Review Article

An efficient method to determine the Hydrophile-Lipophile Balance of surfactants using the phase inversion temperature deviation of C$_i$E$_j$/*n*-octane/water emulsions

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Abstract

OBJECTIVE: The aim of this study was to develop a fast and an efficient method to determine the Hydrophile-Lipophile Balance (HLB) number of cosmetic and pharmaceutics surfactants.
METHODS: This method is based on the deviation of the phase inversion temperature induced by the addition of the test compound, with respect to the phase inversion temperature of a reference system, which includes an ethoxylated surfactant. This method is called PIT-deviation.
RESULTS: Three calibration curves are set up with three reference ethoxylated surfactants. These calibration curves make it possible to evaluate the interfacial behaviour of certain chemicals. More particularly, these curves make it possible to easily determine the surfactant HLB.
CONCLUSION: In this study, a fast and accurate method has been developed to determine the hydrophilic-lipophilic balance (HLB) number of amphiphilic chemicals. This new method can be applied to establish an HLB number of all commercial amphiphilic ingredients. Compounds which have a PIT-deviation close to zero are also discussed.

Résumé

OBJECTIF: Le but de cette étude était de développer une méthode rapide et efficace pour déterminer le nombre Hydrophiles-Lipophiles Balance (HLB) d'agents tensioactifs cosmétiques et pharmaceutiques.
MÉTHODES: Cette méthode est basée sur le déplacement de la température d'inversion de phase induite par l'addition du composé à tester par rapport à la température d'inversion de phase d'un système de référence, comprenant un tensioactif éthoxylé. Cette méthode s'appelle PIT-déviation.
RÉSULTATS: Trois courbes d'étalonnage sont établies avec trois tensioactifs éthoxylés de référence. Ces courbes d'étalonnage permettent d'évaluer le comportement interfacial de certains produits chimiques. Plus particulièrement, ces courbes permettent de déterminer facilement le HLB de tensioactif.

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CONCLUSION: Dans cette étude, une méthode rapide et précise a été développée pour déterminer le Hydrophile-Lipophile Balance (HLB) de produits chimiques amphiphiles. Cette nouvelle méthode peut être appliquée pour établir un HLB de tous les ingrédients amphiphiles. Les composés dont la PIT-deviation est proche de zéro sont également abordés.

Introduction

Chemists and formulators commonly use surfactants. To facilitate their use, they have devised classifications by interfacial properties and in particular the affinity for the aqueous or organic phases. The prevailing notion among surfactant users is the Hydrophile-Lipophile Balance (HLB) number introduced by Griffin. The original use of this classification is for non-ionic surfactant and ester surfactant [1, 2]. This value ranges from 0 to 20, on an increasing scale from least lipophilic (0) to most hydrophilic (20). The 'Griffin' HLB number is calculated using an equation based on ethoxylated alcohols (equation 1) and PEG esters (equation 2) described below:

$$\text{HLB}_{\text{Griffin}} = \frac{M_H}{M_T} * 20, \tag{1}$$

where M_H and M_T correspond to the molecular mass of the hydrophilic part and the molecular mass of the whole molecule respectively.

In practice, formulator use molar mass instead of molecular mass of the surfactants in the equation (1) to calculate the HLB number.

$$\text{HLB}_{\text{Griffin}} = 20\left(1 - \frac{\text{SV}}{\text{AV}}\right), \tag{2}$$

where SV is the saponification value of the ester and AV is the acid value of fatty acid.

However, the limitation of this approach is that numerous surfactants, such as ionic surfactants or compounds with a complex structure cannot be described by equations (1) and (2). Therefore, Davies [3] proposed an equation which takes into account the

contribution of common chemical groups' into the calculation of the HLB number:

$$HLB_{Davies} = 7 + \sum H_{h,i} - \sum H_{l,i}, \qquad (3)$$

where $H_{h,i}$ correspond to the hydrophilic part and $H_{l,i}$ are those of the lipophilic part. Values of common chemical groups are listed in Shinoda and Friberg reports [4].

The HLB number of amphiphilic compounds, and the resulting classification, is widely used in cosmetic and pharmaceutical formulation. It is a criteria which influences the choice of surfactants for an intended formula, that is Water in Oil (W/O) or Oil in Water (O/W) emulsions. The HLB number of numerous non-ionic compounds has been calculated and compiled in the publications 'The HLB system: a time-saving guide to emulsifier selection' or 'The chemistry and manufacture of cosmetics'[5].

For novel amphiphilic compounds or blends, when calculation of the HLB is not appropriate or not suitable, the experimental HLB measurement is necessary. Nevertheless, this experiment is time consuming.

Shinoda and Friberg [6–9] showed that the HLB number of non-ionic surfactants is affected by the temperature of the medium, due to temperature-dependent interactions between water and the hydrophilic group. As a result, the HLB number of non-ionic surfactants is difficult to precisely determine.

