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² Abstract.

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RESEARCH ARTICLES

Hydrophile-Lipophile Balance and Cloud Points of Nonionic Surfactants

HANS SCHOTT

Abstract □ The comparison of the cloud points of 165 nonionic surfactants was based on their calculated hydrophile-lipophile balance (HLB) values. The surfactants were classified according to structure and width of molecular weight distribution. Increasing length of the polyoxyethylene moiety increased the HLB and cloud points. At constant HLB, the following features were found to lower the cloud point: decreasing molecular weight, broader molecular weight distribution (probably due to the presence of fractions of such low degree of polyoxyethylation that they were insoluble in water at all temperatures), branching or greater symmetry of the surfactant molecule, the introduction of olefinic unsaturation, replacement of the terminal hydroxyl by a methoxyl group, and replacement of an ether by an ester bond. The equations for calculating the HLB, which had been derived from emulsification ex-

periments with only a limited number of surfactants, contain the weight-percentage of polyoxyethylene as the sole variable characterizing the surfactant. Therefore, the calculated HLB is not affected by the surfactant characteristics listed above, which largely govern the values of cloud point, CMC, and interfacial tension. Additional HLB measurements are needed to determine whether the equations used to calculate HLB fully describe the emulsifying characteristics of all nonionic surfactants, *i.e.*, whether all experimental HLB values are really independent of the structure of the surfactant molecules.

Keyphrases □ Surfactants, nonionic—HLB, cloud points □ Polyoxyethylene moiety, surfactants—HLB, cloud points □ HLB determination—surfactants □ Cloud point determination, significance—surfactants

"Probably the most important single parameter affecting the type and stability of an emulsion is the puzzling hydrophile-lipophile balance number (HLB). . . One is left with the conviction that the HLB has a

rational interpretation and with a sense of frustration in not being yet able to show its origin conclusively" (1). One such attempt, to find a universal relation between the HLB values and critical micelle concentra-

Table I—Effect of Surfactant Concentration on the Cloud Point^a

Surfactant ^b	Cloud Point, °C., at Concn. (g./l.)			
	2.0	5.0	10	25
C ₁₂ H ₂₅ O(C ₂ H ₄ O) ₇ H	58	58	58.5	59.5
C ₁₂ H ₂₅ O(C ₂ H ₄ O) ₉ H	76	76	76	76.5
C ₁₂ H ₂₅ O(C ₂ H ₄ O) ₁₁ H	99	99	99	99

^a Present work. ^b Normally distributed; POE chain length adjusted by weight increase during EO addition, and verified by acetylation and by NMR.

tions (CMC) of nonionic surfactants, was unsuccessful: while a simple relationship between these two parameters was found for each of two homologous series of surfactants, the two relationships were different (2).

The first objective of the present work was to seek a universal relationship between the HLB value and the cloud point of nonionic surfactants. Griffin, examining a limited number of surfactants, found a nearly linear but somewhat scattered relationship between the two parameters (3). The existence of such a relationship is being reexamined here for the much broader spectrum of nonionic surfactants now available. Since the experimental determination of HLB values is laborious (4), a universal relationship would permit replacing these measurements by the very simple cloud point determinations. It would also provide additional insight into the nature of the HLB.

The second objective was to examine the effect of the structural features of the molecules of nonionic surfactants on their cloud points, using the HLB as a reference scale. The large number of published cloud point values permits a comprehensive survey.

HLB CALCULATIONS

For addition products of p molecules ethylene oxide (EO) to alcohols and phenols of mol. wt. M , the HLB value was calculated (2, 5) by

$$HLB = \frac{4405 p}{5(M + 44.05 p)} \quad (\text{Eq. 1})$$

For esters (mol. wt. E) of fatty acids (mol. wt. M), the equation used (5) was

$$HLB = 20(1 - S/A) \quad (\text{Eq. 2})$$

where S is the saponification number of the ester and A the acid

number of the fatty acid. For monocarboxylic acids, $S/A = M/E$. For monoesters of polyethylene glycols, Eqs. 1 and 2 give the same HLB value. For monoesters of methoxypolyethylene glycols, the mol. wt. of the terminal methyl group was included in the mol. wt. M of the acid in order to obtain the same HLB value from both equations.

In the case of the hydroxystearic acids, Eq. 1 was arbitrarily modified to

$$HLB = \frac{100(44.05 p + 17.01 h)}{5(M + 44.05 p)} \quad (\text{Eq. 1a})$$

where h is the number of hydroxyl groups per molecule, because the hydroxyl group is at least as hydrophilic as the ether group.

