On the relationships between the hydrophilic-lipophilic balance and the nanoarchitecture of nonionic surfactant systems

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On the relationships between the hydrophilic-lipophilic balance and the nanoarchitecture of nonionic surfactant systems

Short Running title: HLB and packing parameter in nonionics

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Abstract

Building links between established parameters for the characterization of surfactant systems is useful not only for the understanding of the underlying phenomena but also for the judicious formulation of products. Herein, we review comprehensively literature data to find correlations between the hydrophilic-lipophilic balance (HLB) and the molecular packing parameter (P) for a variety of nonionic surfactants in water. The interfacial area per surfactant molecule, a fundamental variable to calculate P , follows a power law as a function of the number of ethylene oxide groups in the surfactant. The exponent ranges from 0.3 to 0.7 which may reflect changes in the conformation of the ethylene oxide chain depending on the nature of the hydrophobic group; there is also apparently a transition towards a collapsed conformation of the ethylene oxide chains at high surfactant concentrations. P is found to change linearly with HLB in the range of data studied, although the parameters of the linear fitting depend on the nature of both hydrophobic and hydrophilic moieties of the surfactant; this would also imply a linear relationship between P and the HLB temperature (i.e. Phase Inversion Temperature) according to the Kunieda-Shinoda equations. Analysis of the liquid crystal regions of the surfactant phase diagram at constant temperature indicate that the HLB values required for the morphological phase transitions defined by P increase with surfactant concentration. The present report may serve as contribution for the programmed design of nanoarchitectures in surfactant systems.

Keywords: Nonionic surfactants, Hydrophilic-Lipophilic Balance, HLB, Packing parameter, Phase behavior; Phase diagrams.

Introduction

From long ago, efforts have been devoted in academy and industry to establish structure-property relationships in surfactants (Davis, 1994; Rodríguez-Abreu, 2014). The empirical HLB scale (Griffin, 1949, 1954) is one of the earliest attempts in such direction. It has the advantage of being in principle easy to estimate from a simple equation that is linear and depends only on the weight fraction of hydrophilic groups in the surfactant molecule. Accordingly, low HLBs correspond to hydrophobic surfactants whereas high HLBs correspond to hydrophilic surfactants. However, the HLB scale was initially restricted to certain non-ionic surfactants at room temperature. Moreover, the estimated HLB may be the same for two surfactants that yet may behave differently because of dissimilarities in their chemical structure. Accordingly, other methods different from the Griffin equation were proposed to estimate HLB number (Davies, 1957; Ben-Et, 1972; Rabaron et al., 1993) so that the scale has been extended to ionic surfactants. Later on, more systemic and comprehensive formulation parameters for oil/water/surfactant mixtures have been developed such as the SAD (Surfactant Affinity Difference) and HLD (Hydrophilic-Lipophilic Deviation) concepts (Salager, 2000; Queste, 2007; Acosta, 2008), which take into account effects not considered in the HLB scale such as temperature, salinity, type of oil and cosurfactants. Still, the HLB scale continues to be used in commercial products as a selection guide and therefore is of practical relevance.

A different approach based on a theory linking together thermodynamics, interaction free energies and molecular geometry resulted in the introduction of the surfactant molecular packing parameter P (Israelachvili, 1976). This parameter has been successfully used for the qualitative description and prediction of nanostructures, not only in surfactant solutions but also in surfactant-derived inorganic materials (Huo, 1996).

There have been some attempts to link the surfactant parameters described above. Kunz et al (Kunz, 2009) proposed an equivalence between the spontaneous curvature, the molecular packing parameter, and HLD. Those authors however focused on a particular system, the pentaethylene glycol monododecyl ether/water/*n*-octane system.

Besides the work of Berger et al (Berger, 2005), there is not much literature on the correlation between HLB and P despite they are two relevant surfactant characterization parameters. Herewith, that earlier work is extended to a wider library of experimental data with the aim of filling that gap for the case of nonionic surfactants in water. The interfacial area of the surfactant in aggregates is considered as a key parameter as it much reflects changes in physicochemical conditions and formulation. Further, the important effect of surfactant concentration is considered in the analysis through the use of phase diagrams.

Results and discussion

The packing parameter P (Israelachvili, 1976) is expressed as

$$P = \frac{V}{al} \quad [1]$$

Where V and l are the volume and length of the hydrophobic moiety, respectively, and a is the cross sectional area of the surfactant at the interface. The critical values for morphological transition are $P=1/3$ for spheres, $P=1/2$ for cylinders and $P=1$ for planar bilayers. P is also related with the surfactant layer curvature, so that for $P<1$ the curvature is positive, for $P=1$ is zero and for $P>1$ is negative.

