All the seed samples were relatively rich in oil (20–33%). The calculated protein content of the oil-free meal on a dry basis, 21–34%, is lower than that of the usual oilseed meals, but adequate to be useful as a feed material. Should profitable uses develop for this oil and meal, the variability of germ plasm in this collection offers hope that a breeding program could develop plant forms suitable for mechanical production and harvesting and possibly also could vary the oil composition to increase its value for specific applications.

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The Determination of Hydrophile-Lipophile Balance by Gas-Liquid Chromatography[1]

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Abstract

Measurement of the relative retention time of a pair of liquids, one polar and one nonpolar, permits determination of the polarity of the liquid chromatographic substrate. It is shown that this polarity is a measure of the hydrophile-lipophile balance (HLB) when the substrate is a surface-active agent. The effects of structure, additivity in mixtures, and free polyol are discussed. A GLC apparatus, designed to permit the rapid determination of HLB by this technique, is described.

Introduction

EVER SINCE the concept of HLB-number was introduced by Griffin (1) as a measure of the polar character of emulsifier molecules, attempts have been made to relate this quantity to some basically surface-chemical property of the emulsifying agent. This has been done with two ends in view: first, to attempt to place this admittedly pragmatic index on a firmer theoretical basis and, secondly, to find a method for the rapid and easy determination of the HLB number. Earlier work in this area has been summarized by one of us (2). More recently, attempts have been made to correlate HLB-number (or equivalent indices) with liquid-liquid distribution data (3), stability to centrifugation (4), and to interfacial tension (5).

Employing a simplified picture of the mechanism of emulsion breakdown, Ross, Chen, Becher, and Ranauto (6) demonstrated that a correlation existed between spreading coefficient and HLB-number. It was possible to show that for a given two-phase system the HLB for maximum emulsion stability corresponds to a spreading coefficient which is slightly negative (for oil-in-water emulsions, at least).

Davies (7) has demonstrated that coalescence rates, as measured by the technique of Cockbain and McRoberts (8), can be correlated to HLB-numbers, and that a thermodynamic extension of these observations permits us to calculate HLB-numbers as a sum of structural factors, much in the same way as done with the parachor.

Davies (9) has also shown recently that the HLB-number may be related to the phase ratio at which inversion of an emulsion occurs under dynamic conditions, and has designed an emulsator which permits ready determination of this parameter.

However, recent progress in the area of analytical chemistry, notably in the development of the techniques of GLC, suggests that a more-or-less direct measurement of the polarity (hence, implicitly HLB-number) of the surface-active molecule may be possible, without having recourse to a specifically surface-chemical property. As is well known, the ability of a gas-chromatographic "substrate" to separate the components of a sample depends on the polarity of the substrate with respect to the components of the sample. From this point of view, the use of a surface-active agent as a substrate in GLC might well enable one to carry out a direct determination of HLB-number.

In 1959, Harva, Kivalo, and Keltakallio (10) reported that if one employed a nonionic surface-active agent as the liquid substrate in GLC, there was a linear relationship between the partition coefficient for a particular chromatographic sample material and HLB-numbers of the various substrates. The sample materials studied were water and diisobutylene.

For water, they found that two approximately parallel lines of positive slope were obtained for sorbitan fatty acid esters and polyoxyethylated sorbitan fatty acid esters, respectively, while with diisobutylene a single straight line of negative slope was obtained.

In the last year, Huebner (11) has suggested that a more meaningful measure of polarity is the "polarity index." This is based on the determination of an "apparent carbon number" for methanol. It depends on the well-known fact that the logarithm of the retention volume of each member of a homologous series is a linear function of the number of carbon

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[1] Presented at National Colloid Symposium, Ottawa, June, 1963.