Shinoda has since described a new approach to characterize some surfactants, and in particular, ethoxylated surfactants. This approach establishes the relationship between the HLB number and the phase inversion temperature (PIT) of a non-ionic surfactant. The PIT corresponds to the temperature at which an emulsion switches from O/W to W/O. This phenomenon of a non-ionic ethoxylated surfactant is due to the dehydration of the hydrophilic group during heating, which leads to a decrease in hydrophilicity and packing parameter change causing a phase inversion of the emulsion. Indeed, the packing parameter pp, describing the geometry of the surfactant, defined by equation (4), will change during heating.

$$pp = \frac{V}{a_0 l_c}, \qquad (4)$$

where V is the volume of the hydrophobic portion of the surfactant, a_0 is the effective area per polar head and l_c is the length of the hydrocarbon chains. When pp < 1 the resulting emulsion is oil in water, when pp > 1 resulting emulsion is water in oil and when pp ≈ 1 the system is bicontinuous.

As the temperature increases, a_0 will decrease and so pp will increase. When the temperature becomes large enough, pp becomes greater than 1 which is observable by an inversion of the emulsion [10].

Shinoda *et al.* established a correlation between HLB number and cloud point of ethoxylated surfactant [11, 12] and identified another correlation between the HLB number and the PIT in a water/surfactant/cyclohexane system (Fig. 1). The limit of this technique is reached when the PIT is close to 100°C. This can be avoided by the use of oil in the system which induces a lowering of the PIT [4].

The PIT of a system is influenced by formulation parameters such as the concentration of surfactant, the presence of additives in water
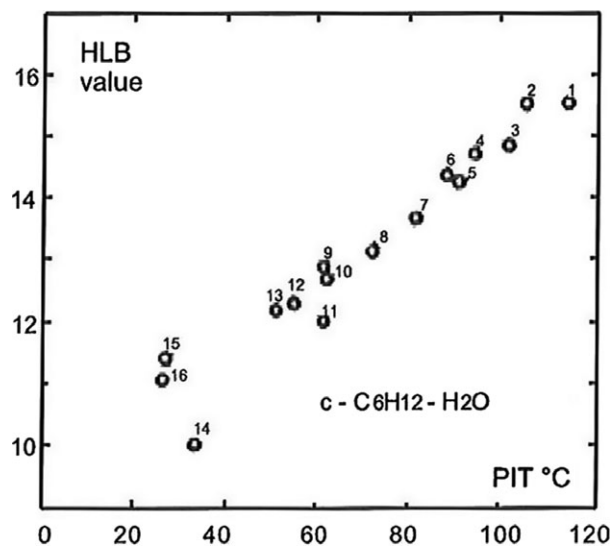

Figure 1 Correlation between the HLB numbers and the PIT of non-ionic surfactants (3% w) in cyclohexane/water emulsions. 1) Tween™ 40; 2) i-$R_9C_6H_4O$-$(CH_2CH_2O)_{17.7}H$; 3) Tween™ 60; 4)i-$R_9C_6H_4O$-$(CH_2CH_2O)_{14}H$; 5) i-$R_{12}C_6H_4O$-$(CH_2CH_2O)_{15}H$; 6) $R_{12}O$-$(CH_2CH_2O)_{10.8}H$; 7) i-$R_8C_6H_4O$-$(CH_2CH_2O)_{8.6}H$; 8) i-$R_9C_6H_4O$-$(CH_2CH_2O)_{9.7}H$; 9) i-$R_8C_6H_4O$-$(CH_2CH_2O)_{8.6}H$; 10) i-$R_{12}C_6H_4O$-$(CH_2CH_2O)_{9.7}H$; 11) $R_{12}O$-$(CH_2CH_2O)_{6.3}H$; 12) i-$R_{12}C_6H_4O$-$(CH_2CH_2O)_{9.4}H$; 13) i-$R_9C_6H_4O$-$(CH_2CH_2O)_{7.4}H$; 14) $R_{12}O$-$(CH_2CH_2O)_{4.2}H$; 15) i-$R_8C_6H_4O$-$(CH_2CH_2O)_6H$; 16) i-$R_9C_6H_4O$-$(CH_2CH_2O)_{6.2}H$ [reproduced from [35]].

or oil, the ratio volumes of water and oil, etc [13–17]. As a result of these observations, Ontiveros *et al.* [18, 19] developed an alternative method based on the phase inversion temperature (PIT) and applied it to several types of surfactants including ethoxylated surfactants, sucroesters, glycerol esters and lecithin [18], carboxylic acids [20] and alcohols [21]. The method is based on calculating the difference between the PIT of a *n*-octane/$C_{10}E_4$/water system and the PIT of a *n*-octane/$C_{10}E_4$/water/tested Surfactant (S). The difference is referred to as the PIT-deviation and is expressed by $dPIT/dX_S$, where X_S is the concentration of the tested surfactant. A negative PIT-deviation value indicates that the tested surfactant has a lower hydrophilicity than $C_{10}E_4$ and a positive value corresponds to a higher hydrophilicity compared with the $C_{10}E_4$.

Ontiveros plotted the PIT-deviation and the HLB number of every compound studied on a unique scale, [19] however, the study was not designed to show a correlation.

Inspired by all the previous research, the purpose of this study was to establish an accurate correlation between the HLB number and the PIT-deviation of all kinds of surfactant.

In the present work, blends of commercial surfactants, for example Span™ and Tween™ products, which are recognized industry standards, are used to determine HLB numbers according to the conventional method. Secondly, the PIT-deviation of these blends is determined using *n*-octane/C_iE_j/brine systems, where C_iE_j is C_8E_4, $C_{10}E_4$ or $C_{12}E_4$.

