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Ionic liquids as herbicides and plant growth regulators

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ABSTRACT

New ILs containing the (2,4-dichlorophenoxy)acetate anion have been synthesized and characterized (properties, chemical and thermal stability, surface activity). Next, the possibility to use them as herbicides and plant growth regulators has been studied. The obtained ILs exhibited higher biological activity than the currently used herbicide (2,4-D salt) and plant growth regulator (CCC).

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1. Introduction

lonic liquids (ILs), due to their properties and enormous potential application still enjoy a great interest in both academia and industry. They are substances composed exclusively of ions, which form phases that are liquids below $100 \circ C.^{1-6}$ ILs, from dependence on the cation, are divided into: imidazolium, ammonium, pyridinium, phosphonium, piperidinium, morpholinium, sulfonium, and lately pyrylium.⁷ They have negligible vapor pressure under ambient conditions and are usually non-flammable. By modification of the cation and/or anion an enormous range of potential ILs is possible. The evaluation of these compounds proceeds very quickly from the first generation (ILs with unique tunable physical properties) to the second generation (ILs with targeted chemical properties combined with selected physical properties), to the third generation (ILs with targeted biological properties combined with physical and chemical properties).^{8,9}

ILs might be easily adapted toward 'designer drugs', since the physical, chemical, and biological properties of a drug can be tuned by choice of the counterion.¹⁰ Recently the third generation phytopharmaceuticals—herbicidal ionic liquids were published.^{11–13} The novel hydrophobic fungicide with thiabendazole and imidazole as ILs, with increased rain persistence and activity against

0040-4020/\$ – see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2013.03.097 potato tuber diseases are also proposed in the agrochemistry field.¹⁴ Enhanced stabilization of the tobacco mosaic virus using protic ILs has recently been described.¹⁵

Chlormequat chloride—2-chloroethyltrimethylammonium chloride (CCC), was prepared in 1910¹⁶ and described as a plant growth regulator by Tolbert in 1960.^{17,18} It is used to prevent lodging and to increase yields in wheat, rye, oats, and triticale. Moreover, CCC is also applied to increase lateral branching and flowering in some ornamental plants and to increase fruit setting in pears, olives, vines, and tomatoes.¹⁹

(2,4-Dichlorophenoxy)acetic acid (2,4-D) was first described by Zimmerman and Hitchcock.²⁰ This phenoxy acid is a systemic herbicide used in the control of broadleaf weeds and is also a synthetic auxin often used in laboratories for plant research.

Due to the toxicity and side effects of 2,4-D and CCC, their use is heavily criticized. However, these are cheap and widely used, especially 2,4-D. Additionally, both have an ionic structure. For this reason we have decided to use them as substrates in the synthesis of the third generation ILs.

The aim of our work was the synthesis of new salts and the study of the possibility to use them as herbicides and plant growth regulators. In our study we have looked for answers to two basic questions. First, whether these compounds are ionic liquids? Second, whether the activities of the cation and anion are maintained? To answer these questions the chemical and thermal stability, surface and biological activity of 2-chloroethyltrimethylammonium and trimethylvinylammonium (2,4-dichlorophenoxy)acetates have been tested.



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2. Results and discussion

The reaction of sodium (2,4-dichlorophenoxy)acetate with 2-chloroethyltrimethylammonium chloride in water gave 2-chloroethyltrimethylammonium (2,4-dichlorophenoxy)acetate— [CC][2,4-D] in 95% yield (Scheme 1).



Scheme 1. Synthesis of 2-chloroethyltrimethylammonium (2,4-dichlorophenoxy) acetate—[CC][2,4-D], 95% yield.

Exchange of the chloride anion in the quaternary ammonium chlorides was effective. Many quaternary ammonium salts are highly hygroscopic, so water should be avoided as a solvent. Very good results were obtained by using anhydrous methanol as a solvent and a stoichiometric amount of a base (e.g., KOH). In this case, KCl came out of reaction mixture and anhydrous product was obtained after evaporation of the solvent under mild conditions.

For [CC][2,4-D] the exchange reaction could not be carried out in methanol with a base because elimination occurred. [CC][2,4-D] has proved to be unstable in an alkaline medium. In contact with base trimethylvinylammonium (2,4-dichlorophenoxy)acetate was formed—[TMVA][2,4-D] as shown in Scheme 2. The yield was 97%.



