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ORIGINAL ARTICLE

# Synthesis and Properties of Sodium Mono-Alkylamide Phthalate Surfactants

**Fu Han · Bao-cai Xu · Zhi-qiang Qu ·
Ya-wen Zhou · Gui-ju Zhang**

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**Abstract** The synthesis of a series of sodium mono-alkylamide phthalate surfactants is described, and the surface activity properties of the surfactants are reported. The mono-alkylamide phthalic acids were synthesized by amidation using primary aliphatic amines (lauryl, myristyl, cetyl) and phthalic anhydride as starting material. They were structurally characterized by IR, $^1$H NMR and MS. The sodium mono-alkylamide phthalate surfactants were prepared by neutralization of the precursor acids with sodium hydroxide. They reduced the surface tension of water to 30–38 mN $m^{-1}$ at concentration levels of $10^{-4}$ mol $L^{-1}$.

**Keywords** Phthalate · Alkylamide · Synthesis · Characterization

## Introduction

It is well known that carboxylate surfactants possess good properties and extensive uses. In recent years the sodium monoester phthalate surfactants have attracted considerable interest because of their many technical applications. The sodium monoester phthalates are synthesized by etherification using fatty alcohol and phthalic anhydride and neutralization with sodium hydroxide. They have superior surface properties such as low surface tension, strong emulsifying capacity and foam capacity [1–9]. However, the ester group in the molecular structure of the surfactants hydrolyzes more easily at high temperature with an acid or base that affects the performance of stability in their application.

The stability could be improved by using an amide group instead of an ester group. The sodium mono-alkylamide phthalate surfactants are useful in a variety of technical applications, such as fastbreak emulsifiers in personal care products, domestic fabric softening agents, foodstuff emulsifiers, various domestic detergents and hard surface cleaners, emulsifiers for Portland cement and concrete, enhanced oil recovery additives, compatibilizers/surfactants for polyurethane/isocyanurate foam systems, wood pulping additives, and other similar uses. However, it has been rarely reported [10].

In this paper, we report the preparation of the sodium mono-alkylamide phthalate surfactants and the study of the surface activity of these compounds by measuring the equilibrium surface tensions of the dilute aqueous solutions. The parameters studied include CMC (critical micelle concentration), $\gamma_{\mathrm{CMC}}$ (the surface tension at the CMC), $\Gamma_{\max}$ (the maximum surface excess concentration at the air/water interface), $a_{\mathrm{m}}^{\mathrm{s}}$ (the minimum area per surfactant molecule at the air/water interface), $\Delta G$ (the standard free energy of micellization).

## Experimental Procedures

### Preparation of Sodium Mono-Alkylamide Phthalate Surfactants

Firstly, 16.3 g (0.11 mol) of phthalic anhydride, 0.04 g ($6.5 \times 10^{-4}$ mol) of boracic acid (catalyst) and 100 mL

F. Han (✉) · B. Xu (✉) · Z. Qu · Y. Zhou · G. Zhang
School of Food and Chemical Engineering, Beijing Technology and Business University, No. 11 Fucheng Road, Haidian District, Beijing 100048, People's Republic of China
e-mail: hanricher@gmail.com

dichloromethane (solvent) were introduced into a 500-mL reaction vessel. Then 0.1 mol of the primary aliphatic amine (dodecylamine, myristyl amine, cetylamine) dissolved in dichloromethane (40 mL) was added slowly dropwise with rapid stirring at 35 °C. After the completion of addition, stirring was continued for 15 min at 35 °C. The crude product was cooled for 2–3 h and the white crystals were precipitated. After being filtered under reduced pressure, the crystals were recrystallized from dichloromethane to give the mono-alkylamide phthalic acid with a yield of 81.8, 85.7 and 76.5%, a purity of 97.0, 98.0 and 98.5%, respectively (Agilent 1200 high-performance liquid chromatography). The structures of the compounds were confirmed by IR, $^1$H NMR and MS. An equal molar quantity of NaOH solution was added to neutralize the mono-alkylamide phthalic acid and the corresponding sodium salts were obtained.

