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Physico-chemical characterization of new amphiphilic ion pairs based on alkylcarboxilic acids

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ABSTRACT

A novel class of ion-pair surfactants (IPS) was prepared through the neutralization of ethanolamine and ter-butylamine by alkyl carboxylic acids by mild reaction conditions. Their aggregation behavior has been studied by surface tensiometry and conductivity. Decreases in the critical micelle concentration (cmc) were obtained, for all studied IPS families, when increasing the anionic alkyl chain length (n). Compared with ([EA][C_nH_{2n+1}COO]) bearing the same hydrocarbon chain, ([tBA][C_nH_{2n+1}COO]) exhibits lower critical micelle concentration (cmc). Conductimetric measurements allowed determination of the degree of ionization of the micelle (α) and the molar conductivity (KM) of these surfactants as a function of n. Changes in the physicochemical, surface and micellar properties of these new IPS can be linked to the nature of the cation. By comparison with classical anionic surfactants having inorganic counter ions, terbutylammonium alkyl carboxylates and ethanolammonium alkyl carboxylates exhibit a higher ability to aggregate in aqueous solution, demonstrating their potential applicability as surfactant.

Keywords: *ion-pair surfactants, ethanolammonium carboxylate, terbutylammonium carboxylate, micellar properties.*

1. INTRODUCTION

The behavior of surfactants in solution or at liquid/fluid interfaces has been widely studied for many years due to their enormous importance in many processes and technologies, such as detergency, food processing, pharmaceutical industry, or cosmetics [1-3]. Most of adsorption studies have been performed at the water/air interface by surface tension measurements [4-6].Micelle formation can be regarded as a choice mechanism to adsorption at the interfaces for dismissal of hydrophobic groups from contact with water, thereby diminishing the free energy of the systems. It is well known that amphiphilic molecules act differently when present in micelles than as free monomers in solution. Ion-pair surfactants (IPS) are electrolytes organic compounds thah have gained attention as a new class of designer surfactants [7-9]. Those formed by the transfer of a proton between a Bronsted acid and a Bronsted base form a protic subgroup in the class of surfactants now referred to as “ion-pair surfactants (IPS)”. The study of the interface and surface interactions is essential to understand micellar properties, technical applications, and environmental impacts of IPS [10–17]. The critical micelle concentration (cmc) is an important factor in the characterization of the of amphiphilic compounds self-aggregation. The formation of micelles is due to the nature of ions constituting the IPS which contain, generally, both hydrophobic and hydrophilic domains. Hence the cmc is dependent on the relative sizes of these domains. A larger hydrophobic domain will result in a lower cmc [18-23]. The purpose of this work is to study the synthesis, characterization and the properties of new alkyl carboxylate surfactants protonated having terbutylammonium and ethanolammonium $C_nH_{2n+1}COO^-$ (n = 8, 10, 12, 14 and 16) as counter anions. The aggregation behavior of this IPS in aqueous solutions has been investigated using surface tension and electrical conductivity measurements at room temperature (298 K). The results can be helpful for their use in a wide range of applications.

2. EXPERIMENTAL SECTION

2.1. Materials.

Carboxylic acids (octanoic, decanoic, dodecanoic, tetradecanoic and hexadecanoic acid), Carboxylic acids sodium salt (dodecanoic, tetradecanoic and hexadecanoic sodium salt), terbutylamine and ethanolamine are commercially available from Fluka (>99.0%) and are used without further purification. Water is purified with Milli-Q 18.3 MX water system.

2.2. Preparation of terbutylammonium and ethanolammonium alkyl carboxylates surfactants. The terbutylammonium alkyl carboxylates ([tBA][C_nH_{2n+1}COO]) and ethanolammonium alkyl carboxylates ([EA][C_nH_{2n+1}COO]), are synthesized by neutralization reactions of terbutilamaine or ethanolamine by the corresponding Bronsted acid (molar ratio of amine/acid = 1/1) according to procedures described elsewhere (Scheme 1) [24–25]. The carboxylic acid dissolved in hexane was added slowly to amine with stirring in a tree-necked round-bottom flask equipped with a dropping funnel and then the stirred to T = 298 K for 4 h. All IPS carboxylates synthesized were dried overnight at 343 K under high vacuum (0.1 Pa) prior to use. Monitoring of the reactions was carried out by FTIR spectrometry (Shimadzu, 8400S) ranging from 4000 to 400 cm-1, with a resolution of 1 cm−1 , comparing the vibration bands of different functional groups of derivative with the fatty acid and amine of departure. For each sample, 2.0 mg sample and 148 mg KBr were weighted and grounded in an agate mortar for 10 min before making the pellets.