In the case of alkyl-type hydrophobic moieties, V and l can be estimated by the following equations (Tanford, 1972)

$$V = 27.4 + 26.9 N \quad [2]$$

$$l = 1.4 + 1.255 N \quad [3]$$

where N is the number of carbons in the alkyl tail. Eq. 3 actually gives the maximum length of the chain, i.e. in its fully extended conformation.

a is a parameter more difficult to estimate, since compared to V and l , it depends much more on physicochemical variables. In the case of nonionics, a changes with the size of the hydrophilic moiety, temperature and surfactant concentration, therefore is a key parameter that determines the nanoarchitecture of surfactant systems.

Although not completely realistic, a first approximation is to take a as the limiting area at the saturated air/water interface (a_s), i.e. at the critical micellar concentration (CMC); there is

plenty of experimental data on a_s from surface tension and neutron reflectivity measurements. As for the dependence on the size of the hydrophilic moiety, the conformation of poly(oxyethylene) chain is expected to play an important role; this conformation is described by the mean field theory of polymer solutions in which polymers are considered as random walks. Accordingly, the radius of gyration (R_g) scales with the degree of polymerization n as $R_g = n^\nu$, where ν is the excluded volume exponent which is 3/5 for fully swollen chains, 1/2 for Gaussian chains, and 1/3 for fully collapsed chains (Hammouda, 2007).

In the case of alkyl polyethoxylates a_s has been found (van Voorst, 1960; Nikas, 1992) to follow a power law as a function of the number of ethylene oxide groups in the surfactant molecule (n), i.e. a_s can be expressed as

$$a_s = k n^x \quad [4]$$

Eq. 4 is in agreement with the scaling law followed by R_g , in despite that the poly(oxyethylene) chains in surfactants are relatively short (oligomeric). Early reports have suggested that $x = 1/2$ and actually this value can be predicted if its assumed that only hydration water remains in the saturated surfactant layer at the water/air interface, and that the poly(ethylene oxide) (EO) chains behave like a Gaussian coil which keeps its size when constrained in the surfactant layer. If other scaling formulas for flexible chains in a good solvent are considered, then x is found to be 6/11 (Sedev, 2001), which is still close to 1/2. Available experimental data of a_s at 25°C were fitted to Eq. 4 and the values of k and x obtained are shown in Table 1 for different nonionic surfactant series (note that both surfactants with homogeneous and polydisperse ethylene oxide chains are included). The fitting is good as indicated by R^2 values close to 1; values of x range from 0.3 to 0.7, suggesting that the conformation of EO chains and therefore a_s depend on the hydrophobic group of the surfactant. For example, in fluorinated surfactants x is low pointing to a nearly collapsed EO chain conformation induced by a very dense packing at the interface (Matos, 1989)

Insert Table 1

Fitting the data of C_jEO_n surfactant areas at the water/octane interface ($j = 6, 8, 10, 12$ and $n = 2, 3, 4, 5, 6$) calculated from Small-Angle Neutron Scattering (SANS) measurements (Sottmann et al, 1997), the values of k and x are estimated at 29.66 and 0.44, respectively.

In comparison to a_s , the values of interfacial areas are actually lower in the aggregates and especially at higher surfactant concentrations, i.e. in the liquid crystal region of the surfactant/water phase diagram. Still, Eq. 4 gives a good fit to the data as shown in Fig. 1. For the case of $C_{12}EO_n$ surfactant series, x appears to decrease with surfactant concentration.

Insert Figure 1

Results from fitting to other non-ionic surfactant systems at high concentrations i.e., in the liquid crystal regions of the surfactant/water phase diagram, are summarized in Table 2. Note the x values are lower than in table 1, which may be attributed to a nearly collapsed conformation of the EO chain when confined in the packed layers of liquid crystals at high surfactant concentrations.

Insert Table 2

Again as a first approximation, the values of a_s (air/water interface) are taken to calculate the packing parameter P from Eqs. 1-3. The Griffin equation (Eq. 5) is then used to construct a plot of P versus HLB for different surfactants series as shown in Fig. 2.

$$HLB = \frac{wt\% \text{ hydrophilic moiety}}{5} \quad [5]$$

From Eq. 4 and 5, one would expect a non-linear relationship between P and HLB for this type of surfactants. However, as can be seen in Fig. 2, in practical terms the data fits well to a linear trend with negative slope for all the surfactants series considered and within the given HLB range. Fig. 2 also shows schematically the loci for the morphological transitions in aggregates: bilayers are favored at low HLB, cylinders at intermediate HLB and spheres at high HLB.

