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Synthesis and surface activities of organic solvent-soluble fluorinated surfactants

Guo-Li Li [a,b], Li-Qiang Zheng [a,*], Jin-Xin Xiao [c,**]

[a] Key Laboratory for Colloid and Interface Chemistry of Education Ministry, Shandong University, Jinan 250100, PR China
[b] School of Light Chemical and Environmental Engineering, Shandong Institute of Light Industry, Jinan 250353, PR China
[c] Beijing FLUOBON Surfactant Institute, Beijing 100080, PR China

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A variety of fluorinated surfactants soluble in organic solvent were prepared, including $C_8F_{17}SO_2NHC_nH_{2n+1}$ ($n = 2, 4, 6, 8, 10$), $C_8F_{17}SO_2NHR$ ($R = C_6H_{11}, C_6H_5$), $C_8F_{17}SO_2N(C_nH_{2n+1})_2$ ($n = 1, 2, 3, 4$) and $C_8F_{17}SO_2NH(CH_2)_nNHO_2SC_8F_{17}$ ($n = 6, 10$). Their surface activities in various organic solvents were determined by surface tension measurement. The results showed that these fluorinated surfactants can reduce the surface tension of both polar and non-polar organic solvents. In general, organic solvents with strong polarity or long alkyl chain are beneficial to increase the surface activity of these polar fluorinated surfactants. By comparing fluorinated surfactants with the same fluorocarbon segment and connecting group, $C_8F_{17}SO_2N(C_nH_{2n+1})_2$ ($n = 1, 2, 3, 4$) showed lower surface activity in organic solvents than $C_8F_{17}SO_2NHC_nH_{2n+1}$ ($n = 2, 4, 6, 8$) with an equal carbon number of the solvophilic group. Through surface tension vs. concentration curves given for *N*-octyl perfluorooctanesulfonamide in various organic solvents, a break point like the critical micelle concentration of ordinary surfactants in aqueous solutions was observed, and the effect of the different types of organic solvents on adsorption and aggregation behavior was also studied.

1. Introduction

Fluorinated surfactants, containing fluorocarbon chains as hydrophobic groups, have a number of special properties such as chemical inertness, thermal stability, high surface activity and water and oil repellence that offer advantages over hydrocarbon surfactants [1]. Among all surfactants, fluorinated surfactants are most effective in reducing the surface tension of aqueous solutions [2]. Their outstanding chemical and thermal stability expands their applications to extreme conditions which are too severe for hydrocarbon surfactants [3].

Utilization of surfactants is most frequently implemented in aqueous systems. However, there are many cases of non-aqueous systems, such as the coating industry, paint industry, petroleum exploitation, and extraction process and micelle catalysis. Conventional surfactants used in aqueous systems that combine two basically different parts, at least one hydrophobic and one hydrophilic group, are not as effective in organic solvents as in water. It is known that conventional surfactants orient with the hydrophilic group away from organic solvent surface, which results in a higher surface energy and an increase of surface tension of the organic solvent [4]. Therefore, structural requirements for a surfactant in organic solvents should be different from those of conventional surfactants.

Previous investigations have shown that fluorinated surfactants consisting of solvophobic and solvophilic segments in the molecule could be adsorbed at organic solvent/air interfaces as monomolecular films, thus depressing the surface tension of the organic solvent. Such investigations have thrown light on the study of fluorinated surfactants in organic solvents [5–12]. Several fluorinated surfactants such as $F[CF(CF_3)CF_2O]_nCF(CF_3)–COAr$, ($Ar$ = aryl group, $n = 1–4$) [13], $F[CF(CF_3)CF_2O]_nCF(CF_3)–C_6H_5$ ($n = 1, 2$) [14], semifluorinated diblock copolymers based on methyl methacrylate and 1*H*, 1*H*, 2*H*, 2*H* perfluoroalkyl methacrylate [15], fluoroalkyl end-capped diacetone (*N*-1,1-dimethyl-3-oxobutylacrylamide) oligomers [16], fluoroalkyl end-capped cooligomers containing polydimethylsiloxane and polyoxyethylene segments [17] were found to be effective in reducing the surface tension of *m*-xylene, while their surface tension curves exhibited a clear break point like the critical micelle concentration of ordinary surfactants in aqueous solutions. These findings suggest that these fluorinated surfactants can form self-assembled molecular aggregates in aromatic solvents. Also some semifluorinated alkanes which possess no charged or polar groups were found to aggregate in either hydrocarbon or fluorocarbon solvents when the incompatibility between the semifluorinated alkanes and solvents is sufficiently strong [18–21].

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[*] Corresponding author. Tel.: +86 531 88366062; fax: +86 531 88564750.
[**] Corresponding author. Tel.: +86 10 62561871; fax: +86 10 62561871.
E-mail addresses: lqzheng@sdu.edu.cn (L.-Q. Zheng), xiaojinxin@pku.edu.cn (J.-X. Xiao).

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Surface activities of fluorinated surfactants at the air/organic solvent interface have been studied since the 1950s [5]. However, rather little work has been reported in recent decades [22–27]. *N*-Alkyl perfluorooctanesulfonamides have been widely used in fabrics and papers, fire retardants, anticorrosion agents, and many other commercial formulations [5,28]. To our knowledge, there is little information available in the literature about the surface activity of derivations of *N*-alkyl perfluoralkylsulfonamides.

In this work, we synthesized a series of *N*-alkyl perfluoralkylsulfonamides as organic solvent-soluble fluorinated surfactants in which straight, branched and cyclic alkyls and phenyl acted as solvophilic segment and single or double fluorocarbon chains as solvophobic segment. Surface activities of these surfactants in organic solvents including aliphatic, aromatic and non-protonic polar solvents were determined by surface tension measurement. Also, the relationship between surface activity and molecular structure of the organic solvent-soluble fluorinated surfactants as well as the type and structure of organic solvents was discussed. The surface adsorption state and surface adsorbed layer of fluorinated surfactants were also discussed.