The FTIR spectra of terbutylammonium dodecanoate and dodecanoic acid respectively (Figure 1) show theasymmetric and symmetric stretching bands for the terbutylammonium dodecanoate molecule at 2562-2208 cm^{-1} for the ammonium group and the deformation band at 1533-1470 cm^{-1} of the respective group corresponding to the protonated amine, while it is observed at 1624 $cm^{-1}$and 1393 cm^{-1} of the asymmetric and symmetric stretching bands for the carboxylate group, respectively, and the deformation band of 719 cm^{-1}. In the FTIR spectrum it is not observed residue of the starting acid or base.

2.3. Surfacetensionmeasurements.

Surface tension measurements were performed at 298 K using the platinum ring method (DuNoüy Central Scientific tensiometer, accuracy ± 0.1 mN m^{-1}). Temperature was controlled at (298 ± 0.2) K using a JULABO thermostated bath. All measurements were repeated at least twice.

2.4. Conductivity measurements.

Conductivity measurements were performed by using a TetraCon®325 conductimeter. The temperature control (at T = 298.15 K) is ensured by a JULABO thermostated bath. The conductimeter was calibrated with a standard solution of known conductivity (0.1 and 0.02) mol dm^{-3} KCl. The conductivity measurements of the IPS carboxylates in aqueous solutions were carried out by continuous addition of pure IPS carboxylates into water. Each conductivity was recorded when its stability was better than 1% within 2 min.

3. RESULTS SECTION

3.1. Surface tension measurements.

The surface tension is a physical property due to the forces of cohesion between molecules of liquids; these superficially active substances are often used in industrial applications and in everyday life. The understanding of thechemical and physical properties of the surfactants is important to define, to choose which is favorable in such chemicals for industrial applications. It is essential to have tools that can describe the physical properties and the behavior of surfactants in hydrophobic and hydrophilic environments phase. Such tools could predict some important characteristics of surfactants, such as the critical micellar concentration (cmc), area minima (A_{min}), surface excess (Γ_{max}) among others, which are dependent on the structure.

Surface tension measurements show no minimum around the cmc, indicating that no unreacted products remain in the synthesized IPSs. The surface tension was measured in order to evaluate the surface activity of the aqueous IPS solutions with regard to their concentrations. Figures 2 and 3 represent a plot of the surface tension (γ) versus ln (C) plot when C is the surfactant molar concentration in aqueous solution; the straight lines are drawn to determine the cmc value. For each IPS, the surface tension progressively decreases with the increase in the IPS concentration up to a plateau region, above which a nearly constant value (γcmc) is obtained. It is worth noting that the absence of a minimum around the breakpoint confirms the high purities of these IPS [26].

Zana found that the surfactants alkyl sulfate and alkyl carboxylate with a counterion of tetrabutylammonium type showed important differences in the phase behavior, self-association in water and microstructure in solution (micelle shape). These differences in micelle ionization degree reflect the fact that the distribution of the electric charge on the sulfate and carboxylate group is quite different, with a greater load on the sulfate group with respect to the carboxylate group [27].

