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Structure–interfacial properties relationship and quantification of the amphiphilicity of well-defined ionic and non-ionic surfactants using the PIT-slope method

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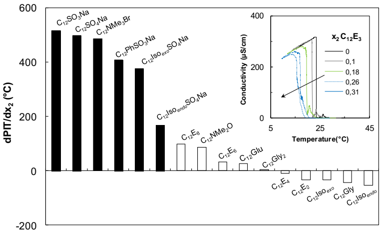
GRAPHICAL ABSTRACT



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ABSTRACT

The Phase Inversion Temperature of a reference $C_{10}E_4$/*n*-Octane/Water system exhibits a quasi-linear variation versus the mole fraction of a second surfactant S_2 added in the mixture. This variation was recently proposed as a classification tool to quantify the Hydrophilic–Lipophilic Balance (HLB) of commercial surfactants. The feasibility of the so-called PIT-slope method for a wide range of well-defined non-ionic and ionic surfactants is investigated. The comparison of various surfactants having the same dodecyl chain tail allows to rank the polar head hydrophilicity as: $SO_3Na \geqslant SO_4Na \geqslant NMe_3Br > E_2SO_3Na \approx CO_2Na \geqslant E_1SO_3Na \geqslant PhSO_3Na > \text{Isosorbide}_{exo}SO_4Na \gg \text{Isosorbide}_{endo}SO_4Na \gg E_8 \geqslant NMe_2O > E_7 > E_6 \geqslant \text{Glucosyl} > E_5 \geqslant \text{Diglyceryl} \geqslant E_4 > E_3 > E_2 \approx \text{Isosorbide}_{exo} > \text{Glyceryl} > \text{Isosorbide}_{endo}$. The influence on the surfactant HLB of other structural parameters, *i.e.* hydrophobic chain length, unsaturation, replacement of Na^+ by K^+ counterion, and isomerism is also investigated. Finally, the method is successfully used to predict the optimal formulation of a new bio-based surfactant, 1-*O*-dodecyldiglycerol, when performing an oil scan at 25 °C.

1. Introduction

The Phase Inversion Temperature (PIT) introduced by Shinoda and Arai [1] corresponds to the temperature at which the affinity of a nonionic ethoxylated surfactant "S" for water and oil switches by dehydration of the polyoxyethylene units during heating, leading to the emulsion phase inversion from O/W to W/O. Shinoda and Arai [1] studied the effect of surfactant polyoxyethylene chain length and hydrocarbon chain length on the PIT and found that the emulsion Phase Inversion Temperature was closely correlated with the cloud point. As defined by these authors, T_{HLB} is the temperature at which an ethoxylated surfactant presents the same affinity for oil and water in a SOW *equilibrated system*, while the PIT corresponds to the change of affinity of a surfactant in an *emulsified system* [2,3]. For a well-defined non-ionic surfactant, the PIT, the

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T_{HLB} and the fish-tail temperature T^* of the so-called "fish diagram" are essentially equivalent at $f_w = 0.5$ [4] but differ significantly when systems are studied at different water/oil ratios, especially at low surfactant concentrations [5].

Recently, a simple and fast method to classify surfactants was proposed, using the variation of the PIT of the 3% $C_{10}E_4$/Octane/Water reference system at $f_w = 0.5$ when a second surfactant S_2 is added [6]. The PIT was found to vary linearly with the second surfactant concentration, and the dPIT/dC parameter was found to allow the estimation of the Hydrophilic Lipophilic Balance of the added surfactant. Well-defined C_iE_j surfactants were studied to validate the classification method and to calibrate an HLB-scale. Then, various technical grade surfactants (Tweens, Spans, lecithin, sucrose esters) were located in this scale.

In the present work, well-defined ionic and nonionic surfactants are investigated in order to extend and complete the precedent scale, to assess the hydrophilicity of a wide variety of polar heads bound to a dodecyl hydrophobic tail, to establish the influence of the alkyl chain length on dPIT/dx_2 (*i.e.*, the PIT variation versus S_2 molar fraction) and to compare the effects of other structural parameters like the counter-ion nature or the isomerism. The described method is also applied to characterize new glycerol and isosorbide-based ionic and non-ionic surfactants. Extending the scale to ionic surfactants permits also to evaluate the robustness of the method when the evaluated and reference surfactants are quite different. Finally, it is shown that dPIT/dx_2 can be used as a guide to determine the "optimal oil" of a given surfactant, which leads to a Winsor III system at 25 °C when mixed with water and the surfactant under study.

2. Experimental

2.1. Chemicals

Pure tetraethyleneglycol monodecyl ether ($C_{10}E_4$) reference surfactant (S_1) was synthesized according to a method described elsewhere [7,8]. Its purity was assessed by NMR and GC analyses (>99%) and by comparing its cloud point temperature [9] (20.4 °C at 2.6 wt.%) with the reference value (20.56 °C at 2.6 wt.%). *n*-Octane (99%) was obtained from Sigma–Aldrich. Sodium chloride NaCl ($\geqslant$99.5%) was supplied by Acros Organics. The commercial surfactants studied in this work (named S_2 in what follows) which are listed in Table 1 were used without further purification. Diethyleneglycol monododecyl ether ($C_{12}E_2$) was synthesized in the same way as $C_{10}E_4$, by reaction of dodecyl bromide with diethyleneglycol. Potassium oleate was prepared by neutralization of oleic acid (Sigma > 99%) in ethanol with ethanolic KOH (Sigma > 90%) followed by solvent evaporation under reduced pressure. 5-*O*-Dodecyl isosorbide, 2-*O*-Dodecyl isosorbide, 5-*O*-Dodecyl isosorbide sodium sulfate, 2-*O*-Dodecyl isosorbide sodium sulfate, 1-*O*-Dodecyl-glycerol and 1-*O*-Dodecyl-diglycerol were synthesized according to a method described elsewhere [10,11]. All synthesized surfactants were obtained with a purity higher than 98% as determined by ^{1}H NMR.