2. Results and discussion

2.1. Surfactant structure

The nature of common surfactants is based on the chemical antipathy of the surfactant head and tail, and on their opposite sympathy for water molecules. The situation is different in organic solvents. Surfactants which operate in organic solvent are generally composed of a solvophobic group and a solvophilic group within the same molecule. The hydrocarbon tail, hydrophobic in water, may be the solvophilic group providing solubility in organic solvents and the fluorinated alkyl tail may be the solvophobic group. Such surfactants are expected to adsorb at the organic solvent/air surface to form a monolayer in which the fluorocarbon segment of the surfactant tilts away from the surface. Thus their surface tension is expected to be reduced to a low value as a result of low cohesive energy density of perfluorocarbons [29]. In this work, perfluorooctanesulfonyl fluoride was used as the raw material in view of its cheapness. Three series of fluorinated surfactants were designed as following:

(1) R_F–Q–R_H. where $R_F = C_8F_{17}$, Q = SO_2NH, $R_H = (CH_2)_nH$ (n = 2, 4, 6, 8, 10), C_6H_{11}, C_6H_5.
(2) R_F–Q–$(R_H)_2$. where $R_F = C_8F_{17}$, Q = SO_2N, $R_H = (CH_2)_nH$ (n = 1, 2, 3, 4).
(3) R_F–Q–R_H–Q–R_F. where $R_F = C_8F_{17}$, Q = SO_2NH, $R_H = (CH_2)_n$ (n = 6, 10).

2.2. The choice of organic solvent

Compared with aqueous solutions, various organic solvents used to dissolve surfactant may enlarge the research system and present diversified properties. Considering the extensive application and the solvent cost, a wide variety of organic solvents including alkanes (*n*-dodecane, *n*-tetradecane, *n*-hexadecane and liquid paraffin), cyclanes (cyclohexane), aromatic hydrocarbons (toluene and *m*-xylene), polar solvents (ethyl acetate, 2-butanone, nitromethane, DMF, and DMSO) were selected for further investigation.

2.3. Surface activity of surfactants in organic solvent

Surface activity results of each synthesized fluorinated surfactant in saturated solutions of various solvents are presented in Table 1′ (see supporting information) and Table 1. In this work, the effectiveness of the fluorinated surfactants was expressed by the maximum reduction of surface tension of the organic solvents, $\Delta\gamma$.

$$\Delta\gamma = \gamma_{\mathrm{solvent}} - \gamma_{\mathrm{solution}} \quad (1)$$

where $\gamma_{\mathrm{solvent}}$ is the surface tension of pure solvent, and $\gamma_{\mathrm{solution}}$ is the surface tension of the saturated solution. Most of surfactant solutions became saturated at concentration lower than 0.05 M. The lower the total concentration at which a small amount of precipitate was observed to appear in solution, the lower the solubility was. And at a same total concentration, more precipitate existed in solution, the lower solubility of surfactant was. However, for some solvents in which surfactants were too soluble, the effectiveness of surfactants was calculated on the basis of a 0.05 M solution (footnote a). For example, the solution of surfactants in DMF remained homogeneous even at 0.2 M. The results in Table 1′ (see supporting information) should be quite comparable because only a small concentration of an effective surfactant can give the maximum possible surface tension lowering of solvents [11]. Besides, the surface tension of a solution containing 0.05 M of surfactant amounts to the value which is very close to the surface tension of a saturated solution.

From Table 1′ (see supporting information), it can be seen that the synthesized fluorinated surfactants can reduce the surface tension of both polar and non-polar organic solvents. In all cases, the surface tension depression is smaller than 21 mN/m. However, common fluorinated surfactants can lower the surface tension of water by more than 50 mN/m. Surfactants are not as effective in organic solvents as in water because of two reasons. First, the initial surface tension of organic solvents, 19–30 mN/m for most of hydrocarbon solvents, is much lower than that of pure water

Table 1
Surface tension of saturated solution of surfactant containing double fluorocarbon chains in various organic solvents at 25 °C.

Surfactant	R_H	Solvent	$\gamma_{\mathrm{solution}}$ (mN m^{-1})	$\Delta\gamma$
$C_8F_{17}SO_2NH–R_H–NHO_2SC_8F_{17}$	$(CH_2)_6$	Toluene	24.6	2.1
		m-xylene	24.3	2.7
		DMSO	24.0	17.5
		Nitromethane	23.7	10.8
		DMF	22.0	12.6
		2-butanone	19.5	2.8
		Ethyl acetate	20.9	1.4
	$(CH_2)_{10}$	Toluene	24.7	2.0
		m-xylene	24.9	2.1
		DMSO	26.6[a]	14.9
		Nitromethane	24.1	10.4
		DMF	28.4[a]	6.2
		2-butanone	20.9	1.4

R_H, the solvophilic group of fluorinated surfactant.
[a] Minimum surface tension at concentration 0.05 mol l^{-1}.

(72 mN/m, 25 °C). Second, the free energy cost of transferring a –CF_2– group from the pure fluorocarbon to an alkane solution is approximately 1.4 kJ/mol, whereas the cost of transferring a –CF_2– from fluorocarbon to water is 6.5 kJ/mol [30].

As expected, there is a close relationship between the structure of the solvophobic and solvophilic constituents of surfactant molecules, the property of organic solvents, and the surface activity of surfactants. That is why a fluorinated surfactant cannot have the same optimum structure for all organic solvents [14]. In order to clarify the effect of surfactant structure on the decrease of surface tension of various organic solvents, Figs. 1–3 were drawn according to corresponding results in Table 1′ (see supporting information).