The cmc and Π_{cmc} values are listed in Table 1. Values of cmc vary notably according to hydrocarbon chain length on the carboxylates. Hence the differences in cmc values for both series of carboxylate IPSs can be attributed to the nature of the counterion. cmc values, listed in Table 1, decrease in the order 1a > 2a > 3a > 4a > 5a, as well as in the ethanolamonium and terbutylammonium series as expected from the increase in hydrophobicity due to the increase of the hydrocarbon chain length. IPSs with longer hydrocarbon chains have significantly lower cmc values, which is a common trend for single-tail ionic surfactants. Indeed IPSs studied in this work have low cmc values compared to cmc values obtained for carboxylates sodium salts [24]. The difference is due to the weaker hydration of the counterion, which more effectively decreases electrostatic repulsion between head groups and in this way facilitates micelle aggregation [20]. At identical hydrocarbon chain length, cmc values obtained for ethanolamonium series are smaller than those obtained for terbutylammonium IPS studied herein. However, both series give cmc values largely lower than their homologue sodium carboxylates. In fact, the studied alkyls IPS have a higher capability to micellize in water than traditional ionic surfactants.

Adsorption and micellization processes of the surfactant molecules are considered as phase transformation either from singly state molecule in the solution into adsorbed molecules at the interface (adsorption) or into the well aggregated molecules in the form of micelles (micellization). According to the Gibbs law, applied to the equilibrium systems, the surfactant adsorption at the air/water interface leads to a surface tension reduction of the solution. The adsorbed amount of surfactants (Γ) for studied IPSs is then calculated by using the following equation [25].

$$\Gamma = -\frac{1}{iRT}\left(\frac{\partial\gamma}{\partial \ln C}\right)_T \qquad (1)$$

where R is the gas constant (8.31 J mol^{-1} K^{-1}), T is the absolute temperature, γ is the surface tension, C is the surfactant concentration, and $\left(\frac{\partial\gamma}{\partial \ln C}\right)_T$ is the slope below the cmc in the surface tension plots (Figs. 2 and 3). The parameter i represent the number of species constituting the surfactant which are adsorbed at the interface. The micellization of the studied IPSs in aqueous solution is a spontaneous process and it means that the free energy of change of this process is negative. ΔG_{mic} for all IPSs are summarized in Table 1. The spontaneity of the process is attributed to the repulsion between the different hydrophobic moieties and the polar solvent. The data show that the negative values of the Gibbs free energy are primarily due to an entropic contribution, an effect common in aggregation processes driven by hydrophobicity.

Figure 4 shows the standard Gibbs energy of aggregation of ethanolamonium carboxylate IPs at 298.15 K as a function of the alkyl chain length of anions. This figure provides the following information: (1) the Gibbs energy change was found to be negative, implying as expected that aggregation of IPs occurs spontaneously once the CMC is reached; (2) the longer the alkyl chain of IPs, the more negative the standard Gibbs energy of aggregation, indicating that the aggregation comes more easily with the increase of the alkyl chain length of IPs; (3) the aggregation is driven by alkyl chain-ion inductive and hydrocarbon-hydrocarbon interactions.

3.2. Conductivity study of terbutylammoniun and ethanolamonium carboxylate in aqueous solution.

Conductivity measurements are commonly used in the study of ionic micellar solutions. For nearly all ionic surfactants in aqueous solutions, there is a substantial change of slope at the onset of aggregation. The obtained parameters from conductivity measurements are summarized in Table 2.

The cmc values of the terbutylammonium and ethanolamonium salts are in agreement within the reported uncertainty, with values obtained from surface tension measurements. Similar observation was made: the cmc values decrease significantly with increasing the alkyl chain length (Figure 5). This behavior reflects a common feature of various single-tail surfactants [18-19].

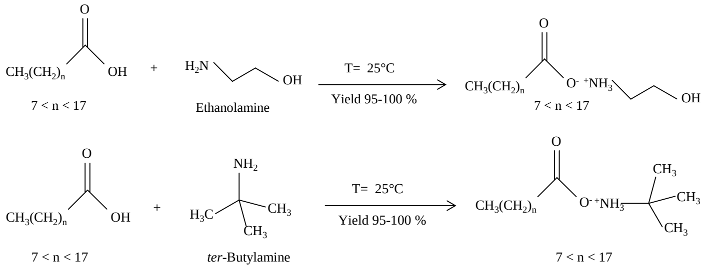
Terbutylammonium and ethanolammonium counterions are much larger and less solvated than small inorganic ions (like Na^+) [3,5,20]. As a result, the terbutylammonium and ethanolamonium cations can be more readily adsorbed on the micellar surface in the Stern layer, decreasing the charge repulsion between cation and polar groups decreasing the cmc compared to sodium carboxylates surfactants [20].

