CALCULATION OF HLB VALUES OF NON-IONIC SURFACTANTS*

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In the past fifteen or twenty years, there has been a tremendous growth in the field of surfactants. The term surfactants, as used here, includes emulsifiers, wetting agents, suspending agents, detergents, anti-foam compounds, and many others. Despite widespread interest in all types of surfactants, there has been no utilitarian method of classifying them. There has been division according to ionization, chemical type, and by popular (often ambiguous) nomenclature.

The surfactant used in practically all formulations prior to the 1930's was soap. In the mid 1930's the supremacy of soap was challenged, first by sulfonates and sulfate-type ionic surfactants, and shortly thereafter by the non-ionics. In the past few years blends of non-ionic and anionic surfactants have become increasingly popular. Throughout this period, cationic surfactants have seen increased use but not to the same degree as that of either anionic or non-ionic products.

The biggest difficulty with surfactants today, at least from the standpoint of those who have to choose them, is the staggering number that are available. Each manufacturer tries to provide one or more of his own products that is suitable for every need and therefore each has a tremendous selection. The large number of surfactants available, coupled with the fact that application problems are becoming increasingly difficult, is making the need for a suitable system of selection of surfactants more and more critical.

Any emulsion chemist who works with surfactants for a few years soon recognizes that there is a correlation between their behavior and their solubility in water. For example, he will use a water-soluble surfactant or blend to make an oil-in-water emulsion. He will also use a water-soluble surfactant for solubilization and an almost completely water-soluble surfactant as a detergent. All the products of these applications may be said to exhibit aqueous characteristics; that is, they dilute readily

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with water and conduct electricity. For these purposes the emulsion chemist would under no circumstances use an oil-soluble surfactant. However, to make a water-in-oil emulsion, to couple water-soluble materials into an oil, or to make a dry-cleaning detergent, all of which are non-aqueous systems, he would choose an oil-soluble surfactant.

This relationship of behavior and water solubility that is followed by most experienced emulsion chemists is so inexact in its usual form that it is only of value as a basis of thinking. We have been successful in assigning numerical values to surfactants, thereby providing a system of classification that is related to their behavior and to their solubility in water. This method, called the HLB method from the term *Hydrophile-Lipophile Balance*, is based on the premise that all surfactants combine hydrophilic and lipophilic groups in one molecule and that the proportion between the weight percentages of these two groups for non-ionic surfactants is an indication of the behavior that may be expected from that product. The HLB value is useful because it allows a prediction of the action that may be expected from a surfactant; for example a low value, about 4, will be a water-in-oil emulsifier; a high value, about 16, will be a solubilizer. What is referred to here *is the type of behavior that can be expected, rather than the efficiency* with which this will be accomplished.

In our laboratory the behavior of surfactants in relationship to their hydrophilic nature was first recognized in emulsion studies. When two non-ionic emulsifiers, one hydrophilic and the other lipophilic, were mixed in varying ratios the efficiency of the blend as an emulsifier for a given oil went through a maximum. Using pairs of different surfactants to emulsify the same oil, it was apparent that this maximum occurred at the same weight percentage of hydrophilic substance in the surfactant blend. Essentially therefore, the HLB value is a function of the weight percentage of the hydrophilic portion of the molecule of a non-ionic surfactant.

HLB values may be calculated for non-ionic surfactants or may be determined experimentally. The experimental procedure is long and laborious and was described a few years ago [J. Soc. Cosmetic Chem., **1**, 311–326 (1949)].

Formulas for calculating HLB values may be based on either analytical or composition data. For most polyhydric alcohol fatty acid esters approximate values may be calculated with the formula

$$\text{HLB} = 20\left(1 - \frac{S}{A}\right)$$

Wherein:

S = saponification number of the ester
A = acid number of the acid

Examples: (A) Atmul 67® glyceryl monostearate (soap free)
S = saponification number, 161
A = acid number of fatty acid, 198

$$\text{HLB} = 20\left(1 - \frac{161}{198}\right) = 3.8$$

(B) Tween 20®, polyoxyethylene sorbitan monolaurate
S = saponification number spec., 45.5 (mid-point)
A = acid number of fatty acid, 276

$$\text{HLB} = 20\left(1 - \frac{45.5}{276}\right) = 16.7$$

Many fatty acid esters do not give good saponification number data; for example, tall oil and rosin esters, beeswax esters, lanolin esters. For these a calculation may be based on the formula:

$$\text{HLB} = \frac{E + P}{5}$$

Wherein:

E = weight percentage of oxyethylene content
P = weight percentage of polyhydric alcohol content (glycerol, sorbitol, etc.)

