tained by the two methods but that sodium borohydride reduction results in somewhat better yields of lauryl alcohol. In addition, catalytic hydrogenation resulted in the production of small amounts of ethyl laurate and diethyl adipate as by-products. Gas liquid chromatographic analyses indicate that both of these products contain small amounts, less than 1%, of lauryl aldehyde though no aldehyde was detected by infrared examination of the lauryl alcohol isolated from the sodium borohydride reduction product. The aldehyde may have been formed by oxidation of lauryl alcohol either during storage or gas liquid chromatographic analysis, but the possibility that it resulted from incomplete reduction of the ozonolysis product cannot be excluded.

In the gas liquid chromatographic analyses, the response factors of lauryl alcohol, ethyl 6-hydroxycaproate, ethyl laurate, and diethyl adipate vary widely even though all of these materials are fatty derivatives. Large errors would be introduced by failure to consider response factors when analyzing mixtures of this type.

The conversion of the sodium salt of 6-hydroxycaproic acid to the free acid with mineral acid leads to the formation of esters in addition to the free hydroxy acid. However, it was found that utilization of a weakly acidic ion exchange resin for acidification of the salt results in little or no ester formation.

Acknowledgments

The authors acknowledge the valuable contributions of the late W. G. Bickford under whose direction this work was initiated. The authors are indebted to R. U. Bayles for preparation of petroselinic acid and to L. E. Brown and V. O. Cirino for some of the analyses.

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[Received April 7, 1962]

Solubilities of Five Triglycerides in Aqueous Ethanol

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Abstract

The solubilities of trilaurin, trimyristin, tripalmitin, tristearin, and triolein in 90, 95.4, 98, and 100% ethanol between 40C and 90C were determined. The data were compared with data calculated by the ideal solution law.

Introduction

DATA on the solubilities of triglycerides in aqueous ethanol at moderate temps are rather limited although work has been reported by Loskit (1), Robinson, et al. (4), and McElry and King (2). Solubility of thirteen vegetable oils and lard in ethanol solutions was determined by Rao and Arnold (3).

In the current studies the solubilities of trilaurin, trimyristin, tripalmitin, tristearin, and triolein in four aqueous ethanol concentrations were determined using the method of Rao and Arnold (3). The ethanol concentrations were: 100, 98.0, 95.4, and 90.0%. The triglycerides were of 95% or greater purity obtained from Hormel Institute. They were prepared by transesterification of the corresponding pure methyl esters with triacetin. The purification consisted of partition between solvents and low temp fractional crystallization. The principal impurity is the corresponding diglyceride. Temperatures varied from 40 to 90C.

