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 peroxide 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 peroxide levels at the time of the peroxide induction point (11, 13).

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 autoxidation 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.

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Solubilities of Vegetable Oils in Aqueous Ethanol and Ethanol-Hexane Mixtures[1]

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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 indigenous 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

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TABLE I

Analysis of Vegetable Oils

Oil	Sp. Gr.	F.F.A.	Iodine value (Wij's)	Saponification value
Mowrah oil..........	0.8566 (0.857 to 0.87)	4.70	58.99 (53 to 70)	194.1 (188 to 200)
Safflower oil.........	0.9146 (0.9243)	0.78	144.00 (140 to 150)	194.9 (188 to 194)
Peanut oil...........	....	1.36 (1.0 to 3.9)	90.78 (83 to 98)	190.6 (185 to 192)
Cottonseed oil (refined)...........	0.9108 (0.91 to 0.918)	1.00 (0.6 to 1.9)	108.30 (100 to 116)	197.4 (190 to 198)

beyond the boiling point. Lowering of solubility temperature is very desirable for varied reasons, hence the effect of n-hexane addition to alcohol on the solubility of vegetable oils is also to be studied so that optimum extraction conditions can be established.

Apparatus and Experimental Procedure

The apparatus employed is essentially the same as described previously (4, 7). It consists of a mild-steel vessel 2 in. in diam. and 5 in. high, closed at the bottom and fitted with a flange at the top. The vessel is closed with another flange, through the center of which passes a steel paddle stirrer. The temperature of the vessel is controlled by a "Sunvic" controller within 0.5°C.

Samples are drawn through a needle valve, located near the bottom. The apparatus is also equipped with a pressure gauge and a thermometer well.

Measured volumes of oil and alcohol were introduced to the apparatus. The ratio of oil to alcohol was such that there was always excess oil except at and beyond the critical point at which complete miscibility occurred. The mixture was stirred at about 250 r.p.m. for 3 hrs. at the desired temperature and allowed to stand for 1 hr. at the same temperature. The samples of the supernatant liquid were taken in tared ice-cooled flasks by opening the needle valve. The flasks were tightly corked and weighed. Alcohol was removed by heating the flask on a water-bath, and the resulting oil was weighed after drying in an oven at 101°C. to a constant weight. Knowing the weight of the solution and the oil, the saturation solubility was calculated and expressed as grams of oil per 100 g. of solvent. Various strengths of aqueous alcoholic solutions were prepared by diluting absolute alcohol, and the strength was determined by finding the Sp. Gr. and was expressed as weight percentage.

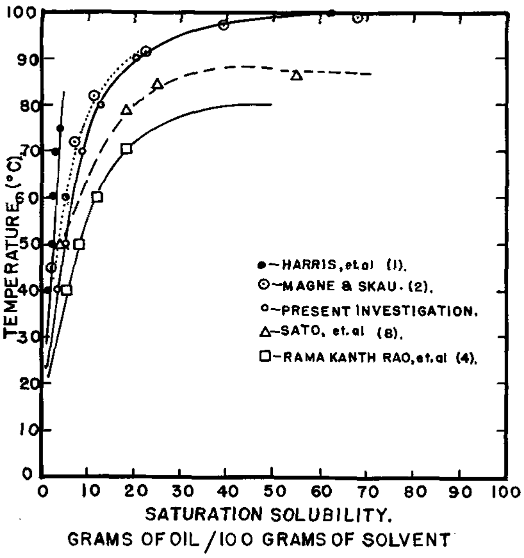

Fig. 1. Comparison of solubility data of cottonseed oil in 95% ethanol.

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 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 spattering of the results is seen. The results of Sato

TABLE II

Saturation Solubilities of Mowrah Oil in Aqueous Solutions of Ethanol

Concentration of ethanol wt. %	Ratio of oil to ethanol by volume	Saturation solubilities expressed as g. of oil per 100 g. of solvent						
		40°C.	50°C.	60°C.	70°C.	80°C.	90°C.	100°C.
85.35..........	1:5 at 50°C. 1:2 at 100°C.	......	0.12	......	......	......	......	4.35
89.38..........	1:5 to 60°C. 1:2 after 60°C.	1.93	2.14	2.72	4.66	5.49	7.27	9.74
95.75..........	1:5 up to 70°C. 1:2 after 70°C. 1:1 at 100°C. also	3.35	4.84	5.94	8.15	14.21	22.93	CM[a]
98.70..........	1:5 up to 60°C. 1:2 after 60°C. 1:1 at 80°C. also	6.72	8.86	12.74	26.86	CM[a]	......	......
99.88..........	1:5 up to 50°C. 1:2 after 50°C. 1:1 at 70°C.	7.98	11.50	23.19	CM[a]	......	......	......

