Acknowledgment

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Alcoholic Extraction of Vegetable Oils. III. Solubilities of Babassu, Coconut, Olive, Palm, Rapeseed, and Sunflower Seed Oils in Aqueous Ethanol

RAMA KANTH RAO and LIONEL K. ARNOLD, Iowa Engineering Experiment Station, Iowa State College, Ames, Iowa

IN EARLIER communications (1, 2) solubility data for seven vegetable oils in aqueous ethanol were reported. This paper deals with similar data for other common vegetable oils for which no data were found in the literature.

Experimental

The apparatus and solubility determination method used were the same as described previously (1).

Commercially available unrefined oils were used in each case. Their characteristics were as follows:

Oil	Acid value	Iodine value Wij's	Sap. value
Babassu	2.82	12.86	248.62
Coconut	2.76	8.82	257.20
Olive	1.12	84.62	190.40
Palm	3.42	53.86	199.64
Rapeseed	2.66	105.62	171.65
Sunflower seed	1.72	123.84	190.76

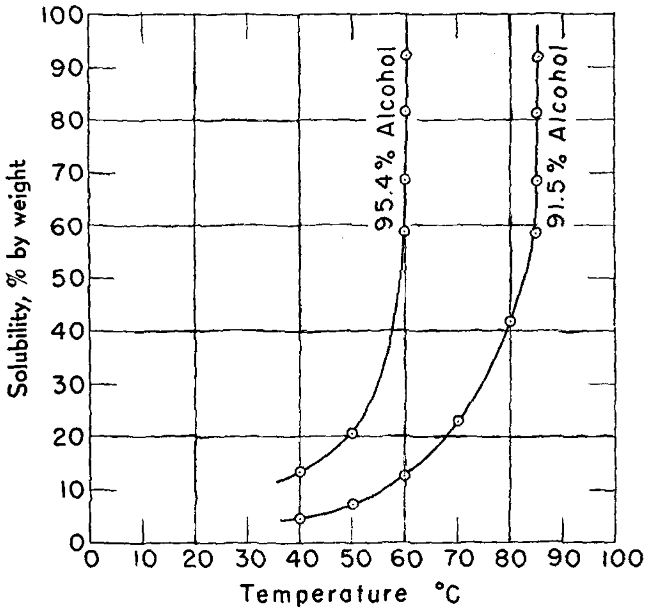

FIG. 1. Solubillity curves for babassu oil.

The various aqueous solutions of ethanol were obtained by diluting absolute alcohol. The concentrations of the alcoholic solutions were determined by determining the densities by the pycnometer method. All the values are reported as weight percentages.

Results

Solubility Data. As might be expected from the similarity in chemical composition, the solubility characteristics of babassu and coconut oils in ethanol are similar. Babassu oil (Figure 1) was miscible in 99.9% ethanol at 30°C., and coconut oil (Figure 2) was miscible at 23°C. In 98.0% ethanol miscibility was attained at 45°C. for babassu oil and at 35°C. for coconut oil. In 95.4% and 91.5% ethanol miscibility temperatures were 60° and 85°C. for babassu oil and 55° C. and 75°C. for coconut oil, respectively.

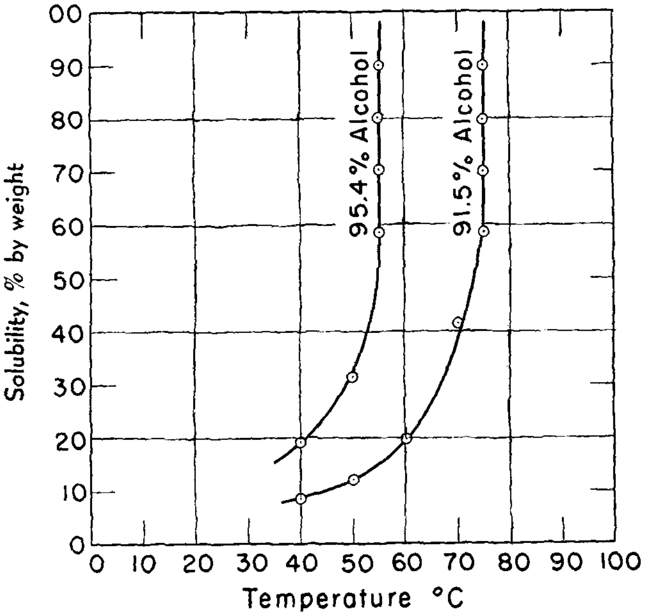

FIG. 2. Solubility curves for coconut oil.