Scheme 2. Synthesis of trimethylvinylammonium (2,4-dichlorophenoxy)acetate---[TMVA][2,4-D], 97% yield.

[CC][2,4-D] and [TMVA][2,4-D] can be made anhydrous by heating at 70 °C in vacuo and storing over P₄O₁₀. The water content in the prepared salts was determined to be less than 500 ppm by coulometric Karl Fischer titration. These salts are stable in air and in contact with water and common organic solvents. They are soluble in DMSO, alcohols (methanol, ethanol, and propanol), chloroform and are insoluble in hexane and diethyl ether. The two new salts were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. Generally, we observed specific signals from the anion and cation. The ¹H NMR spectra of the [CC][2,4-D] and [TMVA][2,4-D] indicate significantly different chemical shifts for the N⁺(CH₃)₃ protons (move over 0.20 ppm). Moreover, signals from protons of 2chloroethyl group—N⁺CH₂CH₂Cl (3.80 and 4.09 ppm) for [CC][2,4-D] are absent on the [TMVA][2,4-D] spectra, which possess three characteristic signals for the vinyl substituent (5.50, 5.80, and 6.77 ppm). The ¹³C NMR spectra present similar differences in chemical shifts of the methyl groups in the cation $-N^+(CH_3)_3$, in the range 0.69 ppm. Signals of the carbons from the 2-chloroethyl group (36.42 and 64.83 ppm) in [CC][2,4-D] spectra are replaced by two peaks characteristic for the vinyl group (111.24 and 143.20 ppm).

The values of $T_{\text{onset5\%}}$ and T_{onset} , determined using TGA, for [CC] [2,4-D] were equal to 180 and 255 °C, respectively, and for [TMVA] [2,4-D]: 170 and 240 °C. Additional physicochemical data were provided by DSC analysis. For [CC][2,4-D] there was only the glass transition temperature at 8 °C. For [TMVA][2,4-D] the glass transition was observed at -16 °C, the temperature of crystallization at 10 °C and the melting point at 16 °C. At room temperature [CC][2,4-D] is a solid and melts at 92–94 °C, and [TMVA][2,4-D] is a liquid of high viscosity. The synthesized [CC][2,4-D] and [TMVA][2,4-D] salts can be classified as ionic liquids. This is the answer to the first question posed at the beginning of our work.

The product of dehydrochlorination of CCC or [CC][2,4-D] via elimination was a vinyl group attached to the nitrogen atom (Scheme 3). The reactions order (*n*) was calculated by the Ostwald–Zawicki method. It has been found that it is an E2 elimination reaction.



Scheme 3. Elimination reaction in 2-chloroethyltrimethylammonium cation, when X=Cl or 2,4-D anion.

The change in concentration as time function during the reaction between CCC or [CC][2,4-D] and potassium hydroxide in water at 30 °C, with 0.100 mol L^{-1} initial concentration of both reactants, is shown in Fig. 1.



Fig. 1. Concentration versus time for the decomposition of CCC and [CC][2,4-D] in water at 30.0 $^\circ C$ (303.2 K).

At low temperatures (20-40 °C) there is a considerable impact on elimination reaction kinetics as is shown in Fig. 1. It is noticeable that the reaction rate of degradation (*k*) for CCC is approximately 2.5 times greater than for [CC][2,4-D] at 30.0 °C (303.2 K). At this temperature [CC][2,4-D] is decomposed much slower than CCC. The linear relationship in the Arrhenius plots demonstrates the correct assumption of the kinetic equation and reaction order (Fig. 2). It means that the reaction with the participation of [CC][2,4-D] is less dependent on the temperature.



Fig. 2. Arrhenius plot of CCC and [CC][2,4-D] E2 elimination reaction in water.

