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Katif A. Peay[a]; Geoffrey D. Bothun[ab]; Alex Anim-Mensah[a]; Shamsuddin Ilias[a]
[a] Department of Mechanical & Chemical Engineering, North Carolina Agricultural & Technical State University, Greensboro, NC, USA [b] Department of Mechanical & Chemical Engineering and NSF Science & Technology Center for Environmentally Responsible Solvents & Processes, North Carolina Agricultural & Technical State University, Greensboro, NC, USA

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Ultrafiltration of W/CO_2 Microemulsions in Ceramic Membranes

Katif A. Peay
Department of Mechanical & Chemical Engineering, North Carolina
Agricultural & Technical State University, Greensboro, NC, USA

Geoffrey D. Bothun
Department of Mechanical & Chemical Engineering and NSF Science
& Technology Center for Environmentally Responsible Solvents &
Processes, North Carolina Agricultural & Technical State University,
Greensboro, NC, USA

Alex Anim-Mensah and Shamsuddin Ilias
Department of Mechanical & Chemical Engineering, North Carolina
Agricultural & Technical State University, Greensboro, NC, USA

Abstract: Water-in-CO_2 (W/CO_2) reverse microemulsions stabilized with 1100 Da poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) block copolymer were recovered using an ultrafiltration ceramic membrane in a custom high-pressure cross-flow separation unit. Viscosity-corrected liquid CO_2 flux (298 K) through the membrane was investigated as a function of time and surfactant concentration to determine the cake layer mass transfer resistance. Rapid CO_2 flux decline was observed with increasing surfactant concentration, denoting cake layer buildup on the membrane surface. For instance, at 0.09 and 0.55 wt% surfactant, the ratio of cake resistance to membrane resistance was 0.4 and 3.8, respectively. Based on our previous work, the reverse-micelles retain their aqueous core and are not altered during filtration. Ultimately, inorganic membrane separations can reduce energy

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Address correspondence to Shamsuddin Ilias, Department of Mechanical & Chemical Engineering, North Carolina Agricultural & Technical State University, Greensboro, NC 27411, USA. E-mail: ilias@ncat.edu

consumption associated with compression/expansion cycles typically used in CO_2-based processes.

Keywords: Inorganic membrane, ceramic membrane, supercritical fluid, ultrafiltration, carbon dioxide

INTRODUCTION

Many conventional industrial solvents are hazardous to the environment, creating a need for more environmentally responsible processing solvents. Liquid and supercritical CO_2 are considered "green" solvents since they are benign, non-toxic, and naturally occur in the atmosphere, making them ideal replacements to organic solvents. When condensed, CO_2 behaves more like an organic solvent than a gas; however, it offers additional benefits such as enhanced mass transfer, low surface tension, tunable solvent strength, and ease of recovery. Given these benefits, CO_2 has gained much attention in extractions, microelectronics fabrication, nanoparticle synthesis, pharmaceutical formulations and polymer synthesis (1–5).

We seek to facilitate continuous CO_2 processes using inorganic membranes, which have high compressible strength, thermal stability, and solvent resistance. At the experimental operating conditions investigated herein (70 bar, 298 K) CO_2 is an apolar liquid solvent. We have previously examined liquid CO_2 transport through mesoporous (2 to 50 nm pore diameter) ceramic membranes to determine permeability coefficients, the application of Darcy's law, and potential CO_2/membrane interactions (6). It has been shown that solvent/ceramic membrane interactions can result in low permeability, relative to water, and deviations from Darcy's law in submicron pores (7, 8). In a subsequent study it was shown that trace amounts of water caused an initial threshold pressure in the permeation of organic solvents through ceramic membranes (9). We have observed similar results for liquid CO_2 as water preferentially adsorbs on pore surfaces, reducing the effective pore size and CO_2 flux (6). This work extends our knowledge of hydrated and dehydrated liquid CO_2 permeation to CO_2-emulsion systems.

