Problems in Understanding the Interaction of Surfactant, Oil and Water

R.C. LITTLE, Combustion and Fuels Branch, Naval Research Laboratory, Washington, DC

ABSTRACT

The limited partition coefficient data presently available on amphiphilic compounds precludes the serious testing of the HOR concept, especially any correlation that it may have with HLB. The HLB scale, on the other hand, has been evolved for complex amphiphile mixtures rather than pure amphiphiles, further complicating the development of a correlation between HLB and other amphiphile-system properties. The paucity of reliable data, then, on the partition coefficient, EACN concept and HLB, especially with respect to reasonably well defined amphiphiles, greatly impedes progress in the development of a rational basis relating surfactant function to molecular structure. The effect of oil, however, in the oil-water-amphiphile system might be assessed through use of the solubility parameter concept since the original HLB scale was based on the stability of a specific oil-water emulsion. Thus, while the physicochemical methods exist to quantitatively establish surfactant-water-oil behavior and to test current theories and correlations, progress in this area must await the cataloging of reliable physicochemical data on reasonably well defined amphiphiles.

BACKGROUND

The correlation of amphiphile function with some physical property of the amphiphile has long preoccupied both the practical chemist interested in evolving new chemical formulations and the research chemist concerned with understanding the sometimes unpredictable interactions of amphiphiles with other components of chemical systems. Some progress was made in correlating function with amphiphile properties when Griffin (1), in 1949, devised the empirical HLB system (hydrophile-lipophile balance) based on a series of exhaustive emulsion tests. Through a series of such emulsion tests on a given amphiphile, an HLB number was assigned to the agent. Using these tests, a large number of amphiphiles were evaluated and it was found that amphiphile function could be reasonably well correlated with the empirical HLB numbers. Since that time, a large number of investigations have been made in an attempt to correlate HLB with almost every conceivable property of the amphiphile. Unfortunately, nearly all the proposed correlations appear to be useful within short ranges of specific chemical families but break down when a wide variety of agents spanning varied chemical types are considered. Hence, one was left with an empirical number which, while related to amphiphile function, was obscure in terms of physical significance.

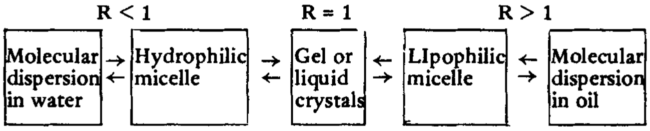
In 1954, Winsor (2) published his R-theory which attempted to explain amphiphile-water-oil behavior in terms of the ratio of amphiphile molecular interactions with water to amphiphile molecular interaction with oil. Unfortunately, the R concept can be used only in a qualitative sense because such molecular interactions cannot be computed directly. Thus, the R concept, while having the potential of being directly related to molecular properties, fails to produce a meaningful numerical evaluation of chemical systems involving amphiphiles, water and oil. Davies (3), in 1957, tried to relate HLB to the distribution coefficient of the amphiphile between the aqueous and oil phases. More recently, Kruglyakov and Koretskii (4) have defined an "HOR" concept directly in terms of the ratio of the amphiphile's work of adsorption in the corresponding oil and aqueous phases, attempting to relate HLB to the HOR concept. This report is concerned with these concepts and problems associated with possible interrelations between them.

Winsor R Concept

The treatment of amphiphilic dispersions by the R concept (2) has remained somewhat descriptive because of the inaccessibility of R to physical measurement either directly or indirectly. The R concept is defined by Winsor as:

$$R = \frac{A_{\bar{c}\bar{o}}}{A_{\bar{c}\bar{w}}}, \qquad [1]$$

where $A_{\bar{c}\bar{o}}$ = molecular interaction energy of the amphiphile $\bar{c}$ with the water-saturated oil phase $\bar{o}$ and $A_{\bar{c}\bar{w}}$ = the molecular interaction energy of the amphiphile with the oil-saturated water phase $\bar{w}$. According to Winsor, $A_{\bar{c}\bar{o}}$ represents molecular interactions promoting miscibility with the oil and $A_{\bar{c}\bar{w}}$ is interactions promoting miscibility with water. The relative contributions of the lipophilic and hydrophilic portions of the amphiphile may be expected to result in corresponding variations in R. A qualitative scheme for such effects may be represented as (from Winsor):



