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CO_2-responsive aliphatic tertiary amine-modified alginate and its application as a switchable surfactant

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ABSTRACT

A new kind of hexyl diethyl tertiary amine-grafted amphiphilic alginate derivative (HDEA-Alg) was synthesized from (6-bromo-hexyl)-diethyl-amine (BHDEA) and sodium alginate (NaAlg) through esterification. The structure of HDEA-Alg was confirmed by FT-IR and NMR spectroscopies. The grafting ratio was calculated according elemental analysis and thermodynamic property was analyzed by TG. The CO_2/N_2-responsive performance of HDEA-Alg in aqueous solution was demonstrated by surface tension and conductivity measurements. Stable emulsions of liquid paraffin were easily prepared in the presence of the HDEA-Alg. These emulsions can be de-emulsified by bubbling CO_2 through the emulsions at 5 °C for 30 min, resulting in complete oil/water phase separations. They can be re-emulsified by bubbling N_2 through the solutions at 50 °C for 30 min with the aid of homogenization.

1. Introduction

In the past decade, switchable surfactants have attracted rapidly growing interest (Jiang, Zhu, Cui, & Binks, 2013) due to their tremendous potential in many industrial applications, such as cleaning, fuel production, oil recovery, oil transport, and emulsion polymerization. By using these surfactants, the emulsions or foam can be stabilized only temporarily and have to be demulsified or defoam at a specific desired stage.

Switchable surfactants are compounds possessing tunable surface activity in response to changes in environmental condition. Common stimuli are pH (Liu, Wang, Zou, Wei, & Tong, 2012), temperature (Hu, Ge, Han, & Guo, 2015; Jochumab & Theato, 2013; Zoppe, Venditti, & Rojas, 2012), light (Jochumab and Theato, 2013; Mirarefi & Ted Lee, 2010), magnetic-field (Czaun, Hevesi, Takafuji, & Ihara, 2008; Melle, Lask, & Fuller, 2005), oxidants/reductants (Cheng, Ren, Gao, Liu, & Tong, 2007; Ghosh, Irvin, & Thayumanavan, 2007). However, it is worth noting that each type of stimuli has its downside (Qian, Zhang, Qiu, & Zhu, 2014). For example, repeated switchable cycles of pH-responsive surfactants require repeated addition of acids and bases to the solution, which may contaminate the system and weaken the switchability due to salt accumulation. Changing the temperature for a large volume sample is also slow and energy consuming. Light is limited to its radiation depth. Magnetic-field intensity trigger is limited to the small application range. And the addition of oxidants or reductants may cause product contamination. More recently, switchable systems that use CO_2 as the trigger have got increasing attention due to their advantages (Pocoví-Martínez et al., 2013). Carbon dioxide (CO_2) is nontoxic, inexpensive, abundant, and an environmentally friendly chemical reagent. And the facile addition of CO_2 allows for a large-scale operation (Liu, Lu, Wang, Li, & Zhu, 2014). Most importantly, it can be readily removed by N_2 or air, which is as well abundant and environmentally friendly. Accordingly, CO_2/N_2–responsive surfactants are useful for green chemical processes such as extraction of organic solvents without distillation (Jessop et al., 2010) and destabilization of colloidal polymer latexes without adding chemicals (Fowler et al., 2011).

Jessop and co-workers have reported a type of CO_2-triggered switchable cationic surfactant containing an amidine group (Liu, Jessop, Cunningham, Eckert, & Liotta, 2006). Acetamidines with a long hydrophobic chain form bicarbonate salts in the presence of CO_2 and water (Jessop, Mercera, & Heldebrant, 2012). These salts are surfactants that stabilize emulsions and could be recovered when bubbling an inert gas like N_2 or Ar through the solution to expel CO_2. However, the amidine group has some drawbacks that might limit its utilization in various applications (Lin & Theato, 2013). The synthesis of amidine-containing monomers or compounds is complex and very challenging. And the costs of amidine groups cannot be neglected. These disadvantages have motivated to investigate amine group instead of amidine group in the preparation of CO_2-responsive polymers. As tertiary amines head groups

