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ORIGINAL ARTICLE

CO_2/N_2 Triggered Switchable Surfactants with Imidazole Group

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Abstract In order to overcome the hydrolysis of 2-alkyl-1-hydroxyethyl imidazoline and its unsatisfactory emulsification–demulsification switchability to water-alkane, the long-chain *N*-alkylimidazole compounds were synthesized by *n*-octyl bromide, *n*-decyl bromide, *n*-dodecyl bromide, *n*-tetradecyl bromide and *n*-hexadecyl bromide with imidazole, respectively and characterized by MS, ^1H NMR and FTIR. The long-chain *N*-alkylimidazole compounds can be reversibly transformed into charged surfactants by exposure to CO_2. Surface tension values indicated that *N*-alkylimidazolium bicarbonates had excellent surface activity compared with corresponding conventional surfactants with a lower γ_{CMC}. The surface behaviors of the five surfactants can be illustrated by A_{min}. Five conductivity cycles by bubbling CO_2 and N_2 alternately indicated that these surfactants could be switched by CO_2 reversibly and repeatedly. Emulsions were repeatedly stabilized for five cycles by *N*-alkylimidazolium bicarbonate and broken by bubbling N_2 through the solutions to reverses the reaction, releasing CO_2.

Keywords Switchable surfactants · CO_2 · *N*-Alkylimidazole · Emulsification

Introduction

Surfactants are often used to stabilize emulsions during certain stages in cleaning, cosmetic, emulsion and microsuspension polymerization, viscous oil transportation, etc. However, the stabilization is usually required only for one step of the whole process, and surfactants and it is desirable that they separate from the emulsion system after stabilization making them environmentally friendly. Lots of industrial applications involving emulsions would benefit from an efficient and rapid method of breaking the emulsion at a specific desired stage. So switchable surfactants whose surface activity can be reversibly altered by a triggering have been developed to allow for stabilized dispersions. The switchability of the reported surfactants can be triggered by altering the pH [1–3], adding redox reagents [4–12] or applying UV and visible-light [13]. Surfactants containing ferrocenyl moieties [4, 6–11] and "pepfactants" [2, 3] are expensive, while those containing viologen [7] moieties are likely to be toxic, and all of the above rely on the addition of oxidants, reductants, acids, or bases to trigger the switch. Photochemical azobenzene surfactants use only light as a trigger but are limited to nonopaque samples. Recently a series of *N*′-alkyl-*N,N*-dimethylacetamidines bearing functional stimuli-responsive groups have been reported and they can be switched alternatively between surface-active and surface-inactive forms by CO_2/N_2 triggering and repeatedly turned "on" and "off" as necessary [14] (Scheme 1, where R is long-chain alkyl). Amidine group reacts with CO_2 to produce the corresponding cationic amidinium bicarbonate, while the bicarbonate decomposes to the neutral amidine by removing CO_2 afterwards by bubbling air, nitrogen, argon or other inert gas under heating. In addition to the properties of conventional surfactants, such as emulsification and foaming, they also show the switchability function. Qin et al. [15] reported the CO_2 switchable surfactant with guanidine headgroups, performing the reversible switchability. Other researchers studied switchable compounds

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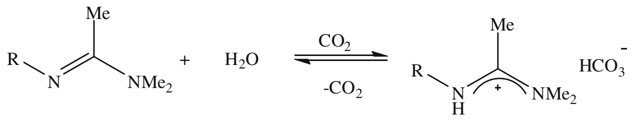


Scheme 1 The "on" and "off" of switchable surfactants

with an amidine or a guanidine group [16–21], as switchable solvents, the solvents can switch reversibly from one state to another.

More recently, we have reported long-chain alkylimidazoline surfactants whose conductivity cycles indicate that the surfactants can be switched reversibly by CO_2 [22]. However, due to the hydrolysis of 2-alkyl-1-hydroxyethylimidazoline and their causing amide emulsification, their emulsification–demulsification switchability to water-alkane was not satisfactory. If the hydrolysis problem of alkylimidazoline can be overcome, the switchability of emulsification–demulsification may be satisfactory. Based on alkylimidazoline, we assume we can connect the alkyl with nitrogen to form *N*-alkyl imidazole instead of with a carbon atom. We conjecture that *N*-alkyl imidazole can not only overcome the hydrolysis problem, but also it would be a kind of effective switchable surfactant which could be triggered by CO_2 due to the N=C–N bond.

