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

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Abstract

As a previous step in their application as emulsifiers, here we performed a study of the hydrophile–lipophile balance (HLB) properties of decyl ($C_{10}H_{21}PO_3H_2$), dodecyl ($C_{12}H_{25}PO_3H_2$), tridecyl ($C_{13}H_{27}PO_3H_2$) 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 $–PO_3H_2$; $–PO_3HNa$ and PO_3Na_2 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.

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 emulsion-stabilizing (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 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

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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-non-ionic 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:

$$\mathrm{HLB}_{\mathrm{mix}} = w_{\mathrm{A}}\mathrm{HLB}_{\mathrm{A}} + w_{\mathrm{B}}\mathrm{HLB}_{\mathrm{B}}, \quad w_{\mathrm{A}} + w_{\mathrm{B}} = 1\,\mathrm{g} \tag{1}$$

where $\mathrm{HLB}_{\mathrm{mix}}$, $\mathrm{HLB}_{\mathrm{A}}$, and $\mathrm{HLB}_{\mathrm{B}}$ are the HLB value for the mixture, surfactant A and the surfactant B (the weights of the 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.

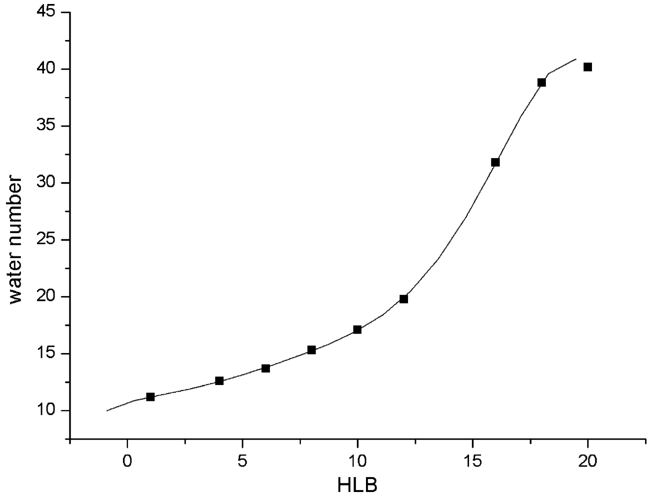

Fig. 1. Greenwald et al. method calibration curve. Water number vs. HLB values obtained from Eq. (1) using oleic acid–sodium oleate and sodium oleate–docecyl sulfate mixtures.

Table 1
Change in water 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)).

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 $(100/m_{\mathrm{e}})/2$ g of water and an equal mass