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have lower basicity and switch off far more quickly than the amidines, in recent years, a lot of studies have been reported on poly (*N*,*N*-(dimethylamino)ethyl methacrylate) (PDMAEMA) which containing tertiary amine groups (Han, Tong, Boissieṙe, & Zhao, 2012; Xu et al., 2013; Zhang, Yu, Wang, Li, & Zhu, 2012). Zhang and co-workers report the synthesis of PDMAEMA-*b*-PMMA diblock copolymer (PDM) (Zhang et al., 2012). Such a polymeric surfactant was prepared by block copolymerization of DMAEMA with a hydrophobic comonomer. The hydrophobic block provides rooting to latex particles, the hydrophilicity of PDMAEMA block could be switched by treating with CO_2. We hypothesized that CO_2-responsive polymeric surfactants could also be prepared by grafting aliphatic tertiary amine onto a hydrophilic alginate. The hydrophobicity of aliphatic tertiary amine could be switched by bubbling CO_2 or N_2. In this paper, we report the synthesis of (6-bromo-hexyl)-diethyl-amine (BHDEA) grafted sodium alginate derivatives (HDEA-Alg) through esterification and using tetrabutyl ammonium bromide (TBAB) as phase transfer catalyst. The product was characterized by FT-IR and ^1H NMR spectroscopies. The surface tension and conductivity of HDEA-Alg in aqueous solution were investigated to assess surfactant switchability. We also demonstrated the applicability of the product as surfactants for the preparation of emulsions and tested the CO_2/N_2-triggered emulsification/demulsification of the emulsion system.

2. Materials and methods

2.1. Materials

Sodium alginate (NaAlg, $\bar{M}_\eta \sim 430$ kDa, M/G = 0.18), diethyl ether (purity ≥99%), Diethylamine (DEA, 99%), *N*,*N*-dimethylformamide (purity ≥99%), and paraffin liquid (purity ≥98.5%) were purchased from Sinopharm Chemical Reagent Co. 1,6-Dibromohexane (purity ≥98%) was provided by Energy Chemical. Tetrabutylammonium bromide (TBAB, 99%) was purchased from Aladdin. Unless specially stated, all materials were guaranteed analytical reagents and used as received without further purification.

2.2. Synthesis and purification of BHDEA

According to the literature (Albrecht, Ehrler, & Mühlebach, 2003), (6-bromo-hexyl)-diethyl-amine (BHDEA) was prepared by reacting 1,6-dibromohexane (61 g, 0.25 mol) with diethylamine (7.8 ml, 75 mmol) in diethyl ether (150 ml) at 25 °C refluxed for 5 days. The reaction mixture was poured into aqueous HCl (0.2 M, 150 ml). The aqueous layer was washed with diethyl ether (2 × 100 ml) and neutralized with NaOH to pH 12. After extraction with diethyl ether (3 × 100 ml), the organic layers were dried over $MgSO_4$ and evaporated to leave BHDEA as a yellow oil.

2.3. Synthesis and characterization of HDEA-Alg

As described by Scheme 1, NaAlg (2.0 g) and BHDEA (5.0 g) were added in 60 ml of acetone/water (5/1,v/v) containing TBAB (2 mmol) by stirring at 60 °C for 30 h. The reaction mixture was filtered and washed with absolute ethanol (2 × 100 ml). The crude product was dissolved into water and then poured into the dialysis bag. The solution was dialyzed against the distilled water for 3 days and lyophilized to get the pure HDEA-Alg. The chemical structure of product was characterized by Fourier transform infrared spectroscopy (FT-IR, Tensor 27, Bruker), NMR spectroscopy (^1H NMR, AVANCE 600, Bruker; ^{13}C AVANCEIII400, Bruker) and thermogravimetric analysis (TG, STA409PC). The grafting ratio ($N_{alkyl}/N_{hexuronic}$) of HDEA-Alg was determined by elemental analysis (Vario EL cube). All tests were carried out according to previous reports (Yang, Zhou, & He, 2013).