As for the synthesis of *N*-alkylimidazoles, Durán-Valle et al. [23] used acidic carbon material as an efficient and selective catalyst in the *N*-alkylation of imidazole. Under alkaline media conditions and reflux, with tetraethylammonium iodide or tetrabutylammonium bromide as phase transfer catalysts, Calvino-Casilda et al. [24] used sonochemical and thermal activations over zeolites to synthesize *N*-alkylimidazoles from imidazole and 1-bromobutane with more than 80 % yields and 100 % selectivity. Khabnadideh et al. [25] reported unsubstituted imidazoles alkylation in high yield from different azole compounds with alkyl bromides. Cuevas-Yanez et al. [26] found that imidazoles were readily *N*-alkylated by a Cu(II)-mediated reaction with α-diazocarbonyl compounds or with diazoalkanes generated *in situ* from the corresponding *p*-toluenesulfonyl hydrazones. The Mitsunobu protocol offered a convenient route from imidazole to *N*-alkyl-substituted imidazole by Kim et al. [27], with the yield from 20 to 94 % by optimization. Wang Xixin and Sun Ruzhong [28] reported preparation of 1-(β-cyanoethyl)imidazole by adding acrylonitrile to imidazole, then conducting an elimination reaction with bromoalkane at a high yield of over 85 %. Compared with the above synthesis methods and considering environmental friendliness, Wang Xixin's method is preferred. In the present work, we focus on surface activities and switchable performance of *N*-alkylimidazoles triggered by CO_2. The switchability of emulsification–demulsification complies with our concept.

Experimental

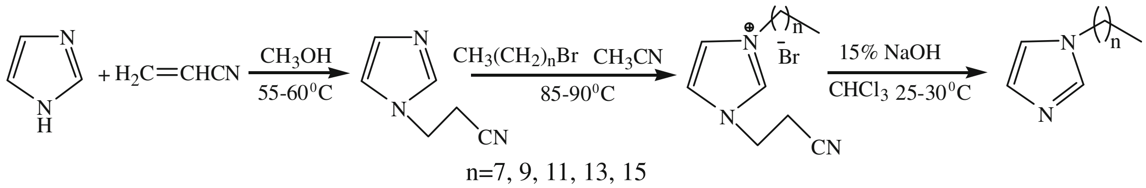
Materials and Measurement Methods

Imidazole with a purity of 99.0 % was obtained from the Sinopharm Chemical Reagent Co., China. *N*-Octyl bromide, *n*-decyl bromide, *n*-dodecyl bromide, *n*-tetradecyl bromide and *n*-hexadecyl bromide were purchased from J&K Chemical and had a purity of 98.0 %. Acetonitrile and methanol (Tianjin Bodi Chemical Co., China) are of analytical grade and both had a purity of 99.5 %. Acrylonitrile with a purity of 98 % was obtained from Tianjin FuCheng Chemical Co. CO_2 and N_2 were purchased from Dalian Guangming Gas Co., and had a purity of 99.999 and 99.99 %, respectively. Sodium hydroxide and chloroform were of analytical grade. Deionized water was purified with a XYJ-250-H Pine-Tree instrument (Beijing Xiangshunyuan Technology Co.) and it was used in all measurements at 25 °C.

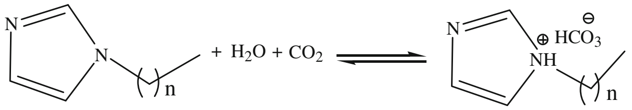
The mass spectrum was obtained with High Performance Liquid Chromatography/Mass Selective Detector (HP, America, HP1100LC/MSD). ^{1}H NMR was recorded on a Bruker 400 MHz instrument (Bruker, France, Model AVANCEII 400 MHz). Infrared spectroscopy was performed with a FT-IR spectrometer (Thermo 60Nicolet, America, Model NEXUS). The surface tension was determined with a tensiometer (0.01 mN m^{-1}, Shanghai Hengping instrument Co., China, Model BZY-2) by the Wilhelmy plate technique. The emulsions of the surfactants were sonicated in the ultrasonic bath KH-300DB (Kunshan He Chuang Ultrasonic Instrument Co). The conductivity was measured by a DDSJ-308A conductivity meter ($\leq \pm 1$ % FS, Shanghai Hongyi Instrument Co., China).

Synthesis and Preparation

The synthesis route of *N*-alkyl imidazoles and preparation of *N*-alkylimidazolium bicarbonates aqueous solution are shown in Schemes 2 and 3, respectively. For a succinct description, the *N*-alkyl imidazoles are recorded as **a,** as shown in Scheme 3. Series of *N*-alkyl imidazoles are named **1a**, **2a**, **3a**, **4a** and **5a** according to their differences in the carbon chain. Correspondingly, their bicarbonates are named as **b**. *N*-alkyl imidazolium bicarbonates are recorded as **1b**, **2b**, **3b**, **4b** and **5b**. Herein, we take the synthesis of *N*-decylimidazole as an example to demonstrate the synthesis method.