SIGNIFICANCE OF THE CLOUD POINT

The polyoxyethylene (POE) moiety of nonionic surfactants is less extensively hydrated at higher temperatures (6). Therefore, heating a dilute solution of a polyoxyethylated surfactant increases its tendency toward self-association; the CMC decreases and the size of the micelles increases. Above a given temperature region, called the threshold temperature, the rate of increase of the micellar mol. wt. with rising temperature becomes very pronounced (7). A further temperature rise of 25–30° results in the sudden appearance of cloudiness followed by the separation of a surfactant-rich phase. The surfactant concentration in the coexisting dilute aqueous phase is approximately equal to the CMC (6). The temperature of incipient cloudiness is the cloud point.

This phase separation is reversible: on cooling, the cloudy suspension reverts to a clear solution. The cloud point is independent of surfactant concentration between rather wide limits (8). This is also shown in Table I.

The θ -point of polymer solutions can be defined as the consolute temperature for polymer molecules of infinite mol. wt. (9). According to this definition, the cloud point of nonionic surfactant solutions is analogous to the θ -temperature. However, an alternate definition of the θ -point is that it is the temperature at which the polymer solutions behave ideally, *i.e.*, at which their second virial coefficient is zero (9). This would liken the θ -temperature to the threshold temperature of surfactant solutions (7).

One can also compare the cloud point with the Krafft point of ionic surfactants. The latter is the temperature at which the solubility reaches the CMC, and above which the solubility increases very rapidly with increasing temperature. It is the melting point of the hydrated solid surfactant; at and above the Krafft point, the solid dissolves largely in the form of micelles (6).

The phase separation in surfactant solutions occurs on heating for nonionic and on cooling for ionic surfactants (6). Their two phase diagrams (8, 10), shown schematically in Fig. 1, bear a remarkable resemblance. Region B corresponds to a solid phase (crystals, curd fibers, or gel) suspended in an isotropic solution. Region B_1 corresponds to two isotropic liquids, one rich and one very low in surfactant. Krafft points have very rarely been reported for nonionic surfactants (11).

RESULTS

Observed cloud points and calculated HLB values are tabulated in Table II. Homogeneous surfactants are those prepared by the Williamson synthesis or other methods which produce a single value for the number p of EO units per surfactant molecule. Surfactants produced by the addition of EO to alcohols, phenols or acids have a range of p values which approximates a Poisson distribution. These are designated normally distributed surfactants.

The following conclusions can be drawn from Table II.

1. An increase in the length of the POE chain of a surfactant makes it more hydrophilic, resulting in higher cloud points and HLB values (4, 6). Within a homologous series based on a given hydrophobic moiety, as p goes up, the increase in cloud point and in HLB per added EO goes down. For instance, adding the eighth EO group in the normally distributed nonylphenol series increased the cloud point by about 28° and the HLB by 0.6 unit. Adding the fifteenth EO group increased the cloud point by 4° and the HLB by 0.3 unit. Figure 2 illustrates this and shows that the breadth of the mol. wt. distribution has a small effect as well. The HLB tends asymptotically toward 20.

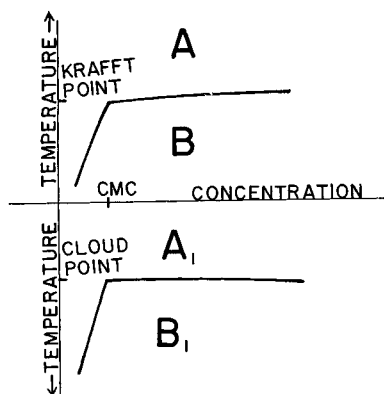


Figure 1—Juxtaposed phase diagrams of a typical anionic (upper) and nonionic (lower) surfactant. Regions A and A_1 represent single-phase, isotropic solutions; regions B and B_1 represent two-phase systems.

Table II—Calculated HLB Values and Experimental Cloud Points for Homologous Series of Nonionic Surfactants