The most intimate mutual dispersion of amphiphile, water and oil occurs when R = 1, where a stable arrangement of lipophilic, amphiphilic and hydrophilic layers pervade the entire dispersion. However, if the hydrophilic portion of the amphiphile is significantly increased in its contribution to the interaction energy relative to the lipophilic section, a molecular dispersion will ultimately result (R << 1). A similar consideration pertains to the effect of increases in the lipophilic contribution relative to the hydrophilic section of the amphiphile resulting in increasing values of R.

Hydrophilic-Oleophilic Energy Relationship and Winsor's R Concept

It is evident that Winsor's use of the R concept is concerned with oil-water systems containing substantial concentrations of amphiphile. It is believed that the determination of R data by direct physical measurement will remain inaccessible over the phenomenological range already outlined. If, however, the concentration of amphiphile is greatly reduced (its concentration in a given phase not to exceed the critical micelle concentration (cmc) of the amphiphile in that phase), treatment of the amphiphile-

TABLE I

Summary of HLB-HOR Data[a]

Compound	HLB	Oil phase	K_{wo}	$\Delta\mu_o$	$\Delta\mu_w$	HOR
OPE_1 (homogeneus)	4.0	Isooctane	1.84×10^{-4}			
OPE_2	5.9		7.17×10^{-4}	7.15	11.55	0.619
OPE_3	7.6		3.13×10^{-3}	7.90	11.4	0.693
OPE_4	9.1		9.83×10^{-3}	8.05	10.84	0.742
OPE_5	10.2		2.42×10^{-2}	8.20	10.45	0.785
OPE_6	11.1		5.92×10^{-2}	8.60	10.32	0.833
OPE_7	11.7		1.82×10^{-1}	8.72	9.74	0.895
OPE_8	12.2		5.04×10^{-1}	8.90	9.32	0.955
OPE_9	12.7		1.42	9.21	9.00	1.023
OPE_{10}	13.4		3.85	9.71	8.90	1.091
NPE_5 (homogeneous)	10.0	Benzene	3.16×10^{-4}	6.10	11.0	0.554
$HPE^1{}_0$	13.3		3.16×10^{-3}	8.5	12.0	0.708
NPE_{15}	15.0		1.60×10^{-2}	9.8	12.3	0.817
NPE_{20}	16.0		1.6×10^{-1}	11.18	12.3	0.909
NPE_5 (homogeneous)	10.0	Heptane	1.62×10^{-2}	8.70	11.30	0.770
NPE_{10}	13.3		1	12.20	12.20	1.000
NPE_{15}	15.0		40	14.32	12.30	1.164
Oleic acid	1.0		1.76×10^{-6}	5.95	13.9	0.428
Octyl alcohol	1.0		5.7×10^{-8}	3.9	13.9	0.280
OPE_2 (normal distribution)	6.0	Isooctane	4.14×10^{-3}	7.48	10.88	0.688
$OPE_{2.98}$	7.6		1.43×10^{-2}	7.95	10.53	0.755
$OPE_{4.07}$	9.0		4.75×10^{-2}	8.55	10.40	0.822
$OPE_{5.01}$	10.2		1.29×10^{-1}	8.60	9.85	0.873
$OPE_{6.03}$	11.1		2.54×10^{-1}	8.70	9.55	0.911
$OPE_{7.05}$	11.7		4.49×10^{-1}	8.90	9.40	0.947
$OPE_{8.03}$	12.3		8.22×10^{-1}	9.00	9.12	0.987
$OPE_{9.06}$	12.8		1.55	9.25	8.98	1.030
$OPE_{9.93}$	13.2		1.89	9.40	9.00	1.044
OPE_{16}	$\sim$16.0		31.3	$\sim$10.9	$\sim$8.9	1.22
OPE_{40}	$\sim$17.8		47.2	$\sim$10.8	$\sim$8.5	1.27