Scheme 2 Synthesis route of long-chain alkyl imidazoles



1a	n=7	**1b**
2a	n=9	**2b**
3a	n=11	**3b**
4a	n=13	**4b**
5a	n=15	**5b**

Scheme 3 The inactive and active reversible process of the switchable surfactants

Synthesis of *N*-decylimidazole

N-decylimidazole was synthesized according to the procedure in the literature [28]: 6.8 g (0.1 mol) imidazole in CH_3OH (7.5 g) and acrylonitrile (7.5 g) were mixed in a three-necked flask and reacted at 50–60 °C for 3 h. Removing the excess acrylonitrile and CH_3OH by vacuum distillation, 1-(β-cyanoethyl)imidazole (light yellow liquid) was obtained. After 17.5 g acetonitrile and *n*-bromodecane had been added dropwise, the temperature was increased to 80–90 °C for another 15 h. Then the solvent was removed by vacuum distillation, after cooling to room temperature, 30 mL chloroform and 40 g sodium hydroxide aqueous solution (15 %) were added and stirred for 1 h. Then the oil phase was separated and washed with deionized water. Then the chloroform was removed by vacuum distillation, and a luminous yellow product was collected and purified by column chromatography from chloroform:methanol = 24:1 (by volume) to give 19.58 g (yield 94.13 %) of a yellow liquid (*N*-decylimidazole). Other *N*-alkylimidazoles were obtained in the same way. The yields of **1a**, **3a**, **4a** and **5a** were 91.5, 90.2, 89.6 and 85.7 %, respectively.

Preparation of *N*-alkylimidazolium Bicarbonates Aqueous Solution

N-decylimidazole was put into a three-necked flask and dispersed in deionized water by magnetic stirring. Then CO_2 was bubbled into the flask. The solubility of *N*-decylimidazole increased along with the bubbling of CO_2. Twenty minutes later, *N*-alkylimidazole had dissolved completely, the liquid was clear. Formation of solutions of the bicarbonate salts was achieved by purging CO_2 through solutions, but their isolation as pure solids was unsuccessful. Therefore, bicarbonate formation in solution was conjectured from the literature [14–22] and confirmed by the changes of the conductivity and emulsifying ability. Other *N*-alkyl imidazolium bicarbonates were obtained in the same way.

Conductivity Measurements

N-alkylimidazoles were dispersed into deionized water at a concentration of 0.025 mol L^{-1} in a flask. Then CO_2 was bubbled into the flask. Conductivities were measured with a DDSJ-308A conductivity meter at 25 ± 0.1 °C, respectively. A corresponding blank test (without *N*-alkimidazoles in the solution) was carried out because the CO_2 could be absorbed slightly in water.

Determination of CMC, γ_{CMC}, Γ_m and A_{min}

The surface tensions of the aqueous solution of alkylimidazolium bicarbonates were measured by a tensiometer at 25 ± 0.1 °C until the experimental error was within 0.20 mN m^{-1}. The solutions were sonicated for 20 min to obtain homogeneous solutions. The curves of surface tension versus the logarithms of the surfactant concentrations (γ-logC) were plotted and the CMC values were determined from the break points. The surface tensions at CMC (γ_{CMC}) were also obtained from the curves of γ-logC. The surface excess concentration (Γ_m) at the air/water surface was calculated by the Gibbs adsorption isotherm equation (Eq. 1), where the value of n (a constant determined by the number of species constituting the surfactant and adsorbed at the interface) is taken as 2, R is the ideal gas constant (8.314 J $mol^{-1}K^{-1}$), T is the absolute temperature (K), and dγ/dlogC is the slope of the curve of surface tension versus logarithm of the surfactant concentration. The minimum average area A_{min} (nm^2) per surfactant molecule on the air/water interface was estimated by Eq. 2, where N is Avogadro's constant.

$$\Gamma_{\mathrm{m}} = \frac{-1}{2.303n\mathrm{RT}}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\log \mathrm{C}}\right) \quad (1)$$

$$A_{\min} = \frac{10^{14}}{N\Gamma_{\mathrm{m}}} \quad (2)$$

The solutions of alkylimidazolium bicarbonates were made with CO_2-saturated water, and CO_2 was bubbled through each solution again for 5 min immediately before the measurement.