Insert Figure 2

Results from the fittings in Fig.2 are summarized in Table 3. It is evident that the data in Fig.2 does not collapse in a single curve but the packing parameter is determined not only by the mass ratio of the hydrophobic and hydrophilic moieties (i.e. HLB) but also by the chemical nature of both moieties in the surfactant molecule (Nagarajan, 2002). For instance, the packing parameter of surfactants with polyglucoside as hydrophile appears to change much less with HLB than those bearing a poly(ethylene oxide) hydrophile. Also, keeping HLB constant, it is possible to have a cylinder-bilayer transition by increasing the length of the hydrophobe in C_jEO_n surfactants.

At this point, it is also possible to make equivalencies with another surfactant characterization parameter, the phase inversion temperature (PIT) or HLB temperature (T_{HLB}), extending this way the approach to surfactant/oil/water systems. In many systems T_{HLB} changes linearly with HLB according to:

$$T_{HLB} = k_{oil} (HLB - N_{oil}) \quad [6]$$

Where k_{oil} and N_{oil} are constants for a given oil (Kunieda, 1985). Eq.6 and Table 3 then indicate that there will also be a linear relationship (with negative slope) between T_{HLB} and P , i.e. low T_{HLB} at high P and high T_{HLB} at high P .

Insert Table 3

Now comes the analysis of the effect of surfactant concentration. The analysis will be based on the Kunieda's phase diagrams, i.e. isothermal diagrams showing the phase regions as a function of the hydrophilic volume fraction in the surfactant and the surfactant concentration (in weight fraction). Herewith, the hydrophilic volume fraction has been replaced by the HLB (estimated by Eq.5), as seen in Fig.3,5 and 6. In these figures, the subscript 1 denotes "hydrophilic" or "normal"-type self-organizing structure or phase, in which the average curvature of surfactant layer is positive and convex toward water. The subscript 2 indicates "lipophilic" or "reverse"- type assemblies. H_1 is a hexagonal liquid crystal; H_2 is a reverse hexagonal liquid; I_1 is a micellar cubic phase; I_2 is a reverse micellar cubic phase; V_1 is a bicontinuous cubic phase; V_2 is a reverse bicontinuous cubic phase; L_α is a lamellar liquid crystal; D_2 is a isotropic bicontinuous surfactant phase (reverse type), also denoted by D' or L_3 phase (Kunieda, 1982, Strey et al, 1990); N is a nematic phase; W_m is an aqueous micellar

phase; O_m is an oily phase such as a reverse micellar solution phase or liquid surfactant; W is an excess water phase; S is a solid-present region.

For C_jEO_n surfactants (Fig.3), it is evident that the morphology and structure of surfactants aggregates and liquid crystals are dependent not only on concentration and HLB, but also on the length of the alkyl chain. On one hand, at constant HLB, a I_1 to H_1 transition ($P=1/3$ to $P=1/2$) is driven by an increase in surfactant concentration for $j=12, 16$ and $18:1$. Also, an increase in surfactant concentration induces a H_1 to L_α transition ($P=1/2$ to $P=1$) for $j=12$ and $18:1$. On the other hand, at constant surfactant concentration, there are a I_1 to H_1 to L_α transitions ($P=1/3$ to $P=1/2$ to $P=1$) by decreasing HLB for $j=12$ and $18:1$. Reverse structures with negative curvature such as the H_2 phase ($P > 1$) are also possible for $j=18:1$ at surfactant weight fractions higher than ca. 0.6 and $HLB < 8$.

Insert Figure 3

The boundaries for morphological transitions in the liquid crystal regions for C_jEO_n surfactants as a function of HLB and surfactant concentration derived from Fig.3 are summarized in Fig. 4. The HLB required for the layer-to-cylinder transition ($P = 1$ to $1/2$) increases non-linearly with surfactant concentration, and it is approximately in the range $HLB = 10-15$, i.e. surfactants with $HLB < 10$ would tend to form bilayers or other structures with low curvature. The HLB required for cylinder-to-sphere transition ($P = 1/2$ to $1/3$) also increases non-linearly with surfactant concentration and it is approximately in the range $HLB = 12-17$.

