Ethylene/ethane separation and mass transfer characteristics through absorption by $AgNO_3$ solutions in microchannels

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ABSTRACT

Chemical absorption using silver ion is a potential way for ethylene recovery, which can be significantly enhanced by the use of microreactors. This work presents an experimental study on the characteristics of absorption of ethylene into aqueous $AgNO_3$ solutions. The effects of several parameters including channel length, channel diameter, flow rates, temperature and $AgNO_3$ concentration are investigated in terms of absorption fraction, molar absorptivity and mass transfer coefficients. It is demonstrated that very high liquid side mass transfer coefficients in the range of $3–85\,s^{-1}$ can be obtained in microchannels, indicating significant process intensification. Based on the results, an empirical correlation was proposed for the prediction of mass transfer coefficients.

1. Introduction

Ethylene is a basic chemical that plays an important role in many chemical synthesis and industrial processes. The general ways of producing ethylene are steam cracking, fluidized catalytic and alkane dehydrogenation [1,2]. Of all these methods, the production obtained is a mixture of many different components [3]. For the recovery of ethylene, cryogenic distillation has been used for decades under considerably low temperature and high pressure, due to the small difference between the relative volatilities of ethane and ethylene. It is costly in terms of both the capital investment and energy consumption. Therefore, there are strong incentives in developing alternative technologies to improve the process. Many methods such as membrane [4–6], adsorption [7,8], extractive distillation [9,10], and chemical/physical absorption [11–14] have been investigated.

Among the above-mentioned processes, chemical absorption of ethylene by transition metal ions has attracted many attentions. Transition metal ions such as silver and copper ions can selectively react with olefins through π-bond complexation between the double bond of olefin and the transition metal ions [3,15]. According to Safarik et al. [16], the predominant complexation of olefin and Ag^+ was a bimolecular reaction that forms $[Ag(C_2H_4)]^+$. Besides, several other kinds of complexation are possible in this system, which forms $[Ag(C_2H_4)_2]^+$, $[Ag_2(C_2H_4)]^{2+}$ and so on. Such complexation is not strong and easy to break by temperature and/or pressure swing, which makes it possible to efficiently separate olefin from paraffin gas streams [3].

Many studies have already revealed considerable insights into the absorption characteristics [11–13,17]. Cho et al. [11] showed that the solubility of ethylene in aqueous $AgNO_3$ solution increases with the increase in pressure and $AgNO_3$ concentration. An increase in temperature can reduce the solubility, but the reaction rate will be increased [13]. Nymeijer et al. found that in a batch reactor the Hatta number and enhancement factor of the absorption with concentrated $AgNO_3$ solutions were 763 and 118, respectively, indicating that the absorption of C_2H_4 is a diffusion-limited process [17]. However, as $AgNO_3$ is not completely dissociated into its ions, the complexation between Ag^+ and ethylene is usually limited by the free Ag^+ concentration in the aqueous solution, especially for low temperature and high salt concentration. Generally, all the studies indicated great potential of using Ag^+ to separate ethylene, which also enabled obviating the need of low temperature operation. Hence, higher efficiency was obtained compared to cryogenic distillation.

It is well known that gas-liquid absorption can be significantly intensified in microreactors [18–22]. Due to the huge interfacial area and short radial diffusion distance in microreactors, the overall mass transfer coefficients can be one or two orders of magnitude higher than in conventional large-scale equipment [18]. For example, CO_2 absorption with amine solutions in microreactors was improved that removal efficiency as high as 90% could be achieved within one second [23,24]. The absorption of ethylene with Ag^+ can also be intensified by microreactors, as the complexation reaction is a fast reaction limited by diffusion rate [17]. Therefore, it is necessary to study the promotion

Nomenclature

a	Specific surface area, m^2/m^3
C	Concentration, mol/L
d	Channel diameter, m
D	Diffusion coefficient, m^2/s
E_A	Enhancement factor calculated by E_∞ and Ha
E_A'	Enhancement factor calculated by experimental data
E_∞	Enhancement factor at infinite reaction rates
H	Henry's constant, kPa
Ha	Hatta number
K	Sechenov constant, L/mol
K_c	Equilibrium constant, L/mol
k	Mass transfer coefficient, m/s
k_{+1}	Kinetic constant of the complexation, $m^3/(mol\cdot s)$
k_L'	Liquid-side mass transfer coefficient of physical absorption, m/s
L	Length of microchannel, m
m	Molecular weight, g/mol
M	Feeding molar ratio of C_2H_4 in the gas to $AgNO_3$ in the liquid phase
P	Pressure, Pa
Q	Flow rate, mL/min