Subsequently, an equation is established to correlate the HLB numbers with the PIT-deviation. Two tested ingredients used in the fields of cosmetic and pharmaceutical formulation are studied and their HLB number is determined by means of the previously established correlation.

Materials and methods

Chemicals

Pure tetraethyleneglycol monodecyl ether ($C_{10}E_4$), tetraethyleneglycol monooctyl ether (C_8E_4) and tetraethyleneglycol monododecyl ether ($C_{12}E_4$) were synthesized according to a method previously described [22]. Bromododecyl (99%) was purchased from Acros. Bromodecyl (99%), Bromooctyl (99%) and Tetraethyleneglycol (99%) were purchased from Alfa Aesar. n-Octane (99%) was purchased from Acros. Dye FD&C blue n° 1 was purchased from Sensient. Sodium chloride NaCl (≥99.5%) was purchased from Sigma-Aldrich. Sorbitan monostearate (Span™ 60), sorbitan monooleate (Span™ 80), polyoxyethylene sorbitan monostearate (Tween™ 60), polyoxyethylene sorbitan monooleate (Tween™ 80), steareth-2 (Brij™ 72), steareth-21 (Brij™ 721) and Cithrol™ DPHS were provided by Croda. Paraffin oil was provided by Univar. Jojoba Oil was purchased from Safic-Alfan. PEG 400 was purchased from Clariant. Tefose® 1500 (PEG-6 stearate and PEG-32 stearate) and Emulium® Mellifera (Polyglyceryl-6 Distearate and Jojoba Esters and Polyglyceryl-3 Beeswax and Cetyl Alcohol) were provided by Gattefossé. Surfhope® C-1216 was provided by Mitsubishi-Chemical Foods Corporation. Stearyl alcohol was purchased from BTC (BASF trading company). Milli-Q water was used in the whole work.

All structures and physical and chemical characteristics are presented in Table I.

Conventional HLB number measurement

The HLB number of an unknown surfactant is generally determined by means of the Griffin or Davies equation or by experimental measurement adapted from the method developed by Griffin [1] (i.e. the conventional method).

In the experimental measurement approach, the tested surfactant (referred to S) is coupled in different proportions with a reference surfactant. Span™ 80 (HLB = 4.3 ± 1) and Tween™ 80 (HLB = 15 ± 1) were chosen as reference surfactants. These are well-documented and are used in cosmetic and pharmaceutical formulations for many years.

If the expected HLB number of 'S' is high, it is combined with Span™ 80. If HLB number is low it is combined with Tween™ 80. Emulsions are prepared with these mixtures, water and paraffin oil (required HLB ≈ 10) [5]. The composition of the emulsions prepared comprises 5%$_w$ of surfactant (or a surfactant mixture), 15%$_w$ of oil and 80%$_w$ of water. The hydrophilic surfactant is solubilized in water and the lipophilic one in oil. Each phase is heated to 80°C for 5 min. The oil phase is dispersed in the aqueous phase at 900 r.p.m. (using a Turbotest homogenizer from VMI Rayneri®) for 15 min; then stirred at 600 r.p.m. for six minutes in a 25°C water bath. At this point, a water-soluble dye (FD&C blue n°1) is added to enable the visual comparison of the stability of each emulsion.

Emulsion stability is evaluated by observing the creaming of the emulsion. The more stable the emulsion the less macroscopic phase separation and vice versa. The more stable emulsion contains the surfactant mixture with an HLB number equal to 10. The HLB number of the tested surfactant is then calculated using the equation (5):

$$\frac{m_s . HLB_S + m_{ref} HLB_{ref}}{m_{tot}} = 10, \tag{5}$$

where m_{ref} and HLB_{ref} are the mass and the HLB of Span™ 80 or Tween™ 80. M_s is the mass of the tested surfactant and $m_{tot} = m_s + m_{ref}$.

This experimental method to determine the HLB number of a tested surfactant is tedious and the resulting values can only be considered approximate.

Synthesis of polyoxyethylene alkyl ether (C_iE_4)

The following procedure is applicable for the synthesis of C_iE_4 surfactants. These surfactants are synthesized according to the procedure described by Gison et al. and Lang et al. [22, 23]. 6.3 g of a 50%w aqueous sodium hydroxide solution and 76.3 g of tetraethylene glycol are introduced in a three neck reactor. The mixture is stirred and heated to 100°C for 30 min. Then, 17.4 g of C_iBr are added drop by drop in the excess of tetraethylene glycol and the medium maintained at 100°C for 24 h. The compounds are purified using a method described in [22] and analysed by GC-FID, resulting in a purity of 98% for C_8E_4; 98% for $C_{10}E_4$ and 97% for $C_{12}E_4$.

PIT deviation measurement of C_iE_4 reference systems

The approach for PIT-deviation measurement is inspired by the study of Pizzino [24] and utilizes a n-Octane/$C_{10}E_4$/water system.

Firstly, the n-Octane/C_iE_4/brine system is prepared in a 20 mL vial, by filling with 4.85 g of brine (NaCl = 10^{-2} M), 4.85 g of n-Octane and 0.3 g of surfactant (C_iE_4), that is 3%$_w$ of the whole reference system. This n-Octane/C_iE_4/brine system was gently hand-shaken for a few seconds and placed in a thermally regulated cell linked to a cryothermostat (UBER ministat 230-NR).