2.4. Assessing surfactant switchability

The reversibility of the conversion from active to inactive form was demonstrated by bubbling CO_2 (at 5 °C for 30 min) followed by N_2 (at 50 °C for 30 min) through solutions of HDEA-Alg and measuring the change in surface tension and conductivity of the solution. The surface tensions and conductivity of NaAlg and HDEA-Alg aqueous solution were measured by a surface tension meter (DCAT11) with a platinum plate and a conductivity meter (DDS-11A) at 20 °C, respectively.

2.5. Emulsions preparation and demulsification

Emulsions were prepared by improving method on literature (Ge, Shao, Lu, & Guo, 2014). Oil in water emulsions were prepared by first mixing the liquid paraffin into the aqueous phase (containing various concentrations of HDEA-Alg) using a superfine homogenizer FA25 (Fluko Equipment Shanghai Co.) at 10,000 rpm for 3 min, followed by an ultrasonic processor VCX 750 (Sonics & Materials Inc.) with the energy output of the probe setting to 300 W for 3 min.

To verify the switchable performance of the emulsions, CO_2 was bubbled into the emulsions at 5 °C for 30 min and switched back by bubbling N_2 through the solution at 50 °C for 30 min, followed by re-homogenization for 3 min.

2.6. Fluorescence microscopy

Images of the emulsion microstructure were acquired using an inversion fluorescence microscope (IX83, Olympus). Approximately 10 ml of emulsion was placed in a test tube, and moderate rhodamine 6G aqueous solution (1 mg/ml) was added and mixed for 30 min. The mixture was then dropped on a microscope slide and covered with a coverslip before observed.

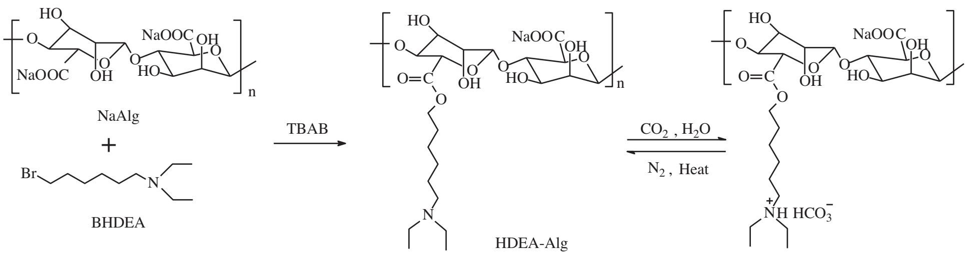
3. Results and discussion

3.1. Characterization of HDEA-Alg

NaAlg was modified by use of the phase transfer catalysis TBAB to form ester linkages between BHDEA molecules and the carboxylate groups on the alginate polymer backbone. The synthesis principle of HDEA-Alg is shown in Scheme 1.

The structures of samples were confirmed by FT-IR as shown in Fig. 1. From the spectrum of NaAlg (Fig. 1a), it is being observed that a broad peak at 3450 cm^{-1} is due to the stretching vibrations of O—H, and a small peak at 2929 cm^{-1} is attributed to the C—H stretching vibrations of methyne groups. The bands at 1096 and 1028 cm^{-1} are assigned to C—O—–C stretching vibrations of the saccharide structure. It is further noted that two strong peaks at 1612 and 1417 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of carboxylate groups. Comparing that of NaAlg, the spectrum of HDEA-Alg (Fig. 1b) contains the characteristic hydroxyl and carboxyl bands, but also features additional peaks. A broad peak appears in HDEA-Alg from 2960 to 2860 cm^{-1} due to the peak overlap of methy, methylene and methyne groups, and the peaks of 1731 and 1250 cm^{-1} are attributed to the C=O and C—O component of an ester bond respectively. Vibrations of C—N is measured to be 1078 cm^{-1} in BHDEA, which overlaps with the peaks of C—O—C stretching vibrations around 1096 and 1028 cm^{-1}. The appearance of the peaks suggests that BHDEA successfully grafted onto alginate.

