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Zwitterionic and mesoionic liquids: Molecular aggregation in 3-methylsydnone

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Ionic liquids are green solvents with interesting properties: displaying low melting points and high boiling points. They offer a new approach applicable in many instances. Nevertheless, the presence of free ions can be a matter in some cases, e.g. for the study of nucleophilic reactions, in electrochemistry, and in each situation where there is a competition between counter ions, as in micellization of ionic surfactants. Neutral compounds having formal unit electrical charges of opposite sign, and the same physical properties than ionic liquids would be a nice alternative to these latter solvents. There are two classes of chemical compounds having these characteristics: zwitterionic liquids (with no uncharged canonical representation) and mesoionic liquids (in which the negative and the positive charges are delocalized). In that last class we have chosen to work with 3-methylsydnone in order to examine, in this aprotic solvent, if it was possible to observe aggregation of surfactants in the same manner as in water. With all kinds of surfactants studied (ionic, zwitterionic and mesoionic) we have been able to demonstrate the formation of direct micelles: hydrogen bonding is thus not mandatory for molecular aggregation. Comparison of the behavior in water and in formamide showed that solvophobic interactions were qualitatively comparable but with a lower intensity.

ionic liquids, zwitterionic liquids, mesoionic liquids, 3-methylsydnone, molecular aggregation, micellization, solvophobicity

1 Introduction

Ionic liquids, salts that are liquid near ambient conditions [1] represent a relatively new class of materials with unique properties. They have a wide range of potential applications, for example as solvents for reactions and material processing [2], as extraction media [3], or as working fluid for chemical devices [4]. The interest in ionic liquids as green solvents has grown enormously in the last few years [5]. They are convenient and economical solvents due to their efficiencies and recyclability. But as some of them are viscous, not very biodegradable and even toxic, they have to be carefully selected according to the desired application. They also display unique physicochemical properties: low melting points and high boiling points.

Ionic liquids offer numerous advantages over conventional organic solvents for carrying out organic reactions. For example: (1) Product recovery is made easier, catalysts can be recycled, Ionic liquids can be reused, rates of reactions are often enhanced and selectivity is frequently increased. (2) The main interest lies in their peculiar properties: absence of flammability, lack of measurable vapor pressure (which can be an advantage for the reduction of VOC for example but a drawback for product separation), good ability to dissolve organic or organometallic compounds, and even some inorganic salts. (3) They are economical solvents!

Ionic liquids are only composed of ions. The most common classes are alkylammonium salts, alkylpyridinium salts and *N*,*N*′-dialkylimidazolium salts. Recently, tunable aryl alkyl ionic liquids (TAAILs) have been synthesized [6] and,

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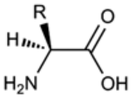
*Corresponding author (email: lattes@chimie.ups-tlse.fr) owing to their properties, authors present them as “the next generation of Ionic Liquids”.

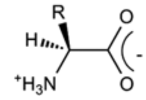
In many cases, the presence of ions does not play an important role on the course of reactions. However, in some cases, ions may be an extra constraint. For example: (1) In electrochemistry, where addition of salts is generally needed to generate carrier ions. With ionic liquids, not only carrier ions, but also ions of the ionic liquids migrate along with potential gradient. (2) In the study of ionic surfactants, for which a rather small quantity of the surfactant (and, of course, a small quantity of the counter ions) is dissolved in a liquid which is composed of different ions in enormous quantity! The surfactant studied is then not the original salt but a new surfactant resulting from the exchange of its counter ions with those of the solvent. (3) In reactivity, as in nucleophilic reactions, where there is a competition between the nucleophile and the anion of the ionic liquid, etc.

For all these reasons, it would be interesting to work with compounds having the same fascinating properties than conventional I.L. (low melting point and high boiling point), but without the presence of free ions. In our laboratory we are interested in the study of surfactants in the wide way; therefore our work will be oriented in the field of “ion-free I.L.”. The first class of compounds answering that condition can be represented by zwitterionic liquids.