No.	<i>m</i>	<i>p</i>	HLB	Cloud Point, °C.	Reference	No.	<i>m</i>	<i>p</i>	HLB	Cloud Point, °C.	Reference
I. Monoethers, Terminal Hydroxyl						B. Normally Distributed					
1. Linear Primary Alcohols						4. Branched Secondary Alcohols					
<i>n</i> -C _{<i>m</i>} H _{2<i>m</i>+1} O(C ₂ H ₄ O) _{<i>p</i>} H						$ \begin{array}{ccccccc} & & \text{CH}_3 & & & \text{CH}_3 & & \text{CH}_3 \\ & & & & & & & \\ \text{H}_3\text{C} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_3 \\ & & & & & & & & & & & & & & & & \\ & & & & & & & & & & \text{O} & & & & & & \\ & & & & & & & & & & \text{(C}_2\text{H}_4\text{O)}_p\text{H} & & & & & & \end{array} $					
A. Homogeneous						B. Normally Distributed					
1	6	3	11.3	37	12	52	12	6	11.7	36, 37	24, 25
2	6	4	12.7	67.5	12	53	12	10	14.1	72, 73	25, 24
3	6	5	13.7	75	12	5. Branched Alkyl-<i>p</i>-Phenols					
4	6	6	14.4	80.5, 83	12, 13	<i>i</i> -C _{<i>m</i>} H _{2<i>m</i>+1} C ₆ H ₄ O(C ₂ H ₄ O) _{<i>p</i>} H					
5	8	4	11.5	35.5	12	A. Homogeneous					
6	8	5	12.6	55	12	54	8	7	12.0	27	26
7	8	6	13.4	68	8	55	8	8	12.6	52	26
8	10	4	10.5	18	12	56	8	9	13.2	67.5	26
9	10	5	11.6	36	12	57	8	10	13.6	78	26
10	10	6	12.5	57, 60, 61	12, 12, 8	B. Distribution Narrowed by Distillation					
11	12	4	9.7	7, 7	12, 14	58	9	6.5	11.3	10	27
12	12	5	10.8	25, 31, 31	12, 12, 14	59	9	7.6	12.1	38.5	27
13	12	6	11.7	48, 48, 51, 52, 55	8, 12, 14, 12, 15	60	9	7.7	12.1	44	27
14	12	7	12.5	65.5, 67, 70	14, 12, 15	61	9	8.3	12.5	75.5	27
15	12	8	13.1	78, 79, 82	14, 12, 15	62	9	8.9	12.8	58.5	27
16	12	9	13.6	87.5, 88	14, 12	63	9	9.7	13.2	73	27
17	12	10	14.1	94, 95, 98	14, 12, 16	64	9	10.7	13.6	83	27
18	12	11	14.4	98, 100	14, 12	C. Normally Distributed					
19	14	6	11.0	42, 45	8, 12	65	8	7	12.0	15	26
20	16	6	10.4	32, 32, 35	12, 7, 8	66	8	7.5	12.3	19, 21	28, 29
21	16	7	11.2	54, 55	7, 11	67	8	8	12.6	33, 44	18, 26
22	16	9	12.4	75	7	68	8	8.9	13.1	60	26
B. Normally Distributed						69	8	9	13.2	62	26
23	10	10	14.7	88	17	70	8	9.5	13.4	65, 68	29, 28
24	12	5.4	11.2	38	18	71	8	9.7	13.5	67	18
25	12	6.2	11.9	34.5	19	72	8	10	13.6	75	26
26	12	6.8	12.3	55	18	73	8	10.85	14.0	81.5	26
27	12	7.0	12.5	58.5	18	74	8	12.5	14.55	88, 90	29, 28
28	12	8.0	13.1	73	18	75	8	13.0	14.7	89	18
29	12	9.0	13.6	76	20	76	9	7	11.7	5	24
30	12	10	14.1	88	20	77	9	7.4	11.9	24, 24	16, 30
31	12	10.1	14.1	93	18	78	9	8.0	12.3	34	18
32	12	11.0	14.4	99	20	79	9	8.1	12.4	42	30
33	14	10	13.5	75	20	80	9	8.3	12.5	31	27
34	16	10	12.9	74	20	81	9	8.5	12.6	30	31
35	18	10	12.4	68	20	82	9	8.9	12.8	48.5	27
<i>n</i> -C _{<i>m</i>} H _{2<i>m</i>-1} O(C ₂ H ₄ O) _{<i>p</i>} H						83	9	9.0	12.9	54, 54, 54	24, 31, 32
36	18	10	12.4	57, 60	20, 16	84	9	9.2	13.0	55, 56	33, 8
(oleyl)						85	9	9.4	13.05	61	18
2. Branched Primary Alcohols						86	9	9.5	13.1	54, 54, 57	21, 28, 29
<i>(n</i> -C _{<i>m</i>} H _{2<i>m</i>+1}) ₂ CHCH ₂ O(C ₂ H ₄ O) _{<i>p</i>} H						87	9	9.6	13.15	62	30
A. Homogeneous						88	9	9.7	13.2	60.5, 63	27, 34
37	1	6	15.6	100	13	89	9	9.8	13.25	58	17
38	2	6	14.4	78	13	90	9	10	13.3	68	32
39	3	6	13.4	53	13	91	9	10.5	13.6	64, 71	24, 31
40	4	6	12.5	27	13	92	9	10.7	13.6	63.5	27
41	4	9	14.3	72	13	93	9	12	14.1	81	21
<i>i</i> -C ₁₈ H ₂₇ O(C ₂ H ₄ O) _{<i>p</i>} H						94	9	12.4	14.25	87	18
B. Normally Distributed						95	9	12.5	14.3	88	29
42	13	9	13.3	62	21	96	9	13	14.4	88	24
43	13	10.1	13.8	61	17	97	9	13.5	14.6	92.5	27
3. Linear Secondary Alcohols						98	9	14.0	14.7	93	30
$ \begin{array}{c} \text{CH}_3 - \text{CH} - \text{C}_{12}\text{H}_{25} \\ \\ \text{O}(\text{C}_2\text{H}_4\text{O})_p\text{H} \end{array} $						99	9	15	15.0	94, 96, 96, 96	21, 24, 28, 31, 32
A. Homogeneous						100	9	15.8	15.2	101	30
44	14	6	11.0	35	14	101	9	17.7	15.6	107, 107	16, 30
45	14	9	13.0	67	14	102	12	9.0	12.0	18, 18, 33	24, 25, 33
46	C ₃ H ₁₁		13.0	31	14	103	12	10.2	12.6	37	17
$ \begin{array}{c} \text{O}(\text{C}_2\text{H}_4\text{O})_p\text{H} \\ \\ \text{CH}_3 - (\text{CH}_2)_a - \text{CH} - (\text{CH}_2)_b - \text{CH}_3 \\ \\ \text{O}(\text{C}_2\text{H}_4\text{O})_p\text{H} \end{array} $						104	12	11.1	13.0	50	18
<i>m</i> = (<i>a</i> + <i>b</i> + 3) from 11 to 16, av. = 13.2						105	12	12	13.4	60, 63	25, 24
						106	12	15.0	14.3	90, 92, 93, >98	18, 25, 24, 17

