New Amphoteric Surfactants Containing the 2-Perfluoroalkyl 2-Hydroxy Ethyl Group and an Amino Acid Residue

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Amphoteric perfluoroalkylated surfactants containing a hydroxyl group were prepared by the addition of 2-perfluoroalkyl-1,2-epoxy ethane to a starting (L,D or L) amino acid (glycine, alanine, β-alanine, serine, 2-amino butyric acid, norvaline, norleucine, methionine, sarcosine, aspartic acid, glutamic acid).

KEY WORDS: Amino acid, amphoteric surfactant, chiral, hydrogen bond, liquid crystal, perfluoroalkyl.

It has already been shown that the essential structural elements of flexible tails, central rigid segments (such as diphenylazomethane, biphenyl, azobenzene or azoxybenzene groups) and hydrophilic heads govern the self-assembling behavior of single-chain surfactants (1-3). Chiral amphiphilic derivatives of glutamic or aspartic acid with long dialkyl groups form a helical super aggregate structure (4-6). Dihelical fibers and gels are also obtained by spontaneous aggregation of chiral N-alkyl gluconamides (7-9).

It has also been established that compounds synthesized by addition of epoxy alkanes (C_{12}, C_{18}) to various amino acids exhibit thermotropic crystalline properties (10,11). Liquid crystal appearance in amphoteric surfactants such as N-(2-hydroxy dodecyl)-β-alanine was observed; it can be assumed that the direction of helicoïdal twist is affected by the ability of the -NH-, -COOH and -OH groups to form intermolecular hydrogen bonds. The presence of hydroxyl groups in the long alkyl chain (*e.g.*, dodecyl) and the asymmetric carbon atom are closely related to the appearance of fibrous aggregates (12).

In this paper we describe the synthesis of perfluoroalkylated homologues of N-(2-hydroxy alkyl) amino acids. With the introduction of a perfluoroalkylated tail in the molecular structure of an amino acid, an increase in hydrophobicity is expected. The presence of perfluoroalkyl groups produces a much more rigid and stable system which, in turn, can lead to higher gel-to-liquid crystal phase transition temperatures. For example, it is known that single-chain and double-chain amphiphiles that possess long perfluoroalkyl chains in the hydrophobic portion can form stable bilayer membranes in water (13).

Recently we reported (14) the synthesis of another series of N-perfluoroalkyl amino acids involving a procedure based on a solid-liquid phase transfer catalysis (SL-PTC) method. Even though the molecules of these compounds are not chiral and do not contain a hydroxyl group, it would be interesting to compare them to the hydroxyl group-containing molecules reported in the present paper with regard to liquid crystal formation.

EXPERIMENTAL PROCEDURES

Materials. The synthesis of N-2-perfluoroalkyl-1,2-epoxy ethanes [**1a-c**] was described elsewhere (15). The amino acids employed as starting materials were of commercial grades (Aldrich Chemical Co., Milwaukee, WI).

Instrumentation. Melting points were measured on a Büchi-Tottoli apparatus (Büchi, Flawil, Switzerland), the values were not corrected. Infrared (IR) spectra were recorded on a Bruker IFS 45 spectrometer (Bruker, Karlsruhe, Germany) with samples as KBr disks. ^{1}H-nuclear magnetic resonance (NMR) spectra were recorded at 200 MHz with a Bruker WH 200 spectrometer on samples in trifluoroacetic acid solution. Mass spectra were run on a Nermag-Ribermag R 10-10 C spectrometer (Nermag, Rueil-Malmaison, France).

Preparation of N-(2-perfluoroalkyl-2-hydroxy ethyl) amino acids (**2a-c** *to* **12a-c**). Triethylamine (1 mmole) dissolved in an aqueous ethanol solution (65 wt% ethanol) is added to amino acid (1 mmole) to protect (as a salt) the carboxyl group of the amino acid. The mixture is stirred at room temperature for 20 min. Subsequently, 2-perfluoroalkyl-1,2-epoxy ethane (1 mmole) is added dropwise, and the mixture is stirred at 50°C for 8 h ($R_F = C_4F_9$, C_6F_{13}) or at 60°C for one night ($R_F = C_8F_{17}$). Then the triethylamine and ethanol are evaporated under *vacuo* (10 mm Hg) at 80°C for 30 min. The residue obtained is washed with water and petroleum ether, then dried under vacuum to afford a white solid of N-(2-perfluoroalkyl-2-hydroxy ethyl) amino acids (**2a-c-12a-c**). The yields and melting points are reported in Tables 1, 2 and 3.

