Separations of Mixtures of Fatty Acids into Individual Components Using a Nanoporous Membrane

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ABSTRACT

We developed the first membrane-based method to separate fatty acids from one another. In this method an amine and a mixture of saturated and cis-fatty acids are placed in solvent on one side of a membrane and allowed to diffuse to the other side of the membrane. The fatty acids permeate the membrane at different rates such that they have different elution times and are readily separated. This method was demonstrated for common fatty acids found in vegetable oils (stearic, oleic, linoleic, linolenic, vaccenic, and petroselinic acid). This method was optimized to isolate each fatty acid from a mixture of fatty acids by changing the amine. Importantly, the same membrane was used throughout the experiments, optimization of the separation required optimizing the amine. This method can be used to quickly and inexpensively separate mixtures of fatty acids using an organic solvent nanofiltration membrane that we developed.

Keywords: membrane, vegetable oils, fatty acids, separation, isolation

1 INTRODUCTION

Vegetable oils represent one of the largest biorenewable feedstocks for the chemical industry. Over 150 million tons of vegetable oils are produced worldwide each year and 96% of this source is used as food for humans and animals or burned as biodiesel. Oils and their fatty acids are used in industry for cosmetics, vitamin supplements, paints, lubricants, and other applications.[1] The amount of fatty acids in industrial applications is expected to grow by double digits for the foreseeable future and reach a market value of $13.5 billion in 2017.

Vegetable oils are composed of a triester of glycerol and three fatty acids (Figure 1).[2] Each source of oil has a different composition of fatty acids; for instance, soybean oil has 10% palmitic acid (a C16 saturated fatty acid), 4% stearic acid, 18% oleic acid, 55% linoleic acid, and 13% linolenic acid. A major challenge in the application of these fatty acids in industrial applications is that the separation of fatty acids is challenging and expensive. Typical methods to purify a mixture of fatty acids into its components include selective precipitation (useful for the purification of saturated fatty acids), distillation, or silver ion chromatography.[3-5] None of these methods can be used to purify unsaturated fatty acids on a large, industrial scale which limits the purity of fatty acids that can be sold. For instance, oleic acid has a market valuation of over $1 billion, but it is typically sold in a purity of 55-70% which is the purity that is obtained from pecan oil, olive oil, or tall oil. A method to quickly and inexpensively purify large quantities of fatty acids would add much value to the field of oleochemicals by allowing the production and sale of fatty acids in high purity (>97%).

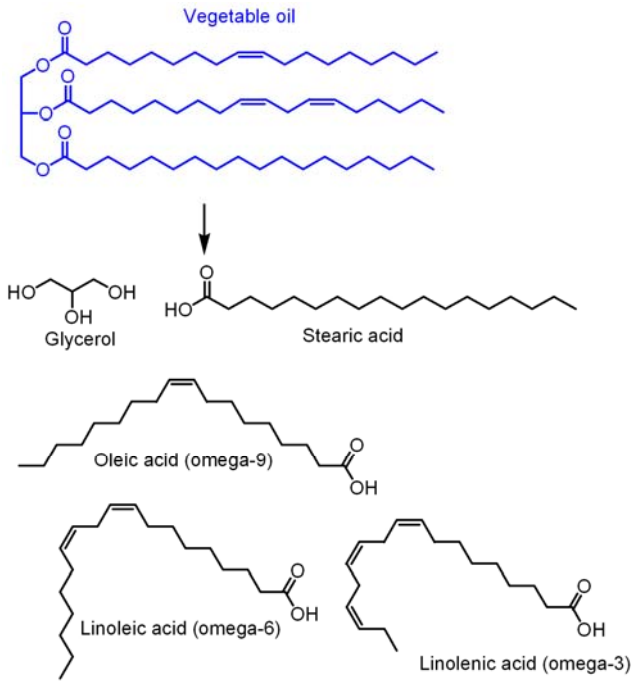

Figure 1. An example of a vegetable oil is shown. Vegetable oils are readily cleaved to yield glycerol and a mixture of fatty acids. Four of the fatty acids found in soybean oil are shown.

We recently developed a method to separate a mixture of fatty acids into individual components using an organic solvent nanofiltration membrane composed of polydicyclopentadiene (PDCPD).[6] This method is simple to

use and, since it is based on a membrane, can be readily scaled up to separate large quantities of fatty acids.

2 RESULTS AND DISCUSSION

2.1 Separation of fatty acid salts using diffusional flux

The permeation of vaccenic acid (a C18 fatty acid with a cis-olefin at C11), elaidic acid (a C18 fatty acid with a trans-olefin at C9), petroselinic acid (a C18 fatty acid with a cis-olefin at C6), and the four fatty acids shown in Figure 1 were studied. A 100 micron-thick membrane composed of PDCPD was placed vertically between two solvent reservoirs. The fatty acids were added to solvent on one side of the membrane – defined as the upstream side – and allowed to permeate to the solvent on the other side of the membrane – defined as the downstream side. The solvent on both sides of the membrane were constantly stirred and the concentrations of the fatty acids in the upstream and downstream solvents were measured every 24 h. The ratio of the downstream to upstream concentrations (Sd/Su) for each fatty acid was determined. Initially, the value for Sd/Su was zero because the fatty acids were added only to the upstream solvent and were not found in the downstream solvent (i.e. Sd = 0). If the fatty acids freely permeated the membrane, their concentrations in the upstream solvent and downstream solvent would be identical and the value for Sd/Su would be 1. A value for Sd/Su of less than one indicated a slowed permeation for a fatty acid.

