# Micelle Formation in Liquid Ammonia

Joseph M. Griffin, John H. Atherton, and Michael I. Page*

IPOS, The Page Laboratories, Department of Chemical and Biological Sciences, The University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, United Kingdom

S Supporting Information

ABSTRACT: Perfluorinated long chain alkyl amides aggregate in liquid ammonia with increasing concentration which reflects micelle-type formation based on changes in ^{19}F NMR chemical shifts. The critical micelle concentrations (cmc) decrease with increasing chain length and give Kleven parameters $A = 0.18$ and $B = 0.19$. The micelles catalyze the ammonolysis of esters in liquid ammonia. The corresponding perfluorinated long chain alkyl carboxylates form ion pairs in liquid ammonia, but the equilibrium dissociation constants indicate favorable interactions between the chains in addition to the electrostatic forces. These perfluorinated carboxylates form micelles in aqueous solution, and their cmc's generate a Kleven B-value = 0.52 compared with 0.30 for the analogous alkyl carboxylates. The differences in hydrophobicity of CH_2 and CF_2 units in water and liquid ammonia are discussed, as is the possible relevance to life forms in liquid ammonia.
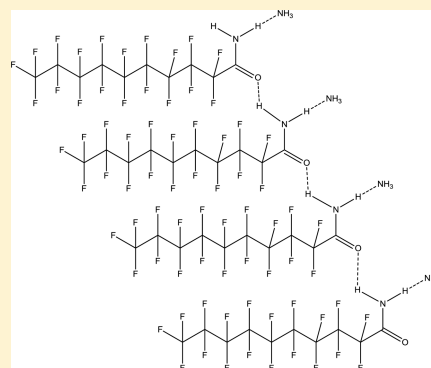
■ INTRODUCTION

It is a commonly held assumption that if life exists beyond Earth it is carbon-based with water as the preferred solvent and utilizes fuels and light as sources of energy to sustain itself.[1] Other suppositions are that life originates quickly if it has the opportunity to do so, but the evolution of multicellularity and intelligence takes a long time and, maybe, is an improbable event so that any extra-terrestrial life is probably unicellular and microbial.[2] Although the definition of life is not easy,[3] one characteristic seems to be that it is liquid based with a self-organizing and bounded local environment not at equilibrium with its surroundings. In fact, the formation of cells appears to be the basis of all living systems characterized by cell membranes formed from the aggregation of monomeric amphiphiles.[4] A major distinction between living and nonliving systems is the presence of biomembranes which establish a boundary enabling different solute concentrations within and outside the cell. The cells of all living organisms on Earth use a selectively permeable membrane to preserve the high free energy state of the system and to encapsulate and confine high concentrations of interacting solutes.

The aggregation of amphiphiles in liquid solution with increasing concentration forms monolayers at the interface of the liquid, micelles, and bilayers to give vesicles.[5] Water is usually assumed to be the universal solvent for life as we know it, as its properties are ideal for the environmental conditions on Earth, in particular the hydrophobicity and hydrophilicity of amphiphilic compounds that favor aggregation in water. In general, the essential condition for solvophobicity is that solvent−solvent interactions be much stronger than solute−solvent ones.[6] The formation of aggregates such as micelles in nonaqueous media and those of reverse micelles from common surfactants in nonpolar, organic solvents are well documented.[7]

The critical micelle concentration (cmc) of surfactants is greatly influenced by the nature of solvent, in particular its polarity/ dielectric constant so that, generally, the cmc decreases with increasing solvent polarity/higher dielectric constant. In the extreme, as the solvent polarity is reduced, solvent−surfactant tail interactions are so favorable and interaction between head group−solvent interactions are so unfavorable that reverse micelle formation is promoted.[8]

The possibility of life based on liquid ammonia has a long history,[9,10] and it has been suggested that metabolism in liquid ammonia is conceivable.[11] Liquid ammonia has some properties similar to water such as the ability to dissolve a diverse range of compounds, and it is excellent at solubilizing polar molecules but not long chained, nonpolar hydrocarbons;[12] so surfactant molecules in liquid ammonia may behave in an analogous manner to that in water. The boiling point of liquid ammonia is −33 °C;[13] it acts like a typical dipolar aprotic solvent at 25 °C, and at a pressure of 10 bar, and can be used to study a wide variety of chemical reactions over a range of temperatures.[14] The dielectric constant of liquid ammonia is only 16.0 at 25 °C,[15] but many salts and organic compounds have good solubility.[16,17] However, some properties of liquid ammonia are very different from those of water. Although ammonia is a good H-bond acceptor and its lone pair can strongly solvate cations,[18] it is not a good hydrogen bond donor.[19] The solvation of anions is weak,[20] and anionic nucleophiles in liquid ammonia are therefore more reactive than in water.[21] The parameters used to characterize these properties of liquid ammonia, such as its normalized donor number,[22] and its autoprotolysis constant highlight significant differences from

water.[23] Salt solutions in liquid ammonia generally have greater electrical conductivity than an aqueous solution of the same salt.[24] Liquid ammonia is about 7-fold less viscous than water at 20 °C,[25] so rates of diffusion are greater in liquid ammonia. Although at atmospheric pressure the temperature range over which ammonia is liquid is only 45 °C, at higher pressures it is greater than that of water; for example, at 60 bar it is 175 °C.[26] Liquid ammonia could present an opportunity for microbial life on numerous colder bodies in the solar system and perhaps in Jovian-type planets where the extreme pressures would make ammonia liquid even at higher temperatures.[27]

