

Processing of Tocopherol and FA Systems Using a Nonporous Denser Polymeric Membrane

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ABSTRACT: Tocopherols permeated preferentially over oleic acid in model systems and over oleic acid and other oil constituents during processing of soy deodorizer distillate (DOD) when using nonporous denser polymeric membranes (i.e., denser than reverse osmosis membranes). This observation was unexpected, since the separation in a denser membrane is generally based on a solution-diffusion mechanism. That tocopherols are less polar than oleic acid appears to have facilitated the preferential permeation of tocopherols through the hydrophobic membrane. Selectivity of the membrane for tocopherols improved with esterified soy DOD. The presence of FAME decreased the viscosity of the feed and thereby increased convective flow, which in turn improved permeate flux. FAME appeared to have exerted positive coupling effects with tocopherols, having better selectivity in spite of the greater solubility of FAME in the membrane material. Membrane selectivity for tocopherols improved upon dilution of the feed material with hexane, perhaps owing to greater solubility of tocopherols in hexane (nonpolar) than other feed constituents.

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KEY WORDS: Deodorizer distillate (DOD), fatty acid methyl esters (FAME), hexane, nonporous denser polymeric composite membrane, observed rejection, oleic acid, permeate flux, solution-diffusion mechanism, viscosity, tocopherols.

Tocopherols are antioxidants naturally present in oilseeds. The α -isomer of tocopherol is used in pharmaceutical formulations as well as in the preparation of cosmetics and health foods. A mixture of α -, β -, γ -, and δ -isomers containing 60% tocopherols is widely used as an additive to various foods (1). The demand for natural tocopherols exceeds that for synthetic ones. Deodorizer distillate (DOD), obtained in the deodorization step of vegetable oil refining, is often used as a source for natural tocopherols. DOD is a complex mixture of TG, FFA, sterols, tocopherols, hydrocarbons, and other unsaponifiable substances (2). Among various crude vegetable oils, wheat germ, canola, sunflower, cottonseed, and soybean oils contain greater amounts of tocopherols than other crude oils. Although sunflower DOD is a rich source of tocopherols, particularly for the α -isomer (9%), soy DOD, which amounts to 0.3-0.5% of the crude oil and contains 2-15% of total tocopherols (rich in γ -isomers), is available in abundance and hence is used as the principal raw material.

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Preparing high-purity concentrates of tocopherols involves a series of physical and chemical treatment steps, designed to separate FFA from the distillate in the initial step, followed by separation of sterols to yield a tocopherol-rich concentrate (3). A number of processes have been developed for manufacturing tocopherols from DOD, including urea adduct formation, liquid-liquid extraction with polar and nonpolar solvent pairs, supercritical CO₂ extraction and molecular distillation (4).

Soy DOD, as such, will not be feasible to use in the aforementioned processes, particularly with supercritical CO₂ extraction, owing to the poor selective solubility of the constituents of soy DOD, and with molecular distillation, as a result of the heat sensitivity of tocopherols, unless soy DOD is modified. Conversion of FFA and FA associated with TG into FAME increases the solubility of soy DOD constituents by four- to sixfold (5). These pretreatment/modification steps are laborious and require close attention to prevent the exposure of tocopherols to molecular oxygen and light. The search for alternative approaches is continuing so as to overcome the drawbacks of the aforementioned processes.

Membrane processes are remarkably simple, offering several advantages, and their applications in the field of nonaqueous processing are expanding. Studies using nonporous denser polymeric composite membranes with undiluted crude vegetable oils and model oil systems revealed that the nonporous denser membranes were effective in reducing phospholipids, color compounds, and oxidation products while retaining beneficial compounds (6). These studies also revealed that tocopherols and FFA permeated preferentially through the membrane as compared to TG. In the present study, attempts were made to assess the suitability of nonporous denser membranes for tocopherol enrichment using real (soy DOD and esterified soy DOD) and model systems with and without dilution with an organic solvent.