Reverse microemulsions are commonly used in liquid and supercritical CO_2 processes, providing a water core to accommodate hydrophilic compounds (W/CO_2 reverse microemulsion). Hence, reductions in CO_2 flux are expected when W/CO_2 microemulsions are recovered using cross-flow filtration. This flux reduction is expected as the microemulsions are rejected, forming a cake layer on the membrane surface. As filtration progresses, the solvent mass transport resistance in the cake layer increases with time, reaching a maximum resistance. The formation of this cake layer is a major obstacle for membrane filtration. Previous investigations have demonstrated the potential for separating reverse micelles in near-critical and supercritical solvents using membranes. However, there have been no detailed studies on mass transfer in these systems (10, 11).

To further understand the impact of cake resistance, cross-flow filtration of W/CO_2 microemulsions stabilized with a poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG, 1100 Da) was performed as a function of time and polymer concentration. PEG-PPG-PEG was selected as a model system with high water solubility. Previous work in our group has shown that water-to-block copolymer ratios of less than 1, and 94% or greater of CO_2 (volume basis) are required to maintain a stable microemulsion at 70 bar and 298 K (12). In the present work, a high pressure liquid CO_2 cross-flow permeation system was used to investigate cake layer resistance on the surface of a mesoporous 1000 Da titania membrane. Darcy's law was combined with the resistance-in-series approach to calculate cake layer resistance.

THEORY

Ultrafiltration processes are controlled by a sieving mechanism. Therefore, transmembrane pressure, ΔP_{TMP}, and solvent flux, J, are expected to exhibit a linear relationship that can be seen by Darcy's law (13):

$$J = \frac{\Delta P_{TMP}}{\eta[R_m + R_c(t)]} \tag{1}$$

where η is the intrinsic solvent viscosity, R_m is the membrane resistance and R_c is the cake layer resistance. Carbon dioxide transport is expressed as a viscosity-corrected volumetric flux (ηJ_{co_2}, $\mathrm{bar} \cdot \mathrm{m}^3 \cdot \mathrm{m}^{-2}$ to account for changes in viscosity and density as a function of pressure (Fig. 1):

$$\eta J_{co_2} = \frac{\Delta P_{TMP}}{R_t} \tag{2}$$

where $R_t = R_m + R_c(t)$ is the total mass transfer resistance. The membrane resistance R_m can be determined from the flux of a pure solvent. By plotting the viscosity corrected flux versus the transmembrane pressure of pure CO_2, the permeability coefficient of the membrane can be calculated from the membrane resistance as $K_m = 1/R_m$. The cake resistance can be determined by the difference between the total resistance and the membrane resistance, which are both determined experimentally.

EXPERIMENTAL

Experiments were carried out using a 1000 Da ceramic membrane with a titania selective layer (Membralox^{TM}, Pall Co.). The selective layer has a thickness, t, of $3.6 \pm 0.9\,\mu\mathrm{m}$ (measured by SEM (6)), a pore radius, r_p, of 1.3 nm and 50% porosity, ε. The pore size was estimated from previous correlations based on PEG rejection (14). Industrial-grade liquid CO_2 (Air Products) was used to