^1H NMR was investigated to further confirm the chemical structure of the graft polymer. The ^1H NMR spectrum of NaAlg and



Scheme 1. The synthesis principle of HDEA-Alg and its CO_2/N_2 responsibility.

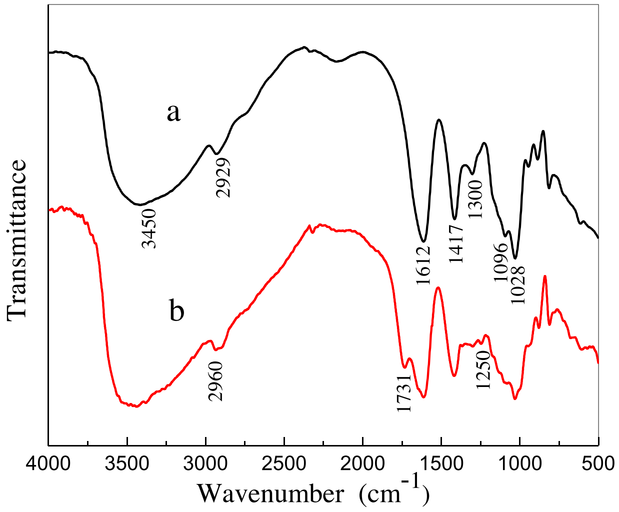


Fig. 1. FT-IR spectra of NaAlg (a) and HDEA-Alg (b).

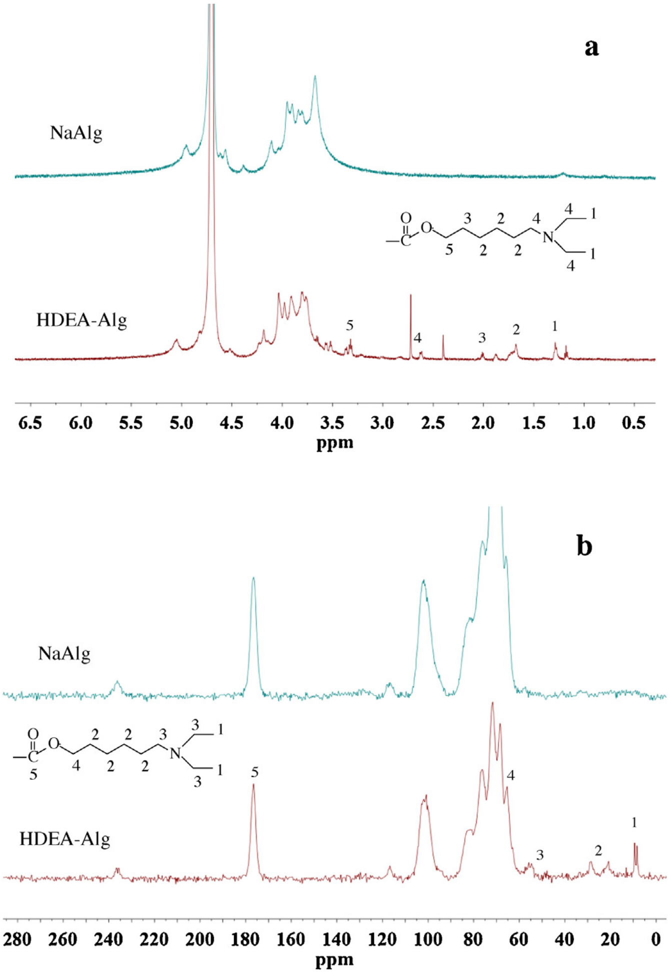


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of NaAlg and HDEA-Alg.