EXPERIMENTAL PROCEDURES

Materials. Soy DOD was procured from Shakthi Soya Ltd. (Pollachi, India). Tocopherol concentrate (assay 71.2%) was obtained through the courtesy of the Henkel Co. (Kankakee, IL). The composition of the tocopherol concentrate was 12.7% α , 1.5% β , 44.2% γ , and 12.8% δ isomers. A FAME standard (mixture) was purchased from Sigma Chemical Co. (St. Louis, MO). Soy FAME were obtained from Sonic Biochem Ltd. (Indore, India).

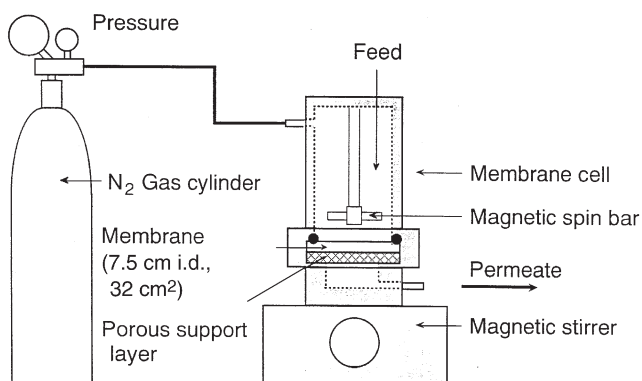
High-speed centrifugation of soy DOD. As a by-product of the oil-refining process soy DOD contains sediment. These sediments, which might otherwise interfere with the performance of the membrane, were first removed by high-speed centrifugation ($15,000 \times g$, 15°C) for 30 min.

Membrane. Nonporous denser polymeric composite membrane, NTGS-2200 with silicone as active layer and polyimide as support layer (Nitto Denko, Kusatsu, Japan), was used in the study. The membranes were cut into circular discs (7.5 cm diameter having a 32 cm^2 effective area) and fitted in the membrane cell in such a way that the active surface came in contact with feed material.

Apparatus. Experiments were conducted using a flat membrane test cell (Model C40-B; Nitto Denko) under a nitrogen atmosphere, and the required pressure was applied by adjusting the pressure regulator of a nitrogen cylinder. The cell was placed on a magnetic stirrer, and the magnetic spin bar fitted into the cell provided the agitation. The cell and magnetic stirrer were placed in a thermostatically controlled incubator. A schematic diagram of the experimental setup is given in Scheme 1. The pressure, temperature, and stirrer spin bar speed were maintained at 3 MPa, 30°C , and 800 rpm, respectively. The unit was operated in batch mode by charging the cell with 50–100 g of sample, and the experiment was stopped after collecting the desired quantity of permeate.

Analyses. Tocopherols were determined by HPLC, generally as per AOCS method Ce 8-89 (8). This method determines the α -, β -, γ -, and δ -tocopherol isomers, by UV detection at three different wavelengths (292, 296, and 298 nm), which gives maximum absorption for the respective tocopherol type by using a diode array detector. The mobile phase consisted of hexane and isopropanol (99.5:0.5 vol/vol). HPLC conditions were: column—silica gel (SBC-SIL), $0.25 \times 15\text{ cm}$ (Shimadzu, Kyoto, Japan); flow—1 mL/min; analysis time—15 min. The total tocopherols content was obtained by summing the four major individual components.

FFA contents in the samples were determined using AOCS method, Ja 6-55 (8). This method determines the FFA in samples by alkali neutralization, and the percentage of FFA is expressed in terms of oleic acid.



SCHEME 1

FAME were determined by using GC. A packed column (15% DEGS, 3 m; Shimadzu) with FID detection and N_2 and H_2 as carrier and detection gases, respectively, were used to analyze the different FAME by running the corresponding FAME standards externally. Analysis was carried out at isocratic temperature conditions, that is, 180, 220, and 240°C for column, injection port, and detector, respectively.

Viscosity measurements of samples were carried out by using a disc spindle measuring system in a digital viscometer. Measurement conditions were: temperature 30°C and spindle speed 100 rpm.

Membrane performance parameters. The performance of the membrane process was expressed in terms of total permeate flux, percent observed rejection (R_o) and selectivity. R_o was determined, assuming that it was constant for each batch of the experiment, by using Equation 1 (9):

$$R_o = \frac{100[\ln(C_{R,f}/C_{R,i})]}{\ln(W_i/W_f)} (\%) \quad [1]$$

where $C_{R,i}$ and $C_{R,f}$ were the initial and final contents of each component in the retentates (mg/kg oil), and W_i and W_f are the initial and final weights of retentate (kg oil), respectively.

