Preparation and Characterization of Polysulfone–Cyclodextrin Composite Nanofiltration Membrane: Solvent Effect

Kundan Baruah, Swapnali Hazarika,* Somiron Borthakur, Narendra Nath Dutta

Chemical Engineering Division, CSIR—North East Institute of Science and Technology, Jorhat 785006, Assam, India

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ABSTRACT: α-Cyclodextrin membranes were prepared by the phase inversion method using four types of casting solvents such as N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethyl acetamide (DMAc), and dimethyl formamide (DMF) herein-after termed as α-CD-NMP, α-CD-DMSO, α-CD-DMAc, and α-CD-DMF, respectively. The membranes were characterized by IR, XRD, TGA-DTA, DSC, and SEM analysis and show that solvents like NMP, DMA, DMF give good uniform morphological membranes and are better than that of DMSO. Thermal decompositions of the pure polymer and composite membranes indicate different range of thermal degradation of the membrane. This study reveals that the casting solvents NMP, DMF, DMAC have nearly same significant effect on morphology and other properties of the membranes. This is explained in terms of demixing behavior of the polymer and the combined effect of solvent volatility and polymer–solvent interactions as estimated from Hansen solubility parameter. Solvent hydrophobicity also affects the performance of the membrane and can be determined in terms of water permeability.

Key words: α-cyclodextrin; NF membrane; solvent effect; membrane morphology; Hansen solubility parameter

INTRODUCTION

Nanofiltration is a relatively new membrane separation technique which is a pressure-driven membrane process normally applicable for separation of dissolved components. The speciality of NF membrane is water softening, treatment of industrial effluents contaminated with organics or heavy metals.1–4 The process is regarded as an innovative and promising water treatment technique, and a potential alternative to conventional water treatment approaches.5–7 Most NF membranes are composite in nature, with a selective layer on the top of the microporous substrate. Many researchers have developed several methods for preparation of selective layer through polymerization.8,9

To make a high-performance separation membrane, it is essential to study the membrane formation procedure which is an important issue in membrane research. The thermodynamic properties of the casting solution and coagulation pairs play a very important role on the structure and performance of a membrane prepared by immersion precipitation.10,11 Different ternary systems result in different membranes with different structures.12,13 Tight NF membrane has a smaller pore size, which is usually adopted for water softening. Properties of solvent can also affect the membrane morphology and performance of membrane. Addition of a volatile solvent along with a non-solvent can change liquid–liquid behavior and as a result membrane morphology may be changed. Again addition of a co-solvent to a polymeric solution can eliminate macrovoid formation during instantaneous demixing and change the morphology of the membrane from finger-like to sponge-like structure. Boussu et al.14 studied the polyethersulfone membrane using DMF and NMP on the casting solvent. This self-made membrane has very good retention for charged compounds in combination with high-permeate flux.

In our present work, we have considered α-cyclodextrin (α-CD) as novel polymer for preparation of NF membrane which is composite with polysulfone. Cyclodextrins are macrocyclic oligomers of α-D-glucose and they are shaped like truncated cones with primary and secondary hydroxyl groups crowning the narrower rim and wider rim respectively. In CD, the glucose units are arranged in such a way that the hydroxymethylene groups are pointing downward, whereas the hydroxyl groups are pointing upward. As a result of this, a hydrophilic outer space and a hydrophobic inner space are formed leading to the particular ability of the cyclodextrins to form host–guest complexes with organic components having appropriate diameters and physical interactions.15,16 It is also used as supramolecular carrier in organometallic reactions and other
areas. To get better understanding of the binding events, a lot of theoretical and experimental methods have been used to study the CD complexes. CD is expected to provide good membrane morphology; however, a very limited study is available in literature. Hence we attempted to study the membrane formation capability of CD composite with polysulfone. In our work, we have been studying the solvent effect on preparation of NF membrane from CD composite with polysulfone and their characterization through investigating the effect of pore size of the membranes in different solvents by measuring pure water permeate flux.

### MATERIALS AND METHODS

#### Chemicals

Commercial grade polysulfone (average mol. wt. 27,000) was supplied by Aldrich Chemical Company, USA. Polyethylene glycol (PEG 1500) was obtained from G. S. Chemical testing and allied industries. Inorganic salt lithium nitrate and α-cyclo-dextrin were supplied from Acros Organics, USA. N-methyl pyrrolidone (NMP) was supplied by RANBAXY Fine Chemicals, New Delhi. N,N-dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMAc) were supplied by Acros Organics. Dimethyl sulfoxide (DMSO) was purchased from MERCK India, Bombay. Deionized water was used as coagulation bath.

#### Methods

**Preparation of membrane**

Flat sheet membranes are prepared by phase inversion method. Polysulfone (PSf) is mixed with a definite amount of α-cyclodextrin, polyethylene glycol, LiNO₃, and then dissolved in different solvents viz., NMP, DMF, DMAc, and DMSO separately at room temperature (28–32°C and relative humidity about 78%) to make the casting solution. The polymer solution is stirred for about 6 h at room temperature (28–27°C) using a magnetic stirrer until a homogeneous solution was achieved. Film was cast on a glass plate with a casting knife of thickness 0.5 mm maintaining the same temperature as in the solution and are exposed for about 5 min to ambient before immersion into a coagulation bath that contains ice-cooled water (maintained at about 6°C). When the cast films changed their color from transparent to white, immediately the plate is immersed into the coagulation bath and the films were separated out from the glass plate after some time. The prepared membrane sheets were washed under running water and kept in deionized water bath overnight. Then the sheets were dried at room temperature. Finally the membranes were characterized by using different analytical methods and kept ready for permeation experiments.

The casted membranes were characterized for porosimetry measurement by standard pressure. The surface morphology and thickness of the membranes were determined by SEM. Pure water permeability for all membranes were measured in a membrane cell of standard design. The membrane with effective area 28.3 cm² was set in the cell and the pure water permeability test was carried out by applying a pressure of 4.9 bar pressure to the feed side. The quantity of water permeated through the membrane was measured as permeation rate. Composition and physical properties such as membrane thickness, pore diameter, surface porosity, and pure water permeability of membranes are shown in Table I.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Membrane thickness (µm)</th>
<th>Pore diameter (nm)</th>
<th>Surface porosity (%)</th>
<th>Pure water permeability (Lm⁻²h⁻¹)</th>
<th>Water uptake (%)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>57.40</td>
<td>1.26</td>
<td>0.19</td>
<td>48</td>
<td>8.36</td>
<td>38</td>
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<tr>
<td>DMAc</td>
<td>13.40</td>
<td>1.64</td>
<td>0.30</td>
<td>40</td>
<td>6.05</td>
<td>41</td>
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<tr>
<td>DMF</td>
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<td>1.81</td>
<td>0.59</td>
<td>32</td>
<td>5.43</td>
<td>49</td>
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<td>2.11</td>
<td>0.22</td>
<td>20</td>
<td>3.21</td>
<td>57</td>
</tr>
</tbody>
</table>

Weight of α-CD = 0.3678%; weight of polysulfone = 10.9874%; weight of additive = 1.0999%; Weight of LiNO₃ = 0.1857%; Weight of solvent added = 87.3592%
vapor pressure, operating at the lowest relative vapor pressure, the pore diameter, contact angle of the liquid with the pore, $D$ is the molar volume of condensed liquid, $Q$ where $c$

100 the wet membranes were dried under vacuum at 100°C overnight, weighed to obtain $W_{dry}$. The water uptake was calculated using the following equation:

\[
\text{Water uptake} = \left( \frac{W_{wet} - W_{dry}}{W_{dry}} \right) \times 100\% \quad (1)
\]

Contact angles of the membranes were measured by bubble formation method applying Poiseuille’s equation which expresses the balance between viscous forces and capillary and hydrostatic forces (neglecting inertial effects).19

Membrane morphology was studied by a scanning electron microscope (LEO 1427VP, UK) which directly provides the visual information of the membrane morphology such as pore shape, size, their distribution, and density.

The thickness of the prepared membranes was measured by a membrane thickness gauge made by Mitutoyo Corporation, Japan.

Pore diameter of the membranes was determined by capillary condensation flow porometer (PMI, Model CCFP-5A). The principle of this process is that at a pressure $P_a$ of vapor, in equilibrium with its liquid, can condense in pores of material. Vapor condenses in all pores smaller than $D$ (pore diameter), determined by the pressure of the vapor20.

\[
D = -\frac{\pi r^2 \cos \theta}{4Q} \ln \left( \frac{P}{P_a} \right) \quad (2)
\]

where $\gamma$ is the surface tension of condensed liquid, $v$ is the molar volume of condensed liquid, $Q$ is the contact angle of the liquid with the pore, $D$ is the pore diameter, $R$ is the gas constant, and $T$ is the absolute test temperature. At the lowest relative vapor pressure, $(P/P_a)$, condensation occurs in the smallest pore. On increase of relative vapor pressure condensation occurs in larger pores. A small increase in pressure on inlet side of the sample causes flow. Measurement of pressure change in outlet side of the sample yields flow rate:

\[
F_{STP} = \frac{\gamma_a T_s}{P_a} \frac{(dp/dt)}{(3)}
\]

After obtaining the value of vapor equilibrated with the sample and rates of pressure change, the pore diameters of the nanopore membrane were obtained.

### RESULTS AND DISCUSSION

#### Primary effect

The interaction between residual solvents and \(\alpha\)-cyclodextrin membrane

The FTIR spectra obtained for polysulfone, \(\alpha\)-cyclodextrin, and the composite membranes in different casting solvents are shown in Figure 1. A broad peak is observed at 3413 cm\(^{-1}\) for \(\alpha\)-CD indicates the presence of –OH group; however, this peak is found to be absent in the composite membrane of \(\alpha\)-CD because of the interaction between the outer surfaces of \(\alpha\)-CD molecule with the polar solvent. For composite membrane, the band in the range 3413–3434 cm\(^{-1}\) indicates the absence of aromaticity of \(\alpha\)-CD, C–O stretching band is obtained in the range 1420–1580 cm\(^{-1}\) for \(\alpha\)-CD-NMP, \(\alpha\)-CD-DMAc, and \(\alpha\)-CD-DMF membranes which is absent in \(\alpha\)-CD-DMSO membrane. Other main bands appearing in the IR spectrum for polymer and composite membranes were assigned and tabulated separately in Table II.

A difference is also observed in \(^1\)H-NMR of \(\alpha\)-CD-NMP membrane where a very intense singlet appeared at 1.7 δ indicating a stronger interaction between \(\alpha\)-CD and NMP compared with the others. The \(^1\)H-NMR spectrums of the composite membranes are shown in Figure 2. All the four membranes show similar intense peaks at 1.61 ppm while some other peaks are also observed due to different chemical environment. The presence of residual solvent in the membrane casting is also identified from the \(^1\)H-NMR spectra even though it is quite a trace amount, the signal at 2.1–2.9 ppm in the \(\alpha\)-CD-NMP, \(\alpha\)-CD-DMAc, and \(\alpha\)-CD-DMF membranes is attributed due to the free –N(CH\(_3\))\(_2\) group. From this observation, it can be concluded that the solvent plasticization effect on membrane properties is negligible as the residual solvent content is too small.21 Also NMP is comparatively less volatile and hence resides on the membrane, indicated by the sharp intense peak at 3.51 ppm which is predicted to be due to the interaction of the solvent (NMP) with \(\alpha\)-CD. The observation of intense peak in \(\alpha\)-CD-NMP membrane can be attributed due to the strong H-bonding which is a main
cause for the difference in membrane properties in different casting solvent. This peak is also present in α-CD-DMAc membrane.

The diffraction pattern of the membranes has been studied by XRD spectra and is shown in Figure 3. The X-ray investigation provided the information about the structural changes induced in α-CD-polymer composite membranes in four different solvents. The patterns for the four membranes showed broad peaks in the range of 7.40–10.12. From the figure, it is seen that the peak position does not depend on the casting solution. However, compared to other three membranes, the pattern of α-CD-NMP membrane shows a broadband peak with a decrease in peak intensity. Broad peak of the composite membrane indicates the amorphous state. The broad peaks also indicate the conformation of complete homogeneity and compatibility among the components of the membrane. This type of observation was reported by Guan et al.\textsuperscript{21} for sulfonated polyether-sulfone (SPES) membrane. The relative degree of the phase can be estimated from the full width at half maximum value (FWHM) given in Table III, wherein d-values and FWHM values are also shown. For α-CD-NMP membrane, FWHM value is 3.8, which is bigger than that of other values of FWHM of other membranes studied in this work. This indicates that stronger hydrogen bonding interaction occurred between α-CD-NMP membranes compared with that between other three solvents with α-CD. The values are different for SPES membrane in different casting solvents as reported by Guan et al.\textsuperscript{21} For blend membranes with sulfonated polystyrene and sulfonated poly(2,6-dimethyl 1,4-phenylene oxide), the electrostatic cross-linking resulting from the ionic groups of sulfonated polymers increases the amorphous region abruptly.\textsuperscript{22,23}

Effect of residual solvents on the thermal behavior of membrane

During the use of composite NF membranes, the stability of them against thermal stress is of great importance. Thus, thermogravimetric analysis was carried out under nitrogen atmosphere at a heating rate of 10°C min\textsuperscript{-1}. The decomposition curves of pure polymer and composite membranes are shown in Figure 4 wherein the derivative curves are shown in Figure 5. For polysulfone, two-step decompositions are at 473.39 and 608.50°C whereas four-step decompositions for α-CD are at 56.02, 127.54, 296.37, and 360.85°C, respectively. For α-CD-NMP, membrane four-step decompositions occur at 122.87, 177.16, 404.68, and 576.44°C whereas for other membranes decomposition occurs in two steps. The decomposition of α-CD-DMAc, α-CD-DMSO, and α-CD-DMF occurs at 465.80 and 576.85, 403.87 and 581.75, and 449.62 and 640.92°C, respectively. DSC measurements of the membranes were carried out at a heating rate of 10°C min\textsuperscript{-1} in nitrogen atmosphere. Melting endothermic peaks obtained at different temperatures for pure polymer and composite membrane were shown in Figure 6. The change in T\textsubscript{g} for composite membranes was strongly influenced by the pore structure and can be explained by the percolation theory\textsuperscript{24} which explains the glass transition behavior in polymer thin film. According to the percolation theory, the polymer sample is composed of domains of fast and slow dynamics, which are each approximately 2 nm in size. The population of slow domains is controlled by the sample temperature. The glass transition occurs on cooling due to the percolation of domains of slow dynamics by thermally induced density fluctuations. The domains of fast dynamics do not affect the overall viscosity. In nanoporous samples, a free-surface interfacial region that surrounds each nanopore results in high polymer chain mobility. These highly mobile regions are dispersed throughout the polymer matrix, and they contribute to the disruption of the percolation of the slow domains when the system is cooled from the polymer melt. In confined systems, such as

