

help in coordinating the collections and providing the data for the correlation studies.

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COMMUNICATIONS

Solubility Studies of Palm Oil in Practical Extraction Solvents

Simple solubility studies for palm oil in common extraction solvents have been made. Solvents used were *n*-hexane and petroleum ether (bp 60–80 °C). Palm oil was miscible in both solvents at concentrations between 5 and 95% mass fraction. The observed maximum miscibility temperature was 45 °C for oil in *n*-hexane and 48.5 °C in petroleum ether. These solvents would, therefore, be expected to be suitable for the primary extraction of palm oil from the fruit.

Palm oil is the fruit coat fat of the oil palm (*Elaeis guineensis*). It has been an export commodity from, and the preferred domestic vegetable oil in, the southern parts of Nigeria for many years.

In spite of this, relatively little change in extraction technology has occurred over these years even though large plantations and new and higher yielding palms are under cultivation and worldwide demand for palm oil is on the rise. With the possible exception of current developments in Malaysia (Berger, 1978) in which some local processing is being attempted, most extraction technology has been geared to the supply of crude palm oil to the industrial markets in Europe and America where the oil is further treated for industrial purposes or refined to a bland, odorless, nonsmoking, and unidentifiable vegetable oil for home consumption.

Most primary extraction processes consist of cooking and pulping the fleshy portions of the fruit, the product of which is then expressed mechanically or blown with live steam to obtain the crude oil.

During refining, the crude oil is subjected to various treatments—degumming, neutralization, deodorization, bleaching, etc.—with the result that carotene, the only source of vitamin (provitamin A), in the oil is also removed, a situation of some significance in the already vitamin deficient diets in developing countries.

Solvent leaching is a well established vegetable oil extraction technique (Treybal, 1980). Yet not much published data seem to be available on the solubility of palm oil, in fact most vegetable oils, in common extraction solvents. Most published data seem to be concerned mainly with the characterization of these oils (Dean, 1973; Perry, 1963), in terms of their composition, free fatty acid content, saponification number, etc.

We were interested in solvent leaching of palm oil from the fruit in a primary extraction step. Reported here, therefore, are preliminary efforts to determine simple solubility phenomena of local market grade edible palm oil in practical extraction solvents as possible pointers to what may be expected from direct extraction of the oil from the fruit.

EXPERIMENTAL SECTION

Characterization of the Oil. Well-known parameters for characterizing vegetable oils were determined at 29 °C, by using standard methods, for fresh palm oil bought from a local market in Enugu, Nigeria. These parameters were specific gravity, refractive index, acid value, and free fatty acid, by the titration method (Lever Brothers of Nigeria, Ltd., 1978), saponification value, also by the titration method, iodine value, by Wij's method, and peroxide value, by the Lea method (Pearson, 1976). Unsaponifiable matter was determined (Codd et al., 1973) by saponification of the oil with alcoholic KOH, separation of soap in water, extraction of the unsaponifiable matter with ether, and evaporation to dryness.

Reagent-grade *n*-hexane and petroleum ether (bp 60–80 °C) (BD Chemicals, Poole, England) were employed as solvents.

Estimates of Hilderbrandt's solubility parameters, δ (Snyder, 1979), for *n*-hexane and palm oil constituents, for which data could be found, were made to determine that the solvent used would not result in significant preferential solubility of some of the oil constituents. The data are shown in Table I.

It should be noted, however, that Hilderbrandt's parameter δ is not the best index of solubility (Snyder, 1978), especially if, in addition to dispersive forces, dipoles and

