂CHO-m-HEC3 with that of HEC, it could be seen that the intensity of peaks at 2924 cm⁻¹ and 2870 cm⁻¹ that were associated with ν_{C-H} of CH₃, CH₂ and CH, and peaks at 1463 cm⁻¹ and 1384 cm⁻¹ that were associated with $\delta_{\nu_{C-H}}$ of CH₃, CH₂ and CH, had become remarkable increased in the FTIR spectrum of DHA(EO)₄CH₂CHO-m-HEC3, and all of these indicated that more methyl, methylene and methyne were present in the structure of DHA(EO)₄CH₂CHO-m-HEC3. Meanwhile, a new peak appeared at *ca.* 1725 cm⁻¹, which could be ascribed to the $\nu_{C=N}$ remained in Schiff-base that had not been reduced completely.

The UV spectra of HEC and DHA(EO)₄CH₂CHO-m-HEC3 were shown in Fig. 4. The ¹H NMR spectrum of DHA(EO)₄CH₂CHO-m-HEC3 was shown in Fig. 5.

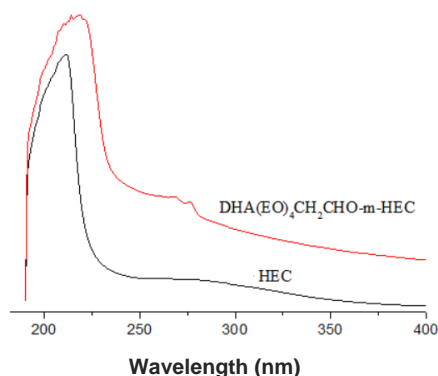


Fig. 4. UV absorption spectra of HEC and DHA(EO)₄CH₂CHO-m-HEC3

It can be seen from Fig. 4 that there were some differences between the UV absorption spectrum of DHA(EO)₄CH₂CHO-m-HEC3 aqueous solution and that of HEC aqueous solution. The appearance of two absorption bands at 269 nm and 277 nm in the UV absorption spectrum of DHA(EO)₄CH₂CHO-m-HEC3 indicated the presence of hydrogenated phenanthrene nucleus in its structure.

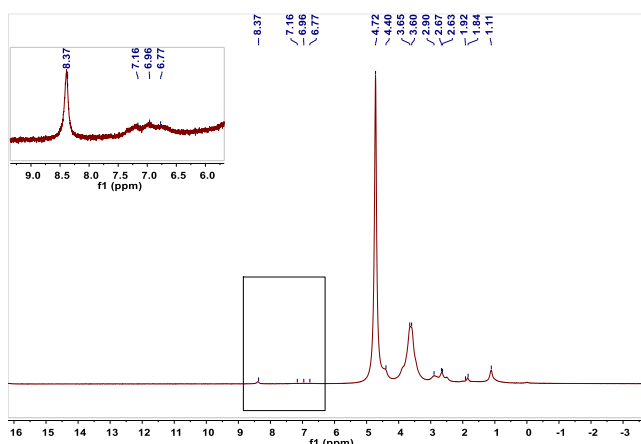


Fig. 5. ¹H NMR spectrum of DHA(EO)₄CH₂CHO-m-HEC3

In the ¹H NMR spectrum of DHA(EO)₄CH₂CHO-m-HEC3, the peak at 8.37 was ascribed to the H of CH of Schiff-base remained in the modified HEC, and that at 7.16, 6.96, and 6.77 were ascribed to the H of benzene ring of the hydrogenated phenanthrene nucleus. The peak at 4.50 to 4.10 represented the proton on C1 of sugar unit, and the peaks

at 4.10 to 3.80 represented the proton on C5 of sugar unit. Peaks at 3.80 to 3.62, and 3.62 to 3.10 represented the proton of methylene of polyoxyethylene chain and hydroxyethyl, and the proton on C2 of sugar unit. The peaks at 3.05 to 2.75, 2.75 to 2.50, and 2.50 to 2.30 were associated with the protons on C4, C3, and C6 of the sugar unit, respectively. The peaks at 1.75 to 2.0 were associated with the protons of hydroxyl and that on C2 of sugar unit of chitosan Schiff-base. The peaks at 1.50 to 0.85 represented the H on methyl, methylene, and methyne of the hydrogenated phenanthrene nucleus. All of these results indicated that the structure of dehydroabietyl polyoxyethylene had been introduced into the sugar chain of HEC.

