

# Determining the Preferred Alkane Carbon Number (PACN) of nonionic surfactants using the PIT-slope method

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## Abstract

In this paper the Phase Inversion Temperature (PIT) of the C<sub>10</sub>E<sub>4</sub>/n-Octane/0.01M NaCl<sub>(aq)</sub> emulsion was used as a reference to determine the changes introduced by adding small amounts of a second surfactant S<sub>2</sub>. The so-called PIT-slope method allowed the calculation of the  $dPIT/dx_2$  value, i.e. the linear variation of PIT with the molar fraction  $x_2$  of second surfactant S<sub>2</sub>. For nonionics polyethoxylated surfactants C<sub>i</sub>E<sub>j</sub>,  $dPIT/dx_2$  showed a linear dependency respect to the Preferred Alkane Carbon Number (PACN), one of the parameters of the HLD equation based on phase behavior. We calculated here the PACN from PIT and  $x_2$  data for C<sub>i</sub>E<sub>j</sub> and other nonionic surfactants derived from isosorbide or glycerol. When possible, the experimental PACN is determined from n-alkane scans at 25°C, and used to validate the proposed estimation method. The effects of changing the oil nature and water salinity on  $dPIT/dx_2$  are discussed in terms of the HLD equation and validates the hypothesis that allows calculate the PACN.

**Keywords:** PIT-slope method, PACN, Surfactants classification, surfactants mixture, HLD, oil scan.

## 1. INTRODUCTION

The Phase Inversion Temperature (PIT) introduced by Shinoda *et al.*[1] corresponds to the temperature at which the hydrophilic/lipophilic character of a nonionic ethoxylated surfactant switches by dehydration of the polyoxyethylene units during heating, leading to the phase inversion of a stirred emulsion from O/W to W/O. For pure nonionic surfactants, with the same weight of oil and water ( $f_w=0.5$ ) this temperature matches with  $T_{HLB}$  [2], the temperature at which an ethoxylated surfactant presents the same affinity for oil and water in a SOW equilibrated system [3,4].

In 2014, a simple and fast method to classify surfactants was proposed, using the PIT variation of the 3 wt% C<sub>10</sub>E<sub>4</sub>/n-octane/0.01M NaCl<sub>(aq)</sub> emulsion at  $f_w=0.5$ , when a second surfactant S<sub>2</sub> is added [5,6]. The PIT was found to vary linearly with the second surfactant concentration (expressed as molar fraction “ $x_2$ ” or mass concentration “C”), and the slope of the straight variation, i.e. the  $dPIT/dC$  [5] or the  $dPIT/dx_2$  [6] parameter, may be used as a comparative criterion to quantify the hydrophilic lipophilic balance change. A positive slope indicates that the S<sub>2</sub> surfactant is more hydrophilic than C<sub>10</sub>E<sub>4</sub>, whereas a negative slope indicates the opposite. Well defined nonionic and ionic surfactants were tested to validate the classification method. Some technical surfactants (Tween, Span, lecithin, sucrose esters) were also placed in this scale. The hydrophilicities of different polar head groups were compared for surfactants with a same dodecyl alkyl chain whereas the effect of the hydrophobic length chain was studied for alkyl trimethyl ammonium bromides and pentaethylene glycol

monoalkyl ethers (C<sub>1</sub>E<sub>5</sub>) amphiphiles. The PIT-slope method is thus an effective and simple experimental approach for [classifying and comparing](#) new surfactants. [5,6]

The Hydrophilic-Lipophilic Deviation [7] equation expresses the effect of the main formulation parameters on the affinity of a given surfactant on the oil and aqueous phases. It takes into account not only the surfactant [characteristics](#), but also salinity (*S*, g/dL of NaCl), temperature (*T*, °C), alcohol concentration (*A*, g/dL) and oil nature (ACN, alkane carbon number) within a semi-empirical equation [drawn](#) from earlier studies on enhanced oil recovery (EOR) [8,9]. When the HLD value is 0, the affinity for oil and aqueous phases is the same and the system is said to be at the “optimal formulation”, a term used because it corresponds to a minimum interfacial tension, which is the optimum formulation for enhanced oil recovery [10]. For nonionic surfactants, the HLD may be expressed as equation 1 [7,8,11].

$$HLD = \beta + bS - kACN + f(A) + c_t(T - 25) \quad (1)$$

$\beta$  is the characteristic parameter to describe the chemical structure of the surfactant. For polyethoxylated alkylphenol and alcohol surfactants  $\beta$  is related to the number of EON groups (“j”) and the length of the hydrocarbon chain (“i”) [4]. *k* and *c<sub>t</sub>* parameters depends on each surfactant, but they are quite similar for each family (*k* ≈ 0.15 and *c<sub>t</sub>* ≈ 0.05°C<sup>-1</sup> for polyethoxylated [nonionic](#) surfactants).

Equation 1 allows the derivation of a more telling parameter, the so-called “Preferred Alkane Carbon Number”, PACN [8,9,11,12]. This parameter indicates the alkane carbon number (ACN) of the oil that produces an optimal formulation at T=25°C in a SOW system without alcohol (*f*(*A*) = 0) nor salt (*S* = 0). From equation 1 at HLD = 0, PACN is equal to the ratio between  $\beta$  and *k* parameters.

$$PACN = \frac{\beta}{k} \quad (2)$$

PACN is an experimental value limited to the range of liquid alkanes, i.e. pentane to hexadecane, which was called *n<sub>min</sub>* in the 1970's. Since the optimum formulation does not necessarily happen within this alkane range, it can be an extrapolated value, even negative. So as to highlight the meaningful concept of PACN, equation 1 is divided by the oil characteristic parameter “*k*”, obtaining a normalized HLD for nonionic surfactants.

$$HLD_u = PACN - ACN + \left( \bar{b}S + \bar{f}(A) + \bar{c}_t(T - 25) \right) \quad (3)$$

where  $\bar{b}$ ,  $\bar{f}(A)$ , and  $\bar{c}_t$  are the parameters *b*, *f*(*A*), and *c<sub>t</sub>* divided by the oil coefficient “*k*”. [Indeed, this change maintains the physical meaning if different equations are combined because the ACN contribution has absolutely the same meaning in all correlations](#) [13]

For new surfactants, the knowledge of PACN is a useful characteristic that would considerably reduce the trial and error experiments in SOW formulation procedure for EOR or demulsifier formulation. The main objective of this [paper](#) is to [determine](#) the relationship between the [quickly](#) available estimated *dPIT/dx<sub>2</sub>* value and the [well-known](#) parameter

PACN for nonionic surfactants. PACN knowledge is also very important in emulsion formulation, since the sign and value of HLD are directly related to emulsion type [14] and its properties. After some physico-chemical and mathematical considerations based on HLD theory, PACN of nonionic surfactants will be estimated from PIT-slope method data. Estimates will then be compared to literature or experimental PACN values when the determination is possible. PACN of one surfactant mixture will also be estimated and compared to experimental results.

