1,1,2-Trichloro-1,2,2-Trifluoroethane for Oilseed Extractions: Demonstration of a Viscosity Effect[1]

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ABSTRACT

Extractions of full fat soy flake and meal were carried out at 5 to 70 C with hexane and 1,1,2-trichloro-1,2,2-trifluoroethane (FC-113) and their corresponding miscellas in order to evaluate FC-113 as a process solvent. In flake extraction, the rate of oil extraction by FC-113 was markedly improved with increasing temperature while extraction by hexane was relatively independent of temperature. In contrast, extraction of flake by the miscellas from both solvents and extraction of meal by fresh solvents gave similar results. A comparison of solvent properties indicates that the differences can be related to the viscosity dependent diffusion into the microporous flakes and suggests similar efficiencies for FC-113 and hexane in countercurrent flow extractors operating at elevated temperatures.

INTRODUCTION

In a preceding publication (1) the use of 1,1,2-trichloro-1,2,2-trifluoroethane, FC-113, as a medium for extractive analyses of oilseeds was investigated as a substitute for flammable hydrocarbons and toxic halocarbons, e.g., carbon tetrachloride. It was concluded that FC-113 gave results similar to, but statistically distinguishable from, hydrocarbon solvents of comparable boiling points. FC-113 was investigated as a process solvent for commercial extraction of oilseeds, where its properties of nonflammability, low toxicity, and chemical stability would also be desirable. It was expected on the basis of the preceding work and earlier work of Kaufman and vom Orde (2), that the extraction profiles of FC-113 and hexane, the most commonly used solvent, would be virtually identical as a function of temperature, particularly since they have virtually identical solubility parameters and dielectric constants. In experimental studies of extraction of flake with pure solvent, differences from the expected behavior were found.

EXPERIMENTAL PROCEDURES

Materials

Full fat soy flake was obtained from the A.E. Staley Co. (Decatur, IL). Portions of the flake were ground to 20-40 mesh particle size just prior to extraction. Hexane was commercial grade (ca. 60% n-hexane) obtained from Phillips Petroleum (Bartlesville, OK). FC-113 was Freon® TF Solvent, > 99.8% pure by gas liquid chromatography (GLC) from E.I. du Pont de Nemours and Company (Wilmington, DE).

Apparatus and Procedure

Column (flow system) extractions were run in water-jacketed columns 1 in. in diameter, 12 in. long. A wire screen kept the flake in place. Solvent was fed from a graduated, water-jacketed dropping funnel equipped with a needle valve flow control. The funnel was also equipped with a vapor by-pass so that the funnel could be stoppered in elevated temperature runs to suppress solvent evaporation. Water was circulated from a "Little Giant" submersible pump immersed in a bucket of ice and water or in a thermostat-controlled water bath through the column jacket to maintain desired extraction temperature. All runs were made with 60 g substrate and 90 ml solvent.

Equilibration studies were run in wide mouth screw cap jars which contained 12.5 g flake and 19 ml solvent or half miscella. The jars were capped and placed in a Magniwhirl Constant Temperature Bath (Blue M Electric Co.) and shaken for periods which ranged from 15 sec (sufficient time to add solvent to flake, shake, quench, and filter) to 55 min. Runs at or below room temperature were then removed from the bath, filtered through Whatman No. 1 paper, and the extracts analyzed by IR. Runs at 38 C and 60 C were quenched for 30 sec in ice-brine bath before filtration. In runs at 60 C, the solvents were kept at 40 C before addition to the flake. Runs at 70 C were made with 16.4 g of flake and 25 ml solvent in 100 ml capacity Fischer-Porter pressure vessels (Fischer-Porter Co., Warminster, PA).

Analytical Procedures

All analyses were run by IR with a Perkin Elmer Model 621 Spectrophotometer. Analysis was made at absorbance at 1748 cm^{-1} (ester carbonyl) with 0.9-1.0 g sample in a 0.2 mm thickness CaF_2 cell. Calibrations were made in both hexane and FC-113 with crude soy oil from the A.E. Staley Co. A blank was run in the pure solvent before each run. The weight percent soy oil in the experimental sample was then calculated to be:

$$\text{for hexane solvent} = \frac{23.2A + 2.9A^2}{W}$$

$$\text{for FC-113 solvent} = \frac{29.19A}{W}$$

where A = absorbance at 1748 cm^{-1}, and W = weight of sample.