### Characterization of the Sodium Mono-Alkylamide Phthalate Surfactants and Surface Activity Measurements

The proton nuclear magnetic resonance ($^1$H NMR) spectra were acquired on a 300 MHz Bruker DRX-300 NMR spectrometer. Samples were prepared in 5-mm OD tubes with deuterated solvents $CDCl_3$. Chemical shifts were referenced to tetramethylsilane. The infrared (IR) spectra were recorded on an Avater FT-IR Spectrometer Tensor 370 (KBr). The mass spectra (MS) were scanned on a Quattro Micro instrument at 70 eV.

Aqueous solution equilibrium surface tension values were obtained by the Wilhelmy plate method using a Dataphysics tensiometer, model DCAT11. The CMC value was taken at the intersection of the linear portions of the plots of the surface tension against the logarithm of the surfactant concentration. Surfactant solutions were prepared with distilled, de-ionized water. The sample temperature was kept at 25 ± 0.2 °C. Prior to measurements on surfactant solutions, the surface tension of the distilled, de-ionized water was measured. These water values were in the range of $72.3 \pm 0.3$ mN m$^{-1}$. Samples were aged 15 min prior to the surface tension measurement.

## Results and Discussion

### Preparation and Spectroscopic Characterization of the Sodium Mono-Alkylamide Phthalate Surfactants

The general formula and process of the sodium mono-alkylamide phthalate surfactants is shown in Scheme 1. Herein, the mono-alkylamide phthalic acids were prepared by amidation using the primary aliphatic amine and phthalic anhydride as starting materials. The boracic acid was added, which restrained the reaction of carboxylic acid and primary aliphatic amine [11].

These compounds were structurally characterized by their IR, $^1$H-NMR and MS spectra. In all cases, the spectra acquired were consistent with the assigned structures of the compounds.

#### *Mono-Laurylamide Phthalic Acid*

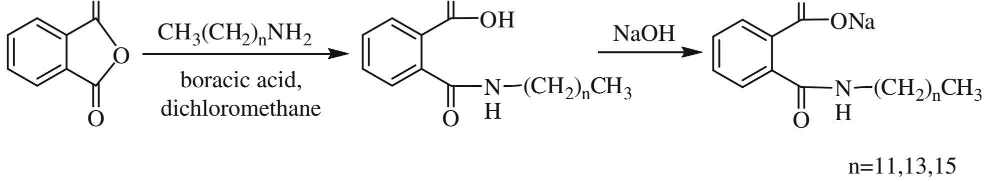
Yield, 81.8%; IR (KBr, $\upsilon$, cm$^{-1}$): 3243 (N–H), 3075 (O–H), 1709 (C = O in –COOH), 1642 (C = O in –NHCO–); $^1$H NMR ($CDCl_3$, 300 MHz, $\delta$ ppm): 0.87 (t, 3H, $CH_3$), 1.25 (m, 18H, $(CH_2)_9$), 1.60 (m, 2H, $CH_2$), 3.42 (t, 2H, $CH_2$), 6.40 (s, 1H, N–H), 7.52–8.06 (m, 4H, benzene ring), 9.60 (s, 1H, O–H); MS: m/z = 334 ($[M + 1]^+$ of mono-laurylamide phthalic acid).

#### *Mono-Myristyl Amide Phthalic Acid*

Yield, 85.7%; IR (KBr, $\upsilon$, cm$^{-1}$): 3308 (N–H), 3092 (O–H), 1711 (C = O in –COOH), 1645 (C = O in –NHCO–); $^1$H NMR ($CDCl_3$, 300 MHz, $\delta$ ppm): 0.89 (t, 3H, $CH_3$), 1.28 (m, 22H, $(CH_2)_{11}$), 1.57 (m, 2H, $CH_2$), 3.38 (t, 2H, $CH_2$), 6.41 (s, 1H, N–H), 7.49–8.11 (m, 4H, benzene ring), 9.62 (s, 1H, O–H); MS: m/z = 362 ($[M + 1]^+$ of mono-myristyl amide phthalic acid).