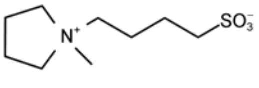
Zwitterionic liquids

Zwitterionic compounds are chemicals that have a total net charge of zero and are thus electrically neutral. They carry formal electrical charges of opposite sign localized on different atoms and then can be considered as inner salts [7]. So amino acids exist mostly as zwitterions in a certain range of pH and the pH at which the average charge is zero is called the molecule’s isoelectric point.





With zwitterionic compounds, cations and anions are tethered covalently. Another example of zwitterionic liquids is imidazolium sulfonate.



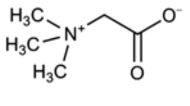
Many zwitterionic compounds are solid at room temperature, but:

(1) It is possible, by structural transformation, to obtain liquids; for example, a new family of zwitterionic liquids has been described arising from a phase transition of ammonium salts containing an ether bond which is effective for lowering the melting point [8].

(2) For some of them they turned liquid at room temperature by adding an appropriate compound (such strategy is operative too with ionic liquids themselves: an appropriate substance may be added to finely tune the physical properties of the system).

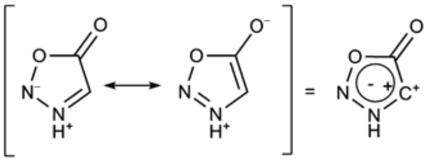
(3) Increasing the length of the hydrocarbon spacer between cation and anion generally lowers the melting point of the zwitterion.

Betaines are a subclass of zwitterionic compounds. A betaine is any neutral chemical compound with both a positively charged cationic functional group: such as an ammonium or a phosphonium ion which bears no hydrogen atom - and a negatively charged functional group (such as carboxylate group which may not be adjacent to the cationic site). A betaine thus may be a specific type of zwitterions; trimethylglycine is a typical example of betaines.

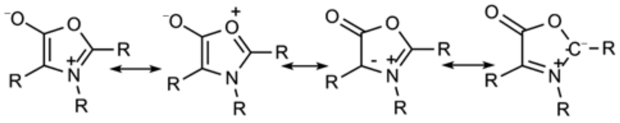


Mesoionic liquids

Mesoionic compounds are a subclass of betaines. They are essentially dipolar five- (or possibly six-) membered heterocyclic compounds in which both the negative and the positive charge are delocalized, and for which a totally covalent structure cannot be written. Therefore they cannot be represented satisfactorily by any sole polar structure. The formal positive charge is associated with the ring atoms, and the formal negative charge is associated with ring atoms or an exocyclic nitrogen or a chalcogen atom [7]. The most representative members of this family are five membered mesomeric betaines: sydnones and munchnones.



sydnone



munchnone

Sydnones constitute a well-defined class of mesoionic compounds: they are the most important and significant mesoionic compounds because they possess different types of physiological activity, depending on the substituents in the heterocyclic ring. Sydnones find their use as anti-inflammatory, antimicrobial, anticancer, and analgesic agents. They were first prepared in 1935 by Earl and Mackney [9].

Owing these interesting properties we have chosen to work with the most simple sydnone: 3-methylsydnone, which possesses the same interesting properties than ionic liquids, and we decided to study the aggregation behavior of surfactants in this compound.

Table 1 Various physicochemical parameters of water, formamide (at 25 °C) and 3-methylsydnone (at 40 °C)

Solvent	mp (°C)	bp (°C/mm Hg)	$\varepsilon/\varepsilon_0$	μ (D)	γ (mN/m)	$\gamma/v^{1/3}$ (mN/m²)
Water	0	100/760	80	1.8	72	2750
Formamide	4	210/760	109.5	3.7	58.5	1700
3-Methylsydnone	36	91/5.10^{-2}	144	7.3	57	1340

3-methylsydnone: A new mesoionic liquid solvent

There is still controversy about micellization in non aqueous polar solvents. Compared to aqueous media, relatively few studies on aggregation of amphiphilic molecules have been carried out in non aqueous structured liquids.

