CALORIMETRIC DETERMINATION OF THE HYDROPHILE-LIPOPHILE BALANCE OF SURFACE-ACTIVE SUBSTANCES

Istvan Racz and Erno Orban

Pharmaceutical Institute, Hungarian University of Medicine, Budapest

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ABSTRACT

The hydrophile-lipophile balance (HLB) of liquid nonionic surface-active agents s linearly related to the measured heat of hydration by the relation

$$HLB = 0.42Q + 7.5,$$

where Q = the heat of hydration in g.-cal./g. In the case of mixtures, this relationhip represents a positive deviation from strictly additive behavior. A simple calorinetric arrangement for the determination of the heat of hydration is described.

INTRODUCTION

In recent years the HLB system introduced by Griffin (1, 2) for the evaluation of the efficiency of surface-active substances has been widely used (3–9). The old concept of the balance existing between polar and nonpolar components of the surface-active substances (10) has been used as the basis for classification in this system. The disadvantage of the technique was the rather considerable amount of time (24–72 hr.) required to determine experimentally the HLB value of a new agent (1, 2, 8. 9). Owing to the practical significance of the problem a number of researchers have attempted to develop a rapid and repeatable technique (11, 12).

It is well known that many useful surface-active substances are derivatives of ethylene oxide. According to Chwala and Martin (13), in an aqueous solution of ethylene oxide derivatives a hydrogen bridge is formed between the ether-like combined oxygen atoms and the water molecules. The simplified process is represented by the formula as follows:

$$-CH_2-\overset{..}{O}-CH_2-$$
$$\updownarrow$$
$$H$$
$$|$$
$$O-H$$
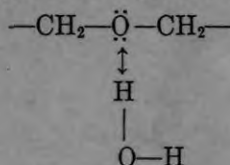
The energy set free in the form of heat is readily measurable by a sensitive calorimetric system. It was deemed probable that in the case of surface-

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Introduction	Results	Summary
Experimental Methods	Discussion	References

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active molecules a relation exists between the number of ethylene oxide groups in the molecule and the size of the lipophilic unit (i.e., the hydrophile-lipophile balance) and the heat of hydration.

EXPERIMENTAL

A schematic diagram of the instrument used to measure the heat of hydration of surface-active substances is shown in Fig. 1. The substances examined were of normal commercial grade, used without any additional purification, and are enumerated in Table I.

The release of the hydration heat was carried out in the liquid-calorimeter (K) formed from a Dewar flask of 200 ml. capacity. The calorimeter was furnished with a 200 r.p.m. paddle stirrer to provide proper mixing of surface-active substance investigated and the calorimeter fluid, and to produce a uniform heat distribution.

The heat released was measured with a thermoelectric pile constructed of copper-constantan thermocouples, the measuring arm of which was immersed in the calorimeter fluid. The auxiliary junction was immersed in the Dewar flask containing water of constant temperature (O).

The changes in the output of the thermoelectric pile were registered by a reflecting galvanometer (G) on a photographic reel adapted from a polarograph (P). The temperature of the calorimeter fluid as well as of the measuring room was $20° \pm 1°C$.

The technique employed in the measurement was as follows: 1.5–1.8 of the surface-active substance under investigation (after having been completely dried) were measured into the small tempering glass vessel made for this specific purpose and furnished with polishing caps. The
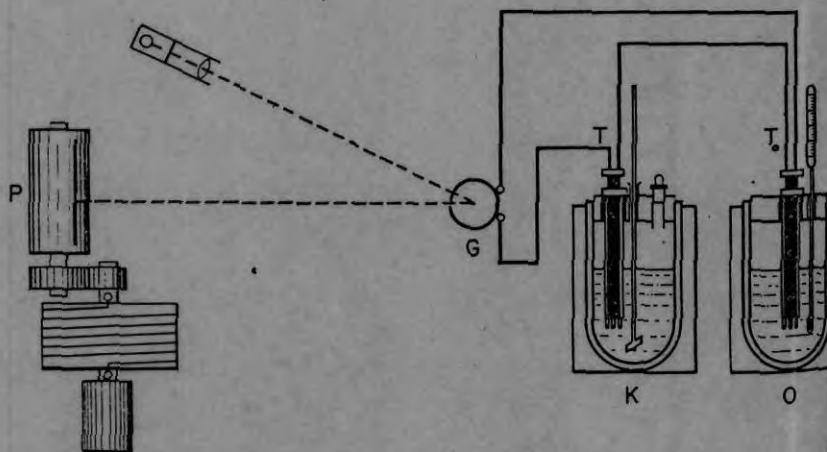

FIG. 1. Schematic diagram of the calorimetric system used for the measurement of heat of hydration.

