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Liquid Membrane Technology: Studies of Sudan Based Chromogenic Ionophores

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ABSTRACT: In chemistry, an ionophore (from Greek ion and -phore 'ion carrier') is a chemical species that reversibly binds ions. Many ionophores are lipid-soluble entities that transport ions across the cell membrane. Ionophores catalyze ion transport across hydrophobic membranes, such as liquid polymeric membranes (carrier-based ion selective electrodes) or lipid bilayers found in the living cells or synthetic vesicles (liposomes). Structurally, an ionophore contains a hydrophilic center and a hydrophobic portion that interacts with the membrane. Some ionophores are synthesized by microorganisms to import ions into their cells. Synthetic ion carriers have also been prepared. Ionophores selective for cations and anions have found many applications in analysis. These compounds have also shown to have various biological effects and a synergistic effect when combined with the ion they bind. Ionophores are chemical compounds that reversibly bind and transport ions through biological membranes in the absence of a protein pore. This can disrupt the membrane potential, and thus these substances could exhibit cytotoxic properties. Ionophores modify the permeability of biological membranes toward certain ions to which they show affinity and selectivity. Many ionophores are lipid-soluble and transport ions across hydrophobic membranes, such as lipid bilayers found in the living cells or synthetic vesicles (liposomes), or liquid polymeric membranes (carrier-based ion selective electrodes). Structurally, an ionophore contains a hydrophilic center and a hydrophobic portion that interacts with the membrane. Ions are bound to the hydrophilic center and form an ionophore-ion complex. The structure of the ionophore-ion complex has been verified by X-ray crystallography.

KEYWORDS: ionophore, sudan, liquid membrane, chromogenic, biological, liposomes, crystallography

I. INTRODUCTION

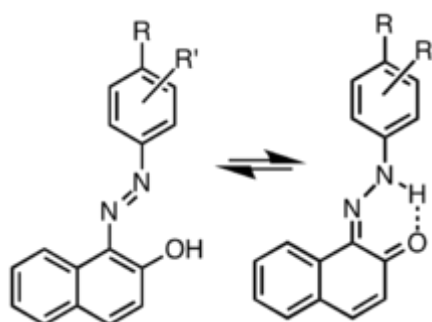
Sudan dyes have high affinity to fats, therefore they are used to demonstrate triglycerides, lipids, and lipoproteins. Alcoholic solutions of Sudan dyes are usually used, however pyridine solutions can be used in some situations as well. Sudan stain test is often used to determine the level of fecal fat to diagnose steatorrhea. A small sample is dissolved in water or saline, glacial acetic acid is added to hydrolyze the insoluble salts of fatty acids, a few drops of alcoholic solution of Sudan III are added, the sample is spread on a microscopic slide, and heated twice to boil. Normally a stool sample should show only a few drops of red-orange stained fat under the microscope. The method is only semiquantitative but, due to its simplicity, it is used for screening. Since they are characteristically oil- and fat-soluble, Sudan dyes are also useful for dyeing plastics and fabrics. Sudan dyes I-IV and Sudan Red G consist of arylazo-substituted naphthols. Such compounds are known to exist as a pair of tautomers:

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Membrane technology encompasses the scientific processes used in the construction and application of membranes. Membranes are used to facilitate the transport or rejection of substances between mediums, and the mechanical separation of gas and liquid streams. In the simplest case, filtration is achieved when the pores of the membrane are smaller than the diameter of the undesired substance, such as a harmful microorganism. Membrane technology is commonly used in industries such as water treatment, chemical and metal processing, pharmaceuticals, biotechnology, the food industry, as well as the removal of environmental pollutants.[1,2]

After membrane construction, there is a need to characterize the prepared membrane to know more about its parameters, like pore size, function group, material properties etc, which are difficult to determine in advance. In this process, instruments such as the Scanning Electron Microscope, the Transmission electron Microscope, the Fourier Transform Infrared Spectroscopy, X-ray Diffraction, and Liquid-Liquid Displacement Porosimetry are utilized.