Re	Reynolds number, $Re = du\rho/\mu$
Sc	Schmidt number, $Sc = \mu/(\rho D)$
Sh	Sherwood number, $Sh = k_L d/D$
T	Temperature, K
y	Molar fraction in the gas phase

Greek symbols

ρ	Density, kg/m^3
η	Absorption fraction
χ	Molar fraction of ethylene in solution

Subscripts

cox	Complex $[Ag(C_2H_4)]^+$
e	Experimental
o	Ethane
=	Ethylene
i	Liquid interface
in	Inlet
out	Outlet
L	Liquid
W	Water

effect on the absorption of ethylene in microreactors, as well as the underlying characteristics and mechanism.

The present work reports experimental study of absorption of ethylene from ethylene-ethane mixture in different microchannels. The performance was mainly characterized with absorption fraction (η), molar ratio of absorbed ethylene to $AgNO_3$ in the liquid phase ($[C_2H_4]_L/[AgNO_3]$), and mass transfer coefficient. The effects of channel diameter, channel length, flow rates, absorption temperature and $AgNO_3$ concentration were investigated for providing further design guidance.

2. Experiments

2.1. Experimental setup

The experimental setup is schematically shown in Fig. 1. Gas flow was provided from a gas cylinder and controlled by a mass flow controller (D07-11C, 0–50 mL/min, Beijing Sevenstar Electronics Co., Ltd.,

China). The liquid flow was pumped by a syringe pump (Longer Precision Pump Co., Ltd., China). Both gas and liquid flows were pre-heated to desired temperature by water bath (Julabo Technology (Beijing) Co., Ltd., China, ± 0.1 °C) for absorption and then mixed in a T-mixer with an inner diameter of 0.5 mm. For each test, the microreactor was a single circular capillary microchannel. The fluid mixture leaving the microchannel was separated in a gas-liquid separator made of glass. The pre-heating tubes, the T-mixer, the microchannel and the lower part of the separator were all immersed in the water bath to ensure isothermal absorption. The mole fractions of C_2H_4 and C_2H_6 in the outlet gas were analyzed with a gas chromatography (Agilent Technologies Inc., China). To reduce the absorption from end effect [18], the end of the microchannel was inserted into the gas-liquid separator directly, without any connecting tubes. The volume of the separator was less than 10 mL and the mixture of both phases was separated by gravity. The liquid in the separator was removed continuously to maintain a constant liquid level. Such arrangement enabled a very short contact time between gas and liquid phases in the separator. Therefore, the end
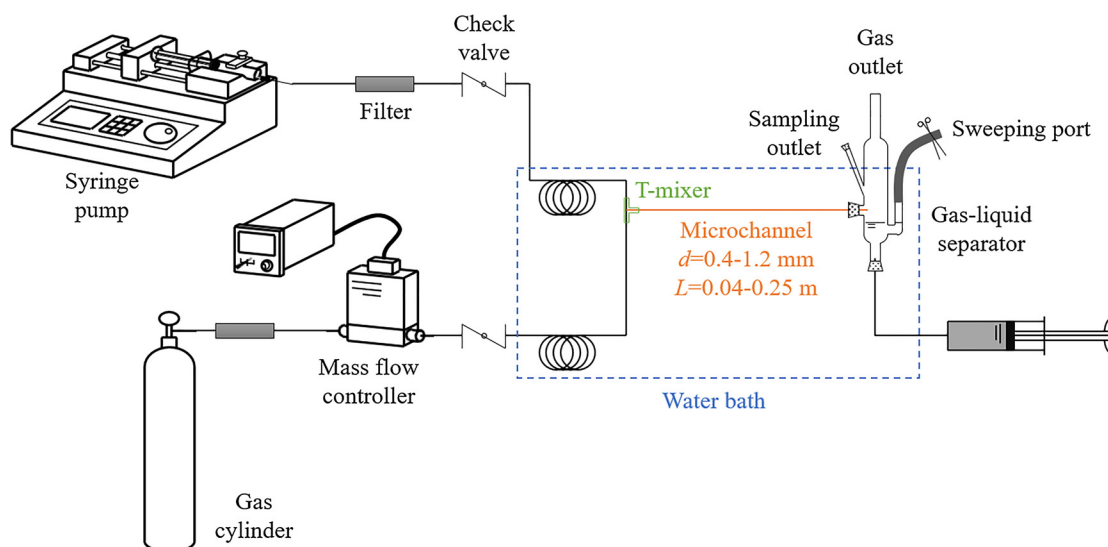

Fig. 1. Schematic of the experimental setup.