Further Comments on the Calculation of Restricted Random Glyceride Distribution[1]

RECENTLY Kartha (JAOCS *39,* 272 [1962]) criticized the method of calculating restricted random glyceride distribution proposed by Hammond and Jones (JAOCS *37,* 376 [1960]). Hammond and Jones had pointed out that Kartha's equations give negative values for GU_3 when the saturated fatty acids exceed 61.8% and GS_3 is reduced to its lowest possible value. In such cases the other glyceride types add up to more than 100%, so that the total is always 100%. In his letter Kartha pointed out that his equations were only approximations and that this had been made clear when the equations were originally published. He also suggests that negative values can be avoided in the example cited by Hammond and Jones by considering the GU_3 to be zero. The remaining glyceride types can then be calculated by a shortcut method which he cites (J. Sci. Ind. Research [India] *13A,* 471 [1954]).

Hammond and Jones had intended to derive an exact calculation of restricted random distribution. The values predicted by this interesting theory had agreed well with the experimental glyceride distribution they had found for cocoa butter. Actually the negative values encountered for GU_3 are quite small, and the results of their equations agree closely with Kartha's equations. The new equations were suggested only in the interests of accuracy. Some further comment, however, seems to be in order.

In calculating restricted random distribution, Kartha starts with a fat in random distribution and calculates how much of the random amount of GS_3 must disappear to reach the observed level of GS_3. The GS_3 which disappears is supposed to react with the GU_3 and GSU_2 in a random manner. The GS_3 and GSU_2 are thereby converted to GS_2U. The GU_3 goes to GSU_2, and some of the GSU_2, thus produced, goes on to GS_2U in a second reaction with GS_3. This conversion of some of the GU_3 to GS_2U is neglected and this approximation was pointed out by Kartha in his original paper. It is obvious, however, that it cannot be the only approximation in the equation, for this approximation would lead to errors only in the amounts of GSU_2 and GS_2U and could not lead to negative values for GU_3. There is a second approximation in Kartha's calculations which is: As the hypothetical random triglyceride mixture proceeds towards a restricted random distribution by the paths Kartha postulates, the ratio of GU_3 to GSU_2 will change continually until it reaches the final restricted random ratio. Since the proportions of GU_3 and GSU_2 which react with the disappearing GS_3 depend on the ratio of GU_3 to GSU_2, the proportions reacting are constantly changing. Kartha assumes that the ratio of GU_3 to GSU_2 remains fixed at the random value during the entire reaction, this leads to the negative values for GU_3 under the conditions cited by Hammond and Jones.

Since Kartha had evidently not considered this second approximation in his equations, Hammond and Jones had to deal with it without guidance from him in their efforts to derive a more exact equation. They attempted to do this within the spirit of his original calculation and the theory he had proposed. Of course, it would be possible to calculate the conversion of a random glyceride mixture to a restricted random one, using only the paths specified by Kartha. But in the light of the above analysis, this now appears to be a trivial case. Since the fat never really exists as a random triglyceride mixture that is then converted to a restricted random one, an exact calculation of such a conversion could not be expected to agree with reality. Thus Hammond and Jones assumed that restricted random distribution deviates from random distribution only in the limitation of the amount of GS_3. This entails the assumption that the unsaturated triglycerides are in equilibrium with each other, and it is this assumption which Kartha has objected to.

In calculating the conversion from a random distribution to a restricted random one, Kartha has assumed that the only reactions occurring are

$$GU_3 + GS_3 \longrightarrow GSU_2 + GS_2U$$
$$GSU_2 + GS_3 \longrightarrow 2GS_2U$$

However, if Kartha postulates that the GS_3 can exchange acyl groups with GU_3 and GSU_2, in the presence of lipase, what is to prevent the unsaturated glycerides from exchanging acyl groups with one another? It is not even necessary for a direct equilibrium to exist among the unsaturated glycerides. If the reactions which Kartha has postulated between GU_3, GSU_2, and GS_3 are reversible, the unsaturated glycerides are indirectly but effectively in equilibrium with each other. Indeed, the unsaturated glycerides may obey the equilibrium relation when they are not even indirectly in equilibrium. In such cases the equilibrium is only a hypothetical one. For example, in a random glyceride mixture, the unsaturated glycerides will be in the proportions that would occur if they were in equilibrium, even though one can imagine ways of obtaining a random glyceride mixture in which the acyl groups are not free to migrate after being attached to the glycerol. In deriving their equation Hammond and Jones could find no justification in Kartha's writings for the assumptions needed to rule out equilibrium among the unsaturated glycerides. On the contrary, one can find such statements as, "Since there is no restriction in interchange of any radicals between GS_2U, GSU_2, and GU_3, the different saturated and unsaturated acids will be distributed in the same ratio in these three glyceride types *(Ibid).*