Herein, it is demonstrated that some surfactants form micelle type structures in liquid ammonia presumably with "ammono-philic" head groups exposed to the ammonia solvent while the "ammonophobic" tails orientate themselves away from the bulk ammonia environment. Comparisons are made with analogous data in aqueous solution. There is also evidence of micelle type catalyzed reactions in liquid ammonia.

■ RESULTS AND DISCUSSION

Aggregation of Perfluoroalkyl Amides $CF_3(CF_2)_nCONH_2$ in Liquid Ammonia. Some properties of fluorinated surfactants are significantly different from those of their hydrocarbon analogues. The surface tensions of aqueous solutions of fluorocarbon surfactants at concentrations above their cmc are much lower than those of analogous hydrocarbon surfactants.[28] The small size of the fluorine atom renders fluorocarbon chains more "rigid" than a hydrocarbon chain.[29] The enhanced hydrophobicity of fluorocarbon chains is reflected in the fact that each CF_2 group has a similar effect on the cmc in water as does 1.6 CH_2 groups.[30] Fluorocarbons pack less densely on surfaces[31] giving rise to poorer van der Waals interactions with water. The free energy of hydration of hydrophobic solutes/surfaces in water is much more dependent on Lennard–Jones interactions than on electrostatic inter-actions, which may not be the case for nonaqueous polar solvents.[32] The energy required for cavity formation in liquids is an important factor in determining solubility and aggregation, and liquid ammonia has a much lower cohesive energy density (0.83 GJ/m^3 at 298 K and 10 bar) than water (2.3 GJ/m^3 at 298 K and 1 bar).[33] Liquid ammonia is a good H-bond acceptor, and therefore it was conjectured that perfluorinated alkyl amides may form stabilized head groups in micelles or similar aggregates.

It was noted during the synthesis of perfluorinated alkyl amides that they showed a large degree of "frothing and foaming" in liquid ammonia, typical of surfactant/micelle systems and a qualitative indicator that these compounds have surface active properties in ammonia and their potential to aggregate into micelles was promising. Amides are well solvated by ammonia with its relatively high normalized donor number (DN^N) of 1.52,[22] and long chain amides are more soluble in liquid ammonia than their analogous carboxylate anions. For example, perfluorododecanoic acid is insoluble in liquid ammonia at 5 mM, whereas perfluorododecanamide is soluble up to 40 mM.

The aggregation of fluorinated surfactants in water has been detected by using the sensitivity of ^{19}F NMR chemical shifts to the environment,[34,35] and so this method was used to investigate the behavior of perfluorinated alkyl amides $CF_3(CF_2)_nCONH_2$ in liquid ammonia for which the terminal (ω)-CF_3 group, its adjacent $-CF_2-$ group, and the α carbon $-CF_2-$ group are readily distinguishable. For example, the ^{19}F

NMR chemical shifts of 16.9 mM perfluorononanamide in liquid ammonia at 25 °C, relative to ammonium trifluoroacetate as an internal standard at $\delta = -75.51$, are for the ω terminal CF_3 triplet −82.2 ppm, with J_{FF} 10.6 Hz, and for the α CF_2 triplet at −120.0 ppm, with J_{FF} 12.2 Hz. However, these chemical shifts vary with the concentration of the perfluori-nated alkyl amide in liquid ammonia. The chemical shift of the terminal CF_3 group in perfluorononanamide is relatively constant at low concentrations (9−32 mM) but above this concentration decreases with increasing concentration of the surfactant (Figure 1). This behavior is typical of micelle
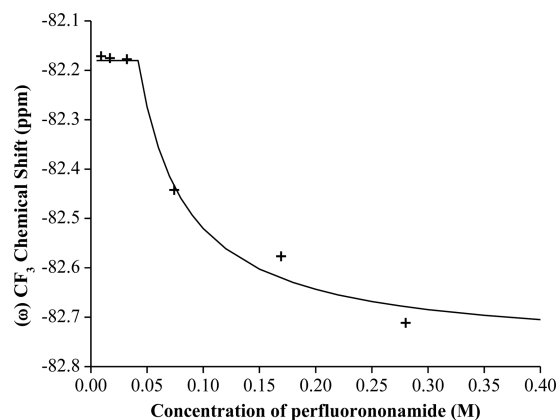

Figure 1. ^{19}F-NMR CF_3 chemical shift as a function of concentration for perfluorononanamide in liquid ammonia at 25 °C.

formation and aggregation.[33] It is also observed with other long chain perfluorinated alkyl amides in liquid ammonia, but not for trifluoroacetamide, which is not expected to aggregate, and for which the ^{19}F NMR chemical shift for CF_3 remains invariant at $\delta = -76.858 \pm 0.002$ up to 0.25 M.