Moreover, even if there are some aprotic ionic liquids known to allow micelle formation, nearly all studies to date on micellization in non aqueous polar solvents have been carried out in protic solvents such as hydrazine [10], ethylammonium nitrate [11], glycols [12] and formamide [13]. A convenient sydnone would be a very interesting aprotic medium for such studies, but precautions have to be taken as sydnones in general have proven to be reprotoxic compounds.

It can be seen from the various physicochemical characteristics of 3-methylsydnone (Table 1) that this compound corresponds to a structured polar medium which could be exploited to investigate molecular aggregation [14]. The highly polar nature of 3-methylsydnone is shown by its high relative dielectric constant $\varepsilon/\varepsilon_0$ and dipole moment μ. The $\gamma/v^{1/3}$(v = molar volume) is also elevated, indicating the structured nature of this solvent. Although it is aprotic, 3-methylsydnone does have properties favoring the aggregation of amphiphiles.

Nevertheless, Evans *et al.* [15] have studied the variation of the surface tension and the conductance of tetradecylpyridinium nitrate and hexadecylpyridinium bromide as well as the diffusive interfacial transport (DIT) of dihexadecyldimethylammonium acetate in 3-methylsydnone. These authors did not observe any discernable modification in the surface tension vs. concentration for neither pyridinium surfactants nor liquid crystalline phases with DIT method [16]. Evans *et al.* concluded: “These results suggest that surfactant self aggregation processes do not occur in 3-methylsydnone and probably not in other aprotic, polar, high cohesive energy density solvents. Hydrogen bonding – leading to solvent structure – must play a decisive role in amphiphilic self assembly”.

But, (1) all these authors experiments with pyridinium surfactants have been carried out at 40 °C; (2) with the double-chained surfactant, the Krafft temperature in water is 34 °C.

All their experiments have been carried out at temperatures above the Krafft point “in water”, but this parameter is different in non aqueous media! The Krafft point can be defined as the temperature of fusion of solvated surfactants: this temperature will depend on the nature of solvent [17]. In general, the Krafft point is lower in water than in other solvent (Table 2).

We have shown that for SDS it is 39 °C and for CTAB 17 °C higher in formamide compared to water (Table 2). In our opinion, Evans *et al.* did not observe aggregation because they worked at a too low temperature. We have been able to detect liquid crystalline phases in the binary system hexadecylpyridinium bromide/3-methylsydnone by optical microscopy and small angle X-ray diffraction: we observed two phases, the first one at 45.4 °C and the second at 55 °C [18]. Our conclusion was: surfactant self aggregation can thus occur in 3-methylsydnone and therefore in an aprotic solvent.

Our purpose here is to demonstrate that molecular aggregation is a general behavior of surfactants, to prove it by studying the micellization of different families of surfactants by different means, and to compare the results obtained in 3-methylsydnone with those obtained in water and formamide. Following that idea, molecular aggregation of ionic, zwitterionic and mesoionic amphiphiles was studied in 3-methylsydnone.

2 Experimental

2.1 General

Formamide (Aldrich 99% spectrophotometric grade) was kept over molecular sieves (3 Å) and used as supplied. The water content (< 1% for solvents and 0.05% for surfactants) was measured by the Karl-Fischer method). Surface tensions were measured using a Prolabo tensiometer (Tensiomat N°3) using the ring detachment method. Microscopic examinations and X-ray scattering experiments have been described elsewhere [14]. 3-Methylsydnone melts at 36 °C, but displays surfusion, therefore measurements below that temperature were determined in the superfused solvent.

2.2 Synthesis of 3-methylsydnone

3-Methylsydnone was synthesized using the procedure described by Earl and Mackney [9].