### TABLE II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vibrational frequency (cm\textsuperscript{-1})</th>
<th>Bond assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone</td>
<td>3434</td>
<td>O–H str that may be arise due to absorption of water during analysis</td>
</tr>
<tr>
<td></td>
<td>2327.79</td>
<td>C=H \text{sym str}</td>
</tr>
<tr>
<td></td>
<td>1644.05</td>
<td>O–C aromatic ring str</td>
</tr>
<tr>
<td></td>
<td>1018.81–1148</td>
<td>C–SO\textsubscript{2}–C \text{sym str}</td>
</tr>
<tr>
<td>α-Cycloextrin</td>
<td>3413.34</td>
<td>O–H str</td>
</tr>
<tr>
<td></td>
<td>2327.79</td>
<td>C–C bend</td>
</tr>
<tr>
<td></td>
<td>1411.25–1644.75</td>
<td>C–O str</td>
</tr>
<tr>
<td></td>
<td>1153.17</td>
<td>C–O str (etheral group)</td>
</tr>
<tr>
<td>α-CD-NMP</td>
<td>2850–3100</td>
<td>N–H str</td>
</tr>
<tr>
<td></td>
<td>1584</td>
<td>C=O str</td>
</tr>
<tr>
<td></td>
<td>1487.9</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>1105.2</td>
<td>C–C str</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>C–SO\textsubscript{2}–C \text{sym str}</td>
</tr>
<tr>
<td>α-CD-DMF</td>
<td>3100–3500</td>
<td>N–H str</td>
</tr>
<tr>
<td></td>
<td>1504–1580</td>
<td>C=O str</td>
</tr>
<tr>
<td></td>
<td>1409–1487</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>1148–1168.6</td>
<td>C–SO\textsubscript{2}–C \text{sym str}</td>
</tr>
<tr>
<td></td>
<td>1013–1104</td>
<td>C–C aromatic str</td>
</tr>
<tr>
<td>α-CD-DMAc</td>
<td>3100–3500</td>
<td>N–H str</td>
</tr>
<tr>
<td></td>
<td>1584.3–1504.9</td>
<td>C=O str</td>
</tr>
<tr>
<td></td>
<td>1487–1404</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>1149–1104</td>
<td>C–SO\textsubscript{2}–C \text{sym str}</td>
</tr>
<tr>
<td></td>
<td>1013–1080.3</td>
<td>C–C bend</td>
</tr>
<tr>
<td>α-CD-DMSO</td>
<td>1582–1506</td>
<td>C–O bend</td>
</tr>
<tr>
<td></td>
<td>1484</td>
<td>C–H str</td>
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<tr>
<td></td>
<td>1323</td>
<td>S=O bend</td>
</tr>
<tr>
<td></td>
<td>1146–1168</td>
<td>C–SO\textsubscript{2}–C \text{sym str}</td>
</tr>
<tr>
<td></td>
<td>1102</td>
<td>C–C bend</td>
</tr>
</tbody>
</table>

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Figure 2  (a) $^1$H-NMR spectra of $\alpha$-CD-NMP membrane; (b): $^1$H-NMR spectra of $\alpha$-CD-DMF membrane; (c): $^1$H-NMR spectra of $\alpha$-CD-DMAc membrane; (d): $^1$H-NMR spectra of $\alpha$-CD-DMSO membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
nanoporous polymers and polymer thin films, the interfacial regions are sufficiently close together that the percolation of the slow domains is restrained by these interfacial regions, and this causes the glass transition to occur at a lower temperature compared with that of the bulk polymer. For this reason, $T_g$ value decreases in case of CD membranes than that of pure polymer. The $T_g$ values for the composite membranes obtained from Figure 6 were plotted with respective pore diameter of the membranes which gives a linear relationship (Fig. 7) represented by following equation:

$$y = 58.021x - 42.243 \quad (4)$$

With a correlation co-efficient 0.97 which may be considered highly significant. The increase in $T_g$ value indicates thermal stability of composite membrane probably due to the formation of van der Waals bonds that exist inside the cavity of $\alpha$-CD and the H-bonding existing between residual –OH on $\alpha$-CD in the respective solvent.

Effect of casting solvents on the surface morphologies of $\alpha$-CD membranes

Membrane morphology for different $\alpha$-CD membranes was studied by SEM analysis and is shown in Figure 8(a) and (b). Figure 8(a) shows the SEM image of the top surface of NF membranes in different casting solvents. The reason for such type of surface morphology may be explained from the concept of quaternary phase diagram of membrane formation. A schematic phase diagram for ternary system is shown in Figure 9. The morphology and properties of the membrane are strongly dependent on the dope position, critical point position, and precipitation path. When precipitation path crosses the binodal curve, phase separation starts with nucleation and growth of the polymer-rich or polymer-lean phase. If the polymer concentration is low, the precipitation path crosses the equilibrium line below the critical point and nucleation of a polymer-rich phase initiates the phase separation process. When the polymer concentration is high, the mentioned

<table>
<thead>
<tr>
<th>Sample</th>
<th>20</th>
<th>$d$</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-CD</td>
<td>9.88</td>
<td>10.395</td>
<td>7.4</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>7.1</td>
<td>14.456</td>
<td>2.7</td>
</tr>
<tr>
<td>$\alpha$-CD-DMF membrane</td>
<td>8.3</td>
<td>10.653</td>
<td>3.1</td>
</tr>
<tr>
<td>$\alpha$-CD-DMAc membrane</td>
<td>9.88</td>
<td>8.952</td>
<td>3.3</td>
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<tr>
<td>$\alpha$-CD-DMSO membrane</td>
<td>7.4</td>
<td>11.946</td>
<td>2.3</td>
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<tr>
<td>$\alpha$-CD-NMP membrane</td>
<td>10.12</td>
<td>8.74</td>
<td>3.8</td>
</tr>
</tbody>
</table>
path passes through the bimodal curve above the critical point. In such cases, nucleation of the polymer-lean phase may occur. On the other hand at high polymer concentrations, the precipitation path bypasses the bimodal curve and phenomena such as vitrification, gelation, or crystallization may occur without polymer-lean phase growth. The time of phase separation initiation after immersion is very important to predict the morphology and separation properties of the membrane. If precipitation is initiated immediately after immersion, i.e., instantaneous demixing, the resulting membranes have a porous top layer and if precipitation begins after measurable time, i.e., delayed demixing, the membrane will be a dense skin layer.

In case of CD-NMP and CD-DMF membranes, precipitation is initiated immediately after immersion and the membranes have a porous top layer confirmed by SEM results. In case of CD-DMSO and CD-DMAc membranes, precipitation begins after measurable time (delayed demixing) and the membranes have dense skin layer as is evident from the SEM results.

The formation of the top surfaces is possibly due to demixing of the casting solution by means of nucleation and growth of the polymer-rich phase. Compared to the images of \(\alpha\)-CD-DMF, \(\alpha\)-CD-DMAc, and \(\alpha\)-CD-DMSO membranes, the SEM image of \(\alpha\)-CD-NMP membrane shows a more regular image of surface morphology. A more continuous morphology is observed in the surface of this membrane than other membranes. The variation of membrane morphologies observed in the four solvents may be due to the differences in the solvent volatility and the interaction between solvents and \(\alpha\)-CD. For rapid evaporation of volatile solvent DMF, it is reported that some grains are produced when the polymer is dissolved in more volatile solvents and can contain large free volume entrapped inside the grains, which cause the formation of large grains. Among the four solvents used in our study DMF is more volatile than other solvents. So \(\alpha\)-CD-DMF gives most irregular morphological structure than other membranes studied in this work. However, in case of DMSO, \(\alpha\)-CD is dissolved in DMSO at higher temperature; as a result the morphology of \(\alpha\)-CD-DMSO membranes is not regular.

In Figure 8(b), the cross-sectional SEM images of NF membranes in different casting solvents are shown. The CD layer is deposited onto the PS layer. It was noticeable that the cross-sectional SEM images, which exhibited a clear variation of CD layer thickness with the variation of casting solvent. Due to the high mutual affinity of the casting solvent for water, instantaneous demixing results, leading to the formation of dense top layer. The skin layer of asymmetric membrane is generated from a region with locally elevated polymer concentration. Volatile solvent in the casting dope can rapidly be driven off under-forced convection conditions and thus due to a selective loss of volatile solvent from the outermost surface of the membrane, the polymer-rich regions are forced to coalesce by capillary pressures. This phenomenon causes the polymer-rich phase to undergo rapid vitrification and hence an oriented membrane skin with few pores or defects will be formed.

The morphological change of four membranes is also correlated to the polymer–solvent interaction which can be explained by three types of interaction: polymer–polymer, solvent–solvent, and polymer–solvent interactions.
Figure 8  (a): SEM photograph of top surface of NF membrane, (b): cross-sectional SEM photograph of NF membrane.
Polymer–solvent interaction has been studied for four solvents used in this study. The relative strength of polymer–solvent interactions determines the properties of casting solvent and presumably the morphologies and properties of the final membranes.32 In a good solvent, the polymer is unfolded, obtaining to the maximum extent, the more favorable polymer–solvent interactions as reported by Guan et al.21

Affinity of solvents to polymers can be estimated by introducing the “solubility parameter” \( \delta \), which is defined as the square root of the cohesive energy density and described the strength of attractive force between molecules. Polymer–solvent interaction in polymer solutions has been evaluated on the basis of the difference between solubility parameters of polymer and solvents, Hansen took the dispersive forces (\( \delta_d \)), permanent dipole–dipole interaction (\( \delta_p \)), and hydrogen bonding forces (\( \delta_H \)) into consideration.21 Thus \( \delta \) is expressed as

\[
\Delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2
\]

The difference in Hansen solubility parameters between solvent and polymer can be calculated by

\[
\Delta = \left[ (\delta_{p1,d} - \delta_{s,d})^2 + (\delta_{p1,p} - \delta_{s,p})^2 + (\delta_{p1,H} - \delta_{s,H})^2 \right]^{1/2}
\]

Where \( P1 \) and \( S \) represent polymer and solvent, respectively. \( d, p \) and \( H \) represent dispersive, polar, and hydrogen bonding components of Hansen solubility parameters, respectively. \( d, p, \) and \( h \) represents dispersive, polar, and hydrogen bonding components of Hansen solubility parameters, respectively. 

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \delta_d (\text{MPa})^{1/2} )</th>
<th>( \delta_p (\text{MPa})^{1/2} )</th>
<th>( \delta_h (\text{MPa})^{1/2} )</th>
<th>( \delta (\text{MPa})^{1/2} )</th>
<th>( \Delta )</th>
</tr>
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<td>24.93</td>
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<td>11.8</td>
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<td>DMSO</td>
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<td>16.4</td>
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<td>24.53</td>
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<tr>
<td>( \alpha )-CD</td>
<td>15.2</td>
<td>9.4</td>
<td>7.5</td>
<td>21.12</td>
<td>-</td>
</tr>
</tbody>
</table>

Effect of solvent hydrophobicity on water permeability of \( \alpha \)-CD membranes

Membrane performance depends on the hydrophobicity of the casting solvent. Solvent hydrophobicity value is the quantitative measure of solvent polarity which is the value of octanol–water partition co-efficient. The correlation of solvent polarity and water permeability of \( \alpha \)-CD membrane in different casting solvents is shown in Figure 10. From the figure, it is seen that rate of performance of the composite membranes depends on \( \log P \) value with a significance correlation of straight line.

Effect of casting solvent on the hydrophilicity of membranes

The hydrophilicity of the membrane can be evaluated from the values of water uptake and contact angle measurement, the values of which are given in Table I. The contact angle of a surface against water reflects its wettability which in turn related with the water uptake of membrane. When water wets the surface, i.e., a small contact angle and high water uptake
value, the surface has the ability to interact with water molecules (dipoles) and make the surface more hydrophilic. The contact angle has often been criticized as a surface characterization method of membranes since membrane surfaces usually have pores and they are rough. The surfaces of NF membranes have proven to be very smooth and practically without pores. Therefore, the contact angle measurements would reflect well the hydrophilicity of an NF membrane surface.\textsuperscript{33,34} In our case, DMSO is the most polar solvent; however, due to some other interactions of polymer composite and solvent; \(\alpha\)-CD-NMP is found to be more hydrophilic in nature.

CONCLUSION

NF membranes have been prepared using four different casting solvents, and the effect of casting solvents on morphologies and performance of the membranes have been studied by means of a series of characterization methods. IR studies of the pure polymer and NF membranes reveal that there are different transition peaks in the pure polymer and composite membranes. XRD study reveals that there are stronger hydrogen bonding interaction which occurred between \(\alpha\)-CD-NMP membrane compared to that of other membranes. Thermal decomposition of the pure polymer and composite membranes indicates different range of thermal degradation of each membrane which also indicates a four-step decomposition of the \(\alpha\)-CD-NMP membrane. SEM results of the membranes show that membrane morphology can be controlled by changing the casting solvent. The morphological change depends on the demixing behavior of the polymer and solvent volatility combined with polymer–solvent interactions which were measured by considering Hansen solubility parameter. Solvent hydrophobicity is another parameter which effects on the membrane performance in terms of water permeability. Membrane hydrophilicity depends on the value of water uptake and contact angle which is explained in the present study.

