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Hydrophile–lipophile balance of alkyl ethoxylated surfactants as a function of intermolecular energies

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SUMMARY

The semiempirical MNDO method has been used in order to examine the variation of the molecular properties of hydrocarbons C_nH_{2n+2} (with $1 \leq n \leq 19$) and ethylene oxide chains $CH_3(CH_2CH_2O)_mCH_3$ (with $1 \leq m \leq 19$) as a function of their molecular length. Least-square fits of those properties have been calculated, along with two mathematical relations between the hydrophile–lipophile balance of alkyl-phenol ethoxylated surfactants and (1) the ratio of molecular lengths between their lipophilic and hydrophilic branches; (2) the intermolecular energies between the molecules of surfactant, water and hexane.

INTRODUCTION

In recent years the use of nonionic surfactants has greatly increased, due to their special property of not releasing toxic substances upon burning. A wise use of commercial surfactants has allowed production of oil–water (O/W) emulsions with very high oil content [1]. However, although the general behavior of most nonionic surfactants is known from experience, the relation between their molecular properties and their ability to stabilize O/W emulsions remains unclear.

Several years ago, Winsor [2] related a quotient of intermolecular energies to the phase behavior of a water–oil–surfactant system. However, a *direct* evaluation of this quotient in terms of bimolecular energies has not been made, probably due to the qualitative nature of the concept, and the usual difficulties found in the quantum-mechanical calculation of fairly large molecules. In contrast, the arbitrary Hydrophile–Lipophile Balance (HLB) scale [3] has become widely used [4], because its formulation implicitly describes an experimental method of evaluation. The purpose of this paper is to report a mathematical relation between the empirical HLB scale and a theoretical Winsor's R-type quotient, calculated for nonyl and octyl ethoxylated surfactants, with the use of the molecular mechanics package Discover 2.0 [5].

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COMPUTATIONAL DETAILS

Since only pairwise interactions between the lipophilic and hydrophilic branches of the alkyl-phenol ethoxylated surfactants are involved in Winsor's R-type quotients, the electronic structures of (1) alkylic chains C_nH_{2n+2} with $1 \leq n \leq 19$; (2) ethylene oxide chains $CH_3(CH_2CH_2O)_mCH_3$ with $1 \leq m \leq 19$; and (3) a water molecule, were calculated with the semiempirical Modified Neglect of Differential Overlap (MNDO) method [6,7], using BFGS [8] geometry optimization. Least-square fits of some molecular properties with respect to the molecular length were obtained. The molecular length was estimated as the longest hydrogen-hydrogen distance in the molecule.

Using a docking procedure, approximate spatial conformations of all possible pairs constituted by hexane, octane, nonane, water and the ethylene oxide chains were found. At this point, the intermolecular interaction was modeled through a Lennard-Jones potential plus a Coulombic term, in which MNDO net atomic charges were introduced. Subsequently, a molecular mechanics calculation was undertaken for each bimolecular configuration, using the CVFF force field [5]. For the final configurations, the van der Waals energies along with the electrostatic contributions were evaluated.

For pairs of equal alkanes and ethylene oxide compounds (EOCs), the dipole-dipole (Debye), dipole-induced dipole (Keesom), and dispersion (London) energies, contributing to the total van der Waals energy, have been calculated, using the well-known analytical formulas and the dipole moments, polarizabilities and ionization potentials resulting from the MNDO calculation.

RESULTS AND DISCUSSION

Molecular properties as a function of molecular length

A number of theoretical studies have attempted to address the issue of surfactant HC chain conformation and its contribution to emulsification behavior [9–13]. Table 1 shows the dependence of the molecular properties of hydrocarbons and ethylene oxide derivatives on their molecular lengths. Those lengths have been measured in the all-trans (elongated) conformation of the molecules, which has been determined to be the most stable conformation from an empirical evaluation of the rotational barriers [14; see also Refs. 15 and 16].