Grams of oil/ml solution were found to be:

$$\text{for hexane} = 6.971 \times 10^{-4}(\text{wt }\%) + 1.35 \times 10^{-6}\ (\text{wt }\%)^2$$

$$\text{for FC-113} = 1.538 \times 10^{-2}\ (\text{wt }\%) - 7.86 \times 10^{-6}\ (\text{wt }\%)^2$$

Total oil in extracts from equilibration studies was calculated as

$$\text{g oil} = \frac{(\text{wt }\%/100)(\text{g solvent})}{1 - (\%/100)}$$

Replicates were run with samples taken at 1, 3, 5, 10, and 50 min.

"Total oil" extractable was determined by running 3-hr extractions in Butt extractors on 10.0 g of 20-40 mesh full fat flake with commercial hexane and by evaporating the solvent until constant weight of oil was obtained. GLC (1) showed less than 0.1% residual solvent.

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[1] Contribution No. 561 of the Research and Development Division, Jackson Laboratory, Organic Chemicals Department, E.I. du Pont de Nemours & Company, Wilmington, DE 19898.

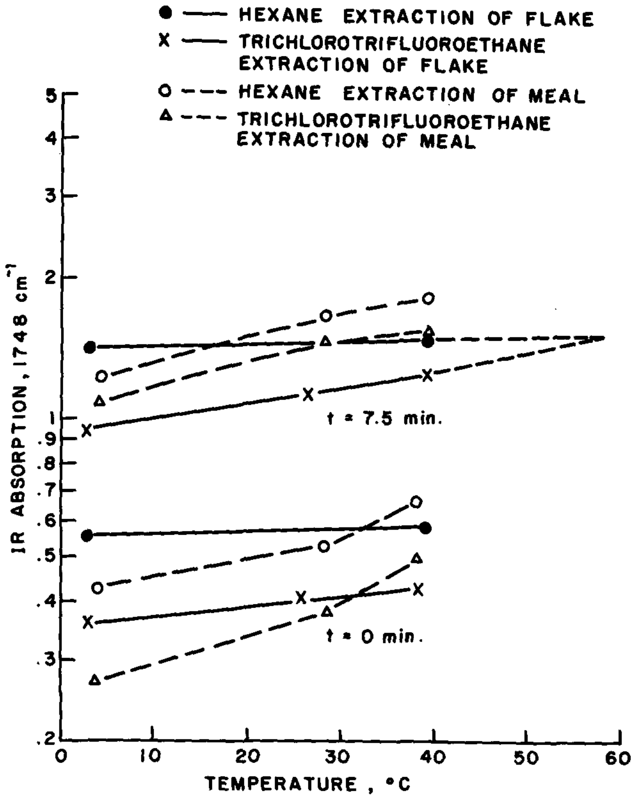

FIG. 1. Extraction of triglyceride from soy flake and meal as a function of time and temperature.

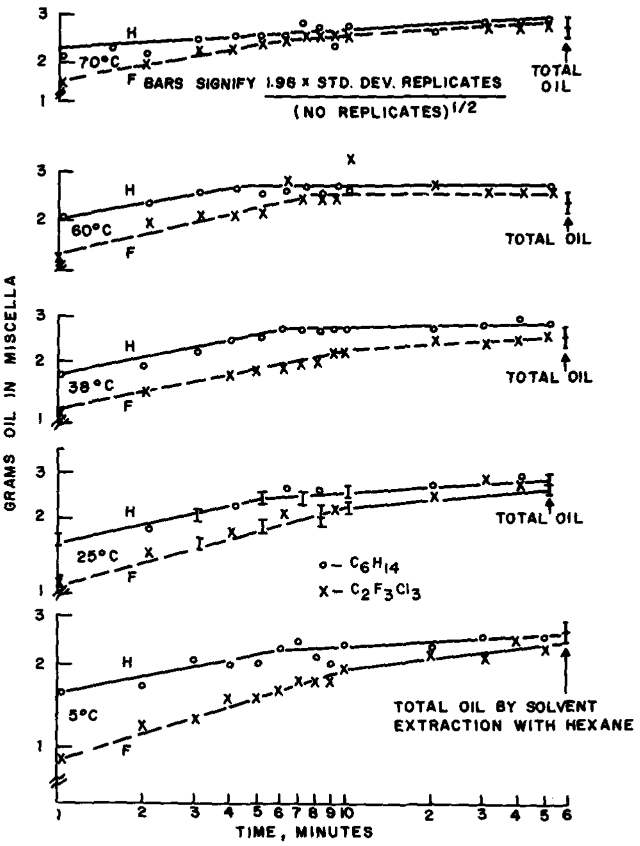

FIG. 2. Equilibration of full fat soy flake with hexane and trichlorotrifluoroethane solvents.