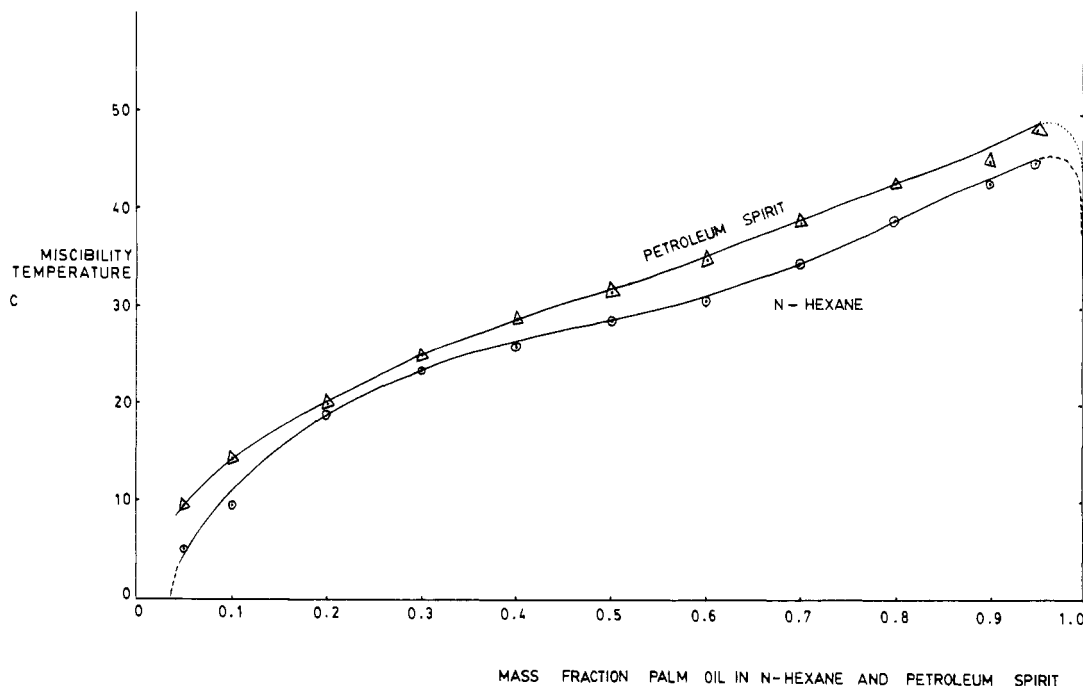


Figure 1. Miscibility of palm oil in *n*-hexane and petroleum ether (bp 60–80 °C).

Table I. Solubility Parameters, δ , for Palm Oil (Snyder, 1979)

com- pound	M_r	density, g/cm ³	ΔE , cal/Gmol ^a	molar vol, cm ³	δ^b
<i>n</i> -hexane	86.18	0.66 (25 °C)	7 540.75	130.58	7.6
myristic acid	228.38	0.85 (25 °C)	18 380.1	268.64	8.3
palmitic acid	256.43	0.85 (70 °C)	17 603.6	301.68	7.6
stearic acid	284.47	0.85 (69 °C)	19 306.6	334.67	7.6
oleic acid	282.47	0.89 (20 °C)	20 326.7	317.38	7.6
linoleic acid	280.45	0.90 (18 °C)	NA ^c	311.61	
carotene	536.89	1.00 (20 °C)	NA	536.89	

^a "Handbook of Chemistry and Physics", 1971–1972.

^b $\delta = (\Delta E/\text{molar volume})^{1/2}$ where ΔE is the heat of vaporization. ^c Not available.

hydrogen-bonding effects are possible. In this work, however, it provided sufficient confirmation that *n*-hexane would extract all of the palm oil since the δ values for *n*-hexane and most of the components are similar.

The red color of fresh palm oil is due to the presence of carotene, a provitamin A, and might be expected to provide a satisfactory method of determining concentrations of palm oil in solvents by spectrophotometric methods. Absorbance vs. wavelength (300–600 nm) and vs. palm oil concentration (0.5–4.5 g/L) were, therefore, measured by using a Pye-Unicam SP6-50 UV spectrophotometer.

Miscibility experiments (Findlay, 1973) were carried out for 5–95% mass fractions of oil in solvent. The results are shown in Figure 1 for oil-*n*-hexane and oil-petroleum ether mixtures.

Solubilities of the oil were measured (Daniels et al., 1962; Findlay, 1973) at different temperatures between 15 and 40 °C. The results are presented in Table II.

RESULTS AND DISCUSSION

Characterization Data. The characterization data obtained were comparable to those in the literature (Codd

Table II. Palm Oil Solubility Data

	palm oil in <i>n</i> -hexane	palm oil in petroleum ether (bp 60–80 °C)
solubility	$S = 1.69$	$S = 1.71$
correlation ^a	$\exp(0.00377T)$ $S' = 1.33$ $\exp(0.00162T)$	$\exp(0.00366T)$ $S' =$ $\exp(0.00145T)$
differential heat of solution	2670 kJ/kmol	2786 kJ/kmol
differential heat of mixing	967 kJ/kmol	900 kJ/kmol

^a S is the solubility expressed as gigamoles of palm oil per kilogram of solvent. S' is the solubility expressed as gigamoles of palm oil per kilogram of solution. T is the absolute temperature in kelvin. M_r of palm oil = 270.00.

et al., 1973; Dean, 1973; "Handbook of Chemistry and Physics", 1971–1972).

The solubility parameter δ for *n*-hexane and palm oil constituents was also comparable. These solvents would, therefore, be expected to extract all palm oil constituents in the proportions in which they occur. The UV-visible absorption spectrophotometry showed a peak at 440 nm and indicated that the Beer-Lambert law was obeyed for the concentration range studied, with an extinction coefficient of 0.38. Concentration of palm oil in these solvents can, therefore, be followed spectrophotometrically.

