The alkyltrimethylammonium bromides were checked for tertiary amine content using TLC. The 20 × 20-cm. glass plates were coated with a 0.25-mm. thickness of aluminum oxide G, using a Desega spreader, and were air dried. For spotting, pure tertiary amines[6] were diluted with ethanol, and the alkyltrimethylammonium bromides were dissolved in water. The dilutions were calculated so that the weight of tertiary amine deposited from a calibrated capillary tube was approximately 0.1% of the weight of quaternary surfactant deposited. The developing solvent was a mixture of acetone and water (100:5), and Dragendorff's reagent was used to color the quaternaries and the tertiary amines orange. The more polar quaternaries were strongly adsorbed onto the substrate and thus moved only a short distance from the point of application. It was estimated that there was less than 0.2% tertiary amine in each quaternary compound examined. These quantities would not significantly alter the analyses based on GLC.

The results for the alkyltrimethylammonium bromides are shown in Table II; they are the mean of at least two analyses, and repetitive runs in general differed by less than 1%.

These results have been used to confirm the validity of Shinoda's equation (14) for predicting the CMC of mixtures of quaternary ammonium surfactants containing up to seven components (15). They have also been used to investigate the mechanism of the self-bodying action of mixed emulsifiers of the type alkyltrimethylammonium bromides–cetostearyl alcohol (5, 6).

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[6] Dimethylaminododecane, dimethylaminotetradecane, and dimethylaminooctadecane, Fluka, Buchs S. G., Switzerland.

Octahedral Hybridization of Hydrogenic Orbitals in Molecular Orbital and Ligand Field Calculations

Keyphrases ☐ Hydrogenic orbitals—octahedral hybridization ☐ Molecular orbital, ligand field calculations—octahedral hybridization of hydrogenic orbitals

Sir:

Various quantum chemical methods have been applied to the correlation of theoretical indexes of drug and biochemical activity with experimentally determined quantities (1). Among these are molecular orbital theory and ligand field theory. The applications of these treatments to any molecular system containing hexacoordinate atoms (*e.g.*, transition metal ions in metalloenzymes) necessarily entails knowledge of a set of six d^2sp^3 hybrid orbitals, composed of linear combinations of the hydrogenic s, p, and d orbitals, to describe the bonding situation and to provide the appropriate orbitals for the calculation of π-electron energies, charge densities, and other indexes of molecular reactivity (2). The construction of d^2sp^3 hybrid orbitals was originally discussed by Pauling (3). The set of d^2sp^3 hybrids given by Pauling is:

$$\psi_1 = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_z \qquad \text{(Eq. 1)}$$

$$\psi_2 = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_z \qquad \text{(Eq. 2)}$$

$$\psi_3 = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{12}}d_z + \frac{1}{2}d_x + \frac{1}{\sqrt{2}}p_x \qquad \text{(Eq. 3)}$$

$$\psi_4 = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{12}}d_z + \frac{1}{2}d_x - \frac{1}{\sqrt{2}}p_x \qquad \text{(Eq. 4)}$$

$$\psi_5 = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{12}}d_z - \frac{1}{2}d_x + \frac{1}{\sqrt{2}}p_y \qquad \text{(Eq. 5)}$$

$$\psi_6 = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{12}}d_z - \frac{1}{2}d_x - \frac{1}{\sqrt{2}}p_y \qquad \text{(Eq. 6)}$$

where ψ_1–ψ_6 are the d^2sp^3 hybrids and s, p_x, p_y, p_z, and d_z are hydrogenic orbitals. Necessary and sufficient conditions for the set ψ_1–ψ_6 to form a complete set of d^2sp^3 orbitals are that the orbitals are equivalent (*i.e.*, they each contain probability density of s, p, and d character in the ratio of 1:3:2), they are normalized (*i.e.*, $\int \psi_i \psi_i dT = 1$, where dT is the volume element in space), and they are orthogonal to one another (*i.e.*, $\int \psi_i \psi_{j \neq i} dT = 0$). Upon examination of the atomic orbital coefficients, it can be seen that the hybrid orbitals fulfill the required conditions of equivalence and normalization but do not form an orthogonal set. For example, the integral of the product of ψ_1 and ψ_4 is not zero but rather $^1/_3$.