Values of cmc , γ_{cmc} , γ_{min} and H_5/H_0 of DHA(EO)₄CH₂CHO-m-HECs in Aqueous Solution

Plots reflecting the relationship between the surface tensions (γ , mN.m⁻¹) of DHA(EO)₄CH₂CHO-m-HECs and their concentration (C, g.L⁻¹) in aqueous solution are shown in Fig. 6. The cmc , γ_{cmc} , γ_{min} and H_5/H_0 of DHA(EO)₄CH₂CHO-m-HECs in aqueous solution are shown in Table 2.

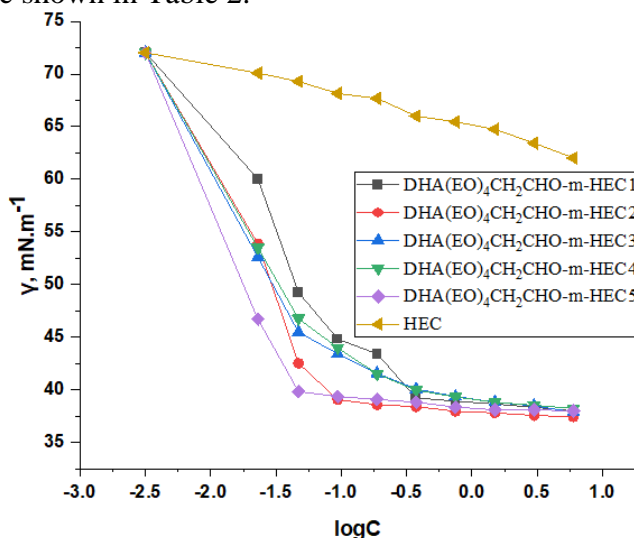


Fig. 6. Relationship between surface tension and concentration of different DHA(EO)₄CH₂CHO-m-HECs in aqueous solution

Table 2. The cmc , γ_{cmc} , γ_{min} and H_5/H_0 Values of DHA(EO)₄CH₂CHO-m-HECs in Aqueous Solution

Sample	cmc , g/L	γ_{cmc} , N/m	γ_{min} , mN/m	H_5/H_0 , mm/mm
DHA(EO) ₄ CH ₂ CHO-g-HEC1	0.077	45.64	37.98	5/85
DHA(EO) ₄ CH ₂ CHO-g-HEC2	0.057	42.13	37.43	10/85
DHA(EO) ₄ CH ₂ CHO-g-HEC3	0.055	44.42	37.87	19/91
DHA(EO) ₄ CH ₂ CHO-g-HEC4	0.042	44.51	38.22	14/88
DHA(EO) ₄ CH ₂ CHO-g-HEC5	0.032	40.52	38.01	13/92
TX-10	0.0313*	29.01*	-	-
HEC	-	-	-	0/10

*Results of literature (Xu *et al.* 2013). "-" means no data.

Combining the data of Table 2 with that of Table 1, it is apparent that the cmc and γ_{cmc} of DHA(EO)₄CH₂CHO-m-HECs in aqueous solution decreased with the increase of DG, and their γ_{min} was nearly equal to each other. It also could be seen from the data of

Table 2 that the cmc of DHA(EO)₄CH₂CHO-g-HEC5 was almost equal to that of TX-10, and its γ_{cmc} was higher than that of TX-10 in aqueous solution. The DHA(EO)₄CH₂CHO-m-HECs was able to form and retain foam retention to some extent, and the capability of DHA(EO)₄CH₂CHO-m-HEC (DG=56.95%) was better than others. These trends were related to the effect of DG on the hydrophobic properties of DHA(EO)₄CH₂CHO-m-HECs. Increased DG resulted in the increase of hydrophobic property of DHA(EO)₄CH₂CHO-m-HECs, and could promote them to migrate to the surface of aqueous solution in some extent. The increase of DG could also improve the capability of DHA(EO)₄CH₂CHO-m-HECs to aggregate together in the solution, so that they formed micelles at lower concentration. The γ_{min} of different DHA(EO)₄CH₂CHO-m-HECs depended on the amount of hydrophobic group of per unit surface at their status of saturated adsorption. Because of the hydrophilic nature and bendable feature of sugar chain of HEC, the DG of DHA(EO)₄CH₂CHO onto HEC for DHA(EO)₄CH₂CHO-m-HECs was less than 100%. Due to the rigidity of hydrogenated phenanthrene nucleus, the amount of hydrophobic group of per unit surface at saturated adsorption for different DHA(EO)₄CH₂CHO-m-HECs was almost equal to each other. Thus, their hydrophobicities at saturated adsorption were almost the same.

Meanwhile, it also could be seen from Fig. 6 that the surface tension of aqueous solution containing HEC decreased with the increase of HEC in the solution to some extent, but there was no obvious inflection point in the γ -log C curve. This result indicated the HEC could not be regarded as surfactant.