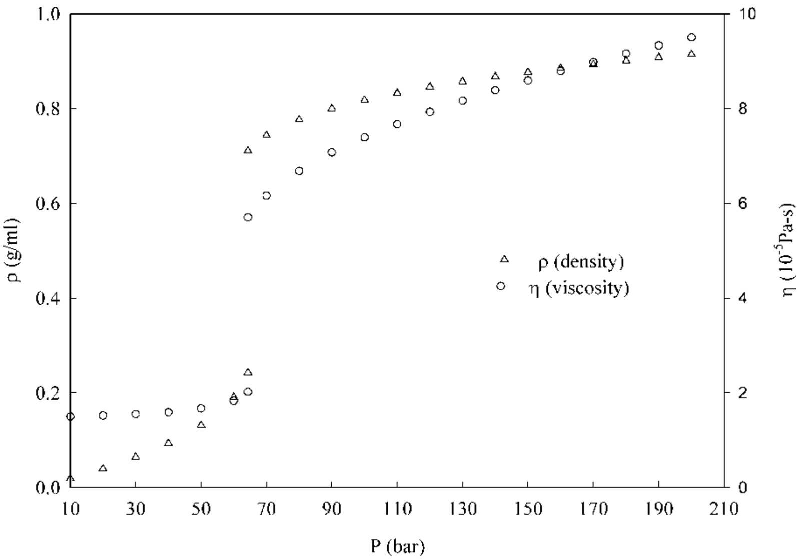

Figure 1. Carbon dioxide density (ρ) and viscosity (η) as a function of pressure at 298 K (data from NIST).

carry out the filtration. The membrane housing was placed in a crossflow configuration using a custom designed high pressure permeation setup (previously described by Photinon et al. (11), Fig. 2). Major components includes 1 L feed tank with a viewing window, reciprocating pump (Thar Designs, Pittsburgh, PA), two automatic back pressure regulators (Thar Designs), one on permeate and other on the retentate side, a permeate flowmeter (Rheonik), and a custom-fabricated stainless steel membrane housing.

Predetermined amounts of PEG-PPG-PEG (Slovanik M-640), water and liquid CO_2 were mixed to form the emulsion system used in these experiments (12). PEG-PPG-PEG and distilled water were mixed in the correct ratio and injected into the feed tank. The feed tank was then charged with liquid CO_2 at approximately 60 bar and mixed until the solution was optically clear, symbolizing the presence of a W/CO_2 reverse microemulsion. Filtration was initiated by setting the transmembrane pressure (4 bar) and feed flowrate using the reciprocating pump and back pressure regulators, respectively. CO_2 permeate flux was recorded as a function of time.

RESULTS AND DISCUSSION

To study the performance of UF membranes in liquid CO_2 filtration in presence of model W/CO_2 reverse microemulsions, CO_2 flux was examined as a function of time and surfactant concentrations. In Fig. 3, typical flux

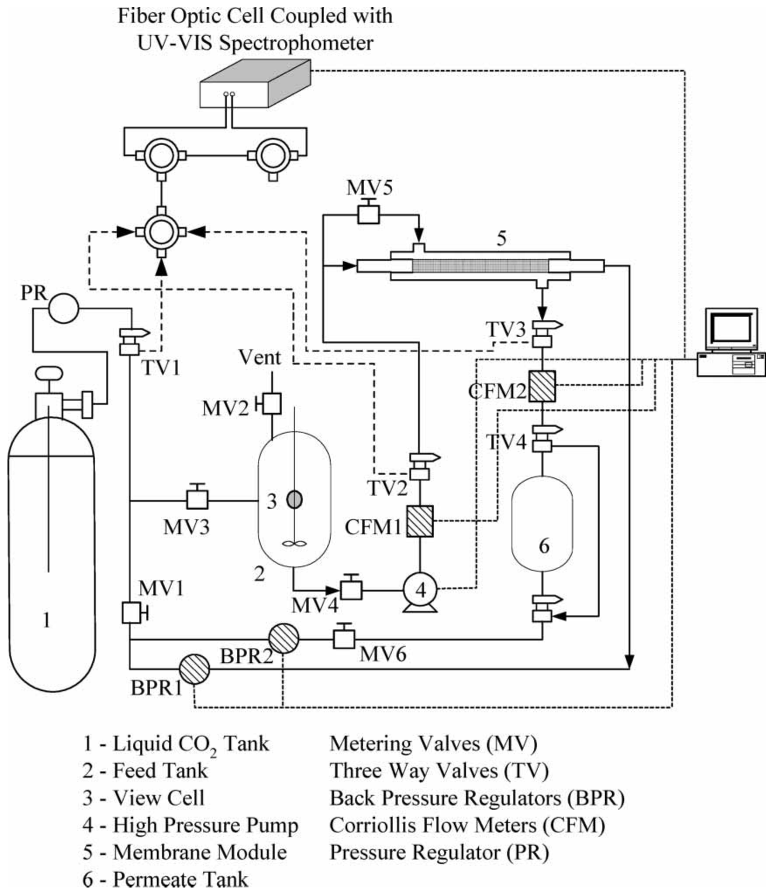

Figure 2. Schematic of high pressure crossflow ultrafiltration system.

