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# Determination of hydrophile-lipophile balance of some polyethoxylated non-ionic surfactants by reversed-phase thin layer chromatography

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**Abstract**

A study has been carried out to verify the applicability of RP-TLC to the determination of the HLB values of some polyethoxylated non-ionic surfactants. Our results show that adsorption phenomena do not significantly affect retention and that a linear relation exists between the HLB value and the lipophilicity parameter $R_{M_0}$. A deviation from this linear correlation was observed for compounds bearing hydrophilic chains with more than 12–13 ethylene oxide units. These exceptions can be explained in terms of methodological limitations and/or conformational properties. RP-TLC method appears to be a simple, rapid and inexpensive way to rank non-ionic amphiphilic substances.

*Keywords:* Hydrophile-lipophile balance; RP-TLC; Nonionic surfactant

## 1. Introduction

The hydrophile-lipophile balance (HLB) is a valuable parameter for the classification of non-ionic surfactants. HLB can be either calculated starting from the surfactant molecular structure or experimentally determined by the so-called 'emulsion comparison method' (Griffin, 1949). Correlations of the empirical HLB values with physicochemical parameters of the surfactants, including dielectric constants, heats of hydration, critical micelle concentrations and phase inversion temperatures of emulsions have been demonstrated. A recent paper summarized the different parameters correlated with HLB value of surface-active agents (Rabaron et al., 1993). HLB values have also been assessed based on water-oil partition coefficients (Greenwald et al., 1961; Schott, 1971), and recently Hahn and Sucker (1989) found that the retention time determined by HPLC on a reversed-phase ($C_{18}$) column, extrapolated to an eluent water content of 100%, can be considered a good predictor of the HLB value.

As for lipophilicity parameters, water-oil partition coefficients can be determined by the so-called 'shake-flask' technique (Leo et al., 1971).

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However, due to some inherent drawbacks and limitations, other procedures, aiming at determining lipophilicity parameters with better accuracy and precision, have been proposed (Dearden and Bresuen, 1988). Among them, techniques based on reversed-phase high performance liquid chromatography (RP-HPLC) (Braumann, 1986) or reversed-phase thin-layer chromatography (Barbaro et al., 1984), as well as centrifugal partition chromatography (Terada et al., 1987; El Tayar et al., 1991), represent good alternatives to the shake-flask technique. Compared with other chromatographic techniques, RP-TLC is less time-consuming and requires less expensive laboratory equipment.

Since the search for easily measurable parameters which could allow estimation of the HLB of surfactants still represents a goal of interest, we undertook a systematic study of the chromatographic behaviour of a number of non-ionic surfactants by RP-TLC, the first objective being the examination of the correlation between HLB and retention data of amphiphilic substances.

## 2. Materials and methods

Two series of non-ionic surfactants were used, namely: (i) octylphenol and nonylphenol ethoxylates of increasing molar ratios of ethylene oxide (Triton X® and Triton N® series of Rohm and Haas); and (ii) polyethoxyl lauryl, stearyl and oleyl ethers (Brij® of ICI Americas). The surfactants were chosen taking into account the work of Schott (1990), which pointed out that, aside from sorbitan esters and polysorbates, the majority of non-ionic surfactants used in industrial, pharmaceutical, and cosmetic emulsions have the structures of polyethoxylated fatty alcohols and polyethoxylated alkylphenols. All surfactants were used as received. The HLB values of these surfactants were taken from the literature (Griffin, 1974; Rohm and Haas Co., 1986) or, in the case of Brij 721, calculated according to Griffin (1974). All the RP-TLC measurements were made at a constant temperature of 30 ± 1°C by using a chromatographic chamber immersed in a water bath. Nano-Sil-$C_{18}$-100 $UV_{254}$ plates $10 \times 5$ cm (from Aldrich) were used as the non-polar stationary phase. Migration of 8 cm was attained on all the plates by cutting the layer at 10 cm and spotting the compounds on a line 1 cm from the lower edge of the plate. The mobile phases (20 ml) used were mixtures of water-miscible organic solvents, namely, acetone for Triton® and tetrahydrofuran for Brij® series, selected among a variety of solvents tested (methanol, acetone, acetonitrile, dioxane, and tetrahydrofuran). A series of solvent volume ratios was used in which the water content ranged from 0 to 45% at 5–10% intervals. In this range of water concentration the $R_M$ values ($R_M = \log(1/R_f - 1)$) of four selected reference compounds (namely, *o*-nitroanisole, methyl and ethyl benzoate, benzophenone) resulted linearly correlated ($r^2 = 0.899$) with the corresponding log $P$ values. The surfactants were dissolved in $CHCl_3$ (1–2 mg/ml) and 5 $\mu$l of solution was spotted on the plates in random positions in order to avoid systematic error. After development, the plates were dried and introduced in a chamber saturated with iodine vapour; within a few minutes brown spots appeared on an intense yellow background. To take into account also the irregular spots observed, we measured the distance moved by the surfactants from the starting point to the front of the solute zone. For each experiment, at least five independent parallel determinations were carried out. The $R_M$ value at zero organic solvent concentration (i.e., $R_{Mo}$) was obtained by extrapolation, using regression calculation, and compared with HLB value.