[a] CM = Completely miscible.

TABLE III
Saturation Solubilities of Safflower Oil in Aqueous Solutions of Ethanol

Concentration of ethanol wt. %	Ratio of oil to ethanol by volume	Saturation solubilities expressed as g. of oil per 100 g. of solvent						
		40°C.	50°C.	60°C.	70°C.	80°C.	90°C.	100°C.
85.36	1:2	......	0.70	......	......	......	......	3.56
90.56	1:5 up to 60°C. 1:2 after 60°C.	1.09	1.29	1.91	2.45	3.73	5.28	......
95.75	1:5 up to 60°C. 1:2 after 60°C. 1:1 at 90°C. also	3.38	4.96	7.10	10.23	17.91	CM[a]	......
98.00	1:5 up to 60°C. 1:2 after 60°C. 1:1 at 80°C. also	6.07	10.60	11.87	20.64	CM[a]	......	......
99.94	1:5 up to 50°C. 1:2 at 60° and 70°C. 1:1 at 70°C. also	10.97	16.52	28.02	CM[a]	......	......	......

[a] CM = Completely miscible.

TABLE IV
Saturation Solubilities of Peanut Oil in Aqueous Solutions of Ethanol

Concentration of ethanol wt. %	Ratio of oil to ethanol by volume	Saturation solubilities expressed as g. of oil per 100 g. of solvent					
		40°C.	50°C.	60°C.	70°C.	80°C.	90°C.
90.00	1:5 up to 60°C. 1:2 after 60°C.	1.37	2.35	2.67	4.23	5.54	9.17
95.00	1:5 up to 60°C. 1:2 after 60°C.	2.40	3.52	6.83	13.77	25.31	CM[a]
98.00	1:5 up to 60°C. 1:2 after 60°C.	8.61	11.48	15.67	64.85	CM[a]	......
99.94	1:5 up to 60°C. 1:2 at 70°C. 1:1 at 70°C. also	8.29	10.26	18.77	CM[a]	......	......

[a] CM = Completely miscible.
(Solubilities in 90, 95, 98% ethanol are recalculated results of Rama Kanth Rao's report submitted to Regional Research Laboratory.)

TABLE V
Saturation Solubilities of Cottonseed Oil in Aqueous Solutions of Ethanol

Concentration of ethanol wt. %	Ratio of oil to ethanol by volume	Saturation solubilities expressed as g. of oil per 100 g. of solvent						
		40°C.	50°C.	60°C.	70°C.	80°C.	90°C.	100°C.
90.00 (crude oil)	1:5 up to 70°C. 1:2 after 70°C.	1.35	2.05	3.02	5.22	7.50	10.50	......
95.00 (refined oil)	1:5 up to 60°C. 1:2 after 60°C. 1:1 at 100°C. also	2.97	4.14	5.54	8.22	12.24	20.86	CM[a]
98.00 (crude oil)	1:5 up to 60°C. 1:2 after 60°C.	10.50	16.20	29.55	CM[a]	......	......	......
99.94 (refined oil)	1:5 up to 60°C. 1:2 after 60°C. 1:1 at 70°C. also	9.12	13.51	21.88	CM[a]	......	......	......

[a] CM = Completely miscible.
(Results of crude oil are recalculated results from Rama Kanth Rao's report submitted to Regional Research Laboratory.)

TABLE VI
Saturation Solubilities of Mowrah Oil in Ethanol (99.88%)—Hexane Mixtures

Composition of mixture by volume	Density of solvent mixture d_4^{30}	Ratio of oil and solvent mixture by volume	Saturation solubility expressed as g. of oil per 100 g. of solvent mixture			
			40°C.	50°C.	60°C.	70°C.
100% ethanol	......	See Table II	7.98	11.50	23.19	CM[a]
90% ethanol + 10% n-hexane	0.76922	1:5 at 40°C. 1:2 at 50 and 60°C. 1:1 at 60°C. also	17.36	29.10	CM[a]	......
80% ethanol + 20% n-hexane	0.75732	1:1 at 40°C. and at 50°C.	45.57	CM[a]	......	......