During the course of the experiments, the system is kept under gentle magnetic stirring. Prior to increasing the temperature, the system is maintained for five minutes at 6°C below the expected PIT. Then heat is applied at a rate of 1°C/min until a temperature of 3°C above the observed PIT is reached. During the study, the viscosity of n-octane and water does not change significantly with the temperature [25] and does not impact the PIT. Moreover, as described by Pizzino [24], the heating rate is set at 1°C/min and C_iE_4 concentration fixed at 3%w. These parameters give reproducible measurements.

The conductivity (χ) and temperature are simultaneously measured by a Radiometer Analytical CDM 210 conductimeter fitted with a probe. The software was custom developed with a LabVIEW 10.0.1 platform. The programme carried out real-time data acquisition at 1 data unit per $\Delta T = 0.1°C$.

The conductivity (χ) as a function of temperature (T) profile was obtained during the heating process (Fig. 2a).

The PIT of the system corresponds to the temperature when $\frac{d^2\chi}{dT^2} = 0$. On the conductivity profile a bump appears just after the first fall, which is usually attributed to the temporary occurrence of liquid crystals [26, 27].

The tested surfactant 'S' was introduced to the system (mass m_S) by successive additions. Equation (6) defines mass fraction X_S of S in the surfactants C_iE_4/S mixture for each addition.

Table I Chemical structure, melting point (MP), saponification index (SV), acid value (AV), density and HLB$_{literature.}$ of studied compounds
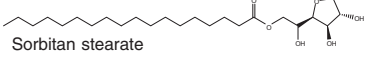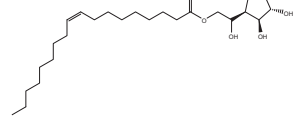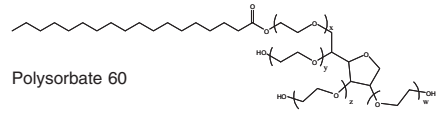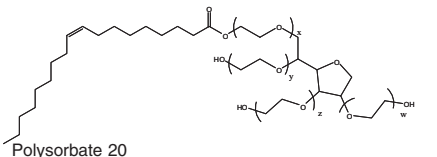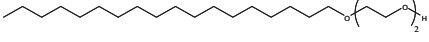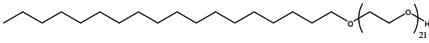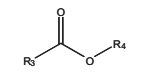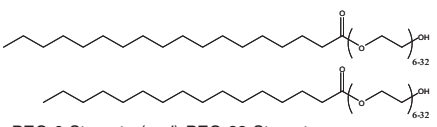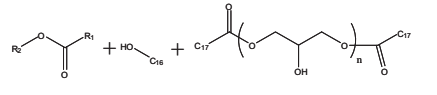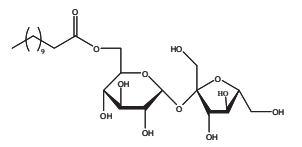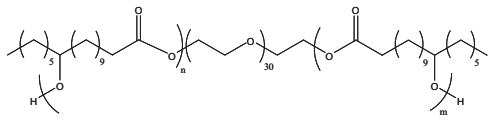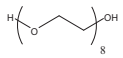
Compounds	Chemical structure/INCI	Density[a] (20°C)	MP[a] (°C)	SV[a] (mgKOH/g)	AV[a] (mgKOH/g)	HLB$_{lit.}$ [36]
Span™60	Sorbitan stearate	1	55	149–160	<8	4.7
Span™ 80	Sorbitan oleate	1	1	149–160	<8	4.3
Tween™ 60	Polysorbate 60	1.1	55–60	45–55	<8	14.9
Tween™ 80	Polysorbate 20	1.07	−20	45–55	<8	15.0
Brij™ 72	Steareth-2	0.89	45	/	<2	4.9
Brij™ 721	Steareth-21	0.89	45	/	<2	15.5
Jojoba oil	R3 : 15 to 25 R4 : 18 to 24 Unsaturated aliphatic ester	0.86–0.88	7	92–95	0–3	6 (for O/W emulsion)[b]
Tefose® 1500	PEG-6 Stearate (and) PEG-32 Stearate	1.03	40–44.4	75–95	<6	/
Emulium® Mellifera	R1:C15 to 31 R2:C16 to 32 Polyglyceryl-6 Distearate (and) Jojoba Esters (and) Polyglyceryl-3 Beeswax (and) Cetyl Alcohol	0.95	48–54	110–30	8.0–12	/
Surfhope® C-1216	Sucrose monolaurate	/	150	/	/	16

Table 1 (continued)

Compounds	Chemical structure/INCI	Density[a] (20°C)	MP[a] (°C)	SV[a] (mgKOH/g)	AV[a] (mgKOH/g)	HLB$_{lit.}$ [36]
Cithrol™ DPHS	PEG-30 Dipolyhydroxystearate	1	40–50	/	/	5.5
PEG 400	Polyethylene glycol	1.1		/	/	/
Paraffin oil	C_nH_{2n+2} $n = 16$–24	0.85	−24	/	/	10 (for O/W emulsions)[b]
Stearyl alcohol		0.81	59.8	0	0	1

[a]Information given in the supplier's technical data sheet.
[b]Required HLB described in the scientific literature [37].

$$X_S = \frac{m_S}{m_w + m_o + m_S + m_{CiE4}}, \qquad (6)$$

where m_s, m_w, m_o and m_{CiE4} are the mass of the tested surfactant, the water, the n-octane and the C_iE_4 respectively. m_w, m_o and m_{CiE4} are constant during all experiments.