As pointed out by Flory [17], the molecular length of a polymer should present a square-root dependence on the number of monomers if free rotation of the bonds around all possible molecular angles is assumed. This is not usually the case, however, since the bond angles are naturally constrained to a range of certain values, in order to avoid unfavorable steric interactions. For the two series of molecules calculated here, for instance, the t-g and t-g' barriers are kinetically accessible at room temperature, but the g-g' rotational barriers are much more restricted, increasing considerably as one moves from the external monomers to the most internal bonds, and reaching top values of 10.95 kcal/mol for *n*-decane, and 30.3 kcal/mol for the O-C rotation of $CH_3(CH_2CH_2O)_6CH_3$ [18]. Since the rotation of external bonds does not appreciably change the molecular length, the percentage of molecules exhibiting marked differences from the most stable molecular length should be quite small, even at room temperature ($\sim e^{-(\Delta E_r/kT)}$). This might explain the fact that the molecular volumes, deduced from the experimental densities (see below), vary linearly with the molecular lengths estimated here, even though molecular dynamics studies [19] on liquid hydrocarbons have shown that between 25 and 30% of the bonds exhibit gauche

TABLE 1
MOLECULAR PROPERTIES OF HYDROCARBONS AND ETHYLENE OXIDE OLIGOMERS

Property	Hydrocarbons C_nH_{2n+2}	Ethylene oxide compounds $CH_3(CH_2CH_2O)_mCH_3$
Length L (Å)	$1.2922 n + 0.491^a$	$3.41 m + 3.8^b$
I.P. (eV)	13.86–11.62	10.85–10.96
Dipole moment (D)	0.0003–0.0060	(odd) 1.1240–1.3818 (even) 0.1361–0.6388 ^c
Polarizability α (Å ³)	$1.1740 n + 0.080^d$ $0.9086 L - 0.366^f$	$3.0471 m + 2.31771^e$ $0.894 L - 1.1^g$
Molecular volume (Å ³)	$22.91 \alpha + 54^h$ $20.82 L + 46^i$	— $18.7 L + 31^j$
Intermolecular distance (Å)	4.70^k 4.57^m	4.36^l 4.32^m

^a 1.2922 ± 0.0005 Å, 0.491 ± 0.007 Å, $r = 0.999998$, SE in estimates: 0.0140388 Å; $1.8035 \leq L \leq 25.0461$ Å.

^b 3.41 ± 0.02 Å, 3.8 ± 0.2 Å, $r = 0.999576$, SE in estimates: 0.575207 Å; $6.3436 \leq L \leq 68.2838$ Å.

^c Dipole moment less than 0.2236 D for $m \leq 8$.

^d 1.1740 ± 0.0007 Å³, 0.080 ± 0.008 Å³, $r = 0.999997$, SE in estimates: 0.0175398 Å³, $1.27568 \leq \alpha \leq 22.40175$ Å³.

^e 3.0471 ± 0.0008 Å³, $2.31771 \pm 1E-8$ Å³, $r = 0.999999$, SE in estimates: 0.0198228 Å³; $5.37721 \leq \alpha \leq 60.28384$ Å³.

^f 0.9086 ± 0.0004 Å³, 0.366 ± 0.006 Å³, $r = 0.999998$, SE in estimates: 0.0133068 Å³.

^g 0.894 ± 0.006 Å³, 1.1 ± 0.3 Å³, $r = 0.999587$, SE in estimates: 0.507679 Å³.

^h 22.91 ± 0.07 Å³, 54 ± 1 Å³, $r = 0.999934$, SE in estimates: 1.43991 Å³.

ⁱ 20.82 ± 0.07 Å³, 46 ± 1 Å³, $r = 0.999924$, SE in estimates: 1.53578 Å³.

^j 18.7 ± 0.1 Å³, 31 ± 5 Å³, $r = 0.999589$, SE in estimates: 10.5845 Å³.

^k $4.60 \leq I.D. \leq 4.86$ Å.

^l $4.19 \leq I.D. \leq 4.41$ Å.

^m Deduced from the tetragonal cell model.

conformations at room temperature, while crystallographic studies on solid polyethylene oxide compounds $H(CH_2)_nO(CH_2CH_2O)_m(CH_2)_nH$ [20–22] support a $7/2$ helix conformation [23], in which seven monomeric units turn twice per fiber period [24,25].

