Reverse Osmosis Membrane Characteristics for Partitioning Triglyceride-Solvent Mixtures[1]

M.S. Kuk*, R.J. Hron, Sr. and **G. Abraham**
Southern Regional Research Center, Agricultural Research Service, USDA, P.O. Box 19687, New Orleans, LA 70179

Residual free gossypol in hexane-extracted cottonseed meal is a frequent concern of the feed industry. It is known that ethanol can efficiently extract the gossypol from cottonseed. However, regeneration of ethanol from ethanol-rich miscellas by conventional evaporation is costly, due to the high latent heat of ethanol. As an alternative to the evaporative regeneration, reverse osmosis (RO) has been investigated. It was found that commercially available RO membranes which have pore diameter around 20 A° (evaluated with deionized water flux) or less perform the necessary partitioning. Among the commercially available RO membranes, cellulose acetate (CA) type membranes with a nominal MWCO (molecular weight cutoff) value between 500 and 1000 were found to be efficient in partitioning the cottonseed triglycerides from the base solvent, but were not chemically compatible with the base solvent. RO membranes made from aromatic polyamide (PA) with MWCO value 1000 were found to have both the chemical stability and the necessary pore characteristics. Experimental results indicated the potential use of RO membranes for the regeneration of ethanol from ethanol miscellas. The required membrane pore characteristics and applicable permeate flux equations are discussed.

Triglycerides, the major components of vegetable oils, have a linear normal alkyl structure in their acyl chains. Since hexane has a similar alkyl chain structure in a smaller molecular volume, it has suitable characteristics to extract vegetable oil from oilseeds. Along with its solubility characteristics and availability, hexane has been the solvent of choice. The efficacy of an extracting agent in oilseed solvent extraction is primarily dependent upon its energy of dissolution with the lipids and the transport properties of the solvent-lipid mixture, as can be seen in the following process sequence: (a) transport of solvent molecules by diffusion to the oilseed lipids through the seed matrix, (b) dissolution of the lipids, and (c) transport of the resulting mixture by diffusion out to the bulk stream. In the case of cottonseed extraction, hexane dissolves readily and extracts triglycerides, whereas some nontriglycerides such as gossypol and afatoxins, are not easily extracted. The energy of dissolution required with these non-triglyceride components are apparently higher than with the triglycerides, and the nontriglyceride components remain in the defatted meal after solvent extraction. Hence, gossypol and aflatoxins are reactively detoxified or physically removed by multiple extractions with polar solvents (1,2).

Even without considering the extremely flammable nature of hexane, it is obvious that an alternative solvent with a capability of removing the toxic components as well as efficiently extracting oil is desirable for cottonseed oil extraction. As a candidate for the alternate solvent, iso-propanol has been extensively investigated by Harris *et al.* (3). Ethanol, the smaller member of linear alcohol homologue, has also been examined (4) and has become a serious candidate to replace hexane because of its capability of extracting gossypol and aflatoxins (5,6). Countering the strategic advantage of availability from renewable resources, ethanol suffers from its higher latent heat in replacing the present extracting agent. The conventional method of solvent regeneration in the extraction process is evaporation, which is economical for hexane. The heat of vaporization for ethanol is two and a half times higher than that of hexane. Hence, a new solvent recovery technique which does not require phase changes is much desired. As an alternative to the energy intensive evaporation, reverse osmosis was investigated for regenerating the solvent from the miscellas.

EXPERIMENTAL METHODS

Reverse osmosis (RO) membranes, both as flat disc and in tubular configuration, with nominal molecular weight cutoff (MWCO) between 500 and 2000, were examined. The examined RO membranes were made of either cellulose acetate (CA) with a typical degree of substitution (DS) of 2.5, or polymers other than CA designated as non-cellulose acetate (NCA) type. NCA type or NCA composite RO membranes are commercially available from a variety of polymeric materials which include polysulfone, polyacrylonitrile, polyester, polyimide, polyamide, polyetheramide, polyetherimine, and polyvinylidene fluoride. Composite membranes made from these polymers have recently been developed to improve chemical and pH stability, permeate characteristics of existing CA membranes, and chlorine resistance of NCA membranes. The porosity characteristics of most commercially available NCA composite membranes were such that applications were aimed at ultrafiltration.