## 2. EXPERIMENTAL

### Chemicals

Pure tetraethyleneglycol monododecyl ether (C<sub>10</sub>E<sub>4</sub>) was synthesized according to a method described elsewhere [15,16]. Its purity was assessed by NMR and GC analyses (>99%) and by comparing its cloud point temperature (20.4°C at 2.6% wt.) with the reference value (20.56°C at 2.6% wt.) [17].

*n*-Octane (>99%) and *n*-nonane (99%) were obtained from Sigma-Aldrich. *N*-Decane (+99%), *n*-hexadecane (99%), squalane (99%) and sodium chloride NaCl (≥99.5%) were supplied by Acros Organics. *n*-Dodecane (+99%) and *n*-tetradecane (99%) were provided by Alfa Aesar. Pentaethylene glycol monotetradecyl ether (C<sub>14</sub>E<sub>5</sub>; 99%) and tetraethylene glycol monododecyl ether (C<sub>12</sub>E<sub>4</sub>; 98%) were supplied by Fluka and TCI, respectively. All these chemicals were used without further purification. 1-O-Dodecyl-glycerol and 1-O-Dodecyl-diglycerol were synthesized according to a method described elsewhere [18]. Both surfactants were obtained with purity greater than 98%, as determined by <sup>1</sup>H NMR.

### Oils scans

1g-samples are prepared in 2 mL vials by weighing successively water (W), oil (O) and surfactant (S). In all the samples, the water/oil ratio equals 1, *i.e.* the water weight fraction  $f_w$ , defined as  $f_w = W/(W+O)$ , equals 0.5. Surfactant concentration is adapted (0.5-3% wt.) to each system in order to avoid precipitates or liquid crystals. The surfactant/oil/water systems are then gently mixed to favor the contact of phases while avoiding emulsification. The vials are then placed in a thermostatic bath HUBER Ministat 125 at 25°C ± 0.1°C until phase separation and equilibrium are reached *i.e.* when the interphases limits are stable. It requires less than 1 month of equilibration.

The determination of the phase behavior is determined by visual inspection so as to classify the systems according to Winsor nomenclature [19]. As linear alkanes higher than hexadecane are not liquid at 25°C, the oil scans for ACN=17 and ACN=18 were performed with mixtures of hexadecane (ACN=16) and squalane (EACN=24) [20].

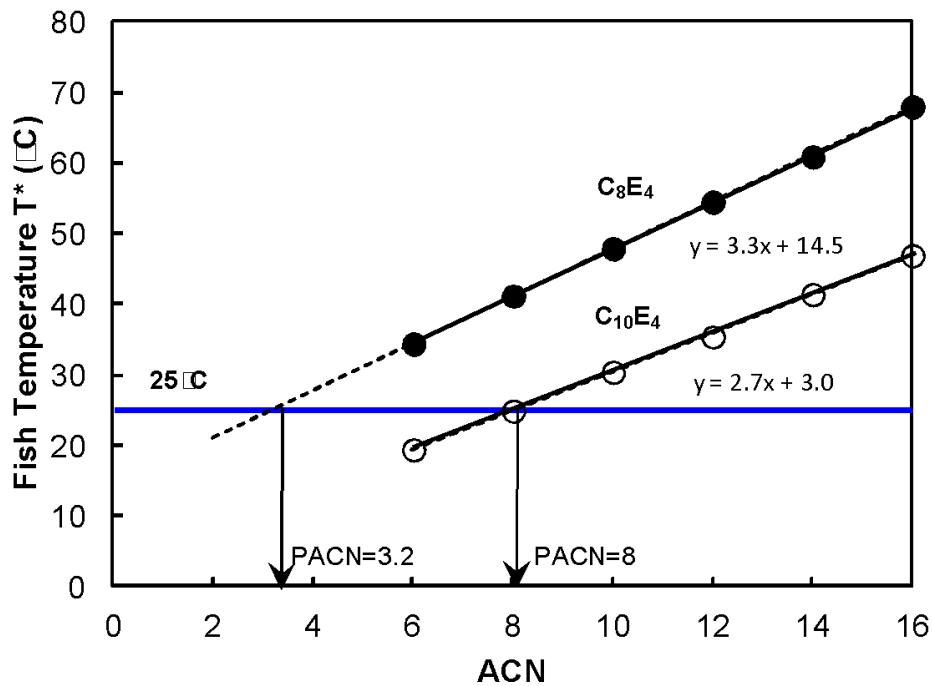
## 3. DISCUSSION

### 3.1 PACN values: from the current method to a simpler one

Kahlweit *et al.* [21] and then Queste [20] and Bouton [22] have studied the Temperature vs. concentration phase behavior, (the so-called fish diagrams), of well-defined C<sub>*i*</sub>E<sub>*j*</sub>/alkane/water systems (without salt or alcohol). For a large series of *n*-alkanes (C<sub>6</sub> to C<sub>28</sub>) each alkane, the T\* and C\* values corresponding to the fish tail point were reported. If we consider that at the fish tail condition (when the Winsor III and IV regions meets) the surfactant has the same affinity for the oily and aqueous phase, equation 3 can be written as follows in the absence of salt and alcohol:

$$HLD_u = 0 = PACN - ACN + \bar{c}_t(T^* - 25) \quad (4)$$

Figure 1 represents the evolution of  $T^*$  as a function of the ACN of the oil for  $C_{10}E_4$ /alkane/water [20] and  $C_8E_4$ /alkane/water [21] systems. In agreement with equation 4,  $T^*$  varies linearly on ACN. Moreover, from these data, PACN and  $\bar{c}_t$  can be easily obtained. PACN corresponds to the ACN value of the oil giving an optimal formulation at  $25^\circ\text{C}$ , and  $\bar{c}_t$  is the reciprocal of the slope.