Table 2 Krafft points (°C)

	SDS	CTAB
Water	16	26
Formamide	55	43

Preparation of N-nitrososarcosine 1)

2 mol of sarcosine in alkaline solution (pH 10) were refluxed for 15 min to remove methylamine. The solution was cooled to 0 °C, and 2 mol of sodium nitrate dissolved in 80 mL of water were then added dropwise. The mixture was acidified with hydrochloric acid to pH 2. The reaction mixture was left to stand for 3 d under stirring at room temperature. The solution was extracted six times with diethyl ether. After drying over $MgSO_4$ and evaporating the ether, a pale yellow liquid, *N*-nitrososarcosine, was obtained (yield 18%; IR 3500 (OH), 1750 (CO), 1470 cm^{-1} (N–N=O)).

Preparation of 3-methylsydnone

5×10^{-1} mol of *N*-nitrososarcosine in 200 mL of freshly distilled acetic anhydride was refluxed for 15 min in a round bottomed flask. The reaction starts rapidly and was carried out without heating, but in the dark. The acetic anhydride was evaporated under vacuum ($T < 60$ °C) and the residue distilled under reduced pressure. 3-Methylsydnone was recovered as a pale yellow liquid (yield 60%; mp: 36 °C; bp: 91 °C/5×10^{-2} mmHg; IR: 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.91 (3p, s, CH_3N); 6.35 (1p, s, CH). Anal. calcd C 36.00; H 4.02; N 27.99; O 31.97. Found for $C_3H_4N_2O_3$: C 35.98; H 4.10; N 27.92; O 31.94.

2.3 Surfactants

Cetylpyridinium bromide (Fluka) was recrystallized four times from ethyl acetate/acetone (50/50, *v*/*v*) and dried in a vacuum oven at 30 °C. Elemental analysis indicated a purity > 99%. Cetyltrimethylammonium bromide (Merck, 99% minimum purity) was used as supplied.

β-Alaninebetaines have been prepared using the method described by Le Berre and Delacroix [19]: reaction of acrylic acid with tertiary amines. 2 mmol of the suitable amine were reacted with 3 mmoles of acrylic acid, at room temperature, in a mixture of 3 mL of diethyl ether and 1 mL of acetonitrile. After one week a precipitate was recovered by filtration.

N-Dodecylalaninebetaine, yield: 68%, mp 135 °C. Anal. calcd C 71.52; H 12.35; N 4.90; O 11.20. Found for $C_{17}H_{35}NO_2$: C 71.47; H 12.34; N 5.01; O 11.18.

N-Hexadecylalaninebetaine, yield: 57%, mp 160 °C. Anal. calcd C 73.84; H 12.68; N 4.10; O 9.36. Found for $C_{21}H_{43}NO_2$: C 73.78; H 12.70; N 4.07; O 9.40.

N-Octadecylalaninebetaine, yield: 55%, mp 179 °C. Anal. calcd C 74.73; H 12.81; N 3.78; O 8.65. Found for $C_{23}H_{47}NO_2$: C 74.80; H 12.78; N 3.82; O 8.62.

2.4 Synthesis of long chain alkyl azides

We employed the method described by Reeves and Bahr [20] involving a liquid-liquid phase transfer reaction between an aqueous solution of sodium azide and an alkyl halide in the absence of organic solvent. Previous work in our laboratory having shown that formamide can be profitably employed instead of water as solvent in various reactions [21], we therefore used formamide in place of water.

The alkyl bromide (8 mmol) was added to a 25% sodium azide (16 mmol) solution in formamide. Aliquat® 336 (0.4 mmol) was then added to the mixture which was heated to 100 °C for 6 h under stirring. After extraction with diethyl ether and distillation, the products were identified by elemental analysis, NMR and IR spectroscopy. Boiling points were in agreement with literature data (yields: 98%–99%).

N-Heptylazide: bp 75 °C/21 mbar. *N*-Decylazide: bp 62 °C/0.02 mbar. *N*-Dodecylazide: bp 71 °C/0.03 mbar.