Preliminary screening has been performed and most of these NCA type RO/UF membranes were excluded from this study, except for RO composite membranes made with aromatic polyamide (PA). The exclusion was based upon the necessary chemical stability and RO porosity characteristics. For instance, our preliminary screening indicated that polysulfone UF/RO membranes with nominal molecular weight cutoff in the range between 1000 and 2000 did not have enough permselectivity to reject the triglycerides.

Conventional stirred cell test units (Amicon models) were used for evaluating the basic transient flux characteristics. A continuous flow small scale pilot unit was used for evaluating the steady state data. A schematic diagram of the pilot unit is given in Figure 1. The direction of bulk flow is orthogonal to that of permeation in both types of the test units as shown in the schematic diagram in Figure 2. The hydrostatic pressure is released across the micropores of the tested RO membranes, which are supported by a steel housing. To avoid the evaporation loss of the base solvent, the feed and permeate removal

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*To whom correspondence should be addressed.

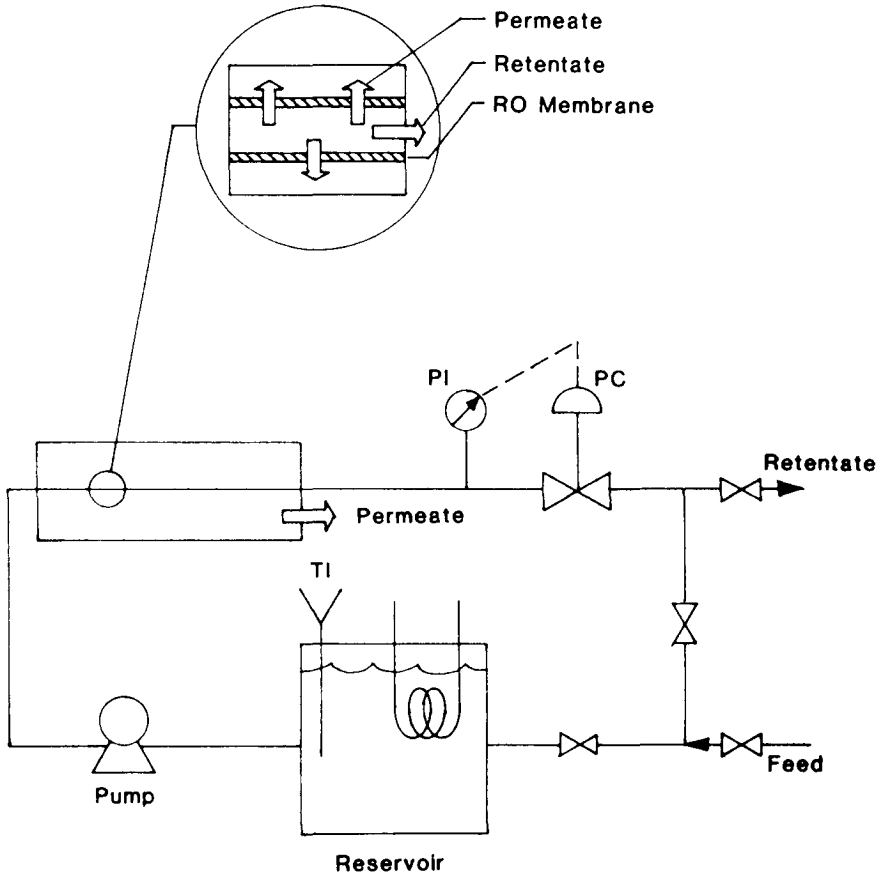

FIG. 1. Schematic diagram of pilot scale continuous membrane test unit.