Emulsifying Stability Tests

In a 10-mL stoppered test tube, 2 mL of deionized water, 2 mL of dodecane and 3 % (mass fraction) of alkylimidazoles were added. Then CO_2 was bubbled into test tube for 20 min. The aqueous solution was vibrated sonically at 32 kHz for 20 min and then shaken for about 30 s by hand. An emulsion was formed and its stability was determined by observing the emulsion separation at room temperature after 5, 10, 30 min, 1, 2, 5, 8, 24 h, respectively.

Switching Performance

Switchability of Conductivities

In 40 mL of deionized water, 0.208 g of **2a** was added. CO_2 was bubbled through the aqueous at a rate of several bubbles per second at 25 °C. The conductivity of the aqueous solution was measured with a conductivity meter at 30 s intervals from the beginning until the conductance value was constant. Then N_2 was bubbled through the aqueous until the conductivity reached the starting value approximately. Five cycles of CO_2 and N_2 bubble alternately was performed.

Switchability of Emulsification-Demulsification

A mixture of 2 mL of decane, 2 mL of deionized water and 0.117 g of **2a** were put into a test tube. After bubbling CO_2 for 20 min, the solution was sonically vibrated at 32 kHz for 20 min and shaken for about 30 s by hand, and then a homogeneous emulsion was obtained. Then the prepared emulsion was broken by bubbling N_2 for another 20 min. The operation was performed for a total of five cycles.

Results and Discussion

Synthesis and Characterization

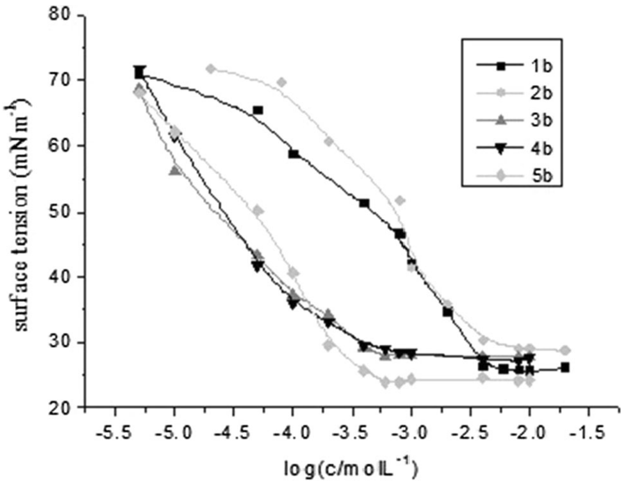


Fig. 1 Surface tension versus logarithmic concentration curve of **1b**–**5b**

The **2a** imidazole was dissolved in $CHCl_3$ and analyzed by a Mass Selective Detector (MSD). The mass spectrum shows peaks of the target product at *m/z* 209.1($M+H^+$) and *m/z* 417.4 ($2M+H^+$). The NMR spectrum was measured in $CDCl_3$. The ^{1}H NMR: 0.88 (t, 3H, CH_2*CH_3*), 1.28 (m, 14H, (*CH_2*)$_7$$CH_3$), 1.78 (m, 2H, *$CH_2$*$CH_2$N), 3.92 (t, 2H, *$CH_2$*N), 6.90 (s, 1H, N*CH*=CH), 7.06 (s, 1H, N*CH*=N), 7.47 (s, 1H, CH=*CH*N). The IR spectrum of **2a** showed a strong absorption of ν(H–C) of long-chain alkyl at 2,925.30 and 2,854.60 cm^{-1} as well as strong absorption of ν(C=N) of imidazole ring at 1,506.91 cm^{-1}. The MS and ^{1}H NMR of other alkylimidazoles were as follow:

1a: MS *m/z* 181.1 ($M+H^+$) and *m/z* 203.1 ($M+Na^+$). ^{1}H NMR: 0.88 (t, 3H, CH_2*CH_3*), 1.28 (m, 10H, (*CH_2*)$_5$$CH_3$), 1.77 (m, 2H, *$CH_2$*$CH_2$N), 3.92 (t, 2H, *$CH_2$*N), 6.91 (s, 1H, N*CH*=CH), 7.06 (s, 1H, N*CH*=N), 7.47 (s, 1H, CH=*CH*N).

3a: MS *m/z* 237.3 ($M+H^+$). ^{1}H NMR: 0.88 (t, 3H, CH_2*CH_3*), 1.28 (m, 18H, (*CH_2*)$_9$$CH_3$), 1.78 (m, 2H, *$CH_2$*$CH_2$N), 3.92 (t, 2H, *$CH_2$*N), 6.90 (s, 1H, N*CH*=CH), 7.05 (s, 1H, N*CH*=N), 7.47 (s, 1H, CH=*CH*N).