Example: Atlas G-1441; polyoxyethylene sorbitol lanolin derivative
E = weight percentage of oxyethylene content, 65.1
P = weight percentage of polyhydric alcohol content, 6.7

$$\text{HLB} = \frac{65.1 + 6.7}{5} = 14$$

In products wherein only ethylene oxide is used as the hydrophilic portion and for fatty alcohol ethylene oxide condensation products, equation 2 may be simplified to

$$\text{HLB} = \frac{E}{5}$$

Example: Myrj 49® polyoxyethylene stearate
E = weight percentage of oxyethylene content, 76

$$\text{HLB} = \frac{76}{5} = 15$$

These formulas are satisfactory for non-ionic surfactants of many types. However, non-ionic surfactants containing propylene oxide, butylene oxide, nitrogen, sulfur, etc., exhibit behavior which has not been related to composition. In addition, the HLB values of ionic surfactants do not follow a weight percentage basis because even though the hydrophilic portion is low in molecular weight the fact that it ionizes lends extra emphasis to that portion and therefore makes the product more hydrophilic. For these products, the experimental method must be used.

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HLB values for a wide variety of surfactants have been calculated or observed and are listed in Table 1. As with any system that deals with surfactants, there are occasional side effects which seem to alter the established value. These are often unique to the test that is being run and there is no explanation for them at the present time.

Because of the difficulty, time, and expense involved in carrying out the experimental procedure, relatively few of the host of available surfactants have had their HLB values determined. However, this is not the disadvantage that it first appears to be, since a rough estimate of the HLB can be made from the degree of water solubility and in many instances this is adequate for screening work.

In its present form, the HLB system lacks exactness. A suitable simple laboratory method of measuring HLB values of surfactants accurately is needed. We have tried a variety of methods including solubility in water, or various solvents, ratio solubility in two solvents, solubilization behavior both for oils and dyes, surface and interfacial tension data, cloud point behavior, and many other properties. Of these the most promising is the determination of the cloud point of an aqueous solution of the surfactant. However, this test still possesses severe limitations.

In addition to hydrophile-lipophile balance, it is believed that surfactants possess a second property which is related to their behavior. We call it chemical type. For example, we may find that esters of a particular fatty acid provide better emulsification in a given system than any other fatty acid esters; or polyoxyalkylene fatty alcohols may give better performance than esters. In all probability, chemical type is related to the attraction of the lipophilic group in the surfactant for the lipophilic material with which the surfactant is being used. This, we believe, governs the efficiency of a surfactant, provided it is of the proper HLB. This second characteristic point, the nature of the hydrophilic and lipophilic groups, also requires further study.

To select a surfactant properly for any application, we believe that one must first have the optimum HLB value and secondly have the correct chemical type. Since, at the moment we have correlation only for the HLB value our procedure is to establish the required HLB and then try a variety of chemical types at that optimum HLB. This procedure eliminates trial of all surfactants that are of the wrong HLB and, thus, reduces the time and effort required to solve a problem.