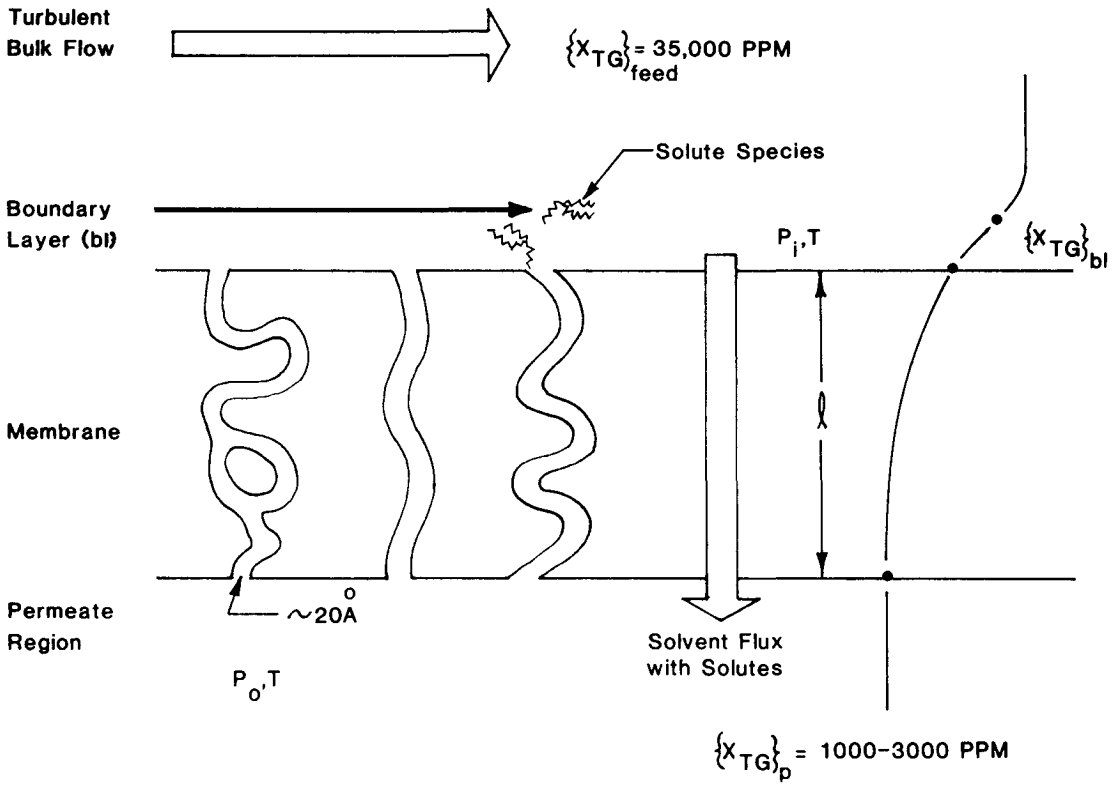

FIG. 2. Diagrammatic representation of transmembrane RO process for regenerating miscella.

operations were performed within the sealed enclosure where the system temperature was controlled. The maximum temperature was limited to 40°C for CA membranes due to the membrane material characteristics. Chemical compatibility tests were conducted with anhydrous ethanol.

Permeation flux data were gathered from deionized water, ethanol, and crude cottonseed oil-solvent mixtures as a function of pressure and temperature. U.S.P. grade anhydrous alcohol was used. Tap water was deionized, and the free chlorine in the deionized water was less than 0.5 ppm. Cottonseed flakes were extracted with the solvent at 78°C to yield the crude cottonseed oil-solvent mixtures. A small pilot plant extractor (Crown) and a benchtop percolating extractor were utilized for producing the crude oil-rich miscellas. The experimental details of ethanol extraction were given elsewhere (5). The maximum equilibrium solubility of the crude cottonseed oil in the miscella mixture is about 13% (wt) at 78°C. Several batches of crude cottonseed oil extracted with anhydrous and azeotrope ethanol were prepared. The resulting crude-miscella mixtures were cooled to room temperature to yield two phases, an oil-rich phase and a solvent-rich phase containing ca. 3.5% of triglycerides and ca. 1% free sugars. The solvent-rich miscella mixture was further sieved with a 20 mesh screen to remove fines and used in the RO partitioning experiments utilizing reverse osmosis membranes. Free fatty acids, free gossypol, oil color and phosphorus were determined by standard AOCS methods (7). The permeate products from the RO membranes were analyzed using a high temperature capillary gas chromatographic (HTCGC) column with a cold on-column injector. The high temperature capillary column was 25 m long and 250 μ i.d. (Chrompack) with a methylphenylpolysiloxane coating of 0.1 μ thickness. Hydrogen was the carrier gas. The permeate samples were introduced to the HTCGC column via a silica-needle injector with 170 μ i.d. bore to avoid the direct contact of triglycerides to a metal surface, thereby eliminating possible catalytic degradation of triglycerides. The HTCGC method allowed direct analyses of triglycerides in the samples without the conventional derivatization.

