

## *Application of HLB to Selected Castor, Hear and Soybean Ethoxylates*

Anthony J. O'Lenick, Jr.

Siltech LLC

Dacula, Ga 30019

### **Abstract**

The HLB system provides a system to predict the emulsification properties and solubilities of surfactants that contain water-soluble groups derived from ethylene oxide. The present paper evaluates three different oils as starting materials for the preparation of surfactant esters. The solubility in water, isopropanol, mineral oil and are evaluated as well as the emulsification properties were studied. The structural differences between the oils and the impact on calculated vs. observed HLB was also evaluated.

### **HLB SYSTEM**

HLB, the so-called Hydrophile - Lipophile Balance, is the ratio of oil soluble and water-soluble portions of a molecule. The system was originally developed for ethoxylated products. Table 1 contains some approximations for the HLB value for surfactants as a function of their solubility in water. Values are assigned based upon that table to form a one-dimensional scale, ranging from 0 to 20. We are using the

generic term "hydrocarbon" to designate the oil-soluble portion of the molecule. This generic term includes the more specific terms fatty, lipid, and alkyl.

Table 1

Solubility in Water -----	HLB Value -----	Description -----
Insoluble	4 - 5 emulsifier	water in oil
Poorly dispersible (milky appearance)	6 - 9	wetting agent
Translucent to clear	10 - 12	detergent
Very soluble	13 - 18 emulsifier	oil in water

There are two basic types of emulsions envisioned by the HLB system. They are the oil in water (O/W) and the water in oil (W/O). The phase listed first is the discontinuous phase. That is it is the phase that is emulsified into the other. Bancroft<sup>3</sup> postulated that upon mixing of the two phases with a surfactant present, the emulsifier forms a third phase as a film at the interface between the two phases being mixed together. He also predicted that the phase in which the emulsifier is most soluble would become the continuous phase. The continuous phase need not be the predominant quantity of material present. There are emulsions where the discontinuous phase makes up a greater weight percent than the continuous phase. A simple test is if the emulsion is readily diluted with water, water is the continuous phase.

It has been stated "The HLB system has made it possible to organize a great deal of rather messy information and to plan fairly efficient systematic approaches to optimize emulsion preparation. If one pursues the concept too far however the system tends to lose itself to complexities."<sup>4</sup>

### CALCULATION OF HLB

The HLB system allows for the calculation of HLB using the following formulation:

$$\text{HLB} = \frac{\% \text{ Hydrophile by weight of molecule}}{5}$$

Example Oleyl alcohol 5 E.O.

M.W. Hydrophile (5) (44) = 220

---

$$\frac{\text{Total M.W of molecule}}{\text{Total M.W of molecule}} = 45.0 \%$$

$$\text{HLB} = 45\% / 5 = 9.0 \quad \text{HLB} = 9.0$$

## APPLICATION OF HLB

One can predict the approximate HLB needed to emulsify a given material and make more intelligent estimates of which surfactant or combination of surfactants is appropriate to a given application. When blends are used the HLB can be estimated by using a weighted average of the surfactants used in the blend.

### HLB NEEDED TO EMULSIFY <sup>2</sup>

Acetophenone	14	Lanolin	12
Acid, Lauric	16	Lauryl amine	12
Acid, Oleic	17	Mineral spirits	10
Beeswax	9	Nonylphenol	14
Benzene	15	Orthodichlorobenzene	13
Butyl Stearate	11	Pine oil	16
Carbon Tetrachloride	16	Toluene	15
Castor oil	14	Xylene	14
Chlorobenzene	13	Kerosene	14
Cottonseed oil	6	Cyclohexane	15
Petrolatum	7	Chloronated paraffin	8

For those materials that are not listed above, it is recommended that the oil be tested using specific blends of known emulsifiers. This allows the formulator to calculate the HLB needed to emulsify the non-listed oil.