data as function of time is shown for 0.09 to 0.55 wt% PEG-PPG-PEG surfactant concentrations at a transmembrane pressure, $\Delta P_{TMP} = 4$ bar. From Fig. 3, we find that CO$_2$ flux declines rapidly within the first 20 minutes of operation denoting cake layer formation at the inner membrane surface, which results in increased total mass-transfer resistance to CO$_2$ transport. We computed these resistances from the flux data presented in Fig. 3. Knowing the membrane resistance from pure CO$_2$ flux data (6) ($R_m = 4.0 \times 10^{13}\text{m}^{-1}$), we can determine the cake layer resistance as a function of time from equation (1).

The cake layer resistance was found to be strongly dependent on surfactant concentration in liquid CO$_2$. A higher surfactant concentration results in a higher number density of reverse-micelles and greater rejection, resulting in added mass transfer resistance. The cake layer resistance as a function of time for 0.09 to 0.55 wt% PEG-PPG-PEG surfactant is shown in Fig. 4. At low concentration (≤ 0.38 wt%), a quasi-steady state cake resistance was

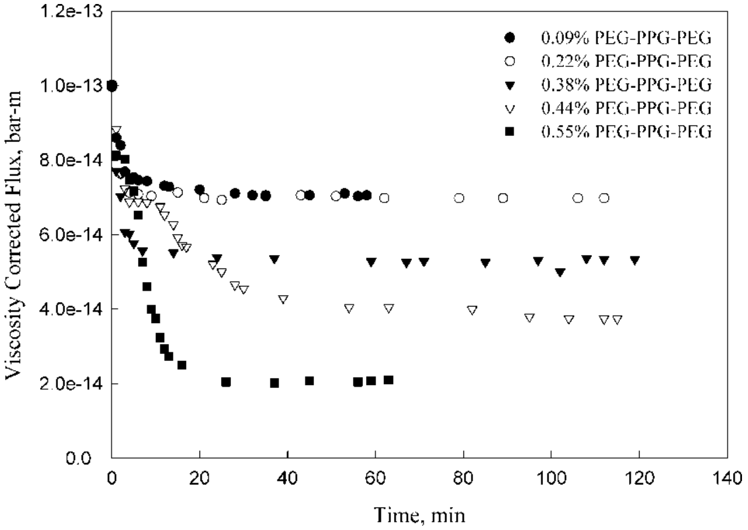

Figure 3. Viscosity corrected liquid CO_2 permeate flux at various PEG-PPG-PEG concentrations as a function of time at $\Delta P_{TMP} = 4$ bar, $T = 298$ K, and 0.28 wt% H_2O.