Kartha also objects to the method of calculation of Hammond and Jones because it "does not take into consideration the fact that the proportions of mono- and diglycerides formed in earlier stages will be those required according to chance distribution. . . . " The equation of Hammond and Jones describes a final state condition. It makes no assumption about the

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nature of mono- and diglycerides which may exist on the way. It is not clear to me why this is objectionable or how Kartha's calculation is any different in this respect. For example, random distribution equations describe the final state of a glyceride mixture equally well whether it was made by reacting a fatty acid mixture with glycerol or by a very specific synthesis of triglycerides which were randomized with a suitable catalyst as a last step.

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Definition of the Word "Detergent"

THE WORD "DETERGENCY" is commonly understood to mean cleansing or removal of soil (or dirt or foreign matter) from a substrate by a liquid medium. Definitions incorporating this concept are so frequent that there seems to be no confusion about the meaning of the word "detergency".

The word "detergent," in contrast, has different meanings for different people. Despite the great amount written about detergents, there have been few attempts at definition. These inconsistencies are well illustrated by the following definitions of "detergent."

Webster's Distionary (1) "A cleansing agent . . ."

Chemist's Dictionary (2) "(1) A substance used for its cleansing action. (2) A particular type of cleansing agent that does not precipitate insoluble sludge. Such detergents often contain organic sulfonates."

Tarring (3) "Broadly, a detergent is any material which, when added to water, assists in the removal and disposal of dirt from substrates."

Schwartz and Perry (4), p. 12, "The newer synthetic surface active agents are most often referred to, for brevity's sake, as detergents and/or wetting agents."

P. 369, "Detergency in its broadest sense merely means cleansing, and a detergent is therefore any agent which cleans."

Bacon and Smith (5) "A substance which when dissolved in water increases the inherent detergent power of water."

American Society for Testing Materials (6) "A composition that removes soil."

McBain (7), p. 100, "The American Society for Testing Materials defines a detergent as 'any material which cleans'. Thus, water through solvent and especially mechanical action, is an important detergent."

P. 103, "The three main classes of detergents are anion active, cation active and non-electrolytic."

Snell (8) "All detergents are surface active agents, the molecules of which concentrate and orient at the interface of a solution."

Durham (9) "Although detergency is a mosaic of many diverse phenomena a unifying element exists in the structure of the detergent ion or molecule. In all cases the detergent molecule has a dual character, in that a part of the molecule has water attracting tendencies, while at the same time the molecule also possesses groups that are hydrophobic. It is because of this peculiar molecular structure that detergent solutions possess good wetting and emulsifying power, that they foam and are capable of cleaning soiled surfaces."

It is apparent that one school of thought limits the use of the word "detergent" to long-chain dipolar compounds although many of these exhibit no power of detergency. Such compounds (amphiphiles) are adequately described by the term "surface-active agent" or similar expressions. It seems preferable that the word "detergent" be restricted to a meaning consistent with that of the unambiguous word "detergency".

Bourne and Jennings (10) consider that the common factor in all detergency is a work requirement. The principal function of a detergent is to reduce the work requirement (detergents are used because they make cleaning easier). Using this concept we propose the following definition:

> A DETERGENT IS ANY SUBSTANCE THAT, EITHER ALONE OR IN A MIXTURE, REDUCES THE WORK REQUIREMENT OF A CLEANING PROCESS.

The definition is consistent with the meaning of the word "detergency". It does not specify any special chemical group of compounds. It includes soap. It includes the surface-active compounds that have some power of detergency, and excludes those that do not. It includes substances (such as sodium hydroxide) that have a strong power of detergency but are not surface-active; substances (such as the polyphosphates) that may have a synergistic effect; and substances (such as sodium carboxymethylcellulose) that restrict redeposition of removed soil. It is broad enough to include detergents that are used in non-aqueous systems. It includes solvents and also cleaners that function by chemical degradation (such as strong acids), since these reduce the work requirement to zero. It does not include abrasives, which do not reduce work requirement but merely increase efficiency with which the work is applied to the soil.

A well found definition of "detergent" should help resolve the confusion that arises when different workers use the same word to mean different things.

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