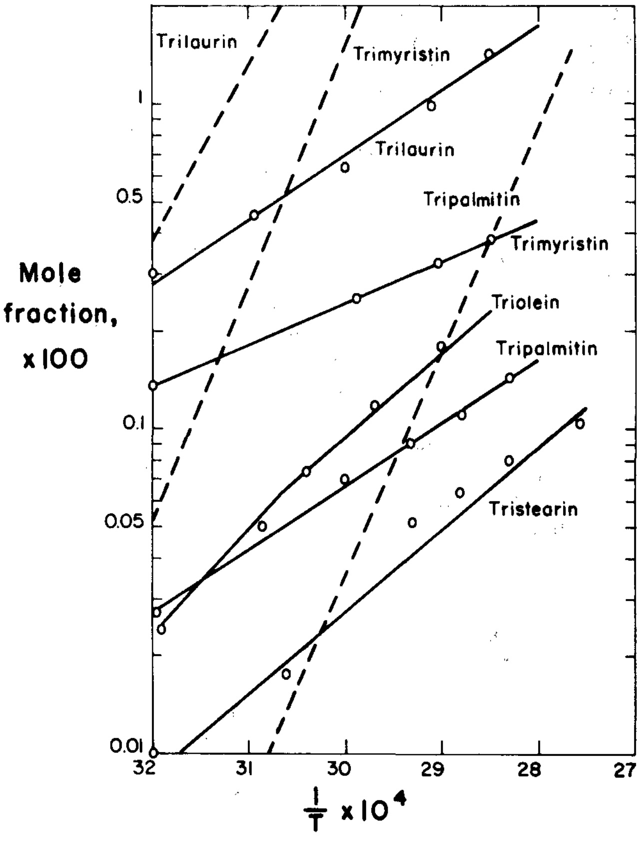

FIG. 1. Solubilities of triglycerides in 90.4% ethanol.
– – – ideal solution
T = degrees Kelvin

The solubility data for the triglycerides in 90.4% ethanol are shown in Figure 1 as the relation between mol fractions dissolved and the reciprocal of the absolute temp. The calculated values for ideal solutions are shown as broken lines for comparison with the experimental data. These values are based on the equation:

$$2.3 \log x_1 = \frac{\triangle H_1{}^F}{R} \left(\frac{1}{T_F} - \frac{1}{T} \right)$$

derived from the Clausius-Clapeyron equation, where X_1 = the mol fraction of the solute, $\triangle H_1{}^F$ = the heat of fusion of the solute, and T = temp in °K. The

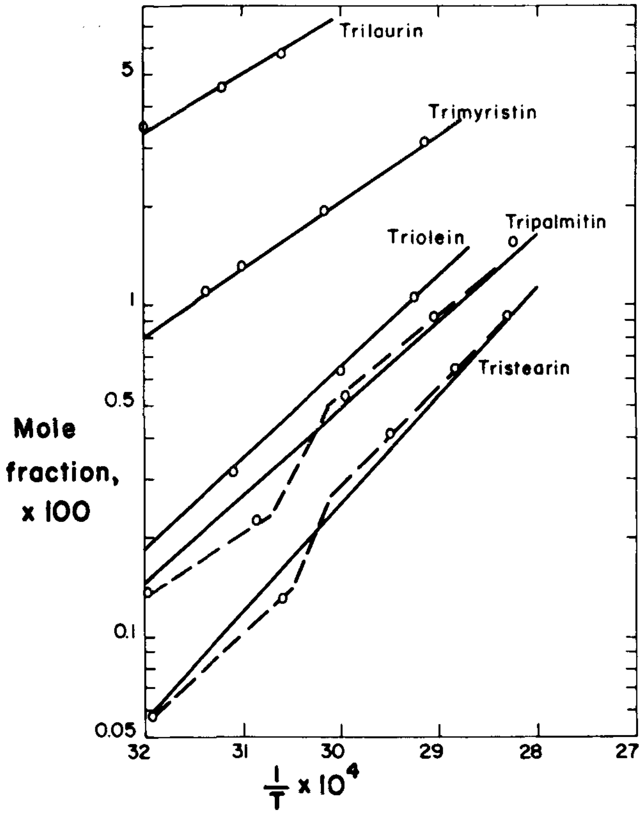

FIG. 2. Solubilities of triglycerides in 100% ethanol. T = degrees Kelvin

experimental values fall along straight lines well except those for tristearin but do not coincide with the ideal values. This variation from ideal behavior is to be expected because of the relatively non-polar nature of the triglycerides in relation to the ethanol solutions. The deviation from the straight line representing the ideal solubility relationship occurs with both tristearin and tripalmitin at all ethanol concentrations but is somewhat more evident at the 100% level as shown in Figure 2. It is significant that the breaks in the curves as shown by the cross over points of the broken lines and the solid lines occur at approximately the melting points of the triglycerides. The probable significance of these breaks is that the solubility of the liquid fat is greater than that of the solid fat, a phenomenon which would be expected. The solubility curves for 95.4 and 98.0% ethanol fall between those shown for 90.4 and 100%. That is, the solubility increases with the increase in ethanol concentration. This solubility increase is similar to that previously secured with various oils (3) and probably results from the decrease in polarity of ethanol solutions with decrease in water content. Within the temp limits studied the triglycerides did not show the critical solution temps observed with oils (3). Since pure triglycerides are the only component in addition to the ethanol they probably present a more ordered arrangement with each other than possible with the mixtures occurring in ordinary fats or oils. The compact arrangement probably does not allow as ready mixing with the ethanol as occurs with the oils. Hence the lower solubility.