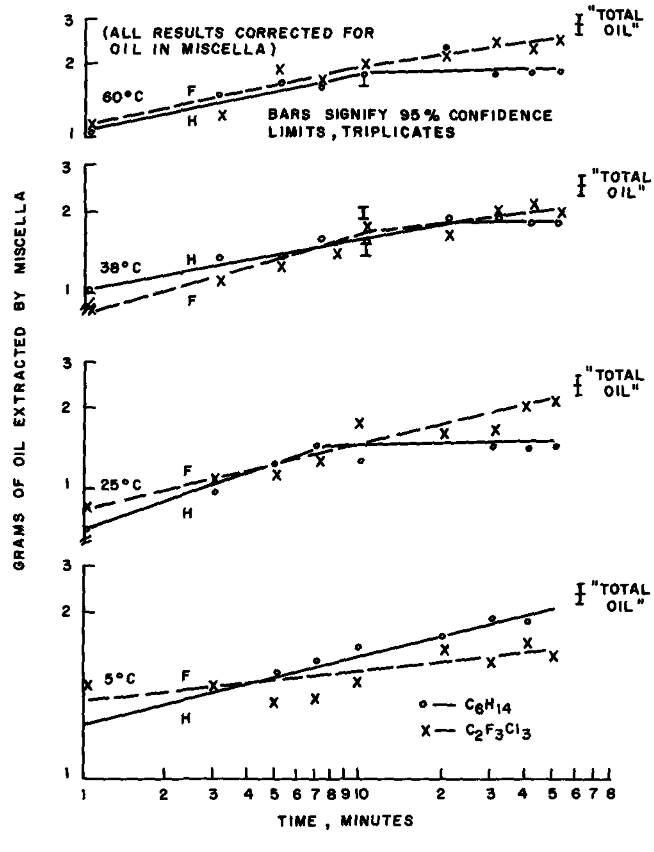

FIG. 3. Equilibration of full fat soy flake with hexane and trichlorotrifluoroethane "miscellas."

Runs with miscella were made in a similar fashion, and the extracted oil = (analytically determined g oil in extracts) – initial (g oil in half-miscella).

RESULTS

Column extractions of soy flake with 15 min and 55 min total elapsed time showed that the amount of oil extracted, as measured by IR absorbance at 1748 cm^{-1}, was dependent on the volume throughput of solvent rather than the flow rate. This dependence suggests that, even at the higher flow rate, there was sufficient time for oil at the surface of the flake to diffuse into the bulk of the solvent. Higher rates than these were not investigated. Figure 1 shows the results as a function of temperature for extraction of 60 g whole and ground soy flake with 90 ml solvent in 15 min elapsed time. The ordinate is given as the IR absorbance becuase the density of the miscella changes with volume of eluate. The $t=0$ mark represents eluate fraction taken at $\leqslant$ 1 min, and $t=7.5$ represents the approximate kinetic half-life time for "total oil" extraction when based upon independent measure of total oil by exhaustive extraction. Note that the slope for the hexane extraction is relatively independent of time and temperature. FC-113 shows a marked temperature dependence, even more pronounced for partially extracted flake.

Equilibration studies with solvent, miscellas, and whole flake show this effect from another perspective, as shown in Figures 2 and 3. Figure 2 shows the g oil extracted in a given time at different temperatures. Hexane extracts oil more rapidly than FC-113, but the gap between solvents narrows until it is barely significant at 60 C. At temperatures of 25 C or more, essentially all the oil is extracted in 10 min.