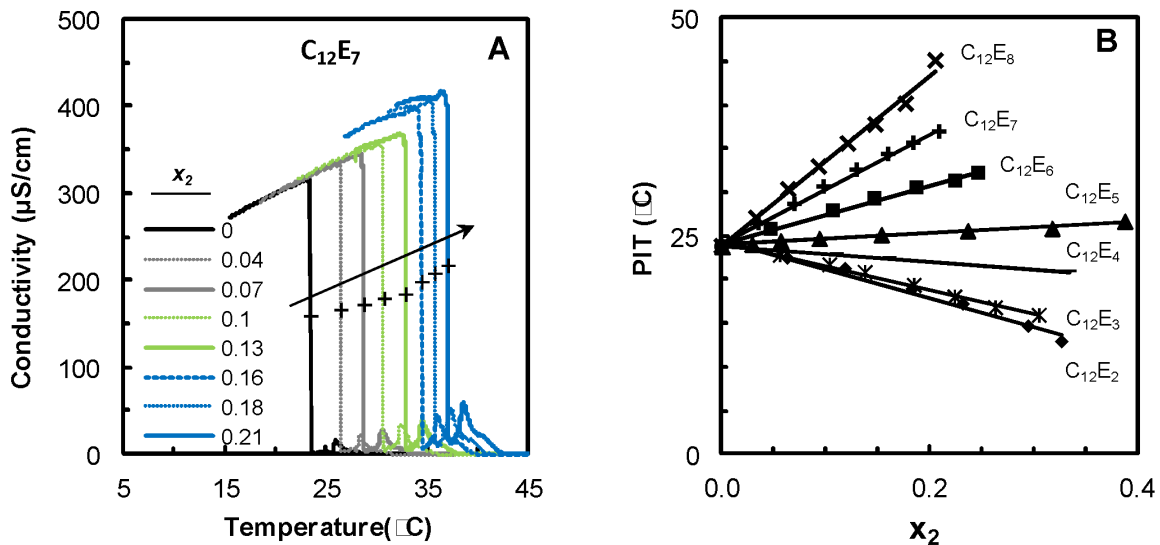
**Fig. 1** Linear evolution of the fish tail temperature  $T^*$  ( $^\circ\text{C}$ ) [20] as a function of the ACN of the oil for  $C_{10}E_4$ /Alkane/Water and  $C_8E_4$ /Alkane/Water systems. The dotted line indicates the extrapolation of the linear fitting for  $C_8E_4$ .

Thus, for  $C_{10}E_4$ ,  $\bar{c}_t$  is 0.36 and the PACN value is 8.0, the oil that makes it possible to obtain a VIII behavior at room temperature without salt or alcohol is the n-octane. For  $C_8E_4$ , the slope is slightly higher ( $\bar{c}_t=0.30$ ). Both  $\bar{c}_t$  values are in agreement with the average value calculated from literature [23]: for  $C_iE_j$ ,  $c_i$  and  $k$  are 0.05 and 0.15, respectively so their ratio is 0.33. This figure also shows that the PACN of some surfactants (such as  $C_8E_4$ ) cannot be experimentally determined with n-alkanes because there is no liquid alkane that gives a VIII system at room temperature. In this case, a less accurate value of PACN can be inferred by extrapolating the straight line to the intersection with the horizontal line at  $25^\circ\text{C}$ . A PACN value of 3.2 is then obtained.

This rigorous method to determine the PACN of a surfactant based on the fish tail temperature is time-consuming and can only be applied to a limited range of surfactants. Indeed, if one wants to use true ternary SOW systems, free of co-surfactants and alcohol, the hydrophilicity of the surfactant must be highly sensitive to temperature since it is the formulation variable

used to tune the hydrophilic/lipophilic balance. In addition, the surfactant should be neither too hydrophilic nor too lipophilic because no n-alkane would be able to provide a WIII behavior.

In a previous report [6] it was shown how conductivity monitoring of a stirred SOW system adding a small amount of a second surfactant  $S_2$  allow to determine  $dPIT/dx_2$ , i.e. the PIT-slope value, which was proposed to quantify the intrinsic hydrophilic-lipophilic balance of surfactants. Figure 2A shows the conductivity profiles that make it possible to determine the Phase Inversion Temperature (PIT) at each concentration of the second surfactant  $S_2$ , whereas Figure 2B represents the evolution of PIT of the mixtures  $C_{10}E_4/C_{12}E_j$  [6]. The slope of these straight lines is called  $dPIT/dx_2$ .



**Fig. 2** A) Conductivity-Temperature profile at several molar fractions  $x_2$  for the  $(C_{10}E_4+C_{12}E_7)/\text{Octane}/(\text{Water}+10^{-2}\text{M NaCl})$  system at  $f_w=0.5$ . The PIT is represented as “+” for different molar fraction  $x_2 = 0$  (—); 0.04 (···); 0.07 (—); 0.1 (···); 0.13 (—); 0.16 (—); 0.18 (···); 0.21 (—). B) Phase inversion temperature (PIT) vs. molar fraction of  $S_2$ :  $C_{12}E_8$  (x);  $C_{12}E_7$  (□);  $C_{12}E_6$  (■);  $C_{12}E_5$  (▲);  $C_{12}E_4$  (—);  $C_{12}E_3$  (◻);  $C_{12}E_2$  (◆). Dotted lines correspond to linear fitting leading to  $dPIT/dx_2$ . [6]

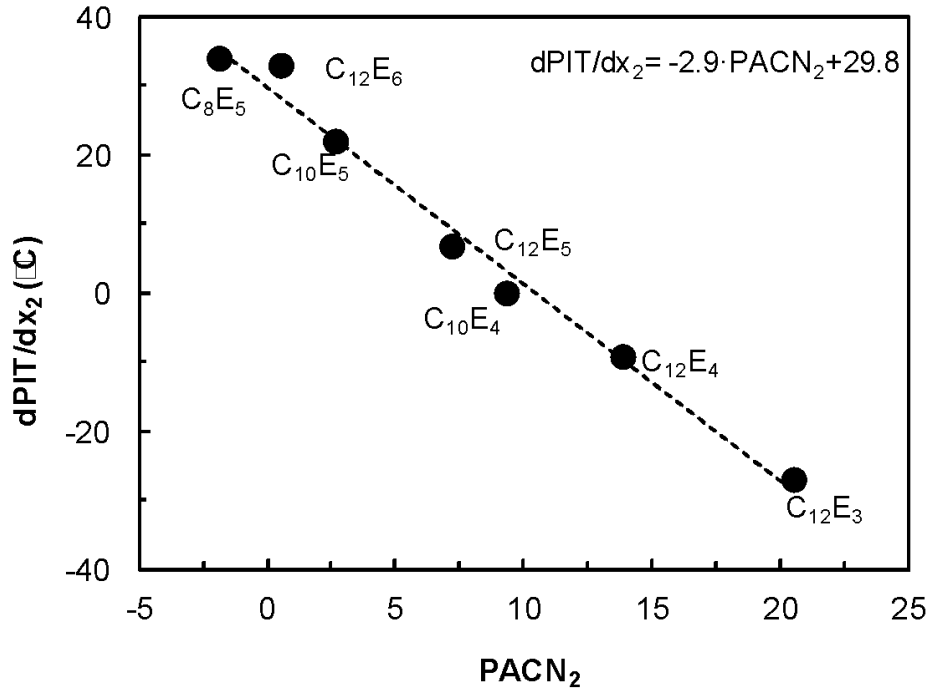
Using the HLD model equation applied to very accurate formulation scan experiments [24] performed with oligomerically pure alcohol ethoxylates  $C_iE_j$ , Salager *et al.* [23] reported in equation 5 a linear fit between  $\beta$  and the structure, i.e., between the number of carbon atoms in the tail (“i” from 8 to 12) and the number of ethylene oxide groups in the polar head EON (“j” from 3 to 6):

$$\beta = 2 + 0.34i - j \quad (5)$$

As a consequence, PACN values of  $C_iE_j$  surfactants may be expressed accord to:

$$PACN = \frac{\beta}{k} = \frac{2+0.34i-j}{k} \quad (6)$$

The figure below shows the parameter  $dPIT/dx_2$  drawn from our previous work [6] as a function of PACN for the  $C_iE_j$  in the mentioned range ( $8 < i < 12$  and  $3 < j < 6$ ) using the reported value of  $k=0.15$  for  $C_iE_j$  [23].