Selectivity (degree of separation) was calculated by using Equation 2 (10):

$$\text{selectivity} = \frac{\text{tocopherols/FFA content in permeate}}{\text{tocopherols/FFA content in retentate}} \quad [2]$$

Data analysis. All experimental runs were carried out in duplicate, and practically no difference was observed ($\pm 0.5\%$). The mean values obtained are reported.

RESULTS AND DISCUSSION

Model systems (undiluted). Model systems consisting of oleic acid and tocopherol concentrate in two different ratios (80:20 and 50:50) as well as soy-FAME and tocopherol concentrate (90:10) were processed using nonporous denser membrane. Tocopherols, FFA, and FAME contents were analyzed in feed, permeate, and retentate streams. The values of feed viscosity; permeate flux; observed rejection for tocopherols, FFA, and FAME; and selectivity are presented in Table 1. The tocopherol concentrate contained 71.2% total tocopherols plus other lipid components (mainly unsaponifiables), including TG. In the two model systems consisting of oleic acid and tocopherols, tocopherols preferentially permeated compared to FFA, which was evident from the higher negative rejection values for tocopherols. In the third model system, the selectivity for tocopherols improved when oleic acid was replaced with soy-FAME.

Denser membrane theory appears to be more applicable than reverse osmosis (RO) theory in qualitatively explaining the differential permeation of oil constituents through nonporous denser membranes wherein solution-diffusion plays a predominant role in the transport (7). In applications such as gas separation, liquid separation, pervaporation, and vapor permeation, the transport in denser membranes is completely controlled by

TABLE 1
Membrane Selectivity and Rejection^a of Tocopherols and Oleic Acid in a Model System (undiluted)

Sample description	Permeate		Viscosity (mPa·s)	R_o		Selectivity	Flux [kg/(m ² ·h)]
	Tocopherols (%)	FFA/FAME (%)		Tocopherols (%)	FFA/FAME (%)		
Oleic acid/tocopherols (80:20)	13.3	83.5	31.0	-25.2	+1.6	1.41	1.20
Oleic acid/tocopherols (50:50)	31.9	55.5	45.9	-27.5	-0.7	1.37	0.72
Soy-FAME/tocopherols (90:10)	10.3	41.1	8.26	-66.6	+6.9	2.16	5.50

^a R_o , observed rejection.

the solution-diffusion mechanism (11). The permeability, P_m , is equal to:

$$P_m = D \cdot S \quad [3]$$

where D is the diffusion coefficient and S the solubility (12).

Solubility values of α -tocopherol, γ -tocopherol, oleic acid, methyl oleate, and hexane were predicted (Figs. 1–5) based on the group-contribution lattice-fluid equation of state (GCLF-EOS) model proposed by Lee and Danner (13). This model provides excellent predictions for solvent activity coefficients in polymers both at infinite dilution and finite concentrations based only on the input of molecular structures in terms of their functional groups. Polydimethyl siloxane (PDMS), which is identical to silicone rubber, was chosen as the polymer for solubility predictions from the database of the above model. The solubility of oleic acid (10) was predicted to be greater than that of γ -tocopherol (1); the latter was predicted to have a solubility about the same as α -tocopherol (1) at unit activity. Diffusion coefficients are inversely proportional to the molar volume of the solutes, according to the Wilke–Chang equation (14). The M.W. of oleic acid is 282 Da, γ -tocopherol is 417 Da, and α -tocopherol is