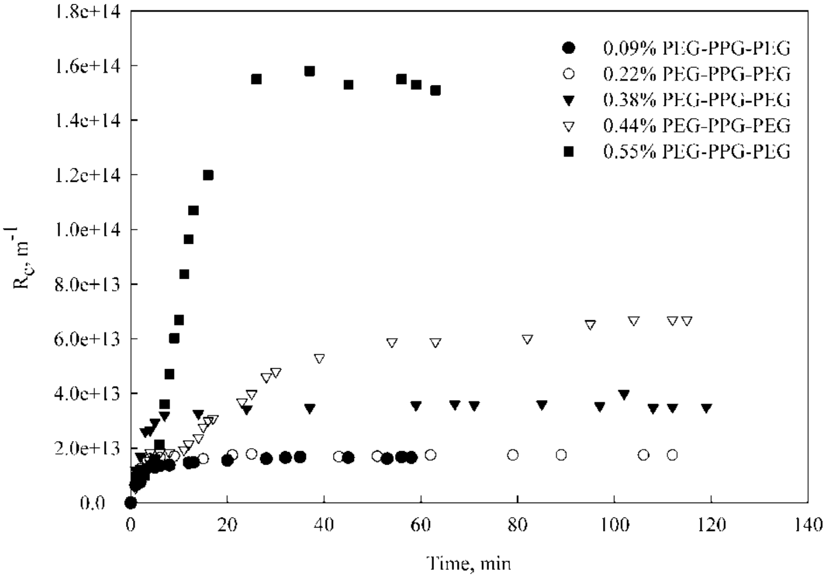

Figure 4. Cake layer resistance as a function of time for various PEG-PPG-PEG concentrations ($\Delta P_{TMP} = 4$ bar, $T = 298$ K, and 0.28 wt% H_2O).

observed within the first ten minutes. At higher concentrations a much greater resistance was observed, which indicated that more time was needed to approach quasi-steady state (Fig. 4).

The relative contributions of membrane resistance and cake layer resistance at the lowest and highest concentrations are shown in Figs. 5, and 6, respectively. In Fig. 5, we observe that at 0.09 wt% PEG-PPG-PEG concentration, the cake layer resistance approaches 29% of the total resistance and the ratio of R_c/R_m is approximately 0.4. In contrast, at 0.55 wt% PEG-PPG-PEG concentration, the cake layer resistance becomes the controlling transport resistance. In this case, we find that the cake layer resistance approaches 79% of the total resistance, which gives $R_c/R_m = 3.8$. Thus we find the contribution of cake layer resistance increases by an order of magnitude when the concentration changes by about six-fold. The contributions of cake layer resistances at quasi-steady state operation for different solute concentrations are given in Table 1.

We can compare these results for PEG-PPG-PEG filtration with our previous results on dehydrated and hydrated liquid CO$_2$ transport to evaluate the potential for:

(i) water stripping from the aqueous core of the reverse micelles followed by
(ii) adsorption onto the pore surface.

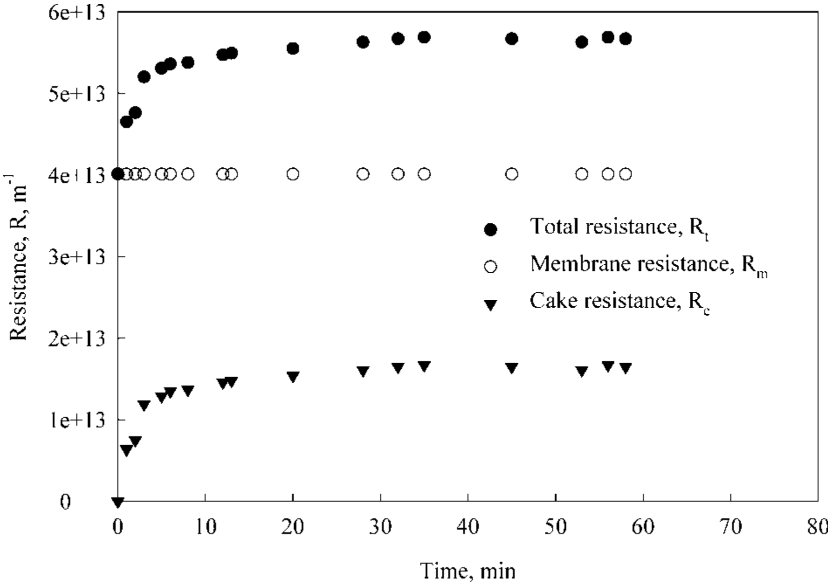

Figure 5. Major resistive contributions resulting from crossflow filtration of 0.09% PEG-PPG-PEG/CO$_2$/H$_2$O emulsion as a function of time at $\Delta P_{TMP} = 4$ bar, $T = 298$ K, and 0.28 wt% H$_2$O.

