

Solubility Parameter and Hydrophilic-Lipophilic Balance of Nonionic Surfactants

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Abstract □ The solubility parameters of various polyoxyethylated nonionic surfactants were compared with their hydrophilic-lipophilic balance (HLB) numbers. The compounds included three homologous surfactant series based on dodecanol, octylphenol, and fatty acid esters of sorbitan, respectively, a polyoxyethylated sorbitol ester, and a polyethylene glycol. Solubility parameters were calculated from measured heats of vaporization for the polyoxyethylated dodecanol series and from molar attraction constants for all three surfactant series. The values remained nearly constant and independent of the degree of polyoxyethylation, increasing at most by $1 \text{ (cal/cm}^3)^{1/2}$ while the HLB increased from 0 to 10. This discrepancy arose because HLB values are based on emulsification experiments, in which the polyoxyethylene or polyol moiety of the surfactants is hydrated, while the solubility parameter was calculated for anhydrous conditions. When the solubility parameter was corrected for hydration by including a hydrogen-bonding component, plots of HLB versus this new solubility parameter were nearly linear and parallel for the three series of surfactants, with slopes of 5.0 ± 0.2 . The three lines were spaced apart only $\sim 1.2 \text{ (cal/cm}^3)^{1/2}$ despite structural differences among the surfactants, indicating that the chemical nature of the hydrocarbon moiety exerts only a limited effect on the solubility parameter. The HLB, which considers only the weight percent of the hydrocarbon moieties of nonionic surfactants and completely disregards differences in structural features, is, therefore, not as bad an approximation as had previously been thought.

Keyphrases □ Solubility parameter—polyoxyethylated nonionic surfactants, comparison with hydrophilic-lipophilic balance □ Hydrophilic-lipophilic balance—polyoxyethylated nonionic surfactants, comparison with solubility parameter □ Surfactants, nonionic—polyoxyethylated, solubility parameters compared with hydrophilic-lipophilic balance values

The hydrophilic-lipophilic balance (HLB) system was developed by Griffin to characterize the emulsifying efficiency of nonionic surfactants (1). Because the experimental determination of HLB values through emulsification experiments is laborious and not very accurate, the following equation was developed (2, 3):

$$\text{HLB} = \frac{E + P}{5} \quad (\text{Eq. 1})$$

where E is the percent (w/w) of polyoxyethylene and P the percent (w/w) of polyhydric alcohols in the surfactant molecule.

A criticism leveled against the HLB concept, as embodied in Eq. 1, was that it disregards the effect of the chemical nature of the hydrocarbon moiety of the surfactants (4). The purpose of this work is to investigate the application of the solubility

Table I—Values of Hydrophilic-Lipophilic Balance and Solubility Parameters for Polyoxyethylated Dodecanols

| p^a | HLB ^b | δ^c | δ^d | δ^e | δ^f |
|-------|------------------|------------|------------|------------|------------|
| 0 | 0 | 8.04 | — | 8.39 | 9.63 |
| 1 | 3.83 | 8.04 | — | 8.38 | 10.39 |
| 2 | 6.42 | 7.97 | — | 8.47 | 11.02 |
| 3 | 8.30 | 8.51 | — | 8.47 | 11.42 |
| 4 | 9.72 | 8.92 | — | 8.45 | 11.70 |
| 6 | 11.73 | — | 9.49 | 8.41 | 12.09 |
| 8 | 13.08 | — | 9.86 | 8.39 | 12.37 |
| 10 | 14.05 | — | — | 8.37 | 12.57 |
| 12 | 14.79 | — | — | 8.37 | 12.73 |

^a Average number of oxyethylene units per molecule. ^b Calculated by Eq. 1. ^c Calculated by Eq. 2 from experimental ΔH values (12). ^d Calculated by Eq. 2 from ΔH values extrapolated with Eq. 3. ^e Calculated from molar attraction constants in Table I and Eq. 7. ^f Calculated by Eq. 8.

parameter concept (5-7) to nonionic surfactants, because it takes into consideration the nature of their hydrophilic as well as their hydrophobic moieties. Even though the solubility parameter is the subject of much current pharmaceutically oriented research (8, 9), it has been investigated only briefly in connection with nonionic surfactants (10, 11).