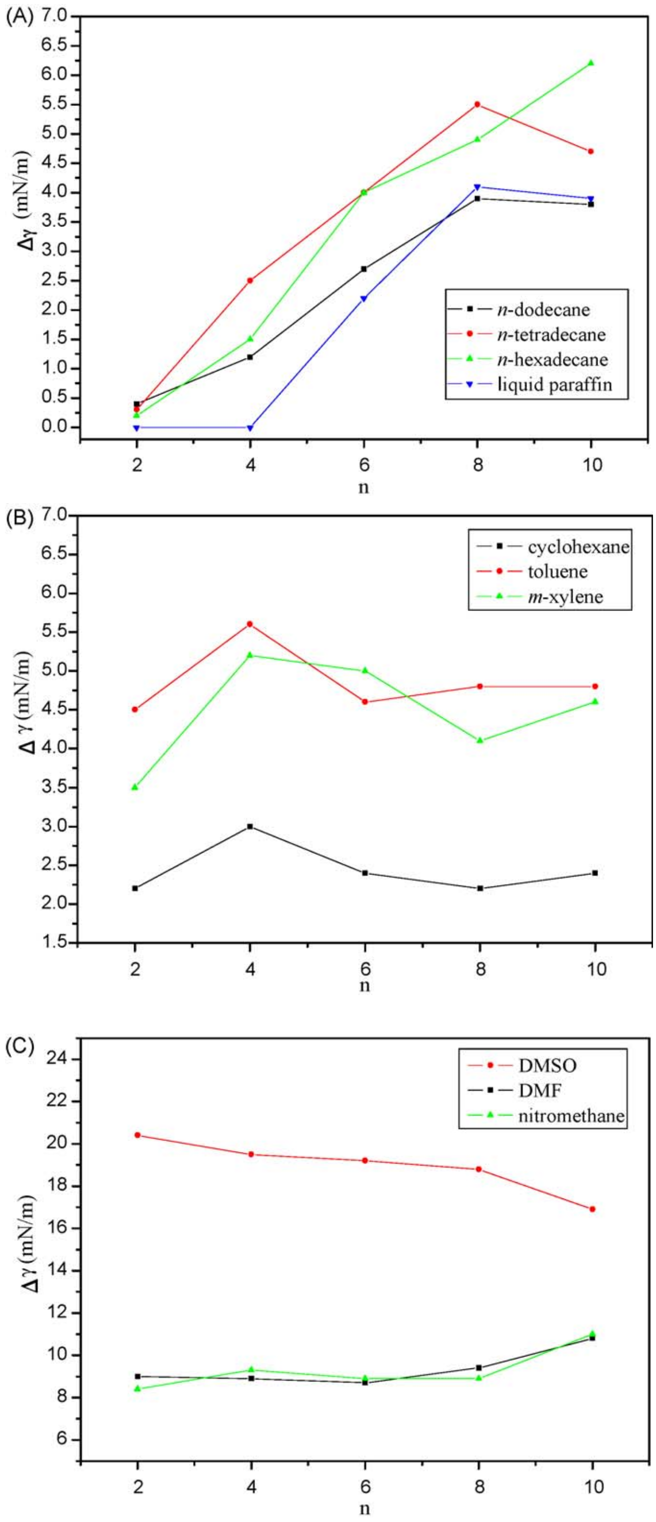

Fig. 1. Relationship between the decrease of surface tension of organic solvents and the carbon atom numbers of single alkyl chain of $C_8F_{17}SO_2NHC_nH_{2n+1}$ at 25 °C. (A) alkanes; (B) cyclohexane and aromatic solvents; (C) polar solvents. $\Delta\gamma = \gamma_{\text{solvent}} - \gamma_{\text{solution}}$ indicates the effectiveness of the surfactant in lowering the surface tension of the solvent; n, the carbon atom numbers of single alkyl of $C_8F_{17}SO_2NHC_nH_{2n+1}$.

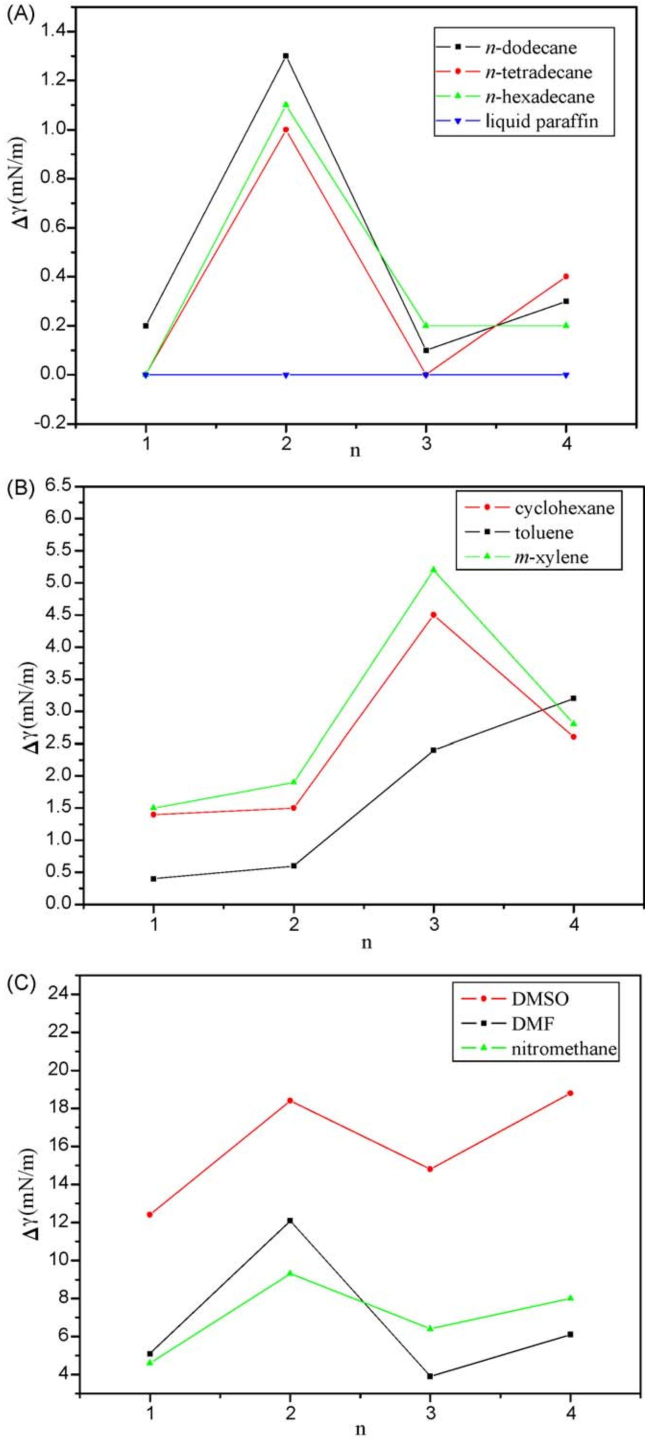

Fig. 2. Relationship between the decrease of surface tension of organic solvents and the carbon atom numbers of double alkyl chains of $C_8F_{17}SO_2N\ (C_nH_{2n+1})_2$ at 25 °C. (A) alkanes; (B) cyclohexane and aromatic solvents; (C) polar solvents. $\Delta\gamma = \gamma_{\text{solvent}} - \gamma_{\text{solution}}$ indicates the effectiveness of the surfactant in lowering the surface tension of the solvent; n, the carbon atom numbers of solvophilic segment of $C_8F_{17}SO_2N\ (C_nH_{2n+1})_2$.

