Approximate HLB values of SMA® Resins and Esters – Anionic Surfactants

The HLB system was designed for nonionic surfactants and typically ranges from 1 (most hydrophobic) to 20 (most hydrophilic). The ranges of HLB values for the different types of nonionic surfactants, based on their water solubility is generally as follows:

Water solubility	HLB range
No dispersibility in water	1-4
Poor dispersion	3-6
Milky dispersion after vigorous shaking	6-8
Stable milky dispersion	8-10
Translucent to clear dispersion	10-13
Clear solution	13+

Generally, the applications for nonionic surfactants within the following HLB ranges are as follows:

HLB range	Application
4– 6	w/o emulsifiers
7- 9	wetting agents
8 – 18	w/o emulsifiers
13 – 15	detergents
10 – 18	solubilizers

Calculations for the HLB of nonionic surfactants take the weight percent of the hydrophilic portion of the molecule and divide by 5. For example a 20 mole ethoxylate(EO) of lauric acid has a total molecular weight of (20 moles EO x 44 g/mole= 880) + 200g/mole (lauric acid) – 18g/mole (esterification water) = 1062g/mole. The hydrophilic weight percent is the EO portion = 880/1062 x 100 = 82.9%. Divide this by 5 to get the HLB value = 82.9/5 = 16.6 HLB value.

Anionic surfactants generally have a much higher HLB value than nonionics due to the higher hydrophilicity of the anionic group. For example sodium lauryl sulfate (SLS) has an HLB of 40, and sodium oleate (Na Oleate) has an HLB of 18. If one were to calculate the HLB of these structures using the nonionic methodology (hydrophilic weight percent portion divided by 5), one would get :

SLS MW = 288.4, hydrophilic portion (SO_4Na = 119)
HLB = ((119/288.4) x 100)/5 = 8.2

Na Oleate MW = 305, hydrophilic portion (COONa = 67)
HLB = ((67/305) x 100)/5 = 4.4

Since the actual SLS HLB value is approximately 4.9x that of the calculated and that for the sodium oleate is about 4.1x that of the calculated, there needs to be a multiplier to account for the higher hydrophilicity of the anionic groups. For SMA®, the multiplier may need to be smaller based on the fact that these are polymeric surfactants, which lowers their ability to migrate to interfaces compared to the monomeric SLS and sodium oleate. If we look at the known applications where the SMA® products are sold and look at the above table of nonionic HLB values and applications, it would appear that the appropriate multiplier for the SMA® products may be about 2.8. Using this assumption, the SMA® product line would have the following HLB values:

Product	Calculated HLB
SMA® 1000	24.1
SMA® 2000	16.5
SMA® 17352	16.2
SMA® 1440	14.4
SMA® 2625	13.8
SMA® 3000 (EF-30)	12.3
SMA® 4000 (EF-40)	10
SMA® 3840	8.4
SMA® 31890	7.7
SMA® 6000 (EF-60)	7.3

An example calculation for the above determinations is as follows:

SMA® 1000

Number average molecular weight as determined by GPC = 2100. The weight of the hydrophilic portion of the molecule (the maleic anhydride portion of the copolymer) is 903 (~8-9 MA groups/chain). Therefore, the hydrophilic weight percent of SMA® 1000 = 903/2100 = 43%. By the nonionic HLB method, we would divide this number by 5 and get HLB = 8.6. Using the theoretical 2.8x multiplier, the HLB value for SMA® 1000 = 24.1. This was done in a similar way for all of the resins. For the esters, the alkyl portion of the ester was counted in the hydrophobic portion of the molecule.

Summary:

HLB values are traditionally calculated for nonionic surfactants and can be determined experimentally by trying to emulsify liquids of known HLB value. In lieu of doing the experiments to determine the HLB values of the anionic SMA® resins and esters, we have used the nonionic method for calculating the values, and applied a correction factor to adjust them into a range where they appear to be consistent with the known applications. The more hydrophilic materials contain more maleic anhydride and/or acid groups and have the higher HLB values. The products that have more styrene and longer ester chains are more hydrophobic and thus have lower HLB values. So even though the values shown in the above table may not be exact values, the trend seems to be consistent with the structures and known applications.