BACKGROUND

The solubility parameter, δ , is the square root of the cohesive energy density, i.e., the molar internal energy of vaporization ΔE per unit volume:

$$\delta = \sqrt{\frac{\Delta E}{V_1}} = \sqrt{\frac{(\Delta H - RT)d}{M_r}} \quad (\text{Eq. 2})$$

where $V_1 = M_r/d$ is the molar volume in the liquid state, d is the density, and M_r is the molecular weight. The molar heat of vaporization ΔH refers to constant pressure P . Therefore, it exceeds the molar energy of vaporization, which refers to constant volume, by the expansion term during vaporization $P(V_g - V_l) \cong PV_g = RT$; V_g is the molar volume in the gaseous state, R is the gas constant, and T is the absolute temperature (5-7).

RESULTS

Solubility Parameters from Heats of Vaporization—Vapor pressure measurements from which heats of vaporization can be calculated require such high temperatures that all but homologues with the lowest degrees of oxyethylation undergo decomposition. For polyoxyethylated dodecanol surfactants, $\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_p\text{H}$, heats of vaporization were measured for p values up to 4 (12). A plot of the ΔH values for surfactants with $p = 2, 3$, and 4 fall on a straight line represented by the equation:

$$\Delta H = 8.4 + 5.65p \quad (\text{Eq. 3})$$

where the units of ΔH are kcal/mol.

The densities, d , of polyoxyethylated dodecanols at 25°C are related to the logarithm of the average number, p , of oxyethylene units per molecule by the equation:

$$\log p = -6.64 + 7.63d \quad (\text{Eq. 4})$$

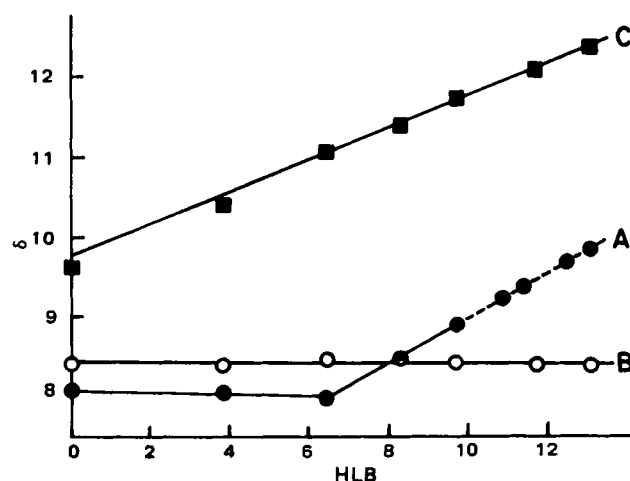


Figure 1—Solubility parameters of polyoxyethylated dodecanols obtained by three methods versus HLB. Key: (●) curve A, δ based on measured (—) and extrapolated (---) heats of vaporization calculated by Eq. 2; (○) curve B, δ calculated from molar attraction constants with Eq. 7; (■) curve C, δ corrected for hydration, based on Eqs. 8 and 9.

For polyoxyethylated *p*-*tert*-octylphenols, the following linear relation holds for *p* values <20:

$$\log p = -12.53 + 12.72d \quad (\text{Eq. 5})$$

Applying Eq. 2 to the measured heats of vaporization (12) of dodecanol-based surfactants with *p* values of 0–4 and to the heats of vaporization extrapolated by Eq. 3 for surfactants with *p* values of 6 and 8 results in the δ values in the third and fourth columns of Table I, respectively, and curve A of Fig. 1. The curve consists of two segments. The first is nearly horizontal. The second, for HLB values >5 (*p* \geq 2), is linear and represented by the equation:

$$\delta = 6.16 + 0.283 \cdot \text{HLB} \quad (\text{Eq. 6})$$

The slopes of both segments are unrealistically small. For the second segment, a change of 1 HLB unit produces a change of only 0.3 (cal/cm³)^{1/2}. The two parameters actually span similar ranges of values: the HLB scale extends from 0 to 20 (Eq. 1) and the δ scale from 5 to 23 (13).

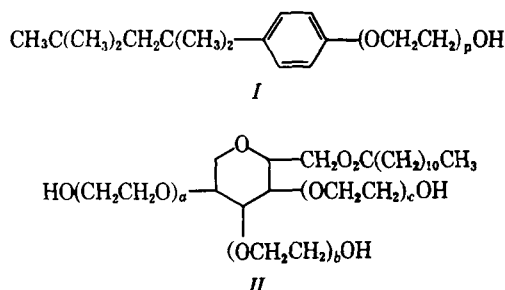
The HLB values of the surfactants in Table I range from 0 to 15, *i.e.*, from surfactants primarily soluble in liquids of low polarity such as vegetable or mineral oils ($\delta \cong 8$) to surfactants primarily soluble in polar liquids like ethyl alcohol ($\delta = 12.8$), propylene glycol ($\delta = 15.0$), and water ($\delta = 23.6$) (1–3). Compounds are most soluble in solvents whose δ values match their own most closely. Since the δ values of the best solvents for the surfactants in Table I cover the range from 8 to at least 15, the δ values of the surfactants should cover a similar range, rather than the more limited range of 8–10 obtained from heats of vaporization. The 8–10 range would indicate highest solubility in liquids of intermediate polarity, such as esters, amines, and ketones (13), for all surfactants. One possible explanation for this discrepancy is that the linear extrapolation by Eq. 3 is unwarranted.