Using the experimental densities of liquid hydrocarbons, molecular volumes were calculated, i.e., the volume per molecule, which is critically dependent on the intermolecular interaction. It was found that these molecular volumes show linear dependences on the molecular lengths and the volumes of polarizability, as shown in Table 1. Using the expression of the polarizability in terms of the number of carbons, methylene and methyl group contributions to the molecular volumes are found to be 26.9 and 55 Å³, respectively. These values are very close to those previously deduced by Nagarajan and Ruckenstein [9] from the dependence of the molecular volume on temperature, i.e., 29.6 and 54.6 Å³, respectively.

A similar relation between the molecular volume and the polarizability of alkanes up to hexane has been reported [26]. In that study, however, molecular volumes strictly equal to the sum of theoretical atomic volumes were considered. Both kinds of relations are expected to hold whenever the dispersion forces predominate in the intermolecular interaction.

The molecular volumes of the ethylene oxide compounds were estimated, using the polarizabilities calculated for these compounds and the molecular volume-vs.-polarizability relation calculated for hydrocarbons. In doing this, it is important to realize that: (1) the ethylene oxide compounds mainly interact through dispersive forces, as do the alkanes, since the Keesom and Debye forces are at least one order of magnitude lower; and (2) the polarizability vs. molecular

TABLE 2
ESTIMATED MOLECULAR VOLUMES AND DENSITIES OF $\text{CH}_3(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_3$ MOLECULES

m	Molecular volume (\AA^3)	Density (g/cc)	m	Molecular volume (\AA^3)	Density (g/cc)
1	178	0.693	11	876	0.976
2	247	0.794	12	946	0.981
3	316	0.852	13	1016	0.986
4	387	0.886	14	1086	0.990
5	457	0.911	15	1155	0.994
6	526	0.929	16	1226	0.996
7	596	0.943	17	1294	1.000
8	666	0.954	18	1365	1.001
9	737	0.961	19	1435	1.003
10	806	0.970			

length relationship for ethylene oxide compounds displays almost the same slope as the corresponding hydrocarbon relation, indicating that the polarizability varies with the molecular length in the same manner for both kinds of molecules.

The calculated molecular volumes for the ethylene oxide compounds, along with their respective densities, are shown in Table 2. As far as we know, the only experimental density reported for the ethylene oxide compounds calculated here is that of methyl propyl ether (0.738 g/cc [27]) which differs 7%. A comparison of the deduced densities with those of similar compounds [28] is presented in Table 3. It is observed that the theoretical densities fall well within the experimental range. Plotting the theoretically deduced molecular volumes of ethylene oxide compounds against their calculated molecular lengths, a linear relationship is found, similar to the alkane case (see Table 1).

We have applied two different methods in order to estimate intermolecular distances between alkane molecules and ethylene oxide compounds, required for the separation of the total van der Waals energy (calculated with Discover) into its component contributions (calculated with the MNDO results):

(1) Using the Docking module of InsightII, approximate configurations between each pair of similar alkane molecules were obtained by minimization of the total intermolecular energy, estimated as a van der Waals energy plus a Coulombic correction. Next, a molecular mechanics calculation was undertaken using the CVFF force field. Finally, the Docking module was again used in order to minimize the total intermolecular energy. This procedure was repeated for all pairs of equal alkane molecules $\text{C}_n\text{H}_{2n+2}$ (with $1 \leq n \leq 19$). An average intermolecular separation of 4.70 \AA was found, very close to the value of 4.6 \AA estimated by Dill and Flory [12] for a lattice representation of the hydrophobic surfactant tails in aggregates.