Table 1 summarizes a series of calculated kinetic parameters: reaction half-life ($\tau_{1/2}$), activation energy (E_a), enthalpy of activation

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Table 1				
Summarv	of	calculated	kinetic	parameters

Table 1

Substrate	Temp [K]	k (L mol ⁻¹ min ⁻¹)	$\tau_{1/2}$ (min)	$E_{\rm a}$ (kJ mol ⁻¹)	ΔH^{\neq} (kJ mol ⁻¹)	ΔS^{\neq} (kJ mol ⁻¹ K ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)
CCC	293.2	0.011	952.4	85.6	83.2	-33.0	92.8
	303.2	0.034	295.0		83.1	-33.1	93.1
	313.2	0.105	95.5		83.0	-33.1	93.4
	323.2	0.261	38.3		82.9	-34.2	94.0
	333.2	0.734	13.6		82.8	-33.8	94.1
[CC][2,4-D]	293.2	0.004	2564.1	81.7	104.4	-47.0	93.1
	303.2	0.014	694.4		104.3	-48.0	93.8
	313.2	0.067	148.4		104.2	-47.7	94.1
	323.2	0.235	42.5		104.2	-48.2	94.6
	333.2	0.691	14.5		104.1	-48.2	95.0

 (ΔH^{\neq}) , entropy of activation (ΔS^{\neq}) , Gibbs free energy of activation (ΔG^{\neq}) . Bimolecular dehydrochlorination of [CC][2,4-D] requires less activation energy by about 4 kJ mol⁻¹ than CCC. The activation entropy is strongly negative. This phenomenon could be explained by the fact that on the route from the initial to the transition state, vibrational, rotational, and translational motion is extremely restricted.

Both growth chamber and field experiments were conducted for [CC][2,4-D] and dimethylammonium (2,4-dichlorophenoxy)acetate (the active ingredient of the commercial used herbicide)—[DMA] [2,4-D]. A preliminary study conducted in a growth chamber indicated that the new form of 2,4-D has a better activity compared with used commercial product. The results of this experiment, presented in Table 2, show that the fresh weight reduction of white mustard (*Sinapis alba*) was higher when [CC][2,4-D] was used. The activity of this IL increased with increasing the concentration from 0.005 M to 0.01 M.

Table 2

Efficacy of [CC][2,4-D] and [DMA][2,4-D] against white mustard (*Sinapis alba*) in growth chamber experiment

Treatments	Concentration	ntration Dose (g ha^{-1})		Fresh weight	
			CCC	reduction (%)	
[CC][2,4-D]	0.005 M	220	158	50	
[CC][2,4-D]	0.01 M	440	316	75	
[DMA][2,4-D]	0.01 M	600 ^a	0	68	

^a Dose recommended in spring cereals.

[CC][2,4-D] used at rate corresponding to 440 g ha⁻¹ of 2,4-D free acid was more active than [DMA][2,4-D] used at rate of 600 g ha⁻¹. The better herbicidal activity of [CC][2,4-D] compared to [DMA][2,4-D] was also confirmed in field experiments carried out in spring wheat and spring barley. The results showed in Table 3 indicate that the control of common lambsquarters (*Chenopodium album*) by the new form of 2,4-D was more effective compared to commercial [DMA][2,4-D]. The differences between treatments were higher in 2011 when there were dramatically low amount of rainfall in spring. In other experiment carried out in spring wheat we obtained similar results. The control of both common lambsquarters and cornflower (*Centaurea cyanus*) was better when [CC] [2,4-D] was used (Table 4).

Table 3

The control of common lambsquarters by different forms of 2,4-D applied in spring barley

Treatments ^a	2011	2012	
	% of fresh weigh	t reduction	
[CC][2,4-D]	95	72	
CCC+[DMA][2,4-D] ^b	—	61	
[DMA][2,4-D]	47	54	
^a In all treatments the rate of 2.4-D was 450 g ha ^{-1} .			

^b Tank mixture of commercial products.

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Table 4

The influence of different forms of 2,4-D on weed control, stems length and yield of spring wheat

Treatments ^a	Chenopodium album	Centaurea cyanus	Stems length (cm)	Yield t ha ⁻¹
	Weed control (%)			
[CC][2,4-D]	87	94	86.2	6.26
CCC+[DMA] [2,4-D] ^b	85	93	90.0	5.98
[DMA][2,4-D]	79	70	101.0	6.15
Untreated check	0	0	101.5	6.23

^a In all treatments the rate of 2,4-D was 450 g ha⁻¹.

^b Tank mixture of commercial products.