Membrane technology covers all engineering approaches for the transport of substances between two fractions with the help of semi-permeable membranes. In general, mechanical separation processes for separating gaseous or liquid streams use membrane technology. Recent years, different methods have been used to remove environmental pollutants, like adsorption, oxidation and membrane separation. Different pollution occurs in the environment like air pollution, waste water pollution etc. As per industry requirement to prevent industrial pollution because more than 70% of environmental pollution occurs due to industries. It is their responsibility to follow government rules of the Air Pollution Control & Prevention Act 1981 to maintain and prevent the harmful chemical release in the environment.[2] Make sure to do prevention & safety processes after that industries are able to release their waste in the environment. Biomass Based Membrane technology are one of the most promising technologies for use as a pollutants removal weapon, because it has low cost, more efficiency, & lack of secondary pollutants.[1] Most probably polysulfone, polyvinylidene fluoride, and polypropylene is used in the membrane preparation process. These membrane materials are non-renewable and non-biodegradable as it will be harmful to the environment and create environmental pollution.[4] Researchers are trying to find a solution to synthesize an eco-friendly membrane which avoids environmental pollution. Synthesis of biodegradable material with the help of naturally available material such as biomass based membrane synthesis can be used to remove pollutants.[5] Membrane separation processes operate without heating and therefore use less energy than conventional thermal separation processes such as distillation, sublimation or crystallization. The separation process is purely physical and both fractions (permeate and retentate) can be obtained as useful products. [3,4] Cold separation using membrane technology is widely used in the food technology, biotechnology and pharmaceutical industries. Furthermore, using membranes enables separations to take place that would be impossible using thermal separation methods. For example, it is impossible to separate the constituents of azeotropic liquids or solutes which form isomorphous crystals by distillation or recrystallization but such separations can be achieved using membrane technology. Depending on the type of membrane, the selective separation of certain individual substances or substance mixtures is possible. Important technical applications include the production of drinking water by reverse osmosis. In waste water treatment, membrane technology is becoming increasingly important. Ultra/microfiltration can be very effective in removing

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colloids and macromolecules from wastewater. This is needed if wastewater is discharged into sensitive waters especially those designated for contact water sports and recreation. About half of the market is in medical applications such as use in artificial kidneys to remove toxic substances by hemodialysis and as artificial lung for bubble-free supply of oxygen in the blood. The importance of membrane technology is growing in the field of environmental protection (Nano-Mem-Pro IPPC Database). Even in modern energy recovery techniques membranes are increasingly used, for example in fuel cells and in osmotic power plants.[5,6]

Two basic models can be distinguished for mass transfer through the membrane:

- the solution-diffusion model and
- the hydrodynamic model.

In real membranes, these two transport mechanisms certainly occur side by side, especially during ultra-filtration.

In the solution-diffusion model, transport occurs only by diffusion. The component that needs to be transported must first be dissolved in the membrane. The general approach of the solution-diffusion model is to assume that the chemical potential of the feed and permeate fluids are in equilibrium with the adjacent membrane surfaces such that appropriate expressions for the chemical potential in the fluid and membrane phases can be equated at the solution-membrane interface. This principle is more important for dense membranes without natural pores such as those used for reverse osmosis and in fuel cells. During the filtration process a boundary layer forms on the membrane. This concentration gradient is created by molecules which cannot pass through the membrane. The effect is referred as concentration polarization and, occurring during the filtration, leads to a reduced trans-membrane flow (flux). Concentration polarization is, in principle, reversible by cleaning the membrane which results in the initial flux being almost totally restored. Using a tangential flow to the membrane (cross-flow filtration) can also minimize concentration polarization.[7,8]

Transport through pores – in the simplest case – is done convectively. This requires the size of the pores to be smaller than the diameter of the two separate components. Membranes which function according to this principle are used mainly in micro- and ultrafiltration. They are used to separate macromolecules from solutions, colloids from a dispersion or remove bacteria. During this process the retained particles or molecules form a pulpy mass (filter cake) on the membrane, and this blockage of the membrane hampers the filtration. This blockage can be reduced by the use of the cross-flow method (cross-flow filtration). Here, the liquid to be filtered flows along the front of the membrane and is separated by the pressure difference between the front and back of the membrane into retentate (the flowing concentrate) on the front and permeate (filtrate) on the back. The tangential flow on the front creates a shear stress that cracks the filter cake and reduces the fouling.[9,10]