These changes in chemical shift of the terminal $-CF_3$ group are consistent with a change in its environment and compatible with a free monomer dominating at low concentrations, but buried deep within a micelle aggregate in a nonpolar fluoroalkane-type environment at higher concentrations. In aqueous solutions of perfluoroheptanoate the ^{19}F NMR chemical shifts also decrease with increasing concentration but the peaks became broader because the rapid exchange of the fluorocarbon surfactant molecules between the monomer species and micelles with an estimated mean lifetime of 10^{-6} s.[34] This peak broadening is not observed with perfluorinated alkyl amides in liquid ammonia which is perhaps indicative of a much slower exchange rate and more structured and/or larger aggregates.

A mass action approximation can be used to relate the observed chemical shift δ_{obs} and the total surfactant molar concentration c to the molar concentration at which micelles or aggregates begin to form, loosely defined as the cmc, and the chemical shift of the free surfactant monomer δ_m and the chemical shift of the micellar or aggregated phase δ_a (eq 1).[36]

$$\delta_{obs} = \delta_a + (cmc/c)(\delta_m - \delta_a) \tag{1}$$

A plot of δ_{obs} against $1/c$ for perfluorononanamide in liquid ammonia consists of two linear segments that intersect at $1/c = 1/cmc$ (Figure 2), and these derived cmc values for various perfluorinated alkyl amides are given in Table 1. As expected, at low concentrations of surfactant ($c <$ cmc) δ_{obs} is independent of concentration and is identified with δ_m, the free monomer
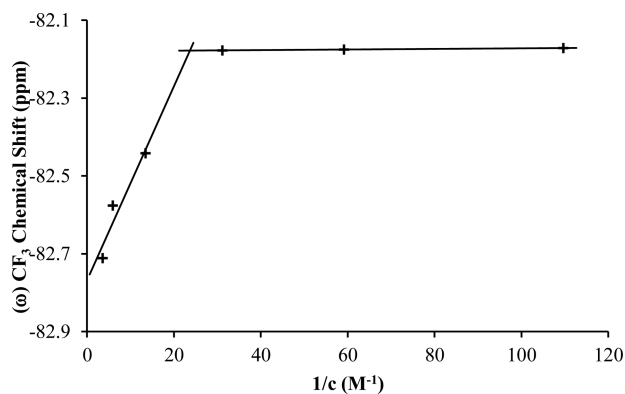
Figure 2. ^{19}F NMR chemical shift of the ω terminal CF$_3$ group as a function of the reciprocal of concentration for perfluorononanamide in liquid ammonia at 25 °C.

Table 1. Cmc Values of Perfluoroalkyl Amides CF$_3$(CF$_2$)$_n$CONH$_2$ in Liquid Ammonia at 25°C

surfactant	$n + 1$	cmc (mM)
perfluoroheptanamide	6	104
perfluorooctanamide	7	66
perfluorononanamide	8	42
perfluorodecanamide	9	27

chemical shift. At higher concentrations (c > cmc), extrapolation to $1/c = 0$ gives the chemical shift of the aggregate, δ_a.

The apparent cmc values for the perfluoroalkyl amides vary as expected with chain length; they decrease with increasing chain length. Klevens rule is an empirical formula[37] that proposes a linear relationship between log(cmc) and surfactant carbon chain length n (eq 2), and it is interesting to note that this applies to perfluorinated alkyl amides in liquid ammonia (Figure 3). The Kleven parameters A and B are 0.18 and 0.19,
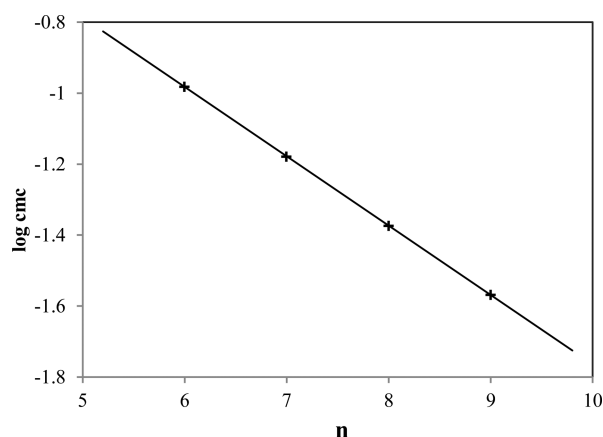
Figure 3. Plot of log(cmc) as a function of the number of carbons in the hydrophobic tail for a series of perfluorinated alkyl amides in liquid ammonia at 25 °C.

respectively, and are discussed and are later compared with parameters obtained for perfluoroalkyl carboxylic acids in water.