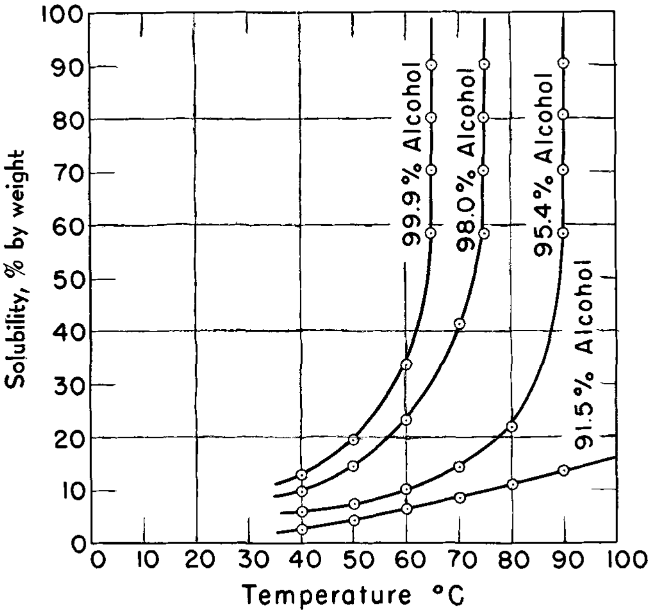

Fig. 3. Solubility curves for palm oil.

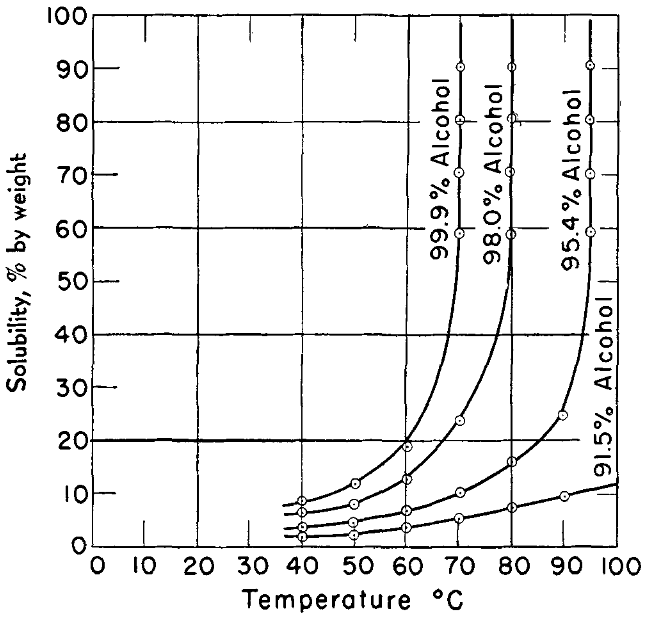

Fig. 5. Solubility curves for olive oil

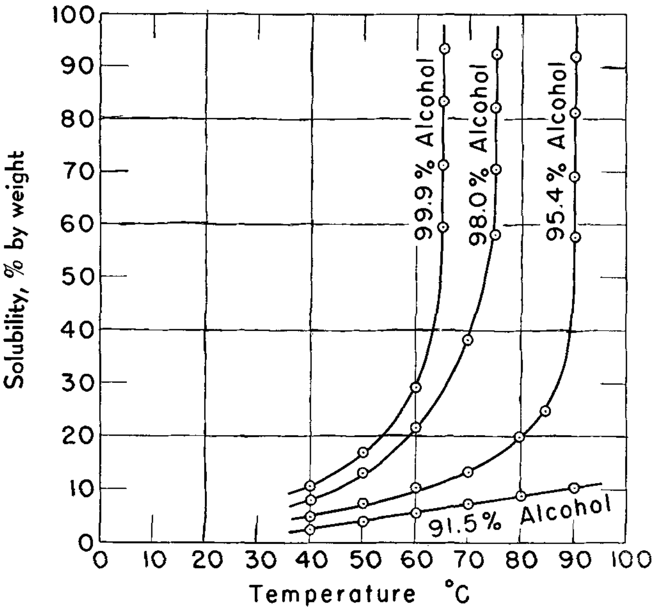

Fig. 4. Solubility curves for sunflower oil.