Since commercial extraction of oilseeds is a countercur-

TABLE I

Comparative Physical Properties of $CFC1_2CF_2C1$ and C_6H_{14}

		$CFC1_2CF_2C1$	C_6H_{14}[a]
Mol wt		187	86
BP (C)		47	69
Density (g/ml/-25 C)		1.56	0.63-0.66
Molar volume		120	130
Coefficient of expansion ml/(-25 C)		2.3×10^{-4}	9.1×10^{-5}
Surface tension (25 C)		17	18
Temperature coefficient of surface tension		-0.1048	-0.1016
Solubility parameter[b]		7.3	8.6
Kauri-butanol number[c]		32	32-33
Dielectric constant (Liquid, 30 C)		2.4[d]	1.9[e]
Dipole moment[f] (Vapor, 25 C)		0.56	0
Viscosity[g], η centistokes (25 C)		0.42	0.44
Coefficients of η[h] $= Ae^{B/T}$	A	0.0178	0.0459
	B	939	684
Miscibility with soy oil		All proportions	All proportions

[a] Commercial n-hexane.
[b] See Ref. 3.
[c] See Ref. 4.
[d] See Ref. 5.
[e] See Ref. 6.
[f] Calculated from the dielectric constant (Ref. 7).
[g] See Ref. 5.
[h] Hexane from Ref. 6, trichlorotrifluoroethane calculated from data in Ref. 5.

TABLE II

Comparison of Physical Properties of Half and Full Miscellas of Soy Oil in Hexane and FC-113

Solvent	Wt percent oil	Mole fraction[a]	Temperature, C	Surface tension (dynes/cm)	Density (g/ml)	Viscosity (cps)
Hexane	10.6	0.0114	0	20.2	1.08	0.84
			25	17.8	0.69	0.43
			40	16.8	0.64	0.35
	17	0.0195	0	20.9	1.11	1.17
			25	18.7	0.71	0.55
			40	17.0	0.65	0.44
$C_2C1_3F_3$	3.7	0.0081	0	20.0	2.37	1.80
			25	17.9	1.52	0.92
			40	16.6	1.40	0.78
$C_2C1_3F_3$	9.3	0.0212	0	20.1	2.29	3.18
			25	18.5	1.37	1.27
			40	16.9	1.37	1.13

[a] As trilinolein.

rent process, extractions of whole flake were carried out with half-miscellas (Fig. 3). Now any difference between corresponding miscellas (as miscellas) is of virtually no statistical significance. The apparent differences at $t > 10$ min at 25 C and 5 C is mainly a reflection of the higher volatility of FC-113, which results in some redepositing of oil on flake and on filter paper during workup. Redeposit of oil because of solvent evaporation also explains the apparently lower overall extraction (compared to "total oil") in miscella extractions.

DISCUSSION

A comparison of extraction of soy flake by FC-113 and hexane offers a unique opportunity for the study of diffusion mechanism because of their similar solvent nature (Table I).

Othmer (8,9) has suggested a model based on a modified Hagen-Poiseuille equation:

$$-\frac{dC}{dt} = K\frac{\gamma\rho}{\mu} f(C)$$

where K is a constant for the experiment, C is the oil content of the flake, γ is the surface tension (dynes/cm^2), ρ is the density (g/ml), and μ is the viscosity (centipoises). Now $\frac{\mu}{\rho}$ is the kinematic viscosity, η, so that $-\frac{dC}{dt} = K\frac{\gamma}{\eta}$. FC-113 and hexane have almost identical surface tensions, and the kinematic viscosities, η, are also similar at 25 C.

The function, $\frac{\delta(\gamma/\eta)}{\partial T}$, for FC-113 is ca. 0.82 relative to hexane in the temperature range studied. As oil is extracted into miscella, there should be a slight increase in γ, an increase in viscosity of both miscellas, but an increase in ρ for hexane and a decrease for FC-113. One would expect $\frac{\gamma}{\eta}$ to be relatively constant with increased extraction for hexane and to decrease for FC-113 as η increases.

The effect should be markedly temperature dependent since γ and ρ are linear functions of temperature, but μ (cps) and hence, η, are exponential functions.

To determine the validity of this hypothesis, the half and full miscellas from countercurrent extractions of soy flake with hexanes and FC-113 were analyzed for oil content, and the surface tension, density, and viscosity were measured at 0, 25, and 40 C. The results are given in Table II.