The molar conductivities of the micellar species Λ_M, and the free species values Λ_∞ are listed in Table 2. In each series of surfactants Λ_M values decrease with an increase in the alkyl chain length. It is seen that the molar conductivities at infinite dilution for the carboxylates anion decrease with increasing the hydrophobic chain length; larger anions have lower mobility. At the same time the molar conductivity at infinite dilution for the ethanolamoniumcation (Λ_∞ = 253.8μS cm^2 mol^{-1}) shows that this ion which is less attached to the carboxylate ion and less solvated by water is more mobile than terbutylamonium cation (Λ_∞ = 73.1 μS cm^2 mol^{-1}).

The ionization degree (α) of micelles was estimated from the ratio of the slopes above and below the cmc [24]. Calculated values are reported in Table 2. As can be seen α remained relatively constant from about $0.65 <\alpha< 0.34$ when going from ethanol ammonium dodecanoate to ethanol ammonium hexadecanoate IPSs and $0.39 <\alpha< 0.20$ when going from terbutyl ammonium dodecanoate to terbutyl ammonium hexadecanoate, presenting thus a similar trend with other sodium carboxylate salt surfactants studied ($0.50 <\alpha< 0.22$ when going from sodium dodecanoate to sodium hexadecanoate) [20,24].

Zana has shown that the change in α when increasing n_c is due to a change in charge density at the micelle surface on increasing chain length [30]. As a longer chain length causes a higher degree of compactness of the aggregate, ultimately the ‘‘heads” tend to approach more together, which implies that a large number of counterions are attracted to the Stern layer decreasing the micelle ionization degree. For studied IPSs, the weak change in α with the alkyl chain length is synonymous to weak attraction between the ‘‘heads” and counterion to the Stern layer around.

Nonetheless, the most outstanding property of these IPSs is the fact that they are capable of forming micelles at room temperature even with hexadecanoic acid (C16) in contrast to the homologous alkali soaps, which are restricted in their solubility. As a consequence of the potential use of longer-chain surfactants, a relatively high surface tension reduction can be obtained.



Scheme 1. Preparation of ethanolammonium and ter-butylammonium alkyl carboxylates surfactants.

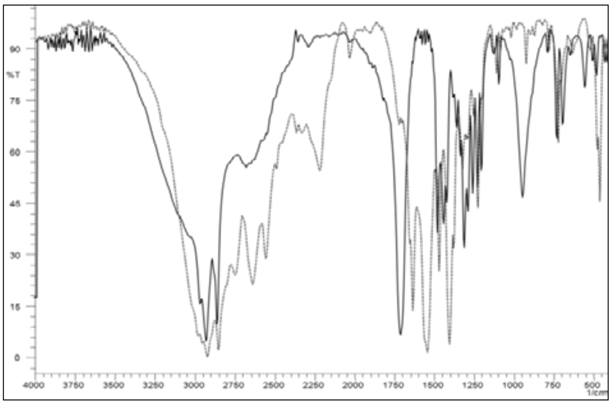


Figure 1. FTIR spectra of terbutylammonium dodecanoate (...); dodecanoic Acid (-).

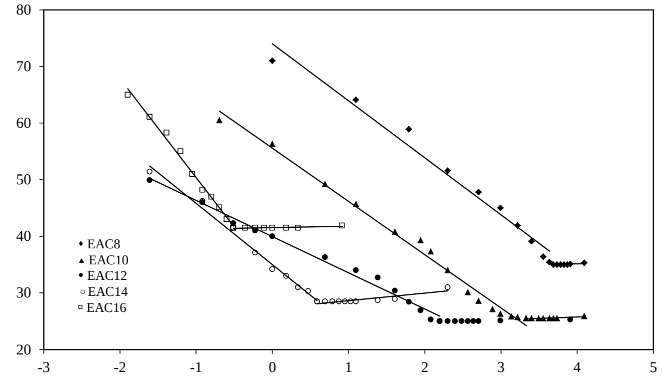


Figure 2. Surface tension as a function of ln (C) for ethanolammonium carboxylates IPS at 298 K: (♦) 1a; (▲) 2a; (●) 3a; (○) 4a; (□) 5a