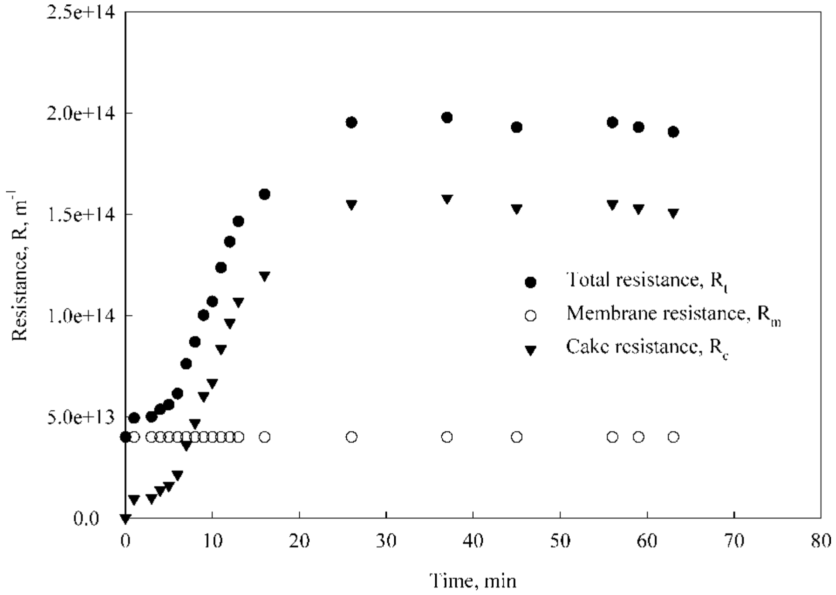

Figure 6. Major resistive contributions resulting from crossflow filtration of 0.55% PEG-PPG-PEG/CO_2/H_2O emulsion as a function of time at $\Delta P_{TMP} = 4$ bar, $T = 298$ K, and 0.28 wt% H_2O.

Water adsorption on membrane pore surfaces reduces the effective pore size, which leads to a decrease in CO_2 permeability. For instance, a 60% decrease in liquid CO_2 flux was observed for partially hydrated CO_2 (0.02 wt%), relative to dehydrated CO_2 at $\Delta P_{TMP} = 4$ bar (6). Comparatively, the water content in the reverse micelle systems is constant at 0.28 wt%. A significant flux decline of at least 60% would be expected if water did strip from the aqueous core and

Table 1. Quasi steady-state mass transfer resistances as a function of PEG-PPG-PEG concentration in W/CO_2 reverse microemulsion systems ($\Delta P_{TMP} = 4$ bar, $T = 298$ K, and 0.28 wt% H_2O)

[PEG-PPG-PEG] (wt%)	R_t[a] (10^{13} m^{-1})	R_c[b] (10^{13} m^{-1})	R_c/R_t	R_c/R_m[c]
0.09	5.7	1.7	0.3	0.4
0.22	5.7	1.7	0.3	0.4
0.38	7.5	3.5	0.5	0.9
0.44	10.7	6.6	0.6	1.7
0.55	19.1	15.1	0.8	3.8

[a] Total mass transfer resistance.

[b] Cake layer mass transfer resistance.

[c] Ratio of cake resistance to membrane resistance.

adsorb on the pore surface. This was not observed as evident from Fig. 3 at low surfactant concentrations. Therefore, mass transfer resistance in this W/CO_2 microemulsion system is due to a cake layer buildup of intact micelles and not due to a pore restriction via water adsorption.

CONCLUSIONS

Inorganic membrane separations may eliminate the need for system depressurization and reduce the energy consumption associated with compression/expansion cycles typically associated with CO_2-based processes. Therefore, the aim of this work was to examine the separation characteristics of a model reverse microemulsion system in liquid CO_2. Ultrafiltration of a W/CO_2 reverse microelumsion stabilized with PEG-PPG-PEG was performed using a 1000 Da ceramic membrane to determine the liquid CO_2 flux behavior and cake layer resistance as a function of time and surfactant concentration. An increase in surfactant concentration increased the cake layer resistance and the time needed to reach quasi steady-state. At high concentrations of PEG-PPG-PEG the total resistance was dominated by the cake layer resistance. In contrast, CO_2 flux at low concentrations was controlled by the membrane mass transfer resistance. By relating the results for reverse micelle recovery to that of dehydrated and partially hydrated liquid CO_2 (no surfactant present), it is apparent that the micelles retain their shape and are not subject to water stripping from the aqueous core.