TABLE 3
EXPERIMENTAL DENSITIES OF SELECTED ETHYLENE OXIDE OLIGOMERS

Oligomer	Density range (g/cc)	n Values
$\text{H}(\text{CH}_2)_n\text{H}$	0.62–0.78	$6 \leq n \leq 43$
$\text{CH}_3(\text{OCH}_2)_n\text{OCH}_3$	0.85–1.10	$1 \leq n \leq 5$
$\text{C}_2\text{H}_5(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	0.84–0.85	$3 \leq n \leq 10$
$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$	1.43–1.47	$1 \leq n \leq 8$

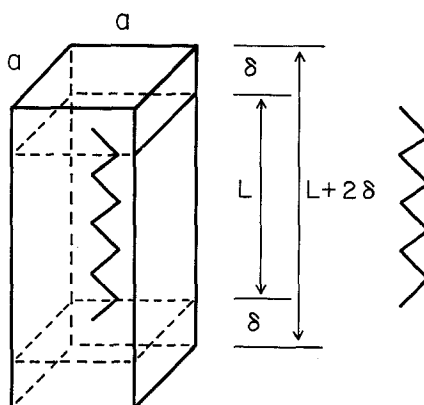


Fig. 1. The tetragonal cell model.

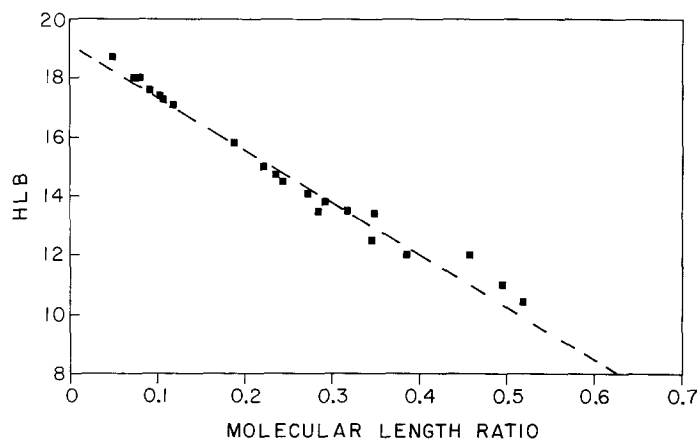
When the same procedure was applied to each pair of equal ethylene oxide molecules $\text{CH}_3-(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_3$ (with $1 \leq m \leq 19$), values between 4.19 and 4.41 Å were obtained, except for $m = 13$ which presented an anomalously high value of 4.94 Å. The average intermolecular separation (leaving out the result for $m = 13$) was 4.36 Å.

(2) Since the conformational analysis as well as the molecular volume vs. molecular length plots suggest that all molecules considered have a greater tendency to be elongated rather than wound, we associated a primitive tetragonal cell with each molecular volume, as shown in Fig. 1. This model allows us to rewrite the former molecular volume dependence ($V = a_1 \times L + a_2$) on the molecular length as:

$$V = a^2 \times (L + 2\delta) \quad (1)$$

where $a_1 = a^2$ and $\delta = (a_2/2a^2)$.

The tetragonal cell model has been inspired by the work of Bennema et al. [29], which shows that the odd n -alkane molecules ($\text{C}_n\text{H}_{2n+2}$, n odd) crystallize in orthorhombic cells, in which the crystallographic c -axis is proportional to the chain length ($c = 2.546 \times n + 3.75$ Å). Since in a

Fig. 2. Plot of HLB vs. L_U/L_H .

tetragonal cell the other two axes, i.e. *a* and *b*, are equal, whereas they differ in the orthorhombic cell, our model is a simplification of Bennema's findings.

According to the tetragonal model, the intermolecular separation would be equal to 'a' (see Fig. 1), which is the distance between reticle points, resulting from the spatial displacement of the tetragonal unit cell. The distance 2δ is then equivalent to a kind of interlamellar separation. Intermolecular distances of 4.57 Å for hydrocarbons and 4.32 Å for ethylene oxide molecules were found, along with interlamellar separations of 2.07 and 1.68 Å, respectively.