II. DISCUSSION

There are two main flow configurations of membrane processes: cross-flow (or tangential flow) and dead-end filtrations. In cross-flow filtration the feed flow is tangential to the surface of membrane, retentate is removed from the same side further downstream, whereas the permeate flow is tracked on the other side. In dead-end filtration the direction of the fluid flow is normal to the membrane surface. Both flow geometries offer some advantages and disadvantages. Generally, dead-end filtration is used for feasibility studies on a laboratory scale. The dead-end membranes are relatively easy to fabricate which reduces the cost of the separation process. The dead-end membrane separation process is easy to implement and the process is usually cheaper than cross-flow membrane filtration. The dead-end filtration process is usually a batch-type process, where the filtering solution is loaded (or slowly fed) into the membrane device, which then allows passage of some particles subject to the driving force. The main disadvantage of a dead end filtration is the extensive membrane fouling and concentration polarization. The fouling is usually induced faster at higher driving forces.[11,12] Membrane fouling and particle retention in a feed solution also builds up a

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concentration gradients and particle back flow (concentration polarization). The tangential flow devices are more cost and labor-intensive, but they are less susceptible to fouling due to the sweeping effects and high shear rates of the passing flow. The most commonly used synthetic membrane devices (modules) are flat sheets/plates, spiral wounds, and hollow fibers. Flat plates are usually constructed as circular thin flat membrane surfaces to be used in dead-end geometry modules. Spiral wounds are constructed from similar flat membranes but in the form of a "pocket" containing two membrane sheets separated by a highly porous support plate.[6] Several such pockets are then wound around a tube to create a tangential flow geometry and to reduce membrane fouling. hollow fiber modules consist of an assembly of self-supporting fibers with dense skin separation layers, and a more open matrix helping to withstand pressure gradients and maintain structural integrity.[6] The hollow fiber modules can contain up to 10,000 fibers ranging from 200 to 2500 μm in diameter; The main advantage of hollow fiber modules is very large surface area within an enclosed volume, increasing the efficiency of the separation process. Membrane separation processes have a very important role in the separation industry. Nevertheless, they were not considered technically important until the mid-1970s. Membrane separation processes differ based on separation mechanisms and size of the separated particles. The widely used membrane processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrolysis, dialysis, electro dialysis, gas separation, vapor permeation, pervaporation, membrane distillation, and membrane contactors.[8] All processes except for pervaporation involve no phase change. All processes except electro dialysis are pressure driven. Microfiltration and ultrafiltration is widely used in food and beverage processing (beer microfiltration, apple juice ultrafiltration), biotechnological applications and pharmaceutical industry (antibiotic production, protein purification), water purification and wastewater treatment, the microelectronics industry, and others. Nanofiltration and reverse osmosis membranes are mainly used for water purification purposes. Dense membranes are utilized for gas separations (removal of CO_2 from natural gas, separating N_2 from air, organic vapor removal from air or a nitrogen stream) and sometimes in membrane distillation. The later process helps in the separation of azeotropic compositions reducing the costs of distillation processes.[13,14]

To determine the pore diameter, physical methods such as porosimeter (mercury, liquid-liquid porosimeter and Bubble Point Test) are also used, but a certain form of the pores (such as cylindrical or concatenated spherical holes) is assumed. Such methods are used for membranes whose pore geometry does not match the ideal, and we get "nominal" pore diameter, which characterizes the membrane, but does not necessarily reflect its actual filtration behavior and selectivity. The selectivity is highly dependent on the separation process, the composition of the membrane and its electrochemical properties in addition to the pore size. With high selectivity, isotopes can be enriched (uranium enrichment) in nuclear engineering or industrial gases like nitrogen can be recovered (gas separation). Ideally, even racemics can be enriched with a suitable membrane. When choosing membranes selectivity has priority over a high permeability, as low flows can easily be offset by increasing the filter surface with a modular structure. In gas phase filtration different deposition mechanisms are operative, so that particles having sizes below the pore size of the membrane can be retained as well.[15,16]

Green membrane or Bio-membrane synthesis is the solution to protected environments which have largely comprehensive performance. Biomass is used in the form of activated carbon nanoparticles, like using cellulose based biomass coconut shell, hazelnut shell, walnut shell, agricultural wastes of corn stalks etc.[4] which improve surface hydrophilicity, larger pore size, more and lower surface roughness therefore, the separation and anti-fouling performance of membranes are also improved simultaneously.[15] A biomass-based membrane is a membrane made from organic materials such as plant fibers.[4] These membranes are often used in water filtration and wastewater treatment applications. The fabrication of a pure biomass-based membrane is a complex process that involves a number of steps. The first step is to create a slurry of the organic materials. This slurry is then cast onto a substrate, such as a glass or metal plate.[16] The cast is then dried, and the resulting membrane is then subjected to a number of treatments, such as chemical or heat treatments, to improve its properties. One of the challenges in the fabrication of biomass-based membranes is to create a membrane with the desired properties.[17]