**Fig. 3**  $dPIT/dx_2$  (°C) [6] vs. PACN ( $\frac{\beta}{k}$ ) obtained from literature [23]). Dotted line indicates linear fitting.

Figure 3 indicates, on the one hand, that there is a linear relationship between  $PACN$  and  $dPIT/dx_2$  and, on the other, that the PIT-slope method is very accurate as a surfactant classification tool, for this group of surfactants. Since such a match is probably not a mere coincidence, it is worth trying to explain it through a simple reasoning based on HLD equation.

### 3.2 $PACN$ estimation using the PIT-slope method.

At the optimal formulation HLD is zero and, if the oil and salinity conditions are fixed, the PIT value does not depend on the concentration of the nonionic surfactant if it is pure.  $T_{HLB}$  is the temperature at which a nonionic surfactant presents the same affinity for oil and water in a SOW equilibrated system. Both temperatures,  $T_{HLB}$  and  $T^*$ , correspond to an equilibrated system while the PIT represents the change of morphology in the emulsified system. The three values are essentially equivalent at  $f_w=0.5$  for pure surfactants [3,4,25]. Based on this premise, and using the emulsion change of type as the detection criteria for optimum formulation, the HLD equation may be written as equation 7:

$$0 = PACN - ACN + \bar{b}S + \bar{c}_t(PIT - 25) \quad (7)$$

The HLD equation has also been used for surfactants mixtures. When the mixed surfactants come from the same chemical family with the same oil and temperature coefficients ( $k$  and  $c_t$ ), e.g. alkylaryl sulfonates, then a linear mixing rule on the surfactant parameter may be assumed. [20] If the mixed surfactants are different and if temperature coefficients are not the same, then the linear rule must be used not for the surfactant coefficient but for the entire HLD equation. For a binary mixture at optimal formulation the following linear rule with the molar fraction " $x_2$ " is used (equation 8) [11]:

$$(HLD_u)_m = (1 - x_2)(HLD_u)_1 + x_2(HLD_u)_2 = 0 \quad (8)$$

This equation can be used to calculate an estimation of the HLD value for surfactant mixtures. Its validity depends on the nature of the mixed surfactants. Anionic surfactants follows a linear mixing rule [26]. As reported elsewhere [27,28], nonionics mixtures of relatively different surfactants (as far as their ethylene oxide number is concerned), might exhibit deviations from linearity due to partition phenomena,. Anionic-nonionic mixtures presents complex phase behaviors and synergistic effects [26,29–34]. As a matter of fact, it **could** be said that a perfect linear mixing on surfactant parameters or HLD overall summation is an exception, unless the mixed species are very similar. However, a linear mixing rule is often a fair approximation that could save a lot of time in formulation research, because it **makes it possible** to avoid trial and error methods.

Consequently, such an approximation through a linear mixing rule is used in what follows, taking as a reference oligomerically pure  $C_{10}E_4$ . If the second surfactant  $S_2$  is also a nonionic polyethoxylated surfactant  $C_iE_j$ , we can **then** assume that HLD coefficients are **identical to those** expected from the reported data, i.e.  $c_{t2} \approx c_{t1} \approx c_{tC_{10}E_4}$  and  $k_2 \approx k_1 \approx k_{C_{10}E_4}$ . The values for k and b reported in **the** literature for  $C_iE_j$  are 0.15 and 0.13, respectively. A linear mixing rule for PACN can be written **as**:

$$PACN = PACN_1(1 - x_2) + PACN_2x_2 \quad (9)$$

where indices 1 and 2 indicate the reference and the added surfactants. This expression for  $PACN$  is introduced on equation 7 and, solving for PIT, the HLD equation can be used to predict the changes of phase inversion temperature in function of the others formulation variables, i.e. the change in PIT when a second surfactant  $S_2$  is added to the reference SOW system.

$$0 = PACN_1(1 - x_2) + PACN_2x_2 - ACN + \left(\frac{b}{k_1}\right)S + \left(\frac{c_{t1}}{k_1}\right)(PIT - 25)$$

$$PIT = \frac{PACN_1 - PACN_2}{c_{t1}}x_2 + \frac{ACN - \bar{b}S - PACN_1}{c_{t1}} + 25 \quad (10)$$

This equation exhibits **linearity** between the PIT and **the molar fraction** of the second surfactant, as was recently described for oligomerically pure nonionics [6]. According to the expression, the derivative  $dPIT/dx_2$ , i.e. the slope of the PIT vs.  $x_2$  lines is found to be:

$$\frac{dPIT}{dx_2} = \frac{PACN_1 - PACN_2}{c_{t1}} \text{ or } \frac{dPIT}{dx_2} = \frac{\beta_1 - \beta_2}{c_{t1}} \quad (11)$$

The straight line variation seen in figure 3 corroborates the accuracy of equation 11 and clearly indicates that  $dPIT/dx_2$  is a comparative yardstick which **makes it possible** to classify a surfactant  $S_2$  **with** respect to a reference surfactant  $S_1$ . If the reference surfactant changes from  $C_{10}E_4$ , then the value of  $dPIT/dx_2$  is likely to change **as well** as  $PACN_1$  appears in equation 11. The zero value of  $dPIT/dx_2$  corresponds to the same characteristic for  $S_2$  and for



the reference surfactant  $S_1$ , i.e.  $PACN_1 = PACN_2$ . Moreover, this equation shows that  $dPIT/dx_2$  values must be independent of oil nature and salt concentration for  $C_iE_j$  mixtures. This aspect will be confirmed and discussed in the [section 3.4](#).

The numerical calculation of the characteristic parameter ( $PACN_2$ ) of nonionics surfactant  $S_2$  from equation 11 requires the values of  $PACN_1$  and  $\overline{c_{t1}}$ . Using equation 10, the data of PIT for every molar fraction  $x_2$  of mixture  $C_{10}E_4/S_2$  can be fitted and the characteristic parameters of HLD estimated ( $\beta_2, \beta_1, c_{t1}$  or  $PACN_2, PACN_1$  and  $\overline{c_{t1}}$ ). The data of PIT and  $x_2$  from  $C_{10}E_4/C_iE_j/n$ -octane/ $10^{-2}$ M NaCl systems were used to this purpose. Values for  $\beta_1, c_{t1}, PACN_1$  and  $\overline{c_{t1}}$  were found to be 1.23, 0.047 ( $^{\circ}C^{-1}$ ), 8.2 and 0.31, respectively.