Just as each surfactant or surfactant blend exhibits an HLB value each lipophilic material or blend of lipophilic materials with which surfactants are used exhibits an optimum required HLB value for any specific formulation or application, Table 2. The determination of required HLB values has also been studied both from the standpoint of calculation and

Table 1—Calculated and Determined HLB Values

Name	Mfr.*	Chemical Designation	Type†	HLB††
Span 85	1	Sorbitan trioleate	N	1.8
Arlacel 85	1	Sorbitan trioleate	N	1.8
Atlas G-1706	1	Polyoxyethylene sorbitol beeswax derivative	N	2
Span 65	1	Sorbitan tristearate	N	2.1
Arlacel 65	1	Sorbitan tristearate	N	2.1
Atlas G-1050	1	Polyoxyethylene sorbitol hexastearate	N	2.6
Emcol EO-50	2	Ethylene glycol fatty acid ester	N	2.7
Emcol ES-50	2	Ethylene glycol fatty acid ester	N	2.7
Atlas G-1704	1	Polyoxyethylene sorbitol beeswax derivative	N	3
Emcol PO-50	2	Propylene glycol fatty acid ester	N	3.4
Atlas G-922	1	Propylene glycol monostearate	N	3.4
"Pure"	6	Propylene glycol monostearate	N	3.4
Atlas G-2158	1	Propylene glycol monostearate	N	3.4
Emcol PS-50	2	Propylene glycol fatty acid ester	N	3.4
Emcol EL-50	2	Ethylene glycol fatty acid ester	N	3.6
Emcol PP-50	2	Propylene glycol fatty acid ester	N	3.7
Arlacel C	1	Sorbitan sesquioleate	N	3.7
Arlacel 83	1	Sorbitan sesquioleate	N	3.7
Atlas G-2859	1	Polyoxyethylene sorbitol 4.5 oleate	N	3.7
Atmul 67	1	Glycerol monostearate	N	3.8
Atmul 84	1	Glycerol monostearate	N	3.8
Tegin 515	5	Glycerol monostearate	N	3.8
Aldo 33	4	Glycerol monostearate	N	3.8
"Pure"	6	Glycerol monostearate	N	3.8
Atlas G-1727	1	Polyoxyethylene sorbitol beeswax derivative	N	4
Emcol PM-50	2	Propylene glycol fatty acid ester	N	4.1
Span 80	1	Sorbitan monoöleate	N	4.3
Arlacel 80	1	Sorbitan monoöleate	N	4.3
Atlas G-917	1	Propylene glycol monolaurate	N	4.5
Atlas G-3851	1	Propylene glycol monolaurate	N	4.5
Emcol PL-50	2	Propylene glycol fatty acid ester	N	4.5
Span 60	1	Sorbitan monostearate	N	4.7
Arlacel 60	1	Sorbitan monostearate	N	4.7
Atlas G-2139	1	Diethylene glycol monoöleate	N	4.7
Emcol DO-50	2	Diethylene glycol fatty acid ester	N	4.7
Atlas G-2146	1	Diethylene glycol monostearate	N	4.7
Emcol DS-50	2	Diethylene glycol fatty acid ester	N	4.7
Atlas G-1702	1	Polyoxyethylene sorbitol beeswax derivative	N	5
Emcol DP-50	2	Diethylene glycol fatty acid ester	N	5.1
Aldo 28	4	Glycerol monostearate (self-emulsifying)	A	5.5
Tegin	5	Glycerol monostearate (self-emulsifying)	A	5.5
Emcol DM-50	2	Diethylene glycol fatty acid ester	N	5.6
Atlas G-1725	1	Polyoxyethylene sorbitol beeswax derivative	N	6
Atlas G-2124	1	Diethylene glycol monolaurate (soap free)	N	6.1
Emcol DL-50	2	Diethylene glycol fatty acid ester	N	6.1
Glaurin	4	Diethylene glycol monolaurate (soap free)	N	6.5
Span 40	1	Sorbitan monopalmitate	N	6.7
Arlacel 40	1	Sorbitan monopalmitate	N	6.7
Atlas G-2242	1	Polyoxyethylene dioleate	N	7.5
Atlas G-2147	1	Tetraethylene glycol monostearate	N	7.7

TABLE 1—(*Continued*)