Solubility Parameters from Molar Attraction Constants—Small (14) treated the solubility parameter as an additive-constitutive property. He noted that the so-called molar attraction constants, $F = (\Delta e \cdot v_1)^{1/2}$, were additive; Δe and v_1 are the contributions of the organic functional groups to the molar energy of vaporization and to the molar volume in the liquid state at 25°C, respectively. Therefore, the solubility parameter of a compound can be calculated from the *F* values of its functional groups according to the following equation (14):

$$\delta = \frac{d \sum F}{M_r} \quad (\text{Eq. 7})$$

The *F* values used here, selected from the various published sets (14, 15), are listed in Table II.

The structures for the three classes of surfactants investigated are CH₃(CH₂)₁₁(OCH₂CH₂)_{*p*}OH, and I and II (shown below). In addition to the lauric acid ester of sorbitan shown (II), the stearic and oleic acid esters are also included. The total number of ethylene oxide molecules added during oxyethylation of the sorbitan monoesters are *a* + *b* + *c* = *p*. As long as the value of *p* remains constant, the value of $\sum F$ is not changed if a polyoxyethylene chain is inserted by transesterification between the ester group of the fatty acid and the hexitan ring during the oxyethylation reaction (16). Sorbitan is a mixture of 5- and 6-membered rings. These two ring structures make the same contribution to $\sum F$.



For dodecanol derivatives, the δ values are represented by curve B in Fig. 1 and the fifth column of Table I. For octylphenol and polyol derivatives, the results are listed in the third columns of Tables III and IV, respectively.

The δ values of the dodecanol derivatives based on heats of vaporization are in good agreement with those calculated from molar attraction constants for derivatives with HLB ≤ 10 (*p* ≤ 4) (compare the solid portion of curve A with curve B in Fig. 1). As the number, *p*, of oxyethylene units increases, the calculated δ values remain constant for the dodecanol derivatives: curve B of Fig. 1 is horizontal. The δ values actually decrease slightly for the octylphenol and sorbitan derivatives. Similar observations have been published (10, 11).

Table II—Molar Attraction Constants *F* for Functional Groups of Nonionic Surfactants

| Group | <i>F</i> , (cal/cm ³) ^{1/2} /mol |
|---|--|
| —CH ₃ | 179 |
| —CH ₂ — | 133 |
| CH \equiv | 67 |
| >C< | 0 |
| —CH=CH— | 231 |
| —C ₆ H ₄ — (<i>o</i> -, <i>m</i> -, or <i>p</i> -phenylene) | 658 |
| Saturated 5- or 6-membered ring | 105 |
| —OH aliphatic hydroxyl | 240 |
| —C(=O)O— ester | 303 |
| —O— ether | 70 |

An empirical parameter, the product of the contribution of the hydrocarbon moiety to $\sum F$ times the weight fraction of that moiety, was developed as a consequence. It was inversely proportional to the HLB (11) and offers, therefore, no advantage over that parameter.

The reason that the solubility parameters obtained from these two approaches are nearly independent of the percentage of oxyethylene in the surfactant molecule or its HLB is that they were computed for anhydrous systems. In the absence of water, the molar attraction constant for the ether oxygen is only 70, *i.e.*, not much larger than that of a hydrogen atom. Consequently, the polyoxyethylene moiety increases the polarity of the nonionic surfactant molecule little or not at all above that of its hydrophobic moiety. It is only in the presence of water, where the ether groups are extensively hydrated, that the polyoxyethylene moiety becomes polar and raises the effective δ of the surfactant.

Emulsification experiments measure the HLB values of hydrated surfactants. Even surfactants dissolved in oil have their polyoxyethylene or polyol moieties immersed in water when they are concentrated at the oil–water interface during emulsification. Hydrogen bonding between water and the ether oxygens and/or hydroxyl groups of nonionic surfactants is responsible for their water solubility or, in the case of oil-soluble surfactants, for their surface activity. The two treatments underestimate the solubility parameters because they do not take into account these intermolecular hydrogen bonds.

