Use of Dielectric Constants in the Classification of Surfactants

By WILLIAM G. GORMAN and GARY D. HALL

The polar balance of a surfactant, as reflected by its hydrophile-lipophile balance (HLB), was found to possess a linear relationship with the log dielectric constant (log DEC) of the surfactant. From this relationship, a rapid method of classifying surfactants was presented. A correlation between the polarity of an oil and that of the required emulsifying system was shown for oil-in-water emulsions. The use of direct DEC measurements for mixed surfactants and mixed oils was presented. Correlations between the DEC system and several phases of the HLB system were shown. Possible uses, advantages, and limitations of the DEC system were discussed.

IT HAS been reported (1) that the most formidable obstacle in the selection of surfactants for any particular application is the staggering number that are available. In order to efficiently and rationally select surfactants from among this number, a suitable method of surfactant classification is required. Such a method should provide a parameter that is easily measured with reliability and reproducibility. In recent years many methods (1–12) have been proposed for the classification of surfactants. Although some of these methods have been successful in limited areas of application, only the hydrophile-lipophile balance (HLB) system (1,2,8–12) appears to have found widespread usage. As its basis for classification, the HLB system successfully utilized the long recognized concept of the balance between the polar and nonpolar portions of the surfactant molecule.

Since a balance of polar and nonpolar groupings in a molecule is essentially an expression of molecular polarity, it follows that any method of measuring molecular polarity should provide a means of surfactant classification. According to Debye (13) the word polarity has been used in different ways to express molecular properties more or less connected with the actual arrangement, or the mobility, of the charges of which molecules are supposed to consist. All definitions of polarity are based on a fundamental picture which represents a molecule as a system of electric charges. Nonuniformity in the distribution of these electric charges results in polar groups which confer upon the molecules containing them a characteristic permanent electric moment, which reveals itself in dielectric phenomena. On this basis, it appeared that the polar balance of a surfactant should be quantitatively reflected in a measurement of its dielectric constant. The exploration of this hypothesis was the object of this investigation.

EXPERIMENTAL

The dielectric constants (DEC's) of commercial grade surfactants were determined using a Sargent model V oscillometer. The instrument was calibrated using the standard procedures as outlined in the manual of instructions (14). All of the surfactants were dried prior to use in a vacuum desiccator containing calcium chloride in order to minimize experimental error due to the presence of moisture which may be significant, especially in the more hydrophilic samples. DEC values for the liquid surfactants were determined at room temperature ($25 \pm 1°$), using the pure samples without further treatment. Because of the low melting points of the few solid surfactants examined in this study, their DEC's were determined at the lowest temperature consistent with the maintenance of the surfactant in a liquid state.

RESULTS AND DISCUSSION

Pure Surfactants.—A comparison of the reported HLB's of a number of surfactants and their experimentally determined DEC's is presented in Table I. An apparent linear relationship between these HLB values and DEC values is shown in Fig. 1, where reported HLB was plotted *vs.* log DEC. This linear relationship lends strong support to the hypothesis that surfactant polarity as inferred by its HLB value is quantitatively expressed by its DEC value.

Surfactant Mixtures.—Besides offering a system for classifying pure surfactants, DEC values also provide a means of directly measuring the polarity of mixed surfactants. The HLB system (2) claims that the HLB values of surfactants are additive in behavior on a weight-to-weight basis and that the HLB value of surfactant mixtures may be calculated accordingly. Linear relationships of an additive nature would be expected for surfactant mixtures only if the individual surfactants behaved independently of each other and exhibited no intermolecular reactions. Since it is seldom that these conditions would actually be met, a strictly additive relationship for the HLB of surfactant mixtures would not usually be expected.