In the deduction of equation 10, and according to the first report on optimum formulation for nonionics surfactants [8],  $k$  and  $c_t$  are supposed to be independent from temperature and molar fraction. However, for polyethoxylated surfactants  $C_iE_j$ , a more recent study has indicated that the temperature coefficient varies slightly with the ethylene oxide number “j” and the temperature [7]:

$$c_t = \frac{2210-450j}{(T+273.15)^2} \quad (12)$$

According to this expression the temperature coefficient for  $C_{10}E_4$  is 0.045 ( $^{\circ}C^{-1}$ ) at 25 $^{\circ}C$  for the 3% $C_{10}E_4$ /Octane/Water system. The  $c_t$  for the mixture with a second surfactant  $S_2$  can be calculated in the same way as  $PACN$  was calculated through equation 9 as:

$$c_t = c_{t_1}(1 - x_2) + c_{t_2}x_2 \quad (13)$$

Equation (12) indicates that the  $c_t$  numerator tends to decrease when the ethoxylation increases. But if the ethoxylation increases, then the PIT increases as well, so at optimum formulation the  $c_t$  denominator tends to increase. As a consequence, changes on average  $c_t$  (equation 11) are not very significant because both EON and PIT associated changes compensate each other. Indeed, the result of 0.047( $^{\circ}C^{-1}$ ) obtained without taking into account “j” and T dependence of  $c_t$  is close to the average in each studied  $C_{10}E_4/C_iE_j$  pair.

Table 1 shows the values of  $PACN_2$  for  $C_iE_j$ , whether one takes into account the “j” and T dependence of  $c_t$  or not.

**Table 1.**  $dPIT/dx_2$  ( $^{\circ}C$ ) and Preferred Alkane Carbon Number for the  $C_iE_j$ .

$C_iE_j$	$dPIT/dx_2$ ( $^{\circ}C$ )	$PACN$ $c_t \approx c_{t_{C_{10}E_4}} \approx cte$	$PACN$ $c_t \approx f(T, j)$	$PACN$ average
$C_{12}E_{10}$	141	-33.2	-31.7	-32.4
$C_{12}E_8$	98	-23.3	-20.7	-22.0
$C_{10}E_8$	102	-22.0	-22.7	-22.3



$C_{12}E_7$	63	-11.3	-11.3	-11.3
$C_8E_5$	34	-2.7	-3.3	-3.0
$C_{12}E_6$	33	-2.0	-2.0	-2.0
$C_{10}E_5$	22	1.5	1.3	1.4
$C_{12}E_5$	6.8	6.0	6.7	6.3
$C_{14}E_5$	1.6	7.3	7.3	7.3
$C_{10}E_4$	0	8.0	-	8.0
$C_{12}E_4$	-9.2	11.3	11.3	11.3
$C_{12}E_3$	-27	17.3	17.3	17.3
$C_{12}E_2$	-34	18.0	17.3	17.7

Table 1 data clearly show that the change of the temperature coefficient “ $c_t$ ” with the number of ethylene oxide “ $j$ ” and PIT does not result in a significant change in PACN. The dependence of PACN with both ethylene oxide number (“ $j$ ”) and the number of carbon in the alkyl chain (“ $i$ ” or SACN) can be considered linear on a certain interval, *i.e.* when the added surfactant and the reference one are close. There is a good correlation between reported values in the literature from SOW equilibrated pure systems and those presented here from emulsion mixtures  $C_{10}E_4/C_iE_j$ .

### 3.3 Experimental determination of Preferred Alkane Carbon Number by oil scans.

a) The second surfactant  $S_2$  is a  $C_iE_j$   
 PACN for  $C_{10}E_4$  matches the experimental results reported in the literature. This surfactant reached a WIII system (with the same quantity of oil and water in the microemulsion [35]) and a minimum interfacial tension phase with octane at 25°C [24]. If the  $C_{12}E_5$  temperature  $T^*$  data for several alkanes reported by Burauer [36] are extrapolated, then the PACN for this surfactant would be pentane; hence the prediction of 6 is fair. In order to validate the method to estimate the PACN an oil scan at 25°C was carried out for oligomerically pure  $C_{14}E_5$  ( $PACN_{\text{predicted}}=7$ ) and  $C_{12}E_4$  ( $PACN_{\text{predicted}}=11.4$ ). For more hydrophilic surfactants the PACN value exhibited in Table 1 is negative, which means that no alkane can achieve the optimal formulation at 25°C and that only some chlorinated oils can.

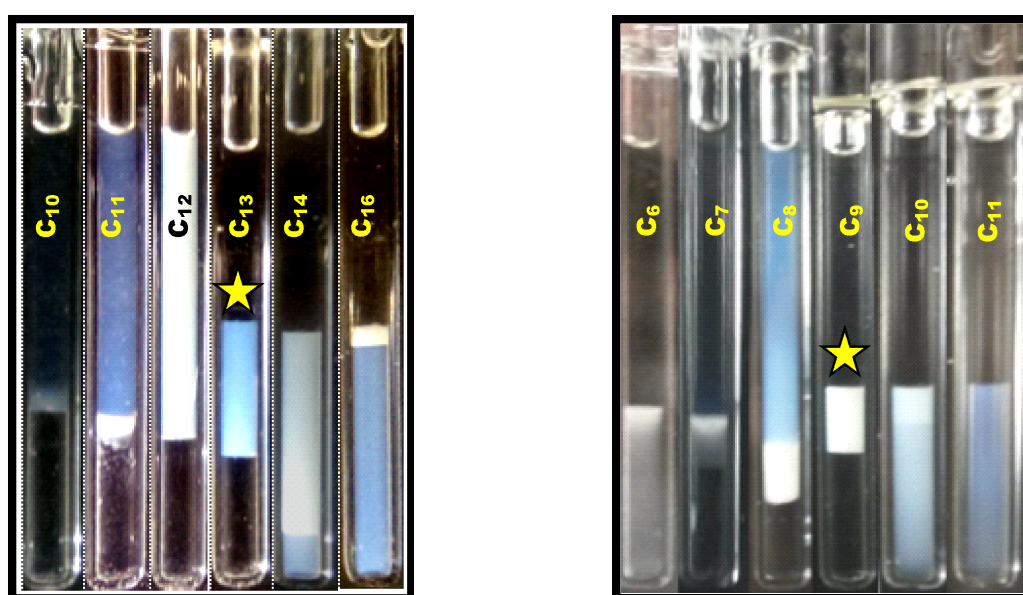


Fig. 4 Phase separation from oil scans in  $C_iE_j$ /Alkane/Water systems equilibrated one month at 25°C. Left: 3% $C_{12}E_4$ ; Right: 1% $C_{14}E_5$ .