Insert Figure 4

The HLB vs surfactant concentration phase diagrams were also constructed for other type of nonionic surfactants. When a trisiloxane chain is present as the hydrophobic moiety in the nonionic surfactant molecule, the L_α phase ($P=1$) tends to shift to higher HLB values as compared to C_jEO_n surfactants (Fig.5a); actually, the L_α phase (bilayer) is dominant in the phase diagram of trisiloxane nonionic surfactants. For longer siloxane chains (Fig.5b) structures with lower curvature are preferred and it is possible to form reverse structures such as H_2 and I_2 ($P > 1$) at $HLB < 7$ and surfactant weight fractions higher than ca. 0.7. Note the existence of liquid crystals in siloxane surfactants at $HLBs < 5$, something not found in C_jEO_n .

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3 surfactants. Contrary to alkyl chains, very long poly(dimethylsiloxane) remain in the liquid
4 state. This allows a wider range of hydrophobicity in aggregates and therefore stronger
5 segregation between the poly(dimethylsiloxane) and poly(ethylene oxide) chains, which
6 favors the formation of reverse liquid crystals.
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11 Insert Figure 5
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14 A change of the type of nonionic hydrophilic group also impacts the relationship between
15 HLB and P , as shown in the phase diagram for polyglyceryl surfactants(Fig.6). In this case,
16 there is no formation of I_1 phase and in general there is much less variety of surfactant self-
17 assembled structures as compared to C_jEO_n surfactants (Fig.3). Poly(glycerol) and
18 poly(ethylene oxide) have different hydration properties, which affects their phase behavior.
19 For example, the cloud point of polyglyceryl surfactants increases much more with HLB than
20 that of C_jEO_n surfactants (Kunieda, 2002).
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27 Insert Figure 6
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31 Conclusions and Outlook

32 Literature data on several nonionic surfactants in water have been fitted to produce power
33 laws for the interfacial area in aggregates and then empirical linear equations between the
34 hydrophile-lipophile balance (HLB) and the molecular packing parameter (P), which also
35 implies linear correlations with the HLB temperature or phase inversion temperature. The
36 parameters of the linear equations depend both on the hydrophilic and hydrophobic groups
37 of the surfactant molecule. The analysis of phase diagrams at constant temperature in the
38 concentrated region indicate that the HLB required for the cylinder-to-sphere ($P = 1/2$ to $1/3$)
39 or layer-to-cylinder transitions ($P = 1$ to $1/2$) increases with surfactant concentration.
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46 The present approach may serve as contribution for the programmed design of
47 nanoarchitectures in surfactant systems. If appropriate equations are derived to estimate the
48 interfacial area and effective hydrophobic length and volume, HLB- P relationships could in
49 principle also be established for ionic surfactants and surfactant/water/oil systems, but it is a
50 challenge.
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Tables

Table 1. Best fittings to the equation $a_s = k n^x$ (air/water interface) for concentrations below or at CMC (25 °C)

Surfactant series	n	k	x	R^2	References
$C_{10}EO_n^{a,b}$	4,5,6,8,10	17.24	0.65	0.9643	Mahajan et al, 2012 Eastoe et al, 1997 Carless et al, 1964 Meguro et al, 1981
$C_{12}EO_n^{a,b}$	2,3,4,5,6,7,8,12	23.51	0.46	0.9234	Lu et al, 1993 Lu et al, 2000 Li et al, 2013 Rosen et al, 1982a Eastoe et al, 1997
$C_{14}EO_n^{a,b}$	1,2,4,6,8	18.40	0.44	0.9565	Pollard et al, 1998 Meguro et al, 1981
$C_{16}EO_n^{a,b}$	2,4,6,7,9,12,15,21,20,30,40	11.51	0.72	0.9841	Pollard et al, 1998 Elworthy et al, 1962
$OPEO_n^c$	3,4,5,6,7,8,9,10	29.10	0.38	0.9586	Crook et al, 1964
$C_6F_{13}EO_n^d$	2,3,5,7	26.99	0.33	0.9673	Matos et al, 1989
$EO_nPO_{50-60}EO_n^e$	17,27,37,132	19.03	0.43	0.9739	Alexandridis et al, 1994
Brij TM series ^f	2,4,5,10,12,20,21,23,25	12.41	0.69	0.9374	Wang et al, 2005 Liu et al, 2006 Horozov et al, 1995 Bardhan et al, 2016 Samanta et al, 2011

^a $C_j = C_jH_{2j+1}$; ^b $EO_n = (OC_2H_4)_nOH$; ^c OP = octyl phenol; ^d $C_6F_{13} = C_6F_{13}C_2H_4SC_2H_4$
^e PO = poly (propylene oxide)
^f Fitted data correspond to Brij 30,35,56,58,72,76,78,93,97, 98 and 721 (they have different alkyl chain length).