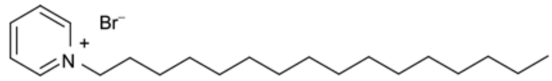
3 Results and discussion

3.1 Ionic surfactants

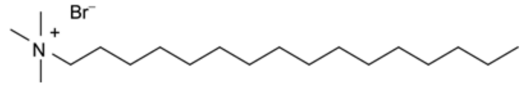
Investigations of the 3-methylsydnone/cetylpyridinium bromide (CPBr: **Ia**) and 3-methylsydnone/cetyltrimethylammonium bromide (CTAB: **Ib**) binary systems by optical microscopy and small angle X-ray diffraction gave different results. The examination of the system with CPBr under polarizing conditions showed the presence of ordered lamellar and hexagonal phases. By contrast, optical microscopic observations have shown only the presence of both isotropic and lamellar phases in the CTAB/3-methylsydnone system. X-ray diffraction studies confirmed these results and the existence of micelles only for the system with CPBr.

CTAB and CPBr differ only in the nature of their polar heads which do not interact in the same way as with the sydnone. This factor, which also depends on the nature of the solvent, is ill-defined. Polar head/solvent interactions have to be investigated.

Ia



Ib



3.2 Zwitterionic surfactants

This study was devoted to β-alaninebetaines (**II**) synthesized using the method described by Le Berre and Delacroix [19]:

$$\mathrm{R{-}N^{+}(CH_3)_2{-}(CH_2)_2{-}CO_2^{-}}$$
$$\mathrm{R} = \mathrm{C_{12}H_{25}}\,(\mathbf{IIa});\ \mathrm{C_{16}H_{33}}\,(\mathbf{IIb});\ \mathrm{C_{18}H_{37}}\,(\mathbf{IIc})$$

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1) Nitroso compounds are known to be carcinogenic; therefore all necessary precautions have to be taken during the synthesis.

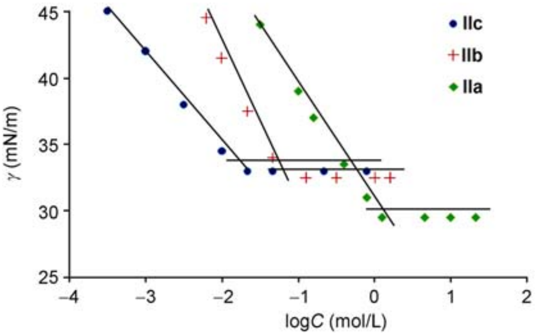

Figure 1 Plot of surface tension against the logarithm of the concentration of β-alaninebetaines in 3-methylsydnone at 60 °C (temperature above the highest Krafft point of these compounds).

We were able to observe micellization of β-alaninebetaines in 3-methylsydnone (Figure 1). As in water and formamide, the critical micelle concentration (CMC) fell with increasing length of the hydrophobic tail. However, for equal chain lengths the CMC was almost double compared to the one observed in formamide.

The values of the dielectric constant ($\varepsilon/\varepsilon_0 = 144$ at 40 °C) and the dipole moment ($\mu = 7.3$ D) of 3-methylsydnone are higher than those of formamide ($\varepsilon/\varepsilon_0 = 109.5$ at 25 °C; $\mu = 3.4$ D). Thus the electrostatic bonds formed by addition of surfactants molecules in the sydnone will tend to favor solvation of these molecules. During micellization, the energy required for the desolvation of these amphiphiles will be higher in 3-methylsydnone than in formamide. For a given homologous series of surfactants, the CMC can be expressed in terms of the following relationship:

$$\log\text{CMC} = a - b(n+1)$$

where a is the contribution of the polar head to micellization, b the increment per CH_2 group, and n+1 the total number of carbon atoms in the hydrophobic tail.