[a]From ref. 4.

oil-water system is correspondingly simplified. According to Winsor, maximal cosolvent effects (R = 1) will be conferred to those amphiphiles which, at lower concentrations, distribute themselves evenly between the oil and water phases. In general, this free energy of transfer of solute between phases will be expressed by the relation:

$$\Delta\mu_A^{w \to o} = RT \ln \frac{a_A^w}{a_A^o} = RT \ln K_{wo}, \qquad [II]$$

where a = the activity of the amphiphile; R = gas constant; K_{wo} = partition coefficient; and A, w, o refers to the amphiphile, water and oil phases, respectively. The hydrophilic-oleophilic energy relation, HOR, is defined (4) as:

$$\text{HOR} = \frac{\Delta\mu_o^o}{\Delta\mu_w^o} = 1 + \frac{RT \ln K_{wo}}{\Delta\mu_w^o} \qquad [III]$$

It is evident that the HOR relation (a) fulfills the energy ratio requirements for the definition of R, and (b) is experimentally accessible. Further, replacing activities by concentrations, it is conceivable that

$$\text{Limit } R_{c_A \to o} = R_o = \frac{1}{\text{HOR}}, \qquad [IV]$$

where R_o is the limiting value of R. Kruglyakov and Koretskii have determined HOR values for published literature data. Table I summarizes these data together with several additional compounds (data taken below cmc of amphiphile). The authors further attempt to relate these HOR data to the HLB system of Griffin (1) as considered in the next section. It should be noted that the HLB system was experimentally evolved using commercial materials rather than homogeneous compounds.

HLB-HOR Relations

Figure 1 is a plot of HLB vs HOR for the normal distribution *p,t*-octylphenoxyethanols (OPE). The partition coefficients are from the data of Crook et al. (5). Included in the figure is the oleic acid point which was determined in a

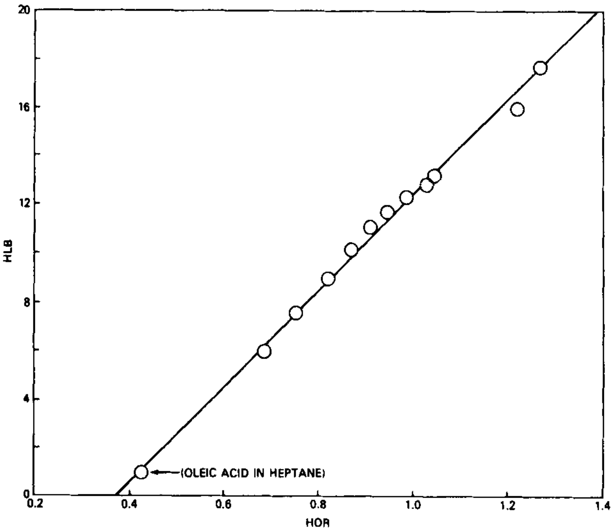


FIG. 1. HLB-HOR plot for normal distribution OPE in the isooctane-water system.

