

Available online at www.sciencedirect.com





Colloids and Surfaces A: Physicochem. Eng. Aspects 316 (2008) 131-135

www.elsevier.com/locate/colsurfa

Hydrophile–lipophile balance (HLB) of *n*-alkane phosphonic acids and theirs salts

Valeria Verdinelli^a, Paula V. Messina^{a,*}, Pablo C. Schulz^a, Bruno Vuano^b

^a Departamento de Química, Universidad Nacional del Sur, 8000 Bahía Blanca, Argentina ^b Universidad Tecnológica Nacional, Facultad Regional Bahía Blanca, Argentina

Received 25 May 2007; received in revised form 17 August 2007; accepted 23 August 2007 Available online 30 August 2007

Abstract

As a previous step in their application as emulsifiers, here we performed a study of the hydrophile–lipophile balance (HLB) properties of decyl $(C_{10}H_{21}PO_{3}H_{2})$, dodecyl $(C_{12}H_{25}PO_{3}H_{2})$, tridecyl $(C_{13}H_{27}PO_{3}H_{2})$ phosphonic acids and their mono and disodic salts. Two different methods (Griffin and Greenwald et al. methods) were applied. The HLB values along with the –PO₃H₂; –PO₃HNa and PO₃Na₂ HLB group numbers found by Greenwald et al. method were comparable to those obtained for similar structure surfactants. The HLB computed by Griffin emulsion technique strongly depends on the nature of the emulsifier mixture compounds, and was shown inappropriate to study this kind of surfactants. This fact is interpreted because of the hydrocarbon/water structure.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrophile-lipophile balance (HLB); Greenwald et al. method; Phosphonic acids; Griffin method

1. Introduction

Emulsions formed with two immiscible liquids usually require the presence of an emulsifier, if stability must be attained. Singly or in combination, hundreds of surface-active agents are available and may potentially aid emulsion formation and stability. Although this variety contributes flexibility, certain principles of selection are needed, if the task of choosing an emulsifier is to be rendered manageable.

Selection of the best surfactant for the stabilization of a particular emulsion is largely a trial and error process aided by classificatory schemes such as the empirical hydrophile–lipophile balance, which is commonly used to express the relative degrees of hydrophilic and lipophilic character possessed by respectively hydrophilic and lipophilic parts of a surfactant molecule.

The need to classify emulsifiers according to their emulsionstabilizing (O/W or W/O) qualities led Griffin [1] to introduce a quantitative but empirical basis for the HLB. A systematic ranking of emulsifiers and of oil with respect to the

0927-7757/\$ – see front matter @ 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.colsurfa.2007.08.040

hydrophile–liphophile balance was undertaken by comparing the type and the stability of an emulsion formed by emulsification of a series of oils in the presence of the surface active agent. The scale chose ranged from 1 (hydrophobic material) to 40 (hydrophilic). Approximately 75 emulsions were made for the determination of each HLB number. The HLB computed by Griffin emulsion technique depended so much on the nature of the emulsifier mixture compounds, implying a change in the oil–water interface structure due to the presence of surfactant of dissimilar structures and demonstrating that such method is only applicable to non-ionic amphiphiles.

Because knowledge of the emulsification properties of different surfactants is of paramount importance in the industry of emulsions, the determination of these properties (such as HLB) in new possible emulsifiers are highly desirable.

Here we present a study of the hydrophile–lipophile balance (HLB) properties of the decyl phosphonic acids and their mono and disodic salts; as a previous step in their application as emulsifiers.

Hence, our aim in this article is to build upon the knowledge in this area in several ways. On one hand $C_{10}H_{21}PO_3H_2$, $C_{12}H_{25}PO_3H_2$ and $C_{13}H_{27}PO_3H_2$ hydrophile–lipophile character was determined by two different methods and the $-PO_3H_2$; $-PO_3HNa$ and PO_3Na_2 HLB group numbers, which

^{*} Corresponding author. Tel.: +54 291 4551447; fax: +54 291 4551447. *E-mail address:* pau423ve@yahoo.com.ar (P.V. Messina).

are unknown until now, were estimated by the employment of Davies and Rideal equation. Furthermore we compared the Griffin method with others applied in the HLB determination, like the proposed by Greenwald, Brown and Fireman. These authors design a solubility scale capable of ranking emulsifiers and oils in a manner commensurable with the matching that results from emulsification experiments.