RESULTS AND DISCUSSION

Figure 3 represents a typical HTCGC chromatogram of triglycerides in the permeate stream produced from the cellulose acetate RO (DS 2.5) membranes with a nominal MWCO value of 500. The peremate flux from this type of RO membrane contained slightly less than one tenth of the triglycerides originally in the feed. The chromatograms shown in Figures 4 and 5 represent a typical permeate product from PA membranes with MWCO of 1000. Figure 4 shows the permeate with 25 ppm of tripalmitolein added as an internal standard (IS). Figure 5 shows the same permeate with tristearin. As seen in these chromatograms, mixed triglycerides with 51, 53, 55, and 57 carbons formed the majority of the permeate stream. As shown in Table 1, the feed contains traces of free fatty acids and phosphorus. The trace of phospholipids in the feed, represented by 30 ppm of phosphorus, contributes to the component concentration gradient, as depicted in Figure 2. However, little variation was observed in the steady state permeate flux rates, with a small increase in the phosphorus content up to 25%. In this region of phosphorus concentration the flux polarization—which could be caused by a gel layer of phospholipids—was not observed. Although it was not investigated in the present application, the gel polarization (8) effects can be determined by examining the relationship between the flux and pressure in a wide range of phospholipids concentration. As indicated by the Lovibond colors of the feed and permeate products (Table 1), there was a significant color contrast between the feed and permeate products. Although gossypol analysis indicated that the feed contained little gossypol, traces of the transformation products of gossypol and gossypol derivatives were believed to exist in the feed, and to be responsible for the feed color (3,9). The chromatographic analysis of the feed (Fig. 6) and the permeate products

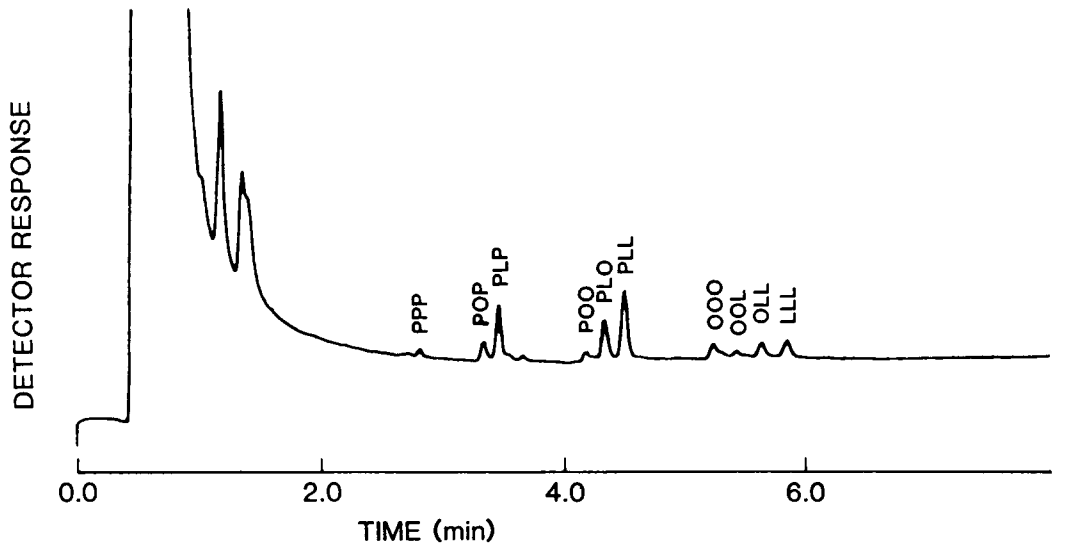

FIG. 3. Capillary gas chromatogram of ethanol-extracted cottonseed triglycerides in permeate stream by CA membranes with MWCO 500.