Financial support from DST-New Delhi, India, has been gratefully acknowledged. Authors gratefully acknowledge Dr. P. G. Rao, Director, NEIST, Jorhat, for his encouragement to carry out the work.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(W_{\text{wet}})</td>
<td>weight of membrane after hydration (mg)</td>
</tr>
<tr>
<td>(W_{\text{dry}})</td>
<td>weight of membrane before hydration (mg)</td>
</tr>
<tr>
<td>(h)</td>
<td>height reached by the liquid (mm)</td>
</tr>
<tr>
<td>(t)</td>
<td>time (s)</td>
</tr>
<tr>
<td>(R_{\text{H}})</td>
<td>mean hydrodynamic radius of pore (nm)</td>
</tr>
<tr>
<td>(v)</td>
<td>rate of liquid penetration (mm s(^{-1}))</td>
</tr>
<tr>
<td>(\eta)</td>
<td>viscosity of the liquid (PaS)</td>
</tr>
<tr>
<td>(\Delta P)</td>
<td>pressure difference (Pa)</td>
</tr>
<tr>
<td>(P)</td>
<td>applied pressure (Pa)</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>surface tension (dynes cm(^{-1}))</td>
</tr>
<tr>
<td>(\rho)</td>
<td>density (g cm(^{-3}))</td>
</tr>
<tr>
<td>(\theta)</td>
<td>contact angle (°)</td>
</tr>
<tr>
<td>(R_s)</td>
<td>mean static radius (mm)</td>
</tr>
<tr>
<td>(\theta_{\text{eq}})</td>
<td>equilibrium contact angle (°)</td>
</tr>
<tr>
<td>(r_m)</td>
<td>mean pore radius (nm)</td>
</tr>
<tr>
<td>(r_i)</td>
<td>radius of pores of different size (nm)</td>
</tr>
<tr>
<td>(n)</td>
<td>number of pores</td>
</tr>
<tr>
<td>(c)</td>
<td>surface porosity</td>
</tr>
<tr>
<td>(d_i)</td>
<td>pore diameter (nm)</td>
</tr>
<tr>
<td>(A)</td>
<td>area of the membrane (cm(^2))</td>
</tr>
<tr>
<td>(l)</td>
<td>thickness of the membrane (mm)</td>
</tr>
<tr>
<td>(J)</td>
<td>permeate flow rate (mmol L(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td>(T_g)</td>
<td>glass transition temperature (°C)</td>
</tr>
<tr>
<td>(d)</td>
<td>dispersive component</td>
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<tr>
<td>(h)</td>
<td>hydrogen bonding component</td>
</tr>
<tr>
<td>(F_{\text{STP}})</td>
<td>flow rate at standard (P_s) and temperature (T_s)</td>
</tr>
<tr>
<td>(\gamma_v)</td>
<td>volume of sample chamber on the outlet side</td>
</tr>
<tr>
<td>(T_s)</td>
<td>test temperature in Kelvin</td>
</tr>
<tr>
<td>(p_s)</td>
<td>pressure on the outlet side of sample</td>
</tr>
<tr>
<td>(T)</td>
<td>time</td>
</tr>
</tbody>
</table>

REFERENCES

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Separation of Acetic Acid from Dilute Aqueous Solution by Nanofiltration Membrane

Kundan Baruah, Swapnali Hazarika
Chemical Engineering Division, CSIR-North East Institute of Science and Technology, Jorhat 785 006, Assam, India
Correspondence to: S. Hazarika (E-mail: shrrljt@yahoo.com)

ABSTRACT: NF membranes have been prepared from α, β, γ-cyclodextrin (CD) composite with polysulfone and characterized by pore size, thickness, pure water permeability, contact angle measurement and membrane morphology study. The permeation performances of the prepared membranes have been tested for separation of acetic acid from dilute aqueous solution. Effect of concentration, pressure, flow rate on flux and rejection have been calculated and interpreted. Different permeation models have been tested for experimental values and validated by comparing the values with the experimental data. It has observed that in β-CD membranes 99% recovery of acetic acid from aqueous solution has been obtained and found to be the best membrane for separation of acetic acid from dilute solution. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 40537.

KEYWORDS: membranes; separation techniques; composites; films

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INTRODUCTION

Owing to their distinctive features such as low costs, low energy, and as a solution to long standing problems in chemical industries, membrane technologies have been widely applied in chemical and biochemical process stream separation, purification, recovery, seawater desalination, removal of heavy metals from waste effluents, purification of potable water, etc. Nanofiltration (NF), which emerged in the mid-1980s, is a pressure-driven process that represents the transition between ultrafiltration (UF) and reverse osmosis (RO). It has the advantage of low operating pressure compared to RO and higher molecular weight retentions compared to UF. For this reason, NF has been widely applied in many industrial fields such as solvent recovery from lube oil and vegetable oil filtrates in pharmaceutical industry and for solvent exchange in the chemical industry.

In Fine chemical industry, organic solvents are liberated with the industrial effluent. Most notably in the process stream of polyester industry and ethanol industry, low concentrated acetic acid is liberated with the process stream. Several methods are available to remove acetic acid from the process stream. Examples of such processes include distillation, extraction, neutralization, over-liming, vacuum evaporation, stream stripping, charcoal adsorption, ion exchange resin adsorption etc. Recently, membrane processes such as adsorptive membrane and membrane extraction have been used to remove acetic acid from the process stream. Processes like distillation, solvent extraction, adsorption etc. are high energy extensive process. As the distribution coefficient and solubility of acetic acid between the two phases (i.e., organic and aqueous system) is low, the amount of solvent required for extraction is very high and economically ineffective. Moreover, distribution coefficient will change due to ionization of acetic acid. Application of membrane technology for removal of acetic acid is an efficient process but still in its infancy. To the best of our knowledge, there are a few investigations on NF separation of acetic acid on downstream processing. However, transport and retention data for NF membranes in organic solvents are very limited in the literature and the mechanism of transport through NF membranes in organic solvent environment is not well understood. Previous studies have shown that nanofiltration (NF) is one of the effective technologies to remove organic compounds when the solute size are larger than the membrane pore size or organic compounds have ionizable functional groups causing electrostatic repulsion. However, these studies have typically considered relatively large compounds (e.g., M.W. > 150 g mol⁻¹) and/or relatively hydrophobic compounds (e.g., Logarithm of octanol-water partition coefficient > 2.0). Only a few studies have investigated the rejection of small uncharged organic compounds by NF membranes. A complete understanding of the transport of small organic compounds through NF membranes is a challenging issue, since solute transport depends on physico-chemical properties of the solvent, solute and membrane. Several recent studies have investigated the transport mechanism of organic solutes through NF membranes. These studies have shown that for organic compounds
the removal depends upon the solute size and shape, polarity or hydrophobicity, the membrane pore size, and charge. Thus, to save energy and improve the quality of product NF technique was introduced for recovery of acetic acid which is a new process in membrane separation and its application have been increasing rapidly in the last decade.

In this article, we report a comprehensive study on NF membrane through removal of acetic acid from dilute aqueous solution of acetic acid (≤3%). NF membranes were prepared indigenously from α, β, and γ-cyclodextrin composite with polysulfone and characterized. Selection of Cyclodextrin is based on unique characteristics of uniform macromolecular structure, molecular self assembling etc.15 Because of its ability to form host guest complexes with organic components having appropriate diameters and physical interactions, it can also be used for studying host guest chemistry.16,17

In the literature, different solvent, solute and membrane parameters influencing the transport model were experimentally identified and different models were developed.12–14,18–24 However, transport models for Nanofiltration system are limited for specific experimental data. Therefore further research and improvement of transport models are highly necessary. For our work, permeation results were analyzed through a suitable permeation model and the effects of solvent membrane parameters were identified.

MATERIALS AND METHODS

Polysulfone (average molecular weight 22,000, purity 99%) was obtained from Aldrich Chemical Company, USA in pellet form. Polyethylene glycol 1500 was supplied by G.S. Chemical testing Lab & Allied Industries, India. α, β, and γ-cyclodextrin hydrate (purity 99%) and lithium nitrate (99% extra pure) were supplied by Acros Organics, USA. N-methyl pyrrolidone (NMP, purity > 99.5%) was procured from Rankem, India. All reagents were used without any further purification.

Membrane Preparation

Flat sheet membranes were prepared by dissolving Polysulfone (PSf) in NMP as solvent at room temperature (28–32°C) with relative humidity about 78% and then mixed with definite amount of Polyethylene glycol (PEG-1500) used as additive, LiNO₃ as swelling gel, and α, β, γ-cyclodextrin separately to make the casting solution. Compositions and physical properties of the casting solution for preparation of membrane are given in Table I. The polymer solution was stirred for about 6 h at room temperature (28–30°C) using a magnetic stirrer until a homogeneous solution was achieved. Films were cast on a glass plate with a casting Knife maintaining the same temperature as in the solution and are exposed for about 5 min to ambient before immersion into a coagulation bath that contains ice-cooled water (maintained at about 6°C). Then the membranes were immersed into the coagulation bath and kept out from the glass plate after sometime. The prepared membrane sheets were washed under running water and kept in deionized water bath overnight. Then the sheets were dried at room temperature. Finally the membranes were characterized by using different analytical methods and kept ready for permeation experiments.

<p>| Table I. Composition and Physical Properties of the Composite NF Membranes |</p>
<table>
<thead>
<tr>
<th>% of membrane material</th>
<th>% of polysulfone</th>
<th>% of LiNO₃</th>
<th>% of PEG</th>
<th>% of NMP</th>
<th>Membrane thickness (μm)</th>
<th>Pore diameter (nm)</th>
<th>Surface porosity (%)</th>
<th>Pure water permeability (L·m⁻²·h⁻¹)</th>
<th>Water uptake (%)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha-CD</td>
<td>0.402</td>
<td>16.166</td>
<td>0.161</td>
<td>0.483</td>
<td>82.836</td>
<td>57.40</td>
<td>32.6</td>
<td>0.14</td>
<td>48 x 10⁻⁵</td>
<td>8.36</td>
</tr>
<tr>
<td>Beta-CD</td>
<td>0.378</td>
<td>11.344</td>
<td>0.196</td>
<td>1.134</td>
<td>86.946</td>
<td>12.30</td>
<td>38.4</td>
<td>0.37</td>
<td>43 x 10⁻⁵</td>
<td>6.29</td>
</tr>
<tr>
<td>Gamma-CD</td>
<td>1.022</td>
<td>15.337</td>
<td>0.306</td>
<td>1.533</td>
<td>84.355</td>
<td>64.80</td>
<td>59.1</td>
<td>0.52</td>
<td>39 x 10⁻⁵</td>
<td>4.98</td>
</tr>
</tbody>
</table>
obtained through SEM and TEM analysis. The cross-sectional morphology of the prepared membranes was obtained by applying compressed high-purity nitrogen gas to the membrane cell made of standard size, their distribution and density. Pure water permeability for membrane morphology such as pore shape, size, their distribution and density. Pure water permeability for membrane was measured in a membrane cell of standard size, their distribution and density. Pure water permeability for membrane morphology such as pore shape, size, their distribution and density. Pure water permeability for membrane were obtained.

The thicknesses of the prepared membranes were measured by a membrane thickness gauge made by Mitutoyo Corporation Japan. Membrane morphology was studied by a scanning electron microscope (SEM) (LEO 1400VP, UK) and Transmission Electron Microscope (TEM) (JEOL, Japan, JEM 2100) at an accelerating voltage of 200 kV, which directly provides the visual information of the membrane morphology such as pore shape, size, their distribution and density. Pure water permeability for all membranes was measured in a membrane cell of standard design. The membranes with effective area of 15 cm² were set in the test cell and the pure water permeability test was carried out by applying compressed high-purity nitrogen gas to the feed side. The quantity of water permeated through the membrane was measured as permeation rate (L m⁻² h⁻¹). Contact angles of the membranes were measured by bubble formation method applying Poiseuille’s equation which expresses the balance between viscous forces and capillary and hydrostatic forces (neglecting inertial effects) and reported in our previous communication. Qualitative information regarding surface and cross-sectional morphology of the prepared membranes was obtained through SEM and TEM analysis.

THEORETICAL BACKGROUND

Permeation Flux and Rejection

The separation performance of NF membranes depends on the operating conditions such as pressure, temperature, flow rate and concentration. For a batch experimental set up the permeation flux was calculated by the following equation,

\[ J = \frac{V}{A \Delta t} \]  

(3)

The percent rejection can be defined by,

\[ R_{\text{obs}} = 1 - \frac{C_p}{C_f} \]  

(4)

Permeation Model

In the nanofiltration systems, some studies support the use of pore flow model and some others support the solution diffusion model. The simplified version of both the models was given by Silva et al.

Pore-Flow Model. As reported by Silva et al., it is assumed that the stable pores to be present inside the membrane and the driving force across the membrane is the pressure. At constant temperature, we can write,

\[ -X_{i(m)} \nabla p \eta \sum_{k} \frac{\zeta_{i,k} X_{k(m)} N_i}{c_{i(m)} (\ell/\tau)} + \zeta_{i,m} \frac{N_i}{c_{i(m)} (\ell/\tau)} \]

(5)

If the pressure gradient contribution is more significant than the activity gradient to the transport then eq. (5) is simplified to

\[ -X_{i(m)} \nabla p \eta \sum_{k} \frac{\zeta_{i,k} X_{k(m)} N_i}{c_{i(m)} (\ell/\tau)} + \zeta_{i,m} \frac{N_i}{c_{i(m)} (\ell/\tau)} \]

(6)

When friction of acetic acid with the membrane is much higher than the friction between acetic acid and water then we can write,

\[ -X_{i(m)} \nabla p \eta \sum_{k} \frac{\zeta_{i,k} X_{k(m)} N_i}{c_{i(m)} (\ell/\tau)} + \zeta_{i,m} \frac{N_i}{c_{i(m)} (\ell/\tau)} \]

(7)

As the first term in the left side of eq. (7) is much lower than the second, thus the equation can be written as,

\[ N_i = -\frac{\zeta_{i,m} X_{i(m)} \beta_i \ell}{\eta} \nabla p \]

(8)

For small permeating species in relation to the pore size, the total volume flux is given by

\[ N_i = \frac{\beta_i \ell}{\eta} \nabla p \]

(9)

where \( \beta_i \) is the specific permeability which is depend on membrane structure. When membrane is composed of more or less cylindrical pores then, Hagen–Poiseuille equation will be obtained,

\[ N_i = -\frac{d_{\text{pore}}^2 \ell}{32 \eta \tau} \nabla p \]

(10)

If membrane consists of packed bed of particles, then Carman Kozeny equation will be obtained.
Solution Diffusion Model. Considering concentration gradient, it is assumed that each permeating molecule dissolves in the membrane phase and diffuses through the membrane. For this type of system, eq. (5) can be written as,

\[ \frac{d^2}{dx^2} \left( \frac{\varepsilon}{1 - \varepsilon} \right) \psi \theta \nabla \mathbf{p} = N_i \]  \tag{11}

Assuming that friction of species with the membrane is greater than the magnitude of the friction between species, then eq. (12) becomes,

\[ -X_i \left( \nabla \cdot \mathbf{p} \right) \psi_i = \sum_k \left( \psi_{i,k} \right) \frac{N_i \psi_{i,k} - N_k \psi_{i,k}}{c_{i,m}} + \psi_{i,m} \frac{N_i \psi_{i,m}}{c_{i,m}} \]  \tag{12}

Neglecting kinetic coupling and approximating the gradient of chemical potential, eq. (13) simplifies to

\[ N_i = -\frac{c_{i,m}}{x_{i,m}} \nabla x_{i,m} \]  \tag{14}

Integrating eq. (14) and applying proper boundary conditions as applied by Silva et al., we obtain

\[ N_i = \frac{p_{\text{molar}}}{x_i} \left( \frac{\gamma_1 \rho}{\gamma_{1,i}} x_i \exp \left( -\frac{\Delta p}{RT} \right) \right) \]  \tag{15}

RESULTS AND DISCUSSION

Characterization of Membrane

CD-membranes were characterized for pore size, porosity, surface morphology, and pure water permeability. Some physical properties such as membrane thickness, pore diameter, surface porosity and pure water permeability of membranes are shown in Table I. Figure 2 shows the SEM image of the cross section of α-CD, β-CD, and γ-CD membranes. It is seen from the figure that α-CD, β-CD, and γ-CD membranes have asymmetric structure consisting of a dense top layer and a porous sub layer. The sub layer seems to have finger-like cavities as well as macrovoid structure. This finger like cavity is due to instantaneous demixing of membrane material in the solvent. The SEM image of β-CD membrane shows a more regular image of surface morphology. A more continuous morphology is observed in the surface of this membrane than α-CD, and γ-CD membranes. The variation of membrane morphology for α-CD, β-CD, and γ-CD membranes is probably due to the difference in interaction between α-CD, β-CD, and γ-CD with the casting solvent. SEM image of top surface of the membranes are presented in Figure 3. The formation of the membrane top surface is probably a result of spinodal demixing because the diffusion processes during formation of the top layer are fast enough for the
polymer solution to become a highly unstable and cross the spinodal curve decomposition. This results in a top surface with much better interconnected pores, which is more prominent in β-CD membrane. Thus, much better interconnectivity of pores in the membranes is achieved due to spinodal decomposition.