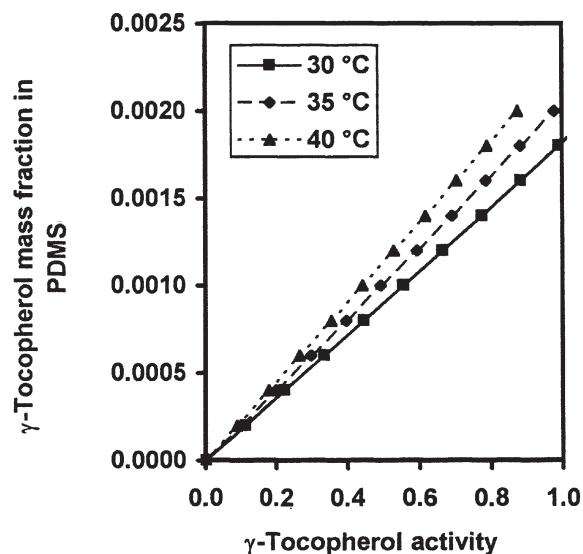


FIG. 2. Prediction of γ -tocopherol solubility in PDMS by a GCLF-EOS model. Data variability: $\pm 0.5\%$ ($n = 2$). For abbreviations see Figure 1.

431 Da. Therefore, by virtue of their M.W., the diffusion coefficient of FA will be greater than for tocopherols in membrane material. In considering both solubility and diffusivity,

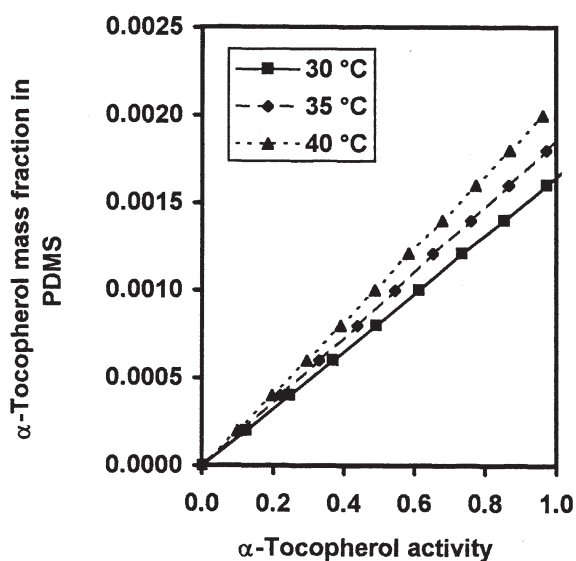


FIG. 1. Prediction of α -tocopherol solubility in polydimethyl siloxane (PDMS) by a group-contribution lattice-fluid equation of state (GCLF-EOS) model. Data variability: $\pm 0.5\%$ ($n = 2$).

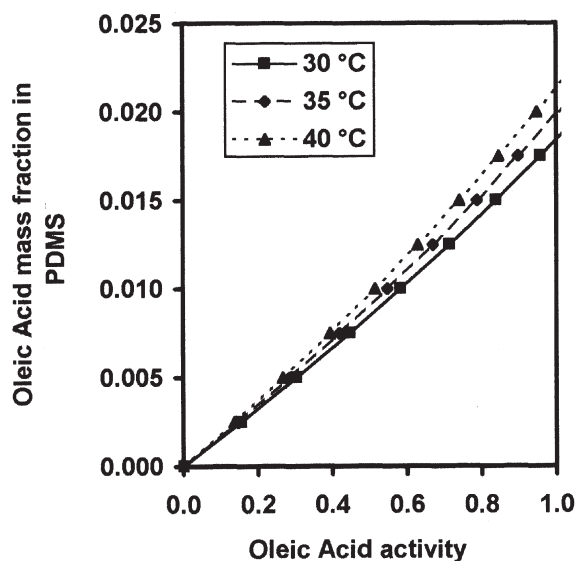


FIG. 3. Prediction of oleic acid solubility in PDMS by a GCLF-EOS model. Data variability: $\pm 0.5\%$ ($n = 2$). For abbreviations see Figure 1.

