Multiregressional Analysis of the Griffin HLB Numbers for Polyoxyethylene Polyoxypropylene Surfactants

By WERNER LOWENTHAL

Using data from 32 polyoxypropylene polyoxyethylene surfactants and the technique of multiregressional analysis, an equation was determined. This equation describes the relationship between Griffin HLB number, percent polyoxyethylene in the total molecule, and the typical molecular weight of the polyoxypropylene. From the equation, given any two variables, the third variable can be readily determined with good accuracy for this series of polymeric surfactants.

POLYOXYETHYLENE POLYOXYPROPYLENE[1] surfactants are block polymers prepared by adding ethylene oxide to a polyoxypropylene chain. This produces a series of compounds that have the following formula: $HO(CH_2CH_2O)_a(CHCH_3CH_2O)_b$-$(CH_2CH_2O)_cH$, where a and c are the number of ethylene oxide units and b is the number of propylene oxide units. Since the chain lengths can be varied, surfactants having different properties may be prepared. The propylene oxide chain is hydrophobic and the ethylene oxide chains are hydrophilic.

RESULTS AND DISCUSSION

A method called the Pluronic Grid which characterizes the available surfactants in this group has been published (1). This grid is actually a graphical plot of percent polyoxyethylene in the total molecule on one axis, and the typical molecular weight of the polyoxypropylene hydrophobic base on the other axis (1). At the points of intersection of the two variables on this grid, the different surfactants available are noted. The Griffin HLB number (2) for 32 of these surfactants is also available. Using these three sets of data, it is possible to calculate a multiregressional analysis to determine the relationships between the molecular weight of the hydrophobic group, the percent of hydrophilic groups in the total molecule, interactions between these two variables, and the HLB number.

The initial equation for which the constants and coefficients were determined using the RPC 4000 computer[2] was written as:

$$Y = b_0 + b_1X_1 + b_{11}X_1^2 + b_2X_2 + b_{22}X_2^2 + b_{12}X_1X_2 \quad \text{(Eq. 1)}$$

where Y is the HLB number, X_1 is the typical molecular weight of the hydrophobic group, X_2 is the percent polyethylene oxide in the total molecule, b_0 is a constant, and the other b values are coefficients. The constant and coefficients were calculated, and t tests (3) showed that only the coefficients for X_1, X_1^2, and X_2 were statistically significant. Equation 1 then reduced to:

$$Y = 3.01 - 0.00231X_1 + 1.94 \times 10^{-7}X_1^2 + 0.371X_2 \quad \text{(Eq. 2)}$$

A more detailed grid was drawn from HLB values obtained by selecting values of X_1 between 950 and

TABLE I—CALCULATED HLB NUMBERS USING EQ. 2

Surfactant	Given HLB No.	Calcd. HLB No.
L31	4.5	4.7
L35	18.5	19.5
F38	30.5	30.7
L42	8.0	7.9
L43	12	11.6
L44	16	15.4
L61	3	3.3
L62	7	7.0
L63	11	10.7
L64	15	14.4
P65	17	18.1
F68	29	29.2
L72	6.5	6.5
P75	16.5	17.6
F77	24.5	25.1
L81	2	2.5
P84	14	13.6
P85	16	17.3
F87	24	24.8
F88	28	28.5
L92	5.5	5.5
P94	13.5	13.0
F98	27.5	27.8
L101	1	1.3
P103	9	8.7
P104	13	12.4
P105	15	16.1
F108	27	27.2
L121	0.5	0.6
L122	4	4.3
P123	8	8.0
F127	22	22.8

4000 and values of X_2 between 10 and 80, substituting these numbers into Eq. 2, and solving for the HLB values. The HLB numbers for each corresponding set of X_1 and X_2 values were then plotted on rectangular coordinate paper and lines drawn connecting equal HLB numbers. The topography of this grid showed that, in the range of values used, a flat plain existed inclining from high HLB numbers at high percent hydrophilic groups and low molecular weight hydrophobic group, to low HLB numbers at low percent hydrophilic groups and high molecular weight hydrophobic group.

Table I shows the values calculated with Eq. 2 and the published values. The numbers in column one are the commercial names of the polyoxyethylene polyoxypropylene surfactants.

The average difference between the given and calculated HLB numbers is 0.45 units, which is probably within the error in determining HLB numbers.