4a: MS *m/z* 265.3 ($M+H^+$) and *m/z* 287.3 ($M+Na^+$). ^{1}H NMR: 0.88 (t, 3H, CH_2*CH_3*), 1.29 (m, 22H, (*CH_2*)$_{11}$$CH_3$), 1.77 (m, 2H, *$CH_2$*$CH_2$N), 3.93 (t, 2H, *$CH_2$*N), 6.91 (s, 1H, N*CH*=CH), 7.07 (s, 1H, N*CH*=N), 7.51 (s, 1H, CH=*CH*N).

5a: MS *m/z* 293.3 ($M+H^+$) and *m/z* 315.2 ($M+Na^+$). ^{1}H NMR: 0.88 (t, 3H, CH_2*CH_3*), 1.29 (m, 26H, (*CH_2*)$_{13}$$CH_3$), 1.77 (m, 2H, *$CH_2$*$CH_2$N), 3.92 (t, 2H, *$CH_2$*N), 6.90 (s, 1H, N*CH*=CH), 7.05 (s, 1H, N*CH*=N), 7.47 (s, 1H, CH=*CH*N).

CMC, γ_{CMC}, Γ_{m}, $A_{\min}$ and pC_{20}

The CMC, γ_{CMC}, Γ_{m}, $A_{\min}$ and pC_{20} are important parameters for surfactants. Figure 1 shows the results of surface tension versus logarithmic concentration of aqueous solutions of five alkylimidazolium bicarbonates.

Table 1 CMC, γ_{CMC}, Γ_m, A_{min} and pC_{20} of alkylimidazolium bicarbonates and alkylimidazolinium bicarbonates

Surfactants	CMC/(mol L^{-1})	γ_{CMC}/(mN m^{-1})	Γ_m/(mol cm^{-2})	A_m/(nm^2)	pC_{20}
Octylimidazolium bicarbonate	5.41×10^{-3}	25.76	1.34×10^{-10}	1.24	3.42
Decylimidazolium bicarbonate	4.56×10^{-3}	29.74	1.70×10^{-10}	0.976	3.17
Dodecylimidazolium bicarbonate	6.05×10^{-4}	28.75	1.74×10^{-10}	0.958	4.75
Tetradecylimidazolium bicarbonate	4.32×10^{-4}	28.09	1.97×10^{-10}	0.844	4.65
Hexadecylimidazolium bicarbonate	3.90×10^{-4}	24.11	2.01×10^{-10}	0.826	4.42
Dodecylimidazolinium bicarbonate	2.04×10^{-3}	29.02	1.53×10^{-10}	1.084	[22]
Tetradecylimidazolinium bicarbonate	1.48×10^{-3}	28.13	1.74×10^{-10}	0.957	[22]
Hexadecylimidazolinium bicarbonate	2.57×10^{-4}	36.37	3.41×10^{-10}	0.487	[22]
Octadecylimidazolinium bicarbonate	1.35×10^{-4}	33.14	2.59×10^{-10}	0.640	[22]

Table 1 lists the values of the CMC, γ_{CMC}, A_{min}, Γ_m and pC_{20} of bicarbonates surfactants.

Generally, CMC values of conventional cationic surfactants decrease as the carbon numbers of hydrophobic chain up to 16 [29]. Table 1 indicates that, from **lb** to **5b**, CMC values of alkylimidazolium bicarbonates decreased from 5.41×10^{-3}, 4.56×10^{-3}, 6.05×10^{-4}, 4.32×10^{-4} to 3.90×10^{-4} mol L^{-1} as the hydrophobic chain increased from 8 to 16, which is consistent with the tendency of the common homologous surfactants [22]. Compared CMC values of alkylimidazolium bicarbonates with alkylimidazolinium bicarbonates which were studied in our previous work [22], also shown in Table 1, as we expected, they all exhibited remarkable physicochemical properties with low CMC and great efficiency in reducing surface tension, but alkylimidazolium bicarbonates presented smaller γ_{CMC} than that of alkylimidazolinium surfactants. It was noteworthy that the CMC values of the alkylimidazolium bicarbonates surfactants were smaller by one order of magnitude while the carbon number of hydrophobic chain increases from 10 to 12. This performance indicates that the surfactants could orient themselves to cause superior surface activity when they absorbed strongly at the air/water interface [30]. The ascending order of γ_{CMC}, Γ_m and A_{min} values were **2b** > **3b** > **4b** > **1b** > **5b**, **5b** > **4b** > **3b** > **2b** > **1b** and **1b** > **2b** > **3b** > **4b** > **5b**, respectively. In Fig. 1, the CMC values of **1b** and **2b** are similar, and the CMC values of **3b**, **4b** and **5b** are close. They are new synthesized CO_2/N_2 triggered switchable surfactants with imidazole group. The difference between them is different length of carbon chains. The changes of CMC between 2**b** and 3**b** caused by the different chain length show that the length at 12 might be a breakpoint of these new surfactants. So before and after the breakpoint the CMC values change slightly. Furthermore, the surface tension of **5b** can reach 24.11 mN m^{-1}. Their surface tensions show conventional rules as the carbon chain increases. The surface tension 24.11 mN m^{-1} of **5b** is a little bit lower for hydrocarbon surfactants, but in our previous work, we also found some lower surface tension as the length of carbon chain increases [31].