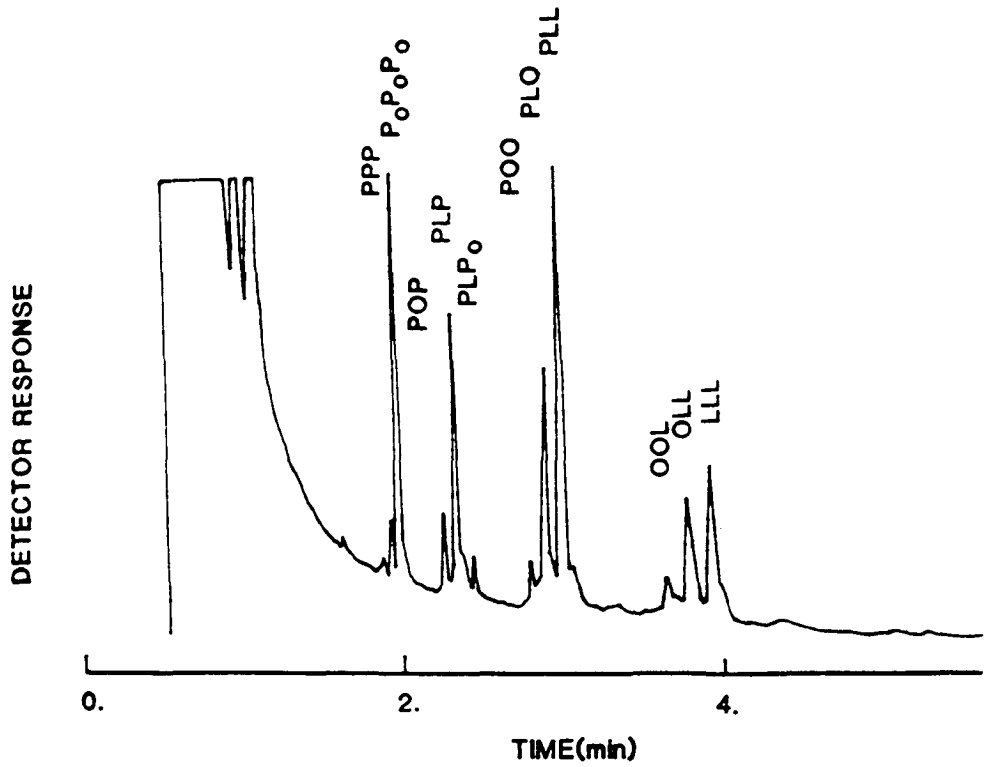

FIG. 4. Ethanol-extracted cottonseed triglycerides in permeate stream by PA membranes with MWCO 1000 (tripalmitolein added as IS).

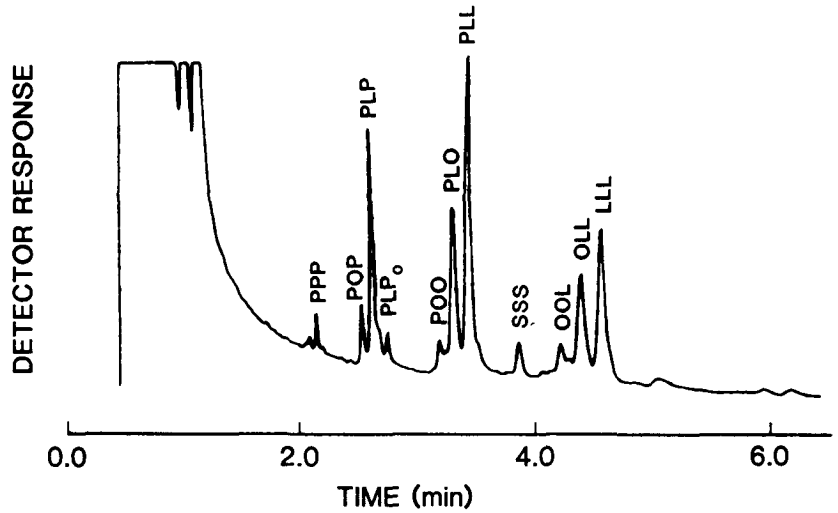

FIG. 5. Ethanol-extracted cottonseed triglycerides in permeate stream by PA membranes with MWCO 1000 (tristearin as IS).

(Figs. 3-5) clearly show that most triglyceride components in the feed are present in a lesser amount in the permeate. Among the monoacid triglycerides in the feed, tristearin was not detected in the permeate products from either CA or PA type membranes. This could be attributed to the fact that tristearin has the highest viscosity of all the triglycerides present. It is apparent that the relatively high viscosity and, in turn, low diffusivity retarded the flow of tristearin molecules through the microporous openings of the membrane, resulting in a permeate stream that was practically free from tristearin.