[CC][2,4-D] showed very good herbicidal activity as well as plant growth inhibition activity. The shorter stems are more resistant to lodging, which can decrease the yield of cereals. Therefore this compound can be used not only for effective weed control in cereals, but also for preventing the crop lodging. The combining the herbicidal activity of this compound with inhibition of cereals stem elongation is a unique solution for growers.

[CC][2,4-D] were selective to the cereals and showed a profitable influence on the spring wheat yield. On the second question posed at the beginning of our work, we have received a positive response. Under the same conditions [TMVA][2,4-D] was tested. This new IL retained only herbicidal activity. The 2-chloroethyl group decides that the compound is classified as a plant growth regulator.

Critical micelle concentration (CMC), surface tension, and contact angle values of the synthesized ILs are shown in Table 5. In addition, surface activities for CCC and [DMA][2,4-D] are given.

Table 5	
The CMC, surface tension (γ_{CMC}), and contact angle CA (paraffin) of aqueous soluti	on
of salts, at 25 °C	

Salt	CMC (mol L^{-1})	$\gamma_{CMC} (mN m^{-1})$	CA (°)
[CC][2,4-D]	0.158	41.5	71.7
[TMVA][2,4-D]	0.079	36.7	63.4
CCC	0.201	47.1	84.7
[DMA][2,4-D]	0.086	52.5	89.1

In comparison with the standard herbicide ([DMA][2,4-D]) and plant growth regulator (CCC) the designed values of surface tension and contact angles for the synthesized ILs were significantly lower. In accordance with our expectations, the results of surface tension measurements were consistent with biological data of [CC][2,4-D] and [TMVA][2,4-D]. The low value of contact angle and surface tension should result in good wetting of plants, enhancing spray retention, absorption, cuticle penetration, and translocation of active ingredient. 4

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3. Conclusion

New ionic liquids: 2-chloroethyltrimethylammonium and trimethylvinylammonium (2,4-dichlorophenoxy)acetates were synthesized in high yields. The obtained salts exhibited higher surface activity than the currently used herbicide (2,4-D salt) and plant growth regulator (CCC). The biological activities of the 2-chloroethyltrimethylammonium cation and (2,4-dichlorophenoxy) acetate anion were maintained in the new IL. In conclusion, [TMVA] [2,4-D] and [CC][2,4-D] showed very good herbicidal activity, and [CC][2,4-D] could also be used as a plant growth regulator.

4. Experimental section

4.1. General

¹H NMR spectra were recorded on a Mercury Gemini 400 spectrometer operating at 400 MHz with tetramethylsilane as the internal standard. ¹³C NMR spectra were obtained with the same instrument at 100 MHz. CHN elemental analyses were performed at Adam Mickiewicz University, Poznan (Poland).

4.2. Preparation

4.2.1. 2-Chloroethyltrimethylammonium (2,4-dichlorophenoxy)-acet ate—[CC][2,4-D]. In a round-bottom flask, equipped with reflux condenser and dropping funnel, the sodium salt of (2,4dichlorophenoxy)acetic acid (0.03 mol), dissolved in distilled water (30 mL) was added. Then a stoichiometric amount of 2chloroethyltrimethylammonioum chloride was added and the mixture was stirred for 3 h at room temperature. The water was evaporated using a rotary evaporator and the residue was dissolved in methanol. The product, deposited in the methanol phase, was separated from the insoluble inorganic salt-sodium chloride. After removal of methanol the product was dried under reduced pressure at 70 °C for 24 h. The obtained compound was solid at room temperature and the reaction yield was 95%. ¹H NMR (DMSO- d_6 , 298 K, 400 MHz) δ ppm=3.18 (s, 9H, (CH₃)₃N⁺), 3.80 (t, J=7.0 Hz, 2H, N⁺CH₂CH₂Cl), 4.09 (t, J=7.0 Hz, 2H, N⁺CH₂CH₂Cl), 4.28 (s, 2H, OCH2COO⁻), 6.84 (d, J=8.9 Hz, 1H, ClCCH=CHC), 7.26 (dd, J^{1,2}=8.8 Hz, J^{1,3}=2.6 Hz, 1H, ClCCH=CHC), 7.47 (d, J=2.6 Hz, 1H, CICCH=CCI); ¹³C NMR (DMSO- d_6 , 298 K, 100 MHz) δ ppm=36.42, 52.59, 64.83, 68.35, 114.95, 121.63, 123.05, 127.51, 128.75, 153.66, 168.79. Elemental analysis calcd (%) for C₁₃H₁₈Cl₃NO₃ (*M*=342.65) C 45.57, H 5.29, N 4.09; found: C 45.83, H 5.22, N 4.15; IR (KBr) *v*_{max}: 3364, 3076, 3023, 2968 (-CH2-CH2Cl, C-Hst, m), 1645, 1606, 1484, 1476, 1464 (-CH₂-CH₂Cl, C-H_δ, m), 1430, 1424, 1389, 1347, 1331, 1283, 1264, 1252, 1231, 1154, 1104, 1066, 1037, 975, 951, 919, 896, 869, 838, 802, 775, 734 (-CH2-CH2Cl, C-Clst, m), 722, 699, 648, 556 cm^{-1} .