HLB as a function of molecular length

It is clear that the HLB [30,31] of a surfactant depends markedly on the length of its hydrophilic and lipophilic chains. These lengths have been found to depend linearly on the number of monomers of the alkanes and ethylene oxide compounds. Since one of the usual definitions of HLB [32,33] relates it directly with the weight percent of ethylene oxide in the surfactant, it is not surprising that the HLBs of nonyl, octyl and dodecyl ethoxylated surfactants depend linearly on the quotient of their lipophilic and hydrophilic lengths (Fig. 2):

$$\text{HLB} = 19.1 - 17.6 \times L_L/L_H \quad (2)$$

(19.1 ± 0.2 , 17.6 ± 0.6 , $r = 0.99088$, standard error in estimates: 0.390663). This relationship holds for molecules whose HLB lies between 10.4 and 18.7 units. The relation is not valid for fairly large hydrophilic branches ($m = 40$), since the small differences between the C-C-O and C-O-C angles cause an appreciable bending in the molecule, even in the all-trans conformation. This curvature has been found to be much less pronounced in alkyl-phenol ethoxylated surfactants than in the alkyl ethoxylated ones.

The HLB values used were those reported by the manufacturers for their commercial surfactants [4], without any reference to the method of evaluation employed [33]. The values are shown in Table 4, along with the molecular lengths of their conforming branches. Since for $\text{HLB} = 10$, L_L/L_H equals ~ 0.51 , an alkyl ethoxylated surfactant would need a lipophilic chain twice as long as the hydrophilic chain in order to present similar affinities for the oil and water phases. For this reason, the usual alkyl-phenol ethoxylated surfactants display HLB values higher than 10, and produce O/W emulsions rather than W/O emulsions.

TABLE 4
HLB VALUES AS A FUNCTION OF MOLECULAR LENGTH

Series	No. of ethylene oxide units	HLB	L_L/L_H	Series	No. of ethylene oxide units	HLB	L_L/L_H
Octyl	5	10.4	0.52	Nonyl	14	14.7	0.23
Nonyl	6	11.0	0.49	Nonyl	15	15.0	0.22
Dodecyl	9	12.0	0.46	Octyl	16	15.8	0.18
Nonyl	8	12.0	0.38	Nonyl	30	17.1	0.11
Octyl	8	12.5	0.34	Octyl	30	17.3	0.10
Nonyl	9	13.4	0.34	Nonyl	35	17.4	0.10
Octyl	10	13.5	0.31	Nonyl	40	17.6	0.09
Octyl	10	13.5	0.28	Nonyl	50	18.0	0.07
Nonyl	11	13.8	0.29	Octyl	40	18.0	0.08
Nonyl	12	14.1	0.27	Octyl	70	18.7	0.04
Octyl	12	14.5	0.24				

TABLE 5
INTERACTION ENERGIES (KCAL/MOL) BETWEEN WATER, HEXANE AND ALKANES

Compounds	van der Waals energy	Electrostatic energy	Total energy
H ₂ O-H ₂ O	-0.19705	-0.73209	-0.92914
C ₆ -C ₆ (oil-oil)	-3.18083	-0.00024	-3.18107
C ₆ -H ₂ O	-0.61721	-0.02696	-0.64417
C ₈ -H ₂ O	-0.69336	-0.03013	-0.72349
C ₉ -H ₂ O	-0.69881	-0.01664	-0.71544
C ₈ -C ₆ (alk-oil)	-3.48232	-0.00002	-3.48234
C ₉ -C ₆ (alk-oil)	-3.75136	-0.00013	-3.75136
C ₈ -C ₈ (alk-alk)	-4.47720	-0.00028	-4.47748
C ₉ -C ₉ (alk-alk)	-6.39374	0.00051	-6.39623

HLB as a function of intermolecular energies

Only recently, thermodynamic models using Winsor's hypothesis have been developed [34–36]. As stated by Bourrel et al. [34], the Winsor model is a free enthalpy relationship and in this respect, the consideration of van der Waals forces and electrostatic interactions is justified. However, it must be recognized that entropic considerations are neglected in the present treatment. It is also worth mentioning that the bimolecular energies calculated here are not expressed per unit area of interface [32], since the estimation of these areas is extremely difficult.

As shown by the bimolecular energies (Tables 5, 6 and 7), all the calculated pairs, except water–water and water–EOCs, interact through van der Waals forces, whose major contribution is due to polarizability (London) forces.