[a] CM = Completely miscible.

et al. (8) are normally expected to be lower than those obtained in the present investigation as there is no proper mixing of oil and alcohol in the sealed-tube method (8). However the results as compared in Figure 1 are higher than the results of present authors. It is likely that they have used crude cottonseed oil for their investigations, and the presence of a fair percentage of free fatty acids in crude oils increases the solubility of the oil in ethanol. The results of Harris *et al.* (1) are lower than those of the authors; however the disparity is lesser at lower temperatures. Magne and Skau's solubility data (2) are higher than those of Harris *et al.* (1) but lower than the results of the present authors. The results of

Rama Kanth Rao *et al.* (4) are higher because of the usage of crude cottonseed oil. Hence the disparity in the results may result from either the method employed or from the quality of the oil used. The effect of various methods of determination of solubility on the solubility of oil is shown in Figure 2. It is seen that the sealed-tube method and flask method (3) give lower solubility results than those of the present apparatus because of improved agitation and elimination of visual observations of turbidity temperatures.

Solubility determinations were also made with various mixtures of different concentrations of alcohol (95.7 and 99.9%) and n-hexane. The critical solubility temperatures are considerably lowered and the solubility of mowrah oil increases with the increase of hexane content (shown in Figure 3 as volume percentage) in the mixture for any particular temperature. It was also observed, as can be seen from Table VI, that the addition of n-hexane to absolute alcohol (99.9%) increases the solubility of mowrah oil considerably and lowers the solubility temperature.

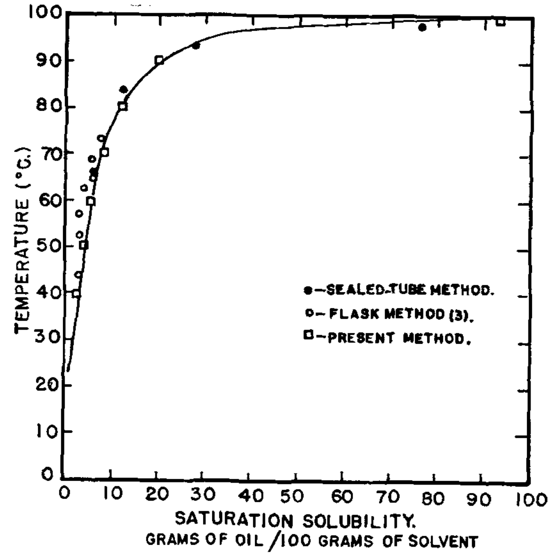

FIG. 2. Solubility of cottonseed oil determined by various methods.

Summary

The solubility of vegetable oils in aqueous ethanol depends on the concentration of alcohol and temperature of the system. At ordinary temperatures even absolute alcohol is not a good solvent for vegetable oils since the solubility is even less than 10 g. of oil per 100 g. of alcohol. Mowrah, safflower, peanut, and cottonseed oils are soluble in absolute alcohol at 70°C. All the oils investigated are found to be miscible above the boiling point of alcohol even if the concentration is 98%. In 95% ethanol they are miscible between 90° and 100°C. Addition of a good solvent, like n-hexane, increases the solubility of oils, and the solubility temperatures are lowered. From the results obtained by various methods of solubility determination it is found that the apparatus employed in the present work yields more reliable results by eliminating the visual observation of turbidity temperatures, ensuring vigorous stirring and allowing sufficient amount of time to attain equilibrium conditions in determining the solubilities of vegetable oils.

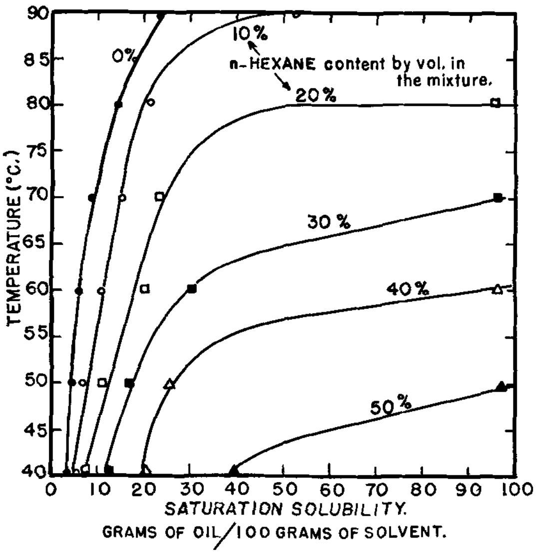

FIG. 3. Solubility of mowrah oil in 95.7% ethanol-hexane mixtures.

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