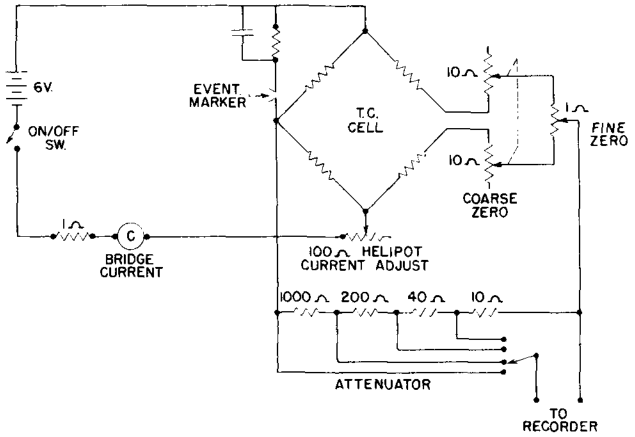

FIG. 1. Electrical circuitry for GLC apparatus.

atoms. Thus, by using a mixture of methanol and a homologous series of hydrocarbons as his sample material, Huebner plots the retention volumes of his hydrocarbons logarithmically, and interpolates the retention volume of the methanol to determine the "carbon number," which is defined as the number of carbon atoms the methanol would have if it were a hydrocarbon with the same retention volume on the particular substrate under test.

The polarity index is then defined in terms of the carbon number as:

$$\text{Polarity Index} = 100 \log (C - 4.7) + 60$$

Huebner was able to show, in a limited way, that the polarity index thus defined was linearly related to the HLB-Number.

Although, in simplicity, this represents a considerable advance over the technique described by Harva and co-workers (10), the determination is still fairly cumbersome. This report details our efforts to simplify still further the determination of HLB-number by gas chromatography.

Experimental

Materials. The surface-active agents examined were all commercial nonionic agents manufactured by Atlas Chemical Industries, Inc. They were all used as-is, with the exception, noted below, that certain of them were treated by aqueous extraction of an ethyl acetate solution to remove the small amounts of free polyol, in order to determine the effect of this parameter.

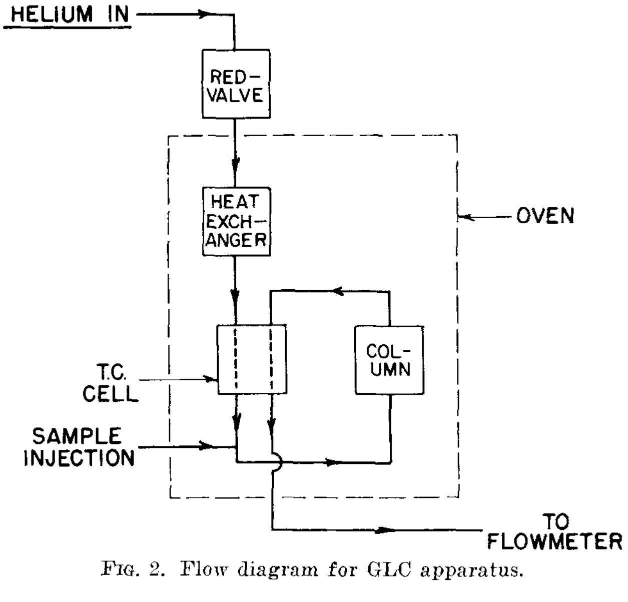

FIG. 2. Flow diagram for GLC apparatus.

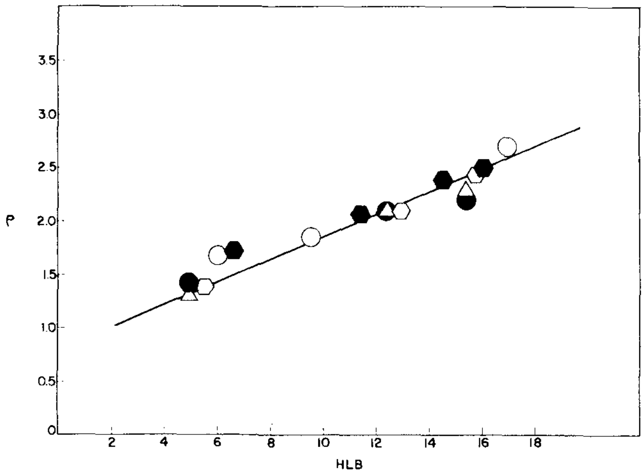

FIG. 3. Retention time ratio, ρ, *vs.* HLB for polyoxyethylated fatty alcohols. Outline circle—lauryl; black hexagon—tridecyl; outline hexagon—cetyl; black circle—stearyl; outline triangle—oleyl.

Apparatus. A survey of the available GLC equipment indicated that there was no inexpensive commercial instrument which was adaptable to our needs. A simple, pilot instrument was constructed, incorporating the degree of control we believed would be required, and after some preliminary studies, a more elaborate, but still simple instrument was built. Figure 1 shows the electrical circuitry employed in these instruments, while Figure 2 shows the piping layout.