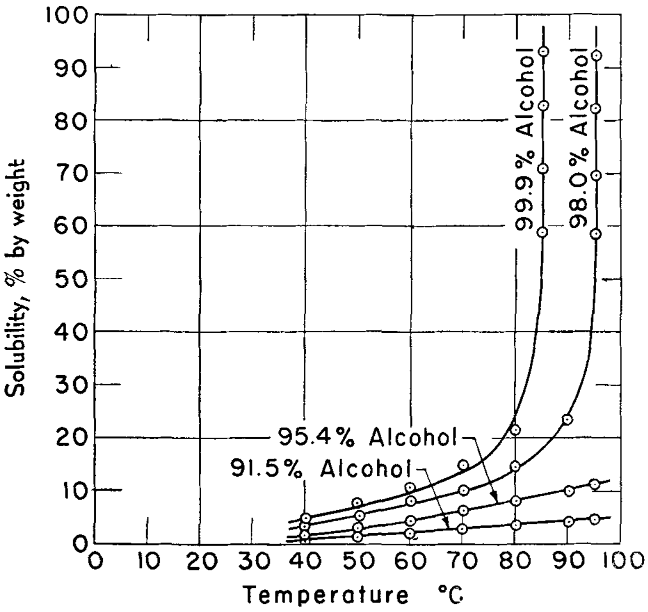

Fig. 6. Solubility curves for rapeseed oil.

The coconut oil was the most soluble of the six oils examined.

Palm oil (Figure 3) and sunflower seed oil (Figure 4) showed identical miscibility temperatures in the three highest concentrations of ethanol as follows: in 99.9% ethanol, 65°C.; in 98.0% ethanol, 75°C.; and in 95.4% ethanol, 90°C. However in 91.5% ethanol the solubility of sunflower seed oil was only 10.17% at 90°C. compared with 13.5% for palm oil at this temperature.

Olive oil (Figure 5) was miscible in 99.9% ethanol at 70°C., in 98.0% at 80°C., and in 95.4% at 95°C., in each case 5°C. above palm and sunflower oils. The least soluble of the group was rapeseed oil (Figure 6) with miscibility in 99.9% ethanol at 85°C. and in 98.0% ethanol at 95°C. The solubility in 95.4% and 91.5% ethanol at 95°C. was only 11.3% and 4.9%, respectively. Thus this oil was the least soluble of the entire group.

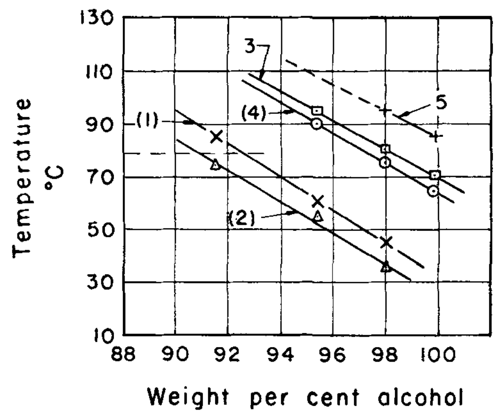

Fig. 7. Variation of critical solution temperature of the six oils with alcohol composition.

1. Babassu oil
2. Coconut oil
3. Olive oil
4. Palm and sunflower oils
5. Rapeseed oil

Critical Solution Temperatures. It can be observed from Figure 7 that the critical solution temperature increased with the water content of ethanol, and in each case the relationship was linear. Similar results have been reported for other oils (1, 2).

Pressure in the System. The maximum pressure, which was the result of both vapor and air pressure in the vessel, was recorded for different alcoholic compositions at various temperatures as shown below in p.s.i.g.

Concentration of alcoholic solution	Temperature °C.					
	50	60	70	80	90	95
95.4%	2	4	8	15	17	20
98.0%	2	4	8	15	18	
99.9%	2	4	10	15		

The maximum pressure to be used for alcoholic extraction of the oils is thus about 20 p.s.i.g. Similar data have been reported for other oils (1, 2) and were determined for use in extraction-equipment design and operation rather than as vapor pressure values.

