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Studies on pervaporative characteristics of bacterial cellulose membrane

Lokesh Kumar Pandey, Chhaya Saxena, Vinita Dubey*

Synthetic Chemistry Division, Defence Research and Development Establishment, Jhansi Road, Gwalior (MP) 474002, India

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Abstract

Cellulose membrane produced by bacterial *Acetobacter xylinum* was deproteinated and investigated for pervaporative separation of aqueous organic mixtures. The permeate flux, selectivity, pervaporation separation index (PSI), solubility and degree of sorption were studied as a function of increasing concentration of organics in the feed. The membrane was found highly selective to water; highest selectivity [α_p = 186] was obtained for a mixture of trihydric alcohol viz. glycerol (Gly) with 40% (v/v) water. The binary system of monohydric alcohol viz. ethanol (EtOH) and water (40% (v/v)) showed the lowest selectivity [α_p = 12] but the highest pervaporative flux of 614 $gm^{-2}\,h^{-1}$ at 35 °C which further increased to 1429 $gm^{-2}\,h^{-1}$ at 75 °C. However, selectivity decreased to 1.3 with the increase in temperature. The pervaporation behaviour was interpreted in terms of sorption and diffusivity of the organics, which in turn, was influenced by the extent of their hydrogen bonding with the cellulose units in the membrane and the plasticization induced by the permeating water present in the binary mixture. Substantially high pervaporative separation index (PSI) of the order of 10^3–10^4 $gm^{-2}\,h^{-1}$ and comparatively lower energy of activation (Ej) of 10 kJ/mol is indicative of the pervaporative potential of the bacterial cellulose membrane (BCM) in the separation of aqueous binary mixtures.

Keywords: Bacterial cellulose membrane; Pervaporation; Flux; Selectivity; Sorption; Separation

1. Introduction

The bacterial cellulose originates as a white gelatinous pellicle on the surface of the liquid medium at about 30 °C, in a static culture containing *Acetobacter xylinum*, a rod shaped, aerobic gram negative bacterium which occurs as a contaminant in vinegar production [1–3]. By controlling the physiological conditions of bacterial growth such as the composition of the culture media, its pH, temperature and oxygen tension, morphologically reproducible pellicle is obtained [2–5] which can be easily flattened, pressed and processed into membranes of desired thickness. The membrane has superior mechanical properties, high resistance to corrosive chemicals, biodegradability, ease of tailorability and economical processing [3,6–7]. Its unique structural features and properties facilitate diverse applications ranging from wound-dressing, carrier for mammalian cell culture, immobilization of enzymes and other biomolecules, to diaphragms in speakers for audio-communication [1–3,7].

The pervaporation potential of the membrane however still remains largely unexplored. The remarkable water flux with reasonable selectivity shown by the membrane especially in the water-lean (<50 wt.% water) regions for the pervaporation of water/alcohol binary mixtures [7] prompted us to investigate the potential of the membrane for the separation of aqueous binary mixtures of organics in the present study. The representative organics chosen for the study ranged from volatile organic chemicals (VOCs) such as acetone (Ac), formalin (HCHO) and ethanol (EtOH) to those forming extensive hydrogen bonding with water such as ethylene glycol (EG) and glycerol (Gly) (Table 1).

The removal of water from organics assumes importance with a view to enrich the process stream in the organic components for their subsequent recycling or recovery. The separation of organics from water also helps to 'clean' the effluents prior to direct discharge of water into the environment. Eco-friendly and economical membrane mediated green separation are attracting considerable attention for 'cleaning technology'. Both hydrophobic and hydrophilic membranes have been explored [6–10] for the purpose. The paper describes the use of hydrophilic water selective BCM for such applications.

* Corresponding author. Tel.: +91 751 2233482; fax: +91 751 2341148.
E-mail address: India_dv@yahoo.com (V. Dubey).