Phosphonic amphiphiles derivate from *n*-alkane phosphonic acids are diprotic substances from which a variety of properties originated from their neutralizing degree (their polar head group charge can be varied from about zero, acting as a quasi-nonionic surfactant, to -2 [2]) can be obtained. These facts would favor their use in practical or theoretical applications. We are especially thinking in emulsions destined to the ambient due to their harmless. In particular, it is interesting their possible use in petroleum emulsions.

2. Materials and methods

2.1. Materials

All reagents were 99% pure and used as received. Phosphonic acids $C_{10}H_{21}PO_3H_2$, $C_{12}H_{25}PO_3H_2$, $C_{13}H_{27}PO_3H_2$ and their salts $C_{10}H_{21}PO_3HNa$, $C_{12}H_{25}PO_3HNa$, $C_{13}H_{27}PO_3HNa$, $C_{10}H_{21}PO_3Na_2$, $C_{12}H_{25}PO_3Na_2$, $C_{13}H_{27}PO_3Na_2$ were synthesized in our laboratory by Roos & Toet and Kossolapoff [3] methods. The obtained product was recrystalized four times in petroleum ether (Cicarelli Laboratories, 60–80 °C) until constant melting point was reached.

2.2. Methods

The hydrophile–lipophile balance (HLB) values were determined by the application of two different methods.

2.2.1. Greenwald, Brown and Fireman method [4]

As the HLB of an oil or emulsifier appear to be related to the solubility characteristics, an index of these was sought. Samples of 1 g of emulsifier were accurately weighed into 125 ml Erlenmeyer flasks and 30 ml of solvent (4% (v/v), benzene (Cicarelli) in dioxane (Cicarelli)) was added to dissolve the sample. To ensure the dissolution, the samples were sonicated in a laboratory ultrasound generator (MADA no. 6000). This clean solution was titrated with double-distilled water from a burette until the first persistent turbidity was obtained. The volume of added water up to the end point is called the water index. Using this procedure, a calibration curve (Fig. 1) was plotted by using oleic acid (Raudo, HLB = 1.0) [5], sodium oleate (PROLABO, HLB = 18 [5], and sodium oleate with sodium docecyl sulfate (Mallinckrodt, HLB = 40) [5] mixtures [6]. To obtain the intermediate HLB values, mixtures of these surfactants were used and the following equation was employed:

$$HLB_{mix} = w_A HLB_A + w_B HLB_B, \quad w_A + w_B = 1 g$$
(1)

where HLB_{mix} , HLB_A , and HLB_B are the HLB value for the mixture, surfactant A and the surfactant B (the weights of the



Fig. 1. Greenwald et al. method calibration curve. Water number vs. HLB values obtained from Eq. (1) using oleic acid–sodium oleate and sodium oleate–docecyl sulfate mixtures.

Table I				
Change in w	ater titration	values for the	different HLB	systems

HLB ^a	Sodium oleate (g)	Oleic acid (g)	SDS (g)	HLB ^b	Water number (mL)
1	0	1.0033	0	1.0033	11.2
4	0.1767	0.8231	0	4.0037	12.9
6	0.2941	0.7061	0	5.9999	14.2
8	0.4118	0.5882	0	8.0006	15.7
10	0.5294	0.4718	0	10.001	17.7
12	0.6471	0.3529	0	12.0007	20.9
16	0.8825	0.1174	0	16.0024	34.0
18	1.0007	0	0	18.0126	41.2
20	0.9090		0.0906	19.986	55.9

^a Theoretical HLB system value.

^b Calculated HLB system value in accordance with the weighted quantities of surfactants (Eq. (1)).

last two in the mixture are w_A and w_B). The different mixtures were then treated as described above to obtain the respective water index, and then the HLB values were plotted as a function of the water index to obtain a calibration curve.

A range of 1–26 HLB values were tested and summarized in Table 1. The phosphonic acids and their salts were then tested following the same procedure.