#### *Mono-Cetyl Amide Phthalic Acid*

Yield, 76.5%; IR (KBr, $\upsilon$, cm$^{-1}$): 3307 (N–H), 3099 (O–H), 1710 (C = O in –COOH), 1647 (C = O in –NHCO–); $^1$H NMR ($CDCl_3$, 300 MHz, $\delta$ ppm): 0.88 (t, 3H, $CH_3$),



**Scheme 1** The general process of the sodium mono-alkylamide phthalate surfactants

1.26 (m, 26H, $(CH_2)_{13}$), 1.54 (m, 2H, $CH_2$), 3.42 (t, 2H, $CH_2$), 6.48 (s, 1H, N–H), 7.48–8.00 (m, 4H, benzene ring), 10.11 (s, 1H, O–H); MS: m/z = 390 ($[M + 1]^+$ of mono-cetyl amide phthalic acid).

### Equilibrium Surface Tension Measurements

The equilibrium surface tensions of dilute aqueous solutions of the sodium mono-alkylamide phthalate surfactants were measured. The minimum surface tension ($\gamma_{CMC}$) values were acquired by analyzing the plateau region of the plots. The critical micelle concentrations (CMC) of the surfactants were acquired by analyzing the intersection point of the plateau region and the steeply downward sloping portion of the plots. The surface excess concentration ($\Gamma_{max}$) and the surface area per molecule ($a_m^s$) were acquired by analyzing the application of the Gibbs equation to the steeply downward sloping section of the plots. A summary of the data is compiled in Table 1 and in Fig. 1. These surfactants all reduced the surface tension of water to a minimum value of approximately 30–38 mN $m^{-1}$ at concentrations of $10^{-4}$ mol $L^{-1}$.

**Table 1** Aqueous surface activity of the sodium mono-alkylamide phthalate surfactants

| Compounds | Laurylamide | Myristyl amide | Cetyl amide |
|---|---|---|---|
| CMC (mol $L^{-1}$) | $7.25 \times 10^{-4}$ | $3.24 \times 10^{-4}$ | $3.11 \times 10^{-4}$ |
| $\gamma_{CMC}$ (mN $m^{-1}$) | 38.19 | 36.06 | 30.28 |
| $\Gamma_{max}$ (μmol $m^{-2}$) | 1.10 | 1.19 | 2.48 |
| $a_m^s$ ($Å^2$ $molecule^{-1}$) | 150.96 | 139.54 | 66.96 |
| $\Delta G$ (KJ $mol^{-1}$) | −27.88 | −29.87 | −29.98 |

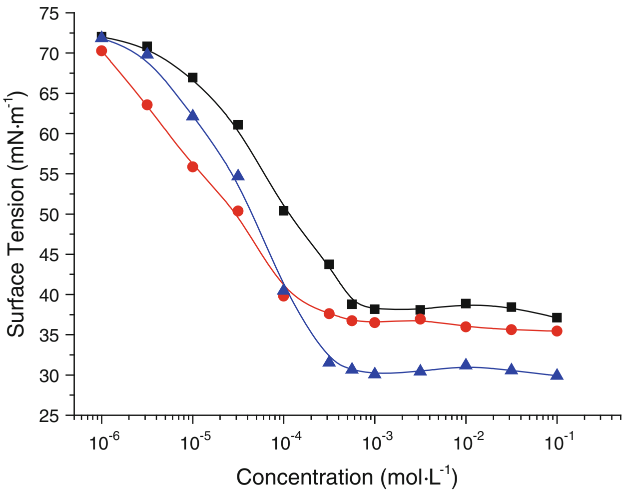


**Fig. 1** Plots of equilibrium surface tensions of aqueous solutions of the sodium mono-alkylamide phthalate surfactants versus log moles concentration. *Filled squares*, laurylamide; *Filled circles* myristyl amide; *Filled triangles*, cetyl amide

Inspection of the data in Table 1 shows that the sodium mono-alkylamide phthalate surfactants significantly reduce the surface tension of the solutions at low concentrations, indicating that these molecules adsorb strongly at the air/water surface and that they are highly effective aqueous surfactants.