The thermal conductivity cell is a commercial *Gow-Mac* Model 9285 cell (pretzel geometry), operated from a 6-v storage battery; the recorder employed is a Varian G-11A 5 mv full-scale instrument.

The final design adopted combined simple circuitry and a layout which permits rapid exchange of columns, together with an oven permitting rapid heat-up and thermal equilibration of the columns.

Methods. The surface-active agent to be studied is deposited from acetone on three times its weight of acid-washed Chromosorb-P (35–80 mesh), and packed into a 3-ft long ¼-in. diam copper column. Normally, the instrument oven, which houses both the column and detector, is operated at 80 ± 0.5C, although it is possible to operate at other temperatures. The filaments are operated at a current of 150 ma.

Rather than use the complex mixture suggested by Huebner, a 50-50 by volume mixture of ethanol and hexane was adopted as the sample to be injected.[2] In the determination, 3.0 μl of the BTM is injected, although in particular cases a smaller or larger amount may be convenient. Two well-defined peaks are obtained, the hexane peak normally appearing first.

The data are reported in terms of the ratio of the retention times of the two components

$$\rho = R_{EtOH}/R_{Hex}$$

where R_{EtOH} is the retention time for ethanol, and R_{Hex} that for hexane.

Results and Discussion

Measurements of the retention-time ratio are plotted as a function of the known HLB for a number of

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[2] It should be noted that there is a terminological problem connected with the discussion of these experiments. In conventional GLC, it is the unknown sample which is injected into the column, containing a substrate of known properties. In the present case, involving as it were inverse GLC, the injected sample is of known composition, while the substrate is the unknown, at least to the extent that we wish to determine its HLB. In order to prevent confusion, the injected mixture will hereafter be referred to as the binary test mixture (BTM).

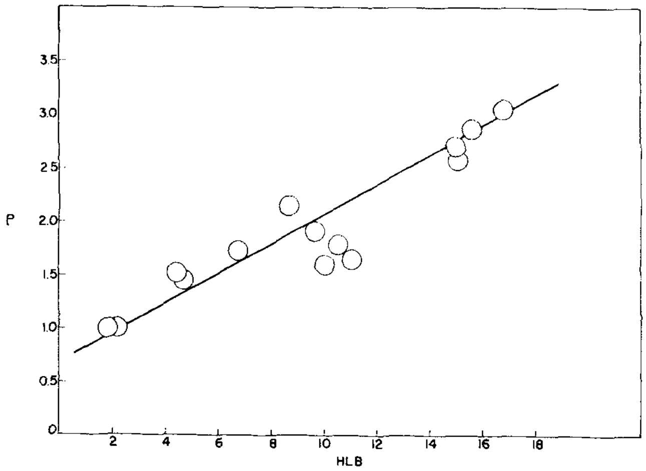

Fig. 4. Retention-time ratio, ρ, *vs.* HLB for sorbitan fatty acid esters and polyoxethylated sorbitan fatty acid esters.

polyoxyethylated fatty alcohols in Figure 3. A satisfactory straight-line relationship between these two parameters was found. Figure 4, which represents similar data for a series of sorbitan fatty acid esters and polyoxyethylated sorbitan fatty acid esters, shows somewhat more scatter, and the best straight line through these points does not coincide with that for the fatty-alcohol derivatives.

Since partial ester emulsifiers normally contain several per cent of free polyol (in varying amounts, depending on the particular agent), it was thought that this might explain the scatter.

The polyol was removed from the sorbitan derivatives by extraction and the measurements repeated. The data for these samples show in Figure 5. As can be seen, the scatter is much reduced, and the line now coincides with that for the alcohol derivatives. It is interesting that the retention time ratio for the extracted polyol is consistent for all samples, being very close to 4.0.

Regression analysis of the data of Figures 3 and 5 yields the relation

$$\text{HLB} = 8.55\rho - 6.36$$

It should be emphasized that this relation may give erroneous results with substances containing substantial free polyol, unless the retention time ratio is corrected for the polyol.

In connection with the question of linearity, it should be pointed out that it has long been assumed that the HLB-number of a mixture of surface-active agents could be calculated on the basis of algebraic additivity.