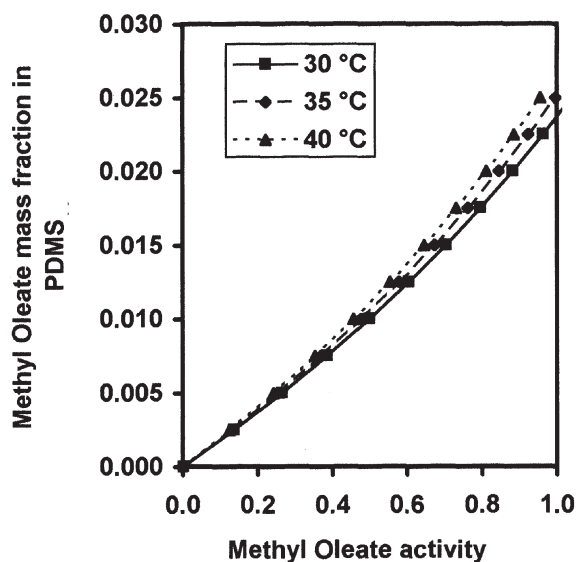


FIG. 4. Prediction of methyl oleate solubility in PDMS by a GCLF-EOS model. Data variability: $\pm 0.5\%$ ($n = 2$). For abbreviations see Figure 1.

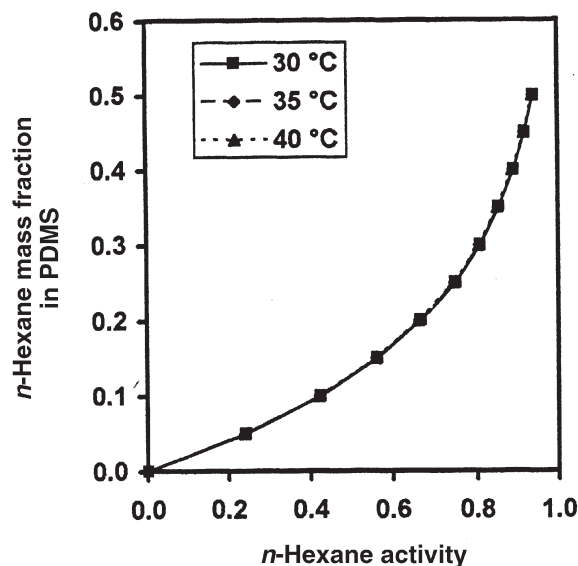


FIG. 5. Prediction of *n*-hexane solubility in PDMS by GCLF-EOS model. Data variability: $\pm 0.5\%$ ($n = 2$). For abbreviations see Figure 1.

the order of preferential permeation in nonporous membranes would be FFA > tocopherols. Higher solubility and higher diffusivity of oleic acid should have resulted in preferential permeation over tocopherols or, in other words, negative rejection greater than tocopherols. However, the observed phenomenon is contrary to this expectation. FFA contain a carboxylic group in their linear structure, which gives rise to relatively high polarity as compared to tocopherols (hydroxyl group linked to an aromatic chromanoxyl ring). This may explain the higher preferential permeation of tocopherols in spite of their greater M.W. as compared to oleic acid, since the membrane used in the study was hydrophobic. In our earlier study on rejection of carotenoids, greater rejection of xanthophylls over β -carotene showed that rejection by the hydrophobic membrane was highly influenced by the polarity of the compounds (15).

Selectivity was only marginally affected when the concentration of tocopherols in the feed was increased from 20 to 50%. The rejection values for tocopherols as well as oleic acid were both negative, which was due to the presence of other oil constituents in the system (ca. 2.5% TG).

When oleic acid was replaced with soy-FAME, preferential permeation of tocopherols increased, which significantly improved the selectivity for tocopherols. Esterification increased the M.W. of the FA and altered other properties (density, viscosity, solubility, polarity) due to association with the methyl groups associated with FFA in FAME. The average M.W. of FAME is 270–326 Da, which is more than the average M.W. of the corresponding FA (256–285 Da) but still lower than the M.W. of the tocopherols. The increased M.W. of FA after esterification decreases the difference between diffusivities of FA and tocopherols. Sorption plays a major role in deciding the selectivity since the difference in diffusivity of components is generally smaller in liquid systems (11). In

the present system of liquid mixtures, the difference in diffusivities did not play much of a role in the separation. Predicted solubility values based on the GCLF-EOS model showed that the solubility of oleic acid in PDMS increased by ca. 1.3-fold after esterification. Association with the methyl groups makes the FA molecules more nonpolar, which increases the permeability of FAME in the hydrophobic membrane, thereby affecting the selectivity. Therefore, other changes due to esterification had a greater influence in improving the membrane selectivity for tocopherols.