Solubility Data. Figure 1 shows the miscibility curves for palm oil-hexane and palm oil-petroleum ether mixtures. The points at zero concentrations of palm oil or solvent were not actually measured but were assumed to be the melting or freezing points of palm oil or solvent respectively. It is difficult to interpret the curves without more data. The curves probably represent some system of conjugate solutions with some upper consolute temperatures.

The extent of the flat portion of the curve through a wide concentration range (5–95% mass fraction) may represent the composite miscibility curve of, perhaps, the saturated (fatty) and unsaturated (oily) components of palm oil (Young, 1978). Again more experiments will be required before definite conclusions can be reached. Palm

oil, however, has significant miscibility in both solvents.

The solubility data indicated that only very narrow temperature and solubility ranges were studied and were correlated by an equation of the form $S = A \exp(KT)$ instead of the usual $S = A \exp[-\Delta H/(RT)]$ where T is the absolute temperature and A and K are constants. The heat of solution (or mixing) was found from a plot of $\ln S$ against $1/T$.

Again, the solubility of palm oil in *n*-hexane and petroleum spirit was found to be comparable and quite high. Heats of solution (or mixing) are also comparable and are seen from Table II to be very small.

CONCLUSION

The solubility of palm oil in *n*-hexane and petroleum ether appears reasonable and does not show unusual phenomena. UV-visible spectrophotometry can be used to monitor the concentration of palm oil in a primary solvent leaching scheme for extracting oil from the fruit. More work needs to be done to determine the rate and efficiency of primary extraction of palm oil from the fruit using these solvents.

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Methoxychlor Metabolism in Goats. 2. Metabolites in Bile and Movement through Skin

[¹⁴C]Methoxychlor [1,1,1-trichloro-2,2-bis(4-methoxyphenyl)ethane] was given orally to a bile-cannulated goat and via skin surface to two other goats. At the end of 3 days, recovery of ¹⁴C in bile, feces, and urine was 7.8%, 35.2%, and 44.4%, respectively, for the bile-cannulated goat given 1 g of methoxychlor (518 μCi). Seven metabolites plus methoxychlor were isolated from the bile and identified by GC-mass spectrometry. These were demethylated, dechlorinated, and dehydrochlorinated products. When 200 mg (545 μCi) of methoxychlor was applied to the skin of each of the two goats, 85% and 76% of the ¹⁴C were recovered in the skin 3 days later. Small amounts of ¹⁴C were recovered in muscle, adipose tissue, liver, and kidneys, and small amounts of ¹⁴C were excreted in the urine and feces.

Although methoxychlor is a relatively old insecticide, it is still frequently used in formulations for home gardeners, for control of certain insects on crops and livestock, and for fly control in farm buildings. Knowledge of the metabolic fate of methoxychlor in farm animals enables one to make better decisions regarding use of the compound. Previously, we reported isolation and identification of methoxychlor metabolites in urine and feces of lactating goats (Davison et al., 1982). We now report isolation and identification of methoxychlor metabolites in goat bile and movement of [¹⁴C]methoxychlor through skin.

MATERIALS AND METHODS

Animals. A castrated male goat (goat 104, weight 39 kg, 1 year old) was anesthetized with halothane. A polyethylene cannula (PE 240 polyethylene tubing 1.67 mm i.d. × 2.42 mm o.d.; Clay Adams, Parsippany, NJ) was then inserted into the bile duct between the liver and the union of the bile duct with the pancreatic duct. The cannula was brought outside the body through a stab in the right flank. The goat was restrained in a metabolism stall (Robbins

and Bakke, 1967), and bile was collected in a graduated cylinder. Ten days after surgery, the goat was given 1 g of 4,4'-methoxychlor, including 518 μCi of [¹⁴C]methoxychlor, bile was collected for 72 h, and the goat was killed.

Bile was not infused into goat 104 to replace that removed. The goat was given a trace-mineralized salt in addition to hay and water ad libitum.

Hair was clipped from an area about 12 cm² on the backs of two castrated male goats (goat 100, weight 63 kg, 2 years old, and goat 105, weight 46 kg, 1 year old). An area 10 cm² was marked within the clipped area, and 200 mg of 4,4'-methoxychlor, including 545 μCi of [¹⁴C]methoxychlor, was applied in 1 mL of dichloromethane. Urine and feces were collected for 72 h from the goats in metabolism stalls. Then, the goats were killed. Various tissues as well as treated and untreated skin patches were collected.

Methoxychlor and [¹⁴C]Methoxychlor. 4,4'-Methoxychlor and [*ring*-U-¹⁴C]methoxychlor have been described (Davison et al., 1982).

Carbon-14 Analysis. Lyophilized tissues and feces were combusted and assayed for ¹⁴C by liquid scintillation