Chun and Martin (6) found negative deviations from linearity in the interfacial tension measurements of Igepal[1] mixtures which suggest positive deviations from linearity of HLB values, thus indicat-

TABLE I.—COMPARISON OF DEC AND HLB VALUES OF SURFACTANTS

No., Fig. 1.	Surfactant[a]	Chemical Composition	Reported HLB Value[b]	DEC	Log DEC
1	Arlacel 83	Sorbitan sesquioleate	3.7	3.86	0.587
2	Span 20	Sorbitan monolaurate	8.6	5.57	0.746
3	Span 40	Sorbitan monopalmitate	6.7	4.88[c]	0.688
4	Span 60	Sorbitan monostearate	4.7	4.28[c]	0.631
5	Span 80	Sorbitan monooleate	4.3	4.16	0.619
6	Span 85	Sorbitan trioleate	1.8	3.37	0.528
7	Brij 30	Polyoxyethylene lauryl ether	9.5–9.7	6.02	0.780
8	PEG 200 Monolaurate	Polyoxyethylene monolaurate	9.1	6.66	0.824
9	PEG 300 Monolaurate	Polyoxyethylene monolaurate	11.3	7.27	0.862
10	PEG 400 Monolaurate	Polyoxyethylene monolaurate	12.9–13.1	7.32	0.864
11	PEG 600 Monolaurate	Polyoxyethylene monolaurate	14.5	8.14	0.911
12	Renex 648	Polyoxyethylene alkyl aryl ether	10.0	6.57	0.818
13	Renex 688	Polyoxyethylene alkyl aryl ether	12.5	7.25	0.860
14	Renex 690	Polyoxyethylene alkyl aryl ether	13.0	7.18	0.856
15	Tween 20	Polyoxyethylene sorbitan monolaurate	16.7	9.89	0.995
16	Tween 40	Polyoxyethylene sorbitan monopalmitate	15.6	9.49	0.977
17	Tween 60	Polyoxyethylene sorbitan monostearate	14.9	8.27	0.918
18	Tween 80	Polyoxyethylene sorbitan monooleate	15.0	8.75	0.942
19	Tween 81	Polyoxyethylene sorbitan monooleate	10.0	7.50	0.875
20	Tween 85	Polyoxyethylene sorbitan trioleate	11.0	7.53	0.877

[a] All surfactants were products of Atlas Chemical Industries, Inc., except the PEG monolaurates, which were products of Kessler Chemical Co.   [b] Reported values as calculated or determined (1,15,16).   [c] Determined at elevated temperatures.

ing that HLB values may not be strictly additive in nature. Likewise, Maclay (17) found some positive deviations from linearity in the cloud points of Pluronic[2] mixtures and Igepal mixtures.

The nonlinearity of the DEC's of mixtures of pure binary organic systems is illustrated by the work of Miller and Maass (18). Although the same deviations are observed in the dielectric constants of mixed surfactant systems, it is possible to make direct measurements even on multicomponent surfactant mixtures. The deviations from linearity of several surfactant mixtures are shown in Fig. 2. It is interesting to note that these mixtures gave positive deviations from linearity which are in general agreement with the previously reported interfacial tension and cloud point findings for other surfactant mixtures. More importantly, however, is the fact that over a considerable portion of the range for mixtures of Tween 20/Span 20 and for Tween 80/Span 80, deviations from linearity of approximately 0.04 log DEC units (approximately 1.3 HLB units) were observed.

Surfactant Solvent Relationships.—Since dielectric constants give relative values in the same numerical system for surfactants as well as for solvents (including water and oils), it is proposed that dielectric constants, in addition to offering a means of classifying surfactants, could provide a means for relating solvents and surfactants. This feature is not offered by the presently employed systems of surfactant classification. The approximate required HLB's for oil-in-water (o/w) emulsions of various oils, empirically determined by trial and error (1,2,9,12,19) have been reported. A comparison of the required HLB for o/w emulsification

of several oils with the log DEC of these oils is presented in Table II. In Fig. 3 the reported required HLB of surfactant for o/w emulsion is plotted against the log DEC of these oils. Using the relationship indicated in Fig. 1, the approxi-
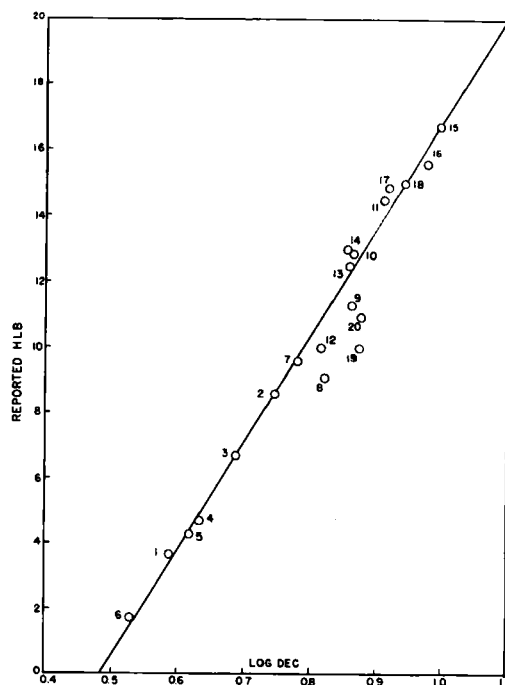