HDEA-Alg are shown in Fig. 2a. The proton peaks from 3.6 to 5.1 ppm contributed to the H of alginate, in which the anomeric protons are observed in the region 4.5–5.1 ppm. In contrast with the spectrum of NaAlg, additional peaks in spectrum of HDEA-Alg are observed from 1.0 to 3.5 ppm, which were assigned to the methyl and methylene protons of aliphatic tertiary amine respectively. Affected by N and O atoms, the chemical shift of methyl protons and methylene protons both increased. The solid-state ^{13}C NMR spectra of NaAlg and HDEA-Alg samples are shown in Fig. 2b. Comparing to NaAlg, a series of peaks appear in HDEA-Alg from 10 to 65 ppm because of the introducing of alkyl tertiary amine chain. The ^{13}C NMR spectra of HDEA-Alg exhibits peaks at 10 ppm (methyl groups), and two peaks at 20 ppm and 28 ppm assigned to methylene groups. Meanwhile, the peaks of 48 ppm and 55 ppm are attributed to C—N and C—O groups. On the basis of the above data, it could be concluded that HDEA-Alg was synthesized.

The grafting ratio (X) of the HDEA-Alg is 12.8% calculated by the following formula, according to percentage content of N in the HDEA-Alg measured by an elemental analyzer.

$$\mathrm{N\%} = \frac{\mathrm{M_3 \cdot X}}{\mathrm{M_1 \cdot X + M_2\,(1 - X)}}$$

$$\mathrm{X(\%)} = \frac{\mathrm{N\% \cdot M_2}}{\mathrm{M_3 - N\% \cdot M_1 + N\% \cdot M_2}}$$

(M_1 represents the sum of the atomic weight of $C_{16}H_{29}O_6N$; M_2 represents the sum of the atomic weight of $C_6H_7O_6Na$; M_3 represents the relative atomic mass of N).

Fig. 3 shows the TG analysis curves of NaAlg and HDEA-Alg. As we know, the first stage region belongs to the loss of combined water of NaAlg in the 30–200 °C, and in the second stage from 220 to 280 °C, the weight loss of NaAlg should be the carboxyl take off CO_2 and neighboring hydroxyl dehydration. The weightlessness of HDEA-Alg in the second stage is obviously higher than the NaAlg because of the thermal scission of the ester and the evolution of tertiary amine molecules. This finding further supports the presence of ester bond formatting between DEHA and NaAlg.

3.2. CO_2/N_2-responsive performance of HDEA-Alg in aqueous solution

Fig. 4a displays the plots of surface tension versus different concentration of NaAlg and HDEA-Alg. Attributing to the introduction of hydrophobic chain by esterification, the synthesized surfactant has lower surface tension than NaAlg in aqueous solution under the same concentration. To assess surfactant switchability, the surface tension of HDEA-Alg (0.4 wt%, the critical micelle concentration) aqueous solutions were observed when CO_2 followed by N_2 were

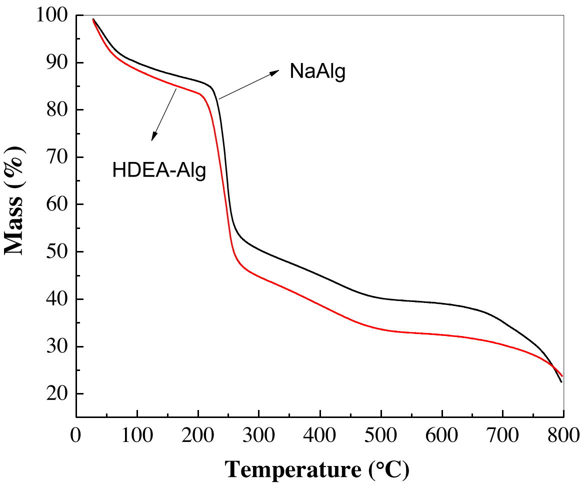


Fig. 3. TG curves of samples.

bubbled through the solution, just as shown in Fig. 4b. CO_2 was bubbled through the solution for 30 min at 5 °C and the surface tension of the solution was measured to be 58.7 mN/m at 20 °C, which implies that the tertiary amine switchable surfactant has been converted to bicarbonate and lead to enhanced hydrophilicity. Following this procedure, N_2 was bubbled through the solution for 30 min at 50 °C and surface tension of the solution decreased to 46.6 mN/m. After another two cycles of bubbling CO_2/N_2, there is no discernible loss in performance.