These errors have been carried over into standard texts on chemical bonding (2, 4). It is, therefore, in order to call attention to this matter; the use of the nonorthogonal set of d^2sp^3 hybrids in molecular orbital and ligand field calculations will result in errors in off-diagonal terms of matrixes used to calculate values of physical variables. A correct set of equivalent, normalized orthogonal d^2sp^3 hybrids is:

$$\psi_1 = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_z \quad \text{(Eq. 7)}$$

$$\psi_2 = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_z \quad \text{(Eq. 8)}$$

$$\psi_3 = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{12}}d_z + \frac{1}{2}d_x + \frac{1}{\sqrt{2}}p_x \quad \text{(Eq. 9)}$$

$$\psi_4 = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{12}}d_z + \frac{1}{2}d_x - \frac{1}{\sqrt{2}}p_x \quad \text{(Eq. 10)}$$

$$\psi_5 = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{12}}d_z - \frac{1}{2}d_x + \frac{1}{\sqrt{2}}p_y \quad \text{(Eq. 11)}$$

$$\psi_6 = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{12}}d_z - \frac{1}{2}d_x - \frac{1}{\sqrt{2}}p_y \quad \text{(Eq. 12)}$$

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Hydrophilic–Lipophilic Balance and Distribution Coefficients of Nonionic Surfactants

Keyphrases ☐ Hydrophilic–lipophilic balance, nonionic surfactants—distribution coefficient correlation ☐ Distribution coefficient correlation—hydrophilic–lipophilic balance, nonionic surfactants ☐ Nonionic surfactants—hydrophilic–lipophilic balance and distribution coefficients

Sir:

The hydrophilic–lipophilic balance (HLB) of nonionic surfactants has been correlated with many of their physical properties such as dielectric constants, heats of hydration, critical micelle concentrations, cloud points, phase inversion temperatures of emulsions, spreading coefficients of oil on water or of water on oil, and interfacial tensions at oil-water interfaces. In general, good correlations were found between the HLB and these properties within a given homologous series of surfactants. However, as soon as the chemical characteristics of the hydrophilic or lipophilic moieties were changed, *e.g.*, by going from a polyoxyethylated surfactant to a sorbitan derivative or from a *n*-alkanol base to an alkylphenol base, different correlations were obtained. So far, the search for a universal correlation between the HLB and another property of the surfactant, which could be determined more readily than the HLB, has not been successful.

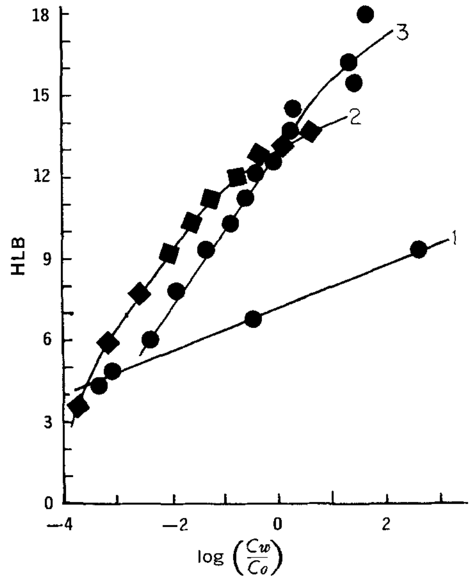

Figure 1—*Relationship between correct HLB values and the logarithms of the water–oil distribution coefficients. Key: Curve 1, sorbitan monoesters; Curve 2, homogeneous polyoxyethylated octylphenols; and Curve 3, normally distributed polyoxyethylated octylphenols.*

Intuitively, the distribution coefficient of the surfactants between water and oil, C_w/C_o, would seem to be well suited for correlation with the balance between their hydrophilic and lipophilic tendencies. Davies and Rideal (1) combined the kinetic treatment of emulsion coalescence with the free energy change of transferring a surfactant molecule from water to oil and arrived at the following correlation:

$$\text{HLB} = 7 + 0.829 \log (C_w/C_o) \quad \text{(Eq. 1)}$$

Table I—Comparison between Experimental HLB Values and Values Derived from Distribution Coefficients

Surfactant	Experimental HLB[a]	$\left(\frac{C_w}{C_o}\right)^b$	HLB from Eq. 1
Sorbitan monooleate[c]	4.3	3.70×10^{-4}	4.2
Sorbitan monostearate[d]	4.7	6.19×10^{-4}	4.3
Sorbitan monopalmitate[e]	6.7	0.314	6.6
Polyoxyethylene sorbitol oleate[f]	9.2	367	9.1
	HLB from Eq. 2*a*	$\left(\frac{C_w}{C_o}\right)^g$	HLB from Eq. 1
Octylphenol(EO)$_1$	3.5	1.84×10^{-4}	3.9
Octylphenol(EO)$_3$	7.8	3.13×10^{-3}	4.9
Octylphenol(EO)$_6$	11.2	5.92×10^{-2}	6.0
Octylphenol(EO)$_{10}$	13.6	3.85	7.5

[a] From *Reference 2.* [b] From *Reference 1.* [c] Span 80. [d] Span 60. [e] Span 40. [f] Atlox 1087. [g] From *Reference 3.*