CONCLUSIONS

The solution of a multiregression equation showed that the Griffin HLB numbers are directly related to the molecular weight of the hydrophobic group and percent of hydrophilic groups in the total molecule,

in polyoxypropylene polyoxyethylene surfactants. The HLB numbers can be calculated from the derived equation which closely agree with the observed values for this series of surfactants. Conversely, part of the molecular structure of the surfactant can be determined, *e.g.*, the molecular weight of the hydrophobic group or the percent hydrophilic groups in the total molecule, when the HLB number and one of the other variables of a particular surfactant of this series are given

REFERENCES

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⊙⟶ *Keyphrases*

Polyoxyethylene polyoxypropylene surfactants
Griffin HLB numbers—multiregressional analysis
Hydrophobic group, M.W.—HLB relation
Hydrophilic group, percent—HLB relation

Cactus Alkaloids IV. Macromerine from *Coryphantha runyonii*

By L. E. BELOW, A. Y. LEUNG, J. L. McLAUGHLIN*, and A. G. PAUL

Macromerine, a β-phenethylamine alkaloid previously isolated from *Coryphantha macromeris*, has been isolated from *Coryphantha runyonii*

HODGKINS *et al.* (1) have recently isolated a new β-phenethylamine, macromerine, from the cactus, *Coryphantha macromeris* (Engelm.) Lemaire. Physiological tests demonstrated that macromerine has potential hallucinogenic and sympatholytic activities. From physical data, spectra, and elemental analysis they proposed that macromerine is *l*-α-3,4-dimethoxyphenyl-β-dimethylaminoethanol, and they have confirmed this structure by synthesis of the racemic mixture.

Working independently in this laboratory using thin-layer chromatography (TLC) several unknown alkaloids were detected in a related species of cactus, *Coryphantha runyonii* Britton and Rose (2). Since the alkaloids detected produced TLC patterns different from those of previously known cactus alkaloids, isolation attempts were initiated.

EXPERIMENTAL

Using large Soxhlet extractors, alkaloids were extracted with ethanol from 1.8 Kg. of dried and pulverized plant material.[1] Nonphenolic alkaloids were isolated from the ethanolic residue using the procedures and ion-exchange column technique of purification method No. 2 (3). The total nonphenolic alkaloid fraction was chromatographed over 560 Gm. of activated alumina in a 40 × 150 cm. column using chloroform as the developer. Eluant fractions of 15–20 ml. each were collected and analyzed by TLC. Those fractions richest in concentrations of the major alkaloid were combined. The crystalline residue obtained (1.314 Gm.; yield 0.07%) was recrystallized several times from ethyl ether (m.p. 65–65.5°; picrate m.p. 159°; optical rotation: $[\alpha]_D^{26} = -54.2$, c = 0.0120 Gm./ml. in methanol).

The isolated alkaloid appeared as a single spot upon TLC analysis in several solvent systems, indicating its homogeneity.

Permanganate oxidation (4) of the alkaloid produced a crystalline derivative which was identified as 3,4-dimethoxybenzoic acid by melting point, mixed melting point, and IR spectral comparison. Elemental analysis[2] of the alkaloid indicated an empirical formula of $C_{12}H_{19}NO_3$.

Calcd. for C, 63.98; H, 8.50; N, 6.22; mol. wt. 225.29. Found: C, 65.02; H, 8.39; N, 6.29.

The UV spectrum (0.016 mg./ml. methanol) showed a λ_{max} at 202 mμ and smaller peaks at 230 mμ and 278 mμ, indicating typical benzene ring absorption. The IR spectrum in KBr revealed a broad band at 3120 cm.$^{-1}$ (hydroxyl). NMR spectra in $CDCl_3$ showed peaks at 6.99 δ and 6.89 δ, indicative of three aromatic hydrogens, and a doublet of doublets centered at 4.67 δ, indicative of a benzylic hydrogen adjacent to two nonequivalent methylene protons (5). An alcohol hydrogen (3.96 δ) showed shifts with varying concentrations and disappeared with D_2O exchange. A doublet centered at 3.90 δ indicated two methoxyl groups, a doublet centered at 2.48 δ indicated a methylene group, and a singlet at 2.35 δ indicated two methyl groups attached to nitrogen.

Analysis by high resolution mass spectrometry[3] showed a weak molecular ion peak at $m/e = 225.1362$, in agreement with the proposed empirical formula. Prominent peaks appeared at $m/e = 208$, 207, 192, 180, 167, 166, 165, 164, and 151, postulated structures of which are compatible with the expected fragmentation pattern of macromerine.

The UV, IR, and NMR spectra of the alkaloid and the spectra of natural *l*-macromerine from *C. macromeris* as well as synthetic *d,l*-macromerine are essentially identical. In addition the melting point of *l*-macromerine (m.p. 65–65.5°) was not depressed by admixture (mixed m.p. 65–65.5°) with the alkaloid isolated from *C. runyonii*.[4]