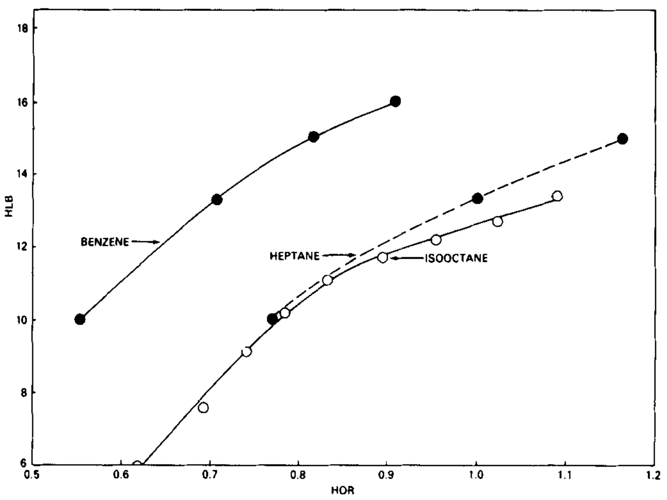


FIG. 2. HLB-HOR plots for homogeneous nonionics in three solvent-water systems: ● = NPE; ○ = OPE.

heptane-water system as opposed to this isooctane-water system used for the OPE. The merit of including the oleic acid point as was done in the original Russian work may be open to criticism as will be seen later in this paper. The apparent linear relationship observed between HLB and HOR seems impressive and an empirical relationship of HLB = 19.80 HOR - 7.38 is obtained for the normal distribution OPE. This appears to be in approximate agreement with the earlier report (4) of Kruglyakov and Koretskii who claim a linear relationship between HLB and HOR.

Some difficulty is obtained, however, when the plots are repeated for the homogeneous OPE (5) and for the narrow cut oxyethylated nonyl phenols (NPE) taken from the data of Petrov and Pazdnyshev (6). Figure 2 reports the data in terms of HLB vs HOR for benzene-water, heptane-water and isooctane-water systems. Two features are immediately evident from the plot. First, there is a definite solvent effect which reveals the implicit bias of the HLB system in terms of the oil chosen for the original emulsion tests by Griffin. Second, there is very pronounced curvature in the plots of the homogeneous nonionics for each solvent-water system. The noncurvature of the plot of HLB vs HOR for the normal distribution OPE may possibly be a result of an additional bias of the HLB system, i.e., that the HLB which are reported were determined for normal distribution nonionics. Thus, the HLB of the homogeneous species may be in doubt because their HLB were assigned on the basis of the performance of the normal distribution nonionics which involve fractionation of species between phases (5). The extraction of the more water-soluble species contained in the normal distribution compounds into the aqueous phase will result in higher values of K_{wo}. Thus, the characteristics of the adsorbed interfacial film will be affected. Unfortunately, HLB data for the homogeneous compounds is presently not available so that the HLB-HOR relationship cannot properly be tested for the homogeneous nonionics reported here.

Partition Coefficient As a Measure of HLB

The concept of the partition coefficient as a measure of HLB is not new; it was first advanced by Davies (3). He considered the work of transfer $\Delta\mu_A^{wo}$ of the amphiphile taking into account the energy contributions from the lipophilic and hydrophilic parts of the molecule. He obtained the equations

$$(\text{HLB} - 7) = 0.36 \ln \left(\frac{c_A^A}{c_A^o}\right) \qquad [V]$$

or

$$\text{HLB} = 0.36 \ln K_{wo} + 7 \qquad [VI]$$

Figure 3 reports an HLB vs ln k_{wo} plot for the normal distribution OPE previously discussed. The correlation is nearly as good as that obtained for the HLB-HOR plot. However, the empirical relationship

$$\text{HLB} = 1.20 \ln K_{wo} + 12.6 \qquad [VII]$$

was obtained, somewhat in disagreement with the results of Davies' theory (Equation VI).