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Table 1
BAT (best available technology) effluent limits (from http://www.epa.gov/)

Pollutant	Permissible concentration (mg/L)		
	Long term mean	Maximum for one day	Monthly average
Ethanol	1.1	3.7	1.8
Formalin	0.01	0.05	0.02
Ethylene glycol	1.1	3.7	1.8
Acetone	0.1	0.4	0.2

2. Experimental

2.1. Materials

BCM grown from *A. xylinum*, as per the earlier reported [7] method was obtained from Biotechnology Division of our establishment. The membranes were dipped for 48 h in a flat-bottomed large petridish containing saturated solution of NaOH for deproteination and were then rinsed several times with distilled water until a neutral pH was attained in the drained liquid. The specimens were dried for a week under vacuum at 60 °C prior to use. The average thickness of the membrane was 80 μm. The membrane was characterised as reported earlier [6]. The organic chemicals namely Ac, HCHO, EtOH, EG and Gly were used as received from E. Merck/Across. Distilled water was used for preparing their binary mixtures.

2.2. Determination of sorption

Membrane specimen of predetermined weight W_d, were immersed in the above mentioned pure organic components and in their respective 40:60 (v/v) aqueous mixtures. After equilibration for 72 h at room temperature, the membranes were removed and superfluous liquid was wiped with tissue paper. The weight W_s of the swollen membrane was determined with an accuracy of 0.1 mg using analytical balance (AW220 Shimadzu, Japan). W_d and W_s were substituted in Eq. (1) to calculate the extent (%) of sorption Q [7–10,13]:

$$Q = \left[\frac{W_s}{W_d} - 1\right] \times 100 \quad (1)$$

2.3. Solubility in the membrane phase

In order to determine the amount of water, in the membrane phase, the above specimens swollen to equilibrium in binary mixtures were desorbed using the cold-finger technique [7]. The specimen was placed in a reservoir at 60 °C under a vacuum of 1.0 mmHg for 2 h. The desorbed vapours were collected in a trap cooled by liquid nitrogen/methanol mixture at a temperature of −70 °C. The composition of condensate was determined by measurement of refractive indices at 30 °C using an Abbe refractometer (Model RCR-1, from M/s Rajdhani Scientific Instruments, New Delhi, India) having an accuracy of ±0.0001 unit and lower detection limit of 1% for binary mixtures. The solubility selectivity (α_s) was calculated using the following equation [7–10,13]:

$$\alpha_s = \frac{Y_m/X_m}{Y_f/X_f} \quad (2)$$

where Y and X are the weight fractions of water and organic component, respectively, in the membrane (Y_m, X_m) and feed (Y_f, X_f).

2.4. Sorption isotherms

The sorption isotherms for organic vapour and water were determined using an automated sorption analyzer termed intelligent gravimetric analyser (IGA) procured from M/s Hiden Analytical Ltd., UK. The instrument [12] is based on the principle of mass relaxation in the polymer accompanying vapour sorption. The concentration ($P/P_0 \sim$ activity or concentration) of the vapours was increased in 12–22 equal steps corresponding to a pressure change of 4–5 mb at a constant temperature of 30 ± 1 °C and the corresponding increase in the weight of the sample was monitored to obtain the sorption kinetics which were fitted into appropriate sorption models [12,14] and converted to the isotherms by the system software.

2.5. Permeation studies

The PV experiments were carried out at 35 ± 1 °C using a batch stirred reactor described by Natke et al. [15]. The membrane was allowed to equilibrate with the feed solution for 24 h. After the attainment of steady state, the permeate was condensed in cold traps immersed in liquid nitrogen. The permeate composition was determined using a Abbe refractometer with an accuracy of ±0.0001 units. The downstream pressure was maintained at 1 mmHg in all experiments. The flux (J) was determined by measuring the weight of the permeate. The permeation selectivity (α_p) was calculated using the following equation [7–10]:

$$\alpha_s = \frac{Y_p/X_p}{Y_f/X_f} \quad (3)$$

where Y and X are the weight fractions of water and organic species respectively in the feed (Y_f, X_f) and permeate (Y_p, X_p).The pervaporation separation index (PSI) was calculated from Eq. (4) proposed by Feng and Huang [16]

$$\text{PSI} = J(\alpha - 1) \quad (4)$$

3. Results and discussion

According to the prevalent solution-diffusion model [8–11], the flux and separation factor of a component in a binary system through a membrane are function of its solubility and diffusivity. Unlike distillation, the separation mechanism in PV is not based on the relative volatility of the constituent