$$\log(\text{cmc}) = A - Bn \qquad (2)$$

As well as using the changes in ^{19}F NMR chemical shifts of the terminal CF$_3$ group of the perfluoro alkyl amides to identify aggregation, those of other residues, particularly the α CF$_2$

adjacent to the amide carbonyl and the CF$_2$ next to the terminal CF$_3$, yielded similar results (Figures 4 and 5). The relative
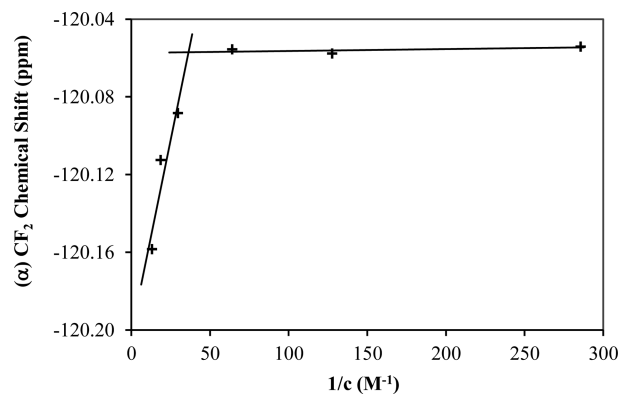
Figure 4. ^{19}F NMR chemical shift of α CF$_2$ group as a function of the reciprocal of the concentration of perfluorodecanamide in liquid ammonia at 25 °C.
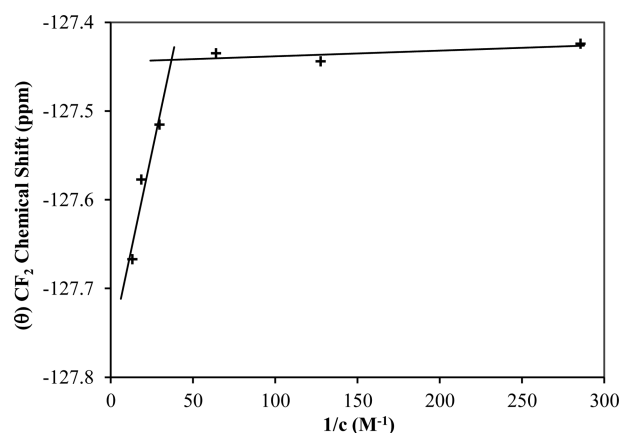
Figure 5. Chemical shift of CF$_2$ group adjacent to the ω CF$_3$ as a function of the reciprocal of the concentration for perfluorodecanamide in liquid ammonia at 25 °C.

changes in chemical shift on going from monomer to aggregate are given by $\delta_m - \delta_a$ and are all positive (Table 2) as there is a

Table 2. ^{19}F Chemical Shifts of Perfluorodecanamide Monomer and Aggregate Peaks in Liquid Ammonia at 25°C

CF group	δ_m	δ_a	$\delta_m - \delta_a$
α CF$_2$	−120.06	−120.20	0.14
CF$_2$(CF$_3$)	−127.44	−127.77	0.33
ω CF$_3$	−82.21	−82.63	0.42

decrease in chemical shift on going from monomer to aggregate. The monomers are surrounded by a relatively polar ammonia environment whereas those in the aggregated micelle are surrounded by neighboring fluorine atoms from the adjacent hydrophobic chains. The magnitude of $\delta_m - \delta_a$ increases with increasing distance from the amide head group. This is compatible with micelle formation, as it suggests that the further along the chain then the deeper the fluorinated chain is buried into the micelle structure. Similar changes in $\delta_m - \delta_a$ that are dependent on the position of the fluoro group in the chain are seen for the other perfluoro alkyl amides, with the magnitude increasing with increasing chain length, which again

is compatible with greater shifts being seen the deeper the reporter group is buried inside the micelle. A simple model envisages the head group amides H-bonded to each other and solvated by liquid ammonia with the fluorocarbon chains packed into an aggregate (Scheme 1).

Scheme 1
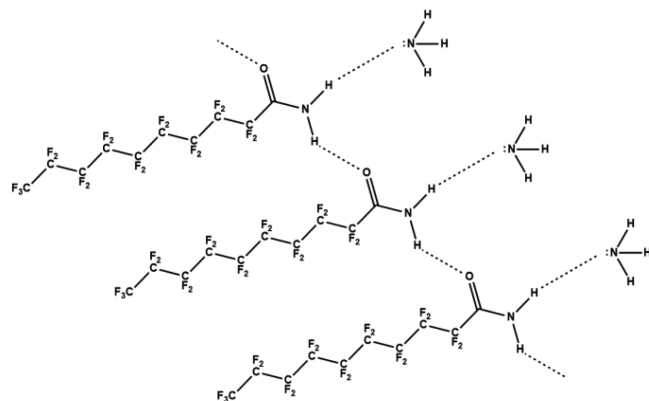
Conductivity of Ionic Surfactants in Liquid Ammonia.