Analytical data. Anal. Calc. for compound **8b** ($C_{11}F_{13}H_{10}NO_3$): C, 29.27; F, 54.77; H, 2.22; N, 3.10. Found: C, 28.88; F, 53.97; H, 2.18; N, 3.04. IR (KBr) ν [cm^{-1}]: 3342 (N-H), 1703 (C=O), 1250-1150 (C-F). ^{1}H NMR (CF_3CO_2D) δ [ppm]: 1.36, (s, 1H), N*H*; 1.84, (d, 3H),

TABLE 1

Yields and Melting Points of Compounds 2a-c to 7a-c

Compound	R_F	R	Yield (%)	m.p. (°C)
2a	C_4F_9	C_2H_5	89	207
2b	C_6F_{13}	C_2H_5	92	185
2c	C_8F_{17}	C_2H_5	83	196
3a	C_4F_9	C_3H_7	85	208
3b	C_6F_{13}	C_3H_7	92	206
3c	C_8F_{17}	C_3H_7	87	186
4a	C_4F_9	C_4H_9	90	212
4b	C_6F_{13}	C_4H_9	95	195
4c	C_8F_{17}	C_4H_9	93	193
5a	C_4F_9	CH_2OH	82	218
5b	C_6F_{13}	CH_2OH	89	215
5c	C_8F_{17}	CH_2OH	89	140
6a	C_4F_9	$C_2H_4SCH_3$	91	200
6b	C_6F_{13}	$C_2H_4SCH_3$	95	173
6c	C_8F_{17}	$C_2H_4SCH_3$	92	180
7a	C_4F_9	CH_2COOH	90	>260
7b	C_6F_{13}	CH_2COOH	89	>260
7c	C_8F_{17}	CH_2COOH	92	—[a]

[a]The product is obtained as a waxy solid.

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TABLE 2

Yields and Melting Points of Compounds 8a-c and 9a-c

Compound	R_F	R	Yield (%)	m.p. (°C)
8a	C_4F_9	CH_3	83	198
8b	C_6F_{13}	CH_3	80	180
8c	C_8F_{17}	CH_3	85	163
9a	C_4F_9	C_2H_4COOH	88	194
9b	C_6F_{13}	C_2H_4COOH	88	184
9c	C_8F_{17}	C_2H_4COOH	91	177

TABLE 3

Yields and Melting Points of Compounds 10a-c to 12a-c

Compound	R_F	Amino acid	n	Yield	m.p. (°C)
10a	C_4F_9	Glycine	1	80	205
10b	C_6F_{13}	Glycine	1	82	182
10c	C_8F_{17}	Glycine	1	94	173
11a	C_4F_9	Sarcosine	1	90	—[a]
11b	C_6F_{13}	Sarcosine	1	88	—[a]
11c	C_8F_{17}	Sarcosine	1	83	143
12a	C_4F_9	β-Alanine	2	83	175
12b	C_6F_{13}	β-Alanine	2	90	166
12c	C_8F_{17}	β-Alanine	2	94	175

[a]The product is obtained as a waxy solid.

CH_3; 3.58, (m, 3H), CH_2NHCH; 4.40, (m, 1H), C_6F_{13}-CH(OH); 4.84 (m, 2H), O*H* and COO*H*. Mass spectra (70 eV): *m/z* (%)452 ($M^{\oplus}$ + 1, 2.75), 406 ($C_6F_{13}CH(OH)$-CH_2N^+H=CH-CH_3, 7.62), 86 (CH_3-CH=$^+$N CH_2-CH-(OH), 9.18), 44 (CH_3-CH=$^+NH_2$, 46.58), 102 (CH_2=$^+$NH-CH(CH_3)-CO_2H, 22.99), 57 (CH_2=$^+$NH-CH-CH_3, 37.63), 56 (CH_2=N=CH-CH_3]$^+$, 100.00), 45 ($^+$O≡C-OH, 10.82), 69 (CF_3^+, 12.65), 119 ($C_2F_5^+$, 2.34), 131 ($C_3F_5^+$, 3.60).

RESULTS AND DISCUSSION

Amino acid-based surfactants usually have the fundamental structures pictured in Figure 1. The structure in Figure 1a corresponds to an N-acylated amino acid, which is essentially an anionic surfactant. The structures in Figure 1b, the carboxylic group of which is converted to ester or amide, are fundamentally cationic surfactants. The structures in Figures 1c and 1d, which have both amino and carboxyl groups as part of the hydrophilic moiety, are amphoteric surfactants.

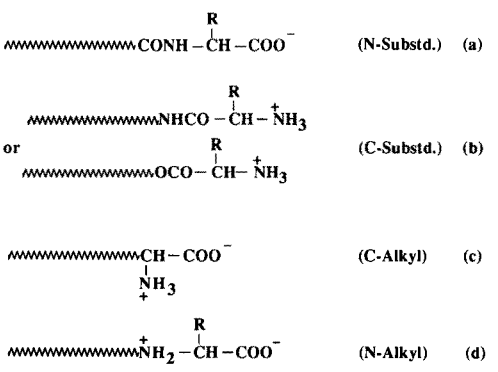

FIG. 1. Fundamental structures of amino acid-based surfactants.