With increased tocopherol concentration in the feed, the total permeate flux decreased. This could be due to the increased viscosity (Table 1). Although denser and RO membranes are nonporous, actually micropores of less than 2 nm size may exist in such membranes. The structures of the RO membranes are not as dense as those of other nonporous membranes used for applications such as gas separation and pervaporation (10). The denser the membrane, the greater the contribution of the solution–diffusion mechanism. Less convective flow is observed in denser membranes than is observed with an RO membrane (6). Although the effect of viscosity is not proportional, it does appear to play a role in permeation rate (6). Therefore, the increased viscosity with an increase in tocopherol content in the feed could be the reason for the observed decrease in the permeate flux (Table 1). When oleic acid was replaced with FAME, preferential permeation of tocopherols as well as total permeate flux increased. Esterification drastically decreased viscosity and thereby improved total permeate flux (Table 1). The flux obtained with the FAME and tocopherol concentrate model system is ca. fivefold higher than the oleic acid and tocopherol system (80:20).

In transport of liquid mixtures, in addition to solubility and diffusivity, coupling has an influence and the coupling coefficients can be either positive or negative (10). FAME in feed greatly decreased the viscosity and thereby increased convective

TABLE 2
Membrane Selectivity and Rejection^a of Tocopherols and Oleic Acid in a Real System (undiluted)

Sample description	Permeate		Viscosity (mPa·s)	R_o		Selectivity	Flux [kg/(m ² ·h)]
	Tocopherols (%)	FFA/FAME (%)		Tocopherols (%)	FFA/FAME (%)		
Soy DOD	3.60	23.9	49.0	-32.2	-13.7	1.23	0.23
Esterified soy DOD	6.35	28.6	9.1	-60.4	-7.1	1.92	2.10

^aDOD, deodorizer distillate; for other abbreviation see Table 1.

flow. It appeared that FAME exerted positive coupling with tocopherols during its transport across the nonporous denser membrane. This positive coupling effect at a higher permeation rate appeared to have enhanced the preferential permeation of tocopherols. The higher solubility of tocopherols in FAME also seemed to play a role in this phenomenon.

Real systems (undiluted). Soy DOD and esterified soy DOD were processed using a nonporous membrane to assess the selectivity in a real system before and after esterification. Tocopherols, FFA, and FAME in feed, permeate, and retentate samples were analyzed. Feed viscosity, permeate flux, and observed rejection for tocopherols, FFA and FAME, and selectivity are given in Table 2.

Tocopherols showed significantly higher negative rejection and preferentially permeated as compared to the FFA in soy DOD and FAME in esterified soy DOD during membrane processing. The membrane exhibited more selectivity with the esterified soy DOD when compared to the unmodified soy DOD. Esterification improved the selectivity in the real system as well as model systems (Table 1). Factors such as the actual composition of feed, increase in M.W. with FAME, and significant improvement in the permeate flux would have contributed to the better selectivity for tocopherols with esterified soy DOD, as explained with model systems.

The permeate flux obtained with esterified soy DOD was *ca.* 10-fold higher than that obtained with soy DOD. The compositions of these two real systems are quite different. TG

(55–60%) was the major constituent in soy DOD along with FFA (25%) and tocopherols. On the other hand, FAME was the major constituent (*ca.* 80%) in esterified soy DOD along with TG (10%) and tocopherols (4%). As already discussed, convective or hydraulic flow exists in these nonporous membranes. Greater FAME content in the feed decreased the viscosity in esterified soy DOD and increased permeate flux (Table 2).

Although NTGS-2200 membrane was a hydrophobic membrane, the flux obtained was very low in the solvent-free real and model nonaqueous lipid systems used in the study. The feed material was basically viscous; hence, the permeation rate through the membrane material was rather low. Attempts were made to improve permeate flux by diluting both real and model systems with hexane to reduce feed viscosity.