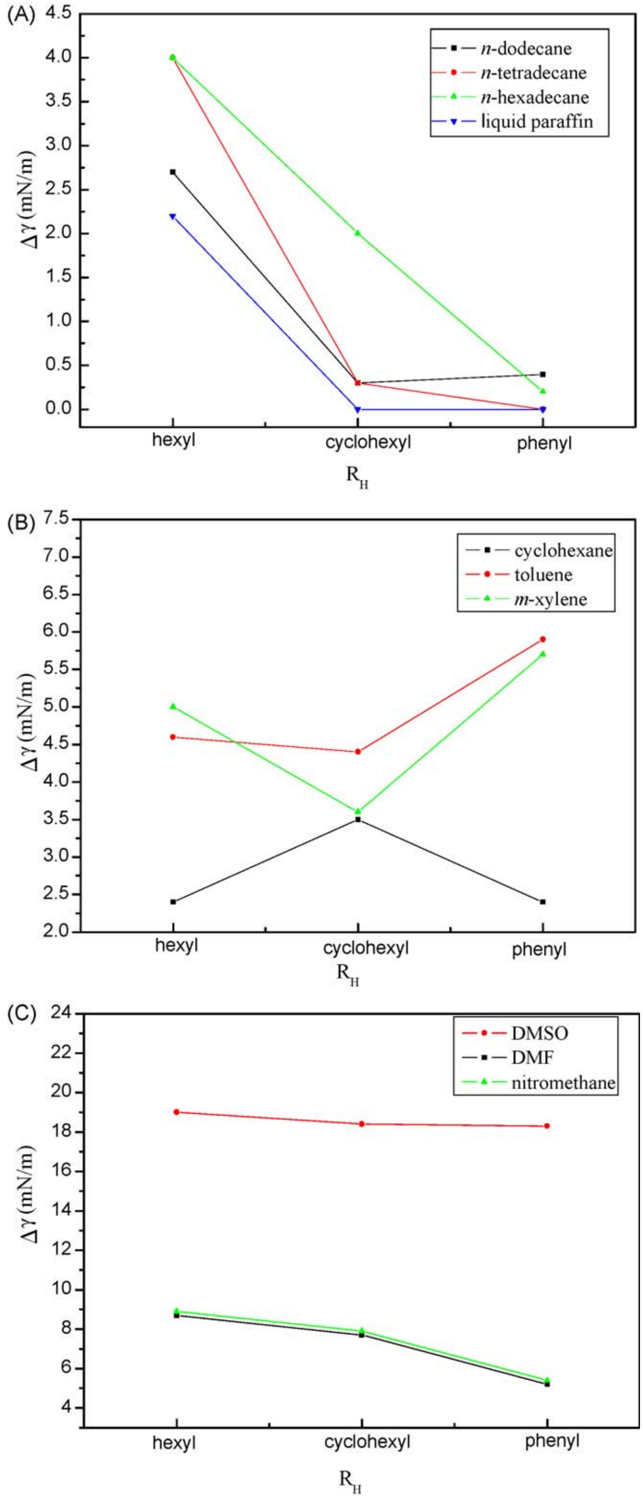

Fig. 3. Relationship between the decrease of surface tension of organic solvents and the structure of solvophilic group of $C_8F_{17}SO_2NH{-}R_H$ (R_H = n-hexyl, cyclohexyl, phenyl) at 25 °C. (A) alkanes; (B) cyclohexane and aromatic solvents; (C) polar solvents. $\Delta\gamma = \gamma_{\text{solvent}} - \gamma_{\text{solution}}$ indicate the effectiveness of the surfactant in lowering the surface tension of the solvent; *n*-Hexyl, cyclohexyl and phenyl, the solvophilic segment of $C_8F_{17}SO_2NH{-}R_H$.

2.3.1. Effect of the length of the solvophilic group

2.3.1.1. Single alkyl solvophilic group structure. Fig. 1 shows the relationship between the decreases of surface tension of organic solvents ($\Delta\gamma$) and the carbon number (n) of $C_8F_{17}SO_2NHC_nH_{2n+1}$. It can be seen from Fig. 1A that in *n*-alkane (dodecane, tetradecane and hexadecane) solutions, surface activity increases with increasing alkyl chain length of the surfactants. Only those $C_8F_{17}SO_2NHC_nH_{2n+1}$ with enough long carbon chain and sufficient solubility can exhibit surface activity in *n*-alkane solutions. For example, in *n*-hexadecane, such a surfactant has the highest surface tension reduction when the solvophilic group is *n*-decyl ($\Delta\gamma$ = 6.2 mN/m). In liquid paraffin, the surfactants with a long alkyl chain, such as *N*-hexyl, *N*-octyl and *N*-decyl perfluorooctanesulfonamide exhibit surface activity whereas surfactants with a short alkyl chain cannot decrease the surface tension of liquid paraffin. The differences in surface activity of surfactants are based on the high solubility of *N*-alkyl perfluorooctanesulfonamide with a long alkyl chain, leading to the adsorption of a high concentration of perfluorocarbon chains at the organic solvent/air interface. Thus, it is not surprising to find that *N*-ethyl perfluorooctanesulfonamide has little surface activity due to the short alkyl chain. However, in *n*-tetradecane and *n*-dodecane, the highest surface tension decrease can be obtained by *N*-octyl perfluorooctanesulfonamide to 5.7 mN/m and 3.9 mN/m, respectively. A possible explanation is that a long alkyl chain favors sufficient solubility, yet a long alkyl chain arranged in zigzag conformation is easier to bend than a short alkyl chain. Because of the increasing steric hindrance between the bending long alkyl chains, a long alkyl chain maybe unfavorable for high packing density of fluorocarbon chains at the interface. Moreover, it can also be inferred from Fig. 1A that $C_8F_{17}SO_2NHC_nH_{2n+1}$ show higher surface activity in long chain *n*-alkane solvents than that in short chain *n*-alkane solvents. For example, the $\Delta\gamma$ of *N*-octyl perfluorooctanesulfonamide, one surfactant of $C_8F_{17}SO_2NHC_nH_{2n+1}$ is 5.5 mN/m in *n*-hexadecane which is higher than the $\Delta\gamma$ in *n*-dodecane. The reason for this trend is quite obvious. Long chain alkane solvents have the contribution to maximize the mutual immiscibility and incompatibility between the fluorocarbon chain and solvent, to promote fluorocarbon chain escaping from the bulk of organic solvent, and thus to increase adsorption [21]. In general, the surface tension decrease of *n*-alkane depends mostly on the length of the solvophilic group of $C_8F_{17}SO_2NHC_nH_{2n+1}$, which exhibits a great decrease when the length of the single alkyl is long enough.

