Journal of Membrane Science 318 (2008) 317–326

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

CO_2 transfer in an aqueous potassium carbonate liquid membrane module with dense polymeric supporting layers: Influence of concentration, circulation flow rate and temperature

M.G. Shalygin[a,b,*], D. Roizard[b], E. Favre[b], V.V. Teplyakov[a]

[a] A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29, Leninskiy Prospect, 119991 Moscow, Russia
[b] Laboratoire des Sciences du Génie Chimique (UPR 6811), Groupe ENSIC, 1, rue Grandville-BP 451 F-54001 Nancy, France

ARTICLE INFO

Article history:
Received 28 November 2006
Received in revised form 14 February 2008
Accepted 26 February 2008
Available online 7 March 2008

Keywords:
CO_2 recovery
Liquid membrane
Facilitated transport
Potassium carbonate

ABSTRACT

Gas–liquid separation systems have already received considerable attention in a great number of situations of industrial interest. The attention paid to membrane contactors and immobilized liquid membranes have recently increased due to their separation performances. For the sake of simplicity, most experiments are usually performed at room temperature. It is, however, obvious that increasing the temperature would increase the reaction rate and thereby also possibly enhance the system's productivity. This work presents a systematic study of CO_2 and H_2 transport in a novel flowing liquid membrane (FLM) module with dense membranes separating layers and aqueous potassium carbonate (concentration 0.1–3 kmol/m^3) solutions in the temperature range 295–353 K. A model of CO_2 transport with reversible chemical reactions through the FLM was developed and compared to a series of experimental data. It was found that increasing the concentration of potassium carbonate as well as the temperature led to large increases in both the CO_2 productivity and the CO_2/H_2 selectivity. The industrial implications of these observations were discussed. Unsteady state transport of CO_2 was also investigated and a simple model of gas transfer in the FLM with physical absorption in the liquid phase was developed.

1. Introduction

The use of liquids' absorption properties in gas separation technologies is not a new concept. The most classical example is based on absorption of a gas into a liquid flowing in a column. Given the intrinsic advantages of membrane separation technologies (e.g. high interfacial areas, no flooding problems, the possibility to achieve absorption and regeneration in a single unit, etc.), a large number of studies have been devoted to separation systems that combine absorption in a liquid with membrane technologies [1,2]. The best-known examples of such gas–liquid–membrane systems (GLMSs) are gas–liquid–membrane contactors (MCs, Fig. 1a) and liquid membranes (LMs). LMs can be either immobile, e.g. immobilized or supported liquid membranes (ILMs, SLMs, Fig. 1b), or mobile, e.g. flowing liquid membranes (FLMs, Fig. 1c). An FLM differs markedly from an ILM in that the liquid layer is capable of flowing. This property of the FLM can be employed for “fine tuning” the separation process or for ternary gas mixture separation [3].

One of the advantages of a GLMSs is its ability to provide and exactly determined geometry of the liquid phase and the gas–(membrane)–liquid interface. Furthermore, the membrane plays the role of a physical barrier between the phases. As a result, it is possible to independently adjust the gas and liquid fluxes as well as to avoid dispersion of one phase into another [2]. These characteristics can explain the technical benefits of such systems.

LMs take direct advantage of the separation properties of a liquid. Moreover, the presence, in the liquid phase, of a chemical absorbent that is capable of reversibly reacting with one of the gas mixture components is a classical means when high separation performances are necessary [4]. Thus, the liquid layer plays the role of an absorbing medium and a part of the reacting component is transferred through the LM following a mechanism known as facilitated transport [5]. LMs can show high productivities and selectivities due to this mechanism. Facilitated transport offers an additional way of transferring a target component in the form of a chemical reaction product.

Reacting liquid absorbents are traditionally used to remove acid gases such as CO_2, and various amines, and carbonate aqueous solu-

---

Abbreviations: LM, liquid membrane; ILM, immobilized liquid membrane; FLM, flowing liquid membrane; GLMS, gas–liquid–membrane system; PVTMS, poly-(vinyltrimethylsilane).

[*] Corresponding author at: A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29, Leninskiy Prospect, 119991 Moscow, Russia.
E-mail address: mshalygin@ips.ac.ru (M.G. Shalygin).

0376-7388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2008.02.062

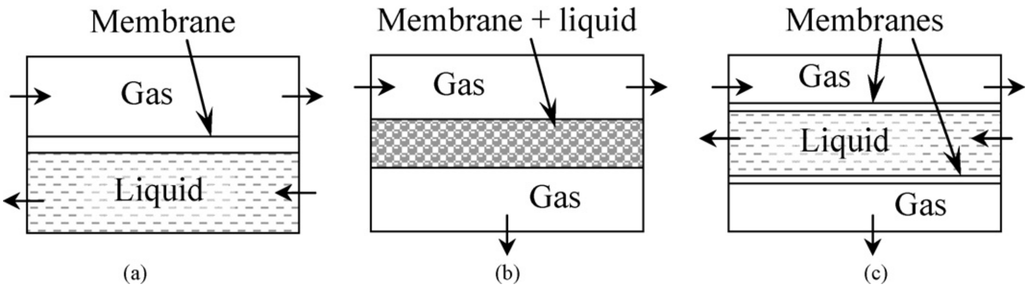

Fig. 1. Three types of gas–liquid–membrane systems: (a) a membrane contactor; (b) an immobilized liquid membrane; (c) a flowing liquid membrane.