TABLE I

The Relation between the HLB Values of Surface-Active Substances and the Hydration Heat of Them

Surface-active substance[a]	Chemical composition	Published HLB value	Hydration heat (g.-cal./g.)
1 TWEEN 20	Polyoxyethylene sorbitan monolaurate	16.7	21.55
2 TWEEN 40	Polyoxyethylene sorbitan mono-palmitate	15.6	19.88
3 TWEEN 60	Polyoxyethylene sorbitan monostearate	14.9	18.69
4 TWEEN 80	Polyoxyethylene sorbitan monooleate	15.0	18.64
5 TWEEN 21	Polyoxyethylene sorbitan monolaurate	13.3	14.05
6 TWEEN 85	Polyoxyethylene sorbitan trioleate	11.0	8.35
7 TWEEN 81	Polyoxyethylene sorbitan monooleate	10.0	6.64

[a] Products of the Atlas Chemical Industries, Inc., Wilmington, Delaware.

tempering period at 20° ± 1°C. is two hours. Thirty minutes operation of the calorimeter was allowed for the establishment of thermal equilibrium. At this point, the initial temperature mark was registered on the photo-paper by switching the registering system. Hereupon, the temperature-equilibrated substance to be investigated was introduced to the calorimeter through a feedway. After 10 minutes running of this system thermo-equilibrium following the hydration process was reached in the calorimeter fluid. The evolution of heat as a function of time was calculated on the basis of the data registered on the photo-paper in the form of a curve representing the temperature changes and taking into account related calibration and water values as well as the specific heat values.

RESULTS AND DISCUSSION

Single Surface-Active Substances

The surface-active substances investigated, reported HLB values (1, 2), and the related heat of hydration values measured calorimetrically are enumerated in Table I. Each datum is the average of six determinations.

From the data in Table I, it is seen that in the investigated HLB range a linear relation exists between the HLB values of the surface-active substances and the heat of hydration.

The relationship may be expressed as:

$$HLB = 0.42Q + 7.5,$$

where: Q = the heat of hydration measured experimentally, expressed in terms of gram-calories per gram.

On the basis of our investigation, it is concluded that this relation applies only to liquid hydrophilic surface-active agents. In the case of surface-

active solids account must be taken of enthalpy changes concomitant
with phase transformations in addition to the hydration process. These
phenomena as well as the application of the method to lipophilic substances
will be discussed in a subsequent paper.

The data presented here are necessarily limited to substances for which
the HLB values are known. It seems, however, that the HLB values of a
number of surface-active liquid materials could be determined by the sug-
gested rapid calorimetric technique.

Mixtures of Surface-Active Substances

According to the HLB system (1, 2) HLB values are algebraically addi-
tive in mixtures of surface-active substances; hence the HLB value of a
mixture can be determined by a simple calculation. On the basis of theo-
retical considerations, however, a linear relation of an additive nature would
be expected from mixtures only when the behavior of each component is
independent, and intermolecular interactions do not occur. Actually, in
the case of mixtures a positive deviation was observed by authors using
different experimental techniques (11–13).

We have investigated the calorimetric behavior of the mixture of SPAN
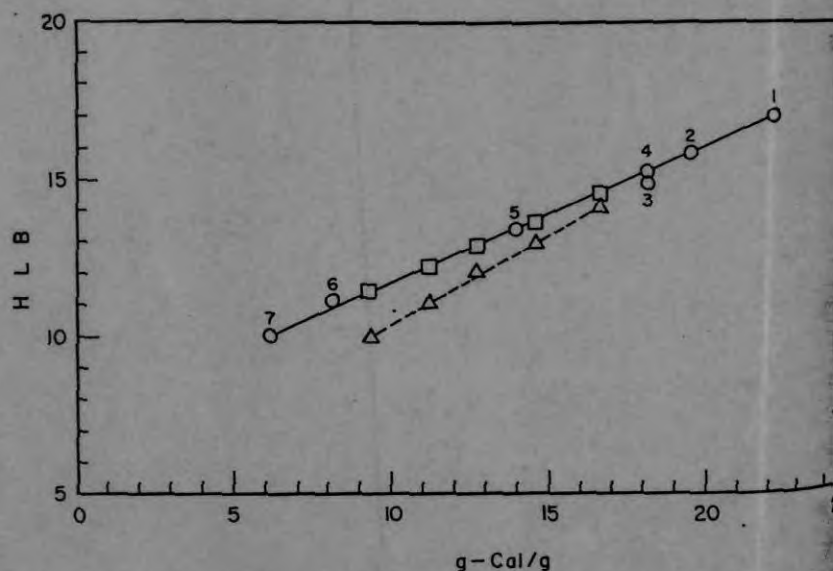80-TWEEN 80 in the region of HLB 10–15. The HLB values calculated

FIG. 2. (O) Relation between HLB values and heat of hydration of hydrophilic
surface-active substances. (△) Relation between heat of hydration of HLB value
for TWEEN 80/SPAN 80 mixtures calculated on the assumption of algebraic addi-
tivity. (□) Relation between heat of hydration and HLB values for TWEEN 80/
SPAN 80 mixtures calculated from the heat equation.

by the equation above on the basis of measured hydration heat differ in a positive sense from the HLB values calculated on the assumption of direct additivity (Fig. 2). This observation corresponds to those previously reported. The conclusion that a strictly additive correlation of HLB values is not to be expected in mixtures of surface-active agents is reasonably established.

SUMMARY

1. A rapid procedure for the experimental determination of HLB values of liquid surface-active agents has been developed.

2. The principle involved is the observation that there is a linear relation between heat of hydration and HLB values of hydrophilic surface-active materials.

3. The technique is suitable for the determination of the HLB values of mixtures of surface-active substances, but in this case the positive deviation of experimental HLB values was observed, in accordance with data recorded previously.

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