In cyclohexane, as can be seen from Fig. 1B, the values of $\Delta\gamma$ for most of $C_8F_{17}SO_2NHC_nH_{2n+1}$ (n = 2, 6, 8, 10) are all small (near 2 mN/m), so the surface activities do not obviously change with an increase of the alkyl chain because of limited solubility. In particular, $\Delta\gamma$ of $C_8F_{17}SO_2NHC_nH_{2n+1}$ (n = 4) is a little higher (3 mN/m) than the other four surfactants, and its solubility is a little higher too. In the case of aromatic solvents, such as toluene and *m*-xylene, $\Delta\gamma$ of $C_8F_{17}SO_2NHC_nH_{2n+1}$ (n = 2, 4, 6, 8, 10) increases, then decreases a bit and increases again with an increase of alkyl chain length. This trend might be ascribed to different solubility of surfactants, and *N*-butyl perfluorooctanesulfonamide has a higher solubility than the other four surfactants. As discussed above, a long alkyl chain in solvophilic group favors sufficient solubility in *n*-alkane solvents with ten or more carbon atoms, such as *n*-dodecane, *n*-tetradecane and *n*-hexadecane. But for cyclohexane and aromatic solvents, the number of carbon atoms is six. Thus compared to *N*-butyl perfluorooctanesulfonamide, other similar surfactants with shorter (n = 2) or longer alkyl chains ($n > 6$) as the solvophilic group have too low a solubility to impart the desired orientation of the surfactant molecule at the interface, resulting in low surface activity.

As shown in Fig. 1C, surfactant with ethyl solvophilic group exhibits the highest surface tension reduction of DMSO. Moreover, the surface activity in DMSO gradually decreases with the increase of the length of alkyl chain. This variation of surface activity may be affected by the result of change of solubility. In strong polar DMSO solvent, the longer the alkyl chain, the lower the solubility of surfactants. During the preparation of solutions, it was found that the solution of *N*-butyl perfluorooctanesulfonamide or *N*-ethyl perfluorooctanesulfonamide in DMSO was homogeneous at 0.05 M, but the solution of other longer alkyl perfluorooctanesulfonamides at the same concentration became supersaturated. These phenomena may support an explanation that the solubility of *N*-alkyl perfluorooctanesulfonamides with longer alkyl chain is too small to obtain high surface activity in DMSO solution.

Known as the “all-purpose dissolvent”, DMF has excellent dissolving ability for $C_8F_{17}SO_2NHC_nH_{2n+1}$. The solution of these surfactants in DMF was still homogeneous even at 0.2 M. But the excessive solvophilic property of surfactants increases the concentration to obtain minimum surface tension of organic solvents, and may prevent the close packing of fluorocarbon chains adsorbed at the interface. Consequently, it is well understood that $\Delta\gamma$ of all surfactants in DMF is less than that in DMSO. Moreover, surfactant with the *n*-decyl solvophilic group exhibits the highest surface tension reduction of DMF.

2.3.1.2. Double alkyl solvophilic groups structure. Fig. 2 shows the relationship between the decrease of surface tension of organic solvents ($\Delta\gamma$) and the carbon atom numbers (n) of $C_8F_{17}SO_2N(C_nH_{2n+1})_2$. Among the four surfactants with double alkyl as solvophilic groups, only *N*,*N*-diethyl perfluorooctanesulfonamide can show surface activity in *n*-alkane and liquid paraffin solutions (see Fig. 2A). These results are not surprising because *N*,*N*-diethyl perfluorooctanesulfonamide has not only sufficient solubility but also low steric hindrance. But surfactant with the dimethyl solvophilic groups has such poor solubility in long chain alkane solvents that the molecule cannot effectively be inserted into the bulk of solvents, resulting in a limited surface activity. For surfactants with dibutyl or dipropyl solvophilic groups, low surface activity may be caused by higher steric hindrance, and thus lower density of fluorocarbon chains packed at the interface.

In toluene and *m*-xylene solutions, it can be seen from Fig. 2B that the surface activity sequence of $C_8F_{17}SO_2N(C_nH_{2n+1})_2$ is *N*,*N*-dipropyl perfluorooctanesulfonamide, *N*,*N*-dibutyl perfluorooctanesulfonamide, *N*,*N*-diethyl perfluorooctanesulfonamide and *N*,*N*-dimethyl perfluorooctanesulfonamide in terms of $\Delta\gamma$ value from high to low. This is because the solubility of the surfactants is controlled by the structural similarity between the solvophobic portion of the solute molecule and the solvent molecules. Among the surfactants with the dialkyl solvophilic groups, the dipropyl structure is similar to the six-membered ring of the solvents, so it shows higher solubility. In cyclohexane, poor solubility of *N*,*N*-dimethyl perfluorooctanesulfonamide limits the maximum surface tension decrease, while surfactants with the dipropyl or dibutyl solvophilic groups have relatively higher surface activity.

As shown in Fig. 2C, in strong polar organic solvents such as nitromethane, DMSO and DMF, *N*,*N*-diethyl perfluorooctanesulfonamide also exhibits higher surface activity than that of other surfactants with the dialkyl solvophilic groups, which might also be explained in the same way as in *n*-alkane and liquid paraffin solutions.

2.3.2. Comparison of single, double and cyclic alkyl and phenyl structure of the solvophilic segment in the surfactant molecule

It can be seen from Figs. 1 and 2 the single alkyl solvophilic group is more effective in lowering surface tension of organic solvents discussed in this paper than the double alkyl structure when the total carbon number of the solvophilic segment are equal. That is, the $\Delta\gamma$ is *n*-octyl > dibutyl, *n*-hexyl > dipropyl, *n*-propyl > diethyl (except for DMF solution) and *n*-ethyl > dimethyl. This can be explained in part by the branching chain effect of the solvophilic segment which increases the steric hindrance between the surfactant molecules, leading to a lower density of fluorocarbon chains at the organic solvent/air interface. That is why only diethyl as the solvophilic segment among $C_8F_{17}SO_2N(C_nH_{2n+1})_2$ shows surface activity in *n*-alkane solutions.