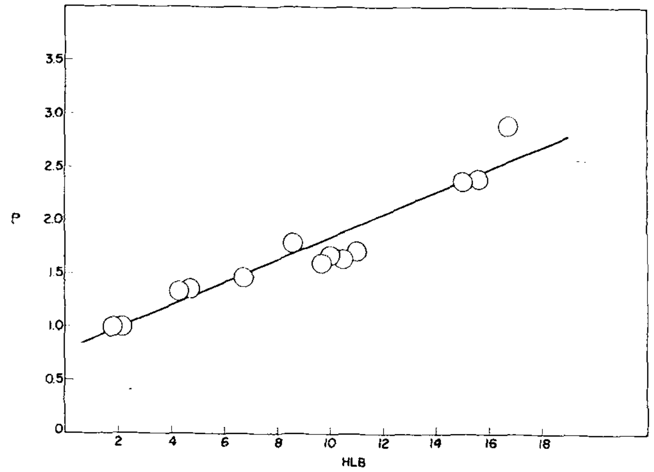

Fig. 5. Retention-time ratio, ρ, vs. HLB for polyol-extracted sorbitan fatty acid esters and polyoxethylated sorbitan fatty acid esters.

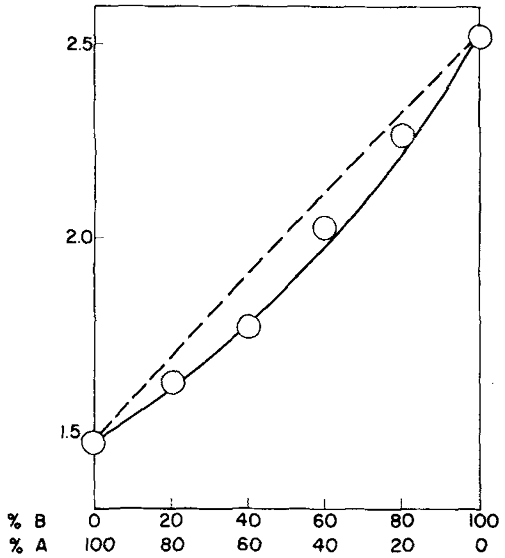

Fig. 6. Retention-time ratio, ρ, *vs.* composition for sorbitan monooleate (A)—polyoxethylated sorbitan monooleate (B) mixtures.

That this is not strictly the case is indicated in Figure 6, where data are given for mixtures of sorbitan monooleate and polyoxyethylated sorbitan monooleate. The dashed line shows the ideal behavior for the mixtures, while the experimental points and solid line indicate the nonideal behavior actually found. It should be emphasized that this deviation from nonlinearity is small, and probably is insignificant in practical applications. Recent careful work has indicated, however, that the effect can be observed under rather special conditions.

In the course of our preliminary studies, it was found that the observed retention time ratio was quite sensitive to column temp and the variability with respect to temp is shown in Figure 7 for sorbitan monooleate and polyoxyethylated sorbitan monooleate. As can be seen, the ratio increases with decrease in temp, the temp coefficient increasing with increasing HLB.

One is rather tempted to speculate as to whether this variation with temp is purely an artifact inherent in the GLC method, or does in fact reflect an actual change of HLB with temperature. If this

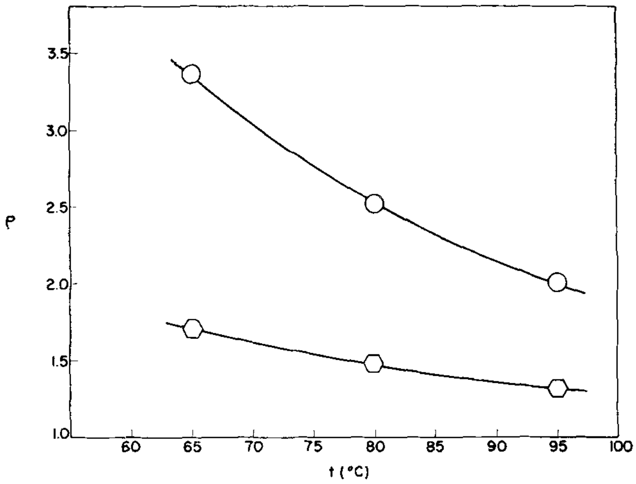

Fig. 7. Retention-time ratio, ρ, *vs.* temperature for sorbitan monooleate (outline hexagon) and polyoxethylated sorbitan monooleate (outline circle).

should turn out to be the case, it might serve to explain some heretofore obscure experimental facts, but, on the other hand, it would probably require a radical reformulation of some of our ideas about emulsion stability.