In Figure 4, TEM pictures of CD membranes are shown. To investigate the similarities and differences among the three membranes qualitatively, image analysis is performed on representative TEM pictures of α-CD, β-CD, and γ-CD membranes. From the TEM pictures, it is seen that β-CD membranes contain more interstitial cavities than α-CD and γ-CD membranes. The interstitial cavities are interconnected in β-CD membranes, forming channels throughout the entire thickness of the membrane. This difference significantly reflected the difference in permeability of the membranes. Thus, creating interstitial mesopores in polymer nanocomposites is important to prepare highly permeable membranes while the aggregate structure has to be carefully designed.

Effect of Concentration of Acetic Acid
To study the effect of concentration of acetic acid on permeation process, experiments were carried out in the concentration range from 0.174 mol L\(^{-1}\) (1 wt%) to 1.223 mol L\(^{-1}\) (7 wt%). From Figure 5, it is seen that the permeation flux declined slowly before the concentration reached at 0.611 mol L\(^{-1}\) (3.5%). The steady permeation flux reached at 83.9 L m\(^{-2}\) h\(^{-1}\) for β-CD membrane at high concentration, indicating that CD-polysulfone composite NF membrane has the potential in commercial applications for recovery of acetic acid from dilute aqueous solution. Similarly, the rejection is high (over 99%) and is scarcely affected by the concentration of acetic acid as shown in the same figure.

Effect of Pressure
Operating pressure is an important factor which influences separation performance. Generally, high operating pressure results in high permeation flux. The relationship between operating pressure and separation performance for CD-polysulfone composite NF membrane is shown in Figure 6. The permeation flux at 1 bar is 84.5 L m\(^{-2}\) h\(^{-1}\) and it increases quickly with rising pressure and reaches 89.2 L m\(^{-2}\) h\(^{-1}\) at 5 bar. The phenomenon of flux increasing with pressure has been observed in other reports also: n-hexane flux increased with pressure as reported by Bhanushali, flux of n-heptane and xylene (mixture of isomers) with pressure as reported by Robinson et al., flux of benzene and toluene went up with pressure were reported in White’s study. This illustrates that pressure boost is an effective method for increasing permeation flux. But it is seen from Figure 6 that permeation flux is not in proportion to the operating pressure. In other words, the increasing rate of the permeation flux diminishes during a rise in pressure. This may result from compressing effect of the membrane, and observed in other membrane separation processes also. The average pore
size of the active separation layer of membrane diminishes at high pressure. This may delay the increase in the transport rate for components with an increase in pressure and can increase the rejection. Therefore, very high pressure is not necessary to get a high transport rate. Higher pressure needs a higher investment of equipment and results in higher operational costs. A suitable operating pressure for this membrane separation system is found to be 3.5 bar. Permeation flux at 3.5 bar is observed to be 88.8 L m⁻² h⁻¹ and slightly less than the permeation flux at 5 bar, which is large enough for commercial

Figure 4. TEM photograph of NF Membrane. Alpha CD, Beta CD, Gama CD.

Figure 5. Flux and Rejection as a function of concentration of acetic acid. Open symbol: Flux, Closed symbol: Rejection.

Figure 6. Flux and rejection as a function of operating pressure. Open symbol: rejection, closed symbol.
The viscosity of the solution at a low concentration, i.e., 2%, is very low. This means the boundary layer conditions are not very thick. The flux of the membrane depends on flow rate of the solution. The fluid velocity near to the membrane surface is very small. A boundary layer exists at the interface of membrane and fluid. Flow in this part of the boundary layer is laminar and the mass transfer coefficient of each component in boundary is small. Thus, the thickness of the boundary layer influences the transport rate of the components from the bulk of feedstock to the surface of the membrane and further affects the permeation rate through the membrane. The thickness of the boundary layer of the membrane is related to the viscosity and the flow pattern of the fluid. With increasing the viscosity of the solution, the thickness of the boundary layer increases, as viscosity is a function of temperature and the operating temperature is restricted by the process conditions and is fixed at a stable value. The flow rate of the solution is a variable in the operation process, a high flow rate brought an ideal turbulent flow with a favorable flow pattern to reduce the thickness of the boundary layer. A high flow rate increases the tangential and radial velocity of fluids. The strong disturbance of fluid can break down the boundary layer at a certain extent. Therefore, increasing the flow rate is an effective factor to raise permeation flux, especially for those solutions where viscosities are not very low.

The effect of flow rate of aqueous acetic acid solution on the separation performance of membrane is shown in Figure 7 within the rejection is also shown for three types of NF membrane. The change in flow has not influenced the rejection; however it has little impact on permeation flux, especially for those solutions where viscosities are not very low. The effect of concentration polarization can give the concentration. This phenomenon is called concentration polarization. The effect of concentration polarization can give the concentration of solution at the surface of the membrane. We have omitted the effect of friction of acetic acid with the porous membrane matrix, at constant temperature and the solution viscosity. In this case, the ratio of the net transmembrane pressure across the membrane is equal to the ratio of the product (P_r) to the pure water permeability (P_w). For pure water permeation, the net transmembrane pressure is considered to be the applied pressure (∇p). This concept can be applied for the Poiseuille flow within the membrane pores or Darcy’s law.

Effects of Operation Time
The expected useful lifetime of membranes is one of the critical questions which determine whether the membrane can be used commercially. Some kinds of polymer membranes have excellent separation performance, but they do not have a good solvent-resistant property, which can be typically found in the significantly decreased rejection after a long period of operation. Experiments were carried out to demonstrate membrane stability in acetic acid and tested long-term performance of the membranes over a period of 4 months. From Figure 8 it is seen that, the separation performance was kept at a high level after a long period of work. Permeation flux decreased from 84.5 L m⁻² h⁻¹ to a steady state of 83.5 L m⁻² h⁻¹. The slight decline of flux is due to membrane compaction at 3 months. The densification of the membrane under pressure reduced the flux through the membrane. Long-term operation has little influence on the rejection of acetic acid as shown in the same figure, which indicates that the solvent-resistant performance of β-CD NF membrane is good.

Effect of Concentration Polarization
In membrane filtration processes, some of the components in the solution are rejected by the membrane and accumulate near the membrane surface. Before reaching a steady state the convective flow of the components to the membrane surface is larger than that due to diffusion back-flow to the bulk solution. This phenomenon is called concentration polarization. The effect of concentration polarization can give the concentration of solution at the surface of the membrane. We have omitted the effect of friction of acetic acid with the porous membrane matrix, at constant temperature and the solution viscosity. In this case, the ratio of the net transmembrane pressure across the membrane is equal to the ratio of the product (P_r) to the pure water permeability (P_w). For pure water permeation, the net transmembrane pressure is considered to be the applied pressure (∇p). This concept can be applied for the Poiseuille flow within the membrane pores or Darcy’s law.

Figure 7. Flux and rejection as a function of flow rate. Open symbol: flux, closed symbol: rejection.

Figure 8. Effect of operation time on permeation flux and rejection (3.5 bar, temp:25°C, feedstock flowrate: 100 mL min⁻¹, concentration of acetic acid: 0.349 mol L⁻¹). Open symbol: flux, closed symbol: rejection.
for describing solute transport through the porous membrane matrix.\(^{39}\)

The actual trans membrane pressure is given by,

\[
\left[ \nabla p - \prod C_i \prod C_f \right], \quad (16)
\]

where \(\Pi C_i\) and \(\Pi C_f\) are the osmotic pressures at the entrance and exit of the membrane pores.

Now,

\[
\frac{P_w}{P_r} = \frac{(\nabla p - (\prod C_i + \prod C_f))}{\nabla p} \quad (17)
\]

Thus, the boundary layer concentration \(C_o\) which accounts for the reduction in product rate is 45 mol L\(^{-1}\), whereas the initial feed concentration is only 1.223 mol L\(^{-1}\). Since the surface concentration which is three orders of magnitude larger than bulk quantities are unreasonable and hence concentration polarization cannot explain in this case.

**Transport Model Fitting and Statistical Analysis**

Two described models mentioned in Permeation Model section have been used to analyze the flux data given in Figure 5. In the Pore Flow model the permeability term \(\frac{d_{\text{ave}}}{32g}\) given in eq. (10) has been determined by the physical properties of the membrane and this value is \(4.2 \times 10^{-15}\) m for acetic acid. The predicted values using both pore flow and solution diffusion models are shown in Figure 9. It is clear that pore flow model provides much better predictions for acetic acid system. However, in case of binary mixtures of the solvent solution diffusion model better predicts the solvent fluxes.\(^{29}\) Better predictions of solution diffusion model than pore flow model in binary solvent system is due to the degree of separation. In pore flow model, no solvent separation is expected while in solution diffusion model small solvent separation occurs through the permeate.\(^{40}\) Thus, transport of acetic acid through β-CD NF membrane follows the pore flow model and can be used for the design of separation device for separating acetic acid from aqueous solution.

**SUMMARY**

NF membranes are prepared from α, β, γ-cyclodextrin composite with polysulfone and characterized. The permeation performances of the prepared membranes were tested for recovery of acetic acid from dilute aqueous solution. Effect of concentration, pressure, flow rate on flux, and rejection are studied and optimum conditions were established. Suitable operating pressure for acetic acid recovery from dilute aqueous solution through polysulfone-composite β-CD membrane is 3.5 bar which is a suitable pressure range for commercial application. The rejection decreases when the feedstock flow rate goes up, which clearly indicates that the permeation flux increases due to the decrease in mass transfer resistance, as a result high flow rate was obtained. The activity of the membranes remains same up to 3 months. From the calculated and experimental values it was established that pore flow model is well fitted for separation of acetic acid from dilute aqueous solution.

**LIST OF SYMBOLS:**

- \(J\) \hspace{1cm} permeation flux (L m\(^{-2}\) h\(^{-1}\))
- \(R_{\text{obs}}\) \hspace{1cm} observed rejection
- \(c\) \hspace{1cm} molar concentration (mol L\(^{-1}\))
- \(d_{\text{pore}}\) \hspace{1cm} pore diameter (nm)
- \(d_{\text{particle}}\) \hspace{1cm} particle diameter (m)
- \(l\) \hspace{1cm} membrane thickness (nm)
- \(N_i\) \hspace{1cm} molar flux (mol m\(^{-2}\) s\(^{-1}\))
- \(N_v\) \hspace{1cm} total volume flux (m s\(^{-1}\))
- \(J\) \hspace{1cm} solvent flux (L m\(^{-2}\) h\(^{-1}\))
- \(\nabla p\) \hspace{1cm} applied pressure (bar)
- \(\Pi\) \hspace{1cm} osmotic pressure (bar)
- \(n\) \hspace{1cm} number of moles of acetic acid
- \(V\) \hspace{1cm} volume of permeate in time \(t\) (mL)
- \(m_{\text{molar}}\) \hspace{1cm} molar permeability (mol m\(^{-2}\) s\(^{-1}\))
- \(R\) \hspace{1cm} ideal gas constant (Pa m\(^{2}\) mol\(^{-1}\) K\(^{-1}\))
- \(t\) \hspace{1cm} time (s)
- \(T\) \hspace{1cm} temperature (K)
- \(w\) \hspace{1cm} mass fraction
- \(x\) \hspace{1cm} molar fraction
- \(A\) \hspace{1cm} membrane area (cm\(^2\))
- \(\Delta C\) \hspace{1cm} concentration variation in the corresponding aqueous solution at the time interval \(\Delta t\)
- \(C_f\) \hspace{1cm} concentration of the feed (mol L\(^{-1}\))
- \(C_p\) \hspace{1cm} concentration of the permeate side (mol L\(^{-1}\))
- \(\mu\) \hspace{1cm} chemical potential (J mol\(^{-1}\))
- \(\rho\) \hspace{1cm} density (kg m\(^{-3}\))
- \(\tau\) \hspace{1cm} tortuosity factor
- \(z\) \hspace{1cm} viscous flow characterization parameter
- \(\beta_o\) \hspace{1cm} membrane viscous flow characterization parameter
- \(\gamma\) \hspace{1cm} molar activity co-efficient
- \(\delta\) \hspace{1cm} Hilderbrand solubility parameter (MPa\(^{1/2}\))
- \(\varepsilon\) \hspace{1cm} porosity
- \(\chi\) \hspace{1cm} Flory–Huggins interaction parameter
- \(\zeta\) \hspace{1cm} friction coefficient (J s\(^{-1}\) m\(^{-2}\) mol\(^{-1}\))
- \(\eta\) \hspace{1cm} viscosity (Pa s\(^{-1}\))

![Figure 9. Comparison of experimental acetic acid flux data in β-CD membrane at pressure 2 bar (calculated values by solution diffusion and pore flow model).](image-url)
\[ \Pi C_o \] osmotic pressure at the entrance of the membrane pores

\[ \Pi C_i \] osmotic pressure at the exit of the membrane pores

Subscripts

\( f \) feed side
\( i, k \) species
\( m, (m) \) membrane

ACKNOWLEDGMENTS

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REFERENCES

Adsorption of Dilute Alcohols onto Cyclodextrin–Polysulfone Membrane: Experimental and Theoretical Analysis

Kundan Baruah,† Pradip Kr. Bhattacharyya,‡ and Swapnali Hazarika*,†

†Chemical Engineering Division, CSIR-North East Institute of Science and Technology, Jorhat 785 006, Assam, India
‡Department of Chemistry, Arya Vidyapeeth College, Guwahati 781016, Assam, India

ABSTRACT: The adsorptive separation of dilute alcohols onto polymeric membrane has been investigated in this work. The adsorption experiments have been performed in a stirred reactor using an indigenously developed membrane. Equilibrium adsorption isotherms and kinetics have also been investigated. The kinetic data experimentally obtained at different concentrations have been analyzed using pseudofirst-order, pseudo-second-order, and an intraparticle diffusion models. The experimental data satisfied the pseudo-second-order model well. Adsorption isotherms have been interpreted from Langmuir, Freundlich, and Temkin isotherms, and Langmuir isotherm exhibited a better fit to the experimental data. It has been observed that the adsorption depends on the different interactions occurring at the solid—liquid interface, i.e., hydrophobic, dipole—dipole, and hydrogen bonding which are interpreted by considering interaction energy between adsorbent and adsorbate using density functional theory and MP2. Physical properties of the adsorbent and quantitative structure—activity relationship properties of the adsorbate play an important role in the equilibrium of adsorption. The experimental value of heat of adsorption (ΔH°) has been determined from the van’t Hoff plot using equilibrium data at different temperatures.