Fig. 3 shows the surface activity of $C_8F_{17}SO_2NH–R_H$ (R_H = *n*-hexyl, cyclohexyl, phenyl) in different organic solvents. It can be found that *N*-cyclohexyl perfluorooctanesulfonamide exhibits the highest surface tension reduction of cyclohexane solution owing to the similar polarity of solvophilic group with solvent molecule (see Fig. 3B). Likewise, *N*-phenyl perfluorooctanesulfonamide has the best surface activity in toluene and *m*-xylene solution (see Fig. 3B), and *N*-hexyl perfluorooctanesulfonamide can effectively decrease the surface tension of *n*-dodecane, *n*-tetradecane and *n*-hexadecane (see Fig. 3A). It can also be found that *N*-cyclohexyl perfluorooctanesulfonamide is only effective in decreasing the surface tension of *n*-hexadecane. As for surfactants with phenyl or dipropyl as the solvophilic segment, they are all not effective in decreasing the surface tension of *n*-alkane solvents. This different ability in lowering the surface tension of *n*-alkane solvents might be not only caused by insufficient solubility, but also due to the increased steric hindrance of cyclohexyl, phenyl and dipropyl groups in surfactant molecules as shown in Fig. 4.

2.3.3. Comparison of single fluorocarbon chain and double fluorocarbon chains of the solvophobic segment

As is known, long fluoroalkylated compounds exhibit a strong repellent property against water or hydrocarbons. Therefore, compounds containing two fluorinated chains listed in Table 1 were designed and the surface activity was examined in a series of organic solvents. Effect of the number of solvophobic groups on the decrease of surface tension of organic solvents can be obtained by comparing results in Figs. 1–3 and Table 1. Results show that the most effective surfactant that lowers the surface tension of nitromethane and DMF is $C_8F_{17}SO_2NHC_6H_{12}NHO_2SC_8F_{17}$ among all synthesized surfactants. Especially, in 2-butanone and ethyl acetate, surfactants with a single fluorocarbon chain as the solvophobic group cannot play a role due to excessive solubility in these solvents. However, the $\Delta\gamma$ values of $C_8F_{17}SO_2NHC_6H_{12}NHO_2SC_8F_{17}$ are both higher than 1 mN/m, which suggests that this fluorocarbon compound can function as a surfactant in these solvents. Consequently, the use of fluorinated surfactants in industrial applications may be widened. The discrepancy between the ability of surfactants containing different fluorinated chains may reflect the differences in adsorption states. It is believed that

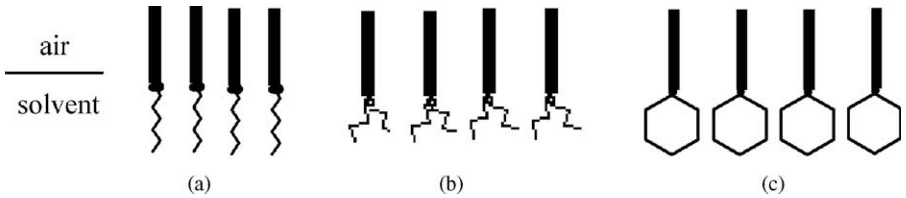

Fig. 4. Schematic illustration of the adsorption of $C_8F_{17}SO_2NH(CH_2)_5CH_3$, $C_8F_{17}SO_2N(CH_2CH_2CH_3)_2$ and $C_8F_{17}SO_2NHC_6H_{11}$ in *n*-alkane solvent. Bent curves depict alkyl groups, shaded blocks represent fluorinated chains, and dark dots indicate the connecting group.

an increase of the solvophobic part in surfactant molecules may decrease the solubility and lead to closer packing at the surface.

2.4. Adsorption at interface and the adsorbing state of surfactant molecules

The orientation and packing of fluorinated surfactant molecules at the organic solvent/air interface prominently depend upon the molecular structure, solubility and extent of association of the solute and solvent molecules. As described above, *N*-octyl perfluorooctanesulfonamide exhibits remarkably decrease the surface tension of various organic solvents, so special attention was paid to the adsorption of *N*-octyl perfluorooctanesulfonamide in some representative organic solvents including *n*-tetradecane, *n*-hexadecane, DMF, DMSO and nitromethane. As shown in Fig. 5, the surface tension curves (γ-log c curves) of *N*-octyl perfluorooctanesulfonamide solutions in five organic solvents at 25 °C, are similar to those of common surfactants in aqueous solution. The initial decrease of the surface tension is followed by an abrupt change in the slope of the surface tension curve. After the break point, the surface tension of the solutions no longer changes, suggesting the aggregation of surfactant molecules in the organic solvent. The intersection in the surface tension curves can be defined as critical aggregate concentrations (cac), and the corresponding surface tension is defined as γ_{cac}. The main difference between these curves and the analogous curves for common surfactants in aqueous solutions is that the initial surface tensions of the pure organic solvents are much lower than that of pure water.

The values of cac and γ_{cac} for $C_8F_{17}SO_2NHC_8H_{17}$ in various organic solvents at 25 °C are shown in Table 2. It is evident that the cac values increase and then decrease with an increase of polarity of organic solvents, which agrees with the idea that excessive solubility increases the concentration to obtain minimum surface tension.

To investigate the adsorbing state of surfactant molecules at the organic solvent/air interface, the maximum surface excess concentration, $\Gamma_{\max}$, and the area occupied by a single surfactant molecule at the organic solvent/air interface, $A_{\min}$, were both estimated from the Gibbs adsorption isotherm of nonionic surfactants [11] and also shown in Table 2.

$$\Gamma_{\max} = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_T \tag{2}$$

$$A_{\min} = \frac{10^{14}}{(\Gamma_{\max} \cdot N_o)} \tag{3}$$

where C is the concentration of surfactant, $(\partial\gamma/\partial \ln C)_T$ is the slope in the surface tension isotherm when the concentration is near the cac. R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature and N_o is the Avogadro constant.