Summary

Solubilities of babassu, coconut, olive, palm, rapeseed, and sunflower seed oils in aqueous alcoholic solutions at various temperatures were determined by a direct and simple method. Solubility curves for the six oils are presented.

The critical solution temperatures increase with the water content of the alcohol, and in each case the relationship is linear. The pressure in the system also varies with the temperature, the maximum being about 20 p.s.i.g.

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Epoxy Fatty Acid Ester Plasticizers. Preparation and Properties[1]

FRANK P. GREENSPAN and RALPH J. GALL, Becco Chemical Division, Food Machinery and Chemical Corporation, Buffalo, New York

IN THE FEW SHORT YEARS since their introduction epoxy fatty acid ester plasticizers have achieved an important place in the vinyl plasticizer field. Based upon abundantly available and cheap raw materials, these plasticizers are produced by the epoxidation of unsaturated fatty acid esters.

Preparation

Epoxidation reactions with peracids have been widely described in the literature (1–3, 15). The earliest method of preparation of epoxy esters utilized a preformed peracid, peracetic acid (6, 11, 17); the peracetic acid was prepared by reaction of hydrogen peroxide with acetic anhydride (16) or glacial acetic acid (9). The latter procedure in recent years has largely displaced the use of acetic anhydride for this purpose. Reaction of hydrogen peroxide with acetic acid is an equilibrium reaction:

$$H_2O_2 + HOAc \overset{H^+}{\rightleftarrows} HOOAc + H_2O$$

All four components are present at equilibrium along with the strong acid employed to catalyze the reaction. The degree of conversion to the peracid is dependent upon the respective molar ratios and concentrations of acetic acid to hydrogen peroxide.

Epoxidations with a preformed peracid are generally run at relatively low temperatures, *i.e.*, below 25°C. A number of improvements have been made in this mode of epoxidation. A modified, preformed peracid procedure giving low iodine number epoxy end products has recently been described (11). This process utilizes a short high temperature reaction period, at the conclusion of a normal epoxidation run, to reduce residual unsaturation. Table I illustrates results of reactions with a preformed peracid with (modified Becco Process) and without (Standard Process) a final high temperature reaction period.

TABLE I

Epoxidation of Unsaturated Esters with Preformed Peracetic Acid

Epoxy Ester	Standard Process[a] Oxirane Oxygen %	Iodine Value	Modified Becco Process[b] Oxirane Oxygen %	Iodine Value
Butyl Epoxystearate	4.1	5.4	4.2	1.4
Epoxy Soybean Oil	6.1	18.2	6.5	3.2

[a] A preformed peracetic acid (40%—1.04 moles) was reacted with the unsaturated ester (1.0 mole of ethylenic unsaturation) at 20°–25° C. for 4 to 5 hrs.

[b] A preformed peracetic acid (40%—1.04 moles) was reacted with the unsaturated ester (1.0 mole of ethylenic unsaturation) at 20°–25° C. for 3 to 4 hrs., completing the reaction at 50°–60°C. in an additional hour.

Although the use of a preformed peracetic acid for epoxidation is an excellent preparative method, considerable interest in recent years has been focussed on the development of *in-situ* epoxidation processes. The motivation has been essentially an economic one. When a preformed peracetic acid is employed for epoxidation purposes, the strong acid catalyst component of the peracid must be buffered to depress undesired ring opening of the epoxide. Accordingly, further formation of peracid during the reaction is negligible, and only the peracid component of the peracetic acid equilibrium mixture is effectively utilized. The hydrogen peroxide fraction (22% of the total active oxygen for the commercial 40% peracetic acid [4]) is largely wasted and discarded at the end of the reaction.

It was reasoned that if hydrogen peroxide were added to an aliphatic acid solution of an olefinic material, proper conditions could be found to effect formation of peracid accompanied by concurrent reaction of the peracid with the double bond to give the desired epoxide. Similar procedures have long been in use for hydroxylation reactions. Unfortunately this is complicated by the fact that the very conditions that favor peracid formation, notably the presence of a strong acid catalyst, high molar ratio of aliphatic acid to hydrogen peroxide, high tempera-

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[1] Presented at the 28th fall meeting, American Oil Chemists' Society, October 1954, Minneapolis, Minn.