The total content of triglycerides in Figures 3-5 represents approximately 0.1-0.3%, which is slightly less than 10% of triglycerides in the feed. It is an industry standard that the residual lipids in cottonseed meal be less than 1%. In an earlier study of cottonseed extraction with

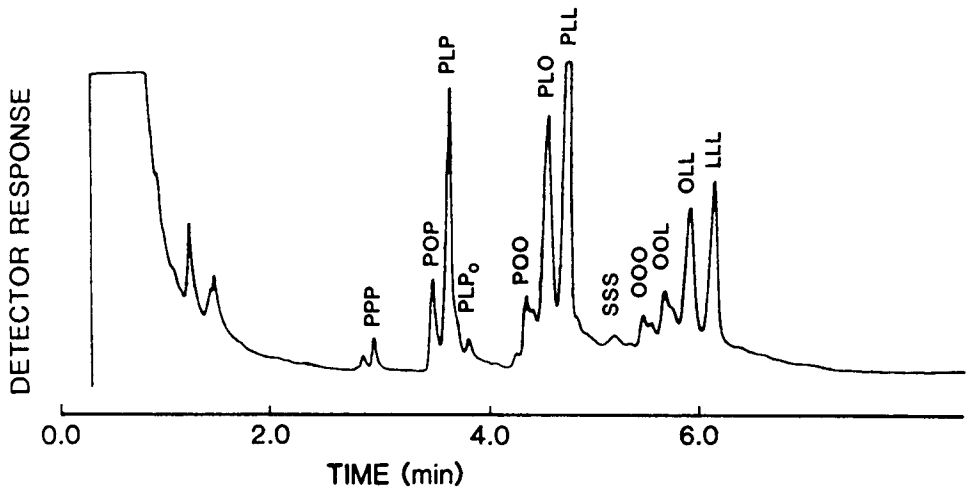

FIG. 6. Ethanol-extracted cottonseed triglycerides in feedstocks used for regenerating the solvent by reverse osmosis membranes.

TABLE 1

Analysis of Ethanol-Rich Miscella Feed to Reverse Osmosis Test Unit

	Triglycerides (%)	FFA[a] (%)	Lovibond color	Phosphorus (ppm)
Feed to RO	3.5	0.4	40Y 4.5R[b]	30
Permeate	>0.3	0.2	1Y 0.2R	—
Refined oil	99+	trace	35Y 3.0R	2.3

[a]Free fatty acid.

[b]Measure with 1" long glass.

ethanol (10), it was determined that the regenerated solvent purity should be higher than 99% to achieve a residual lipid content of less than 1%. Therefore, these experimental results indicate the high potential of the tested RO membranes for use in regenerating ethanol miscellas.

The permeate rate of solutes can theoretically be predicted by Fick's first law, in which the solute rates are primarily dependent upon the molecular diffusivity and the solute concentration gradient near and across the membrane surface. The permeate flux of solvent with solutes can be described by the following equation when there is significant osmotic pressure from the solute in the permeate and retentate stream: $J = K(\Delta P - \Delta\Omega)/(R_m + R_p)/\Delta X$, where J represents the permeant flux with solutes; K, the permation coefficient; R_m, the intrinsic membrane resistance term (determined by the physicochemical properties of the membrane); R_p, the resistance term (determined by the solvent and solute concentration profile); ΔP, the hydrostatic pressure differential between permeate and retentate; and $\Delta\Omega$, the osmotic pressure differential. K is strongly dependent upon the solvent molar volume and diffusivity. A limiting case of this permeate flux equation, where the osmotic pressure differential is negligible, essentially conforms to the Hagen-Poiseuille model for viscous flow in a capillary pore: $J = (\epsilon^* D_p{}^{2*} \Delta P)/(32^* \Delta X^* \eta)/\tau$, where ϵ represents porosity; D_p, the pore diameter; ΔX, the membrane barrier thickness; η, the viscosity; and τ, the tortuosity. As shown in Figure 7, the permeate flux rates with the base solvent, ethanol, were linearly proportional to pressure, as indicated by the Hagen-Poiseuille equation. The flux variation with temperature is closely related to viscosity dependency on temperature as follows:

$$\text{Flux}(T_1)/\text{Flux}(T_2) = \exp\{1/(273+T_1) - 1/(273+T_2)\}^*\text{constant},$$

where T represents temperature.