Table II—(Continued)

Table II—(Continued)

No.	<i>m</i>	<i>p</i>	HLB	Cloud Point, °C.	Reference
6. Branched Dialkyl Phenols					
$\begin{array}{c} C_6H_{2a+1} \\ \diagdown \\ C_6H_5O(C_2H_4O)_{30}H \\ \diagup \\ C_6H_{2b+1} \\ m = a + b = 29 \end{array}$					
B. Normally Distributed					
107	29	30	14.5	95	28
7. Acetylenic Branched Glycols					
$\begin{array}{ccccccc} & CH_3 & & CH_3 & & CH_3 & & CH_3 \\ & & & & & & & \\ CH_3- & CH & -CH_2- & C & -C \equiv & C & -CH_2- & CH-CH_3 \\ & & & & & & & \\ & H(OH_4C_2)_aO & & & & & & O(C_2H_4O)_bH \\ & & & & & & & p = a + b \end{array}$					
B. Normally Distributed					
108	14	5.1	10.0	5	35
109	14	9.5	13.0	63	35
110	14	15.4	15.0	85	35
8. Sorbitan Monoesters					
B. Normally Distributed					
No.	Acid	<i>p</i>	HLB	Cloud Point, °C.	Reference
111	Lauric	20	16.7	95	36
112	Stearic	20	14.9	76	36
113	Oleic	20	15.0	93	36
II. Monoesters, Terminal Hydroxyl					
B. Normally Distributed					
114	Lauric	10	13.75	46	20
115	Lauric	15	15.35	70	20
116	Lauric	20	16.3	79	20
117	Lauric	25	16.9	83	20
118	Lauric	30	17.4	85	20
119	Lauric	35	17.7	87	20
120	Myristic	15	14.9	65	20
121	Myristic	20	15.9	80	20
122	Myristic	25	16.6	86	20
123	Myristic	30	17.05	89	20
124	Myristic	35	17.4	92	20
125	Palmitic	10	12.6	54	20
126	Palmitic	15	14.4	70	20
127	Palmitic	20	15.5	85	20
No.	Acid	<i>p</i>	HLB	Cloud Point, °C.	Reference
128	Stearic	15	14.0	75	20
129	Stearic	20	15.1	92	20
130	Stearic	25	15.9	94	20
131	Oleic	15	14.0	82	20
132	Oleic	20	15.15	85	20
133	Oleic	25	15.9	87	20
134	Oleic	30	16.5	89	20
135	Oleic	35	16.9	92	20
136	Hydroxystearic	15	14.1	39	20
137	Hydroxystearic	20	15.2	67	20
138	Hydroxystearic	25	16.0	87	20
139	Hydroxystearic	30	16.5	91	20
140	Hydroxystearic	35	16.9	93	20
141	9,10-Dihydroxystearic	10	12.5	32	20
142	9,10-Dihydroxystearic	15	14.2	47	20
143	9,10-Dihydroxystearic	20	15.3	62	20
144	9,10-Dihydroxystearic	25	16.0	72	20
145	9,10-Dihydroxystearic	30	16.6	78	20
146	9,10-Dihydroxystearic	35	17.0	83	20
147	Phenylstearic	15	12.9	49	20
148	Phenylstearic	20	14.2	65	20
149	Phenylstearic	25	15.1	78	20
150	Phenylstearic	30	15.7	89	20
151	<i>o</i> -Xylylstearyl	20	13.9	63	20
152	<i>o</i> -Xylylstearyl	25	14.8	75	20
153	<i>o</i> -Xylylstearyl	30	15.5	82	20
154	<i>o</i> -Xylylstearyl	35	16.0	87	20
III. Diethers, Terminal Methoxyl					
$n-C_mH_{2m+1}O(C_2H_4O)_pCH_3$					
A. Homogeneous					
No.	<i>m</i>	<i>p</i>	HLB	Cloud Point, °C.	Reference
155	10	10	14.4	69.5	12
156	10	12	15.1	76	8
157	12	12	14.5	78	8
IV. Ester-Ethers, Terminal Methoxyl					
$n-C_mH_{2m+1}COO(C_2H_4O)_pCH_3$					
B. Distribution Narrowed by Distillation of Methoxypolyethylene Glycols					
158	7	7.6	13.6	44	6
159	9	7.0	12.5	44	6
160	9	10.3	14.2	65	6
161	9	11.9	14.8	74	6
162	11	6.0	11.05	31	6
163	11	8.4	12.7	53	6
164	11	11.2	13.9	74	6
165	11	12.5	14.4	79	6