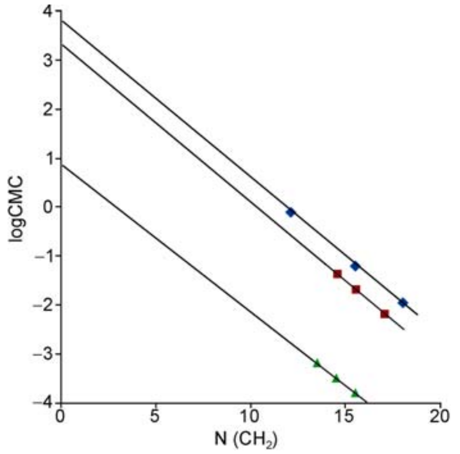

Figure 2 Plot of logarithm of CMC against the number of carbon atoms in the hydrophobic chain of β-alaninebetaines in water (▲), formamide (■) and 3-methylsydnone (◆).

A plot of logCMC of the β-alaninebetaines vs. the number of carbon atoms in the hydrophobic tail, in water, formamide, and 3-methylsydnone is shown in Figure 2.

It can be seen that in all these three media, there was a linear relationship between logCMC and the length of the hydrocarbon chain. From the slopes we could evaluate the respective incremental contribution a and b of the polar heads and CH_2 groups to micellization. The values of these parameters are listed in Table 3.

In this table we observe that parameter b is essentially the same in all three solvents. This shows that solvophobic interactions in formamide and 3-methylsydnone are similar to those in water. In contrast, parameter a is not the same in the different solvents.

3.3 Mesoionic surfactants

We then investigated a series of mesoionic compounds of original structures, the alkylazides (**III**):

$$\text{R–N}^{-}\text{–N}^{+}\text{=N} \leftrightarrow \text{R–N=N}^{+}\text{=N}^{-}$$

$$\text{R} = C_7H_{15}\,(\textbf{IIIa});\ C_{10}H_{21}\,(\textbf{IIIb});\ C_{12}H_{25}\,(\textbf{IIIc})$$

The long-chain azides were synthesized using a method developed in our laboratory involving a liquid/liquid phase transfer reaction in formamide [21]. The CMC of these long-chain alkyl azides were measured in 3-methylsydnone at 40 °C, which is above the highest of the Krafft point for these compounds. These alkyl azides are insoluble in water. Nevertheless, they display surfactant properties in both formamide and 3-methylsydnone. In a previous study, we observed surfactant properties of water-insoluble amphiphiles (the long-chain phosphonium salts) in formamide [22]. The present results are a further example of the generality of surfactant behavior in non aqueous solvent systems.

The surface tension results for the alkyl azides in formamide and 3-methylsydnone are shown in Figure 3.

The CMC values are listed in Table 4.

As found with the betaines, the CMCs of the azides for equal chain length were higher in 3-methylsydnone than in formamide. Figure 4 shows the plot of the logCMC against the number of carbon atoms in the chain.

The values of parameters a and b are listed in Table 5. It

Table 3 Values of parameters a and b, representing the contributions of polar heads and CH_2 groups, respectively, to micellization of betaines in water, formamide and *N*-methylsydnone

Compound	Parameter	
	a	*b*
Water	0.9	−0.32
Formamide	3.58	−0.33
N-methylsydnone	3.72	−0.29