Table 1. Obtained parameters from surface tension measurements for ethanolammoniumcarboxyltes [EA][$CnH_{2n+1}CO_2$], n = 8 (1a), n = 10 (2a), n = 12 (3a), n = 14 (4a), n = 16 (5a); and terbutylammonium carboxylates [tBA][$CnH_{2n+1}CO_2$], n = 8 (1b), n = 10 (2b), n = 12 (3b), n = 14 (4b), n = 16 (5b) in aqueous solution at 298 K.

IPS	cmc^a (mmol L^{-1})	γ_{cmc} ± 0.1 % (dinas cm^{-1})	Π_{cmc}± 0.1 % (dinas cm^{-1})	Γ_{max}± 0.1 % (μmol m^{-2})	Amin± 0.01 (nm^2)	ΔG˚ ads (Kj mol^{-1})	ΔG˚ mic (Kj mol^{-1})
1a	48.0	35.0	37.06	0.403	0.398	-22.24	-5.49
2a	26.4	25.5	46.56	0.344	0.482	-30.52	-8.05
3a	10.2	25.0	47.06	0.266	0.600	-39.57	-10.76
4a	1.8	28.5	43.56	0.435	0.420	-32.23	-15.61
5a	0.6	41.1	31.01	0.625	0.260	-26.39	-18.15
1b	58.0	45.0	27.1	0.366	0.61	-26.7	-10.1
2b	39.9	25.4	41.7	0.354	0.69	-31.6	-9.14
3b	10.8	27.6	44.1	0.344	0.76	-40.4	-5.89
4b	3.4	28.0	45.1	0.320	0.78	-43.4	-3.02
5b	1.0	25.0	46.7	0.269	0.81	-45.1	-2.35

^{a}The estimated errors for cmc obtained from surface tension are less than 5%.

Table 2. Obtained parameters from conductivity measurements for ethanolammoniumcarboxyltes [EA][$CnH_{2n+1}CO_2$], n = 8 (1a), n = 10 (2a), n = 12 (3a), n = 14 (4a), n = 16 (5a); terbutylammonium carboxylates [tBA][$CnH_{2n+1}CO_2$], n = 8 (1b), n = 10 (2b), n = 12 (3b), n = 14 (4b), n = 16 (5b) and sodium alkylcarboxylates [Na][$CnH_{2n+1}CO_2$], n = 12 (1c), n = 14 (2c), n = 16 (3c) in aqueous solution at 298 K.

IPS	cmc^a (mmol L^{-1})	k (μS cm^{-1})	α	Λ_∞ (μS cm^2mol^{-1})	Λ_M (μS cm^2mol^{-1})
1a	46.01	1836.61	0.91	70.19	107.97
2a	38.24	1738.45	0.74	71.24	71.77
3a	11.50	715.69	0.65	253.80	56.88
4a	1.86	112.34	0.46	122.00	30.63
5a	0.99	41.56	0.34	94.80	4.05
1b	49.98	1964.16	0.61	96.1	123.5
2b	41.2	1827.3	0.53	88.4	90.1
3b	11.9	599.8	0.39	73.1	77.7
4b	2.88	154.2	0.27	66.8	51.1
5b	1.31	51.7	0.20	54.9	29.3
1c	26.04	1593.2	0.50	77.0	84.3
2c	9.54	627.7	0.33	68.5	76.9
3c	3.26	222.1	0.22	64.3	73.3

^{a}The estimated errors for cmc obtained from conductivity are less than 5%.

