COLLOIDS
AND
SURFACES

A

Hydrophile–lipophile balance and solubility parameter of cationic surfactants

Z.E. Proverbio [a], S.M. Bardavid [b], E.L. Arancibia [b], P.C. Schulz [a],*

[a] *Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, (8000) Bahía Blanca, Argentina*
[b] *Departamento de Química, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán, Av. Independencia 1800, (4000) San Miguel de Tucumán, Argentina*

Abstract

By using hydrophile–lipophile balance (HLB) values of cationic surfactants obtained from literature, two methods to determine this property were tested to verify if they are applicable to such amphiphiles: Little's method with the surfactant solubility parameter (δ) and the water number of Greenwald et al., related to their ability to promote inversion of emulsions. Cationic surfactants did not follow the behaviour of anionic and non-ionic surfactants. Little's method gave non-realistic values of HLB for cationic surfactants, whereas the Greenwald et al. treatment gave a non-linear relationship. However, both δ and water numbers are related with the HLB values, but these relations are different from those for anionic and non-ionic surfactants. This is not surprising on dealing with water number (anionic and non-ionic surfactants follow different equations in the paper of Greenwald et al.), but in the case of δ, Little has shown that both, anionic and non-ionic surfactants, follow the same equation. The solubility parameters of dodecyltrimethylammonium and dioctadecyldimethymammonium bromides, and the HLB value of dodecylpyridinium chloride are reported.
© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the most important properties of surface-active agents is their hydrophile–lipophile balance (HLB). Since the concept of HLB number was introduced by Griffin[1,2] as a measure of the polar character of surfactants, many workers have attempted to develop a rapid and reproducible technique to determine experimentally the HLB of any new surfactant. Many investigators, attempting to relate HLB to various properties of surfactant molecules and to further develop methods of measurement of this number, have done much work [3–10]. HLB values of emulsifiers were originally obtained by a time-consuming and laborious determination of emulsion stability, the original method of Griffin [1].

---

* Corresponding author. Tel.: +54-291-4528-034; fax: +54-291-4561-447

E-mail address: pschulz@criba.edu.ar (P.C. Schulz).

There is little information about HLB values for cationic surfactants in the literature. The HLB values of surfactants are related to several other properties such as the cmc, the solubility parameter (δ) and their ability to promote inversion of emulsions. In spite of the several methods to determine the HLB value (e.g. see the list given by Becher [11]), in general it is difficult to determine this property by direct methods. Some indirect, simpler methods need calibration with surfactants having known HLB values. As an example, Becher and Birkmeier [12] developed a simplified chromatographic method to measure the polarity of the substrate (the surfactant) by injection of a test mixture of a polar and a non-polar solvent. One of the most useful mixtures is an equal-volume mixture of ethanol and hexane. The polarity ρ of the surface-active substrate is defined in terms of the ratio of the retention time for ethanol ($t_{R,EtOH}$) and that for hexane ($t_{R,Hex}$), $\rho = t_{R,EtOH}/t_{R,Hex}$. For a number of non-ionic surfactants, there is a linear relationship between the HLB and the polarity.

On the basis of the Davies HLB numbers obtained by O [13] for cationic surfactants, we intended to relate HLB to δ following Little's method [14], and with the water number of Greenwald et al. [15] procedure.

2. Experimental

The employed surfactants were analytical grade decyltrimethylammonum bromide (DTAB); dodecyltrimethylammonium bromide (LTAB); didodecyldimethylammonium bromide (DDAB); dioctadecyldimethylammonium bromide (DODAB); hexadecyltrimethylammonium tosilate (CTATOS) and dodecylpyridinium chloride (LPC). All of them were used as received from Sigma.

The Greenwald et al. method [15] modified by Olano and Martínez [16] was employed to determine the water number of each surfactant. 0.166 g of each surfactant was dissolved in 5 ml of 4 % v/v of benzene in dioxane mixture contained in a 25 ml Erlenmeyer flask. Then the stirred solution was titrated with double-distilled water from a micro-burette until a persistent turbidity was obtained. The amount of water added at this point is known as the 'water number' (WN). Greenwald et al. [15] gave a figure with the linear relationships between HLB and WN for 18 surface active in two families of polyhydric alcohol esters: ethylene oxide adducts and those without ethylene oxide. From that figure, we obtained the following equations, in which the WN have been translated to the values obtained with the modification of Olano and Martínez [16].

For ethylene oxide adducts:

$$HLB = 9.58WN - 3.43$$

For adducts without ethylene oxide:

$$HLB = 7.10WN + 2.81$$

Three runs were made with each surfactant. First, we have employed the method with anionic and non-ionic surfactants and we have found the same linear relationships between HLB and WN values obtained by Greenwald et al. Then, the cationic surfactants were studied with the same method. All experiments were performed at 25 °C.