2.2.2. Griffin method [1]

First the required HLB value of petroleum ether (60–80 °C) was determined. For this, different petroleum ether/water emulsions were prepared using an emulsifier mixture that HLB was equal to 14.0 (the approximately required HLB value expected for petroleum ether O/W emulsions according to literature [7]). This was made to determine the appropriate concentration of emulsifier. The emulsifiers used were mixtures of Tween 20 (PROLABO, HLB = 16.7) and Span 20 (Importadora Técnica Industrial S.R.L., HLB = 8.6). Emulsions with 0%, 0.01%, 0.05%, 0.1%, 0.2%, 0.3%, and 0.4% content of emulsifier mixtures were prepared. The emulsions were prepared in graduate tubes of 100 ml, adding $(100/m_e)/2$ g of water and an equal mass

of petroleum ether in which m_e gram of emulsifier mixture were dissolved. The tubes were plugged and shaken twice by hand (immediately they were prepared and 10 min later). The separated water phase volumes were measured at 24 h. As it was mentioned above, petroleum ether/water emulsions were prepared using emulsifier mixtures of HLB values from 12.5 to 16.7. The percentage of emulsifier mixtures was the previously determined. The weight percent (wt%) of Tween 20 in the emulsifier mixture for a certain HLB value were calculated as follows

Tween 20 (wt%) =
$$\left(\frac{\text{HLB} - \text{HLB}_{\text{Span 20}}}{\text{HLB}_{\text{Tween 20}} - \text{HLB}_{\text{Span 20}}}\right) \times 100$$
 (2)

To determine the HLB values of phosphonic acids and their salts, it was followed the same protocol but Span 20 or Tween 20 (depending of the prepared emulsifier mixture) was replaced conveniently. Other surfactants used were Span 80 (Importadora Técnica Industrial S.R.L., HLB = 4.7), oleic acid, sodium oleate, and dodecanoic acid (Asay Alfa Aear, HLB = 3.8).

The HLB value was calculated by the following equation:

$$\text{HLB}_{\text{ac}} = \frac{\text{HLB}_{\text{ether}} - \text{HLB}_{\text{S}} f_{\text{T}}}{1 - f_{\text{T}}} \tag{3}$$

where $\text{HLB}_{\text{ether}}$ is the obtained required HLB value of petroleum ether, f_{T} the weight fraction of phosphonic acid or salt in emulsifier mixture which provide the minimum or maximum water phase volume separation, and HLB_{S} is the HLB of the surfactant employed in the emulsified mixture.

3. Results and discussion

3.1. HLB values by Greenwald et al. method

Fig. 2 shows the HLB values computed by the water index method vs. surfactant chain length. It can be seen that HLB value augmented with the neutralization degree and diminished with the increment of the number of C atoms in the analogue series, as expected. The HLB value is dependent on the relative tendency of surfactant molecules to transfer them from an aqueous



Fig. 2. HLB values computed by the water index method vs. surfactant chain length.

Table 2

Separated aqueous phase volume from petroleum ether/water emulsions containing different proportions of an emulsifier mixture of Tween 20 and Span 20

% emulsifier mixture (Tween 20–Span 20) (HLB = 14)	Separated volume (mL)		
0	50		
0.01	19		
0.05	18		
0.10	14		
0.20	0		
0.30	0		
0.40	0		

environment to a hydrocarbon environment and vice versa. This is quantified in Davies equation [8]:

$$HLB = \sum (\text{group number}) + 7 \tag{4}$$

which for straight chain hydrocarbon surfactants with *n* equal to the number of methylene groups in the chain become [9]:

HLB =
$$\sum$$
(hydrophilic group number) - $\left(\frac{\phi' n}{2.303kT}\right)$ + 7
(5)

where ϕ' is the free energy change involved in the transfer of an aliphatic –CH₂-group from an aqueous to a hydrocarbon phase ($\phi' = 1.09kT[10]$), *k* the Boltzmann constant and *T* is the absolute temperature. For a given homologous surfactant series the HLB number decreases as the number of carbon atoms in the chain increases. For a homologous series of surfactants, ϕ' is almost independent on chain length [10].

Eq. (5) has a fundamental significance in terms of free energy of micellization and its validity has been tested for anionic and cationic straight chain surfactants [10]. By the employ of this equation the $-PO_3H_2$; $-PO_3HNa$ and PO_3Na_2 HLB group numbers were calculated as 13.27 ± 0.04 , 14.53 ± 0.96 , 16.39 ± 0.16 , respectively. The PO_3Na_2 HLB group numbers was in accordance with the computed in a previous work [11] for a related surfactant (sodium dioctylphosphinate, $(C_8H_{17})_2PO_2Na_2$).