Changes in conductivity with concentration are often used as analytical tools to identify aggregation, and so such measurements of ionic solutes in liquid ammonia were performed but at −15 °C due to the pressure limit on the conductivity cell. The change in conductivity with the concentration of ionic surfactants such as perfluorinated carboxylates, sodium dodecyl sulfate (SDS), and Aerosol OT (dioctyl sodium sulfosuccinate) in liquid ammonia are all nonlinear; however, they do not show the distinct break expected if aggregation occurs (Figure 6).
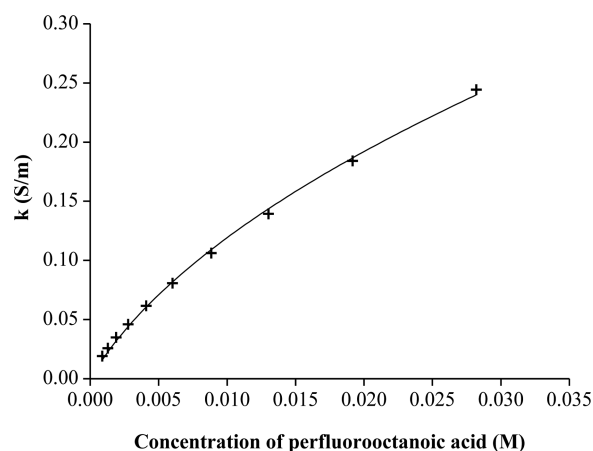
Figure 6. Conductivity as a function of the concentration of perfluorooctanoic acid in liquid ammonia at −15 °C; the continuous line is calculated using eq 3.

Although this behavior is similar to that observed for a weak electrolyte, such as acetic acid in water, the data for the surfactants in liquid ammonia do not fit with Ostwald's dilution law or Kohlrausch's law for fully ionized species (see Supporting Information). The data appear more compatible with ion-pair formation in liquid ammonia which is only moderately polar compared with water (the dielectric constant of ammonia = 16.7 compared with 80 for water at 25 °C). Ion-pair formation (Scheme 2) in liquid ammonia is thus expected to be much more favorable compared with that in water, and

Scheme 2
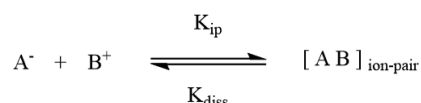
this is reflected in conductivity data. For example, whereas the conductivity of ammonium chloride in water increases linearly with concentration, that in liquid ammonia is nonlinear (Figure 7). The observed conductivity κ can be related to the molar
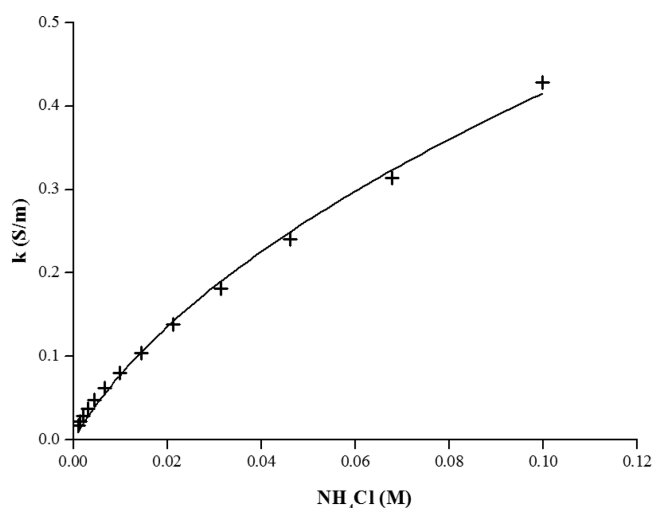
Figure 7. Conductivity as a function of the concentration of ammonium chloride in liquid ammonia at −15 °C; the continuous line is calculated using eq 3.

conductance Λ using the mass balance, and the equilibrium constant for dissociation of the ion-pair formation K_{diss} (eq 3) and the derived values are given in Table 3.

$$\kappa = \lambda + \Lambda \frac{-K_{diss} + \sqrt{K_{diss}^2 - (4 \times K_{diss} \times [A^-]_{tot})}}{2} \quad (3)$$

Although there is no strong evidence for aggregation of the ionic surfactants, there does appear to be some favorable interactions between the perfluorinated alkyl chains in liquid ammonia. As the chain length of the perfluorinated alkyl

Table 3. Equilibrium Constants K_{diss}, K_{ip}, and Molar Conductance Values ε for Ion Pairing of Surfactants and Salts in Liquid Ammonia at −15°C

Salt/surfactant	$10^3 \cdot K_{diss}$ (M)	K_{ip} (M^{-1})	Λ (Sm^{-1}M^{-1})
NH$_4$Cl	31.09	32.2	9.82
TBAB	15.8	63.3	17.3
Aerosol OT	6.06	165.0	23.0
Sodium dodecyl sulfate	5.90	169.5	17.6
Trifluoroacetic acid (C2)	12.9	77.5	28.1
Perfluorooctanoic acid (C8)	9.18	108.9	19.8
Perfluorononanoic acid (C9)	6.89	145.1	21.5
Perfluorodecanoic acid (C10)	4.18	239.2	23.2
Perfluoroundecanoic acid (C11)	2.36	423.7	24.0
Perfluorododecanoic acid (C12)	0.26	3914	51.0
Pefluorooctanesulfonate (Et$_4$N)	1.43	699.3	35.2
Decyltrimethyl ammonium iodide (DTAI)	1.49	671.1	49.3

carboxylate surfactants increases, K_{diss} decreases (50-fold from C2 to C12) (Table 3) with the most dramatic change occurring between C11 and C12. This indicates that more than just electrostatic interactions between the head groups and counterion contribute to the energetics of ion pairing. It may suggest that the longer chained ionic perfluoro surfactants are forming higher aggregates such as dimers or trimers, although not forming typical larger micelle type structures. A possible reason why the ionized perfluorinated carboxylates, unlike the analogous perfluorinated amides, do not show significant aggregation/micelle formation in liquid ammonia is the expected greater repulsion between the similarly charged head groups due to the low dielectric constant of ammonia.