## 3. Results and discussion

For the Triton® products the organic constituent of the mobile phase was acetone, whereas for the Brij® products tetrahydrofuran (THF) was found as the organic modifier that more selectively discriminated the examined substances. For each surfactant, retardation factors ($R_f$) at several different acetone (or THF)/water mixtures were experimentally determined. When the surfactant spot remained at the start ($R_f < 0.1$), or was very close to the front ($R_f > 0.9$), or the relative standard deviation of the determina-

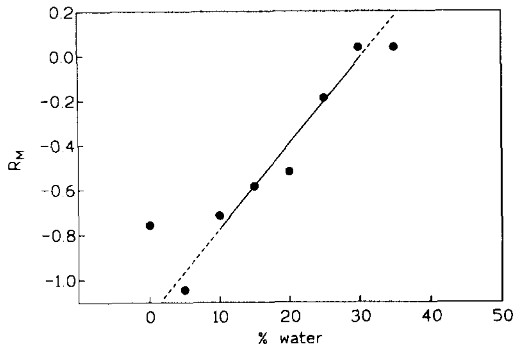


Fig. 1. Dependence of $R_M$ value of TX 405 on the water concentration (vol.%) in the mobile phase.

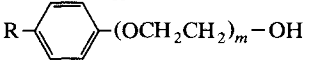
tions was higher than 5%, the data were omitted from calculations. $R_M$ values were plotted against the water content of the mobile phase (see Fig. 1 as an example) and $R_{Mo}$ was calculated from the following linear relationship:

$$R_M = R_{Mo} + b\phi$$

where $b$ is the slope and $\phi$ is the % of organic modifier times $1 \times 10^{-2}$. The parameters of the equation describing the dependence of $R_M$ values on the organic modifier concentration are given in Table 1. All the amphiphilic substances in both groups examined showed a linear decrease in retention with increasing mobile phase ratio (Fig. 1). At high modifier contents (i.e., % water < 5%) the experimental retention data deviated from linearity, likely due to the increasing contribution of adsorptive properties of silica matrix (the so-called 'silanophilic effects') (Bij et al., 1981; Altomare et al., 1993). It has been shown that adsorptive effects, revealable by an incre-

Table 1

Parameters of correlation between the $R_M$ values of surfactants and the organic solvent [a] concentration in the mobile phase on reversed ($C_{18}$) stationary phases



$R-(OCH_2CH_2)_m-OH$

Triton X $R = C_8H_{17}$
Triton N $R = C_9H_{19}$

Brij 92, 96, 99: $R = C_{18}H_{35}$
Brij 72, 76, 78, 721: $R = C_{18}H_{37}$
Brij 30: $R = C_{12}H_{23}$

| Surfactant | $m$ | HLB | $R_{Mo}$ | $b$ | $n$ [b] | $r^2$ |
|---|---|---|---|---|---|---|
| Triton® series | | | | | | |
| TX15 | 1 | 3.6 | 4.33 | −5.59 | 4 | 0.966 |
| TX35 | 3 | 7.8 | 4.06 | −5.26 | 4 | 0.997 |
| TX45 | 5 | 10.4 | 3.90 | −5.10 | 4 | 0.998 |
| TX114 | 7– 8 | 12.4 | 3.60 | −4.77 | 4 | 0.999 |
| TX100 | 9–10 | 13.5 | 3.62 | −4.84 | 4 | 0.998 |
| TX102 | 12–13 | 14.6 | 3.57 | −4.79 | 8 | 0.991 |
| TX165 | 16 | 15.8 | 3.85 | −5.22 | 4 | 0.995 |
| TX405 | 40 | 17.9 | 2.61 | −3.76 | 7 | 0.964 |
| TN42 | 4 | 9.1 | 3.90 | −5.08 | 4 | 0.999 |
| TN57 | 5 | 10.0 | 3.74 | −4.93 | 4 | 0.998 |
| TN60 | 6 | 10.9 | 3.71 | −4.90 | 4 | 0.988 |
| Brij® series | | | | | | |
| Brij 92 | 2 | 4.9 | 3.03 | −4.39 | 4 | 0.929 |
| Brij 96 | 10 | 12.4 | 2.25 | −3.40 | 4 | 0.988 |
| Brij 99 | 20 | 15.3 | 2.01 | −3.34 | 4 | 0.961 |
| Brij 72 | 2 | 4.9 | 2.93 | −4.50 | 4 | 0.954 |
| Brij 30 | 4 | 9.7 | 2.19 | −3.61 | 4 | 0.968 |
| Brij 76 | 10 | 12.4 | 2.09 | −3.21 | 4 | 0.954 |
| Brij 78 | 20 | 15.3 | 2.18 | −3.32 | 6 | 0.967 |
| Brij 721 | 21 | 15.5 | 1.39 | −2.47 | 4 | 0.950 |

[a] Acetone and THF for Triton® and Brij® series, respectively.