Most commercially available CA type RO membranes (including regenerated cellulose) with nominal MWCO values between 500 and 1000 were able to efficiently reject the triglycerides from the miscella mixtures. The base flux rate of CA type or regenerated cellulosic RO membranes with deionized water was measured to be in the neighborhood of 3 L/SQ M/HR/ATM, which is in agreement with previously reported values (11,12) at room temperature. The base flux rates with ethanol were measured at 25°C for CA and PA type RO membranes. The exposure of CA membranes to anhydrous and aqueous ethanol, however, significantly degraded their performance. This was possibly due to alcoholysis. The degradation was immediate upon exposure to the solvent, and steadily progressed to the point where the RO capabilities were seriously damaged.

In the case of aromatic polyamide RO membranes with a nominal MWCO of 1000, the base permeate flux with deionized water was in the same order of magnitude as CA type RO membranes with the corresponding MWCO. The permeate rate with 100% ethanol was slightly lower than that of the deionized water flux at the same condition (Fig. 7), indicating that PA membranes were somewhat more swollen in ethanol than water. It normally requires about two hours to establish steady state flow at an elevated pressure. During the transient state, the solvent flux rates were twice as high as the steady state rates. This indicates that during the incipient period the pore resistance to the capillary flow was not fully developed, even though the test membranes were stored for 24 hours in the test solution prior to the flux measurement.

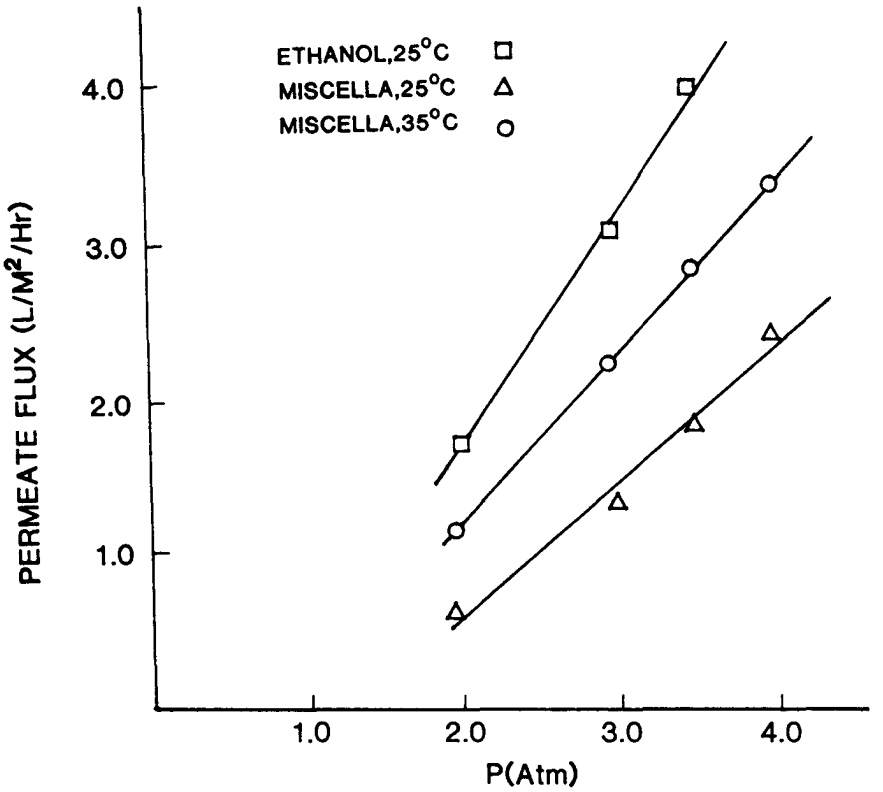

FIG. 7. Isothermal permeate flux rates of polyamide RO membranes with MWCO of 1000.

Figure 7 also shows that the permeate rates of the regenerated miscellas are linearly related to the hydrostatic pressure differential. This linear dependency indicates that the differential osmotic pressure of triglycerides between the feed (3.5%) and the permeate stream (0.3%) is small compared to the hydrostatic pressure differential. Since the upper limit of allowed triglycerides in the regenerated permeate stream is 1%, a higher permeate flux is expected with a higher hydrostatic pressure.

