Miscibility of Glycerol with Fatty Acids and Glycerides

THE FORMATION of monoglycerides being a function of the miscibility of fats (or fatty acids) with glycerol the extent of this miscibility is of theoretical and practical importance. Nevertheless, only a few relevant data have been published. Earlier work by Feuge and Bailey (1) established the maximum total amount of glycerol reactable and miscible with hydrogenated cottonseed oil but their actual miscibility cannot be readily assessed therefrom. More recently Choudhury (2) reported that in the presence of 0.1% NaOH the solubility of glycerol in a number of fats amounted to 18–24 weight percent glycerol on the fat basis between 175–200C. No data on the miscibility of glycerol with fatty acids could be found in the literature. Certain observations in this laboratory incompatible with Choudhury's results have led to a re-examination of his data. In addition to the miscibility of glycerol with a number of natural fats and synthetic triglycerides its miscibility with various pure fatty acids and monoglycerides has been determined and is reported here.

The determinations were carried out at 180 and 200C in test tubes of 10 mm immersed in a thermostat. The reactants were stirred by hand with a glass rod for 5 min or alternatively by bubbling nitrogen, which gave similar results. Approximately equal amounts of preheated glycerol and fats were used. After 5 min settling samples were drawn off with a preheated pipette, weighed, taken up in a mixture of chloroform and 5% aqueous acetic acid and the amount of uncombined glycerol was estimated following essentially Pohle and Mehlenbacher's periodate method (3). No appreciable glycerolysis or esterification were found to occur under these conditions. The influence of 0.1% NaOH on the miscibility was found insignificant and the catalyst was therefore omitted. Some typical results are shown in Table I in which Choudhury's corresponding figures appear in brackets. The great difference between them, despite an otherwise not dissimilar procedure, may be due to Choudhury's using a high speed (1000 r.p.m.) stirrer with ensuing emulsification.

Table I shows that on the absolute percentage basis the molecular weight has little influence on the miscibility of glycerol with triglycerides containing acids with more than 10 carbon atoms. The effect of molecular weight is more pronounced in fatty acids and greater still in monoglycerides. Incidentally the data in Table I explain some results obtained in Choudhury's recent studies on the preparation of monoglycerides (4,5) better than his own miscibility figures.

TABLE I
Miscibility of glycerol with fatty acids and glycerides at 180C and 200C

Material	Percent weight of dissolved glycerol on the fat basis	
	180C	200C
Refined groundnut oil	0.9 (Choudhury at 175C:18.0)	1.2 (Choudhury: 22.3)
Refined coconut oil	1.3 (Choudhury at 175C:19.8)	1.6 (Choudhury: 23.8)
Tristearin	0.9	1.2
Trilaurin	1.2	1.6
Tricaprylin	3.6	6.0
Stearic acid	5.1	7.0
Oleic acid	5.8	7.9
Palmitic acid	7.6	9.6
Myristic acid	11.7	16.5
Lauric acid	23.0	31.4
Caprylic acid	Completely miscible	
1-Monostearin	32.7	
1-Monolaurin	Completely miscible	

The complete miscibility of 1-monolaurin with glycerol at 180C appeared to offer a possibility of preparing monoglycerides of about 90% purity by direct esterification of lauric acid or by reacting coconut oil with a large excess of glycerol. However, this was found impractical owing to the disproportionation of monoglycerides at 180C. This was confirmed by heating pure 1-monolaurin with twice its weight of glycerol for 3 hr at 180C which resulted in a product containing only 74.5% 1-monoglycerides in the fatty portion.

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Utilization Potential of *Crambe abyssinica*

THE CALCULATIONS expressed in our recent appraisal of the economics of *Crambe abyssinica* Utilization [JAOCS, *40*, 1 (1963)], completed over a year ago, included fairly wide ranges of assumptions. Using the *most conservative* figures in regard to sales prices of the brassylic acid and by-products, it was estimated that the chemical industry could afford to pay about 7.7¢/lb for the Crambe oil. This figure appears to have been regarded as our estimate of the likely return that the oil could bring. To correct this impression we have developed a new estimate (taking advantage of all information that has meanwhile come to hand) which we regard as realistic. These calculations indicate that the chemical industry might afford to pay 9.4¢/lb for Crambe oil. They assume a return of 40¢/lb for the brassylic acid and $50/T for the by-product feed.

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