The maximum surface excess concentration ($\Gamma_{\max}$) reflects the degree of packing and orientation of the adsorbed surfactant molecules at the interface. As shown in Table 2, the values of $\Gamma_{\max}$ in *n*-tetradecane, *n*-hexadecane, nitromethane and DMSO is higher than that in DMF, therefore, the area occupied by a single surfactant molecule at organic solvent/air interface ($A_{\min}$) of these four systems is found to be smaller than that at DMF/air interface. A larger $\Gamma_{\max}$ means that there are more surfactant molecules adsorbed on the surface of the solution, which also means a lower surface tension. The lowest value of $A_{\min}$ obtained from *n*-tetradecane system is 0.44 nm^2, which suggests adsorption of surfactant with the solvophobic fluorocarbon chain oriented away from the liquid in a more tilted position, approaching to the cross sectional area of the fluorocarbon chain (28.3 Å^2) [31]. The sulfonamide group of the surfactant molecule coexisting at the organic solvent/air interface increases the steric hindrance between fluorocarbon chains, thus inevitably increases the area occupied by a single surfactant molecule at the interface. And it is reasonable for the high $A_{\min}$ data calculated from *N*-octyl perfluorooctanesulfonamide in *n*-hexadecane, nitromethane and DMSO. For example, the $A_{\min}$ data (0.87 nm^2) of *N*-octyl perfluorooctanesulfonamide in nitromethane is basically coincident with the literature data (0.84 nm^2) of perfluorinatedoctyl ethanesulfonate in nitromethane [11]. However, a high $A_{\min}$ data suggest incompact adsorption of fluorocarbon chains at interface or incomplete surface coverage by a fluorocarbon film, even though the fluorinated chains are oriented away from the liquid surface. When *N*-octyl perfluorooctanesulfonamide dissolves in DMF, it is evident that $\Gamma_{\max}$ values are the minimum, cac is the maximum, and $A_{\min}$ is the maximum (even up to 1.33 nm^2). These results may be due to the excessive solubility of the surfactant in DMF to prevent the close packing of fluorocarbon chains adsorbed at the interface. Therefore, the adsorbed molecules fail to form close-packed condensed monolayer even at cac. At the same time, the fluorinated groups probably lie flat on the surface when they are adsorbed.

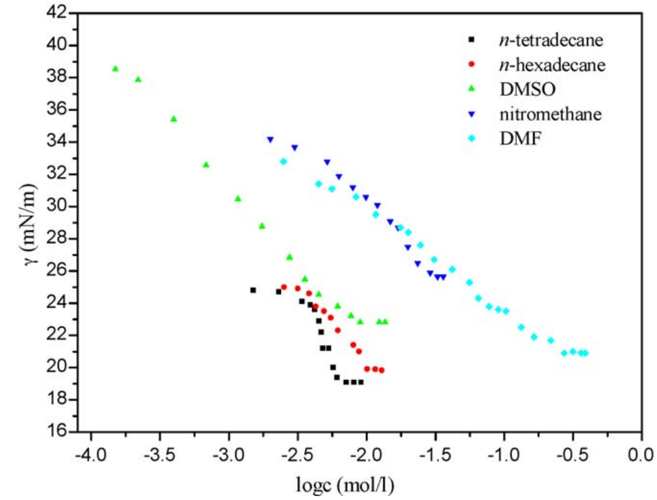

Fig. 5. Surface tension curves of $C_8F_{17}SO_2NHC_8H_{17}$ in various organic solvents at 25 °C.

For conventional surfactants in water, the driving force for micellization and adsorption derives from the unfavorable contact between water and the hydrocarbon chain, called the hydrophobic effect of surfactant. The magnitude of this hydrophobic effect can be quantified in terms of the standard free energy of transfer of the hydrocarbon chain from bulk alkane to water. In organic solvents, the adsorption and aggregation of an organic solvent-soluble surfactant can be attributed to the solvophobic driving force of the fluorocarbon chain. And the magnitude of the driving force can be estimated from the approximate Eq. (4) [30,32].

$$\Delta G^{\theta}_{\text{agg}} = -RT \ln S \tag{4}$$

where S is the solubility of the surfactant in organic solvents in mole fraction units and $\Delta G^{\theta}_{\text{agg}}$ is the standard free energy of aggregation. As illustrated in Table 2, the values of $\Delta G^{\theta}_{\text{agg}}$ in *n*-tetradecane, *n*-hexadecane, nitromethane and DMSO are higher than that in DMF, indicative of higher solvophobic driving force of the fluorocarbon chain in *n*-tetradecane, *n*-hexadecane, nitromethane and DMSO. However, the driving force of aggregation and adsorption in DMF are lower than *n*-alkanes in spite of an increase

Table 2
Surface properties of $C_8F_{17}SO_2NHC_8H_{17}$ in various organic solvents at 25 °C.

Solvent	Dielectric constant [36]	*cac* (mol l^{-1})	γ_{cac} (mN m^{-1})	Γ_{cac} (mol cm^{-2})	A_{min} (nm^2)	ΔG^{θ}_{agg}(kJ/mol)
n-tetradecane	0	0.0065	19.1	3.77×10^{-10}	0.44	15.81
n-hexadecane		0.010	19.8	2.15×10^{-10}	0.77	14.44
Nitromethane	35.9[c]	0.031	25.6	1.79×10^{-10}	0.87	15.85
DMF	36.7[b]	0.24	20.9	1.25×10^{-10}	1.33	9.89
DMSO	46.9[a]	0.0067	22.8	2.04×10^{-10}	0.81	18.88

[a] 20 °C.
[b] 25 °C.
[c] 30 °C.

in the polarity and surface tension of the pure organic solvent. That is, polarity of the organic solvents cannot fully explain the extents of the spontaneous process of aggregation and adsorption. Instead, the solvophobic driving force highly depends upon the proper solubility and extent of association of the solute and solvent molecules. It is well worth noting that Eq. (4) is applicable for those systems with a high aggregation number. Hence, ΔG^{θ}_{agg} maybe an estimated value due to an unknown aggregation number of the surfactant systems at present.