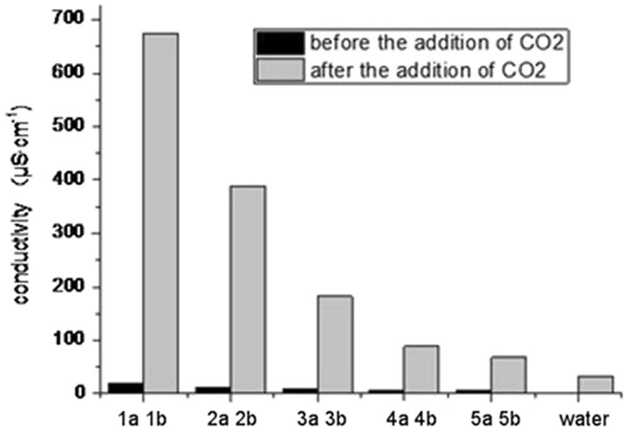


Fig. 2 Conductivity changes before (*black bar*) and after (*gray bar*) addition of CO_2 (**a** and **b** are the changes of blank test)

Conductivity

Alkylimidazoles are neutral and no apparent conductive properties should be shown. After adding CO_2, they are converted into alkylimidazolium bicarbonates cationic surfactants that can be conductive. The conductivity increased almost immediately when CO_2 was bubbled through the solution and decreased again when N_2 was bubbled through. The conductivity changes are compared

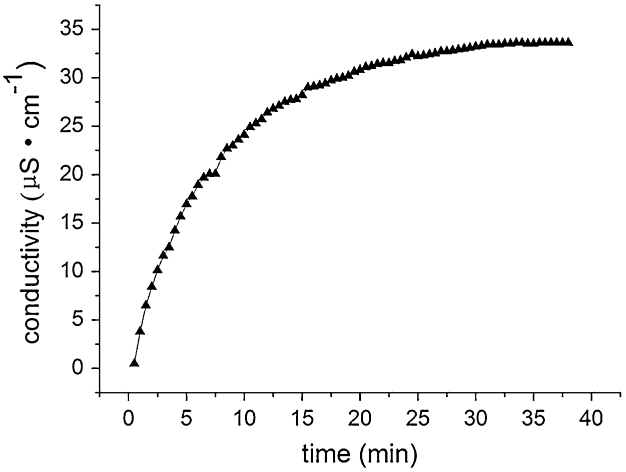


Fig. 3 The conductivity of a deionized water sample treated with CO_2 at 25 °C

in Fig. 2. Figure 2 shows that alkylimidazoles converted into alkylimidazolium bicarbonates after the addition of CO_2, and the resulting conductivity varied greatly. After bubbling CO_2 through **1a, 2a, 3a, 4a,** and **5a** for 20 min, the maximum conductivities reached 674, 388, 182, 88.6 and 68.3 μS cm^{-1}, respectively. After bubbling N_2 through **1b, 2b, 3b, 4b,** and **5b** for 20 min, the minimum conductivities reached 19.8, 12.1, 8.8, 7.1 and 6.5 μS cm^{-1}, respectively.

The conductivity of the deionized water before and after bubbling CO_2 through was measured as a blank control group. Though the conductivity of the blank test changed before and after addition of CO_2, no obvious changes were shown while bubbling CO_2 beyond 15 min. The maximum conductivity reached 33.6 μS cm^{-1} (Fig. 3) while the absorption of CO_2 reaches the maximum. The conductivity variation decreases from 654.2 to 61.8 μS cm^{-1} after bubbling CO_2 as the length of hydrophobic chains increases from 8 to 16. And the variation may be caused by decreases in the solubility and the steric hindrance because of increasingly hydrophobic chains.