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III. RESULTS

An artificial membrane, or synthetic membrane, is a synthetically created membrane which is usually intended for separation purposes in laboratory or in industry. Synthetic membranes have been successfully used for small and large-scale industrial processes since the middle of twentieth century.[1] A wide variety of synthetic membranes is known.[2] They can be produced from organic materials such as polymers and liquids, as well as inorganic materials. The most of commercially utilized synthetic membranes in separation industry are made of polymeric structures. They can be classified based on their surface chemistry, bulk structure, morphology, and production method. The chemical and physical properties of synthetic membranes and separated particles as well as a choice of driving force define a particular membrane separation process. The most commonly used driving forces of a membrane process in industry are pressure and concentration gradients. The respective membrane process is therefore known as filtration. Synthetic membranes utilized in a separation process can be of different geometry and of respective flow configuration. They can also be categorized based on their application and separation regime.[2] The best known synthetic membrane separation processes include water purification, reverse osmosis, dehydrogenation of natural gas, removal of cell particles by microfiltration and ultrafiltration, removal of microorganisms from dairy products, and Dialysis. Liquid membranes refer to synthetic membranes made of non-rigid materials. [17,18] Several types of liquid membranes can be encountered in industry: emulsion liquid membranes, immobilized (supported) liquid membranes, molten salts, and hollow-fiber contained liquid membranes. Liquid membranes have been extensively studied but thus far have limited commercial applications. Maintaining adequate long-term stability is the problem, due to the tendency of membrane liquids to evaporate or dissolve in the phases in contact with them.[17]

Synthetic membranes can be also categorized based on their structure (morphology). Three such types of synthetic membranes are commonly used in separation industry: dense membranes, porous membranes, and asymmetric membranes. Dense and porous membranes are distinct from each other based on the size of separated molecules. Dense membrane is usually a thin layer of dense material utilized in the separation processes of small molecules (usually in gas or liquid phase). Dense membranes are widely used in industry for gas separations and reverse osmosis applications.[19,20]

Dense membranes can be synthesized as amorphous or heterogeneous structures. Polymeric dense membranes such as polytetrafluoroethylene and cellulose esters are usually fabricated by compression molding, solvent casting, and spraying of a polymer solution. The membrane structure of a dense membrane can be in a rubbery or a glassy state at a given temperature depending on its glass transition temperature .[2] Porous membranes are intended on separation of larger molecules such as solid colloidal particles, large biomolecules (proteins, DNA, RNA) and cells from the filtering media. Porous membranes find use in the microfiltration, ultrafiltration, and dialysis applications. There is some controversy in defining a "membrane pore". The most commonly used theory assumes a cylindrical pore for simplicity. This model assumes that pores have the shape of parallel, nonintersecting cylindrical capillaries.[18] But in reality a typical pore is a random network of the unevenly shaped structures of different sizes. The formation of a pore can be induced by the dissolution of a "better" solvent into a "poorer" solvent in a polymer solution.[2] Other types of pore structure can be produced by stretching of crystalline structure polymers. The structure of porous membrane is related to the characteristics of the interacting polymer and solvent, components concentration, molecular weight, temperature, and storing time in solution.[2] The thicker porous membranes sometimes provide support for the thin dense membrane layers, forming the asymmetric membrane structures. The latter are usually produced by a lamination of dense and porous membranes. The stabilized liquid membrane device (SLMD) is a passive, integrative sampler that provides an alternative or complementary approach to the conventional water sampling of aqueous metals. The simple device is composed of nonporous low-density plastic lay-flat tubing, which is filled with a chemical mixture containing a chelating agent (metal-binding agent) and a long chain organic acid. [21,22] The water-insoluble chelating agent-organic acid mixture diffuses in a controlled manner to the exterior surface of the sampler membrane and binds to