Table 2. Best fittings to the equation $a = k n^x$ (aggregate's surface) for concentrations at which liquid crystals are formed in water at 25°C

Surfactant series	n	k	x	R^2	References
$C_{12}EO_n$	2,3,4,6,7,8,9,12	26.82	0.31	0.9845	Kunieda et al (1999); Sakya et al (1997)
$C_{18:1}EO_n$	2-20 ^a	27.39	0.29	0.9566	Kunieda et al (1997)
Si_3EO_n	6-10 ^a	25.56	0.33	0.9240	Kunieda et al (1998)

^a surfactants with different n were mixed to obtain average $\bar{n}$ values within the indicated range.

$C_{18:1}$ = oleyl chain. Si_3 =trisiloxane.

Table 3: Best fittings of data in Fig.2 to the equation $P = b \text{ HLB} + c$

Surfactant series	b	c	R^2
$C_{10}EO_n$	-0.0535	1.0492	0.9390
$C_{12}EO_n$	-0.0382	0.8345	0.9849
$C_{14}EO_n$	-0.0721	1.3196	0.9780
$C_{16}EO_n$	-0.0711	1.2889	0.9939
OPEO _n	-0.0411	0.9853	0.9757
Alkyl polyglucosides	-0.0121	0.5671	0.9669
Brij TM series	-0.0836	1.5059	0.9321

Figure legends:

Figure 1. Plot of interfacial area a as a function of ethylene oxide number n for $C_{12}EO_n$ surfactant series. Data are derived from SAXS measurements in lamellar ($n=2,3,4$) and hexagonal ($n = 6,7,8,9$) liquid crystals in water. The water/ethylene oxide weight ratio is constant at 1.25. Data from Kunieda et al (1999)

Figure 2. Plot of packing parameter P versus HLB for various series of nonionic surfactants

Figure 3. Phase diagrams of C_jEO_n surfactants in water as a function of HLB, n and surfactant concentration at 25 °C. (a) $j = 12$ (b) $j = 12$ (c) $j = 16$ (d) $j = 18:1$ (oleyl chain). Diagrams (a) and (c) have been built using data from Clunie et al (1967), Ali& Mulley (1978), Lang&Morgan (1980), Nibu et al (1997), Huang et al (1998), and Nibu & Inoue (1998). Diagram (b) is adapted by permission from Springer, Progress in Colloid and Polymer Science **110**:171-174, "Phase behavior of polyoxyethylene dodecyl ether-water systems", Huang et al, Copyright (1998). Diagram (d) is adapted with permission from Kunieda et al, The Journal of Physical Chemistry B, 101: 7952-7957, Copyright (1997) American Chemical Society.

Fig.4 Boundaries for morphological transitions in C_jEO_n surfactants (a) layer-to-cylinder transition ($P = 1$ to $1/2$) (b) cylinder-to-sphere transition ($P = 1/2$ to $1/3$). $C_{18:1}$ denotes an oleyl chain.

Fig.5 Phase diagrams of (a) trisiloxane-EO and (b) poly(dimethylsiloxane)-EO surfactants in water as a function of HLB, n and surfactant concentration at 25 °C. The diagrams are adapted with permission from Kunieda et al, Langmuir, 14:5113-5120, Copyright (1998) American Chemical Society and Kunieda et al, The Journal of Physical Chemistry B, 105:5419-5426, Copyright (2001) American Chemical Society. Si_3 = trisiloxane; Si_{14} = $(CH_3)_3SiO((CH_3)_2SiO)_{12}(CH_3)_2SiCH_2CH_2CH_2$

Figure 6 Phase diagram polyglyceryl didodecanoate $(C_{11})_2G_n$ surfactants in water as a function of HLB, n and surfactant concentration at 25 °C. The diagram is adapted from Journal of Colloid and Interface Science, 245, Kunieda et al "Phase Behavior of Polyglycerol Didodecanoates in Water", pp. 365–370, Copyright (2002) with permission from Elsevier.

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