For each addition of tested surfactant, corresponding to a fraction X_S, a heating cycle was applied to determine the PIT value. As shown in Fig. 2b, the deviation of the phase inversion temperature is proportional to the fraction of tested surfactant. Hence, the slope $dPIT/dX_S$, where X_S is the fraction of tested surfactant, is named PIT-deviation or PITd. The percentage of tested compound never exceeds 1%w of the whole system.

As an example (Fig. 2b), the value of PITd of Tween™ 60 in the $C_{10}E_4/n$-Octane/water system is 6.1 (Table II). This means Tween™ 60 has a higher hydrophilicity than $C_{10}E_4$ [18].

Results and discussions

Measurement of HLB number of commercial surfactants

The HLB number of several commercial surfactants: Span™ 60, Tween™ 60, Brij™ 72, Brij™ 721, Emulium® Mellifera and Tefose® 1500 was determined by the conventional method. This selection of surfactants enables different kinds of chemical groups to be evaluated: ethoxylated fatty alcohol, PEG esters, polyglycerol esters and sorbitol esters.

Screening of the HLB number was performed using the combinations of Tween™ 80/Emulium® Mellifera and Span™ 80/Tefose® 1500 (Table III). Emulsions of paraffin oil (HLB required $\approx$ 10) were formulated for each mix of surfactants (Fig. 3), A to G for Tween™ 80/Emulium® Mellifera combination and A' to G' for the Span™ 80/Tefose® 1500 combination.

A first series of emulsions was prepared to determine the HLB number of Emulium® Mellifera (series 1). Emulsion C gave the best stability, corresponding to 40%$_w$ of Tween™ 80 and 60%$_w$ of Emulium® Mellifera.

A second series was prepared to determine the HLB number of Tefose® 1500. In this series Emulsions E' and F' showed a similar stability. The best stability is between emulsions E' and F', that is corresponding to 70%$_w$ of Span™ 80 and 30%$_w$ of Tefose® 1500. The HLB numbers are given by the equation (5): eight for Emulium® Mellifera and 12 for Tefose® 1500.

Similarly, the HLB numbers of Span™ 60, Tween™ 60, Brij™ 72, Brij™ 712, Emulium® Mellifera and Tefose® 1500 are determined and reported in Table IV.

Span™80 (HLB = 4.3) and Span™ 60 (4.7) are classified as lipophilic surfactants, Brij™ 72 (HLB = 8.0) and Emulium® Mellifera (HLB = 8.0) as intermediate surfactants; Tween™ 60 (HLB = 14.9) and Tween™ 80 (15) Brij™ 721 (18.5) and Tefose® 1500 (12) as hydrophilic surfactants. The HLB numbers for Brij™ 72 and Brij™ 721 resulting from this screening do not match the values provided by the supplier and the literature. This difference is most likely due to the fact that the values reported in the literature are based on a calculated HLB number using the equation (1) and not from the conventional (experimental) method. HLB numbers obtained by the conventional method are used for the purpose of this study.

PIT deviation as an extensive value

The PIT-deviation of surfactant blends was measured. The corresponding HLB number was calculated, using equation (5), starting from 4.3 up to 18.5. The blends are Span™ 80/Tween™ 80, Span™ 60/Tween™ 60 and Brij™ 72/Brij™ 721. HLB numbers and PITd experimental determined with n-Octane/$C_{10}E_4$/brine (0.02N NaCl) of the different blends are shown in Table V.

For each blend, the PIT-deviation was also determined using three references systems: 3%w C_iE_4 (C_8E_4, $C_{10}E_4$ and $C_{12}E_4$)/n-octane/brine (0.02N NaCl).