To determine the solubility parameter (δ) we used gas–liquid chromatography. The studied surfactants (DDAB and DODAB) were used as stationary phase and they were deposited on Chromosorb W, NAW, 60/80, which was employed as solid support. The column filler was prepared in a rotary evaporator under a flow of dry nitrogen and was kept in a dry atmosphere before filling the columns (inoxidizable steel pipes). The solubility parameter were obtained using a column of 100 cm long, 1/4 inch external diameter, charged with DDAB containing 7.9285 g of filler with 9.04 % surfactant. That of DODAB had 7.3291 g of filler having 9.00 % of stationary phase. The measurement of retention time for each solute was performed with a Perkin Elmer, Sigma 300 gas chromatograph having a thermal conductivity detector and employing hydrogen as carrier gas. Solutes were injected with a micrometric syringe as vapours in equilibrium with pure liquid. A bubble flow meter was employed at the detector exit. The employed solutes were *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohex-

ane, benzene, toluene, and ethyl acetate. Experiments were performed within a temperature range from 80 to 120 °C.

The specific retention volume V_g° for each solute was computed by [17]:

$$V_g^\circ = j(F_f/w)(273.15/T_f)(t_R - t_0)(p_0 - p_w)/p_0 \quad (1)$$

where

$$j = (2/3)\frac{[(p_i/p_0)^3 - 1]}{[(p_i/p_0)^2 - 1]} \quad (2)$$

p_i and p_0 are the pressure at the column entry and exit (the latest is the atmospheric pressure); F_f is the average flow at p_0 and the temperature T_f (in K) in the flow meter. The mass of stationary phase in the column is w, and p_w is the vapour pressure of water at T_f. The dead time t_0 was computed from the air peak obtained from the thermal conductivity detector.

The Scatchard and Hildebrand [18] solute–solvent interaction parameter $\chi_{1,2}^\infty$ is then computed by:

$$\chi_{1,2}^\infty = \ln[273.15R/p_1^0 V_g^\circ M_1] - p_1^0(B_{11} - v_1^0)/RT \quad (3)$$

where p_1^0, v_1^0 and M_1 are the vapour pressure, molar volume and molar weight of the solute (e.g. n-hexane, n-heptane, etc.) and B_{11} is the second virial coefficient for solute-solute interactions. R is the gas constant and T the absolute temperature. The vapour pressures were computed by Antoine's equation using the coefficients from Riddik et al. [19]. We used literature densities for the solvents [20]. The effect of the solute molar volume to solvent molar volume ratio was not taken into account.

To obtain the surfactant solubility parameter (δ_2) we employed the Di Paola-Baranyi et al. [21,22] procedure, who used the Scatchard and Hildebrand [18] solute–solvent interaction parameter $\chi_{1,2}^\infty$ to determine the solubility parameter of non−volatile substances:

$$\chi_{1,2}^\infty = \frac{v_1^0(\delta_1 - \delta_2)^2}{RT} + \chi_S^\infty \quad (4)$$

where δ_1 and δ_2 are the solubility parameters of solute and solvent (i.e. the surfactant), χ_S^∞ is the entropy factor of the interaction parameter. By

division by v_1^0 and rearranging:

$$\delta_1^2/RT - \chi_{1,2}^\infty/v_1^0$$
$$= (2\delta_2/RT)\delta_1 - (\delta_2^2/RT + \chi_S^\infty/v_1^0) \quad (5)$$

By plotting $[\delta_1^2/RT - \chi_{1,2}^\infty/v_1^0]$ as a function of the solvent solubility parameter δ_1 the surfactant solubility parameter δ_2 may be obtained from the slope. The solubility parameter is expressed in (cal ml^{-1})$^{1/2}$, a dimension originated in the definition of the solubility parameter as $\delta = (\Delta E^V/V)^{1/2}$, $\Delta E^V/V$ being the condensation energy per unit volume [23].

The Student t function was employed to compute the error intervals. Confidence level was 0.90.

3. Theory

In literature [24,25] it is shown that HLB is of the nature of free energy, essentially the free energy involved in the assembly of surfactant molecules, whether in micelles or in macro- or microemulsions. In particular, HLB may be written:

$$HLB = C_1 + \frac{C_2 \Delta G_{m,l}}{RT} + \frac{C_2 \Delta G_{m,h}}{RT} \quad (6)$$

where $\Delta G_{m,l}$ and $\Delta G_{m,h}$ are the free energy of micellisation associated with the lipophilic and the hydrophilic moieties. C_1 and C_2 are simply scaling factors.