The sodium mono-alkylamide phthalate surfactants solutions were aged a week and their surface tensions at different concentrations did not increase, indicating that these surfactants are stable in water.

A dramatic change in slope of the surface tension versus log surfactant concentration curves is generally interpreted as the onset of surfactant aggregation into micelles in bulk aqueous solution. By use of these criteria, inspection of the curves in Fig. 1 suggests that the species of the sodium mono-alkylamide phthalate surfactants are forming micelles.

The sodium mono-alkylamide phthalate surfactants show small CMC values. This indicates that these compounds aggregate easily. Micellization takes place at a concentration of about $10^{-4}$ mol $L^{-1}$. The CMC values decrease as the length of their carbon chains increase because the hydrophobic interaction increase between the surfactants as the length of their carbon chains increase.

The saturation adsorption values, $\Gamma_{max}$, at the air/water interface and the minimum area per surfactant molecule, $a_m^s$, at the air/water interface were obtained from the slope of the surface tension versus log concentration plots (Fig. 1) by using the approximate form of the Gibbs adsorption isotherm equations (Eqs. 1 and 2).

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{\partial \gamma}{\partial \log C}\right)_T \tag{1}$$

$$a_m^s = \frac{10^{16}}{N_A \Gamma_{max}} \tag{2}$$

$$\Delta G = RT \ln\left(\frac{CMC}{55.5}\right) \tag{3}$$

where $R = 8.3144$ J $mol^{-1}K^{-1}$, $N_A$ = Avogadro's number, $\Gamma_{max}$ is in $10^7$ μmol $m^{-2}$, and $a_m^s$ is in $10^2$ $nm^2$ $molecule^{-1}$. In our solution, we were able to set $n = 2$ [12].

It was to be expected, and was confirmed by the $a_m^s$ values in Table 1, that the surface area per molecule ($a_m^s$) (Eq. 2) of the sodium mono-alkylamide phthalate surfactants at the interface decrease as the length of their carbon chain increases. The surfactants at the interface can be packed much tighter as the hydrophobic interaction increase between the surfactants, and the $a_m^s$ would be smaller.

The free energy of micellization ($\Delta G$) (Eq. 3) of the sodium mono-alkylamide phthalate surfactants decreases as the length of their carbon chain increases, indicating that the processes are thermodynamically favored.

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## Author Biographies

**Fu Han** received a B.Sc. in chemical engineering from the East China University of Technology, an M.Sc. in physicochemistry from the China Research Institute of Daily Chemical Industry, and a Ph.D. in physicochemistry from Wuhan University. His research interests are synthesis and properties of novel surfactants.

**Bao-cai Xu** received a B.Sc. and an M.Sc. in applied chemistry from the Beijing Technology and Business University, and a Ph.D. in applied chemistry from the Beijing Institute of Technology. His research interests are synthesis and properties of novel surfactants.

**Zhi-qiang Qu** received a B.Sc. and an M.Sc. in applied chemistry from the Beijing Technology and Business University. His research interests are synthesis and properties of surfactants.

**Ya-wen Zhou** received a B.Sc. in organic chemistry from the Yaiyuan University of Technology and an M.Sc. in applied chemistry from the China Research Institute of Daily Chemical Industry. Her research interests are synthesis and properties of surfactants.

**Gui-ju Zhang** received a B.Sc. and an M.Sc. in applied chemistry from the Beijing Technology and Business University, and a Ph.D. in organic chemistry from the Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences. Her research interests are synthesis and properties of surfactants.