Although the partitioning of non-ionic surfactant blend between brine and oil is reported in literature [28–31], a linear correlation between PIT-deviation and the weight percentage of Brij™ 72 is observed with the blend of Brij™ 72/Brij™ 721 (Fig. 4). This linear correlation suggests that the partitioning does not impact the brine/n-octane interphase. The surfactant blend
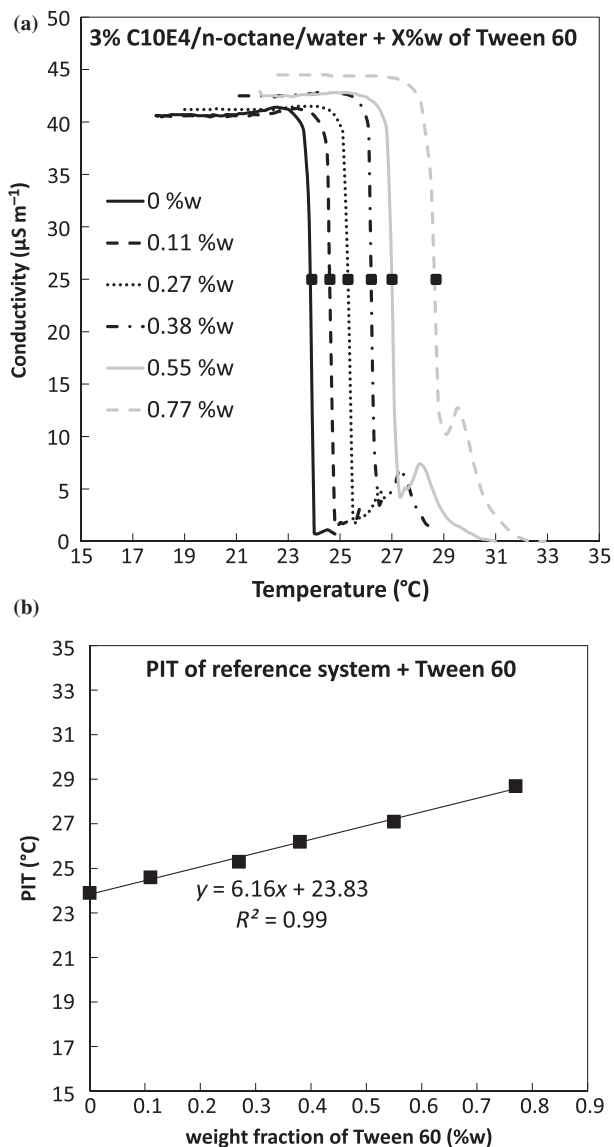
Figure 2 (a) Conductivity vs temperature of the emulsion formed with 3% $C_{10}E_4$/n-octane/brine + x%w of Tween™60 b) PIT of 3% $C_{10}E_4$/n-octane/brine + x%w of the Tween™ 60 system.

acts as a single phase at the interface, as described in previous studies [32].

Moreover, this linearity between PITd and the weight ratio of surfactants can be described by the equation:

$$PITd_{calc} = \frac{m_A \cdot PITd_A + m_B \cdot PITd_B}{m_A + m_B}, \qquad (7)$$

where $PITd_{calc}$ is the PITd of the mixture of two surfactants A and B. The mass of the surfactant A is m_A, the mass of the surfactant B is m_B. PITd of the surfactant A is $PITd_A$ and PITd of the surfactant B is $PITd_B$.

This equation is validated by the equivalence between values of $PITd_{exp.}$ and $PITd_{calc.}$

Table II Data and equation of the PITd measurement of tween™ 60 in *n*-Octane/$C_{10}E_4$/brine system

	Initial	1st add	2nd add	3rd add	4th add	5th add
X_S (%w)	0	0.11	0.27	0.38	0.55	0.77
PIT	23.9	24.6	25.3	26.2	27	28.7
Equation of PITd		PITD = (PIT − $PIT_{initial}$)/X_s				
		PIT = $6.1X_S$ + 23.8	R^2 = 0.993			

Table III Emulsions containing Emulium® Mellifera and Tefose® 1500 to determine their HLB number

Emulsions series 1	A	B	C	D	E	F	G
%wTween™ 80	0	20	40	50	60	80	100
%wEmulium® Mellifera	100	80	60	50	40	20	0

Emulsions series 2	A'	B'	C'	D'	E'	F'	G'
%wSpan™ 80	0	20	40	50	60	80	100
%wTefose® 1500	100	80	60	50	40	20	0

PITd is an extensive value and can be calculated through a simple mixing rule like the HLB number.

This extensive property will not be used in this work, but this property can be useful to design or modulate a surfactant in order to reach an expected HLB number.

Correlation between PIT deviation and HLB number

The HLB number versus PIT-deviation of each blend cited in Table V is represented in Fig. 5. For all C_iE_4, there is a good correlation between the HLB number and the PIT-deviation. This correlation can be described by the equations provided by linear regression reported in the Table VI.

These equations enable the efficient and accurate calculation of the HLB number based on a PIT-deviation measurement.

These equations are validated by HLB measurements obtained by the PIT-deviation and the conventional HLB measurement method ($HLB_{measured}$). The studied compounds are Emulium® Mellifera, Tefose® 1500, Cithrol™ DPHS and Surfhope® C-1216 in *n*-octane/$C_{10}E_4$/brine system. HLB_{PIT} from PIT-deviation are obtained by equation (9), and are reported in Table VII.

The HLB numbers from conventional measurements or calculated using equation (9) give same results (Table VII). Thus, the equation HLB_{PIT} = f(PIT-deviation) is validated for compounds with interfacial activity.

This correlation is valid for surface active compound mixtures regardless of their chemical nature, notably surfactants, fatty alcohols and fatty acids.

Special case: PIT-deviation is close to zero

1 When the PIT-deviation of the *n*-octane/$C_{10}E_4$/brine + tested compound is close to zero (−1 to +1), three explanations are proposed: Tested compound has the same affinity for oil and

Figure 3 Emulsion of paraffin oil stabilized by a mixture of Tween™ 80/Emulium® Mellifera and Span™ 80/Tefose® 1500 (see Table III).