One of the interesting implications of the predictive value of the HLB system is its assumption that the percentage ethylene oxide in the molecule is the sole determining factor in the emulsification properties of a given hydrophobe. With this in mind we undertook a study to determine the effect of (a) hydrophobe structure on HLB of molecules having the same percentage in the molecule and (b) the effect of molecular structure of dimeric species on HLB. Comparing the observed and the calculated HLB allows for interesting evaluations of the structural effects of the oil evaluated.

### ***1. Hydrophobe Structure***

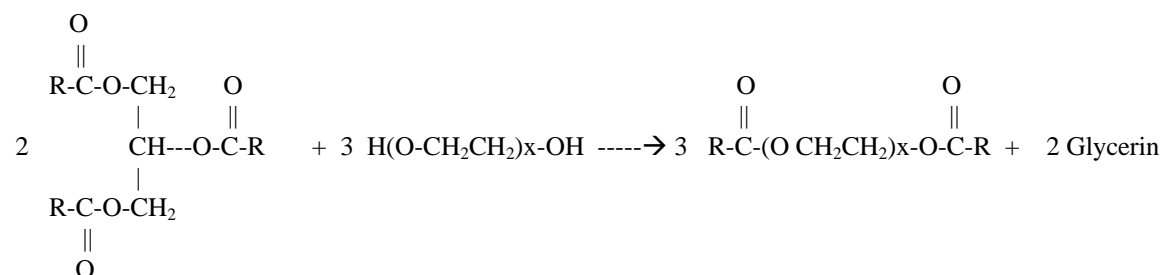
This part of the study was aimed at evaluation of properties of PEG diester based upon oils having different structures. The oils chosen for this evaluation were (a) HEAR oil (also known as Rapeseed oil), Soybean oil, and castor oil. The composition and structures of each are as follows;

[Insert oil compositions]

The reason for the selection of the particular oils chosen was that the castor oil has a hydroxyl group in addition to unsaturation, making it the most polar of the oils evaluated. Castor oil ethoxylates are commonly used as emulsifiers in many applications. Soybean oil was chosen for evaluation since it has unsaturation and on average eighteen carbon atoms. Finally, HEAR oil was chosen since it has unsaturation and a high concentration of eurucic (C22) content.

If the HLB theory applies in its simple form, if the same percentage of water-soluble portion is present in each molecule, the HLB (calculated) should be identical.

### ***Reaction***



### ***Experimental Design***

The three oils were reacted with the same percentage PEG compound as shown above. The prediction from simple HLB evaluation would be that the solubility should be molecules made with an identical weight percentage of ethylene oxide would in fact have identical HLB values. This would in turn result in identical or nearly identical solubility in water and other solvents and identical or nearly identical emulsification properties.

***Products***

The products evaluated were prepared by the reaction of polyoxyalkylene glycol having the molecular weight shown below. The triglycerides were reacted at a temperature of 190° C in the presence of catalyst. The reaction mass was analyzed for free glycerin as a measure of percentage reaction. All reactions were run to 97% of theoretical reaction.

Recalling that the calculated HLB for the materials is determined by using the formula:

$$\% \text{ PEG} / 5 = \text{HLB (calculated)}$$

All materials having the same % of the same PEG, should have the same HLB.

<b><i>Products</i></b>			<b><i>% PEG</i></b>	<b><i>HLB Calculated</i></b>
-----			-----	-----
<b><i>S-1</i></b>	<b><i>C-1</i></b>	<b><i>H-1</i></b>	<b><i>23.0</i></b>	<b><i>4.6</i></b>
<b><i>S-2</i></b>	<b><i>C-2</i></b>	<b><i>H-2</i></b>	<b><i>36.0</i></b>	<b><i>7.2</i></b>
<b><i>S-3</i></b>	<b><i>C-3</i></b>	<b><i>H-3</i></b>	<b><i>47.0</i></b>	<b><i>9.4</i></b>
<b><i>S-4</i></b>	<b><i>C-4</i></b>	<b><i>H-4</i></b>	<b><i>60.0</i></b>	<b><i>12.0</i></b>
<b><i>S-5</i></b>	<b><i>C-5</i></b>	<b><i>H-5</i></b>	<b><i>68.0</i></b>	<b><i>13.6</i></b>
<b><i>S-6</i></b>	<b><i>C-6</i></b>	<b><i>H-6</i></b>	<b><i>84.2</i></b>	<b><i>16.8</i></b>