In initial experiments all of the fatty acids readily permeated the membrane at similar rates. This was expected because the PDCPD membrane separated molecules based on their smallest cross-sectional areas that we labeled as "critical areas".[7,8] The PDCPD membrane was highly cross-linked with nanometer and sub-nanometer sized pores between the polymer chains which allowed the fatty acids to diffuse through. Molecules with large critical areas had slowed permeation but molecules with small critical areas readily permeated through the pores. All of the fatty acids had critical areas that were small enough that they readily permeated through the pores in PDCPD and had similar values for flux.

To increase the critical areas of the fatty acids to the size range where PDCPD membranes separated molecules, we added amines to the upstream solvent. Amines and acids spontaneously formed salts based on a hydrogen transfer to the nitrogen as shown in Figure 2. We hypothesized that the addition of an amine would increase the critical areas of the fatty acids and provide a method to differentiate between saturated and unsaturated fatty acids. Furthermore, we hypothesized that the separation of the fatty acids could be optimized by the selection of an appropriate amine.

In initial experiments the separation of oleic and elaidic acid was studied. These fatty acids have the same chemical composition and an olefin at the C9 position. Oleic acid is a cis-olefin and elaidic acid is a trans-olefin. Both fatty acids readily permeated the membrane (Figure 3). When triethylamine was added, the permeation of the two fatty acid salts was unchanged. A difference in permeation was observed when tripropylamine and triisobutylamine were used. In these experiments, the flux of the oleic acid salt was slowed relative to the flux of elaidic acid which was unchanged. The best results were obtained with triisobutylamine where the value for Sd/Su was 0.07 for the oleic acid salt and 1.01 for the elaidic acid salt. When tributylamine was used, no evidence of the fatty acids was found in the downstream solvent. This result was expected because tributylamine did not permeate the membranes as shown in prior work.

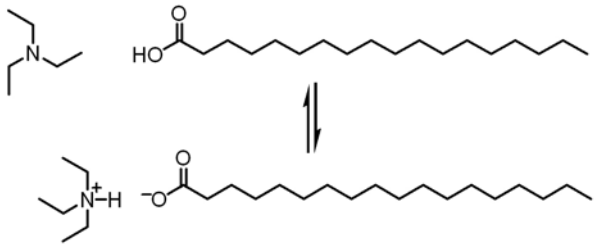

Figure 2. Fatty acids and amines reversibly form salt pairs. The free amine and fatty acid are in equilibrium with the salt but the equilibrium heavily favors the salt in organic solvents.

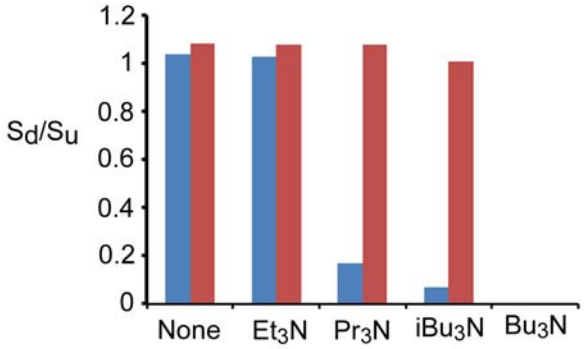

Figure 3. The values for Sd/Su after 72 h were investigated for a mixture of oleic (shown in blue on the left) and elaidic acid (shown in red on the right) with the addition of no amine or the addition of Et_3N, Pr_3N, iBu_3N, or Bu_3N.

The flux of salts formed by the addition of triisobutylamine to seven different fatty acids (linolenic, linoleic, vaccenic, petroselinic, elaidic, oleic, and stearic acid) was investigated (Figure 4). All seven fatty acids permeated the membrane in the absence of an amine. When triisobutylamine was added to the upstream solvent with the fatty acids, the flux of all of the cis-fatty acids was greatly reduced but the flux of the saturated and trans-fatty acids was unchanged.

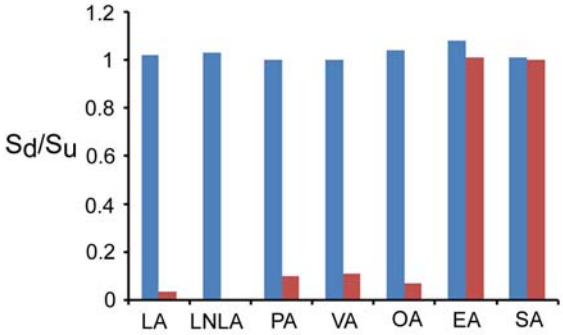

Figure 4. The values for Sd/Su after 72 h for the free fatty acids in the absence of amines are shown in blue (on the left). The Sd/Su value for the fatty acid salts formed by the addition of iBu_3N is shown in red on the right. LA = linoleic acid, LNLA = linolenic acid, PA = petroselinic acid, VA = vaccenic acid, OA = oleic acid, EA = elaidic acid, SA = stearic acid.