Figure 4 plots HLB vs ln K_{wo} for single species in benzene-water, heptane-water and isooctane-water systems. The correlation again is not linear, probably for the same reasons as before, i.e., improper assignment of HLB numbers to the homogeneous species. Interestingly, the oleic acid partition coefficient in heptane-water (estimated from the HLB data) appears to fall in line with the NPE rather than with the OPE, contrary to previously reported results (6). The divergence of the plots in the various solvents is of

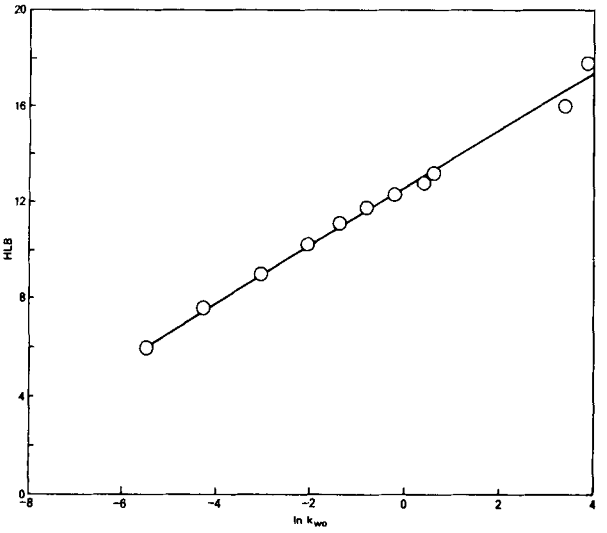


FIG. 3. HLB vs ln K_{wo} for normal distribution OPE in the isooctane-water system.

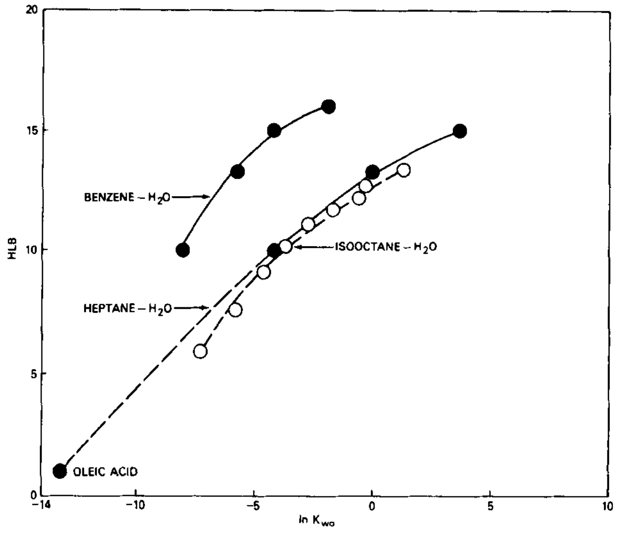


FIG. 4. HLB vs ln K_{wo} for homogeneous nonionics in three solvent water systems: ● = NPE; ○ = OPE.

interest and it may be worthwhile to determine if solvent effects on K_{wo} may be estimated through use of the solubility parameter concept (7).

Extrapolated Alkane Carbon Number Concept

Wade et al. have evolved the concept of $EACN_{min}$ (Extrapolated Alkane Carbon Number at the minimal tension) using interfacial tension plots for a given amphiphile solution against a series of hydrocarbons or hydrocarbon mixtures (8,9). Recently, they have attempted to correlate the $EACN_{min}$ experimental data with the HLB numbers for two series of ethoxylated dinynol phenols and tridecanols (9). A range of ca. 7 HLB units was covered in each amphiphile series. While the plotted data are of great interest, it should be noted that there are separate curves for each series of amphiphiles. This suggests that the correlation of itself may not contain all of the relevant parameters. The authors, moreover, note that anionics are even more troublesome to treat in this fashion when attempting to correlate the $EACN_{min}$ and HLB concepts. What seems to be needed is the influence of structural information (as contributed from both the lipophilic and hydrophilic moieties) upon the $EACN_{min}$ data. Again, the same point is reached—good data are required on well defined amphiphiles to properly test the concepts briefly reviewed in this paper.