NOMENCLATURE

J	Volumetric solvent flux ($m^3 \cdot m^{-2} \cdot s^{-1}$)
K_m	Membrane permeability coefficient (m)
ΔP_{TMP}	Trans-membrane pressure (bar)
r_p	Membrane pore radius (nm)
R_t	Total resistance (m^{-1})
R_m	Membrane resistance (m^{-1})
R_c	Cake layer resistance (m^{-1})
t	Membrane thickness (μm)
t	Membrane porosity (%)
η	Viscosity (Pa's)

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REFERENCES

1. King, J.W. and Williams, L.L. (2003) Utilization of critical fluids in processing semiconductors and their related materials. *Curr. Opin. Solid State & Mat. Sci.*, 7: 413.
2. Jung, J. and Perrut, M. (2001) Particle design using supercritical fluids: Literature and patent survey. *J. Supercritical Fluids*, 20: 179.
3. Shah, P.S., Hanrath, T., Johnston, K.P., and Korgel, B.A. (2004) Nanocrystal and nanowire synthesis and dispersibility in supercritical fluids. *J. Phys. Chem. B*, 108: 9574.
4. Cansell, F., Aymonier, C., and Loppinet-Serani, A. (2003) Review on materials science and supercritical fluids. *Curr. Opin. Solid State & Mat. Sci.*, 7: 331.
5. Cooper, A.I. (2000) Polymer synthesis and processing using supercritical carbon dioxide. *J. Materials Chem.*, 10: 207.
6. Bothun, G.D., Ilias, S., and Nelson, K. (2006) Adsorption and hydration effects on liquid carbon dioxide transport through mesoporous γ-alumina and titania membranes. *Journal of Membrane Science*, in press.
7. Chowdhury, S.R., Schmuhl, R., Keizer, K., Elsof, J.E., and Blank, D.H.A. (2003) Pore size and surface chemistry effects on the transport of hydrophobic and hydrophilic solvents through mesoporous γ-alumina and silica MCM-48. *J. Membrane Sci.*, 225: 177.
8. Garcia, A., Alvarez, S., Riera, F., Alvarez, R., and Coca, J. (2005) Water and hexane permeate flux through organic and ceramic membranes: Effect of pretreatment on hexane permeate flux. *J. Membrane Sci.*, 253: 139.
9. Chowdhury, S.R., Keizer, K., Elsof, J.E., and Blank, D.H.A. (2004) Effect of trace amounts of water on organic solvent transport through γ-alumina membranes with varying pore sizes. *Langmuir*, 20: 4548.
10. Yonker, C.R., Fulton, J.L., Phelps, M.R., and Bowman, L.E. (2003) Membrane separations using reverse micelles in nearcritical and supercritical fluid solvents. *J. Supercrit. Fluids*, 25: 225.
11. Photinon, K., Boddu, A., and Ilias, S. (2003) Recovery of liquid CO_2 from cleaning solutions without phase change using ultrafiltration and microfiltration membranes. *Separations Science and Technology*, 38: 2951.
12. Anim-Mensah, A.R. (2003) Separation and recovery of liquid carbon dioxide from process solutions without phase change through enhanced micellar crossflow microfiltration. MS Thesis. North Carolina Agricultural and Technical State University.
13. Ho, W.S. and Sirkar, K. (Eds.) (1992) *Membrane Handbook*; Van Norstrand Reinhold: New York, NY.
14. Okazaki, I., Ohya, H., Semenova, S.I., Aihara, M., and Negishi, Y. (1998) Study on molecular weight cut-off performance of asymmetric aromatic polyimide membrane—effect of the additive agents. *J. Membrane Sci.*, 141: 277.