Solubility Parameters Corrected for Hydrogen Bonding—Intermolecular forces affecting the cohesive energy density of surfactants in the presence of water include not only the dispersion forces (subscript D), which constitute the major components of the *F* values of Table II, but also the dipole–dipole forces (subscript P) and the hydrogen-bonding forces (subscript H). The overall solubility parameter δ_O is calculated from these three components according to (7, 15, 17, 18):

$$\delta_O = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad (\text{Eq. 8})$$

The contribution of the polar forces, δ_P , can be neglected because it is small in relation to the hydrogen-bonding forces (18, 19). Furthermore, the *p* oxygen–carbon dipoles in a randomly coiled polyoxyethylene moiety weaken each other to the point of annihilation (15).

On the assumptions that each hydrogen bond contributes 5000 cal/mol to the energy of vaporization and that each of the *p* ether groups and each hydroxyl group forms one hydrogen bond with water, the hydrogen-bonding component of the solubility parameter is calculated (20) as:

$$\delta_H = \sqrt{\frac{5000(p+1)d}{M_r}} \quad (\text{Eq. 9})$$

Table III—Values of Hydrophilic–Lipophilic Balance and Solubility Parameters for Polyoxyethylated Octylphenols

| <i>p</i> ^a | HLB ^b | δ^c | δ_O^d |
|-----------------------|------------------|------------|--------------|
| 0 | 0 | 8.85 | 10.06 |
| 1 | 3.52 | 8.90 | 10.89 |
| 2 | 5.98 | 8.90 | 11.43 |
| 3 | 7.81 | 8.87 | 11.80 |
| 4 | 9.21 | 8.83 | 12.06 |
| 6 | 11.23 | 8.77 | 12.44 |
| 8 | 12.61 | 8.73 | 12.70 |
| 10 | 13.62 | 8.70 | 12.89 |
| 13 | 14.70 | 8.67 | 13.10 |

^a Average number of oxyethylene units per molecule. ^b Calculated by Eq. 1. ^c Calculated from molar attraction constants in Table II and Eq. 7. ^d Calculated by Eq. 8.

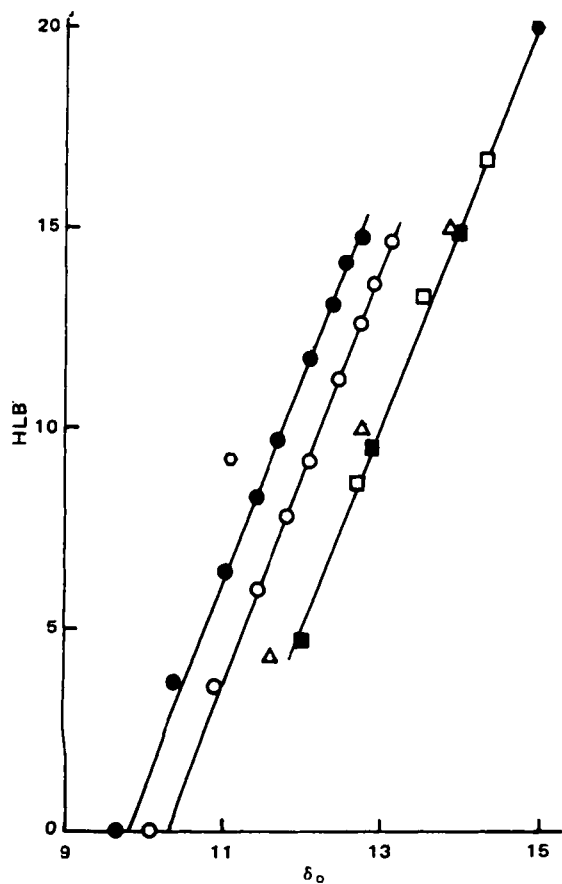


Figure 2—Relationship between HLB and δ_O for three classes of polyoxyethylated surfactants. Key: (●) dodecanol derivatives; (○) octylphenol derivatives; (△) sorbitan monooleate derivatives; (■) sorbitan monostearate derivatives; (□) sorbitan monolaurate derivatives; (○) polyoxyl 40 sorbitol septaoleate; (●) polyethylene glycol 3350.

for the dodecanol and octylphenol derivatives, which have one hydroxyl group per molecule. For sorbitan derivatives containing p oxyethylene units, the coefficient is $p + 4$ to account for the ether linkage in the ring and the three hydroxyl groups. For a polyethylene glycol formed by adding p ethylene oxide molecules to one water molecule, it is $p + 1$ since the compound contains $p - 1$ ether linkages and two hydroxyl groups.