Micelle Catalyzed Ammonolysis of Esters. Changes in organic reactivity in aqueous solutions of micelles[38] have been used to explore the structure of micelles themselves and as models for simple cells.[39] The interior of micelles in water and the head group/solvent interface act as pseudophases distinct from the bulk solvent and can accelerate or inhibit reactions, depending on the mechanism and the rate constants and reactant concentrations in the two regions.[40] It is therefore of interest to explore organic reactivity in liquid ammonia in the presence of aggregates/micelles. The solvolysis of a series of alkyl benzoates and alkyl phenylacetates and aryl benzoates in liquid ammonia gives the corresponding amide and alcohol/phenol.[41] The observed pseudo-first-order rate constant for the ammonolysis of propargyl benzoate in liquid ammonia at 25 °C was studied over a range of perfluorononanamide concentrations and showed no change in the rate up to 38 mM surfactant but then increases at higher concentrations (Supporting Information). The rate increase coincides with concentrations around the cmc obtained from the NMR studies, 42 mM. There is a 14-fold increase in the rate in the presence of 90 mM perfluorononanamide, but trifluoroacetamide has no effect. The modest rate enhancement seen in the presence of the surfactant is typical of the magnitude seen in aqueous micelle catalyzed reactions and further evidence of aggregation of the perfluoroalkyl amides in liquid ammonia. The rate limiting step in the uncatalysed solvolysis reaction involves late formation of the zwitterionic tetrahedral intermediate or a reaction of the neutral tetrahedral intermediate with little C−OR bond fission in the transition state.[40] Presumably, this transition state is stabilized at the micelle−ammonia interface either because of increased polarity of the region or due to direct H-bond interaction between the amide and the tetrahedral intermediate (Scheme 3).

Aggregation of Perfluoralkyl Carboxylates $CF_3(CF_2)_nCO_2^-$ in Water. In order to compare the data obtained for the aggregation of perfluoralkyl amides $CF_3(CF_2)_nCONH_2$ in liquid ammonia, the behavior of the analogous perfluoralkyl carboxylates $CF_3(CF_2)_nCO_2^-$ in water was examined using conductivity. Perfluorooctanoic acid is a strong acid with a pK_a of ~0 and hence is fully ionized in water behaving as a strong electrolyte; a 5 mM solution in water generates a pH of 2.4. The change in conductivity of increasing concentrations of perfluorooctanoic acid in water at 25 °C shows the typical behavior of aggregation to form micelles (Figure 8).

As the concentration of the perfluorooctanoic acid surfactant is increased, an inflection in the conductivity isotherm is observed at the point of micellization when the thermodynamically stable aggregates form, and this concentration can be assigned as the cmc of the surfactant in water. The cmc of

Scheme 3
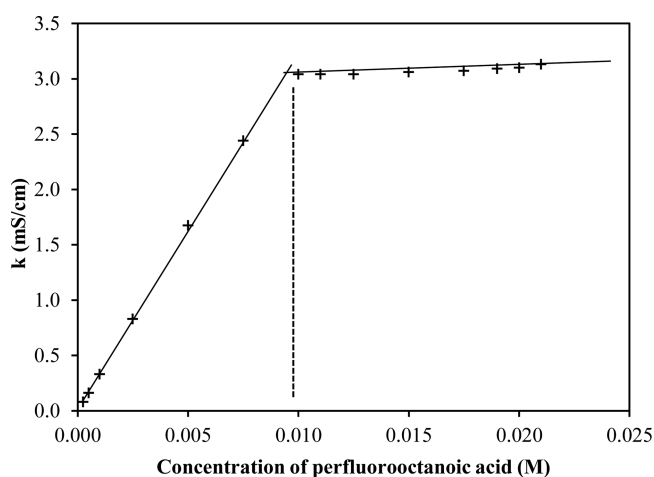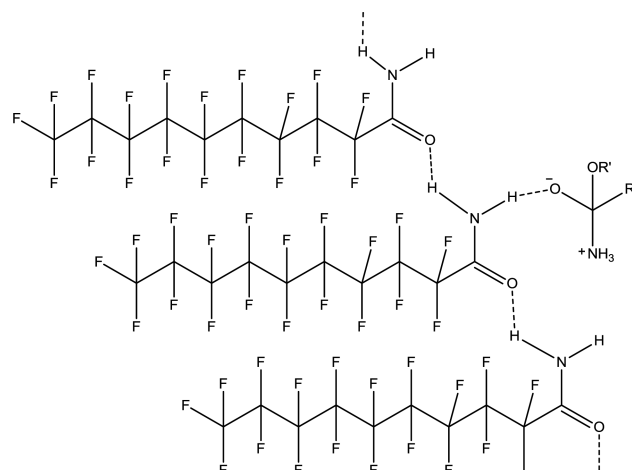
Figure 8. Conductivity of perfluorooctanoic acid as a function of concentration in water at 25 °C.