The solubilities of the four saturated triglycerides decreased with increase in number of carbon atoms as shown in Figure 3. As the chains of the acid groups become longer the polar effect of the carboxyl groups becomes relatively less resulting in less similarity with the polar ethanol and less solubility. The greater solubility of the triolein over the tristearin results from the presence of a double bond in each acid chain of the former. Double bonds are somewhat polar in their effect on the chain.

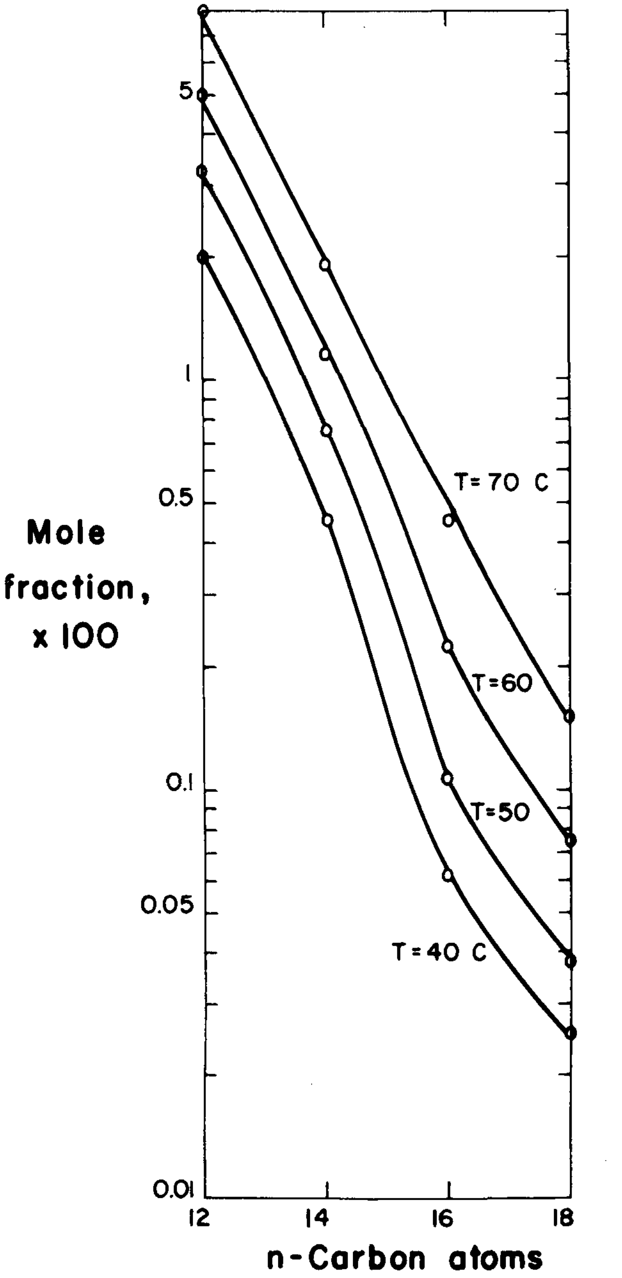

FIG. 3. Relation of number of carbon atoms to the solubilities of saturated triglycerides in 100% ethanol.

Summary

The solubilities of the pure glycerides in ethanol solutions plotted as the mole fraction of the solute versus the reciprocal of the absolute Centigrade temp are straight lines but they deviate from the ideal solubility lines. There is a straight line relation between mol fractions and the number of carbon atoms with a decrease in solubility as the number of carbon atoms increases.

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[Received June 1, 1962]