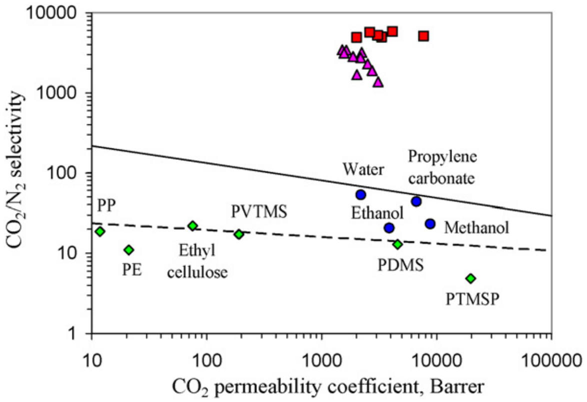

Fig. 2. Separation properties of polymers and liquids for the CO_2/N_2 gas pair: (--) statistical upper bound [6]; (—) theoretical upper bound [8]; (♦) polymers; (●) liquids; (▲) ILM [9]; (■) ILM [10].

tions are used for this purpose. Fig. 2 demonstrates a comparison between the separation properties of polymers and liquids for the CO_2/N_2 gas pair. The statistical upper bound, described by Robeson [6] (dotted line), is an empirical expression relating to polymeric materials that is obtained from numerous experimental results. It is thus subject to change provided that more selective membrane materials are identified [7].

The theoretical upper bound (solid line) shown in Fig. 2 results from a theoretical approach developed by Freeman [8]. This computation is based on correlations proposed for estimating the solubility and diffusivity in polymers under the hypothesis of a strict physical process (no chemical reaction). As can be seen from the figure, traditional membrane separation performances reside below the statistical upper bound, whereas physical liquid solvents remain below the theoretical upper bound. Conversely, the separation performances of chemical liquid absorbents used in ILMs [9,10] are considerably higher and far above the upper bounds. This mode of representation clearly establishes the potential of chemically reacting systems in the liquid phase, and explains why these attract attention.

The development of experimental and theoretical approaches dedicated to LM systems is an essential prerequisite in order to achieve a rigorous design for a given application. Table 1 summarizes a series of experimental studies that have been reported in the area of CO_2 recovery by LM systems.

The main problem that has been identified in theoretical description of CO_2 transfer concerns gas transfer with reversible chemical reaction. The determination of the flux of the reacting component in such a system demands that a series of differential equations be solved. Unfortunately, in most cases, these equations have no analytical solution. The papers presented in Table 1 all describe simplified models of CO_2 transport in order for an analytical solution to be obtained. Such an approach can be of interest for predicting mass transfer rates with low concentrations of carrier and/or penetrating component. All the studies, with the exception of [11], report adequate predictions for these (low concentration) conditions and have been carried out at room temperature. It is obvious, however, that a large carrier concentration is needed for real applications in order to enhance the efficiency of the system. Another strategy consists in increasing the operating temperature, thus promoting chemical reaction rates. In fact, absorption columns for CO_2 recovery from gas mixtures usually work in the temperature range of 40–120 °C [15,16].

High temperature conditions are practically unrealizable for ILMs as the liquid would evaporate and thus induce a rapid degradation of the liquid layer. This problem is absent in FLMs which allow a refreshing of the liquid between the membranes, thereby displaying a much better stability. This was demonstrated by Teramoto et al. [17] in an example of ethane/ethylene separation by ILM and FLM with an $AgNO_3$ solution.

The present article describes a theoretical and experimental study of gas transport in an FLM within a large range of temperatures (295–353 K) and carrier concentrations (0.1–3 kmol/m^3 of K_2CO_3). More specifically, the transport of CO_2 and H_2 in an FLM with water and a solution of potassium carbonate were investigated. In addition, asymmetric polymeric membranes with dense layers facing the liquid side were selected and assembled in a flat cell without a net-spacer in the liquid phase. Such a system can be of interest for the separation of CO_2/H_2 gas mixtures,

Table 1
A list of experimental studies dedicated to CO_2 transport in LM systems

Gas	Chemical absorbent in liquid phase	Gas transfer model	Concentration of absorbent (mol/l)	Liquid layer thickness (mm)	Temperature (K)	Reference
CO_2, N_2	Glycerol–Na_2CO_3	–	0–4	0.1	296	[9]
CO_2, N_2	(1) Glycerol–Na_2CO_3; (2) glycine–Na–glycerol	–	(1) 1; (2) 3	0.01–0.28	296	[10]
CO_2, CH_4	Different amines	AAS[a]	0–4	0.1	298–318	[11]
CO_2, N_2	Na_2CO_3 solution	AAS	0–1	0.2–1	298	[12]
CO_2	K_2CO_3 solution (+enzyme)	AAS	0–1	0.1–1	298	[13]
CO_2	Na_2CO_3 solution	AAS	0–0.35	0.75–1	297	[14]
CO_2, H_2	K_2CO_3 solution	Numerical solution	0–3	0.21–0.26	295–353	This work

[a] Approximate analytical solution.