If the tested membranes are reasonably homogenous throughout their "skin barrier" thickness, then the pore density population and porosity (void area fraction) can be predicted by using the deionized water flux data and the Hagen-Poiseuille equation. By taking tortuosity equal to unity (for the sake of simplicity), the average pore radii equal to 10 A° (as projected for the RO membranes with MWCO around 1000 [13,14]), and a membrane skin barrier of 0.2 μ (15), one can predict a pore population density on the order of 10^{12} per sq cm, and a porosity ca. 8%. Merin and Cheryan (16) reported a pore population density, as measured by electron microscopy (TEM), of about 4×10^{11}/sq cm and a porosity of 7-12% from a polysulfone membrane with a MWCO of 10,000. The pore density calculated in the present study indicates that the estimated value, 10 A°, for the pore radii of RO membranes with the nominal MWCO between 500 and 1000 is reasonable (the manufacturer's value for the average pore radii of the RO membranes with MWCO values of 500 and 1000 were 10.5 and 12 A°, respectively [14]).

According to Sarbolouki's (13,14) slit model for capillary flows in RO membranes, a correlation exists between solute radii and molecular weight cut-off, and, in turn, another correlation between the average pore radii and the solute's molecular weight (MW). Sarbolouki's correlations indicated that when solute molecules with a MW of 1000 are exposed to RO membranes with an average pore diameter of 18-22 A°, ca. 95 to 80% of the solutes are retained in an aqueous RO process. Using the Hagen-Poiseuille equation with the ethanol flux data given in Figure 7 and the same values used previously for the membrane properties, one can predict that the average pore diameter used in this study is ca. 16 A°. This estimation indicates the swollen state of the membrane pores in ethanol as compared to that in water. Since more than 90% of the solutes are retained in this study, the average pore diameter for a MWCO value between 800 and 900 should be ca. 16 A°. The MW of cottonseed triglycerides in this application are distributed between 800 and 900.

The liquid state structures of triglycerides are not as well defined as the various crystalline forms (17-21). According to a qualitative model suggested by Larrson (21), the liquid triglyceride configurations near the melting points can be approximated by those in the solid state. However, it is expected that in the temperature region higher than the melting point, a considerable population of gauche conformations exist in their alkyl chain structures, whereas all-*trans* structures are known to exist in the solid state (20). The Raman spectral data of a liquid state dipalmitoyl lecithin, by Lippert and Peticolas (22), indicated the appearance of gauche conformations at a temperature near 40°C. Liquid state n-heptane was reported to have 13 possible conformations with various gauche-*trans* combinations, including an all-*trans* conformer (23). Even in a simple alkane as liquid n-butane, the gauche and *trans* configuration exist simultaneously at a given state (24). The exact data revealing the

population of gauche and *trans* bonds—and their resulting structures in the liquid state triglycerides—are not available. However, it is expected that more gauche conformations exist in the liquid than in the solid. Increasing gauche bonds in the acyl chains tends to make the solute molecules more global in the liquid state. In the case of the unsaturated monoacid and mixed triglycerides, the solutes should take a further kinked shape because of the *cis-cis* configurations in their acyl chains (19,21). Consequently, the dimension of liquid triglycerides in the direction of short spacing must be larger than that in the solid state. The approximate dimension of short spacing of an all-*trans* configuration is about 5 A° in the solid state (17,20). Hence, it is expected that a portion of the solute population may pass through the pores, and that the partitioning of the solutes is determined by Stoke's radii of the solutes. The Stoke's radii of the solutes vary, depending upon the combination of the gauche-*trans* configurations. Sarbolouki's (13) correlations indicated that a polysaccharide with a MW of 1000 has a Stoke's radii of 10 A°. As indicated by the chromatographic analysis of permeate products, one can postulate that the permeated molecules (less than 10% of the total solute population) have molecular radii small enough to pass through the pores of the tested membranes.

From the experimental results presented in Figures 3-5 and the pore analysis, it is evident that RO membranes with an average pore diameter of about 20 A° (evaluated with deionized water flux) or less and a pore population density of ca. 10^{12} per sq cm have a high potential to replace the conventional method of miscella regeneration.

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