The conductivity of NaAlg and HDEA-Alg aqueous solutions of different concentration was also measured as shown in Fig. 5a. The conductivity all increase with the increase of concentration. It is worth noting that the HDEA-Alg aqueous solutions have lower conductivity than NaAlg aqueous solutions when the concentration is same, indicating that Na^+ of NaAlg has been substituted by the hydrophobic alkyl tertiary amine chain. Formation of the bicarbonate salts was achieved when CO_2 was bubbled at 5 °C for 30 min through the solution, the conductivity increased. And it decreased again after bubbling with N_2 at 50 °C for 30 min. The CO_2/N_2 cycle was performed three times to demonstrate the repeatability of the switching process, and there is no discernible loss in performance as shown in Fig. 5b. Both surface tension and conductivity analysis demonstrated CO_2/N_2-responsive performance of HDEA-Alg in aqueous solution.

3.3. CO_2/N_2-responsive performance of emulsions stabilized by HDEA-Alg

The HDEA-Alg was employed as surfactants with different concentrations in water for the preparation of emulsions. Paraffin liquid was used as the oil phase. And the emulsifying performance was found to increase with increasing concentration of HDEA-Alg from 0.4 to 1.0 wt% as shown in Fig. 6a–d. A stable emulsion could be prepared until the concentration of HDEA-Alg reaches about 1.0 wt%. To verify the switchable performance of the emulsions, emulsion d was bubbled with CO_2 at 5 °C for 30 min and switched back by bubbling N_2 through the solution at 50 °C. Both were observed after 24 h. On one hand, HDEA-Alg in emulsions lost their surface activity by bubbling CO_2 and returned to the water phase and no stable emulsion could be formed after re-homogenization (Fig. 6e). On the other hand, once N_2 was bubbled through the mixture at 50 °C for 30 min, the stability of the emulsions was reestablished after re-homogenization (Fig. 6f). Moderate rhodamine 6 G aqueous solution (1 mg/ml) was added and mixed for 30 min to observe emulsion d and emulsion e. Fig. 6g shows the fluorescence microscopy images of O/W emulsion d, we could clearly observe a yellow ring encompassing a dark spot. Because of opposite charges attracted, the fluorescent dye of Rh6G with positive charges bound to the HDEA-Alg with the negative charges, so that the region of macromolecules appeared yellow under ultraviolet light. Oil droplets, however, appeared nonfluoresced black spherical area because there was no interaction between Rh6G and the molecules of oily phase. The bright layer outside oil droplet showed that the macromolecular membrane formed due to the HDEA-Alg molecular adsorption at the oil/water interface. But in fluorescence microscopy images of O/W emulsion e (Fig. 6h), a large area appeared yellow and oil droplets were coalesced significantly. We know that HDEA-Alg with bicarbonate is a kind of water-soluble macromolecules, so distributes homogeneously in continuous phase of the emulsion.

4. Conclusion

Through grafting aliphatic tertiary amine (*N*,*N*-diethylhexylamine) onto water soluble NaAlg, a novel CO_2/N_2 switchable surfactant (HDEA-Alg) have been successfully synthesized. The grafting rate is 12.8% calculated according to the content of nitrogen by elemental analysis. The aqueous solutions of HDEA-Alg were proved to be CO_2/N_2 responsive. Employing this surfactant, we prepared reversibly emulsion to use CO_2/N_2 as a “green” trigger. This work represents an innovative approach in developing alginate smart materials.