Fig. 1.—Reported HLB *versus* log DEC of pure surfactants.

[2] Trade name for ethylene oxide condensates of polypropylene glycols marketed by Wyandotte Chemicals Corp.
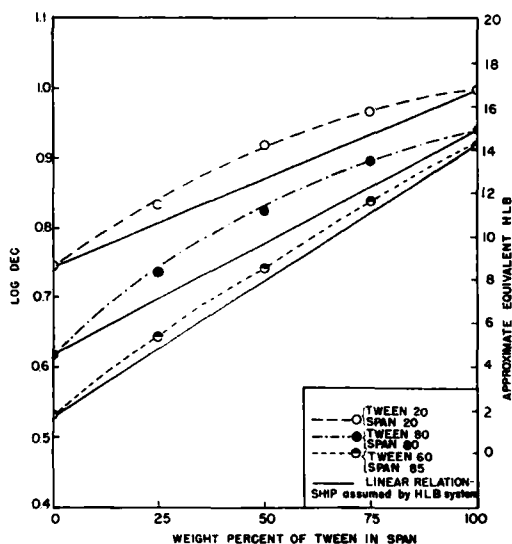
Fig. 2.—Log DEC of surfactant mixtures.

mate equivalent log DEC of surfactant is plotted as a second ordinate. Considering the fact that the required HLB values are reported as whole numbers with a range of approximately ±1 HLB unit, Fig. 3 illustrates the following interesting relationships:

1. A linear relationship exists between the log DEC of these oils and (a) the required HLB of surfactant for o/w emulsion and (b) the approximate equivalent log DEC of surfactant.

2. A proportional relationship is apparent between polarity of the oil (log DEC) and polarity (log DEC) of the surfactant required to effect o/w emulsion. The relationship suggests that for o/w emulsions, the higher the DEC of the oil, the higher would be the required DEC of the emulsifying *surfactant.*

3. The DEC of surfactant required for producing an o/w emulsion of any oil can be approximated from the graph by determining the DEC of the oil.

Solvent Mixtures.—The polarities of a series of oil mixtures, as indicated by their log DEC values, are reported in Fig. 4. Although these mixtures in general approximated additive or linear relationships more closely than the surfactant mixtures, there were still some deviations from linearity as shown by the kerosene-pine oil mixture, which exhibited a slight negative deviation.

The required DEC for producing o/w emulsions of oil mixtures can also be approximated, as described above, by determining the DEC of the oil mixture.

DISCUSSION

Although the data presented in this paper have been necessarily restricted to a limited number of surfactants with known HLB values, it appears that measurements of surfactant balance or polarity can be obtained for many surfactants from dielectric constant data. Such data offer distinct advantages over many of the presently employed systems since DEC's provide physical-chemical values (rather than empirical numbers) which can be duplicated experimentally with a minimum of effort and time.

In comparing DEC and HLB values, preference was given to the HLB values determined experimentally in Griffin's earlier work. It was felt that although the experimental method of determining HLB is tedious and has certain inherent weaknesses, the resulting HLB values are more significant than those calculated from the equations given in the literature (1,8,11). This seems reasonable when we consider that these equations are approximations which appear to have been empirically derived from data based on experimentally determined HLB values.