TABLE 6
INTERACTION ENERGIES (KCAL/MOL) BETWEEN THE EOCs, WATER AND OIL

Compounds	van der Waals energy	Electrostatic energy	Total energy
EOC ₄ -H ₂ O	-0.77705	-0.43748	-1.21453
EOC ₅ -H ₂ O	-0.78977	-0.30803	-1.09780
EOC ₆ -H ₂ O	-0.78919	-0.44174	-1.23093
EOC ₈ -H ₂ O	-0.79082	-0.32962	-1.12044
EOC ₉ -H ₂ O	-0.81362	-1.29286	-2.10648
EOC ₁₀ -H ₂ O	-0.81434	-1.29099	-2.10533
EOC ₁₁ -H ₂ O	-0.81374	-1.29224	-2.10598
EOC ₁₂ -H ₂ O	-0.81451	-1.28920	-2.10371
EOC ₁₄ -H ₂ O	0.00781	-4.71444	-4.70663
EOC ₁₅ -H ₂ O	-0.02383	-4.90054	-4.87671
EOC ₁₆ -H ₂ O	-0.15524	-3.58196	-3.73720
EOC ₄ -C ₆	-3.71219	-0.00584	-3.71803
EOC ₅ -C ₆	-3.86585	0.00956	-3.85629
EOC ₆ -C ₆	-4.16478	-0.00488	-4.16966
EOC ₈ -C ₆	-3.77942	-0.00464	-3.78406
EOC ₉ -C ₆	-3.90851	0.01011	-3.89839
EOC ₁₀ -C ₆	-4.16019	-0.00361	-4.16380
EOC ₁₁ -C ₆	-4.15979	-0.00355	-4.16334
EOC ₁₂ -C ₆	-4.16330	-0.00354	-4.16330
EOC ₁₄ -C ₆	-5.14413	-0.00311	-5.14724
EOC ₁₅ -C ₆	-5.17052	-0.00327	-5.17379
EOC ₁₆ -C ₆	-5.18038	-0.00378	-5.18416

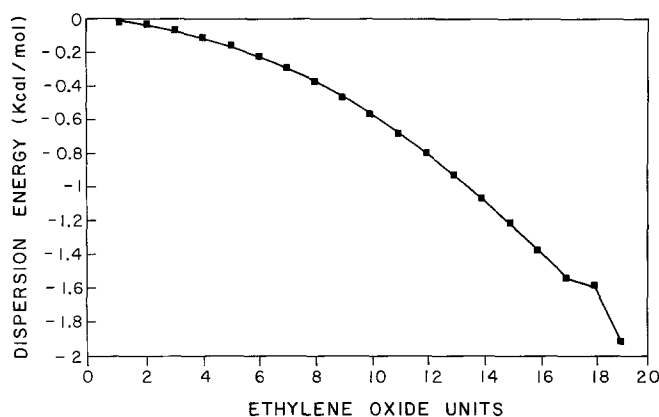


Fig. 3. Dispersion energy of EOCs as a function of molecular length.

As expected, the absolute value of the total (van der Waals + electrostatic) energy for pairs of hydrocarbons increases with the number of carbons, ranging from -0.04 kcal/mol for butane up to -12.0 kcal/mol for eicosane. Although the pairs of ethylene oxide compounds (Table 7) mainly interact through van der Waals forces, whose major contribution is due to dispersion energies (Fig. 3), the intermolecular interaction between each ethylene oxide compound and a water molecule depends on chain size. Thus, for molecules with more than eight ethylene oxide units, the electrostatic contribution predominates, although for smaller molecules the van der Waals energy is at least twice as high (Table 6). For large EOCs ($m > 14$), the electrostatic interaction appears to be far more important than the van der Waals energy.