2. The calculated HLB is the weight-ratio of hydrophilic to hydrophobic + hydrophobic moieties of a surfactant. It is independent of the absolute size of these moieties and of the mol. wt. of the surfactant. This is not true of the cloud point: staying within a given class of surfactants (e.g., *n*-alkanol adducts) and maintaining the calculated HLB constant, the cloud point generally rises as the hydrophilic and hydrophobic moieties increase in size. This is seen in Figs. 3-6, except that in the case of the *n*-alkanol adducts, the plots went through minima for *p* values in the range of 5-6 and for *m* values of 8-10.

For this reason, all subsequent conclusions are based on com-

parisons between surfactants having not only the same HLB but also comparable molecular weights.

3. Within a homologous series of surfactants having the same hydrophobic moiety and varying *p*, the relation between cloud point and HLB is not quite linear. Most plots are slightly concave toward the HLB axis, indicating that the cloud point does not increase quite as fast as the HLB with increasing *p*.

The constants for the equation

$$\text{cloud point (°C.)} = a + b \text{ HLB} + c (\text{HLB})^2 \quad (\text{Eq. 3})$$

obtained by the method of least squares for different homologous

Table III—Effect of Surfactant Homogeneity on Cloud Points

Hydrophobic Moiety	Surfactant Numbers	ΔT^a °C. at <i>p</i> Values						
		6	7	8	9	10	10.7	11
<i>n</i> -Dodecanol	12-18 vs. 24-32	18	12	10	8	3	1	0
<i>i</i> -Octylphenol	54-57 vs. 65-75		13	13	6	5		
<i>i</i> -Nonylphenol	58-64 ^b vs. 76-101		22	18	15	13	12	

^a Difference in cloud point between a homogeneous surfactant and a normally distributed surfactant of the same nominal composition. ^b Products fractionated by molecular distillation (27).

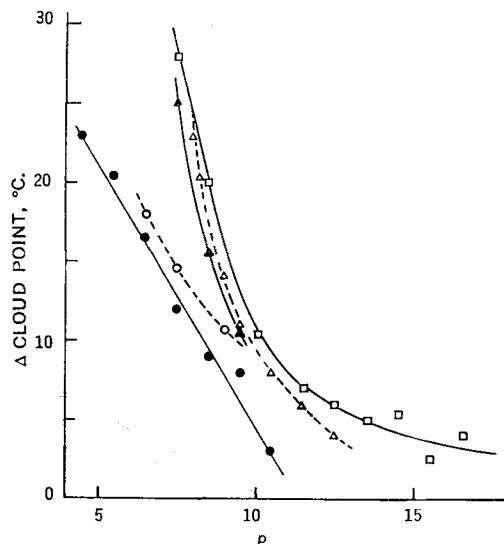


Figure 2—Cloud point increment per EO group as a function of the number p of EO groups per surfactant molecule. Key: n -dodecanol adducts—homogeneous, ●; normally distributed, ○; i -octylphenol adducts—homogeneous, ▲; normally distributed, △; i -nonylphenol adducts—normally distributed, □.

series, were as follows: for the normally distributed nonylphenol series (Nos. 76–101), $a = -874.6$, $b = 114.65$, and $c = -3.323$. For the normally distributed octylphenol series (Nos. 65–75), $a = -1880.1$, $b = 261.60$, and $c = -8.679$. For the homogeneous dodecanol adducts (Nos. 11–18), $a = -323.7$, $b = 43.098$, and $c = -0.9474$. The standard errors of the estimate were 2.8, 3.7, and 2.5, respectively.

For normally distributed dodecanol adducts (Nos. 24–32), a linear relation gave the best fit:

$$\text{cloud point (}^{\circ}\text{C.)} = -197.5 + 20.415 \text{ HLB} \quad (\text{Eq. 4})$$

4. Homogeneous surfactants and surfactants of narrowed mol. wt. distribution have higher cloud points than the corresponding normally distributed surfactants with the same average composition. The cloud point differences decrease as p increases, because the increase in cloud point per added EO group decreases in that direction. This is seen in Table III, based on interpolated cloud point values. The lower cloud points of the normally distributed surfactants are most likely due to the presence of a fraction of very low degree of polyoxyethylation, which is insoluble in water at all temperatures. This fraction is solubilized by micelles of the bulk of the surfactant. Most solubilizes lower the cloud point of dodecanol adducts (Fig. 2.33 of Reference 6). Solubilizes containing an aromatic ring or a hydroxyl group lower the cloud point of alkylphenol adducts (Table I of Reference 8 and Fig. 2.32 of Reference 6); both features are present in the water-insoluble fraction of these surfactants.