Name	Mfr.*	Chemical Designation	Type†	HLB††
Atlas G-2140	1	Tetraethylene glycol monoöleate	N	7.7
Atlas G-2800	1	Polyoxypropylene mannitol dioleate	N	8
Atlas G-1493	1	Polyoxyethylene sorbitol lanolin oleate derivative	N	8
Atlas G-1425	1	Polyoxyethylene sorbitol lanolin derivative	N	8
Atlas G-3608	1	Polyoxypropylene stearate	N	8
Span 20	1	Sorbitan monolaurate	N	8.6
Arlacel 20	1	Sorbitan monolaurate	N	8.6
Emulphor VN-430	3	Polyoxyethylene fatty acid	N	9
Atlas G-1734	1	Polyoxyethylene sorbitol beeswax derivative	N	9
Atlas G-2111	1	Polyoxyethylene oxypropylene oleate	N	9
Atlas G-2125	1	Tetraethylene glycol monolaurate	N	9.4
Brij 30	1	Polyoxyethylene lauryl ether	N	9.5
Tween 61	1	Polyoxyethylene sorbitan monostearate	N	9.6
Atlas G-2154	1	Hexaethylene glycol monostearate	N	9.6
Tween 81	1	Polyoxyethylene sorbitan monoöleate	N	10.0
Atlas G-1218	1	Polyoxyethylene esters of mixed fatty and resin acids	N	10.2
Atlas G-3806	1	Polyoxyethylene cetyl ether	N	10.3
Tween 65	1	Polyoxyethylene sorbitan tristearate	N	10.5
Atlas G-3705	1	Polyoxyethylene lauryl ether	N	10.8
Tween 85	1	Polyoxyethylene sorbitan trioleate	N	11
Atlas G-2116	1	Polyoxyethylene oxypropylene oleate	N	11
Atlas G-1790	1	Polyoxyethylene lanolin derivative	N	11
Atlas G-2142	1	Polyoxyethylene monoöleate	N	11.1
Myrj 45	1	Polyoxyethylene monostearate	N	11.1
Atlas G-2141	1	Polyoxyethylene monoöleate	N	11.4
P.E.G. 400 monooleate	6	Polyoxyethylene monoöleate	N	11.4
P.E.G. 400 monooleate	7	Polyoxyethylene monoöleate	N	11.4
Atlas G-2076	1	Polyoxyethylene monopalmitate	N	11.6
S-541	4	Polyoxyethylene monostearate	N	11.6
P.E.G. 400 monostearate	6	Polyoxyethylene monostearate	N	11.6
P.E.G. 400 monostearate	7	Polyoxyethylene monostearate	N	11.6
Atlas G-3300	1	Alkyl aryl sulfonate	A	11.7
		Triethanolamine oleate	A	12
Atlas G-2127	1	Polyoxyethylene monolaurate	N	12.8
Igepal CA-630	3	Polyoxyethylene alkyl phenol	N	12.8
Atlas G-1431	1	Poloxyethylene sorbitol lanolin derivative	N	13
Atlas G-1690	1	Polyoxyethylene alkyl aryl ether	N	13
S-307	4	Polyoxyethylene monolaurate	N	13.1
P.E.G. 400 monolaurate	6	Polyoxyethylene monolaurate	N	13.1
Atlas G-2133	1	Polyoxyethylene lauryl ether	N	13.1
Atlas G-1794	1	Polyoxyethylene castor oil	N	13.3
Emulphor EL-719	3	Polyoxyethylene vegetable oil	N	13.3
Tween 21	1	Polyoxyethylene sorbitan monolaurate	N	13.3

TABLE 1—(*Continued*)