3.2. HLB values according to Griffin method

The measured aqueous separated phase volumes from petroleum ether/water emulsions containing different proportions of an emulsifier mixture of Tween 20 and Span 20 are summarized in Table 2. Such values indicated that the adequate emulsifier mixture weight proportion for obtaining the required HLB_{ether} by Griffin method was of 0.1%.

Fig. 3 shows separated water phase volumes from ether/water emulsions stabilized by 0.1 wt% of different HLB emulsifier mixtures. A second-order polynomial analysis of such plot was used and the required HLB_{ether} was found from the maximum of the derived regression function. The obtained value was 13.9 ± 0.2 in accordance with literature [7].

Figs. 4-6 represent the separated water volume from ether/water emulsion as a function of the surfactant wt%



Fig. 3. Separated water phase volumes from ether/water emulsions stabilized with 0.1 wt% of different HLB emulsifier mixtures. The curve corresponds to the second-order polynomial fitting.



Fig. 4. Variation of separated water volume from ether/water emulsion vs. dodecanoic wt% present in a $C_{10}H_{23}PO_3$, dodecanoic acid emulsifier mixture.



Fig. 5. Variation of separated water volume from ether/water emulsion vs. sodium oleate wt% present in a $C_{10}H_{21}PO_3HNa$, sodium oleate emulsifier mixture.



Fig. 6. Variation of separated water volume from ether/water emulsion vs. sodium oleate wt% present in a $C_{10}H_{21}PO_3Na_2$, sodium oleate emulsifier mixture.

in $C_{10}H_{21}PO_3H_2$, dodecanoic acid; $C_{10}H_{21}PO_3HN_a$, sodium oleate and $C_{10}H_{21}PO_3Na_2$, sodium oleate emulsifier mixtures. Many emulsifier mixtures were essayed and similar plots were obtained.

The same procedure applied in the determination of required HLB_{ether} was used to select $f_{\rm T}$. Then it was replaced in Eq. (3) to compute the HLB values of the three tested phosphonic acids and their salts. Results are summarized in Table 3. Fig. 7 shows the HLB values calculated by Griffin method plotted vs. chain length. It can be seen that as happened with Greenwald et al. method, HLB value decreased with the increase in number of $-CH_2$ -groups in the hydrocarbon tail, but on contrary, HLB augmented with the diminution of neutralizing degree. The different HLB values were also strongly dependent on the emulsifier mixture composition. This fact is related to differences in the water/oil phase structure due to the presence of surfactant of dissimilar structures. In a hydrocarbon mixture one of the surfactants could be more surface active and would concentrate at



Fig. 7. HLB values calculated by Griffin method vs. surfactant chain length.

B	A						
	Tween 20	Span 20	Span 80	Oleic acid	Sodium oleate	Dodecanoic acid	
C ₁₀ H ₂₃ PO ₃	12.19				11.08	24.10	
C ₁₀ H ₂₂ PO ₃ Na					13.22		
C ₁₀ H ₂₁ PO ₃ Na ₂				25.88	11.44		
C ₁₂ H ₂₇ PO ₃	11.67	19.01	24.77		8.34	20.79	
C ₁₂ H ₂₆ PO ₃ Na					11.61		
C12H25PO3Na2				25.74	11.33		
C13H29PO3		19.94	34.17		12.12	20.04	
C ₁₃ H ₂₈ PO ₃ Na					8.61		
$C_{13}H_{27}PO_3Na_2$				34.37	6.78		

Phosphonic acid, sodium phosphonate and disodium phosphonate HLB values computed using Eq. (3) for the different (A-B) emulsion mixtures tested

the interface. Moreover, the structure of the micelle/water polar interface in micelles of alkane phosphonic acids and their salts is different [12,13]. Alkane phosphonic acids micelles have a polar interface in which the -PO₃H₂-groups are strongly interacting by hydrogen bonds, these interaction remaining in monosodic salts micelles while disodic salts micelles have a Stern layer similar to that of other common ionic surfactants. In the Greenwald et al. method (in which pure surfactants are used) the hydrocarbon/water interface structure is similar to that of micelles, while Griffin procedure, the inclusion of a second surfactant in the mixture will alter the interface structure in an extension that depends on the nature and amount of the second component. This fact is probably the cause of the failure of Griffin's method in the systems here studied. Since the phosphonic acid head groups are strongly interacting by H-bonds, probably they predominate at the water/hydrocarbon interface releasing the other component of the mixture to the bulk of one of the coexisting phases, thus giving an HLB value similar to that obtained from Greenwald et al. technique. Therefore, HLB would reflect the activity of a given surface active compound in the mixture leading an erroneous value.