The variation in the cloud point values published for a given homogeneous surfactant attests to the difficulty of preparing these compounds in chemically pure form. For No. 12, there is a 6° spread among the reported cloud points, and a 7° spread for No. 13.

5. At a comparable molecular formula, branching of the hydrophobic moiety lowers the cloud point (see Table IV). Compare also the interpolated cloud points of normally distributed dodecanol and tridecanol adducts of HLB = 14.1, namely: 91° for the adduct of the linear primary C_{12} alcohol (interpolated in Nos. 24–32); 81° for the adduct of the linear secondary $C_{13.2}$ alcohol (interpolated in Nos. 47–51); and 72.5° for the adduct of the branched secondary C_{12} alcohol (No. 53). A drastic drop in cloud point with increasing molecular symmetry was found between the isomeric homogeneous surfactants Nos. 45 and 46, and a smaller drop between Nos. 19 and 44.

6. The introduction of a double bond into the hydrocarbon moiety of a surfactant, while raising the calculated HLB value by 0.05 unit or less, produces significant changes in the cloud point. These changes vary in direction and magnitude. The following values have been found for the difference Δ = cloud point of saturated

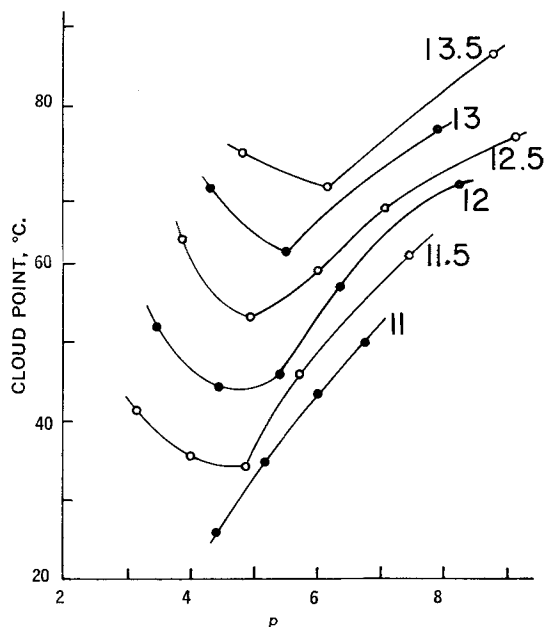


Figure 3—Cloud point versus p at constant HLB for homogeneous $C_m H_{2m+1} O(C_2 H_4 O)_p H$ surfactants. Numbers on curves are HLB values.

surfactant — cloud point of corresponding unsaturated surfactant. $\Delta = 10^{\circ}$ for octadecanol adducts (Nos. 35 and 36); -17° for sorbitan ester adducts (Nos. 112 and 113); -7° , $+7^{\circ}$, $+7^{\circ}$, and more than 11° for octadecanoic esters containing 15, 20, 25, and 30 EO units, respectively (Nos. 128–134). Similar reversals in direction have been found when comparing surface and interfacial tensions of stearyl and oleyl-based polyoxyethylated surfactants as a function of p (20).

7. The introduction of a triple bond into the hydrophobic moiety seems to raise the cloud point; the interpolated cloud points of acetylenic secondary diol adducts (Nos. 108–110) are 3° above the cloud points of saturated secondary monoalcohol adducts (Nos. 52 and 53) of comparable HLB, despite the greater branching of the former due to the existence of two POE chains.

8. It is difficult to assess the effect of a phenyl group in the main chain of the hydrophobic moiety on the cloud point, because of differences in the amount of branching of the alkyl group attached to the phenol and in the alkanol. At comparable HLB and mol.

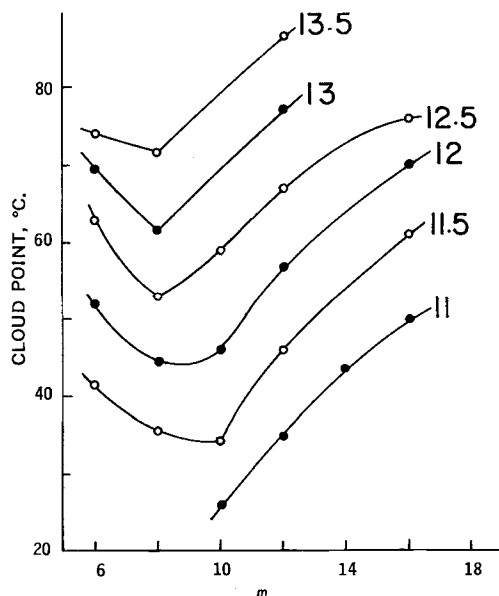


Figure 4—Cloud point versus m at constant HLB for homogeneous $C_m H_{2m+1} O(C_2 H_4 O)_p H$ surfactants. Numbers on curves are HLB values.