Name	Mfr.*	Chemical Designation	Type†	HLB††
Renex 20	1	Polyoxyethylene esters of mixed fatty and resin acids	N	13.5
Atlas G-1441	1	Polyoxyethylene sorbitol lanolin derivative	N	14
Atlas G-7596J	1	Polyoxyethylene sorbitan monolaurate	N	14.9
Tween 60	1	Polyoxyethylene sorbitan monostearate	N	14.9
Tween 80	1	Polyoxyethylene sorbitan monooleate	N	15
Myrj 49	1	Polyoxyethylene monostearate	N	15.0
Atlas G-2144	1	Polyoxyethylene monoöleate	N	15.1
Atlas G-3915	1	Polyoxyethylene oleyl ether	N	15.3
Atlas G-3720	1	Polyoxyethylene stearyl alcohol	N	15.3
Atlas G-3920	1	Polyoxyethylene oleyl alcohol	N	15.4
Emulphor ON-870	3	Polyoxyethylene fatty alcohol	N	15.4
Atlas G-2079	1	Polyoxyethylene glycol monopalmitate	N	15.5
Tween 40	1	Polyoxyethylene sorbitan monopalmitate	N	15.6
Atlas G-3820	1	Polyoxyethylene cetyl alcohol	N	15.7
Atlas G-2162	1	Polyoxyethylene oxypropylene stearate	N	15.7
Atlas G-1471	1	Polyoxyethylene sorbitol lanolin derivative	N	16
Myrj 51	1	Polyoxyethylene monostearate	N	16.0
Atlas G-7596P	1	Polyoxyethylene sorbitan monolaurate	N	16.3
Atlas G-2129	1	Polyoxyethylene monolaurate	N	16.3
Atlas G-3930	1	Polyoxyethylene oleyl ether	N	16.6
Tween 20	1	Polyoxyethylene sorbitan monolaurate	N	16.7
Brij 35	1	Polyoxyethylene lauryl ether	N	16.9
Myrj 52	1	Polyoxyethylene monostearate	N	16.9
Myrj 53	1	Polyoxyethylene monostearate	N	17.9
		Sodium oleate	A	18
Atlas G-2159	1	Polyoxyethylene monostearate	N	18.8
		Potassium oleate	A	20
Atlas G-263	1	*N*-cetyl *N*-ethyl morpholinium ethosulfate	C	25–30
	1	Pure sodium lauryl sulfate	A	App. 40

* 1 = Atlas Powder Company, 2 = Emulsol Corporation, 3 = General Aniline & Film Corporation, 4 = Glyco Products Company, Inc., 5 = Goldschmidt Chemical Corporation, 6 = Kessler Chemical Company, Inc., 7 = W. C. Hardesty Company, Inc.

† A = Anionic, C = Cationic, N = Non-ionic.

†† HLB values, either calculated or determined, believed to be correct to ±1.

a variety of physical tests. There appears to be a correlation of required HLB value with chemical composition, though there are insufficient data to show a fixed relationship at the present time.

It seems possible that, given (1) a suitable sorting-coding system for surfactants based on (a) HLB, and (b) chemical type, and (2) a more or less parallel or complementary sorting-coding system for the lipophilic ma-

TABLE 2—"REQUIRED HLB" VALUES

	W/O Emulsion	O/W Emulsion	Solubilizing*
Acid, stearic	..	17	...
Alcohol, cetyl	..	13	...
Lanolin, anhydrous	8	15	...
Oil			
Cottonseed	..	7.5	...
Essential	..	...	16.5
Mineral, heavy	4	10.5	...
Mineral, light	4	10–12	15.5
Vitamin (with fats or oils)	..	...	15
Vitamin (fat free)	..	...	16.5
Petrolatum	4	10.5	...
Vitamins			
Esters	..	...	14
Oils (see "Oils" above)			
Wax			
Beeswax	5	10–16	...
Microcrystalline	..	9.5	...
Paraffin (household)	4	9	...

* O/W, i.e., solubilizing in water.

terials used with surfactants, a cross relationship could be set up. With such a system, it should be possible to screen all the available surfactants in a few minutes and select a few that are worthy of extensive study.

In summary, two conditions usually must be satisfied in choosing a surfactant for any desired formulation. First, the proper HLB or hydrophilic content of the surfactant must be used, and second the proper chemical type of the surfactant must be chosen. Random choice, i.e., the old trial-and-error method, can lead to many selections that are wrong in two ways; that is, both by chemical type and HLB. By first determining the optimum HLB value and then selecting and testing a variety of chemical types at this particular value a large number of wrong trials can be eliminated. The HLB method permits a more systematized trial than possible previously. HLB values may be calculated from analytical or composition data or the system may be used without calculating or determining exact value since it is a method of operation that has some correlation with water solubility of the surfactants. There is need for further work in this field to establish a rapid, more exact experimental procedure for observing HLB values, for determining "required HLB's," and for classifying and correlating chemical types of surfactants.