As can be seen in Figure 4, from an oil scan at 25°C, the experimental PACN for C<sub>12</sub>E<sub>4</sub> is 13. Longer alkanes, like tetradecane, increase the oil-oil interactions and promote a Winsor I phase behavior, i.e. an aqueous microemulsion in equilibrium with an oil excess phase. Shorter alkanes, such as n-decane promotes a Winsor II behavior, since the surfactant affinity for the oil phase is enhanced. Moreover, Figure 4 indicates that the PACN for C<sub>14</sub>E<sub>5</sub> is 9. For both surfactants the calculated PACN and the experimental value have two units of difference. For C<sub>14</sub>E<sub>5</sub>, the oils scan is made at 1% of surfactant concentration in order to avoid highly viscous microemulsions phases or liquid crystals.

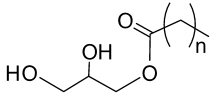
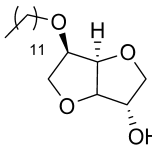
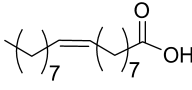
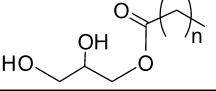
b) The second surfactant S<sub>2</sub> is a nonionic surfactant different from C<sub>i</sub>E<sub>j</sub>. The procedure to calculate PACN for the C<sub>i</sub>E<sub>j</sub> can be applied to estimate it for the other nonionics surfactants. In this case, two approaches can be used. In the first one, the one we called here “Method 1”, it is assumed that the temperature and oil coefficients for the second surfactant are the same as those for C<sub>10</sub>E<sub>4</sub>, i.e.,  $c_{t2} \approx c_{t1}$  and  $k_2 \approx k_1$ . These assumptions are reasonable for two C<sub>i</sub>E<sub>j</sub>, but when the structure of the second surfactant is different from C<sub>10</sub>E<sub>4</sub>, the coefficients are likely to be different; this approach could then be less accurate. The second method consists in assuming that  $k_2 \approx k_1$  as this is very likely, but the temperature coefficients are different, which is found to happen particularly if S<sub>2</sub> is not an ethoxylated nonionic surfactant. The new expression for PIT replacing equation 10, then is

$$PIT = 25 - \frac{PACN_1(1-x_2)+PACN_2x_2-ACN+\bar{bS}}{\bar{c}_{t1}(1-x_2)+\bar{c}_{t2}x_2} \quad (14)$$

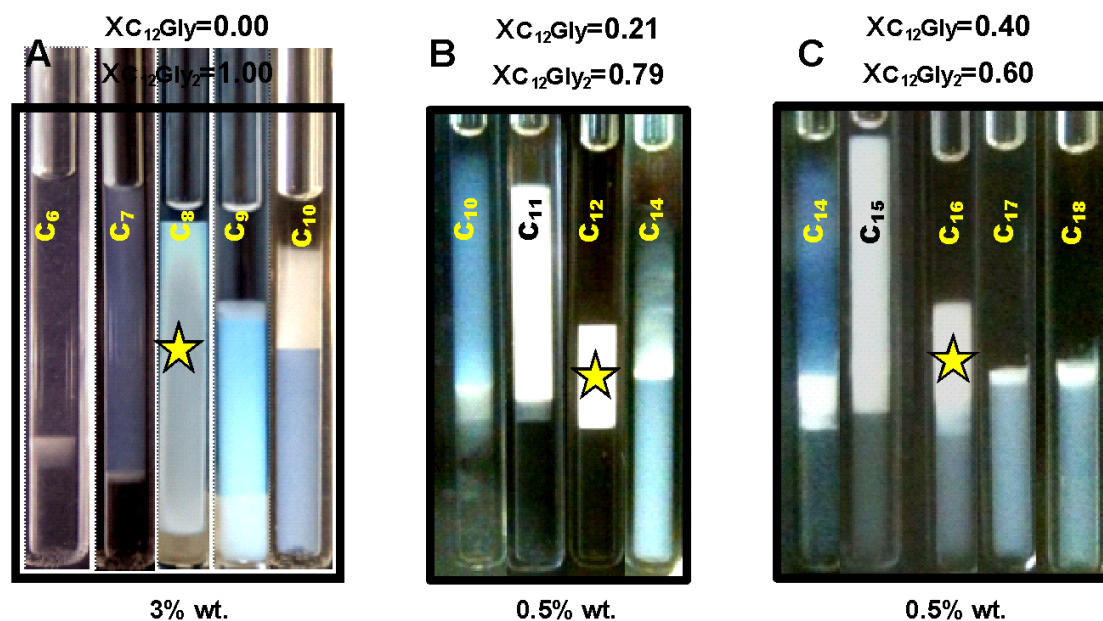
As with C<sub>i</sub>E<sub>j</sub>, PIT vs. molar fraction data are used to estimate PACN<sub>2</sub> by these two methods, using the previously calculated values of PACN<sub>1</sub> and  $\bar{c}_{t1}$ . Table 2 displays the results for PACN<sub>2</sub>.

**Table 2.** Preferred Alkane Carbon Number for nonionics surfactants different from C<sub>i</sub>E<sub>j</sub>

Surfactant (Abbreviation)	Structure	PACN <sub>2</sub>		PACN <sub>2</sub>
		Method 1 $c_t \approx 0,047$	Method 2 $ct = c_{t1}(1 - x_2) + c_t$	
n-Dodecyl- β-D-glucopyranoside (C <sub>12</sub> Glu)		0.3	1.5	0.9
1-O-Dodecyl-diglycero 1 (C <sub>12</sub> Gly <sub>2</sub> )		7.3	7.2	7.2
2-O-dodecyl isosorbide (C <sub>12</sub> Iso <sub>exo</sub> )		17.9	15.5	16.7
1-O-Dodecyl-glycerol (C <sub>12</sub> Gly)		22.5	23.9	23.2

Surfactant (Abbreviation)	Structure	PACN <sub>2</sub>		PACN <sub>2</sub>
		Method 1 $c_t \approx 0,047$	Method 2 $ct = c_{t1}(1 - x_2) + c_t$	
Glycerol Monolaurate	 n=10	21.7	25.2	23.5
5- <i>O</i> -dodecyl isosorbide (C <sub>12</sub> Iso <sub>endo</sub> )	 n=11	25.3	26.2	25.8
Oleic Acid	 n=7	27.3	31.3	29.3
Glycerol Monopalmitate	 n=14	29.1	29.5	29.3

With the results displayed on table 2, we decided to carry out the experimental determination of PACN for C<sub>12</sub>DiGly since it is the only one expected to be within the experimental range of n-alkanes. The n-alkane scan at 25°C showed in figure 5A, indicates that the actual PACN for C<sub>12</sub>DiGly is 8 (octane), a good match with the estimate of 7.2 from the PIT-slope data. One of the initial hypotheses is that the PACN follows a linear mixture rule (equation 9). In order to verify this hypothesis and the results presented in Table 2, an oil scan was performed to mixtures of C<sub>12</sub>Gly and C<sub>12</sub>Gly<sub>2</sub> at two different molar fractions ( $x_{C_{12}Gly}=0.21$  and  $x_{C_{12}Gly}=0.40$ ) at a total concentration of 0.5% wt.