1. INTRODUCTION

From chemical industries, organic solvents are liberated with industrial effluents and cause environmental problems. In industries such as polyester, ethanol, chemical, petrochemical, food, and pharmaceutical, low concentrated alcohols are liberated with the process effluent and there are several methods available to remove them from the process stream. Examples of such processes include distillation, extraction, neutralization, overliming, vacuum evaporation, stream stripping, and charcoal adsorption, etc.1,2 However, separation of the alcohols from the effluents encounters difficulties because of their presence in lower concentration. Polymeric membranes in the nanofiltration (NF) range can be used for separation of such solvents in low concentrations. The high internal surface areas of membranes can adsorb and desorb a wide variety of different compounds depending on the environmental uses. Nowadays, demands for polymeric adsorbents are increasing for some selective separations because of their functionality, surface area, and porosity, etc. The separation techniques based on adsorption, whether it is membrane adsorption or others, are the most promising separation methods due to their non-denaturing capability, high selectivity, energy efficiency, and cost effectiveness for bulk separation and purification of molecules in industries. Membrane based adsorptions are attractive due to their recycling characteristics, low toxicity, green process, high separations from very dilute aqueous solutions, and selectivity. Studies on adsorption of certain important molecules have been reported in the literature considering polymeric resins and membranes as the adsorbent.3–5 From our knowledge, there are a few studies that have been made on nanofiltration separation from dilute aqueous alcohol in a downstream processing study.6 In adsorption process, the molecules are accumulated in the external and internal surfaces of the adsorbent from the bulk solution due to various interactions such as hydrophobic, electrostatic attraction and hydrogen bonding.

We have been pursuing membrane research for separation of organics under ongoing research activities. In the present study, we have reported the recovery of alcohols from dilute aqueous solution of alcohols in the range of 1% to 3% using an adsorption process on membrane. NF membranes were prepared in our laboratory from β-cyclodextrin (β-CD) composite with polysulfone and characterized.7 We have selected the cyclodextrin as the membrane material for its unique characteristics of uniform macromolecular structure, molecular self-assembling, and so on. To know the role of interactions between adsorbent (membrane components) and adsorbate (alcohols) in adsorption process, we have performed density functional theory (DFT) and second-order Möller–Plesset (MP2) calculations. These methods are widely used to

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quantify interactions, and their success in this aspect is documented well in the literature. 8,9 Because of inclusion of electron correlation, MP2 method gives better interaction energies and is useful in understanding molecular interactions. Both methods are expensive in terms of computational time and extremely difficult to apply to large molecular systems. The choice of such methods is carried out according to interaction which is assumed to occur in the system. Earlier computational works comprise application of AM1 and PM3. 10 However, these two methods are not useful in determining interaction energies. Our prepared membranes contain cyclodextrin works comprise application of AM1 and PM3. 10 However, choice of such methods is carried out according to interaction Both methods are expensive in terms of computational time and is useful in understanding molecular interactions. Electron correlation, MP2 method gives better interaction energies and is useful in understanding molecular interactions. Our prepared membranes contain cyclodextrin works comprise application of AM1 and PM3. 10 However, choice of such methods is carried out according to interaction.

2. EXPERIMENTAL SECTION

2.1. Materials. Polysulphone (average molecular weight, Mw 22,000), purchased from Aldrich Chemical Co., St. Louis, MO, USA in pellet form, and polyethylene glycol 1500 supplied by G.S. Chemical Testing Lab & Allied Industries, New Delhi, India, were used as received. β-Cyclodextrin hydrate (purity 99%) and lithium nitrate (99% extra pure) were obtained from Renu Organics, Morris Plains, NJ, USA; N-methylypyrrolidone (purity > 99.5%) was supplied from Macer, Gurgaon, India and used as received. Deionized water obtained from a Milli-Q system was used throughout the whole experiment.

2.2. Preparation of Membrane and Characterization. Membranes were prepared and characterized by the methods reported in our previous publications. 7,11 Composition for membrane preparation and physical properties of the membranes are shown in Table 1.

Table 1. Composition and Physical Properties of CD-PS Membrane

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>% of membrane</th>
<th>% of polysulphone</th>
<th>% of LiNO3</th>
<th>% of PEG</th>
<th>% of NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-CD</td>
<td>0.378</td>
<td>11.344</td>
<td>0.196</td>
<td>1.134</td>
<td>86.946</td>
</tr>
</tbody>
</table>

2.3. Adsorption Kinetics. The adsorption study depended on time and was made by addition of 0.0185 g of adsorbent to 250 mL of the aqueous solution containing 0.741 mol·L⁻¹ methanol, 0.514 mol·L⁻¹ ethanol, and 0.328 mol·L⁻¹ of butanol in different conical flasks. Adsorption experiments were carried out using a shaker (Kuworth AG IRC-1-U) at 200 rpm and 298 K. Each experiment was continued for 2 h of time, and after each experiment, the adsorbents were removed by spatula and alcohol concentration was measured from the calibration curve drawn from the values of refractive index and concentration of alcohols. Refractive index of the samples was measured by a digital refractometer (Model RZ-02941-35, Cole Parmer). For calculating the equilibrium adsorption capacity of the adsorbent the mass balance equation was applied. The amount of alcohols adsorbed onto membranes was determined by following:

\[ q_t = \frac{(C_i - C_f)V}{w} \]  

where \( C_i \) is the initial concentration of alcohol (mmol·L⁻¹), \( C_f \) is the concentration of alcohol at time \( t \) (mmol·L⁻¹), \( q \) is the adsorption density at a definite time \( t \), \( V \) is the total volume of the reaction mixture (L), and \( w \) is the mass of adsorbent (g).

In order to study the kinetics of adsorption of alcohols onto the membrane, different kinetic models such as pseudo-first-order, 12 pseudo-second-order, 13 and intraparticle diffusion 14 models were used.

2.3.1. Pseudo-first-order Model. The pseudo-first-order model expresses the adsorption rate of an adsorbate from a liquid phase, is called the Lagergren rate equation, 12 and is represented as

\[ \frac{dq}{dt} = k_1(q_e - q_t) \]  

where \( q_e (\text{mg}·\text{g}^{-1}) \) is adsorption capacity at equilibrium, \( q_t (\text{mg}·\text{g}^{-1}) \) is adsorption capacity at \( t \), and \( k_1 \) (min⁻¹) is the rate constant. Integrating eq 2 at \( q = 0, t = 0 \), and \( q = q_e, t = t \) eq 2 becomes

\[ \log(q_e - q_t) = \log q_e - (k_1/2.303) \]  

The value of the adsorption rate constant \( (k_1) \) is determined from the plot of \( \log(q_e - q_t) \) vs \( t \).

2.3.2. Pseudo-second-order Model. This model was developed by Ho and McKay, 15 and the rate of adsorption is given as

\[ \left( \frac{dq}{dt} \right) = k_2(q_e - q_t)^2 \]  

where \( k_2 \) (g·mg⁻¹·min⁻¹) is the rate constant for the pseudo-second-order adsorption reaction and other symbols are the same as those given in eq 2. At boundary condition the second-order rate equation becomes

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} \]  

The value of \( q_e \) and \( k_2 \) can be evaluated from the linear plot of eq 5.

2.3.3. Intraparticle Diffusion Model. This model is called Weber’s diffusion model, 12 and, according to which, the adsorbate particle is transported to the adsorbent surface through several steps such as external surface diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface or it may be a combination of one or more steps. For a rapidly stirred batch process, the diffusive mass transfer is related to the apparent diffusion coefficient. If the adsorption rate is dependent on the rate of diffusion, then the process is diffusion-controlled. Weber’s diffusion model is expressed by

\[ q_t = k_{intra}t^{1/2} + C \]  

where \( q_e (\text{mg}·\text{g}^{-1}) \) is the concentration of adsorbate in the solid phase at time \( t \) (min), \( k_{intra} (\text{mg}·\text{g}^{-1}·\text{min}^{-1/2}) \) is the rate constant of intraparticle diffusion, and \( C \) is a constant. Plot of \( q_t \) vs \( t^{1/2} \) gives a straight line from where \( C \) and \( k_{intra} \) can be calculated. With an increasing value of \( C \), the boundary effect increases.

2.4. Equilibrium Study. For adsorption isotherms, experiments were carried out by taking a fixed amount of adsorbent (0.0185 g) in 250 mL of aqueous alcohol solutions at natural
pH with a concentration range of (0.247 to 0.865) mol·L⁻¹ for methanol, (0.171 to 0.6) mol·L⁻¹ for ethanol, and (0.109 to 0.382) mol·L⁻¹ for butanol in a thermostated shaker maintained at (30 ± 0.5) °C. The equilibrium time for adsorption isotherms was considered as 60 min which was confirmed from the kinetics study. The pH of the solution was in the range of pH (4 to 8) by using buffer reagents of appropriate dosages. After reaching equilibrium, the aqueous phase was analyzed by a refractometer. Here we used three different models, viz., Langmuir, Freundlich, and Temkin models, to study the equilibrium adsorption data.

2.4.1. Langmuir Isotherm. Langmuir adsorption isotherm gives a quantitative representation of a monolayer formation of adsorbate on the outer surface of the adsorbent until saturation. Also uniform energies of adsorption onto the adsorbent surface can be obtained by this model. The model equation is represented as

\[ q_e = \frac{q_m K_c C_e}{1 + K_c C_e} \]  

(7)

The adsorption parameters were determined by following linear equation

\[ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_c C_e} \]  

(8)

where \( q_e \) is the equilibrium concentration of the adsorbate (mmol·L⁻¹), \( q_m \) is the amount of alcohol adsorbed per gram of the adsorbent at equilibrium (mmol·g⁻¹), \( q_m \) is the maximum monolayer coverage capacity (mmol·g⁻¹), and \( K_c \) is the Langmuir isotherm constant (L·mg⁻¹).

The slope and intercept of \( 1/q_e \) vs \( 1/C_e \) plot gives the values of \( q_m \) and \( K_c \), respectively. The equilibrium parameter \( R_L \) is a dimensionless constant represented as the separation factor or equilibrium parameter and is given as

\[ R_L = \frac{1}{1 + K_c C_0} \]  

(9)

where \( C_0 \) is the initial concentration.

Here, \( R_L \) indicates the nature of the adsorption. When \( R_L > 1 \), the nature of the adsorption is unfavorable; if \( R_L = 1 \), it is linear; if \( 0 < R_L < 1 \), the nature of the adsorption is favorable; and when \( R_L = 0 \), the nature of the adsorption is irreversible.

2.4.2. Freundlich Isotherm. Freundlich adsorption isotherm is usually used to describe the adsorption characteristics onto the heterogeneous surface. The model equation is

\[ q_e = K_f C_e^{1/n} \]  

(10)

where \( K_f \) is the Freundlich isotherm constant (mmol·g⁻¹), \( n \) is the adsorption intensity, \( C_e \) is the equilibrium concentration of the adsorbate (mmol·L⁻¹), and \( q_e \) is the amount of alcohol adsorbed per gram of the adsorbent at equilibrium (mmol·g⁻¹).

From eq 10 we have

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

(11)

Here \( K_f \) is an approximate indicator of adsorption capacity and \( 1/n \) is a function of strength of adsorption.

The Freundlich model is suitable for highly heterogeneous surfaces and gives good representation of data for a restricted range of concentration only. When it is fitted for high and moderate concentrations, it gives a poor fit for adsorption data at low concentrations.

2.4.3. Temkin Isotherm. The Temkin isotherm model has been used for chemisorptions of the adsorbate onto the adsorbent assuming that the heat of adsorption for all of the molecules in the layer decreases linearly with the coverage due to the interactions between adsorbate and adsorbent. The equation is represented as

\[ q_e = \frac{RT}{b} \ln(K_T C_e) \]  

(12)

and in linear form

\[ q_e = B \ln K_T + B \ln C_e \]  

(13)

where \( B = RT/b \), \( b \) (mol·kJ⁻¹) is the Temkin isotherm constant, \( K_T \) (L·mg⁻¹) is the binding constant, \( q_e \) (mg·g⁻¹) is the solute concentration in solid phase, \( C_e \) (mg·L⁻¹) is the solute concentrations in liquid phase, \( T \) is temperature (K), and \( R \) ((8.314 × 10⁻³) kJ·mol⁻¹·K⁻¹) is the gas constant. The isotherm parameters, \( b \) and \( K_T \), can be calculated from the linear plot of \( q_e \) vs \( \ln C_e \) in eq 13 whose slope and intercept give the values of \( b \) and \( K_T \), respectively.

2.5. Determination of Enthalpies. Enthalpies of the adsorption process can be determined by using the van’t Hoff method. The equation is

\[ \Delta G^0 = -RT \ln K = -RT \ln(\Psi q/C_e) \]  

(14)

where \( \Delta G^0 \), \( R \), \( T \), and \( K \) are the standard free energy change of adsorption, the universal gas constant, temperature, and the equilibrium constant, respectively. When adsorption is limited to the linear region of the isotherm, i.e., at low concentration of solute, the equilibrium constant is related to the adsorption affinity \( (\Psi q/C_e) \). \( \Psi \) is the term for the activity coefficient of the solute in the two phases and activity of the unbound sites. When the solute concentration is low, \( \Psi \) remains constant.