perfluorooctanoate is 9.3 mM, similar to the value obtained from surface tension.[29,42] The cmc values of other perfluoralkyl carboxylates $CF_3(CF_2)_nCO_2^-$ in water were similarly obtained using conductivity data (Table 4). As expected, the longer the

Table 4. Cmc's of Perfluoralkyl Carboxylates $CF_3(CF_2)_nCO_2^-$ in Water at 25°C

Surfactant	cmc (mM)	Surfactant	cmc (mM)
$CF_3(CF_2)_5COO^-H^+$	25[a]	$CF_3(CF_2)_5COO^-Na^+$	83[a]
$CF_3(CF_2)_6COO^-H^+$	9.3	$CF_3(CF_2)_6COO^-Na^+$	35[a]
$CF_3(CF_2)_7COO^-H^+$	3.4	$CF_3(CF_2)_7COO^-Na^+$	11.8
$CF_3(CF_2)_8COO^-H^+$	1.1	$CF_3(CF_2)_8COO^-Na^+$	3.1
$CF_3(CF_2)_9COO^-H^+$	0.23	$CF_3(CF_2)_9COO^-Na^+$	0.55
$CF_3(CF_2)_{10}COO^-H^+$	0.11	$CF_3(CF_2)_{10}COO^-Na^+$	0.2

[a]W. Guo, T. Brown and B. Fung, *J. Phys. Chem.* **1991**, *95*, 1829−1836.

hydrophobic tail of the surfactant, the lower the cmc value which follows (Figure 9) the empirical Klevens rule[36] (eq 2). For the hydronium salts of the perfluoralkyl carboxylates, the constant $A = 1.38$ and reflects the specific nature of the hydrophilic head group and its interactions with the solvent, which shows the relative effect on the cmc of each additional $-CF_2$ unit. For the corresponding sodium salts, $A = 2.31$ and $B = 0.54$. These A value for the analogous alkyl carboxylates is
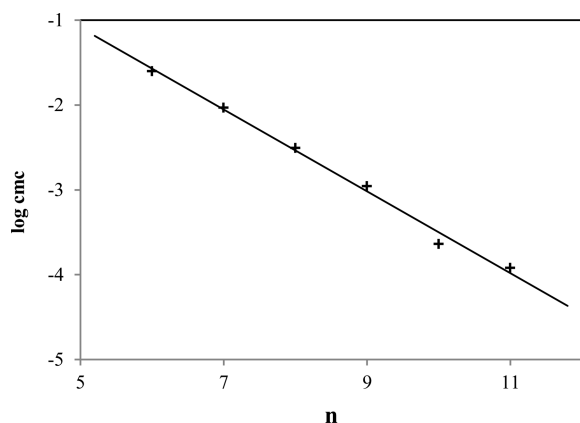
Figure 9. Klevens plot of log(cmc) (M) as a function of the number of carbon atoms in the hydrophobic tail for a series of hydronium salts of perfluorinated carboxylates in water at 25 °C.

1.80, whereas the *B*-values for the perfluoralkyl carboxylates (0.52 ± 0.02) are significantly greater than the 0.30 seen for the alkyl derivatives.[43]

The *B*-values for alkyl chains in water are constant for a variety of surfactants with different polar head groups; for alkyl-*N*-methylpyrrolidinium bromides, *B* = 0.30, and for alkyl-1-sulfonates, *B* = 0.29.[36] This reflects that the cmc is roughly halved with each additional methylene unit added. However, the effect of introducing extra $-CF_2-$ groups into the fluorinated surfactant chain has a greater effect on the cmc due to the greater hydrophobicity of fluorocarbons, such that one $-CF_2-$ group is approximately equivalent to 1.73 $-CH_2-$ units; a fluorosurfactant with 8 carbons behaves like a hydrocarbon surfactant with 14 carbons. It is interesting to compare these *B*-values with those for the perfluorinated alkyl amides in liquid ammonia (Table 5).

Table 5. Klevens *B*-values for Various Surfactants in Water and Liquid Ammonia

Surfactant chain type/solvent	Klevens *B*-value
Alkyl carboxylates in water	0.30
Perfluorinated alkyl carboxylates in water	0.52
Perfluorinated alkyl amides in liquid ammonia	0.19

The *B*-value of 0.19 obtained for the perfluorinated alkyl chain in liquid ammonia is much lower than those for both the simple alkyl and fluorinated chains in water. Effectively, the *B*-values are an indication of the free-energy of transfer of the monomer in the solvent to the aggregate micelle, so the transfer of a CF_2 group from liquid ammonia to its aggregate is less than half of the corresponding transfer from water. This is due to the much greater changes in the Lennard–Jones interactions between the fluorocarbon and water compared with those in liquid ammonia.[31,44]