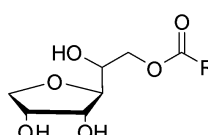
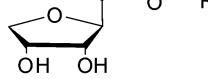
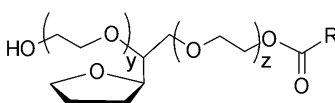
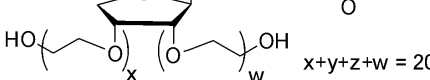
**Fig. 5** Phase separation from oil scans of C<sub>12</sub>Gly<sub>2</sub>+ C<sub>12</sub>Gly/Alkane/Water systems equilibrated one month at 25°C.

In these experiments, the total concentration of surfactant is only 0.5% because the solubility of C<sub>12</sub>Gly is small. Indeed, for the C<sub>12</sub>Gly<sub>2</sub>+ C<sub>12</sub>Gly/C<sub>18</sub>/Water system (the right tube on Figure 5C) the surfactant is precipitated at the water/oil interface. It is clear that is not possible to increase neither the molar fraction of C<sub>12</sub>Gly nor the total weight concentration.

Increasing the molar fraction of the lipophilic surfactant also increases the length of the alkane needed to reach the “optimal formulation”. For mixtures with a molar fraction of 0.21 and 0.40 for C<sub>12</sub>Gly the PACN calculated following equation 9 (*i.e.* using the experimental value  $PACN_{C_{12}Gly_2} = 8$  and  $PACN_{C_{12}Gly} = 23.2$  from Table 2) are 11.2 and 14 respectively. From figures 5B and 5C, the oil scan shows values of 12 and 16 approximately. The estimate error is then approximately 2 units on ACN.

If the method can be applied to any pure nonionic surfactant, its application for commercial mixtures would then be possible, but with an increase of the uncertainty of the results. The molar weight must be estimated for the commercial mixture but partition phenomena at different concentrations and temperatures complicate the analysis. Table 3 shows the estimated PACN for sorbitan alkyl esters, polyethoxylates or not (Tween/Span). These values are consistent with their chemical structure: oleate has higher PACN than laurate and polyethoxylated surfactants have lower values of PACN than corresponding non ethoxylated sorbitan alkyl esters. For all these surfactants, the high hydrophilicity (Tween) or lipophilicity (Span) did not allow us to perform an oil scan at 25°C to determine experimentally their PACN.

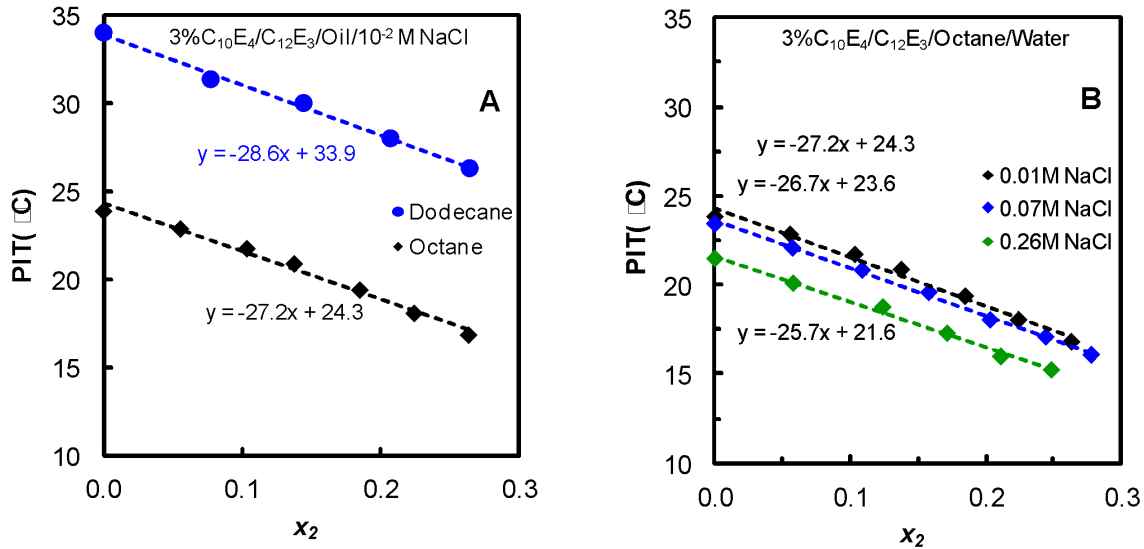
**Table 3.** Preferred Alkane Carbon Number for nonionics commercial surfactants

Surfactant (Abbreviation)	Structure	PACN <sub>2</sub>		
		Method 1 $c_t \approx 0,047$	Method 2 $ct = c_{t1}(1 - x_2)$	PACN <sub>2</sub>
Span 80 (R=C <sub>18:1</sub> )		29.9	27.3	28.6
Span 20 (R=C <sub>12</sub> )		23.7	22.4	23.0
Tween 80 (R=C <sub>18:1</sub> )		-30.3	-29.7	-30.0
Tween 20 (R=C <sub>12</sub> )		-35.3	-35.2	-35.3

Zarate-Muñoz *et al.* [37] calculated the “characteristic curvature”, another name for the  $\beta$  parameter, from salinity scans using a commercial alkyl ethoxylated surfactant as reference. The reference surfactants were previously characterized by oil, salinity and temperature scans. The second surfactant was added and the HLD=0 condition was followed through an emulsion stability test or interfacial tension measurements. Several molar fractions of the second surfactant were tested and the data allows calculate  $\beta$ . Both methods, salinity scan [37] or PIT-scan at different molar fractions, gave  $\beta$  values in the same trend. From these values the differences by the two methods on PACN are between 1.3 and 10 ACN units.

### 3.4 Oil, salinity, and $C_{10}E_4$ concentration effect on $dPIT/dx_2$

The independence of  $dPIT/dx_2$  from oil nature and salinity suggested in equation 11 was experimentally corroborated for  $C_{10}E_4$ - $C_{12}E_3$  mixtures. Figure 6 shows the PIT variation vs. molar fraction of  $C_{12}E_3$  in different experimental conditions for oil (figure 6A) and salinity (figure 6B) compared with the reference system (Octane and NaCl 0.01M).