Results of Emulsifying Experiment for DAGE-g-N,O-HECTs

The intervals for separating 10.0 mL of aqueous solution from emulsions after the last vibration with various DHA(EO)₄CH₂CHO-m-HECs as emulsifying agent are shown in Fig. 7.

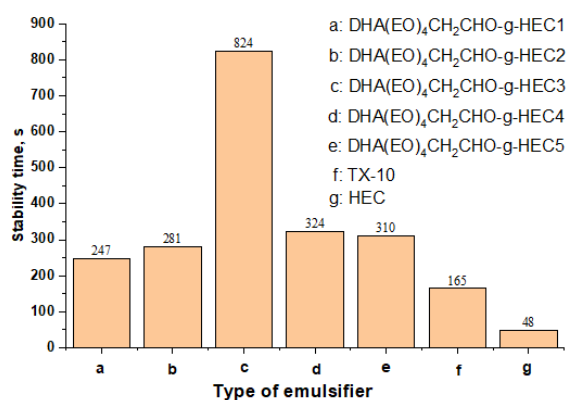


Fig. 7. Stability time of emulsion with different DHA(EO)₄CH₂CHO-m-HECs as emulsifier

The results of emulsifying experiments showed that all the stability time of emulsion with DHA(EO)₄CH₂CHO-m-HECs as emulsifier was longer than that with TX-10 as emulsifier under the experimental conditions. When the DG was lower than 56.95%, its increase could result in the increase of stability time of emulsion with DAGE-g-N,O-HECTs as emulsifier. The stability time of emulsion with DHA(EO)₄CH₂CHO-m-HEC (DG=57.0%) as emulsifier was the longest one among all of investigated emulsion. The reasons resulted in these trends may relate to the influence of DG on the surface activities, the properties of hydrophile-lipophile balance of DHA(EO)₄CH₂CHO-m-HECs, and the

stability of membrane existed on the interface between aqueous solution and liquid paraffin. The increase of DG could result in the increase of surface activities of DHA(EO)₄CH₂CHO-m-HECs and favored a decrease of interfacial tension of paraffin-water interface. The increase of DG could also result in the improvement of mechanical strength of an interfacial film present between paraffin and water, and lead to the increase of resistance of dispersed liquid paraffin to aggregate into oil phase. All of these were favorable for increasing the stability of emulsion. Meanwhile, because the HLB value of the emulsifier is closer to the HLB value required for the oil to be emulsified to form an oil in water (O/W) emulsion, the more stable it is to use this emulsifier to promote the oil to form an O/W emulsion (Ren *et al.* 2001). When the DG of DHA(EO)₄CH₂CHO-m-HEC was *ca.* 57%, its HLB value could close to the HLB value required for liquid paraffin to form O/W emulsion, so the emulsion consisting of the aqueous solution of DHA(EO)₄CH₂CHO-m-HEC3 and liquid paraffin behaved the better stability.

CONCLUSIONS

1. Dehydroabietyl polyethylene glycol(5) aldehyde modified hydroxyethyl chitosan (DHA(EO)₄CH₂CHO-m-HEC) could be prepared with mono dehydroabietyl polyethylene glycol(5) ether (DHA(EO)₅H) and hydroxyethyl chitosan (HEC) as basic materials through a three-step process: DHA(EO)₅H was oxidized into dehydroabietyl polyethylene glycol aldehyde (DHA(EO)₄CH₂CHO) using activated MnO₂ firstly, then the DHA(EO)₄CH₂CHO was reacted with HEC and converted into Schiff-base, and the final product was obtained by reducing the Schiff-base with sodium borohydride.
2. The grafting degree (DG) of DHA(EO)₄CH₂CHO onto HEC for DHA(EO)₄CH₂CHO-m-HEC increased with the increase of the mass ratio of DHA(EO)₄CH₂CHO *versus* sugar unit of HEC.
3. DHA(EO)₄CH₂CHO-m-HEC compounds in aqueous solution could exhibit typical behaviour of polymeric surfactants, and their surface activities increased with the increase of DG.
4. The DHA(EO)₄CH₂CHO-m-HECs could exhibit foaming property and foam retention to some extent, and the capability of DHA(EO)₄CH₂CHO-m-HEC with DG of 57.0% was greater than others.
5. The DHA(EO)₄CH₂CHO-m-HECs could be utilized as emulsifier for improving the stability of emulsion composed of water and liquid paraffin. All of their ability to stabilize the emulsion was better than that of TX-10 under the experimental condition. In addition the stability time of emulsion using DHA(EO)₄CH₂CHO-m-HEC with DG of 57.0% as emulsifier was the longest one among all investigated emulsion.

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