2.2. Sample preparation

24 h before the experiment, 10 mL of the $C_{10}E_4$/*n*-Octane/Water system were prepared in a 20 mL vial ($d = 2.5$ cm, $h = 5.5$ cm) by pouring a mass m_w (4.25 g) of NaCl 10^{-2} M aqueous brine, a mass m_o (4.25 g) of *n*-Octane, and then a mass of surfactant $S_1 = C_{10}E_4$ (0.263 g).

This $C_{10}E_4$/*n*-Octane/Water system was hand-shaken during a few seconds and left to pre-equilibrate 24 h at room temperature. A first heating–cooling cycle was performed (see next paragraph) and then the second surfactant S_2 was added (mass m_{S2}). The amount of $C_{10}E_4$ was then adjusted to m_{S1} so that the proportion of S_1 surfactant remains constant at 3 wt.% of the whole system in all experiments.

Table 1
List of the studied surfactants S_2.

Surfactant	Abbreviation	Supplier	Purity
Pentaethylene glycol monotetradecyl ether	$C_{14}E_5$	Fluka	>99%
Diethylene glycol monododecyl ether	$C_{12}E_2$	Synthesized	>99%
Triethylene glycol monododecyl ether	$C_{12}E_3$	TCI	>95%
Tetraethylene glycol monododecyl ether	$C_{12}E_4$	TCI	>98%
Pentaethylene glycol monododecyl ether	$C_{12}E_5$	Fluka	>98%
Hexaethylene glycol monododecyl ether	$C_{12}E_6$	Sigma	>98%
Heptathylene glycol monododecyl ether	$C_{12}E_7$	TCI	>95%
Octaethylene glycol monododecyl ether	$C_{12}E_8$	TCI	>95%
Tetraethylene glycol monodecyl ether	$C_{10}E_4$	Synthesized	>99%
Pentaethylene glycol monodecyl ether	$C_{10}E_5$	Sigma	>97%
Octaethylene glycol monodecyl ether	$C_{10}E_8$	Sigma	>98%
Pentaethylene glycol monoctyl ether	C_8E_5	Sigma	>98%
Oleic Acid	$C_{17:1}CO_2H$	Sigma	>99%
n-Dodecyl-β-D-glucopyranoside	$C_{12}Glu$	Sigma	>98%
1-*O*-Dodecyl glycerol	$C_{12}Gly$	Synthesized	>98%
1-*O*-Dodecyl diglycerol	$C_{12}Gly_2$	Synthesized	>98%
5-*O*-Dodecyl isosorbide	$C_{12}Iso_{endo}$	Synthesized	>98%
2-*O*-Dodecyl isosorbide	$C_{12}Iso_{exo}$	Synthesized	>98%
N,N dimethyl Dodecylamine N-oxide	C_{12} Me_2NO	Sigma	>99%
Sodium Dodecyl Sulfate	$C_{12}SO_4Na$	Acros	99%
Sodium 1-Dodecane Sulfonate	$C_{12}SO_3Na$	Alfa Aesar	99%
Lauric Acid Sodium Salt	$C_{11}CO_2Na$	Acros	98%
Sodium Lauryl Ether Sulfate	$C_{12}(EO)_1SO_4Na$	Synthesized	>98%
Sodium Lauryl Diether Sulfate	C_{12} $(EO)_2SO_4Na$	Synthesized	>98%
Sodium dodecylbenzenesulfonate	$C_{12}PhSO_3Na$	TCI	>98%
5-*O*-Dodecyl isosorbide Sodium Sulfate	$C_{12}Iso_{endo}SO_4Na$	Synthesized	>98%
2-*O*-Dodecyl isosorbide Sodium Sulfate	$C_{12}Iso_{exo}SO_4Na$	Synthesized	>98%
Sodium Oleate	$C_{17:1}CO_2Na$	Sigma	>99%
Potassium Oleate	$C_{17:1}CO_2K$	Synthesized	>98%
Hexyl Trimethyl Ammonium Bromide	C_6NMe_3Br	TCI	>98%
Octyl Trimethyl Ammonium Bromide	C_8 NMe_3Br	TCI	98%
Decyl Trimethyl Ammonium Bromide	$C_{10}NMe_3Br$	TCI	>99%
Dodecyl Trimethyl Ammonium Bromide	$C_{12}NMe_3Br$	Alfa Aesar	99%
Myristyl Trimethyl Ammonium Bromide	$C_{14}NMe_3Br$	Sigma	>99%
Hexadecyl Trimethyl Ammonium Bromide	$C_{16}NMe_3Br$	Aldrich	>98%
Didodecyl Dimethyl Ammonium Bromide	$(C_{12})_2NMe_2Br$	Fluka	>98%

Eq. (1) defines S_2 surfactant molar fraction in the surfactant mixture.

$$x_2 = \frac{m_{S2}/MW_2}{m_{S1}/MW_1 + m_{S2}/MW_2} \tag{1}$$

The water weight fraction f_w defined by Eq. (2) is 0.5 in all systems.

$$f_w = \frac{m_w}{m_w + m_o} \tag{2}$$