Synthetic routes to hydrocarbon long-chain amino acid-based surfactants (Fig. 1) are varied (16)—a long-chain fatty acyl group is introduced on the amino part of amino acids by using an acid chloride (17). To obtain amino acid esters or amides, the carboxyl part of amino acids are reacted with fatty alcohols or amines, respectively.

C-alkylation of an amino acid is obtained, for example, by the reaction of α-bromo fatty acid with ammonia or by a transimination reaction of the amino part of the amino ester with a stable Schiff base, followed by deprotonation with a strong base, alkylation with an alkyl halide and followed finally by hydrolysis (18). N-alkylation of an amino acid is generally obtained by the reaction of fatty amines with monochloroacetic acid, methyl acrylate, maleic acid or by addition of 1,2-epoxy alkane to amino acids (19,20).

In the fluorocarbon series, the opening reaction of perfluoroalkylated epoxide by amino acids received considerably less attention. The literature reports only the addition of 3-perfluorononyl-1,2-epoxy propane to potassium salt of sarcosine (21).

In this work, we obtained new amphoteric perfluoroalkylated surfactants containing a hydroxyl group, located at the carbon bearing the perfluoroalkyl group, and an asymmetric carbon atom, by addition of racemic 2-perfluoroalkyl-1,2-epoxy ethanes to various α-amino acids (Figs. 2 and 3). The amino acids used were the (L,D) forms of serine, 2-amino butyric acid, norvaline, norleucine, methionine, aspartic acid and the (L) forms of alanine and glutamic acids as well as glycine, sarcosine or β-alanine, which do not possess asymmetric carbon atoms.

The compounds obtained have the following characteristic structural features: (i) they contain an amino acid

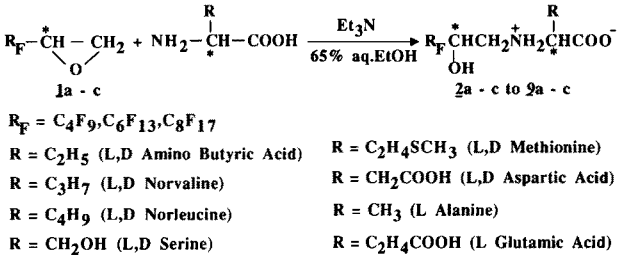

FIG. 2. Schematic synthesis of N-(2-F-alkyl-2-hydroxy ethyl) amino acids 2a-c-9a-c.

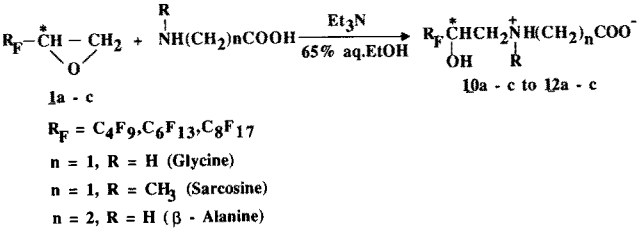

FIG. 3. Schematic synthesis of N-(2-F-alkyl-2-hydroxy ethyl) amino acids 10a-c-12a-c.

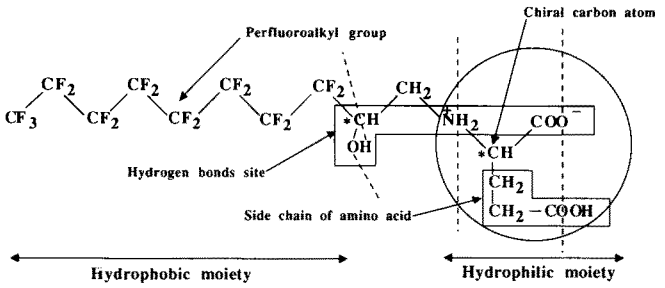

FIG. 4. Structural model of N-(2-F-octyl 2-hydroxy ethyl) glutamic acid (compound 9c).

side-chain group in the hydrophobic moiety; (ii) they have a hydroxyl group between the hydrophobic and hydrophilic moieties, which has a hydrogen-bonding ability; (iii) they possess a chiral carbon atom in the amino acid moiety (except for glycine, sarcosine and β-alanine) which creates a chiral aggregates-forming ability; and (iv) they have the potential ability to produce a rod-like dimer formed by a pair of strong intermolecular hydrogen bonds of $^{+}NH_2...^{-}O_2C$ to make an oligomer or crystal.

Figure 4 summarizes the different elements of N-(2-perfluorooctyl 2-hydroxy ethyl) glutamic acid (Table 2, compound 9c). The yields and the melting points of different compounds are collected in Tables 1, 2 and 3.

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