The second thermodynamic relationship used in the van’t Hoff method is

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  

(15)

where \( \Delta H^0 \) is the standard enthalpy change and \( \Delta S^0 \) is the standard entropy change of adsorption. Combining the two eqs 14 and 15, the following equation is obtained

\[ \ln(q/C_e) = -\Delta H^0/RT + [\Delta S^0/R - \ln \Psi] \]  

(16)

Thus, a plot of \( \ln(q/C_e) \) vs \( 1/T \) should give a straight line with a slope of \( -\Delta H^0/R \), from which \( -\Delta H^0 \) can be calculated under the assumption that \( \Delta H^0 \), \( \Delta S^0 \), and \( \Psi \) are constant over the temperature range of study.

2.6. Computational Details. The gas phase geometrical minima of the species are optimized without any constraints using exchange-correlation functional with gradient corrected correlation provided by Lee, Yang, and Parr (B3LYP) with the 6-31++G(d,p) basis set. The interaction energy between alcohols and cyclodextrins, polysulphone were calculated using the supermolecular approach given as follows:

\[ \Delta E_{AB} = E_A - E_B - E_{AB} \]  

(17)

Additionally, to check the consistency in results, we repeatedly did the calculations at BHandH/6-31++G(d,p) and MP2/6-31++G(d,p) levels of theory. Interaction between the components mainly involves hydrogen bonding between the OH group of the alcohol and O sites in the membrane components. Therefore, we have used the density based functional BHandH; the efficiency of this functional to handle
hydrogen-bonded systems is well documented.\textsuperscript{20–22} MP2/6-311++G (d,p) calculations also give better interaction energies due to high electron correlations. We have considered this basis set to obtain the reliable properties for hydrogen-bonded systems as it is required to employ the same that possess sufficient diffuseness and angular flexibility. In all cases care was taken for basis set superposition error (BSSE) using counterpoise correction method. All calculations were performed in Gaussian 09.\textsuperscript{23}

3. RESULTS AND DISCUSSION

3.1. Kinetic Study. The kinetics of adsorption of the aqueous solution at a fixed initial concentration of alcohols

(0.741 mol\textperiodcentered L\textsuperscript{-1} methanol, 0.514 mol\textperiodcentered L\textsuperscript{-1} ethanol, and 0.328 mol\textperiodcentered L\textsuperscript{-1} butanol) at pH (pH = 6.03) on the membrane was performed to get an idea of the adsorption process and presented in Figure 1. The values of the pseudo-first-order adsorption rate constant $k_f$ are determined using eq 3 by plotting $\log(q_e - q_t)$ against $t$ for adsorption onto the membrane at 293 K for the first 35 min only (Figure 2).

When we plot $t/q_t$ vs $t$ from eq 5 to get the kinetic parameters of the pseudo-second-order model, the experimental data are fitted very well (Figure 3).

The values of $q_{exp}$ and $q_{cal}$ for the pseudo-first-order and pseudo-second-order models are tabulated in Table 2. The values of $q_{exp}$ and $q_{cal}$ calculated by using the pseudo-second-order model are close to each other, wherein the correlation coefficients are closer to unity for this model indicating that the adsorption process follows the pseudo-second-order kinetic model.

Figure 4 represents the plot of $q_t$ vs $t^{1/2}$, eq 6, for the adsorption of alcohols to get Weber–Morris kinetic parameters. The intraparticle diffusion curves give the linear fitting; however, they do not pass through the origin for all three alcohol systems which indicates that intraparticle diffusion is not the rate-controlling step for this adsorption process.

3.2. Adsorption Study. Adsorption isotherms measured for alcohols applying the Langmuir isotherm model are shown in Figure 5, wherein the trends of other alcohols are also the same. It shows that methanol has higher $q_e$ values than ethanol. Again, compared to butanol, ethanol has higher $q_e$ values at all aqueous residual concentrations. The observed effect of the adsorbate on CD membrane as adsorbent is noteworthy. In general, cyclodextrin provides high adsorption behavior for alcohols owing to their predominantly hydroxyl groups which may probably interact through hydrogen bonding. Polysulfone may also provide the hydrogen bonding with alcohol molecules via its S atom. This type of mechanism was also observed for adsorption of alcohols from aqueous solutions on membrane.\textsuperscript{24}

To optimize the adsorption system, it is highly essential to establish the most appropriate relationship for the equilibrium curves, and hence we interpreted the adsorption equilibria from Langmuir, Freundlich, and Temkin models.

The values of the calculated Langmuir parameters and corresponding correlation coefficients ($R^2$) are given in Table 3. From the table it is seen that $R_L$ values are greater than 0 but less than 1, indicating that Langmuir isotherm is favorable in this work.

The Freundlich isotherm model (eq 11) was examined by plotting ln $q_e$ vs ln $C_e$ and the calculated values of $R^2$ are shown in Table 3. The values of $1/n$ for observed alcohols are found to

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{Adsorption density as a function of time.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image2.png}
\caption{Pseudo-first-order plot.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image3.png}
\caption{Pseudo-second-order plot.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image4.png}
\caption{Adsorption density as a function of time.}
\end{figure}
be less than unity, indicating that the adsorption process is favorable.

The Temkin isotherm constants for alcohol adsorption onto the CD membrane obtained from the plots has also been given in Table 3. It is observed that the values of the correlation coefficients ($R^2$) are in the range of 0.974–0.991, signifying a satisfactory representation of the Temkin model.

Comparing the correlation coefficients ($R^2$) of the models, it is observed that Langmuir isotherm gives the most satisfactory representation for almost all experimental data, and it is observed that the calculated values of $q_m$ are close to experimental values while using Langmuir isotherm. The maximum monolayer coverage capacity ($q_m$) shows that the adsorption trend follows the order methanol > ethanol > butanol.

The adsorption process is affected by external physicochemical parameters such as pH, temperature, competing compounds in solution, the chemical structure of the adsorbent and adsorbate, the polarity of the adsorbent, the specific surface area, and the pore volume distribution, etc. It is also noted that surface area and pore radius depend linearly on adsorption capacity with pore radius $\leq$ 90 Å. In our adsorption process, the chemical nature of the adsorbents play a more important role than the physical structure. Cyclodextrin has torous-shaped cyclic oligosaccharides containing six or more glucose units.

Table 3. Isotherm Constants for Adsorption of Alcohols in Cyclodextrin Membrane

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$q_{e,exp}$ (mmol·g$^{-1}$)</th>
<th>$q_m$ (mmol·g$^{-1}$)</th>
<th>$K_L$ (g·mmol$^{-1}$)</th>
<th>$R^2$</th>
<th>$R_L$</th>
<th>$1/n$</th>
<th>$K_f$ (mmol·g$^{-1}$)</th>
<th>$R^2$</th>
<th>$B$</th>
<th>$K_T$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>2.108</td>
<td>2.36</td>
<td>12.46</td>
<td>0.997</td>
<td>0.084</td>
<td>0.215</td>
<td>2.33</td>
<td>0.965</td>
<td>0.387</td>
<td>366.12</td>
<td>0.978</td>
</tr>
<tr>
<td>ethanol</td>
<td>1.121</td>
<td>1.39</td>
<td>9.10</td>
<td>0.995</td>
<td>0.167</td>
<td>0.312</td>
<td>1.44</td>
<td>0.960</td>
<td>0.286</td>
<td>105.64</td>
<td>0.974</td>
</tr>
<tr>
<td>butanol</td>
<td>0.959</td>
<td>1.19</td>
<td>13.55</td>
<td>0.999</td>
<td>0.16</td>
<td>0.345</td>
<td>1.49</td>
<td>0.975</td>
<td>0.260</td>
<td>136.03</td>
<td>0.991</td>
</tr>
</tbody>
</table>

Figure 4. Intraparticle diffusion model plot.

Figure 5. Adsorption isotherm of methanol.

Figure 6. Adsorption of methanol as a function of pH.
which are connected by \( \alpha \)-1,4-glycosidic linkages. In cyclodextrins, glucose units are arranged in such a way that the hydroxyl methylene groups are pointing downward and hydroxyl groups are pointing upward, resulting in host–guest complexes with organic components. Hence, a high affinity for all of the adsorbate molecules on cyclodextrin membrane may be due to the hydrophilic nature of hydroxyl groups in alcohols and can be reduced by increasing the number of -CH\(_2\)- groups which are hydrophobic in nature.

The effect of pH on adsorption is shown in Figure 6. It is seen from the figure that the variation is marginal only. Higher adsorption at acidic pH may be due to the polar–polar interactions between alcohols and cyclodextrin molecule. The adsorption was found to be a maximum at pH 4 for hydrogen bonding. At higher pH, the hydrogen interactions decrease and dissociate to form H\(^+\) and their corresponding anions.

Figure 7 and Figure 8 show the SEM photographs of the CD membrane before and after adsorption. From Figure 7 (before
adsorption), it is observed that the membrane has a porous structure throughout and has a rough surface. The higher degree of roughness is attributed to more adsorption capacity.

3.3. Adsorption Enthalpy. Temperature dependence of adsorption equilibria was determined by measuring the adsorption at three different temperatures, viz., (25, 30, and 35) °C and at constant pH 6.03. The adsorption isotherms of alcohols onto the CD membrane at three different temperatures have been shown in Figure 9 to Figure 11, and it is seen that the adsorption intensity increases with a decrease in temperature, indicating an exothermic adsorption process.

The temperature dependent adsorption affinity (q/Ce) was evident from the slopes of isotherms which were interpreted from the van’t Hoff equation given by eq 16. Figure 12 to Figure 14 show van’t Hoff plots and estimate the values of ΔH° which are found to be −15.13 kcal·mol⁻¹ (R² = 0.996), −14.02 kcal·mol⁻¹ (R² = 0.999), and −12.61 kcal·mol⁻¹ (R² = 0.99) for methanol, ethanol, and butanol, respectively. As we know, the adsorption enthalpy determines the strength of solute–sorbent binding interaction which significantly affects the adsorption affinity. Thus, the adsorbate which shows the highest affinity gives the highest adsorption enthalpy and the adsorbate having the lowest affinity gives the lowest adsorption enthalpy.

3.4. Adsorptive Interaction. Calculated BSSE corrected interaction energies²⁶,²⁷ between membrane components and solvent molecules (methanol, ethanol, and butanol) at three different levels of theory, B3LYP/6-31++G(d,p), MP2/6-31+ +G(d,p), and BHandH/6-31++G(d,p) are presented in Table 4.

To assign the electronegative sites in polysulfone and CD, initially we performed Hirshfeld population²⁸,²⁹ analyses and estimated charges at different sites. In glucopyranose unit, atom number O-16 (Figure 15) bears more negative charges (−0.185 au) whereas, in the polysulfone unit, atom number O-54 possesses a more negative charge (−0.323 au) compared to other positions. This reflects interaction in which these positions exhibit more affinity toward the -OH groups in alcohols. We have considered the total interaction energy between alcohols CD and PS and observed their trends. In all of the three levels of theory, the trend of total interaction energy is in the order methanol > ethanol > butanol, a trend which is also observed in the case of experimental adsorption affinity values. A higher value of interaction energy leads to stronger adsorption,³⁰ and it plays the key role on adsorption. Thus, interaction energy is an index of the strength of adsorptive interaction on the adsorbent surface. However,
membrane material and pore size can be affected in the adsorption of solvents.

Quantitative structure activity relationship (QSAR) analysis of the three alcohols has also been done. Different values such as log \( P \), dipole moment, electron affinity, ionization potential, and molar refractivity are evaluated using Scigress software version 2.4 and plotted with adsorptive affinity values (Figure 16). From the figure it is seen that they follow a linear relationship with the following equations.

\[
y = -1.319x + 1.388, \quad R^2 = 0.953 \quad (\text{log } P \text{ vs } q_e) \quad (18)
\]

\[
y = 6.839x - 10.44, \quad R^2 = 0.983 \quad (\text{dipole moment vs } q_e) \quad (19)
\]

\[
y = 6.568x + 7.371, \quad R^2 = 0.971 \quad (\text{electron affinity vs } q_e) \quad (20)
\]

\[
y = -19.44x - 114.1, \quad R^2 = 0.988 \quad (\text{ionization potential vs } q_e) \quad (21)
\]

\[
y = -0.102x + 2.767, \quad R^2 = 0.963 \quad (\text{molar refractivity vs } q_e) \quad (22)
\]
3.5. Correlation of Adsorptive Affinity with Interaction Energy. The adsorptive interaction energies between adsorbate and adsorbent, $\Delta E$, were correlated with adsorption affinity (Figure 17). The figure indicates the relationship between adsorptive affinity and adsorptive interaction for all three tested alcohols in this work. Thus, adsorption equilibrium is a function of solute–sorbent binding interaction. This observation is similar to some other adsorption processes reported elsewhere.

3.6. Correlation of Adsorptive Enthalpy with Interaction Energy. A plot of adsorption enthalpies ($\Delta H^0$) of the three alcohols against interaction energies ($\Delta E$) gives a linear relationship (Figure 18), indicating the dependency of enthalpies of adsorption on adsorptive interaction energy. The enthalpy determines the strength of the solute–sorbent binding interaction, and thus solute–sorbent binding interaction significantly affects the adsorption affinity of the process which may be considered as an enthalpic process.

4. CONCLUSION

The adsorption of alcohols onto the membranes was studied for adsorption of alcohols from dilute aqueous solution. It was observed that the adsorption process was affected by parameters such as pH, the initial concentration of the alcohol, and temperature. The kinetics and adsorption isotherms were investigated, and the adsorption behavior of the systems was best fitted with the Langmuir isotherm. The kinetics of adsorption followed the pseudo-second-order reaction, where the adsorption rate is proportional to the concentration of adsorbate and the remaining number of vacant sites of adsorbent. The adsorptive affinity follows the order methanol > ethanol > butanol onto the $\beta$-CD membrane. The adsorption intensity is weakly dependent on the aqueous phase pH. Adsorptive interaction is strongly related to the interaction energy between adsorbent and adsorbate.

ASSOCIATED CONTENT

Supporting Information

Figures showing adsorption isotherms of ethanol and butanol, adsorption of ethanol and butanol as a function pH, and typical van’t Hoff plots for adsorption of 0.171 mol·L$^{-1}$ ethanol and 0.109 mol·L$^{-1}$ butanol. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/je501032v.

AUTHOR INFORMATION

Corresponding Author

*E-mail: shrrljt@yahoo.com.