In its original form, as devised by Griffin [1,2], the HLB value was a relative effectivity index, ranging from 0 to 20. A practical drawback of the HLB index as defined by Griffin is its limitation to non-ionic types (or natures) of surfactants. Griffin's method does not allow for indexing ionic surfactants [13]. In the system proposed by Davies [26,27] this limitation was eliminated. Davies [26,27] proposed a method to compute the HLB based on the surfactant structure by assigning group numbers (GN) to various structural elements and combining them according to the equation:

$$HLB_D = 7 + \Sigma\, GN \quad (7)$$

The formal agreement between Eqs. (6) and (7)

is obvious. Davies [26] has shown that the agreement between HLB numbers calculated using the above equation and those determined experimentally is quite satisfactory. Davies' method is, however, different to Griffin's in principle. It ranks surfactants by their effective polarity.

Davies' method reproduces Griffin's HLB values for sorbitan esters and ethoxylated sorbitan esthers almost quantitatively; however, the two methods substantially disagree for ethoxylated alcohols and alkylphenols. In particular, if the lipophilic contribution is large enough, Davies' equation can give negative HLB values. This contrasts with Griffin's values, which always lie between 0 and 20 [28,29]. In spite of these inconsistencies, the Davies method is widely used in emulsion technology, and the determination of GN is of practical interest [13,30].

Davies gave the GN for several chemical hydrophobic and hydrophilic groups. But the hydrophilic groups were only anionic and non-ionic, and the hydrophobic groups, hydrocarbon ones. O [13] published some GN for anionic and cationic hydrophilic groups. The O GN values are 22.5 for $> N^+(CH_3)_2Cl^-$ and 22.0 for $- N^+(CH_3)_3Cl^-$. For methyl and methylene groups, $GN = -0.475$ [24,25]. Lin [31] gave GN values for fluorocarbon hydrophobic groups.

Little [14] proposed the following relationship between the solubility parameter and the HLB value, which was tested with anionic and non-ionic surfactants:

$$HLB = \frac{54(\delta - 8.2)}{(\delta - 6.0)} \qquad (8)$$

4. Results

From the chromatographic experiments we obtained $\delta_{DDAB} = 6.8 \pm 0.5$ (cal ml^{-1})$^{1/2}$ (variation coefficient 7.1 %) and $\delta_{DODAB} = 7.1 \pm 0.6$ (cal ml^{-1})$^{1/2}$ (variation coefficient 8.4 %) at 100 °C. From measurements at different temperatures, we found that δ_{DDAB} (cal ml^{-1})$^{1/2} = 8.2563 - 0.0143t$ (°C), and δ_{DDAB} (cal ml^{-1})$^{1/2} = 12.8515 - 0.0510t$

(°C). This gave $\delta_{DDAB} = 7.9 \pm 0.5$ (cal ml^{-1})$^{1/2}$ and $\delta_{DODAB} = 11.6 \pm 0.6$ (cal ml^{-1})$^{1/2}$ at 25 °C. Using Eq. (8), we found $HLB_{DDAB} = -6.00 \pm 0.05$ and $HLB_{DODAB} = 33 \pm 3$. These results show that Eq. (8) is not applicable to cationic surfactants, because a negative HLB value has not sense, and HLB_{DDAB} ought to be larger than HLB_{DODAB}. Moreover, the HLB values computed with Eq. (7) were $HLB_{DDAB} = 18.1$ and $HLB_{DODAB} = 12.4$ (we neglected the difference between chloride and bromide counterions).

The water titration method gave the water numbers shown in Table 1 together with the Davies HLB numbers computed with Eq. (7) and the GN from Davies [24,25] for the hydrophobic groups and O [11] for the cationic ones (we neglected the difference between chloride and bromide counterions). The data were also plotted in Fig. 1. This figure shows that the HLB–WN relationship is not linear for cationic surfactants. This is a difference when compared with the behaviour of anionic and non-ionic surfactants, which showed linear relationships, although different for each amphiphile kind [15]. Using the WN of dodecylpyridinium chloride and Fig. 1, we estimated $HLB_{LPC} = 16.4$, which gave $GM = 15.1$ for the pyridinium chloride headgroup. However, we could not determine the hexadecyltrimethylammonium tosilate HLB number, because its WN value fell out of the explored range for surfactants having known HLB values.

Table 1
Water number and HLB values computed by the Davies and Rideal procedure

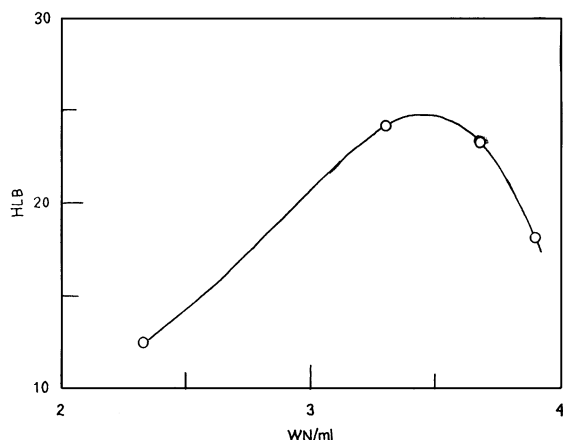| Surfactant	HLB$_{DR}$	WN (ml)
CTATOS		5.370
DDAB	18.1	3.900
LTAB	23.3	3.678
DTAB	24.25	3.300
LPC		2.733
DODAB	12.4	2.330

Fig. 1. The HLB–water number relationship for cationic surfactants.