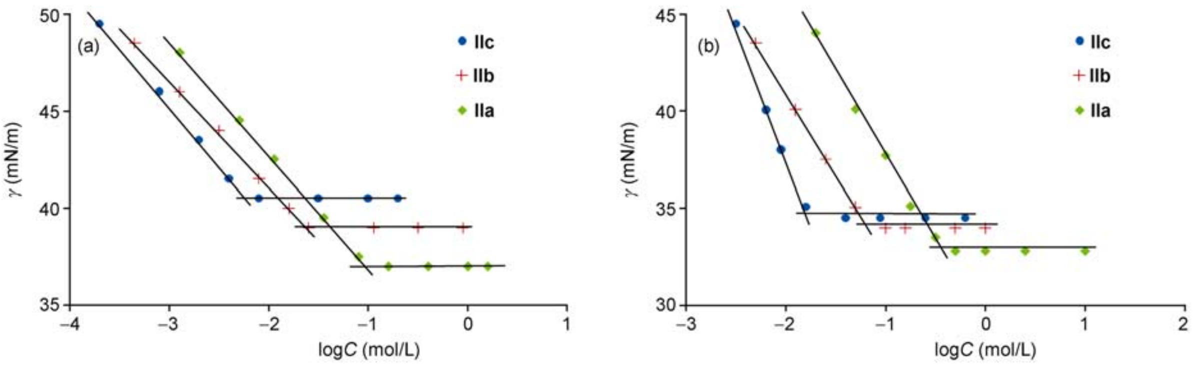

Figure 3 Plot of surface tension against the logarithm of the concentration of compounds IIIa, IIIb and IIIc in formamide (a) and in 3-methylsydnone (b) at 40 °C.

Table 4 CMC values of alkyl azides in formamide and 3-methylsydnone

Compound	CMC (mol/L)		
	IIIa	**IIIb**	**IIIc**
Formamide	0.125	2.3×10^{-2}	6×10^{-3}
3-Methylsydnone	0.400	6.6×10^{-2}	2.5×10^{-2}

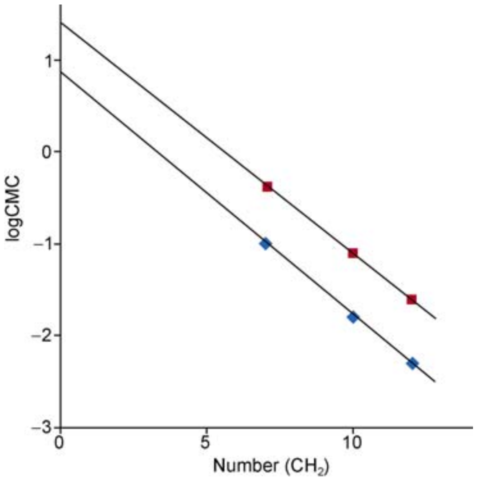

Figure 4 Plot of logarithm of CMC against the number of carbon atoms in the hydrocarbon chain of alkyl azides in formamide (◆) and 3-methylsydnone (■).

Table 5 Parameters *a* and *b*, corresponding to the respective contributions of polar heads and CH_2 groups to micellization of alkyl azides in formamide and *N*-methylsydnone

Compound	Parameter	
	a	*b*
Formamide	0.9	–0.25
N-Methylsydnone	1.3	–0.24

can be seen that parameter *a* was not the same in the two solvents, whereas parameter *b* was identical in formamide and 3-methylsydnone, indicating that solvophobic interactions were comparable in both solvents.

4 Conclusions

In this paper we have shown that synthesized ionic, zwitterionic and mesoionic amphiphiles displayed surfactant properties in 3-methylsydnone, which is a polar and aprotic solvent. Moreover, we found that solvophobic interactions in formamide and 3-methylsydnone were comparable to the hydrophobic interactions encountered in water. Since the solvophobic interactions seemed identical in these media, the interactions between the polar heads of the surfactants and the solvent would tend to have the greatest influence on micellization. Therefore, we showed that parameter *a*, representing the contribution of the polar head to micellization, was different in the different media, and also differed between the zwitterionic and mesoionic surfactants. The values of *a* were comparable in formamide and in 3-methylsydnone, both being considerably higher than in water. This phenomenon can be accounted for by interactions stemming essentially from solvation. In aqueous medium, micellization of surfactants involves mainly the formation of hydrogen bonds with water, whereas dipole-dipole interactions predominate in formamide and in 3-methylsydnone, which have similarly delocalized electronic structures, these interactions being more difficult to break than hydrogen bonds. Since the molecular aggregation depends on the nature of the surfactants, the nature of the solvent and strongly on the interactions between both, micelles production hinges on the optimal choice of the surfactant-solvent pair [23].

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