It was found that for nonyl- and octyl-phenol ethoxylated surfactants, the HLB depends linearly on the interaction energy ratio R_M (Fig. 4):

$$\text{HLB} = 18.2 - 6.5 \times R_M \quad (3)$$

The interaction energy ratio can be expressed as:

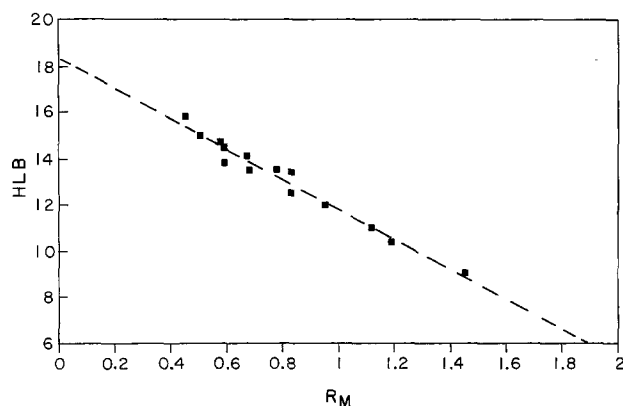


Fig. 4. HLB as a function of intermolecular energies.

TABLE 7
INTERACTION ENERGIES (KCAL/MOL) BETWEEN PAIRS OF EOCs

Compounds	van der Waals energy	Electrostatic energy	Total energy
EOC ₄ -EOC ₄	-7.30498	-1.61962	-8.92460
EOC ₅ -EOC ₅	-9.08330	-0.82175	-9.90505
EOC ₆ -EOC ₆	-10.56770	-2.29209	-12.85980
EOC ₈ -EOC ₈	-14.02480	-1.32066	-15.34550
EOC ₉ -EOC ₉	-15.67974	-1.49586	-17.17560
EOC ₁₀ -EOC ₁₀	-17.32700	-1.66096	-18.98800
EOC ₁₁ -EOC ₁₁	-24.48535	-1.70205	-26.18740
EOC ₁₂ -EOC ₁₂	-20.73521	-1.88980	-22.62501
EOC ₁₄ -EOC ₁₄	-24.07056	-2.17444	-26.24500
EOC ₁₅ -EOC ₁₅	-28.30846	-2.45924	-30.76770
EOC ₁₆ -EOC ₁₆	-26.72476	-3.16094	-29.88570

$$R_M = \frac{E_{\text{ALK-HEX}} + E_{\text{ETOX-HEX}} + E_{\text{HEX-HEX}} + E_{\text{ALK-ALK}}}{E_{\text{ALK-WATER}} + E_{\text{ETOX-WATER}} + E_{\text{WATER-WATER}} + E_{\text{ETOX-ETOX}}} \quad (4)$$

(18.2 ± 0.3, 6.5 ± 0.3, r = 0.985959, standard error in estimates: 0.331871)

It should be noticed that, although the $E_{\text{ETOX-ETOX}}$ term predominates, no other linear relation with the calculated molecules was found if fewer energy terms were considered, since most of the terms do not exhibit monotonic variations with chain length. This might be a consequence of the method of calculation, since it was observed that the van der Waals energy is very sensitive to the intermolecular separation. In order to avoid local minima, several initial configurations were used, all of which were optimized afterwards using Biosym's CVFF [5] force field. The presented interaction energies belong to the most stable configurations calculated.

The R_M ratio differs from the usual Winsor's R-type quotients in the sign of the terms that measure the cohesive energies between alkanes, hexane (oil), water and EOCs, respectively. In this case, those terms are not subtracted from the rest, but rather added.

Finally, it should be noticed that most ethylene oxide compounds calculated here have R_M values lower than 1, which means that they have a higher affinity for water than for oil (hexane). This is in agreement with the tendency of these compounds to produce O/W emulsions rather than W/O emulsions. According to Eq. 3, equal tendencies of the surfactant for the oil and water phases ($R_M = 1$) would be found for a HLB value of 11.75.

CONCLUSIONS

Two mathematical relations between the HLB and molecular properties have been presented. The expression of HLB as a function of molecular length, along with the relations between the molecular length of the hydrophilic and hydrophobic branches and their number of repeating segments, allows substitution of a given non-ethylene oxide surfactant by an ethylene oxide surfactant of equal HLB. Relations between HLB and Winsor R-type quotients, like that of Eq. 3, are aimed to help substitute a given surfactant X by another surfactant Y, independently of their chemical structure, allowing estimation of an approximate HLB value for a potentially useful surfactant, designed computationally. However, no proof has been forwarded of the generality of Eq. 3, although the Winsor concept has proved very useful for a wide variety of chemically different surfactants.

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