### Compositions of Products

H-1	%	S-1	%	C-1	%
HEAR	77.0	Soybean	77.0	Castor	77.0
PEG 200	23.0	PEG 200	23.0	PEG 200	23.0
Catalyst	0.1	Catalyst	0.1		0.1
H-2	%	S-2	%	C-2	%
HEAR	64.0	Soybean	64.0	Castor	64.0
PEG 400	36.0	PEG 400	36.0	PEG 400	36.0
Catalyst	0.1	Catalyst	0.1	Catalyst	0.1
H-3	%	S-3	%	C-3	%
HEAR	53.0	Soybean	53.0	Castor	53.0
PEG 600	47.0	PEG 600	47.0	PEG 600	47.0
Catalyst	0.1	Catalyst	0.1	Catalyst	0.1
H-4	%	S-4	%	C-4	%
HEAR	40.0	Soybean	40	Castor	40
PEG 1000	60.0	PEG 1000	60.0	PEG 1000	60.0
Catalyst	0.1	Catalyst	0.1	Catalyst	0.1
H-5	%	S-5	%	C-5	%
HEAR	32.0	Soybean	32.0	Castor	32
PEG 1450	68.0	PEG 1450	68.0	PEG 1450	68
Catalyst	0.1	Catalyst	0.1	Catalyst	0.1
H-6	%	S-6	%	C-6	%
HEAR	15.8	Soybean	15.8	Castor	15.8
PEG 3350	84.2	PEG 3350	84.2	PEG 3350	84.2
Catalyst	0.1	Catalyst	0.1	Catalyst	0.1

### RESULTS and DISCUSSION

#### Infra Red Analysis

The FTIR spectra of the esters were similar between most of the samples containing the same amount and type of PEG, except for the samples in the 10- and 14.5-series. Each sample of the 10- and 14.5-series mainly varied in peak appearance in the 2800 – 2900  $\text{cm}^{-1}$  (probably alkyl groups) and in the 1100  $\text{cm}^{-1}$  regions (possibly ester C—O bond):

a) S-10 appeared to have a slight bud for a third peak in the 2800 – 2900  $\text{cm}^{-1}$ , whereas, C-10 and H-10 only had two peaks. S-10 and H-10 had three peaks in the 1100  $\text{cm}^{-1}$  but C-10 only had one jagged peak.



b) C-14.5 had a more intense -OH peak in the  $3400\text{ cm}^{-1}$  region than H-14.5 or S-14.5. The peaks found in the  $2800 - 2900\text{ cm}^{-1}$  region of C-14.5 looked like a double peak, whereas, in H-14.5 and S-14.5, these set of peaks could be separated into three individual peaks. And in the  $1100\text{ cm}^{-1}$  region, H-14.5 and S-14.5 each had a set of sharp and narrow triple peaks, but C-14.5 had one jagged, broad peak.

The FTIR spectra of the esters also revealed trends for each oil series. As the amount of PEG was increased within each oil series, the intensity of each of the peaks in the  $2800 - 2900\text{ cm}^{-1}$  region shifted. The peak found around  $2854\text{ cm}^{-1}$  increased in intensity relative to its neighboring peak found at  $2924\text{ cm}^{-1}$ , which was an indication of an increasing amount of  $-\text{CH}_2$  groups, probably contributed by the increasing PEG chain length over the series. Also, the peak found around  $1100\text{ cm}^{-1}$  increased in intensity and went from being an undefined, jagged peak to three sharp and defined peaks by the end of the series. Another ester peak, most likely contributed by the C=O bond, was found around  $1735\text{ cm}^{-1}$  and decreased in intensity by the end of the series. (*see attached FTIR spectra*)

The following three tables include various physical properties of Castor oil, HEAR oil, and Soybean oil PEG esters. Predictable trends to notice with increased amounts of PEG are: a) increased water solubility, decreased oil solubility, b) increased cloud point, c) increased melting point/range, and d) increased HLB value.