Notes

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QM/MM Studies on Cyclodextrin-Alcohol Interaction

Kundan Baruah\textsuperscript{a}, Sourab Sinha\textsuperscript{a}, Swapnali Hazarika\textsuperscript{b} & Pradip Kr. Bhattacharyya\textsuperscript{a}
\textsuperscript{a} Department of Chemistry, Arya Vidyapeeth College, Guwahati-781016, Assam, India
\textsuperscript{b} Chemical Engineering Division, CSIR-North East Institute of Science and Technology, Jorhat-785006, Assam, India
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QM/MM Studies on Cyclodextrin-Alcohol Interaction

KUNDAN BARUAH\textsuperscript{1}, SOURAB SINHA\textsuperscript{1}, SWAPNALI HAZARIKA\textsuperscript{2},
and PRADIP KR. BHATTACHARYYA\textsuperscript{1,*}

\textsuperscript{1}Department of Chemistry, Arya Vidyapeeth College, Guwahati-781016, Assam, India
\textsuperscript{2}Chemical Engineering Division, CSIR-North East Institute of Science and Technology, Jorhat-785006, Assam, India

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The main objective of this study is to provide an insight into the interactions involved during adsorption of the alcohols on \( \beta \)-CD composite nanostructured membrane. Interactions between \( \beta \)-cyclodextrin (\( \beta \)-CD) and alcohols (methanol, ethanol and butanol) are studied using the QM/MM method. Magnitude of interaction energies show that the alcohols are adsorbed on the membrane. In addition, the thermochemical analysis suggests that the formation of these host-guest complexes is enthalpy driven.

\textbf{Keywords:} Cyclodextrin, membrane, QM/MM, host-guest interaction, interaction energy

\textbf{1 Introduction}

Cyclodextrins (CDs) are cyclic oligomers of \( \alpha \)-D-glucose units that consist of six or more glucose rings connected via \( \alpha \)-1,4-glycosidic bond. In all cyclodextrins, the glucose units are arranged in such a way that the hydroxymethylene groups are pointing downwards, whereas the hydroxyl groups are pointing upwards. As a result, a hydrophilic outer space and a hydrophobic inner space (Fig. 1) are formed leading to the particular ability of the \( \beta \)-CD to form host–guest complexes with organic components having appropriate diameters and physical interactions (1, 2). Apart from that it has a remarkable capacity to form inclusion complexes in solution or, in the solid state with organic molecules through host-guest interactions (1) with unique self-assembling behavior. Taking into account of the host-guest interaction in \( \beta \)-CD, it has found widespread applicability in membrane science (3). As a novel molecule, it is used to prepare membrane (4). \( \beta \)-CD membranes are used in extraction techniques and CDs are very attractive components for the enhancement of the selectivity for a specific membrane polymer towards aromatic components. Different aspects of CD chemistry are documented well in the earlier literatures (3). Earlier we used cyclodextrin for preparation of nanofiltration membranes for its specific properties and found that it provides good membrane membrane morphology (4). Apart from pore size, interaction between the membrane material and the substrate play an important role in the adsorption process. Strong interactions (hydrogen bonding or electrostatic) between adsorbent and adsorbate allow the rate of adsorption of alcohols whereas repulsive interactions do not allow the adsorption on the membrane. Thus understanding the interaction between adsorbent and adsorbate becomes utmost important for designing of new adsorbent.

Quantum mechanical methods such as density functional theory are quite useful in understanding the both type of interactions (hydrogen bonding and electrostatic). Even though \( \beta \)-CD drew the attention of many researchers, due to its large size, only a few computational studies have been reported (5–8). Recently, Stachowicz et al. have made DFT studies on cation binding of \( \beta \)-CD (9). A number of theoretical methods are used in molecular modeling for supermolecular systems such as the complexes of CDs or their derivatives with guest molecules (10–22). Among these methods, molecular mechanics (MM) (10, 11), molecular dynamics (MD) (12–15), semi-empirical methods (such as AM1, PM3 etc.) (16–22) and a hybrid Own N-layer Integrated Orbital Molecular Mechanics (ONIOM) methods (23–32) have been widely used for relatively larger sized CDs and their derivatives. Out of these frequently used methods, a hybrid ONIOM method, developed by Morokuma et al. (21–23), has been used widely as it can treat different parts of a system simultaneously with good accuracy and lower computational cost compared to ab-initio and DFT, and it has proven to be effective and reliable for investigating inclusion interaction of CDs or their derivatives with guests molecules (27–30). MM methods based on classical empirical potentials have been proven to provide an effective mean for simulating...
complex molecules. Alternatively, description of classical reactions (i.e., bond-forming and bond-breaking) and other processes that involve changes in the electronic structure, such as charge transfer or electronic excitation, transition state etc. require QM methods. However, due to high computational cost, QM methods have limitations in the case of larger systems. Therefore, it is suitable to use a QM method for the chemically active region and combine it with an MM treatment for the surroundings. By doing this, we can treat a large system into a QM region and a MM region, such that only a part of the system can be analyzed by the QM methods, but still retains the effects of the surrounding environment.

In this article, we have aimed to give an insight into the extent of interaction between $\beta$-CD and alcohols during adsorption of the alcohols on CD membrane. Our emphasis is to interpret interaction of the alcohols with different centers in CD. Sakurai et al. used CNDO method to CD chemistry (33). Lei Liu et al. applied AM1 and PM3 methods to study the structures of CD complexes (34). However, these methods are not useful in estimating the interaction energies. To gain a better understanding on the role of interactions between adsorbate and adsorbent, we have carried out QM/MM methods (35). These methods are widely used to quantify interactions in large systems and their success in this aspect is well documented (36).

2 Computational Details

The gas phase geometrical minima of the species are optimized using the (QM/MM) method. We considered the alcohol and two glucose units in the QM region and applied a polarized triple zeta basis set with diffused and polarized functions, 6-311++G(d,p) with Becke three parameter exchange and Lee, Yang and Parr correlation functional, B3LYP (37, 38) in this region, the rest of the glucose units are considered in the MM region and we used MM force field (PM3) in this region. To check the consistency in results, we repeated our calculation at BHandH/6-311++G(d,p):PM3 level of theory. Choice of the basis set is based on the consideration that in order to obtain reliable properties for hydrogen bonded systems, it is essential to employ basis sets that possess sufficient diffuseness and angular flexibility. Vibrational frequency analysis was performed in all cases to ensure that the species possess no imaginary frequency. Interaction energies are calculated between three alcohols viz. methanol, ethanol, butanol and cyclodextrin using supermolecular approach, (for a process $A + B \rightarrow AB$, interaction energy is defined as, $\Delta E_{int} = E_{AB} - E_A - E_B$, where, $E_A$, $E_B$ and $E_{AB}$ are the energies of the corresponding species), (39). To observe the thermodynamic driving force, we calculated enthalpy of adducts formation ($\Delta H_{AB} = H_{AB} - H_A - H_B$). All calculations are performed in Gaussian09 (40).

3 Results and Discussion

Hydrogen bonding interactions have generated substantial interest given its relevance in the field of chemistry and biology (41). In surface chemistry, interaction between the membrane material as adsorbent and alcohol as adsorbate are important. $\beta$-CD is the most important component of our earlier prepared membrane (4) and it is expected that as the alcohol molecules get adsorbed on the membrane, hydrogen bonds can be formed between the two components, alcohols and $\beta$-CD and this interactions might influence the adsorption process.

The oxygen atoms in cyclodextrin molecule provide space for interactions as can be seen from electron density isosurface (Fig. 2). The red color indicates the negatively

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Fig. 1. Cyclodextrin-alcohol H-bonding interaction.

Fig. 2. Cyclodextrin-alcohol H-bonding interaction.

Fig. 2. Electron density isosurfaces of cyclodextrin.
charged region which is available for interaction in the cyclodextrin molecule forming a host-guest complex. This structural feature make CD molecule very useful for adsorption. The interaction mostly involves hydrogen bonding between O centers in cyclodextrin and OH group of the alcohol and between OH groups in cyclodextrin and O sites of alcohol. Consequently, we have calculated interaction energy between cyclodextrin and alcohol molecules using super molecular approach. Enthalpy involved during interactions are also calculated. The optimized structures along with some important parameters (bond lengths between O-CD and OH group of alcohol, bond lengths between H-CD and O of OH group of alcohol, O-H-O bond angles) are presented in Figure 3 and gas phase interaction energy and enthalpies are presented in Table 1.

We observed that the bond length between O-1 of β-CD with H (in OH group) of methanol, ethanol, and butanol are 1.80 Å, 1.82 Å, 1.83 Å, respectively. In O-2, O-3 and O-4 positions, these values are 1.82 Å, 1.82 Å, 1.83 Å (in O-2 position), 2.06 Å, 2.07 Å, 2.07 Å (in O-3 position) and 2.02 Å, 2.02 Å, 1.98 Å (in O-4 position), respectively. On the other hand, when we considered the hydrogen bonding between O-atom of OH group (indicated by O-5 in Fig. 3) of alcohol with H atom of OH group of β-CD (attached to O-1 position), the observed bond length is 1.87 Å in methanol and 1.88 Å in ethanol and butanol. Shorter bond lengths in the case of O-1, O-2 and O-5 interactions indicate a stronger interaction compared to O-3 or O-4 position and interaction energy values provided in Table 1 also reflected the fact. The O-H-O bond angles in the case of O-1, O-5 and O-2 interactions are observed to be ~165°, ~164° and ~162°, respectively. However, in the case of O-3 interactions, these values are ~149° and with O-4 centers these values are in the range 152°–156°. Structural parameters play important role in strength of a hydrogen bonding and thus are important (42). Usually, it is a general observation that a shorter O-H bond lengths and higher O-H-O (close to 180°) facilitate a stronger hydrogen bonding. Our results agreed with this fact and we observed stronger hydrogen bonding (higher interaction energy) in the case of O-1, O-5 and O-2 interactions where the O-H bond lengths are comparatively shorter and O-H-O bond angles are larger (Fig. 3, Table 1).

Interaction energies at different O-centers reveal that the interactions are not very strong. At B3LYP/6-311++G(d,p):PM3 level of theory, interaction energies are observed to be ~−10 kcal/mol. The order of interaction energy at the four O-centers at both the two levels of theory is observed to be O-1>O-2>O-3>O-4. Steric factor is observed to play a major role on the interactions; O-3 and O-4 positions are sterically hindered and we observe lower interaction energies compared to O-1 and O-2. At BHandH/6-311++G(d,p):PM3 level of theory observed values of interaction energies are comparatively higher. These values of interaction energies are important; a
Table 1. Gas phase interaction energy and enthalpy (in kcal/mol) at two different levels of theories

<table>
<thead>
<tr>
<th>Adducts</th>
<th>( \Delta E_{\text{int}} ) (B3LYP/6-311++G(d,p):PM3)</th>
<th>( \Delta E_{\text{int}} ) (BHandH/6-311++G(d,p):PM)</th>
<th>( \Delta H ) (B3LYP/6-311++G(d,p):PM3)</th>
<th>( \Delta H ) (BHandH/6-311++G(d,p):PM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )-CD-1m</td>
<td>-9.74</td>
<td>-33.86</td>
<td>-4.15</td>
<td>-26.35</td>
</tr>
<tr>
<td>( \beta )-CD-2m</td>
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<td>-10.27</td>
<td>-3.90</td>
<td>-8.74</td>
</tr>
<tr>
<td>( \beta )-CD-3m</td>
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<td>-9.86</td>
<td>-3.77</td>
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</tr>
<tr>
<td>( \beta )-CD-4m</td>
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<td>-8.98</td>
<td>-3.00</td>
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</tr>
<tr>
<td>( \beta )-CD-5m</td>
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<td>-4.10</td>
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</tr>
<tr>
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<td>-8.40</td>
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<tr>
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<td>-3.57</td>
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<td>-25.16</td>
<td>-2.86</td>
<td>-9.32</td>
</tr>
</tbody>
</table>

stronger interaction favors adsorption, moreover a repulsive interaction also make it difficult to adsorb the molecule on the membrane. The interaction energy calculated at O-5 center of alcohol is found to be in between O-1 and O-2 centers. Thus, interaction energy implies that the \( \beta \)-CD component of the membrane allows the alcohol components to adsorb. Interestingly, the enthalpy gain during the interactions is exothermic, indicating presence of thermodynamic driving force in the formation of the host-guest complexes. Trend in case of enthalpy is observed to be similar to that of interaction energy.

We also examined the relationship between the charge density at the O-centers and interaction energies. We performed Hirshfeld population analysis to estimate charges at different sites. The charge density at O-1, O-2, O-3, and O-4 centers are observed to be -0.177 a.u., -0.166 a.u., -0.148 a.u. and -0.128 a.u., respectively. This reflects that these positions will exhibit more affinity towards the –OH groups in alcohols. Interaction energy is found to be more in O-1 and O-2 positions in all three CD-alcohol systems. The presence of +I (electron donating group) alkyl groups decrease the electronegativity of ethereal type oxygen in O-3 and O-4 position. Hence, the hydrogen bonds with these positions are considerably weaker and therefore the magnitude of interactions are less compared to that in O-1 and O-2 positions. Again, compared to O-4 position, interaction energy is found to be more in O-3 position. The O-3 center is exposed more due to fluxional of the glucopyranose ring and so, interaction is stronger. On the other hand, O-4 center is rigid. A similar trend is found in the case of enthalpy. It is also observed that the possibility of interaction from the inside of CD is very difficult because of steric hindrance and hydrophobicity.

4 Conclusions

Our study reveals formation of hydrogen bonding between the CD and alcohols. An intermediate value of interaction energy indicates that the rate of adsorption is governed by the host-guest interaction. Interaction energy is calculated to be higher at O-1 and O-2 centers of the CD and at O-5 center of alcohol. In addition, the thermochemical analysis suggests that the formations of these inclusion complexes are enthalpy driven. The overall theoretical results suggest that hydrogen bonding plays an important role in the adsorption on membrane.

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Effect of external electric field on Cyclodextrin-Alcohol adducts: A DFT study

KUNDAN BARUAH and PRADIP KR BHATTACHARYYA*
Department of Chemistry, Arya Vidyapeeth College, Guwahati 781 016, Assam, India
e-mail: prdpbhatt@yahoo.com

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Abstract. Effect of external electric fields on the interaction energy between cyclodextrin and alcohol was analyzed in the light of density functional theory (DFT) and density functional reactivity theory (DFRT). Stability of the cyclodextrin-alcohol adducts was measured in terms of DFT based reactivity descriptor, global hardness, electrophilicity, and energy of the HOMO. Stability of adducts was observed to be sensitive towards the strength as well as direction of the applied external electric field. In addition, reactivity pattern follows the maximum hardness and minimum electrophilicity principles.

Keywords. Membrane; electric field; DFT; reactivity descriptor; MHP.

1. Introduction

Cyclodextrins (CDs) are natural biomolecules which are derived from starch and have a remarkable capacity to form inclusion complexes in solution or in the solid state with organic molecules through host-guest interactions with unique self assembling behaviour.1 The glucose units in CDs are arranged in such a way that hydroxymethylene groups are pointing downwards, whereas hydroxyl groups are pointing upwards. As a result of this, a hydrophilic outer space and a hydrophobic inner space are formed leading to the particular ability of the CDs to form host-guest complexes with organic components having appropriate diameters and physical interactions.