4. Conclusion

Table 3

In this work hydrophile–lipophile balance (HLB) values as well as head groups HLB group numbers for three phosphonic acids and theirs mono and disodic salts were determined. Two different methods were applied for such determinations: those of Griffin and Greenwald et al. From the obtained results it can be seen that the HLB values found by Greenwald et al. method were comparable to those obtained for similar structure surfactants and as expected from the relative hydrophobicity, augmented in the series phosphonic acid, monosodic phosphonate, disodic phosphonate and for the same neutralizing degree decreased with the increase of the hydrocarbon chain length.

On the other hand, by Griffin emulsion technique it was found that HLB value for *n*-dodecane phosphonic acid is similar to that obtained with titration method. Nevertheless for the other tested acid and all salts, the HLB data strongly depended on the nature of the emulsifier mixture compounds. Such fact is assumed as related to a change in the oil–water interface structure and composition. As a consequence, the HLB values here obtained with this method are not reliable demonstrating that Griffin technique is applicable only to non-ionic amphiphiles.

Acknowledgements

This work was financed by grant of the Universidad Nacional del Sur and the Agencia Nacional de Promoción Científica y Tecnológica of Argentina (ANPCyT) by the grant BID 1728 OC-AR PICT No. 10-14560. PM is an assistant researcher of the Concejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET). VV has a fellowship of ANPCyT.

References

- W.C. Griffin, Classification of surface-active agents by "HLB", J. Soc. Cosmetic Chem. 1 (1949) 311–326.
- [2] P.C. Schulz, Fosfonatos, una familia de tensioactivos con inusuales propiedades, Revista Iberoamericana de Polímeros, http://www.ehu.es/reviberpol.
- [3] G. Kossolapoff, Organic Reactions VI, Wiley, New York, 1951, pp. 273.
- [4] H.L. Greenwald, G.L. Brown, M.N. Fireman, Determination of hydrophile–lipophile character of surface active agents and oil by a water titration, Anal. Chem. 28 (1956) 1693–1697.
- [5] P.M. Kruglyakov, Hydrophile–liphophile balance of surfactants and solid particles: physicochemical aspects and applications, in: Studies in Interface Science Series, Elsevier, Amsterdam, 2000.
- [6] D.H. Melik, H.S. Fogler, Turbidimetric determination of particle size distributions of colloidal systems, J. Colloid Interf. Sci. 92 (1983) 161–180.
- [7] P. Becher, Encyclopedia of Emulsion Technology, Dekker, New York, 1988.
- [8] J.T. Davies, E.K. Rideal, Interfacial Phenomena, Academic, New York, 1961.
- [9] I.J. Lin, Hydrophile–lipophile balance (HLB) of fluorocarbon surfactants and its relation to the critical micelle concentration (cmc), J. Phys. Chem. 76 (1972) 2019–2023.
- [10] I.J. Lin, J.P. Friend, Y. Zimmels, The effect of structural modifications on the hydrophile–lipophile balance of ionic surfactants, J. Colloid Interf. Sci 45 (2) (1973) 378–385.
- [11] P.V. Messina, V. Verdinelli, P.C. Schulz, Dioctylphosphinate emulsifier properties, Colloid Polym. Sci. 285 (2006) 251–261.
- [12] P.C. Schulz, R.M. Minardi, B. Vuano, Solubilization of styrene in the cationic system dodecyltrimethylammonium hydroxide-*n*-dodecane phosphonica acid, Colloid Polym. Sci. 276 (1998) 278–281.
- [13] R.M. Minardi, P.C. Schulz, B. Vuano, The effect of surfactant charge on micellization behavior, Colloid Polym. Sci. 275 (1997) 754–759.