Model systems (diluted). Two model systems, consisting of oleic acid and tocopherol concentrate in the ratios of 80:20 and 50:50, were diluted with hexane at 1:1 and 1:2, respectively, and processed using a nonporous denser membrane. The values of permeate flux and observed rejections for tocopherols and FFA as well as the selectivity obtained in the membrane process are given in Table 3. In both model systems, tocopherols preferentially permeated as compared to FFA. The permeate flux significantly improved (hexane-free basis), *ca.* fourfold with a 1:1 dilution and *ca.* sevenfold with a 1:2 dilution, in comparison with the respective undiluted experimental runs (Table 1). When the hexane dilution was

TABLE 3
Membrane Selectivity and Rejection of Tocopherols and Oleic Acid in a Model System (diluted)

Sample description	Hexane dilution	Permeate		R_o		Selectivity	Flux ^a [kg/(m ² ·h)]
		Tocopherols (%)	FFA/FAME (%)	Tocopherols (%)	FFA/FAME (%)		
Oleic acid/tocopherols (80:20)	1:1	15.1	82.5	-44.5	-3.1	1.55	4.32
Oleic acid/tocopherols (50:50)	1:2	33.3	50.5	-42.5	+9.1	1.95	6.59

^aHexane-free basis; for abbreviations see Table 1.

TABLE 4
Membrane Selectivity and Rejection of Tocopherols and Oleic Acid in a Real System (diluted)

Sample description	Hexane dilution	Permeate		R_o		Selectivity	Flux ^a [kg/(m ² ·h)]
		Tocopherols (%)	FFA/FAME (%)	Tocopherols (%)	FFA/FAME (%)		
Soy DOD	1:1	3.8	23.8	-32.6	+8.1	1.53	1.3
Soy DOD	1:2	6.5	23.7	-33.6	+10.0	1.55	1.8

^aHexane-free basis; for abbreviations see Tables 1 and 2.

increased from 1:1 to 1:2, the permeate flux increased by nearly 1.5-fold (Table 3). That hexane has a higher permeability than any of the oil constituents through the membrane owing to its very high solubility in membrane material (Fig. 5). The increased permeate flux in both systems could be due to the better solubility of tocopherols and oleic acid in hexane and hence better permeability through the membrane material. Selectivity increased with dilution and improved slightly with the amount of dilution. Selectivity in a multi-component system involving a solvent is dependent on the solubility of the individual components in the solvent in addition to their solubility and diffusivity in the membrane material. The improved selectivity on dilution of the feed material with hexane could be due to the greater solubility of tocopherols in hexane as compared to FA, since hexane is a nonpolar solvent.

Real systems (diluted). Soy DOD samples were processed using the nonporous membrane at two different hexane dilutions (1:1 and 1:2). The values of permeate flux, observed rejection for tocopherols and FFA/FAME, and selectivity are presented in Table 4. There was a significant improvement in the permeate flux, nearly sixfold with 1:1 dilution and eightfold with 1:2 dilution, in comparison with undiluted soy-DOD. The selectivity for tocopherols improved but did not change with the level of hexane dilution. This system behaved similarly to that of the model system (hexane-diluted), and the explanation for the improved permeate flux provided in the earlier section applies to this system as well.

Earlier studies with membrane processing of vegetable oils (6) showed that FFA and tocopherols, which are relatively low-M.W. compounds compared to TG, preferentially permeated in nonporous polymeric membranes or, in other words, were negatively rejected. The present study with undiluted model and real systems revealed that tocopherols preferentially permeated through the hydrophobic nonporous denser membrane, as compared to other low-M.W. oil constituents (FFA and FAME), which was evident from the higher negative rejection values for tocopherols in all the experimental runs. The membrane showed better selectivity for tocopherols with esterified soy DOD than soy DOD as feed material. Dilution of feed with hexane also improved selectivity for tocopherols compared to the undiluted feed, as well as improved permeate flux.

Tocopherols, being less polar than FA, permeated preferentially in the hydrophobic membrane. FAME appeared to have exerted a positive coupling effect with tocopherols, resulting in better selectivity in spite of greater solubility of FAME in membrane material. The presence of a third component (TG) in the feed and addition of solvent (hexane) also played crucial role in the permeation of oil constituents and selectivity of membrane besides solubility and diffusivity in membrane material that normally controls permeability and selectivity in nonporous membranes.

The membrane process appears to have potential in enriching tocopherols in soy DOD and esterified soy DOD. How-

ever, pilot-scale experiments will be necessary to improve the process and obtain plant design data relating to the life of membrane, cleaning cycles, and purity of product.

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