Table IV Surfactants used for the correlation between the PIT deviation and the HLB number from experiment and literature

Surfactant	HLB$_{number}$	HLB$_{supplier}$[a]
Span™ 60	4.7 ± 1	4.7
Tween™ 60	14.9 ± 1	14.9
Span™ 80	4.3 ± 1	4.3
Tween™ 80	15.0 ± 1	15.0
Brij™ 72	8.0 ± 1	4.9
Brij™ 721	18.5 ± 1	15.5
Emulium® Mellifera	8.0 ± 1	8.0
Tefose® 1500	12 ± 1	12
Cithrol™ DPHS	5.5 ± 1[a]	5.5
Surfhope® C-1216	16 ± 1[a]	16

[a]Data obtained from supplier technical data sheet.

water as $C_{10}E_4$ and the same HLB number. The PIT is not influenced by the addition of the tested compound.

2 Tested compound is totally soluble in water and does not have any impact on the interface. It slightly changes the polarity of water and the affinity of $C_{10}E_4$ with the aqueous phase.

3 Tested compound is totally soluble in *n*-octane and does not adsorb at the interface or does not change the near interfacial structure such as the lipophilic linker does [33, 34].

To determine which explanation is applicable, it is possible to measure the PIT deviation of the tested compound with another C_iE_4 than $C_{10}E_4$.

Three examples of tested compounds are presented in Table VIII, each having a PIT deviation close to zero with the reference system *n*-octane/$C_{10}E_4$/brine.

Tefose® 1500 CG reflects case i). Tefose® 1500 CG, which is PEG-6 Stearate and PEG-32 Stearate, has a PIT-deviation close to zero with the *n*-octane/$C_{10}E_4$/brine system that corresponds to HLB=12.4. In a *n*-octane/C_8E_4/brine system, Tefose® 1500 CG has

Table V Screening of HLB number with several blends of Tween™ 60/Span™ 60, Tween™ 80/Span™ 80 and Brij™ 721/Brij™ 72

| %$_w$ of lipophilic surfactant	0	20	40	50	60	80	100
	Brij™ 72+ Brij™ 721						
HLB	18.5 ± 1	16.4 ± 1	14.3 ± 1	13.3 ± 1	12.2 ± 1	10.1 ± 1	8 ± 1
PITd exp.	11.2 ± 1	7.4 ± 1	3.7 ± 1	1.1 ± 1	−1.0 ± 1	−4.5 ± 1	−8.8 ± 1
PITd calc.	11.2 ± 1	7.1 ± 1	3.2 ± 1	1.2 ± 1	−0.9 ± 1	−4.8 ± 1	−8.8 ± 1
	Span™ 80+ Tween™ 80						
HLB	15.0 ± 1	12.9 ± 1	10.7 ± 1	9.7 ± 1	8.6 ± 1	6.4 ± 1	4.3 ± 1
PITd exp.	6.8 ± 1	2.4 ± 1	−3.1 ± 1	−5.4 ± 1	−8.2 ± 1	−12.0 ± 1	−17.0 ± 1
PITd calc.	6.8 ± 1	2.0 ± 1	−2.7 ± 1	−5.1 ± 1	−7.5 ± 1	−12.2 ± 1	−17.0 ± 1
	Span™ 60+ Tween™ 60						
HLB	14.9 ± 1	12.8 ± 1	10.8 ± 1	9.8 ± 1	8.8 ± 1	6.7 ± 1	4.7 ± 1
PITd exp.	6.1 ± 1	2.5 ± 1	−2.4 ± 1	−4.3 ± 1	−6.8 ± 1	−11.5 ± 1	−16.9 ± 1
PITd calc.	6.1 ± 1	1.6 ± 1	−3.1 ± 1	−5.4 ± 1	−7.7 ± 1	−12.4 ± 1	−16.9 ± 1
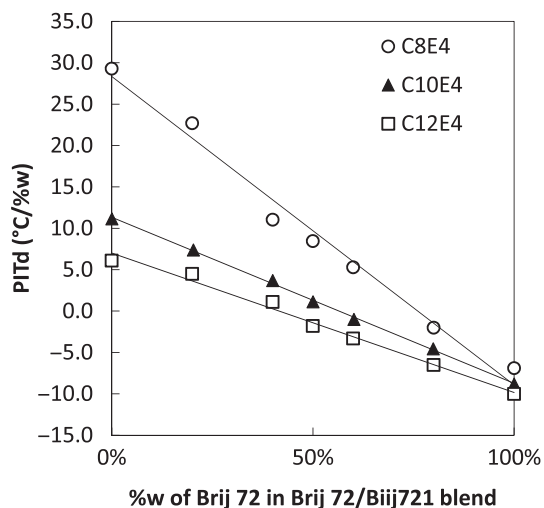
Figure 4 PITd of several blends of Brij™ 72 and Brij™ 721 as a function of the percentage of lipophilic ones in the blend. ○ reference system with C_8E_4, ▲reference system with $C_{10}E_4$, □ reference system with $C_{12}E_4$.
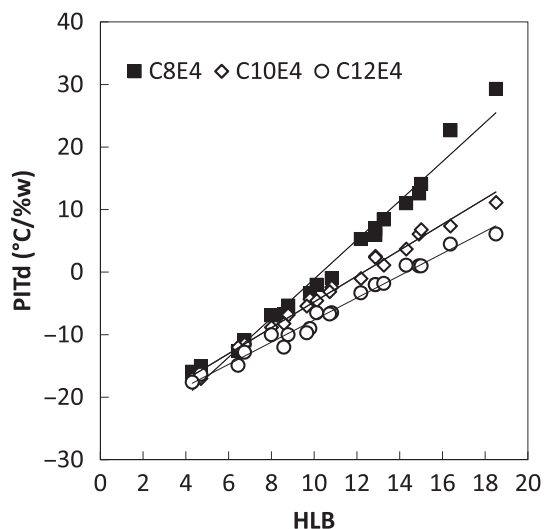