3. Conclusions

In this work, a series of perfluoroalkyl-sulfonamide derivatives were designed and synthesized. These compounds can reduce the surface tension of polar and non-polar organic solvents, exhibit surfactant properties in various organic solvents, and break a new path for the diversified uses of fluorinated surfactants. The relationships between surface activity and molecular structure of surfactants as well as the property of organic solvents are quite complicated owing to the structural diversity of both the fluorinated surfactants and the organic solvents. Proper balance between solvophilic and solvophobic segment can be seen as a function of solubility, which is of importance to obtain the maximum decrease of surface tension of organic solvents. In general, it was found that long chain *n*-alkane solvents are beneficial to increase the surface activity of these fluorinated surfactants because of stronger incompatibility between the fluorocarbon segment of the surfactant and the solvent molecules. And polar organic solvent can improve solubility and surface activity of these polar surfactants. Among these synthesized surfactants, $C_8F_{17}SO_2N(C_nH_{2n+1})_2$ ($n = 1, 2, 3, 4$) shows lower surface activity than $C_8F_{17}SO_2NHC_nH_{2n+1}$ ($n = 2, 4, 6, 8$) with an equal carbon number of the solvophilic group due to enlarging steric hindrance between surfactant molecules. Similarly, $C_8F_{17}SO_2NHC_6H_{11}$ and $C_8F_{17}SO_2NHC_6H_5$ exhibit lower surface activity than $C_8F_{17}SO_2NHC_6H_{13}$ in organic solvents (except for cyclohexane and aromatic solvents).

The surface tension-concentration curves of *N*-octyl perfluorooctanesulfonamide in various organic solvents exhibit a break point like the critical micelle concentration of ordinary surfactants in aqueous solutions. A quiet compact adsorption of fluorocarbon chains was found at *n*-tetradecane solution surface, while the fluorocarbon chains probably lay flat on the DMF solution/air interface resulting in an incomplete surface coverage by fluorocarbon film.

4. Experiments

4.1. Materials

Perfluorooctanesulfonyl fluoride was purchased from Aldrich, containing 74% of the linear isomer and 28% of branched isomers [33]. All the amines including ethylamine (alcohol solution), *n*-butylamine, *n*-hexylamine, *n*-octylamine, *n*-decylamine, dimethylamine (alcohol solution), diethylamine, di-*n*-propylamine, di-*n*-butylamine, triethylamine, cyclohexylamine, aniline, 1,6-hexanediamine and 1,10-diaminodecane were of AR grade from Sinopharm Chemical Reagent Beijing Co., Ltd. *n*-Dodecane, *n*-tetradecane and *n*-hexadecane were products of Haltermann, their purities were 97%, 99% and 99% respectively. Cyclohexane, toluene, *m*-xylene, ethanol, 2-butanone, nitromethane, DMF, DMSO, ethyl acetate and isopropyl ether were of AR grade and liquid paraffin was of chemical grade from Sinopharm Chemical Reagent Beijing Co., Ltd. The water for the experiment was secondary distilled water.

4.2. General procedure for the synthesis of fluorocarbon surfactants [34]

The surfactants $C_8F_{17}SO_2NHR$ and $C_8F_{17}SO_2NH(R)_2$ were prepared by the following reactions:

$$C_8F_{17}SO_2F + NH_2R + N(C_2H_5)_3 \rightarrow C_8F_{17}SO_2NHR + [NH(C_2H_5)_3]F$$

$$R = (CH_2)_nH(n = 2, 4, 6, 8, 10),\ C_6H_{11},\ C_6H_5$$

$$C_8F_{17}SO_2F + NH(R)_2 + N(C_2H_5)_3 \rightarrow C_8F_{17}SO_2N(R)_2 + [NH(C_2H_5)_3]F$$

$$R = (CH_2)_nH(n = 1, 2, 3, 4)$$

The reaction was carried out in a reactor of 500 ml volume equipped with stirrer, thermometer, reflux condenser and dropping funnel. Fluorinated surfactants were typically synthesized by reaction of perfluorooctanesulfonyl fluoride (0.05 mol) with an excess of the respective alkyl amine (0.075 mol) or dialkyl amine (0.075 mol), with triethylamine (0.075 mol) as a base. All materials were used after pre-drying by anhydrous magnesium sulfate. Perfluorooctanesulfonyl fluoride was slowly dropped into the mixed solution of amine and triethylamine, controlling the mole ratio of perfluorooctanesulfonyl fluoride to amine and triethylamine as 1:1.5:1.5. Isopropyl ether (50 ml) was used as the solvent. The mixture was refluxed for 4 h. Solvent and excess amines were removed by distillation under reduced pressure, and the residue was washed with dilute hydrochloric acid and water successively. The washing times were determined by monitoring the surface tension of the washing water (supernatant liquid). Once the surface tension of washing water remains constant and does not increase with the increasing of washing times, the desired pure product is obtained. For example, pure *N*-butyl perfluorooctanesulfonamide (identified by Elemental analysis, NMR spectra and IR spectra) was obtained after seven times of water washing to remove the high surface active impurity, and the surface tension of washing water remains about 53 mN/m at 25 °C. Finally, the products were dried in a vacuum.

The surfactants $C_8F_{17}SO_2NH(CH_2)_nNHO_2SC_8F_{17}$ were prepared by the following reactions:

$$2C_8F_{17}SO_2F + H_2N(CH_2)_nNH_2 + 2N(C_2H_5)_3 \\ \rightarrow C_8F_{17}SO_2NH(CH_2)_nNHO_2SC_8F_{17} + 2[NH(C_2H_5)_3]F \\ n = 6, 10$$

The most synthesis procedure of fluorinated surfactants containing two fluorinated chains was similar to that of mono/dialkylated perfluorooctanesulfonamides. Perfluorooctanesulfonyl fluoride (2.2 mol) was slowly dropped into the mixed solution of 1,6-hexanediamine or 1,10-diaminodecane (1 mol) and triethylamine (2.2 mol). Isopropyl ether (50 ml) was used as the solvent. During the process of synthesizing 1,10-decyl diperfluorooctanesulfonamide, ethanol (50 ml) was applied as a suitable solvent because of the excellent solubility of 1,10-Diaminododecane in it.

4.3. Measurements

Infrared spectra were recorded on a PerkinElmer FT-IR 1720X spectrometer. ^1H and ^{19}F NMR spectra were obtained on a Varian ARX 400 MHz spectrometer with tetramethylsilane as an internal standard. Elemental analyses were performed by Elementar Vario EL III. The surface tension was measured by the drop-volume method [35].

4.4. Characterization

The structures of the fluorinated surfactants were determine by infrared spectrum (IR), nuclear magnetic resonance (NMR), and elemental analysis (EA). The analytical results can be seen from supporting information.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2009.05.006.

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