Emulsifying Capacity

The emulsifying capacity and emulsion stability of **1b–5b** were confirmed by observing the emulsion states at different times under the same conditions. The results show that all the alkylimidazolium bicarbonates can emulsify decane/water systems with a high-efficiency. The capacity of **2b** for stabilizing the emulsion was evaluated (shown in Fig. 4). From Fig. 4, an emulsion was formed with **2a**, but all the solutions on the left were clearly separated into two layers within 5 min after shaking was stopped. However, if the solution was treated with CO_2 for 20 min (on the right, containing **2b**) before the ultrasonic treatment and shaking, the emulsion was much more stable. There was no evidence of separation for 5 h. At this point a very thin layer of opaque liquid began to appear at the top of test tube. The emulsion still occupied 78 % of the liquid volume even after 1 day (Fig. 4f). The emulsions that were prepared with **1b**, **3b, 4b** and **5b** respectively were all quite stable for more than 5 h.

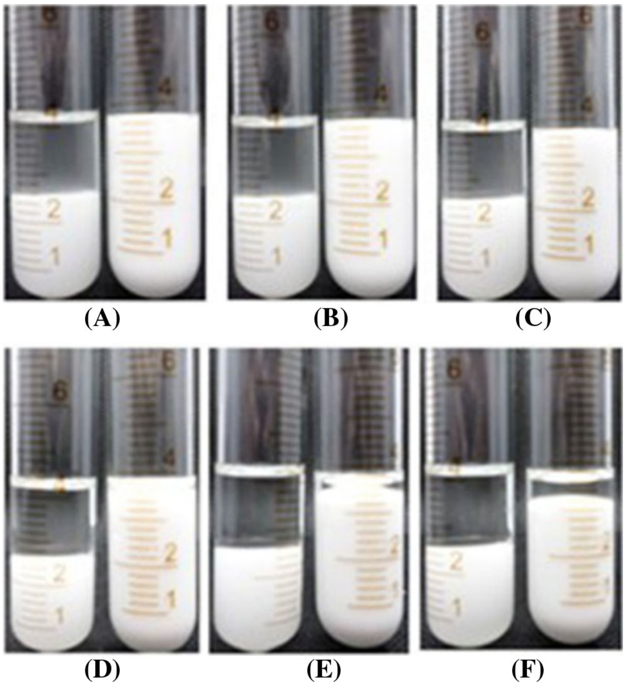


Fig. 4 Photographs of 1:1 (v/v) decane/water mixtures containing **2a** (*left*) and containing **2b** (*right*) after 20 min of ultrasonic treatment and 5 min of shaking followed by a waiting period of **a** 5 min, **b** 30 min, **c** 2 h, **d** 5 h, **e** 15 h and **f** 1 day

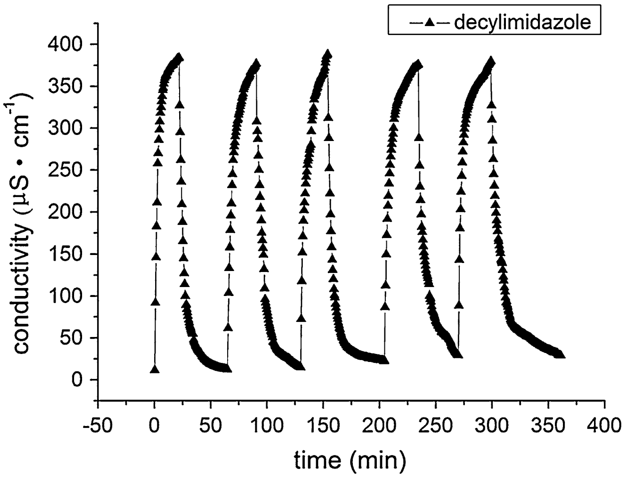


Fig. 5 The conductivity of water solution of **2a** at 25 °C during five cycles of treatment with CO_2 followed by N_2