CONCLUSION

Perfluorinated long chain alkyl amides aggregate in liquid ammonia with increasing concentration, which reflects micelle-type formation in this solvent. The critical micelle concentrations (cmc) decrease with increasing chain length and give Kleven parameters *A* = 0.18 and *B* = 0.19. Although long chain perfluoroalkyl amides aggregate and form micelles in liquid ammonia this is probably not good evidence to support the

claim that life processes could take place in this solvent, as it is difficult to envisage how such perfluorinated systems could readily be formed. The micelles catalyze the ammonolysis of esters in liquid ammonia. The corresponding perfluorinated long chain alkyl carboxylates form ion pairs in liquid ammonia, but the equilibrium dissociation constants indicate favorable interactions between the chains in addition to the electrostatic forces. These perfluorinated carboxylates form micelles in aqueous solution, and their cmc's generate a Kleven *B*-value = 0.52 compared with 0.30 for the analogous alkyl carboxylates. There are significant differences in solvophobicity of CH_2 and CF_2 units in water and liquid ammonia. The free-energy of transfer of a CF_2 group from liquid ammonia to its aggregate is less than half the value of the corresponding transfer from water. The effect of introducing extra $-CF_2-$ groups into the fluorinated surfactant chain has a greater effect on the cmc due to the greater hydrophobicity of fluorocarbons: one $-CF_2-$ group is approximately equivalent to 1.73 $-CH_2-$ units.

■ EXPERIMENTAL SECTION

Synthesis. *Decyl Trimethylammonium Iodide (DTAI).* *N,N*-Dimethyldecylamine (2 mL, 0.00841 mol) was reacted with excess methyl iodide (5 mL, 0.0807 mol) at room temperature for 1 h. The white solid product was washed repeatedly with dichloromethane and filtered under vacuum. Excess solvent was removed by oven drying to constant mass (90 °C, 72 h). Mass (yield %) = 2.41 g (87%). GC-MS analysis showed no methyl iodide or *N,N*-dimethyldecylamine present. ^1H NMR (D$_2$O) δ ppm 0.90 (3H, t), 1.3 (14H, m), 1.81 (2H, t), 3.10 (s, 9H), 3.30 (2H, t). ESI-MS *m/z* 200.2375.

Perfluorinated Amides. Long chained perfluorinated carboxylic acid methyl ester (2.0 g, 0.005 mol) was reacted in liquid ammonia (20 mL) at room temperature for 24 h. Ammonia was allowed to evaporate, and the white powdered product was solubilized in dichloromethane and washed with water. After drying and rotary evaporation to remove the solid, perfluorinated amide was oven-dried to constant mass (90 °C, 48 h). Mass amide (yield %): C$_7$ = 1.54 g (88%); C$_8$ = 1.82 g (89%); C$_9$ = 2.28 g (93%);C$_{10}$ = 1.82 g (86%). GC-MS showed purity was >99%. ESI-MS: perfluoroheptanamide *m/z* 364.0006[M + H]$^+$; perfluorooctanamide *m/z* 413.9974[M + H]$^+$; perfluorononanamide *m/z* 481.0214[M + NH$_4$]$^+$; perfluoro-decanamide *m/z* 513.9908[M + H]$^+$. ^{19}F NMR (DMF with trifluoroacetic acid as the internal standard set to δ = −75.5100 ppm) δ ppm: perfluoroheptanamide −80.4 (3F, t), −118.4 (2F, t), −121.3 to −122.3 (6F, m), −125.7 (2F, m); perfluorooctanamide −80.6 (3F, t), −118.3 (2F, t), −121.3 to −122.3 (8F, m), −125.7 (2F, m); perfluorononanamide −80.8 (3F, t), 118.6 (2F, t), −121.4−122.4 (10F, m), −125.8 (2F, m); perfluorodecanamide −80.8 (3F, t), −118.6 (2F, t), −121.5 to −122.5 (12F, m), −125.9 ppm (2F, m).

Preparation of Liquid Ammonia Surfactant Solutions. The equipment and methodology for charging the vessel with liquid ammonia was as previously described.[41]

^{19}F NMR in Liquid Ammonia. Liquid ammonia solutions of surfactants contained a small amount of deuterated standard (<1%) such as DMSO-d_6 for a lock and ammonium trifluoroacetate (<1%) as the internal standard. High pressure, quick valve NMR tubes were pressure rated to 14 bar (200 psi) designed specifically for 500 MHz NMR instruments with a tube length of 7 in., outside diameter (O.D.) of 5 mm, and wall thickness of 0.38 mm. The top inlet valve of the pressure tube has a standard Swagelok connection allowing for easy connection to the Omnifit apparatus and so practical and safe charging of the NMR tube from the reaction vessel. The tube was cooled in an ice−water slurry, and the liquid ammonia was transferred carefully from the reaction vessel (at room temperature) to the chilled tube. It was then allowed to warm to room temperature before transfer to the NMR instrument. Spectra were recorded at a regulated temperature of 25 °C on a spectrometer operating at 470.5 MHz. ^{19}F chemical shifts