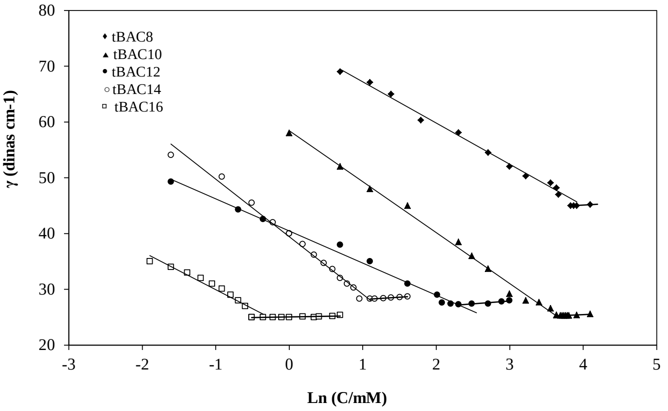


Figure 3. Surface tension as a function of ln (C) for terbutylammonium carboxylates IPS at 298 K: (♦) 1b; (▲) 2b; (●) 3b; (○) 4b; (□) 5b

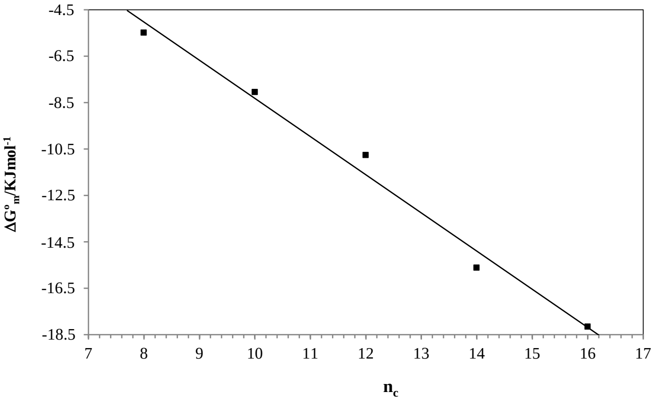


Figure 4. Linear plot between ΔG^o_m of [EA][$CnH_{2n+1}CO_2$], at 298.15 K and the number of carbons in the alkyl chains

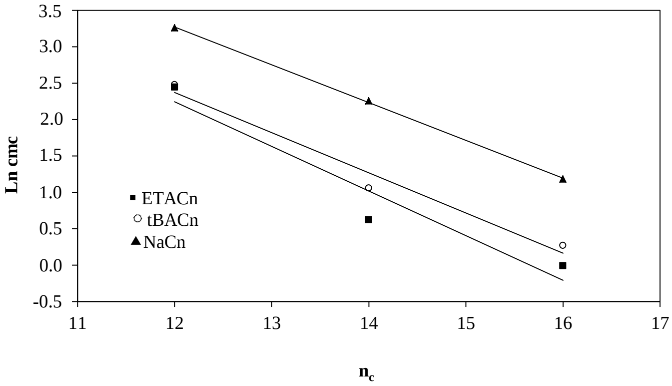


Figure 5. Ln (cmc) against the number of carbon atoms of the alkyl chain, nc, for the terbutylammonium carboxylate family, tba (□), ethanolammonium carboxylate family, eta (■) and sodium carboxylate family, NaCn (▲) as obtained from conductivity method

4. CONCLUSIONS

Ethanol ammonium alkyl carboxylates ([ETA][CnH2n+1COO]) and terbutyl ammonium alkylcarboxylates ([tBA][CnH2n+1COO]), with n = 8–16, were prepared and studied as potential new surfactants in aqueous media. Decreases in the critical micelle concentration (cmc) were obtained, for all studied IPS families, when increasing the anionic alkyl chain length (n). Conductimetric measurements allowed determination of the degree of ionization of the micelle (α) and the molar conductivity (KM) of these surfactants as a function of n. Changes in the physicochemical, surface and micellar properties of these new IPS can be linked to the nature of the cation. By comparison with classical anionic surfactants having inorganic counterions, terbutyl ammonium alkyl carboxylates and ethanol ammonium alkyl carboxylates exhibit a higher ability to aggregate in aqueous solution at room temperature in contrast to the homologous alkali soaps, which are restricted in their solubility, demonstrating their potential applicability as surfactant.

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