Because hydrogen bonding is an unsymmetrical interaction, two δ_H parameters are sometimes employed, one for proton donation or acid character, the other for acceptor or base effects (18). In the present study, almost all donors are water molecules and all acceptor groups are ether linkages. Therefore, the acid nature of the donor groups and the basic nature of the acceptor groups were constant in all surfactant systems, justifying the use of a single δ_H parameter and the assumption of a constant contribution of 5000 cal/mol for all hydrogen bonds to the molar energies of vaporization (20).

The overall solubility parameter δ_O was calculated according to Eq. 8 as follows. The δ values based on the molar attraction constants and Eq. 7 were used as the dispersion component δ_D ; δ_P was neglected, and δ_H was calculated by Eq. 9. The δ_O values for the three classes of surfactants are listed in the last columns of Tables I, III, and IV. For the dodecanol derivatives, they are plotted in Fig. 1 on curve C. They include the effect of hydration on the polarity of the nonionic surfactants, *i.e.*, they are corrected for intermolecular hydrogen bonds.

For polyethylene glycol 3350¹, δ or δ_D is 9.28 and δ_O is 14.96. These two values are in good agreement with the experimental δ values determined for this compound, namely, 8.9 as the lower end of the range in poorly hydrogen-bonded solvents and 14.5 as the upper end of the range in strongly hydrogen-bonded solvents, especially, water (18). The former value corresponds to δ_D and the latter to δ_O . This agreement validates the methods for computing δ_O , δ_D , and δ_H .

¹ Carbowax 4000; Union Carbide Corp.

Table IV—Values of Hydrophilic-Lipophilic Balance and Solubility Parameters for Polyoxyethylated Polyols

| Polyol | p^a | HLB ^b | δ^c | δ_O^d |
|-----------------------------------|-------|------------------|------------|--------------|
| Sorbitan monolaurate | 0 | 8.6 | 10.02 | 12.73 |
| | 4 | 13.3 | 9.83 | 13.51 |
| | 20 | 16.7 | 9.50 | 14.31 |
| Sorbitan monostearate | 0 | 4.7 | 9.77 | 11.99 |
| | 4 | 9.6 | 9.68 | 12.87 |
| | 20 | 14.9 | 9.44 | 13.94 |
| Sorbitan monooleate | 0 | 4.3 | 9.36 | 11.59 |
| | 5 | 10.0 | 9.38 | 12.74 |
| | 20 | 15.0 | 9.34 | 13.85 |
| Sorbitol septaoleate ^e | 40 | 9.2 | 8.41 | 11.10 |

^a Average number of oxyethylene units per molecule. ^b Taken from "General Characteristics of Surfactants," ICI Americas, Inc., Wilmington, Del., 1979. ^c Calculated from molar attraction constants in Table II and Eq. 7. ^d Calculated by Eq. 8. ^e Atlox 1087; ICI Americas, Inc., Wilmington, Del.

CONCLUSIONS

The δ_O values for the nonionic surfactants based on dodecanol, octylphenol, and sorbitan are plotted against their HLB values in Fig. 2. The points for the three classes of sorbitan esters based on lauric, stearic, and oleic acid, respectively, nearly fall on a single straight line which also includes polyethylene glycol 3350. The curves for the dodecanol and octylphenol derivatives are linear down to HLB values of 6. The three straight lines are parallel with slopes, $d\text{HLB}/d\delta_O$, of 5.0 ± 0.2 ; the \pm sign precedes the range of values.

The surprising fact is that the three curves belonging to three different categories of surfactants are spaced only ~ 1.2 (cal/cm³)^{1/2} apart despite the structural differences. This observation indicates that the nature of the hydrocarbon moiety of nonionic surfactants affects their solubility parameter only to a limited extent. The objection that the HLB calculated by Eq. 1 does not take into account the nature of the hydrocarbon moiety but only its weight percentage (or the weight percentage of the polyoxyethylene or polyol moiety, E or P) (4) has only limited validity. The solubility parameter takes the nature of the hydrocarbon moiety into account. Yet, at comparable HLB values, solubility parameters for different classes of surfactants based on different types of hydrocarbons are identical within limits that are narrower than ± 1 (cal/cm³)^{1/2}.

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