Table IV—Effect of Branching on the Cloud Points of Primary Alcohol Adducts of Comparable Molecular Formulas

Hydrophobic Moiety	Surfactant Numbers	<i>p</i>	ΔT^a , °C.
Hexanol	4 vs. 38	6 ^b	4
Octanol	7 vs. 39	6 ^b	15
Decanol	10 vs. 40	6 ^b	32
		HLB	
Dodecanol through } Tetradecanol }	24-33 vs. 42	13.3 ^c	11
	24-33 vs. 43	13.8 ^c	22

^a Difference in cloud point between a linear and a branched surfactant of the same HLB and of similar molecular weights. ^b Homogeneous. ^c Normally distributed.

wt., normally distributed *n*-alkanol adducts have cloud points from 6–28° higher than the corresponding *i*-octylphenol and *i*-nonylphenol adducts, but at least part of this difference is due to branching of the side-chain. On the other hand, at an HLB of 13.8, branched primary $C_{13}H_{27}O(C_2H_4O)_{10.1}H$ (No. 43) has a cloud point 16° below that interpolated for normally distributed $i-C_8H_{17}C_6H_4O(C_2H_4O)_{10.4}H$. At an HLB of 14.1, branched secondary $C_{12}H_{25}O(C_2H_4O)_{10}H$ (No. 53) has a cloud point 10° below that interpolated for $i-C_8H_{17}C_6H_4O(C_2H_4O)_{11.2}H$.

9. A pending phenyl group lowers the cloud point: phenylstearic esters (Nos. 147–150) have cloud points between 5 and 14° lower than stearic esters (Nos. 128–130) of comparable HLB, even though their mol. wts. are higher. This could merely be considered another example of lowering of the cloud point through branching.

10. The introduction of a hydroxyl group into POE stearate surfactants reduced the cloud point; a second hydroxyl reduced it even more. This effect is surprising in view of the extensive hydration of that group (37). It suggests that the hydroxyl groups added EO in competition with the carboxylic acid group, producing branched molecules. This is corroborated by the greater initial rate of EO addition to octadecanol than to stearic acid (20).

Replacing the terminal hydroxyl by a methoxyl group depressed the cloud point considerably. At an HLB of 14.5, the cloud point of $n-C_{12}H_{25}O(C_2H_4O)_{12}CH_3$ (No. 157) was 22° below that interpolated for homogeneous $n-C_{12}H_{25}O(C_2H_4O)_{11.15}H$.

11. Polyethylene glycol esters have considerably lower cloud points than adducts of the corresponding alcohols having comparable HLB values. In the range where the HLB values of normally distributed lauric acid and *n*-dodecanol adducts overlap, the cloud points of the former are 40° or more below those of the latter. The

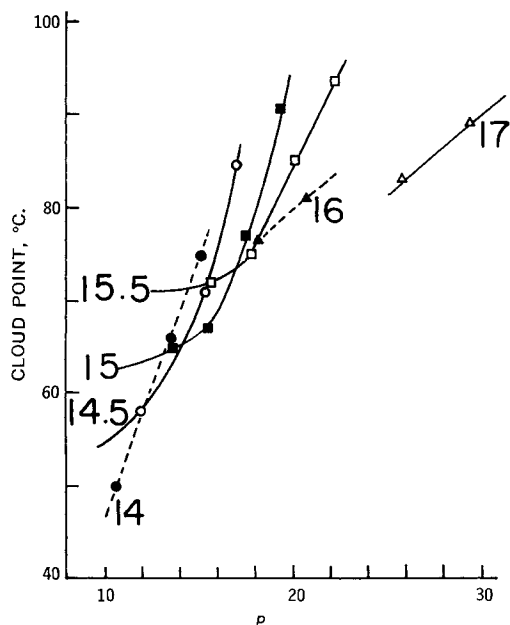


Figure 5—Cloud point versus *p* at constant HLB for normally distributed $C_{m-1}H_{2m-1}COO(C_2H_4O)_pH$ surfactants. Numbers on curves are HLB values.