4.2.2. Trimethylvinylammonium (2,4-dichlorophenoxy)acetate— [TMVA][2,4-D]. In a round-bottom flask 2-chloroethyltrimethylammonioum (2,4-dichlorophenoxy)acetate (0.02 mol) was dissolved in distilled water (15 mL). Then, a stoichiometric amount of KOH, dissolved in distilled water, was added and the mixture was stirred for 24 h at 50 °C. Then, water was evaporated using a rotary evaporator and the residue was dissolved in acetonitrile. The inorganic by-product (potassium chloride) precipitated as a white solid and was separated carefully from the solution. After removal of acetonitrile the product was dried under reduced pressure at 70 °C for 24 h. The reaction yield was 97%. ¹H NMR (DMSO-*d*₆, 298 K, 400 MHz) δ ppm=3.38 (s, 9H, (CH₃)₃N⁺), 4.23 (s, 2H, OCH₂COO⁻), 5.50 (m, 1H, N⁺CH=CHH), 5.80 (d, J=15.3 Hz, 1H, N⁺CH=CHH), 6.77 (m, 1H, N⁺CH=CH₂), 6.84 (d, J=9.0 Hz, 1H, CICCH=CHC), 7.29 (dd, J^{1,2}=9.0 Hz, J^{1,3}=2.7 Hz, 1H, CICCH=CHC),

7.47 (d, *J*=2.6 Hz, 1H, ClCC*H*=CCl); ¹³C NMR (DMSO-*d*₆, 298 K, 100 MHz) δ ppm=53.28, 68.67, 111.24, 114.97, 121.56, 122.88, 127.50, 128.68, 143.20, 153.76, 168.67. Elemental analysis calcd (%) for C₁₃H₁₇Cl₂NO₃ (*M*=306.18) C 51.00, H 5.60, N 4.57; found: C 50.79, H 5.41, N 4.41; IR (KBr) ν_{max} : 3306, 3087 (-CH=CH₂, C-H_{st}, m), 3018, 2970, 2926, 1657 (-CH=CH₂, C=C_{st}, m), 1644, 1609, 1483, 1430, 1424, 1390, 1347, 1282, 1266, 1244, 1231, 1159, 1107, 1064, 1044, 950 (-CH=CH₂, C=H_{\delta}, m), 895, 868, 836, 801, 764, 722, 715, 697, 685, 647, 556 cm⁻¹.

4.3. Thermal analysis

Thermal transitions of the prepared salts were determined by DSC, with a Mettler Toledo Star^e TGA/DSC1 (Leicester, UK) unit, under nitrogen. Samples between 5 and 15 mg were placed in aluminum pans and heated from 25 to 120 °C at a heating rate of 10 °C min⁻¹ and cooled with an intracooler at a cooling rate of 10 °C min⁻¹ to -100 °C. Thermogravimetric analysis was performed using a Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK) under nitrogen. Samples between 2 and 10 mg were placed in aluminum pans and heated from 30 to 450 °C at a heating rate of 10 °C min⁻¹.