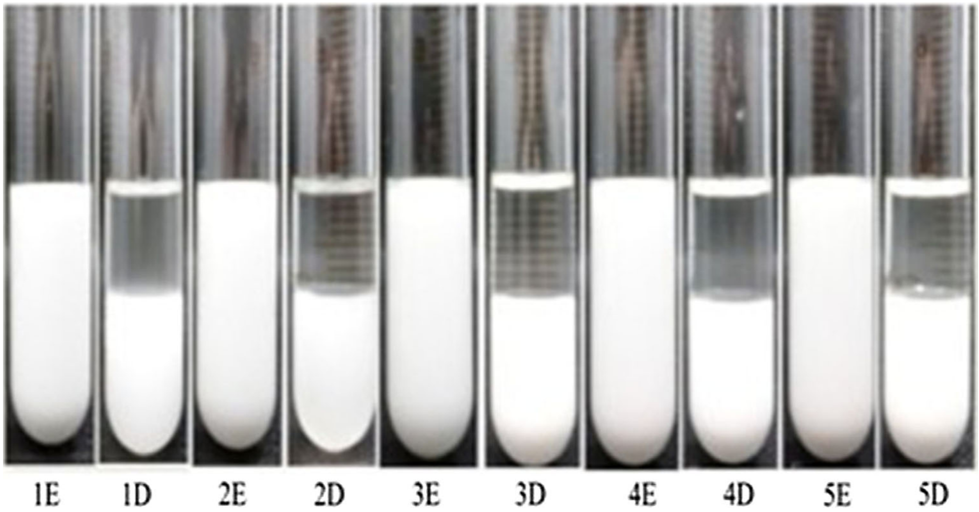


Fig. 6 Photographs of 1:1 (v/v) decane/water mixtures containing **2a** during five cycles of treatment with CO_2 followed by N_2 (E stands for emulsification and D stands for demulsification). *E* Bubbling CO_2 and ultrasonication for 20 min, respectively. *D* Bubbling N_2 for 20 min

Switchable Performance

The reversibility and repeatability of the conversion between uncharged base and cationic surfactant were demonstrated by alternatively bubbling CO_2 and N_2 for five cycles to aqueous solution of **2a** (Fig. 5) and measuring the changes in conductivity of the solution. From Fig. 5, when CO_2 was bubbled through the solution, the conductivity immediately increased, however it declined when N_2 was bubbled. The same processes were repeated for five cycles, and the same observation was observed in all of the repeated cycles. The conductivity changes reversibly, repeatedly and regularly. The variation of conductivity of the blank control group is shown in Fig. 3. The results suggested that the absorption of CO_2 in water did not impact the formation of *N*-alkylimidazolium bicarbonates.

Generally, an interfacial film is formed while surfactants adsorb on the water/oil interface. It has a certain intensity, which can prevent the droplet from aggregating by collision under Brownian motion. So the cationic surfactants, *N*-alkylimidazolium bicarbonates (**1b–5b**) can emulsify a decane/water mixture. By bubbling N_2, the cationic surfactants released CO_2 to convert to neutral alkylimidazoles. The emulsion should be broken. Therefore, we tried to further confirm the switching ability of **2b** by an emulsification–demulsification experiment (shown in Fig. 6). On the one hand, the decane/water mixtures can be emulsified when CO_2 is passed into the test tube followed by ultrasonic treatment for 20 min. On the other hand, the emulsion is demulsified when CO_2 is removed by bubbling N_2 which are only under gravity, meaning a poor emulsion stability because of the decreasing surface activities. The emulsification and demulsification processes were repeated five cycles, and the same observation was taken in all of the repeat cycles.

The results (Fig. 6) show that the emulsification and demulsification of the mixture are reversible, repeatable, and controlled. The key factor is the alkylimidazole group in the system. Alkylimidazole group in the mixture can be switched between a charged state **2b** and an uncharged state **2a** using CO_2/N_2 as the trigger. During the cycles, restoration of the charge is still not sufficient to achieve re-emulsification; the ultrasonic treatment could add some necessary energy to the system, presumably to overcome the free energy required to increase the interfacial area between the two phases and disperse oil finely in the water.

Another important aspect worth noting is that the emulsions are sufficiently stable, no rigorous air-free conditions are necessary, and the condition of demulsification was only the bubbling of N_2 without heating or any other additional measures.

Conclusion

We successfully developed a kind of CO_2/N_2 triggered switchable alkylimidazoles surfactants. This kind of surfactants shows superior surface activity. The CMC and γ_{CMC} of **5b** reach 3.90×10^{-4} mol L^{-1} and 24.11 mN m^{-1}. Conductivities of the surfactants increased almost immediately when CO_2 was bubbled through the solution and decreased rapidly when bubbled through with N_2. The reversible operation could be repeated at least 5 times. The conductivities change greatly after bubbling CO_2. The conductivities of **1a** and **1b** were 19.8 and 674 μS cm^{-1}, respectively. The research reflected the interface behaviors, for example, Γ_m and A_{min} indicated the adsorption ability of the surfactants at the air/water interface. The surfactant molecules acted as an effective stabilizer in the emulsion and it could be easily demulsified by bubbling N_2 at least 5 times without salt, acid, or base as often as required. The emulsions that were prepared with the bicarbonates were all quite stable for more than 5 h. And the emulsion prepared with **2b** occupied 78 % of the liquid volume even after 1 day. By alternatively bubbling CO_2 and N_2 and the alkylimidazole being shifted between cationic and neutral states, the surfactants can easily realize the reversibly switch which was reflected by the conductivity cycles and the emulsification–demulsification switchability.

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