Combination of host-guest complex formation ability and structural features of CDs make them as novel polymer for membrane preparations, which are used extensively in separation science offering a good choice for separation of compounds and extraction processes.2 CDs are very attractive components for the enhancement of the selectivity for a specific membrane polymer towards aromatic/aliphatic components.3 During filtration process, interaction between the membrane components and substrates is important. Usually, stronger adsorption of the substrate slows down the filtration process. Strong interactions (hydrogen bonding or electrostatic) between adsorbent and adsorbate allow the rate of adsorption of alcohols whereas repulsive interactions do not allow the adsorption on the membrane.

Accordingly, apart from the pore size, interaction between membrane material and substrate plays an important role in adsorption processes. Understanding the interaction between adsorbent and adsorbate becomes an important factor for designing new adsorbents. Quantum mechanical methods such as Hartree-Fock or density functional theory (DFT) are quite useful in understanding the interactions in molecular systems (hydrogen bonding and electrostatic in the present case). Even though β-CD drew the attention of many researchers, because of computational cost only a few computational studies have been reported so far.4–16 Different methods are used to understand the host-guest interactions in larger systems like complexes of CDs or their derivatives.7–15 Recently we have studied CD-alcohol interactions using QM-MM method.16 An intermediate value of interaction energy indicates that the rate of adsorption of alcohols on CD membrane is governed by the host-guest interaction.16

In recent years, density functional theory (DFT) has proved its applicability to interpret chemical reactivity in complex phenomenon.17 Moreover, density functional reactivity theory (DFRT) is used to estimate reactivity parameters. The reactivity descriptors, defined within the framework of DFT are global hardness, global electrophilicity, chemical potential, local softness, Fukui functions, etc.18 These descriptors have been tested and studied by several research groups and are found to be very useful in explaining the reactivity patterns in the molecular systems.19–21

Recently, a number of theoretical studies have been made to understand the effects of external electric
field on absorption.\textsuperscript{22–27} Effect of external electric field on hydrogen adsorption over activated carbon separated by dielectric materials was studied by Zhang.\textsuperscript{23} Farmanzadeh and Ghazanfary investigated the interaction between the glycine molecule with the (6,0) zigzag model of single-walled boron nitride nanotubes (BNNTs) with H-terminated at the open end in presence of an external electric field.\textsuperscript{24} Effects of electric field on the adsorption of CO on gold and graphene nanodot were also studied.\textsuperscript{25,26} Thus, it is expected that the adsorption of the CDs are affected by the presence of external electric field which might affect the filtration process.

Application of external electric field influences both physical and chemical properties of various molecular systems. The effect of electric field on the chemical reactivity has also been carried out in several earlier studies.\textsuperscript{27–35} Pal and co-workers have studied the behavior of these descriptors in presence of external electric field as well as solvent media.\textsuperscript{29} Chattaraj and co-workers have monitored the effect of electric field on the global and local reactivity indices and confirmed that electric field considerably affects all the local reactivity indices.\textsuperscript{35} Thus, one might expect that the site of attack and selectivity be affected by external electric field.

In the present work, we have considered the CD-alcohol adduct and studied the variation of interaction energy in presence of an external electric field. We have attempted to exploit the DFRT to study the variation of their reactivity in presence of such external electric fields. To reduce the computational cost, we have considered only one glucopyranose unit of cyclodextrin molecule.

2. Theoretical and Computational

Interaction energy is an important parameter usually used to estimate the stability of a system. However, calculation of the interaction energy in the presence of an external electric field is a challenge to the theoretical chemists. The time-independent non-relativistic electronic Hamiltonian, under the Born–Oppenheimer approximation can be written as:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i,A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

In the Hamiltonian the external electric field is introduced as a perturbation parameter. The dipolar interaction of the Hamiltonian with the electric field, $F$ can be written as,

$$\hat{H} = \hat{H}_0 - \hat{d} \cdot \vec{F}$$

where, $\hat{H}_0$ is the unperturbed Hamiltonian and $\hat{d}$ is the dipole moment operator. In the presence of such external perturbation like external electric field the total energy of the system can be witten as,

$$E = E_0 - \sum_i d_i F_i$$

where, $E_0$ is the energy of the system at zero field, $d_i$ is the permanent dipole moment and $F_i$ is the strength of the field.

Conceptual density functional theory defines the chemical potential $\mu$ as the first derivative of energy with respect to the number of electrons\textsuperscript{36}

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{v(\vec{r})}$$

and hardness ($\eta$)\textsuperscript{37}

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_{v(\vec{r})}$$

where $E$ is the energy and $N$ is the number of electrons of an electronic system at constant external potential, $v(\vec{r})$.

In most numerical applications, chemical potential ($\mu$) and chemical hardness ($\eta$) are calculated using finite difference approximation in terms of ionization potential (IP) and electron affinity (EA) and therefore, $\mu$ and $\eta$, given below, can be used as working formulae

$$\mu = -\frac{(IP + EA)}{2}$$

$$\eta = \frac{(IP - EA)}{2}$$

Approximations, involving the use of Koopmans’ theorem,\textsuperscript{38} defines the IP and EA in terms of the energies of highest occupied molecular orbital ($\varepsilon_{HOMO}$) and lowest unoccupied molecular orbitals ($\varepsilon_{LUMO}$)

$$IP = -\varepsilon_{HOMO}$$

$$EA = -\varepsilon_{LUMO}$$

and therefore, $\mu$ and $\eta$ can be expressed as:

$$\eta = \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{2}$$

and

$$\mu = \frac{\varepsilon_{LUMO} + \varepsilon_{HOMO}}{2}$$

Parr and co-workers proposed electrophilicity ($\omega$) as a measure of electrophilic power of a ligand and its propensity to soak up electrons.\textsuperscript{39}

$$\omega = \mu^2/(2\eta)$$
The geometrical minima of the species are obtained using 6-31++G(d,p) basis set with Becke three parameter exchange and Lee, Yang and Parr correlation functional (B3LYP) and is confirmed by the absence of any imaginary frequency. Thereafter single point calculations are carried out at different external electric field values along six directions (along positive and negative directions of the three Cartesian axes, the + sign means that the field is applied along + direction of the axis and – sign means that the field is applied along the – direction of the axis). The range of the strength of external field is chosen from 0.00 a.u. to 0.02 a.u. [1 a.u. = 51.4 V/Å = 51.4 × 10¹⁰Vm⁻¹]. The global reactivity descriptors (chemical potential, global hardness and electrophilicity) are calculated using equations mentioned above. To check the consistency in results, we repeated our calculation at CAM-B3LYP/6-31++G(d,p) level of theory. Choice of the basis set is based on the consideration that in order to obtain reliable properties for hydrogen bonded systems, it is essential to employ basis sets that possess sufficient diffuseness and angular flexibility. All calculations are performed in Gaussian09.

3. Results and Discussion

Interaction energy between adsorbent and adsorbate plays the most important role in adsorption process and we emphasized on the effect of variation of electric field on interaction energy between the two. Further, stability of adducts are discussed and validity of the maximum hardness and minimum electrophilicity principle have been tested.

3.1 Effect of the external electric field on interaction energy

To examine the effect of external electric field on interaction energy between CD and alcohols, initially we have calculated the interaction energy in absence of any external electric field. Super molecular approach has been adopted in calculating interaction energy [for A + B → AB, \( \Delta E_{\text{int}} = (E_{AB}) - (E_A + E_B) \), where, \( E \) is the total energy of the corresponding species]. In all cases, we have taken care of basis set superposition error (BSSE) using counterpoise correction methodCalculated BSSE corrected gas phase interaction energies in adducts (figure 1) are found to be \(-33.737, -33.597\) and \(-33.552\) kcal/mol for CD-methanol, CD-ethanol and CD-butanol respectively at B3LYP/631++G(d,p) level of theory. Effect of external electric field on the interaction energy is presented in figures 2 and 3.

On applying an electric field upon the CD-alcohol adducts, interaction energy is observed to influence significantly and the variation is not same along all the directions. On application of the electric field along \(-x\) direction, interaction energy in case of ethanol-CD adduct is observed to increase (more negative), imparting stability to the adduct. Interaction energy is calculated to be \(-39.11\) kcal/mol in presence of field of strength of 0.01 a.u. applied along \(-x\) direction, figure 2a. Variation of interaction energy in case of CD-methanol and CD-butanol adducts are opposite to that of CD-ethanol adduct; exhibited more interactions.
Figure 2. Variation of interaction energy along (a) $x$-axis, (b) $y$-axis and (c) $z$-axis with external electric field at B3LYP/6-31++G(d,p) level of theory.

Figure 3. Variation of interaction energy along (a) $x$-axis, (b) $y$-axis and (c) $z$-axis with external electric field at CAM-B3LYP/6-31++G(d,p) level of theory.
on application of the field along +x direction. Interaction energy is $-47.583$ kcal/mol and $-47.530$ kcal/mol in presence of field of strength of 0.01 a.u. for CD-methanol and CD-butanol respectively and opposite trend resulted along −x direction (figure 2a). Thus, the results confirmed the sensitivity of the interaction energy toward the direction of the applied field. In addition, application of the field along −z direction stabilizes CD-methanol and CD-butanol adducts and reverse is the case for CD-ethanol adduct. Exactly same trend is observed in both the cases (CD-methanol and CD-butanol adducts) figure 2c. On the other hand, along y-axis, variation of interaction energy in case of CD-methanol adduct is opposite to that of CD-ethanol and CD-butanol adducts (figure 2b). Same results were observed in CAM-B3LYP/6-31++G(d,p) level of theory (figure 3).

### 3.2 Variation of the global reactivity descriptors

Stability of adducts in presence an external electric field is studied using their global hardness values by varying the field strength, results are presented in figure 4. The global hardness values are found to be 0.117 a.u., 0.116 a.u. and 0.115 a.u. for CD-methanol, CD-ethanol and CD-butanol respectively in absence of electric field. When the external electric field is varied from −0.02 a.u. to +0.02 a.u. along the two axes, the global hardness passes through a maximum and the maxima occurs at around zero field value. Thus according to maximum hardness principle, (maximum hardness refers to maximum stability according to maximum hardness principle) the CD-alcohol adduct attains maximum stability when the external field is absent. Hardness is found to be 0.053 a.u., 0.052 a.u. and 0.029 a.u. for

**Figure 4.** Variation of global hardness, electrophilicity with external field at B3LYP/6-31++G(d,p) level of theory (a)–(c) CD-Methanol along x, y and z axis, (d)–(f) CD-ethanol along x, y and z axis, (g)–(i) CD-butanol along x, y and z-axis.
CD-methanol, CD-ethanol, and CD-butanol respectively in presence of field strength of 0.01 a.u. along +x direction. The corresponding values along +y direction and +z direction are 0.0804 a.u., 0.0802 a.u., 0.078 a.u. and 0.095 a.u., 0.099 a.u., 0.094 a.u. respectively. The variation of hardness along both directions of y-axis and z-axis is found to be similar to that along x-axis. On the other hand, as the value of external electric field increases, irrespective of the direction of the field, electrophilicity of the adduct increases in both axes, figure 4a–f. The electrophilicity values found to be 0.1803 a.u., 0.176 a.u. and 0.127 a.u., 0.120 a.u., 0.26 a.u. for the corresponding adducts which are comparatively lesser than along +x direction. It is observed that the electrophilicity passes through a minimum when the external electric field is varied and the minima occurs at zero field value; satisfying minimum electrophilicity principle. Results clearly indicate that the CD-alcohol adducts become unstable in presence of external electric field which might affect the filtration process. Similar results are observed in CAM-B3LYP/6-31+G(d,p) level of theory (figure 5).

3.3 Variation of HOMO energy ($E_{HOMO}$) with applied field strengths

Variation of $E_{HOMO}$ of the CD-alcohol with the applied field strengths is presented in figure 6. $E_{HOMO}$ is found to be 0.255 a.u., 0.253 a.u. and 0.252 a.u. for

![Graphs showing variation of hardness and electrophilicity with electric field.](image-url)

Figure 5. Variation of global hardness, electrophilicity with external field at CAMB3LYP/6-31+G(d,p) level of theory (a)–(c) CD-Methanol along x, y and z axis, (d)–(f) CD-ethanol along x, y and i axis, (g)–(i) CD-butanol along x, y and z-axis.
Cyclodextrin-alcohol adducts

Figure 6. Variation of HOMO Energy (a.u.) of CD-alcohols along (a) x-axis, (b) y-axis and (c) z-axis with external electric field at B3LYP/6-31++G(d,p) level of theory.

Figure 7. Variation of HOMO Energy (a.u.) of CD-alcohols along (a) x-axis, (b) y-axis and (c) z-axis with external electric field at CAMB3LYP/6-31++G(d,p) level of theory.
CD-methanol, CD-ethanol and CD-butanol respectively in absence of electric field. Figure 6 advocates a significant impact of the strength of the applied electric field.

However, the variation is not same along all the directions. Upon application of the electric field along $-x$ direction, $E_{\text{HOMO}}$ in case of CD-ethanol adduct is observed to decrease (more negative), imparting overall stability to adducts. HOMO energy is $-0.241$ a.u. in presence of field of strength 0.01 a.u. along $-x$ direction, figure 6a. Variation of HOMO energy in case of CD- methanol and CD- butanol adducts is opposite to that of CD- ethanol adduct ($-0.160$ a.u. and $-0.173$ a.u. for CD- methanol and CD- butanol respectively) figure 6a-c. The results confirmed the sensitivity of the HOMO energy toward the direction of the applied field. Observations along y-axis show the same trend as along $x$-axis. In addition, application of the field along $-z$ direction stabilizes CD- methanol and CD- butanol adducts and reverse is the case for CD- ethanol adduct. Similar observations were made in CAM-B3LYP/6-31++G(d,p) level of theory (figure 7).

4. Conclusions

We studied the response of CD-alcohol adduct towards external electric fields. Our study was mainly focused on the variation of interaction energy with the variation of electric field and is observed to depend on the strength and direction of the applied field. Additionally, we analyzed the variation in the stability and reactivity of the CD-alcohol adducts using density based reactivity descriptors. Moreover, stability and $E_{\text{HOMO}}$ were observed to be responsive towards the strength and direction of the applied electric field. Our observations reveal that the stability of CD-alcohol adduct is highly sensitive towards electric field. The observations advocate that one can tune the filtration of alcohols through CD composite membrane.

Supplementary Information

Cartesian coordinates of the CD-alcohol complexes are given in table table S1–S3. Normal modes of the complexes are provided in table S4. Supplementary Information is available at www.ias.ac.in/chemsci.

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