5. Concluding remarks

The Little HLB–solubility parameter relationship, which holds for anionic and non-ionic surfactants, is not with cationic ones.

The Greenwald et al. titration method gave a non-linear water number–HLB relationship, which is different to those for anionic and non-ionic surfactants.

The dodecylpyridinium chloride HLB was estimated as 16.4, and the Davies and Rideal pyridinium chloride group number as 15.1.

Acknowledgements

References

[1] W.C. Griffin, J. Soc. Cosmet. Chem. 1 (1949) 311.
[2] W.C. Griffin, J. Soc. Cosmet. Chem. 5 (1954) 4.
[3] E. Nakache, N. Poulain, 2nd World Congress on Emulsion (23–26 September, 1997), Congress Proc. Bordeaux, France, vol. 1, 1997, p. 249.
[4] H. Kunieda, J. Colloid Interface Sci. 114 (1986) 378.
[5] G. Urbina-Villalba, E. Rogel, M.L. Márquez, I. Reif, J. Comput.-Aided Mol. Des. 8 (1994) 273.
[6] M. Balcan, D.F. Anghel, A. Voicu, M. Cornilescu, Rev. Roumaine Chim. 44 (4) (1999) 369.
[7] S. Yamaguchi, H. Kunieda, Langmuir 13 (1997) 6995.
[8] M. Iida, H. Er, N. Hisamatsu, T. Tanase, Chem. Lett. 2000 (2000) 518.
[9] X. Barril, J. Muñoz, F.J. Luque, M. Orozco, Phys. Chem. Chem. Phys. 2 (2000) 4897.
[10] P. Becherin, P. Becher (Eds.), Encyclopedia of Emulsion Technology, Marcel Dekker, New York and Basel, Ch. 8, vol. 2, pp. 425–521 and vol. 3, Appendix, pp. 397–437, 1988.
[11] P. Becher, in: K.L. Mittal, B. Lindman (Eds.), Surfactants in Solution, vol. 3, Plenum Press, New York, 1984, p. 1927.
[12] P. Becher, R.L. Bierkmeier, J. Am. Oil Chem. Soc. 41 (1964) 169.
[13] B.H. O, J. Colloid Interface Sci. 198 (1998) 249.
[14] R.C. Little, J. Colloid Interface Sci. 65 (1978) 587.
[15] H.L. Greenwald, G.L. Brown, M.N. Fineman, Anal. Chem. 28 (1956) 1963.
[16] A. Olano, M. Martínez, Tenside Detergents 12 (1973) 334.
[17] R.C. Castells, G.D. Mazza, E.L. Arancibia, An. Asoc. Quím. Argentina 73 (1985) 519.
[18] J.H. Hildebrand, R.L. Scott, The Solubility of Nonelectrolytes, 3rd ed., Reinhold, New York, 1950.
[19] A.R. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents. Techniques of Chemistry, 4th ed., Wiley–Interscience, New York, 1986.
[20] R.R. Dreisbach, Advances Chemistry Series, vol. 15, ACS, Washington, DC, 1955.
[21] G. Di Paola-Baranyi, J.M. Braun, J.E. Guillet, Macromolecules 11 (1978) 224.
[22] G. Di Paola-Baranyi, J.E. Guillet, Macromolecules 11 (1978) 228.
[23] K. Shinoda, Principles of Solution and Solubility, Marcel Dekker, New York, 1978, p. 64.
[24] P. Becher, Proceedings of the International Symposium on Surfactants Solutions, Lund, Plenum, New York, 1982, p. 1984.
[25] P. Becher, J. Dispersion Sci. Technol. 5 (1) (1984) 81.
[26] T. Davies, Proc. Int. Congr. Surface Activ. Lond. 1 (1957) 426.
[27] J.T. Davies, E.K. Rideal, Interfacial Phenomena, Academic Press, New York, 1961.
[28] B.W. Davis, in: P. Bacher (Ed.), Encyclopedia of Emulsion Technology, Ch. 3, vol. 3, Marcel Dekker, New York, 1988, p. 364.
[29] H. Kunieda, Y. Sato, in: S.E. Friberg, B. Lindman (Eds.), Organized Solutions, Ch. 6, Marcel Dekker, New York, 1992, p. 69.
[30] R. Sowada, J.C. McGowan, Tenside Surfactants Deterg. 29 (1992) 109.