2.2 Critical areas and partitioning coefficients

The permeation of molecules through highly cross-linked membranes can be understood in terms of partitioning coefficients and rates of diffusion.[9,10] The partitioning coefficient of a molecule is the ratio of its concentration in a solvent divided by its concentration within the matrix of the membrane at equilibrium. This value is important to consider because for a molecule to permeate through a membrane it must be soluble within that membrane. All of the fatty acids and their salts with triisobutylamine had similar values for their partitioning coefficients so they were not the reason for the difference in flux for the fatty acid salts.

The difference in flux of the fatty acid salts was due to their rates of diffusion within the membranes. The equations that describe rates of diffusion are complex, but a simple method to understand them is to look at the critical areas of the molecules. Large molecules cannot pass through small pores, so their rates of diffusion are lowered relative to small molecules. In Table 1 the critical areas of the free fatty acids and the fatty acid salts with triisobutylamine are shown. Two noticeable trends stand out. The critical areas of the free fatty acids were all similar (0.067 to 0.36 nm^2) and below the size range that PDCPD membranes have been shown to separate molecules. In contrast, the addition of triisobutylamine increased the critical areas of each fatty acid and increased the range in areas obtained for each of the seven fatty acids (0.38 to 1.27 nm^2).

The reason for the difference in critical areas of the fatty acid salts is due to the "kink" in the structures of the cis-fatty acids. The saturated and trans-fatty acids adopted linear shapes and were eclipsed by the larger amine when the critical areas were measured. The cis-fatty acids all possessed kinks or bends in their shapes that were not completely eclipsed by the amine. The omega ends of the cis-fatty acids increased the critical areas of the cis-fatty acid salts and were responsible for their diminished flux.

Table 1. The critical areas were measured *in silico* as describe in prior work.

Molecule	Critical area of free fatty acid (nm^2)	Critical area of fatty acid salt (nm^2)
Elaidic acid	0.12	0.38
Stearic acid	0.067	0.38
Vaccenic acid	0.24	0.47
Linolenic acid	0.36	0.74
Oleic acid	0.21	0.95
Linoleic acid	0.34	0.97
Petroselinic acid	0.20	1.27

2.3 Separation of fatty acid salts using pressure

In the experiments described previously, the fatty acid salts were added to solvent on one side of a membrane and allowed to diffuse to solvent on the other side of the membrane. No pressure was applied and the values for the flux were very low. To increase the flux, we investigated the use of pressure. In these experiments the membrane was placed horizontally within a metal apparatus, the fatty acid salts were added in solvent to one side of the membrane, and pressure was applied. The separation of a 1:1 mixture of oleic acid:stearic acid salts with iBu_3N was investigated.

When 90 psi of pressure was applied, the flux of the salts was rapid. The value for the flux of the solvent was 39 L m^{-2} h^{-1} which is a desired flux for many industrial separations. The selectivity for the retention of oleic acid salts was maintained. After permeation through two PDCPD membranes under pressure, the original 1:1 mixture of oleic acid:stearic acid was found to be 1:13 in the downstream solvent and 30:1 for the fatty acid salts that were retained.

2.4 Separation of a mixture of oleic, linoleic, and linolenic acids into separate components

Oleic, linoleic, and linolenic acid are the main components of soybean oil and very challenging to purify from one another. The separation of these cis-fatty acids using a membrane would be an important advance in this field. In the talk associated with this paper, the separation of a mixture of these fatty acids will be described.

3 CONCLUSIONS

The significance of this method is that it is the first description of the use of a membrane to separate mixtures of fatty acids into its individual components. The keys to the success of these experiments were the use of amines and nanofiltration membranes based on PDCPD. The amines were important because the fatty acid salts had critical areas that fell in the range where PDCPD membranes separated molecules so the fatty acids salts could be differentiated from one another. Because there are many amines that may be used, the optimization of the separation to isolate each fatty acid salt required only the addition of different amines to test their effect on the permeation of fatty acids. This result is important because we developed methods to separate a mixture of stearic, oleic, linoleic, and linolenic acid into the separate components by the optimization of the amine.

We believe this method will bring added value to vegetable oils by allowing for the simple, inexpensive purification of fatty acids. The oleochemical market is projected to grow in the double digits in the next several years and already exceeds $10 billion. Clearly, this market is important and the purification of the fatty acids represents an important advance. Although the separation of fatty acids based on soybean oil was studied, it may be possible to separate any mixture of cis-fatty acids by the optimization of the amine.

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