ACKNOWLEDGMENTS

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Evaluation of Butyl Stearate, Butyl Oleate, Butyl Ricinoleate, and Methyl Linoleate as Poly(vinyl Chloride) Plasticizers[1]

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Abstract

An investigation of butyl stearate, butyl oleate, butyl ricinoleate, and methyl linoleate was made to determine the extent of their compatibility with poly(vinyl chloride) and their plasticizing effects on the physical properties of the resulting molded sheets. These monoesters were evaluated as the sole plasticizer and in combination with DOP. The results showed the materials to have limited compatibility in general, being less than 10% of the total mix. In combination with DOP these compounds were found to improve the plasticizer efficiency, color, low temperature flexibility, and heat stability of the molded poly(vinyl chloride) sheets over those containing DOP as the sole plasticizer. Tensile strength, per cent elongation, and light stability properties were essentially comparable to those found for pure DOP.

Introduction

THE PLASTICIZER literature contains numerous references to the limited compatibility of monoesters such as butyl stearate and butyl oleate with poly (vinyl chloride) resins. Doolittle (1) states that the quantity of butyl stearate that can be added to vinyl chloride compositions is very small since the resulting material tends to exude and develop an oil film on the surface and that butyl oleate is slightly more compatible, owing to its double bond; however, the extent of compatibility and the resulting properties are not discussed in the literature. Therefore, several monoesters of fatty acids were studied in order to determine the extent of compatibility and the effect on physical properties of poly(vinyl chloride). In addition, it has been stated that compounds containing free hydroxy groups have limited compatibility (2); an exception to this is the citrate esters. One of the compounds studied contains in addition to unsaturation a free hydroxyl group.

Experimental

Materials. The materials used in this investigation are all commercial.

Material	Source	Iodine number		% FFA
		Theory	Experimental	
Butyl Stearate	Ohio Apex	0	1.46	0.44
Butyl Oleate	Wilson-Martin	74.98	75.98	0.80
Butyl Ricinoleate	Baker Castor	71.59	74.95	1.75
Methyl Linoleate	Pacific Vegetable Oil	172.40	138.86	0.71

Plasticizer Evaluation. A three-component formulation of resin, plasticizer and stabilizer was used. The resin was Geon 101 poly(vinyl chloride). Two plasticizer formulations were employed, one (A) in which the plasticizer was varied from 4–34% with respect to the resin, and the other (B) using a total of 34% plasticizer of which the amount of the monoester varied from 4½–29½% combined with the necessary amount of DOP (di-2-ethylhexylphthalate) to bring the total plasticizer to 34% of the total mix.

A barium-cadmium liquid phenate stabilizer system (Mark M) was used at 1% of the total mix for all the formulations. Since the primary purpose of the study was to determine compatibility and effect on mechanical properties no attempt was made to attain maximum heat and light stability. The formulations were milled at 160C for 7 min except where low compatibility prevented fusion, thereby requiring a longer time on the mill. Samples requiring more than 5 min to fuse and form a complete band were milled an additional 3 min after forming a complete band. Compatibility was determined by observation of the time of fusion during milling and the time for exudation to appear after molding. Samples were

TABLE I
Fusion Time (Min)

%	Butyl stearate	Butyl oleate	Butyl ricinoleate	Methyl linoleate	DOP
Formulation A					
4	3	2	2	2	1½
9	5	3	2½	1½	1½
14	..	7	2½	2	½
19	..	..	5	2	½
24	..	..	5½	2	½
29	..	..	..	2½	½
34	..	..	..	3	½
Formulation B (Total plasticizer 34%)					
4½	½	½	½	½	..
9½	½	½	½	½	..
14½	½	½	½	½	..
19½	2	1½	1	½	..
24½	3½[a]	12	3	1	..
29½	..	..	7	2	..

[a] 22% butyl stearate.

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[1] Presented at the AOCS Meeting, Minneapolis, 1963.
[2] A laboratory of E. Utiliz. Res. and Dev. Div., ARS, USDA.