TABLE II.—COMPARISON OF DEC OF VARIOUS OILS AND THE REPORTED HLB REQUIRED FOR PRODUCING O/W EMULSIONS

No., Fig. 3	Oil	DEC	Log DEC	Required HLB for o/w Emulsion[a]	HLB Ref.
1	Methyl salicylate	9.00	0.954	14	12
2	Dimethyl phthalate	8.51	0.930	15	12
3	Tricresyl phosphate	6.90	0.839	13	12
4	Lauryl alcohol	6.50	0.813	13	12
5	Castor oil	4.67	0.669	12	12
6	Pine oil	4.38	0.642	13	12
7	Isopropyl palmitate	3.15	0.498	10	12
8	Butyl stearate	3.14	0.497	11	12
	Cottonseed oil[b]	3.10	0.491	10	9
				12	12
				7.5	1, 2
9	Silicone oil	2.2–2.8	0.342–0.447	10.5	2
				11	12
10	Oleic acid	2.46	0.391	11	12
11	Toluene	2.38	0.377	9	19
12	Xylene	2.30	0.362	10	12
13	Carbon tetrachloride	2.24	0.350	9	12
14	Kerosene	2.10	0.322	12	12
				12.5	2
	Mineral oil[b]	2.10	0.322	10–12	1
				10–13	12
				10–10.5	2
				12	9

[a] Reported estimate of reliability ±1 HLB unit.   [b] These oils have been omitted from Fig. 3 since there appears to be considerable variation in the reported required HLB values.
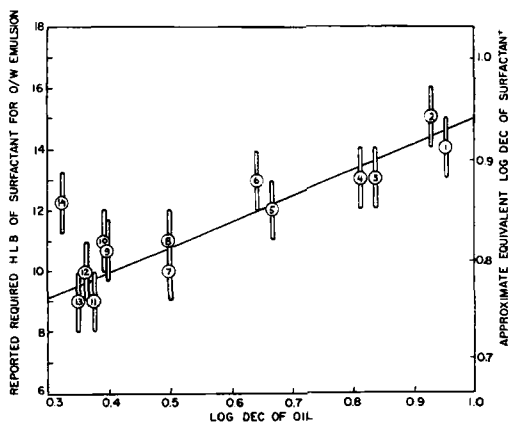
Fig. 3.—Reported required HLB of surfactant for o/w emulsion *versus* log DEC of oil.

The DEC values obtained for some solid surfactants containing large polyethylene oxide chains (usually >10 moles) were frequently lower than anticipated by their reported HLB values. This is probably due to the fact that DEC values of the pure surfactants are representative of the polar balance of the surfactant molecule alone without the influence of an aqueous or solvent environment. Since Maclay (17) reports that the high water solubility of the polyethylene oxide chain is due to hydrogen bonding between the solvent and the ether oxygen atoms in the chain, such interactions might not be apparent from DEC measurements in a solvent free environment. It is probable, however, that the extent of such solvent interactions could be determined from DEC measurements of the pure compounds and of solutions of these compounds in the solvents in question.

Since the "required HLB" of an emulsion is usually determined using a particular pair of surfactants before other groups of surfactants are considered, any deviation of the actual HLB from its theoretical value could be misleading. The positive deviations from linearity observed in the DEC values of surfactant mixtures suggest that the actual HLB's frequently deviate from the theoretical values assumed for such mixtures. These deviations were apparent whether. DEC's or log DEC's were plotted *vs.* concentration, expressed in terms of % w/w, % v/v, or mole fractions. The use of DEC's could be extremely useful in the study of such mixed surfactant systems.

Expressed in terms of dielectric constants, most surfactants would have a value in the range of 3–13. However, it should be remembered that a surfactant must also have certain other properties. The molecule of a surfactant must contain one portion which is strongly attracted by the first phase or excluded by the second and another portion which should be excluded by the first phase or attracted by the second. For most systems this usually requires a lipophilic portion of substantial molecular size. Griffin (8) states that compounds should have molecular weights of at least 200 to be surfactants, while materials with molecular weights below 200 in the HLB (DEC) range of surfactants are often some of our best solvents.

Although this present investigation was intended mainly to introduce the concept and application of DEC measurements in the areas of surfactant classification and usage, there are many related applications which have not been covered in this study. Besides the general correlation of DEC values with HLB values, there also appear to be some correlations of DEC values with cloud point data, interfacial tension measurements, surface tension measurements, foaming properties, the solubilization of liquids and solids in other liquids, and critical micelle concentrations of some surfactants.