Since the surface tensions are so similar at comparable temperature and mole fraction $\frac{\gamma\rho}{\mu}$ or $\frac{\gamma}{\eta}$ will be closely approximated by $\frac{1}{\eta}$ and a plot of η as a function of concentra-

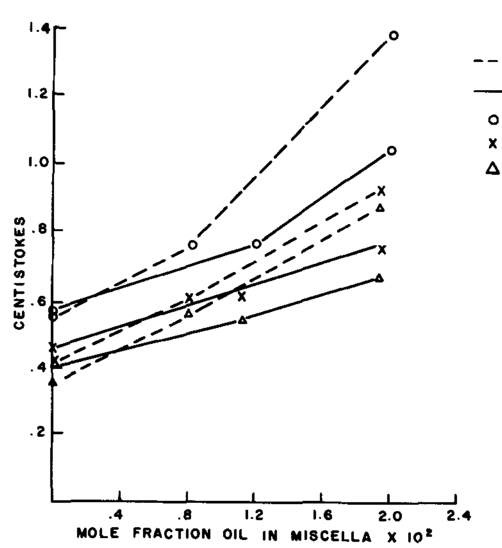

FIG. 4. Kinematic viscosity of miscella as a function of oil concentration.

tion and temperature should, therefore, be the inverse of $\frac{\gamma\rho}{\mu}$. This is shown in Figure 4. It is immediately apparent that η varies with concentration and temperature for both solvents, but the concentration dependency is greater for FC-113. A comparison of the temperature dependency of η and therefore $\frac{\gamma}{\eta}$ shows almost congruent behavior for the half-miscellas. Figure 5 shows η vs. T (C) for solvents and miscellas.

The results seem to be in agreement with extraction data but would require some adjustment of Othmer's hypothesis. Extractions of ground flake should eliminate the complexities of capillary flow, and extraction should be explainable by liquid diffusion theory, which for binary solutions of simple nonelectrolytes can be described by

$$D_{1,2} = K T \sqrt{\varphi M_2}/\mu_2 V_1^{0.6}$$

where K is a constant, T is temperature (°Kelvin), φ is an association parameter (assumed = 1 for nonassociating liquids), M_2 is the molecular weight of the solvent, μ_2 the viscosity of the solution, and V_1 the molar volume of the solute at its normal boiling point (10). For dilute solutions, μ_2 is approximately the viscosity of the solvent. For a comparison of solvents,

$$\frac{D_{Hexane}}{D_{C_2F_2Cl_3}} = \frac{\sqrt{\frac{86}{187}}\,\mu_{C_2F_3Cl_3}}{\mu_{Hexane}} = \frac{0.67\mu_{C_2F_3Cl_2}}{\mu_{Hexane}}$$

$\cong$ 1.3 in the range 25-60 C. For diffusion in a microporous medium, the relationship is much more complex than suggested by Othmer's equations because both liquid mixture diffusion and viscosity theory are presently inadequate to deal with the locally high concentrations of solution formed in the interstices of the flake or with the complex, high molecular weight mixture that is soy oil. A more general relation should be one that takes the changes in viscosity with oil concentration into account.

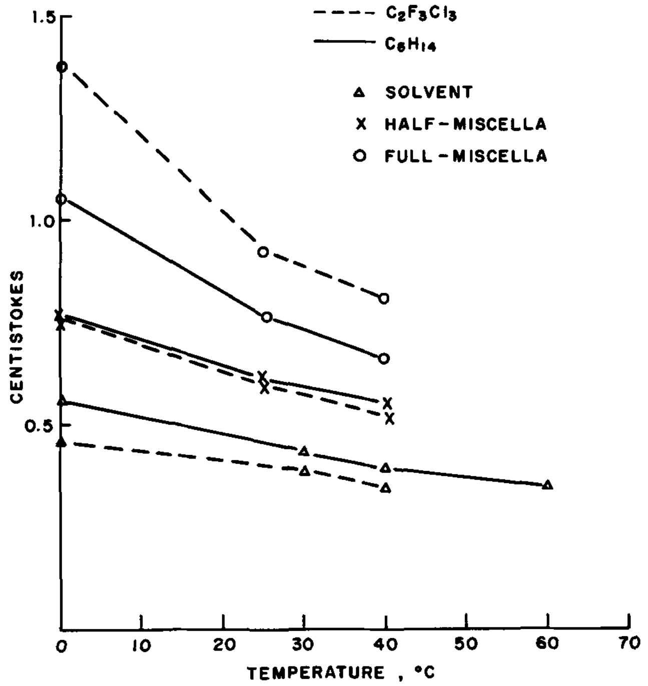

FIG. 5. Temperature dependence of viscosity.

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