[b] $n$, number of data points within the observed range of linearity.

ment of $R_M$ with increasing organic solvent concentration, can occur in reversed-phase chromatography, especially in the case of solutes bearing polar groups (Braumann, 1986; Altomare et al., 1989; Cserhati, 1992). Our results indicated that, within the compositions of the mobile phases used for reliably measuring $R_M$ values of most of the surfactants examined ($5 \leq \%$ water $\leq 30$), retention was not significantly affected by adsorptive side-effects due to free silanol groups.

The existence of a high degree of correlation between $b$ and $R_{Mo}$ values in Table 1 ($r^2 = 0.986$ and 0.964 for Triton® and Brij® sets, respectively) indicated that both of the chromatographic parameters should possess a similar information content and, hence, have a similar influence on the lipophilicity of the examined surfactants.

Plots of $R_{Mo}$ values, measured in this study by RP-TLC, vs HLB values show that the two sets of parameters are fairly well correlated. Exceptions to the linear relationship between $R_{Mo}$ and HLB values for Triton® products are represented by surfactants (Triton® X-165 and X-405) having HLB values higher than 15.3. Excluding them from the regression analysis, the following linear equation was derived:

$$R_{Mo} = -0.07(\pm 0.01)\mathrm{HLB} + 4.58(\pm 0.08)$$

$$n = 9 \quad r^2 = 0.982 \quad s = 0.071$$

which allows one to estimate the HLB value from readily measurable $R_M$ values. The two exceptions reported above could be rationalized in terms of methodological limitations and/or in terms of conformational factors. As for the methodological limitations, increasing hydrophilicity of substances decreases retention on RP stationary phases and, consequently, extrapolation to 100% water could be affected by greater uncertainty. We believe that this greater uncertainty in the $R_{Mo}$ value might lead to a loss of reliability of the RP-TLC method in the HLB assessment of the most hydrophilic substances.

In addition, it cannot be ruled out that changes in the conformational behaviour of surfactants having more than 12–13 ethylene oxide units ($m$ in Table 1) may determine significant changes in their chromatographic behaviour. Rowe (1992) invoked significant changes in chain conformation (i.e., coiling of the longer chains (Rosch, 1966)), occurring in solution for substances bearing hydrophilic chains with more than 10 ethylene oxide units, to explain the results from calorimetric studies. The deviation from the linear correlation between HLB and $R_{Mo}$ observed for Triton® X-165 and X-405 ($m = 16$ and 40, respectively) may be due to changes in their conformational behaviour. This point needs further investigations.

Even though the Brij® data points are limited in number and not regularly spanned, a certain degree of correlation between the chromatographic parameters $R_{Mo}$ and HLB values was exhibited by the examined products. Excluding from the regression analysis the compounds with the highest HLB values (15.3), the following linear equation was derived:

$$R_{Mo} = -0.11(\pm 0.02)\mathrm{HLB} + 3.49(\pm 0.20)$$

$$n = 5 \quad r^2 = 0.904 \quad s = 0.159$$

Once again, the uncertainty of the extrapolation to $R_{Mo}$, as well as changes in the conformational behaviour, for the compounds with the longest ethylene oxide chains could explain the large deviation from linearity of Brij® 78 (HLB = 15.3; $m = 20$) and Brij® 721 (HLB = 15.5; $m = 21$).

## 4. Conclusion

The main conclusion emerging from the correlation analysis presented in this paper is that $R_{Mo}$ values could be useful parameters to assess HLB values of non-ionic surfactants. The most critical point is the choice of the range of organic modifier concentrations to be used in obtaining $R_M$ values from which $R_{Mo}$ is calculated. For the two classes of non-ionic surfactants (Triton® and Brij®) examined, our results demonstrated that the linear relationship between $R_M$ values and the appropriate organic modifier concentration holds fairly well up to high organic solvent concentrations (80–95%).

Provided that an inverse linear correlation between $R_M$ and organic solvent concentration in the mobile phase demonstrates that adsorption phenomena do not significantly affect retention, RP-TLC can be used as simple, rapid and inexpensive method to assess the hydrophile-lipophile balance of amphiphilic substances.

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