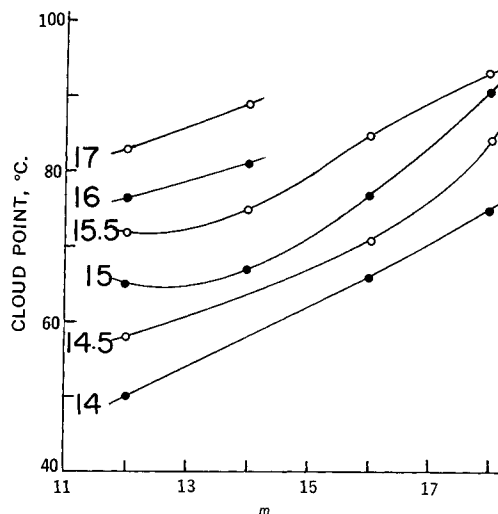


Figure 6—Cloud point versus *m* at constant HLB for normally distributed $C_{m-1}H_{2m-1}COO(C_2H_4O)_pH$ surfactants. Numbers on curves are HLB values.

difference is 18° for palmitic acid and cetyl alcohol adducts of comparable HLB values.

12. Comparison of polyoxyethylated sorbitan esters (Nos. 111–113) with polyethylene glycol esters of the same acid at the same HLB indicates the following: the adducts of sorbitan laurate and oleate have higher cloud points than the corresponding polyethylene glycol laurate and oleate by 13 and 8°, respectively. The cloud point of polyethylene glycol stearate, on the other hand, exceeds that of the corresponding sorbitan stearate by 14°. Since it is not known how many free hydroxyl groups and how many polyethylene glycol chains are present in a polysorbate¹ molecule, it is not possible to ascribe these differences to any structural features.

DISCUSSION

Experimental cloud points were found to be far more sensitive to mol. wt., polydispersity, and structural features of the surfactant molecules than calculated HLB values. Thus, there is no universal relation between the two parameters. A graph correlating them consists not of a line but of a band. For normally distributed surfactants, the width of the band increased from 2 to 3 HLB units with increasing cloud points. The lowest HLB values for a given cloud point belonged to the *n*-dodecanol adducts, the highest to lauric acid adducts. For homogeneous surfactants, the band was 1–1.5 HLB units wide, ranging from *n*-hexadecanol adducts at low HLB to methoxylated lauric acid esters at high HLB.

The foregoing raises the question whether the HLB values calculated by means of Eqs. 1 and 2 are an accurate measure of the emulsifying activity of nonionic surfactants. Alternatively, there is the possibility that the definition of HLB based only on the weight fraction of POE is an oversimplification and does not adequately characterize the wide array of nonionic surfactants developed since Griffin deduced Eqs. 1 and 2 twenty years ago. The true HLB values, like the cloud points, CMC values, and interfacial tensions, may well depend also on structural features, mol. wt. and width of the mol. wt. distribution of the surfactant, which are not contained in Griffin's equations. To decide whether these equations need to be thus modified requires experimental HLB determinations of surfactants differing by one of the following features: high and low molecular weights at constant POE content; broad and narrow mol. wt. distributions at the same average molecular weight; termination by a hydroxyl and an alkoxy group; linear and branched structures; fatty acids and fatty alcohols as hydrophobic moieties, etc.

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Study of Density Gradients in Certain Oil-in-Water Emulsions Using Multichannel Gamma Ray Analysis

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Abstract □ Variations in the attenuation of the 0.084 Mev. total absorption gamma photopeak of ^{170}Tm result when o/w emulsions exhibiting any separation (not necessarily visible) are placed in plastic parallel-sided containers and moved vertically between a radioactive source and a scintillation detector arranged horizontally. Slow raising or lowering of emulsion systems allows the making of an attenuation "map" of the system when data are accumulated using a multichannel analyzer in multiscale mode, and read out via a tape printer. Curves showing log attenuation (and hence density) versus channel number, their first differences, and equations are presented.

Keyphrases □ Density gradients oil-in-water emulsions—analysis □ Analysis, multichannel gamma ray—density gradient □ Emulsions, curves—Pearl-Reed versus Gompertz

The application of the photoextinction method (1, 2) to the state of matter through which visible and other radiation passes has been explored in detail. It has the obvious limitation that unless relative transparency to the incident radiation exists, it is insensitive. Disperse systems are, in general, opaque to visible light,

equally nonconducting to UV radiation, and, since they usually contain some water, are not amenable to IR evaluation unless attenuated total reflectance techniques are employed. Gamma photons of appropriate energy (0.01–0.10 Mev) are a usable source of radiation for the study of disperse systems of pharmaceutical interest whose optical properties forbid the use of visible light, and whose phase densities vary by not more than 0.20 grams per milliliter (3). Studies using scintillation detectors and monoenergetic gamma photons have been carried out (4) which indicate that the logarithm of the radiation intensity attenuation by the intervening system is proportional to the logarithm of the density or the specific gravity of that system. Thus, the ratio of the logarithm of the attenuated or reduced activity to the logarithm of the density of a given system is a constant. This study is concerned with the activity attenuation profiles of certain systems and their relationship to (a) position of maximum change within the system; (b) time dependency of attenuation change, and (c) the rate at which the attenuation change occurs at a given instant or position within a system.