Prediction of Solvent Effects

Partition coefficients may be estimated in other nonpolar solvent-water systems when data have been determined for a reference solvent provided the solubility parameters are used for the amphiphiles (10). The equation

$$-\ln \frac{K_{X,S}}{K_{X,R}} = \frac{V_A}{RT}[(\delta_A - \Delta_R)^2 - (\delta_A - \delta_S)^2], \qquad [VIII]$$

where $K_{X,S}$ = partition coefficient in untried solvent S; $K_{X,R}$ = partition coefficient in reference solvent R; V_A = molar volume of amphiphile; R = gas constant; T = absolute temperature; δ = solubility parameter; A = amphiphile, may be of use in such estimates. In the present case the water-benzene data have been used together with the water-heptane data to determine what value the modified solubility parameter of the amphiphile should have in order to be consistent with the observed partition coefficient values (based on mole fraction). Table II summarizes the results of this exercise. The increased solubility parameters for the amphiphiles which would be necessary for use in Equation VIII to bring predicated partition coefficients in line with observed partition coefficient data may be interpreted in terms of the incomplete dehydration of the polyethylene oxide chains. That is, when the amphiphile enters the hydrocarbon medium from the aqueous phase, the association of several water molecules with the polyethylene oxide chains might account for the increased solubility parameters necessary to bring calculated data from Equation VIII in line with calculated solubility parameter data from HLB-δ relation (11) recently reported, i.e., δ = 118.8 ÷ 54-HLB + 6.0. At any rate, Equation VIII would appear to provide only the crudest estimate of amphiphile solubility parameter when partition coefficients are known, or conversely, a crude estimate of the partition coefficient when using "unadjusted" δ values. Use of the solubility parameter concept to obtain such information for highly polar solutes violates the principles and assumptions upon which the regular solution theory for nonelectrolytes was built. Nonetheless, the solubility parameter results listed in Table II are in rough agreement with an average difference of 0.9 solubility parameter units beteen corresponding values. These data suggest that a modified amphiphile solubility parameter may be useful in predicting its partition coefficient in other oil-water systems. This would be useful in reducing the oil bias of the HLB system (4) and allow more meaningful comparisons to be made between the concepts mentioned here.

TABLE II

Calculated Solubility Parameters of Oxyethylated Nonyl Phenols

Compound	HLB	δ^a	δ^b	$\Delta\delta$
NPE_5	10.0	8.7	9.7	1.0
NPE_{10}	13.3	8.9	9.7 (5)	0.9
NPE_{15}	15.0	9.0	9.8	0.8

[a] From HLB-δ relationship of ref. 11.
[b] Equation of ref. 10.

REFERENCES

1. Griffin W.C., J. Soc. Cosmet. Chem. 1:311 (1949).
2. Winsor, P.A., "Solvent Properties of Amphiphilic Compounds," Butterworth Sci., London, 1954.
3. Davies, J.T., Proc. Int. Congr. Surf. Act. (2nd London) 1:426 (1957).
4. Kruglyakov, P.M., and A.F. Koretskii, Dokl. Akad. Nauk SSSR 197:1106 (1971).
5. Crook, E.H., D.B. Fardyu and G.F. Trebbi, J. Colloid Sci. 20:191 (1965).
6. Petrov, A.A., and G.N. Pozdnyshev, Kolloidn. Zh. 28:858 (1966).
7. Hildebrand, J.H., and R.L. Scott, "The Solubility of Nonelectrolytes," 3rd Edition, Reinhold, New York, 1950.
8. Cash, L., J.L. Cayias, G. Fournier, D. Macallister, T. Schares, R.S. Schechter and W.H. Wade, J. Colloid Interface Sci. 59:39 (1977).
9. Hayes, M.E., M. El-Emary, R.S. Schechter and W.H. Wade, Ibid. 68:591 (1979).
10. Siekierski, S., and R. Olzer, Inorg. Nucl. Chem. 25:1351 (1963).
11. Little, R.C., J. Colloid Interface Sci. 65:587 (1978).

[Received April 7, 1980]