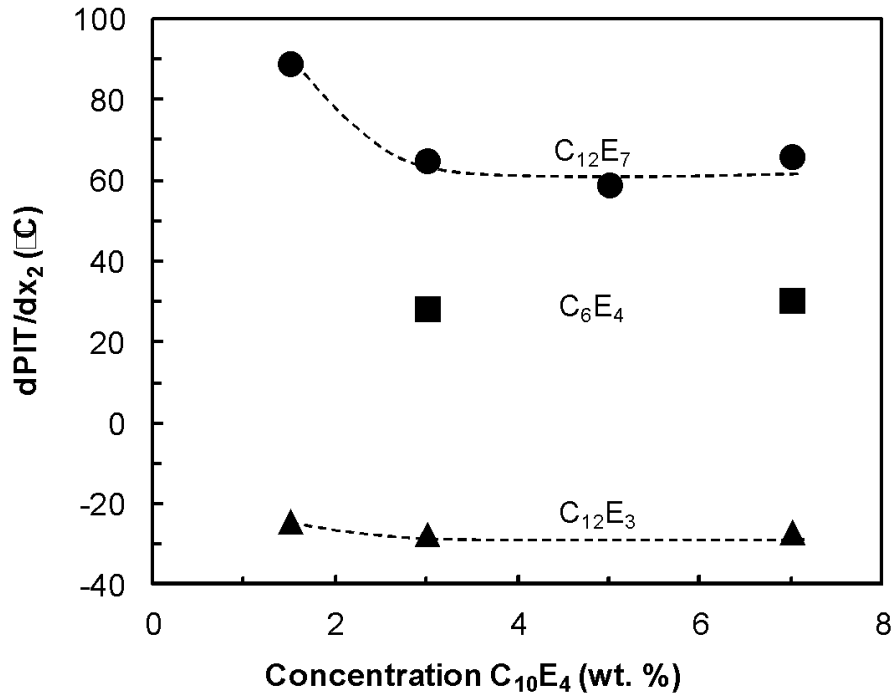


**Fig. 6** Phase inversion temperature (PIT) vs. molar fraction  $x_2$  of  $C_{12}E_3$  for the system 3% $C_{10}E_4/C_{12}E_3/Oil/Water$  at  $f_w=0.5$ . A) Octane (◆) and Dodecane (●) B) 0.01M NaCl (◆) and 0.07M NaCl (●).

As can be seen in Fig 6A, the increase in oil length (ACN passing from 8 to 12) diminishes the surfactant affinity for the oil phase and the PIT increases as expected. If equation 5 is used to predict the increase in PIT with an increase of 4 units on ACN, a  $12.8^\circ\text{C}$  ( $\Delta PIT = \frac{k}{c_{t1}} \times \Delta ACN$ ) is calculated, which is similar to the  $10^\circ\text{C}$  found experimentally in Fig 6A. Although the PIT changes considerably, the slope of the straight line fit remains constant ( $-27.2^\circ\text{C}$  and  $-28.6^\circ\text{C}$ ).

Figure 6B puts forth that a salinity increase from 0.01M to 0.26M diminishes the PIT values, as established for nonionic surfactants ( $\Delta PIT = \frac{-b}{c_{t1}} \times \Delta S$ ) [8]. In this case, the surfactant affinity for aqueous phase decreases, and then the PIT decreases as well. The slope of the PIT vs.  $x_2$  remains in the same order of magnitude ( $-27.2^\circ\text{C}$  and  $-25.7^\circ\text{C}$ ). This corroborates the independence of  $dPIT/dx_2$  from the oil and salinity suggested in equation 11 and validates the hypothesis that allows calculate the PACN.

The PIT-slope method is based on the perturbation of a reference system at 3% $C_{10}E_4$ . The effect of changing this concentration on  $dPIT/dx_2$  values was studied when  $C_{12}E_7$  and  $C_{12}E_3$  are added to the reference system. Lukowicz [38] reported the  $dPIT/dx_2$  for  $C_6E_4$  using 3% and 7% of  $C_{10}E_4$ . These values are also represented in Figure 7.



**Fig. 7**  $dPIT/dx_2$  (°C) of  $C_{12}E_7$ ,  $C_{12}E_3$  and  $C_6E_4$  [38] vs.  $C_{10}E_4$  weight concentration.

Figure 7 clearly shows that, from 3% $C_{10}E_4$  until 7% $C_{10}E_4$  the value of  $dPIT/dx_2$  is almost constant, at least for the  $C_iE_j$ . At 1.5% of  $C_{10}E_4$ , the value of  $dPIT/dx_2$  is greater than other concentrations. In equilibrated systems, the phase behavior of two nonionic  $C_iE_j$  surfactants shows a higher hydrophilicity at low concentrations due to partition phenomena [11,13,14]. The low concentration of the  $C_{10}E_4$  increases the sensibility of the reference system to increase or decrease the PIT when a second surfactant is added.

Even if the  $dPIT/dx_2$  value is constant from 3% $C_{10}E_4$ , it is not the case from  $dPIT/dC$  parameter, based on weight concentration and not on molar fraction. The values expressed on molar fraction are more reliable; however for commercial mixtures with oligomers its estimation is less accurate and  $dPIT/dC$  must be used [5].

## 4 CONCLUSION

The PIT-slope method allows a preliminary and reasonable estimation of PACN (or  $\beta$ ) for well-defined nonionic surfactants like oligomerically pure alcohol ethoxylates. This is an attractive feature since these characteristic parameters are usually calculated from equilibrium phase behavior experiments, *i.e.* it is a time-consuming procedure.

Adding different amounts of a second surfactant to 3% $C_{10}E_4$ /n-Octane/0.01M  $NaCl_{(aq)}$  emulsion, and using the PIT and molar fraction of the second surfactant  $S_2$  data allows the calculus of PACN. The PACN prediction for  $C_{12}E_4$ ,  $C_{14}E_5$  and 1-*O*-Dodecyl-diglycerol are experimentally demonstrated with oils scans at 25°C without salt or alcohol, with an accuracy of at least 2 ACN units. Estimated PACN for a binary  $C_{12}Gly$  and  $C_{12}Gly_2$  mixture was also in agreement with experimental value. The method described is a fast and simple way to classify



the surfactants and determine important parameters for HLD equation.

Lastly, the influence of oil, salinity and surfactant concentration on  $dPIT/dx_2$  was studied.

Replacing octane by dodecane, or changing salinity from 0.01M to 0.26M change the PIT value but not the slope characteristic value for non-ionic surfactants. When the concentration of the reference surfactant  $C_{10}E_4$  is 1.5% the value of  $dPIT/dx_2$  is greater than that reported for 3% as a consequence of an enhanced effect of partition.

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