Figure 5 PIT-deviation of Brij™ 72/Brij™ 721, Span™ 80/Tween™ 80 and Span™ 60/Tween™ 60 blends vs HLB of these blends for different C_iE_4/n-octane/brine systems.

a PIT-deviation of 3.1, corresponding to an HLB number of 11.5. The very similar HLB numbers (margin of ±1) are due to a similar activity of $C_{10}E_4$ at the brine/n-octane interphase.

PEG 400 illustrates case ii). With the n-octane/$C_{10}E_4$/brine system, PEG 400 should have an HLB number of 11.9 based on the correlation from the curve in Fig. 5. However, PEG 400 is water soluble and therefore should not have interfacial properties. To clarify, an experiment is performed with C_8E_4 and the PIT-deviation is also close to 0, corresponding to HLB = 10.2. We conclude, therefore, that PEG 400 has no influence on the interface because it is water soluble.

Table VI Equation linking HLB number and PITd provide by the linear regression

C_iE_4/n-octane/brine (0.02N NaCl)	equation	N°	R^2
C_8E_4/n-octane/brine (0.02N NaCl)	PIT$_d$ = 3.1 HLB-32.4	(8)	0.98
$C_{10}E_4/n$-octane/brine (0.02N NaCl)	PIT$_d$ = 2.1 HLB-25.4	(9)	0.99
$C_{12}E_4/n$-octane/brine (0.02N NaCl)	PIT$_d$ = 1.8 HLB-25.4	(10)	0.98

Table VII HLB numbers of four compounds determined by two methods: PIT-deviation and the conventional measurement

	PIT-deviation	HLB$_{PIT}$	HLB measured
Emulium Mellifera®	−9.6	7.7	8 ± 1
Tefose® 1500	0.5	12.5	12 ± 1
Cithrol™ DPHS	−13.8	5.6	5.5 ± 1
Surfhope® C-1216	10.8	17	16 ± 1

Table VIII Three compounds that lead to a PIT deviation close to zero with n-octane/$C_{10}E_4$/brine system

Compound	Jojoba wax	Tefose® 1500 CG	PEG400
Reference system			
C_8E_4/n-octane/brine	0.7	3.1	−0.6
$C_{10}E_4/n$-octane/brine	0.2	0.5	−0.8

Jojoba wax reflects case iii). With the n-octane/$C_{10}E_4$/brine system, jojoba wax should have an HLB number of 12.6 according to the correlation from the curve in Fig. 5. However, jojoba wax in oil and should not exhibit interfacial properties. A second experiment is performed with C_8E_4 and the PIT-deviation is also close to 0, corresponding to an HLB number of 10.5. We conclude that jojoba wax has no influence on the interface because it is oil soluble.

When a tested compound presents a PIT-deviation close to 0 in the system n-octane/$C_{10}E_4$/brine, a second experiment with another C_iE_4 (i.e. C_8E_4) must be performed to confirm the HLB number and the interfacial activity.

Conclusion

The classification of surfactants by HLB number has a long and broad history in cosmetic and pharmaceutical formulation. The HLB number is commonly determined by a well-known conventional method which is approximate and requires many experiments. PIT is another value used to characterize surfactants, but it is limited to ethoxylated surfactants.

PIT-deviation is a recent method based on calculating the difference between the PIT of a n-octane/CiE$_4$/brine system and the PIT of a n-octane/C_iE_4/brine tested surfactant. Until now no link has been proven between PIT-deviation and HLB number.

In this study, we have shown a correlation between PIT-deviation and HLB number. This correlation is established with reference surfactants (Span™, Tween™ and Brij™ series) and three reference systems: *n*-octane/3%w C$_8$E$_4$/brine, *n*-octane/3%w C$_{10}$E$_4$/brine and *n*-octane/3%w C$_{12}$E$_4$/brine. The correlation is linear for each C$_i$E$_4$ with three different slopes.

HLB numbers were determined for four commercial surfactants spread over the whole range of HLB number, by applying the conventional method, and the PIT-deviation method using the C$_{10}$E$_4$ correlation curve. For all surfactants, the same result of HLB number was obtained, validating the correlation. Furthermore, these results prove the validity of this method for all types of amphiphilic compounds including ethoxylated types.

For PIT-deviation values close to 0, it is necessary to carry out additional experiments with *n*-octane/3%w C$_8$E$_4$/brine or *n*-octane/3%w C$_{12}$E$_4$/brine systems to attribute to the tested compound one of the following properties: water soluble, oil soluble or HLB number of 12 equivalent to C$_{10}$E$_4$.

Beyond the determination of the HLB number, the extensive property of the PIT-deviation allows this method to be extended to the quality control of the amphiphilic products and will also facilitate to the preparation of complex surfactant mixtures.

Acknowledgements

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