hundreds of curves representing each type of glyceride molecule present in the substrate. Tocopherol oxidation curves are probably different for each type of glyceride even though iodine values of the substrates are the same. Kinetic studies made on such a heterogeneous substrate as a hydrogenated fat cannot be unequivocally interpreted.

The antioxidant efficiency of natural tocopherol in hydrogenated soybean oil cannot be considered high if it is evaluated in terms of preventing peroxide development. In trace-metal-contaminated fats its effectiveness is low. Uri (15) regards tocopherol as much inferior to butylated hydroxyanisole or propyl gallate, and he does not regard it as the most powerful of the natural antioxidants present in vegetable oils. Peroxides develop to rather high levels for edible fats by the time the rapid autocatalytic stage is reached. In all cases where the fat is protected by citric acid, the tocopherol levels are more than 100 before the tocopherol levels are reduced to 50% of their initial value. It must also be borne in mind that the initial tocopherol level in soybean oil is 0.15%, which is higher than that normally used in the evaluation of antioxidants. This level may be pro-oxidant in its effect and higher than the optimum level, which is also a factor in the development of high tocopherol levels at the time of the peroxide induction point (11, 19).

Summary

The destruction of tocopherol was studied during autoxidation of a series of hydrogenated soybean oils of decreasing unsaturation. The presence of trace amounts of residual hydrogenation catalyst markedly increased the rates of oxidation of the fat and the destruction of the tocopherol to such an extent that the induction period was entirely eliminated. The catalytic effect of the residual hydrogenation catalyst was eliminated by the use of 0.01% citric acid. Tocopherol antioxidation curves obtained with citric acid-protected fats are typical autocatalytic rate curves showing a distinct induction period. The initial rate of loss of tocopherol is increased at iodine values of 112 and 101, then decreased as the iodine values of the fat are lowered to 90 and below. The time of the tocopherol induction period increases with the decrease in iodine values of the hydrogenated fat.

Increase in the time of the induction period is more closely associated with the linoleic acid content of the fat than to the over-all iodine value. The autocatalytic rates of destruction of tocopherol, i.e., rates beyond the induction period, decreased with the degree of hydrogenation of the fat and show a rapid change at iodine values where a marked lowering of the linoleic acid occurs. When essentially all of the linoleic acid has been removed from the oil, the autocatalytic phase of tocopherol destruction has also been eliminated, and at this iodine value the tocopherol oxidizes at a constant rate.

The disappearance of tocopherol per unit of peroxide accumulated was shown to increase appreciably with the degree of hydrogenation. The greater destruction of tocopherol is attributed to reactions with the more stable fat hydroperoxides, which accumulate to a greater extent in the hydrogenated soybean oil than in the original oil.

Acknowledgment

The technical assistance of C. R. Schofield in determining the spectral analysis of the fats is gratefully acknowledged.

REFERENCES

8. Golumbic, Calvin, Oil and Soap, 29, 105-107 (1943).
16. Unpublished data of the authors.

[Received August 7, 1958]

Solubilities of Vegetable Oils in Aqueous Ethanol and Ethanol-Hexane Mixtures

RAMALINGAM KAPARTHI and K. S. CHARI, Department of Chemical Engineering, University of Cincinnati, Cincinnati, Ohio

A RATIONAL APPROACH to the design of an efficient extraction unit to extract vegetable oils from oleaginous materials requires a knowledge of the solubilities of various vegetable oils in the proposed solvent. The published data on the solubilities of oils in ethanol are scanty. Taylor, Larson, and Johnson (10) made a phase-rule study of different systems of oils and alcohols to determine the amount of oleic acid necessary for complete miscibility with 90% alcohol and absolute alcohol at 25°C. Solubilities of soybean oil (4, 9), cottonseed oil (1, 2, 4, 8), peanut oil (4, 8), and other oils, like sesame (4, 8), corn, linseed, and tung oils, are reported in the literature (5, 6). The miscibility data were obtained for different oils by the sealed-tube method (2, 8, 9, 10). The purpose of the present investigation is to determine the solubilities of edible and nonedible vegetable oils in various concentrations of alcohols at different temperatures. It is known that alcohol is a good solvent for oil extraction at elevated temperatures, mostly...
Aqueous Solutions of Ethanol

Results and Discussion

The analyses of vegetable oils employed for the solubility determination are given in Table I. The usual range of values of the oils are shown in parentheses in Table I.

The saturation solubilities of the oils were determined from 40° to 100°C in 85 to 99.9% ethanol. The results are presented in Tables II to V.

From Tables II to V it is seen that the saturation solubility of vegetable oil depends on the concentration and the temperature of aqueous ethanol. The solubilities are very low at low temperatures in all tests and increase tremendously as the critical temperature is reached at any particular concentration. All the investigated oils have complete miscibility at 70°C in absolute alcohol (99.9%). As the alcohol concentration is decreased, the solubility temperature increases. At 80°C, safflower, mowrah, and refined peanut oils have complete miscibility in about 98% ethyl alcohol. In about 95% ethanol, mowrah and refined cottonseed oils are soluble at 100°C, and safflower and peanut oils at 90°C. The solubility results of cottonseed oil in 95% ethanol obtained by the authors are compared with reported data in Figure 1. Some scattering of the results is seen. The results of Sato

### Table I

<table>
<thead>
<tr>
<th>Oil</th>
<th>Sp. Gr. (0.91 to 0.918)</th>
<th>F.F.A. (1.0 to 3.9)</th>
<th>Iodine value (Wt./%)</th>
<th>Saponification value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mowrhah oil</td>
<td>0.9256</td>
<td>4.79</td>
<td>58.98</td>
<td>194.4</td>
</tr>
<tr>
<td>Safflower oil</td>
<td>0.9146</td>
<td>0.78</td>
<td>144.00</td>
<td>194.9</td>
</tr>
<tr>
<td>Peanut oil</td>
<td>0.9115</td>
<td>1.35</td>
<td>90.78</td>
<td>190.6</td>
</tr>
<tr>
<td>Cottonseed oil (refined)</td>
<td>0.9166</td>
<td>1.99</td>
<td>109.30</td>
<td>197.4</td>
</tr>
</tbody>
</table>

### Table II

<table>
<thead>
<tr>
<th>Concentration of ethanol wt. %</th>
<th>Saturation solubilities expressed as g. of oil per 100 g. of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>85.38%</td>
<td>1: 5 at 50°C, 1: 2 at 100°C</td>
</tr>
<tr>
<td>89.28%</td>
<td>1: 5 at 70°C</td>
</tr>
<tr>
<td>95.75%</td>
<td>1: 5 up to 70°C</td>
</tr>
<tr>
<td>98.70%</td>
<td>1: 5 up to 80°C</td>
</tr>
<tr>
<td>99.88%</td>
<td>1: 5 up to 80°C</td>
</tr>
</tbody>
</table>

*CM = Completely miscible.