4.4. Kinetics analysis

During the kinetics measurements, constant temperature was maintained with an accuracy of 0.1 °C. Concentration of reactants in water was determined using a new generation of semi-automated reactor system for the laboratory synthesis—EasyMax[™] from Mettler Toledo. The temperature of the reactor contents was controlled with an accuracy of 0.01 °C using a Pt100 sensor. Connecting SevenMulti Mettler Toledo instrument, equipped with a suitable electrode allowed for precise measurement of decrease in pH of the mixture as a result of proceeding reaction.

The reactions order (n) was calculated by the Ostwald–Zawicki method, using the equation:

$$n = 1 + \frac{\log\left(\frac{\tau_{1/2, l}}{\tau_{1/2, l}}\right)}{\log\left(\frac{Cm_{0, l}}{Cm_{0, l}}\right)}$$

where: $\tau_{1/2}$ is the reaction half-life, and Cm₀ is the initial concentration of reactants. Measurements of $\tau_{1/2}$ were performed both in water at initial concentrations of both reactants equal to 0.100 and 0.050 mol L⁻¹.

Activation energy (E_a) and entropy (ΔS^{\neq}) were calculated from the equation of Arrhenius and Eyring.

4.5. Growth chamber experiment

The seeds of white mustard (*Sinapis alba*) were sown into soilfilled plastic pots to the depth of 1 cm. After emergence the plants were thinned to 5 plants in each pot. The treatments were applied at fourth leaf stage using a spray chamber with Tee Jet 1102 flat-fan nozzles delivering 200 L of spray solution per 1 ha at 0.2 MPa pressure. The sprayer was moving above the plants at a constant speed of 3.1 m s⁻¹. The distance from nozzles to the tips of the plant was 40 cm. The plants were treated once with a water solution of tested herbicides and they were placed in a growth chamber at a temperature of 20 °C, humidity of 60% and photoperiod (day/night hours)—16/8. The standard herbicide was the commercial product containing [DMA][2,4-D] (Aminopielik Standard 600 SL—600 g 2,4-D per 1 L).

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The study was carried out in 4 replications in a completely randomized setup. After 2 weeks, the plants were cut to soil level and weighed (0.1 g accuracy). The reduction of plant fresh weight as compared to control (no sprayed plants) was measured.

4.6. Field experiments

The field trials were carried out in spring wheat (2009) and spring barley (2011 and 2012) at the Experimental Station in Winna Gora, western Poland (E: $17^{\circ}26'$, N: $52^{\circ}12'$). Cereals were cultivated according to the local agricultural practice. Plot size was 16.5 m^2 . The experimental design was a randomized block with four replications. The water solutions of the tested herbicides were applied at the end of tillering (BBCH 30) using a small plot spraying equipment with XR 11003 flat-fan nozzles with a water volume of 200 L ha⁻¹ and an operating pressure of 0.3 MPa. The standard products were the herbicide containing [DMA][2,4-D] (Aminopielik Standard 600 SL—600 g 2,4-D per 1 L) and plant growth regulator containing chlormequat chloride—CCC (Antywylegacz Plynny 725 SL—725 g CCC per 1 L). The doses used in the experiments were showed in the Tables with results.

Weed control was evaluated visually 4 weeks after herbicide application using a scale of 0 (no control) to 100% (complete weed destruction). In spring barley the reduction of weed species fresh weight as compared to control (no sprayed plants) was measured. In this case 4 weeks after treatments the plants were cut right to the soil level and weighed (0.1 g accuracy). The stem lengths of 25 randomly chosen plants on each plot were measured from soil level to the tip of ears at growth stage when grains reached final size (scale BBCH 77).

4.7. Surface activity

Surface tension measurements were carried out by the use of a DSA 100 analyzer (Krüss, Germany, accuracy+0.01 mN m⁻¹), at 25 °C. The surface tension was determined using the shape drop method. Basically, the principle of this method is to form an axisymmetric drop at the tip of a needle of a syringe. The image of the drop (3 mL) is taken from a CCD camera and digitized. The surface tension (g in mN m⁻¹) is calculated by analyzing the profile of the drop according to the Laplace equation. Temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy +0.1 °C). The values of the critical micelle concentration (CMC) and the surface tension at the CMC (γ_{CMC}) were determined from the intersection of the two straight lines drawn in low and high concentration regions in surface tension curves (γ vs log *C* curves) using a linear regression analysis method.

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