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environmental metals. In practice, the SLMD provides for continuous sequestration of bioavailable forms of trace metals, such as, cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). The SLMD can also be utilized for in-laboratory preconcentration and speciation of bioavailable trace metals from grab water samples.[1] Exposure to ionic metals has been shown to result in deleterious effects for aquatic organisms[2] and may induce oxidative stress, cause DNA damage,[3] and decrease enzyme activity.[4] In contrast, some metals under certain environmental conditions have potential moderating effects on other more toxic metals; one example being zinc (Zn), which has been shown to reduce copper (Cu) toxicity when both metals are present.[5] Given that the presence of particular aqueous metals may have a wide array of effects on organisms, aquatic toxicologists have developed various methods for sampling them. Passive, or in situ, environmental sampling is an important tool used by toxicologists for evaluating toxicants that may exist in very small concentrations—not easily detectable via grab samples. One passive sampler, the semipermeable membrane device, or SPMD, is commonly used to measure organic contaminants in aquatic ecosystems. The SLMD was developed as a counterpart device for sampling metals.[6] Passive sampling for trace metals is more complex than for organic toxicants as most dissolved metals can simultaneously exist in any of several ionic, complex-ion, and organically bound states.[7] Metals can also bind with suspended or dissolved organic matter and exist as ultra-fine colloids,[8] or lipophilic complexes.[9] First developed by Petty, Brumbaugh, Huckins, May, and Wiedmeyer, the SLMD is used to monitor ionic metals in aquatic environments. Due to anthropogenic factors such as mining, metal refining, and industrial activity, global emissions of metals has significantly increased within the last 100 years, and will likely continue to increase during the foreseeable future.[10] The simple device can be created in the laboratory using a nonporous polymeric tube, such as low-density polyethylene (LDPE) plastic[19,20]. A sequestration medium within the tube slowly diffuses through the membrane, binding to ionic metals creating non-mobile metals species that can later be extracted from the other membrane. The sequestration medium generally consists of a metal binding agent, or chelating agent, and a long chain organic acid, commonly oleic acid.[10] The SLMD tube is flat with a membrane thickness that can vary between 2 and 500 μm depending on the application. The approximate width of the SLMD is 2.5 cm and approximate length is 15 cm (these dimensions may vary based on application). The sequestration medium reagent is typically composed of an equal mixture of oleic acid (cis-9-octadecenoic acid) and Kelex-100 (ethyl-methyl-octyl, 8-quinolinol), however other chemicals may be used to perform similar functions. After deployment, the immobilized metal species can then be extracted from the outer membrane.[21,22] The metal species can be identified and analyzed using widely recognized standard techniques (e.g., digestion, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, etc.). In this regard, any procedure or analytical technique applicable to measuring ionic or complexed metal species is suitable for determining metal concentrations sequestered by the SLMD.[10]

IV. CONCLUSIONS

Sudan IV (C₂₄H₂₀N₄O) is a lysochrome (fat-soluble dye) diazo dye used for the staining of lipids, triglycerides and lipoproteins on frozen paraffin sections. It has the appearance of reddish brown crystals with melting point 199 °C and maximum absorption at 520(357) nm. Sudan IV is one of the dyes used for Sudan staining. Similar dyes include Oil Red O, Sudan III, and Sudan Black B. Staining is an important biochemical technique, offering the ability to visually qualify the presence of the fatty compound of interest without isolating it. For staining purposes, Sudan IV can be made up in propylene glycol.[1] Alternatively, authors have reported using the dye saturated in isopropyl alcohol, 95% ethanol, or 0.05% by weight in acetone:ethanol:water (50:35:15) The idea is to use a moderately apolar solvent to solubilize the dye allowing it to partition into the highly apolar fat without the solvent solubilizing the fat to be stained. Sudan I, Sudan III, and Sudan IV have been classified as category 3 carcinogen by the International Agency for Research on Cancer.[2] In its purified form it is called Biebrich scarlet R, which should not be confused with the water-soluble Biebrich scarlet. In industry, it is used to color nonpolar substances like oils, fats, waxes, greases, various hydrocarbon products, and acrylic emulsions. Sudan IV is also used in United Kingdom as a fuel dye to dye lower-taxed heating oil; because of that it is also known as Oil Tax Red. As a food dye, Sudan IV is considered an illegal dye,

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mainly because of its harmful effect over a long period of time, as it is a carcinogen. It was ruled unsafe in the 1995 food safety regulations report.[23]

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