PROPERTY	C-2	C-4	C-6	C-10	C-14.5	C-33.5
Cloud point, °C (1.0% w/w)	N/A	N/A <sup>c</sup>	37 - 41	68 - 72	68 - 73	96 - 97
Foam power/stability, mm (1.0% w/w, 49°C)	N/A	NT	NT	42/15	120/23	98/55
Solubility <sup>a</sup> (0.1/1.0% w/w, 24°C)						
Water	I/I	D/D	S/D	S/S	S/S	S/S
Propylene Glycol	S/D	S/D	S/D	S/D	S/S	S/I
Mineral Oil	S/S	S/S	S/S	S/D	S/I	I/I
Calculated HLB value	7.9	11.4	13.3	15.4	16.5	18.3
Observed HLB value (+/- 1)	10.5	11 - 12	14	15.5	16.1	18.1
Emulsion Stability <sup>b</sup> (1 hr/24 hr, 25°C)						
In F-350	NT	NT	NT	3/3	3/3	3/3
In Mineral Oil	NT	NT	NT	3/3	3/3	3/3
Melting Point, °C	N/A	N/A	N/A	30 - 40	>37 - 40	>47 - 50

a = Key: S = soluble, D = dispersible, I = insoluble

b = Ratio for emulsion is Water/Oil/Sample 76/19/5 % (w/w)

c = Sample appears milky at 0°C

N/A = Not applicable (sample insoluble in water)

NT = Not tested

PROPERTY	H-2	H-4	H-6	H-10	H-14.5	H-33.5
Cloud point, °C (1.0% w/w)	N/A	N/A	N/A <sup>c</sup>	86 - 90	88	97
Foam power/stability, mm (1.0% w/w, 49°C)	N/A	N/A	NT	41/31	51/43	94/92
Solubility <sup>a</sup> (0.1/1.0% w/w, 24°C)						
Water	D/I	D/I	S/D	S/S	S/S	S/S
Propylene Glycol	D/D	D/D	S/D	S/D	S/D	S/D
Mineral Oil	S/S	S/S	S/D	S/I	S/I	I/I
Calculated HLB value	7.3	10.7	12.6	14.9	16.1	18.1
Observed HLB value (+/- 1)	8	10	13.3	14.9	16.2	18.1
Emulsion Stability <sup>b</sup> (1 hr/24 hr, 25°C)						
In F-350	NT	NT	NT	3/3	3/3	3/3
In Mineral Oil	NT	NT	NT	3/3	3/3	3/3
Melting Point, °C	N/A	N/A	N/A	30 - 40	>35 - 37	>45 - 47

a = Key: S = soluble, D = dispersible, I = insoluble

b = Ratio for emulsion is Water/Oil/Sample 76/19/5 % (w/w)

c = Sample appears milky at 0°C

N/A = Not applicable (sample insoluble in water)

NT = Not tested

PROPERTY	S-2	S-4	S-6	S-10	S-14.5	S-33.5
Cloud point, °C (1.0% w/w)	N/A	N/A	N/A <sup>c</sup>	64 – 70	82 – 83	90 - 92
Foam power/stability, mm (1.0% w/w, 49°C)	N/A	N/A	NT	NT	72/60	100/97
Solubility <sup>a</sup> (0.1/1.0% w/w, 24°C)						
Water	D/I	D/I	S/D	S/D	S/S	S/S
Propylene Glycol	D/D	D/D	D/D	S/D	S/D	S/D
Mineral Oil	S/S	S/S	S/S	S/D	S/I	I/I
Calculated HLB value	8.3	11.7	13.6	15.7	16.7	18.4
Observed HLB value (+/- 1)	NT	11	NT	15 – 16	NT	26 <sup>d</sup>
Emulsion Stability <sup>b</sup> (1 hr/24 hr, 25°C)						
In F-350	NT	NT	NT	3/3	3/3	3/3
In Mineral Oil	NT	NT	NT	3/3	3/3	3/3
Melting Point, °C	N/A	N/A	N/A	28 - 33	>37 - 40	>45 - 47

a = Key: S = soluble, D = dispersible, I = insoluble

b = Ratio for emulsion is Water/Oil/Sample 76/19/5 % (w/w)

c = Sample appears milky at 0°C

d = S-33.5 was blended with Tween 80 and calculated to have an Observed HLB of 26

