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Experimental results versus model predictions for dense gas extraction using a hollow fiber membrane contactor

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Abstract

Hollow fiber membrane contactors offer a number of advantages over dispersed phase contactors for extraction of aqueous feeds. In addition, dense gases provide benefits that traditional extraction solvents do not. In a previous paper we described the development of a mathematical model of a membrane contactor, and showed that model predictions were reasonably close to experimental data obtained in our laboratory for the extraction of isopropanol or acetone from water into dense CO_2.

In this paper, results obtained by others upon extraction of various solutes from aqueous solution into dense CO_2 or propane were also compared to model predictions. Solutes studied ranged from low m_A (i.e., partition coefficient) compounds like caffeine, ethanol, and dimethylformamide, to high m_A ones such as 1,2-dichloroethane and ethyl acetate. Again the predicted mass transfer coefficients and yields were reasonably close to the actual ones, except for the data obtained using a membrane module that was particularly susceptible to flow maldistribution.

With higher m_A solutes, most of the mass transfer resistance was in the aqueous phase boundary layer. On the other hand, some of the resistance encountered with lower m_A compounds shifted to the solvent-filled pore and the solvent phase boundary layer, although the aqueous resistance was still significant in most cases. In general, mass transfer coefficients and yields were higher for solutes with higher partition coefficients, and aqueous boundary layer penetration was more rapid.

The results presented in this and in our previous paper validate the ability of the model to predict hollow fiber membrane contactor performance in dense gas extraction. This validation confirms the utility of the model for screening potential applications of the technology, with considerable reduction in the required amount of expensive laboratory experimentation.

Keywords: Membrane contactor; Hollow fiber; Supercritical fluid; Dense gas; Extraction; Mathematical model

1. Introduction

Gas/liquid and liquid/liquid contacting operations are traditionally done using some type of tower or column. Although such towers have been workhorses of the chemical industry for decades, an important disadvantage is the interdependence of the two fluid phases to be contacted, which sometimes leads to difficulties such as emulsions, foaming, unloading and flooding. As explained in our previous paper [1], non-dispersive contact via a microporous membrane is an alternative technology that overcomes these disadvantages and also offers substantially more interfacial area per unit volume than columns. Using a suitable membrane configuration such as a hollow fiber, fluids to be contacted flow on opposite sides of the membrane and the fluid/fluid interface forms at the mouth of each membrane pore. Hollow fiber membrane contactors have been studied extensively since the mid-1980s for a diverse range of applications. Numerous examples are given in our previous paper [1], in Gabelman's dissertation [2] and in several recent review articles [3–9].

A particularly interesting application of membrane contactors is extraction with dense gases (e.g., near critical or supercritical fluids). Like liquids, dense gases offer high sol-

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Nomenclature

a	interfacial area ($cm^2\ cm^{-3}$)
d	diameter (cm)
Gz	Graetz number
k	individual mass transfer coefficient (cm/s)
K	overall mass transfer coefficient (cm/s)
m	ratio of equilibrium solute density in the dense gas to the aqueous phase $(g/cm^3)_{solvent}/(g/cm^3)_{aqueous}$
Q	flow rate (cm^3/s)
r^*	dimensionless radius
V	module volume (cm^3)
z^*	dimensionless length
ρ	density (g/cm^3)

Subscripts

A	component A
i	inside
lm	log mean
m	membrane
o	outside; solvent phase
s	shell side
t	tube side
w	aqueous phase

ubility of many solutes of interest, yet they also offer the high mass transfer rate and low pressure drop enjoyed with gases. Furthermore, solubility is usually a strong function of density, so that the dense gas is easily separated from dissolved solutes simply by reducing the pressure [10,11]. Carbon dioxide or propane is often the solvent of choice in supercritical fluid extraction. While most of the published work on membrane contactors was done with ordinary fluids, there are a few articles [1,2,12–17] and one patent [18] on the use of these devices in dense gas extraction.

In our earlier paper [1], we developed a first principles mathematical model that predicts the steady state velocity and concentration profiles in a hollow fiber contactor. The model was partially validated by demonstrating that predicted Sherwood numbers for tube flow agreed with those obtained from the classical equations [19–21], which have been confirmed many times with experimental data. The model was further validated by comparing its predictions to data obtained in our laboratory upon extraction of isopropanol or acetone from water into near critical or supercritical carbon dioxide [1,2]. Over 100 extractions were performed in that work, and in general the model predictions agreed reasonably well with the observed results. For isopropanol, the average absolute errors in the predicted mass transfer coefficient and yield (the portion of incoming solute that was extracted) were 29% and 31%, respectively, while for acetone the errors were 39% and 11%.

Table 1
Modules used for experimental work[a]

	Module no.		
	1	2	3
Fiber material	Polypropylene	Polypropylene	Polypropylene
Used by	[18]	[16]	[12]
Tubesheet material	Polypropylene	Polypropylene	Polypropylene
Sealing mechanism[b]	*O*-ring (Buna-N)	*O*-ring (Buna-N)	None[c]
Flow pattern	Parallel	Parallel	Parallel
Fiber i.d. (mm)	0.60	0.60	0.60
Fiber o.d. (mm)	1.0	1.0	1.0
Shell i.d. (cm)	1.27	1.27	0.18
Length (cm)	40.3	40.3	106.7
Number of fibers	3	120	1
Packing density	0.10[d]	0.74	0.31
Porosity[e]	0.75	0.75	0.75
Tortuosity[f]	1.3	1.3	1.3
Average pore diameter[g] (μm)	0.18	0.18	0.18

[a] All models were manufactured by Porocrit LLC (Berkeley, CA) or its predecessor, Setec, Inc. (Livermore, CA).

[b] Refers to the method of sealing the shell to the housing.

[c] The housing served as the shell, so no seal was necessary.

[d] To increase the packing density, a polypropylene rod (diameter: 0.32 cm) was placed along the length of this module, in the center of the cross-section [45]. To calculate the packing density, the cross-sectional area of this rod was subtracted from the area of the shell.

[e] According to the supplier.

[f] Obtained from the Wakao–Smith relationship, which states that the tortuosity is the reciprocal of the porosity [41,42].

[g] As determined by Porous Materials, Inc. (Ithaca, NY) by capillary flow porometry.

In this paper, we further validate the model by comparing its predictions to experimental data obtained by others. The solutes studied cover a range of partition coefficients (m_A), including low m_A compounds like caffeine and ethanol, medium m_A solutes such as acetone, and high m_A ones like ethyl acetate and 1,2-dichloroethane. Experiments were carried out over a variety of fluid flow rates, using modules with packing densities ranging from 0.1 to 0.74, and a length of 40 or 107 cm. Mass transfer coefficient, yield, solute and overall mass balances, and distribution of mass transfer resistance were calculated as described in our previous paper [1] and in Gabelman's dissertation [2]. The resistance-in-series model used to determine the mass transfer coefficient and distribution of resistance is reviewed briefly below. Methods used to estimate fluid physical properties needed to run the model are also explained in [2]. Modules are described in Table 1.

2. Determination of mass transfer coefficients

The overall mass transfer coefficient K can be expressed in terms of the individual mass transfer coefficients that characterize the three resistances encountered by the solute upon transfer from the aqueous to the dense gas phase [22]. For a hydrophobic membrane with the aqueous phase on the tube side, the governing resistance-in-series equation based on the