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LETTERS TO THE EDITOR

Hydrophilic-lipophilic balance and partial molal volume of non-ionic surfactants

Since the introduction of the hydrophilic-lipophilic balance (HLB) system of classifying surfactants, various attempts have been made to correlate HLB values with physical properties of the surfactant molecules. The search for a universal correlation between the HLB and another property of the surfactant, has not been successful. An attempt to remedy this situation is now presented.

One factor which does not appear to have been considered is the partial molal volume (PMV). The PMV is a reasonable approximation of the true value of the molecular or molar volume. The PMV of many monomeric and micellar surfactants was recently calculated by the addition of partial atomic values (Yalkowsky & Zografi, 1972) (see Table 1). The calculated PMV values of monomeric surfactants are in good agreement with the literature values. For micellar surfactants, the covolume must be included in the calculation of the PMV. It is obvious that the PMV is an additive and constitutive property of a given molecule.

Davies (1957) assigned HLB group numbers (see Table 1) to the various functional groups that make up surfactant molecules, giving positive values to the hydrophilic groups and negative values to the lipophilic ones. The summation of the products of group numbers gives the HLBD. According to Davies one can express the HLBD by:

$$\text{HLB}_D = \Sigma \text{ (hydrophilic group numbers)} - \Sigma \text{ (hydrophobic group numbers)} + 7 \quad (1)$$

While Davies treats HLB as an additive and constitutive property of a given surfactant molecule, neither the Griffin HLB (Griffin, 1954) nor the Kawakami HLB (Kawakami, 1953) are so treated.

Intuitively, the PMV of the surfactants would seem to be well suited for correlation with the HLBD. The PMV can be expressed by:

$$\text{PMV} = \text{PMV}_L + \text{PMV}_H \quad (2)$$

where PMVL is partial molal volume for hydrophobic groups and PMVH is partial molal volume for hydrophilic groups.

On the other hand, from Table 1 it is obvious that an increase in the PMVL value

Table 1. *Partial molal volumes* (from Yalkowsky & Zografi, 1972) *and HLB group numbers* (from Davies, 1957) *of some common atoms and groups.*

Atom or group	PMV ($cm^3\ mol^{-1}$)	HLBD group numbers
C	9·9	
H	3·1	
O /–OH/	2·3	1·9
CH_3	19·3	0·475
CH_2–	16·2	0·475
–CH=	13·1	0·475
one ring	– 8·1	2·85
CH_2CH_2O	37·9	0·33

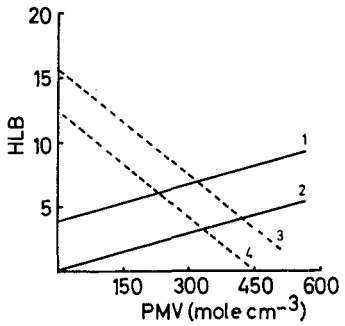

FIG. 1. A plot of PMV against HLB for a selected series of non-ionic ethylene oxide adducts: ——PMV$_L$ = const ; — — PMV$_H$ = const. 1, $C_{10}E_y$; 2, $C_{18}E_y$; 3, C_xE_{20} ; 4, C_xE_{10}

by 34·1 cm^3 mol^{-1} for aliphatic homologous series results in the decrease of HLB$_D$ by 1. This may be written as: Σ (hydrophobic group numbers) $= \frac{PMV_L}{34{\cdot}1}$

Similarly, using data from Table 1, it may be found that an increase in the PMV$_H$ value by 114·8 cm^3 mol^{-1} for homologous series of ethylene oxide adducts results in the increase of HLB$_D$ by 1. This can be expressed by:

$$\Sigma \text{ (hydrophilic group numbers)} = \frac{PMV_H}{114{\cdot}8}$$

Substituting calculated values into equation 1 and adding a group number for the –OH group, for aliphatic homologous series of ethylene oxide adducts, gives the following relations between the HLB$_D$ and the PMV:

$$HLB_D = \frac{PMV_H}{114{\cdot}8} - \frac{PMV_L}{34{\cdot}1} + 8{\cdot}9 \qquad (3)$$

For example, the volume of monomeric compounds of type: $CH_3[CH_2]_x[CH_2CH_2O]_yOH$, where $x = 11$ and $y = 12$, is PMV$_H$ = 12 (37·9) = 354·8; PMV$_L$ = 1 (19·3) + 11 (16·2) = 197·5. The group number for –OH is included in the constant 8·9. HLB$_D$ values calculated according to equations 1 and 3, are 7·16 and 7·06 respectively. From this example it is obvious (assuming that the typical surfactant molecule consists of at least 8–10 carbon atoms) that the PMV value of one hydrogen atom of the terminal CH_3 group has no practical influence on the final result. A similar case occurs when a molecule possesses an unsaturated bond. A plot of PMV against HLB for a selected series of non-ionic ethylene oxide adducts is shown in Fig. 1.

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