SUMMARY

1. The polar balance of a surfactant, as reflected by its hydrophile-lipophile balance (HLB), was found to possess a linear relationship with the log dielectric constant (log DEC) of the surfactant.

2. A rapid method of surfactant classification based on dielectric constants has been presented.

3. The use of this system for the direct measurement of surfactant mixtures was shown. Positive deviations from linearity were observed on the mixtures studied.

4. The use of the DEC system for the measurement of several oil mixtures and a range of polar and nonpolar solvents was described.

5. In the preparation of oil-in-water emulsions, a correlation between the DEC of the oil and that of a required surfactant system has been demonstrated. It was shown that the more polar the oil the more polar the emulsifying system required.
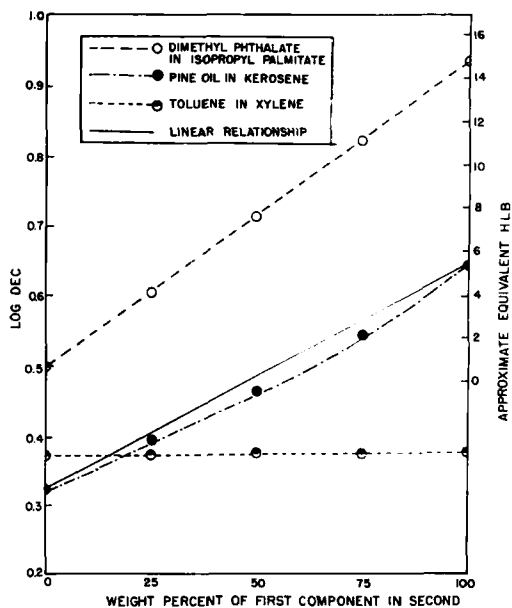

Fig. 4.—Log DEC of oil mixtures.

6. General agreement between phases of the DEC system and the HLB system was noted.

7. The DEC system was presented as offering values which can be measured directly and which can be reproduced in any laboratory by the use of established procedures.

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Antitussive Activity of a Series of Dialkylaminodiphenylbutanol Esters

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The effect of structural modifications upon the antitussive activity of a series of dialkylaminodiphenylbutanol esters was examined. In an attempt to investigate a possible correlation of pharmacological activities, the compounds were also evaluated for their spasmogenic effect upon the intestine and their analgesic activity. Antitussive activity was determined in guinea pigs by means of SO_2-induced cough. Spasmogenic activity was determined by inserting a balloon into the duodenum of anesthetized dogs. Analgesic activity was determined by the rat-tail heat method. The optimum antitussive structure tested within this series was α-*dl*-2-propionoxy-1,2-diphenyl-3-methyl-4-dimethylaminobutane hydrochloride. The optimum analgesic structure tested in this series was the 2-acetoxy analog of the same compound. Some degree of correlation was shown among the activities, although exceptions were noted.

THE PRIMARY purpose of this study was to investigate the influence of certain structural modifications upon the antitussive activity of dialkylaminodiphenylbutanol esters. Since it had been observed that these compounds exhibited analgesic and spasmogenic activities, the possibility of correlations among these activities also was investigated. The antitussive evaluation was made using a new method which will be described in detail.

The compounds chosen for this study were from

a series of dialkylaminodiphenylbutanol esters prepared by Pohland and Sullivan (1) of The Lilly Research Laboratories. All of these compounds were racemic mixtures, and were synthesized by the same general procedure from their corresponding ketones. The compounds used in this study are listed in Table I with their respective melting points.

EXPERIMENTAL

Antitussive Testing Method.—Many problems are associated with the evaluation of antitussive agents and a variety of methods have been employed in an attempt to overcome these difficulties. The major problem is in evoking a reproducible cough. This reproducible cough must be responsive to known antitussive agents, and the method must be sensitive enough to discriminate among varying doses of these compounds. Often this discrimination is not good and results in a flat dosage-response relationship. The numerous disadvantages and problems of most methods led to the development of the following procedure which was used to determine the antitussive activity of the diphenylbutanol esters.