N/A = Not applicable (sample insoluble in water)

NT = Not tested

## Conclusions

HLB theory has provided a basis for evaluation of potential surfactants as emulsifiers for many years. The theory provides a simple approach to a complicated problem. As such it provides an approximation for emulsification work. The theory would predict that all molecules having the same amount of water-soluble group present in the molecule, should have the same HLB. Consequently, the surfactants prepared regardless of fatty source should also have the same solubilities. Clearly, this was not the case.

The specific structure of the hydrophobe used to make the ester has an effect upon the solubility of the resulting surfactant. The percentage by weight of the water-soluble portion of the molecule was not the only factor as predicted by HLB theory. For example, PEG 600 castor forms a microemulsion in water at 5% by weight. Both the HEAR

product and the soybean product required more water-soluble group (i.e. higher PEG) to achieve solubility in water.

All materials evaluated was soluble in isopropanol, but only the HEAR product produced a gel with isopropanol when reacted with PEG 3350.

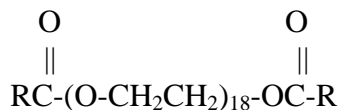
The solubility in light mineral oil, was also different. The presence of the polar hydroxyl group in the castor molecule results no mineral oil soluble products. The HEAR and soybean based products had a number of mineral oil soluble products, with HEAR based products having more solubility over a wider range of products..

The calculated HLB and the observed HLB

## ***2. Dimeric Species***

The second part of the study was undertaken to determine if dimeric PEG esters having twice the molecular weight as the mono-substituted PEG ester, but the same percentage ethylene oxide, had the same HLB. The HLB theory also predicts that these materials would have the same emulsification properties and solubilities, despite the difference in molecular weight.

Consider the following materials. They should have nearly identical HLB values



In all cases R is C<sub>17</sub>H<sub>34</sub>

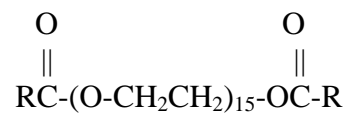
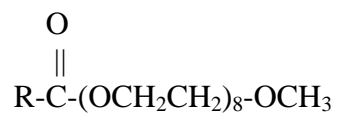
C <sub>36</sub> H <sub>71</sub> O <sub>11</sub>	Emp. Formula	C <sub>72</sub> H <sub>140</sub> O <sub>21</sub>
679	Molecular Weight	1340
679	Equiv Molecular Weight	670
396/679 = 58.32%	Water Soluble	792/1340= 59.1%
11.7	HLB	11.8

The practical difficulty is to obtain nearly pure monoester. All attempts to make monoester result in a mixture of monoester, diester and free polyoxyethyleneglycol (PEG). In order to overcome this difficulty, we used a methanol ethoxylate having the following structure;



Reaction of a 1:1 ratio of this material to oil does not results in a mixture. We needed to modify the molecular structure somewhat to match the percentage of ethylene oxide portion in each molecule. This would result in molecules that should have identical or nearly identical HLB values, albeit dramatically different total molecular weights.

We have chosen and synthesized the following materials for evaluation:



In all cases R is C<sub>17</sub>H<sub>34</sub>

C <sub>35</sub> H <sub>69</sub> O <sub>10</sub>	Emp. Formula	C <sub>66</sub> H <sub>128</sub> O <sub>18</sub>
649	Molecular Weight	1208
649	Equiv Molecular Weight	604
352/649 = 54.2%	Water Soluble	660/1208= 54.6 %
10.8	HLB	10.9