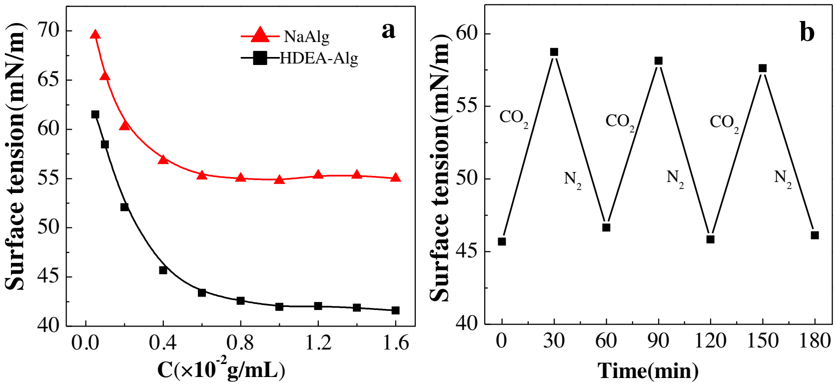


Fig. 4. Surface tension of NaAlg and HDEA-Alg aqueous solutions (a) and reversible change of the solution surface tension of HDEA-Alg (0.4 wt%) when purging with CO_2 and N_2, respectively (b).

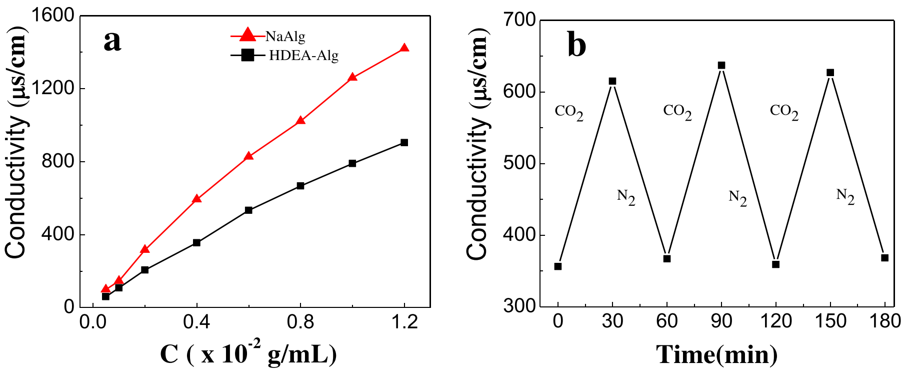


Fig. 5. Conductivity of NaAlg and HDEA-Alg aqueous solutions (a) and reversible change of the solution conductivity of HDEA-Alg (0.4 wt%) when purging with CO_2 and N_2, respectively (b).

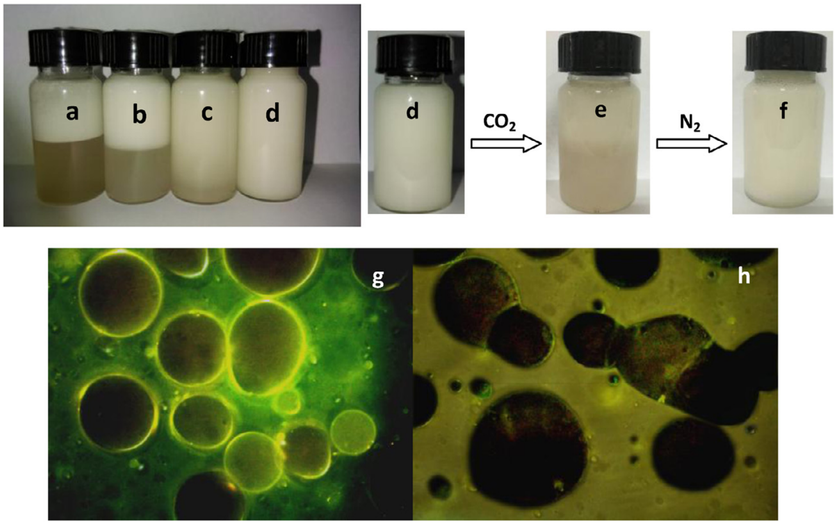


Fig. 6. Digital photographs of paraffin liquid-in-water emulsions (3/7, v/v) stabilized by HDEA-Alg, that were taken one week after preparation. The HDEA-Alg concentrations in water from a to d are 0.4, 0.6, 0.8, 1.0 wt%; Bubbling CO_2 through the emulsion d at 5 °C for 30 min (e), then bubbling N_2 through the emulsion e at 50 °C for 30 min, followed by re-homogenization for 3 min, 24 h later (f); The fluorescence photomicrograph of the emulsion d (g) and e (h).

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