



Separation of propylene and propane by functional mixture of imidazolium chloride ionic liquid – Organic solvent – Cuprous salt



Xiaolong Shen^a, Rashid Abro^a, Ibrahim A. Alhumaydhi^{a,b}, Ahmed A. Abdeltawab^c, Abdullah M. Al-Enizi^c, Xiaochun Chen^a, Guangren Yu^{a,*}

^a Beijing Key Laboratory of Membrane Science and Technology & College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

^b National Petrochemical Technology Center, Materials Science Research Institute, King Abdulaziz City for Science and Technology, Riyadh 11442, Saudi Arabia

^c Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

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ABSTRACT

To lower viscosity and possible negative effect on mass/heat transfer in industrial operation, we prepared a new absorption system to separate propylene from propane, i.e., ionic liquids (ILs)-organic solvent-cuprous salt. The absorption system is constructed by IL of 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]); organic solvent of pyridine, N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP); cuprous chloride (CuCl). We experimentally measured the absorption capability and selectivity of such a new system for pure propylene, propane or their mixture at 1–7 bar and 298–318 K. We investigated different factors such as temperature, pressure, species of organic solvent, Cu⁺ concentration and regeneration and recycling of absorbents. The addition of organic solvent significantly lowers the viscosity of absorption system (approximately one order of magnitude lower). Organic solvent interestingly enhances the absorption capability for propylene while suppresses the absorption selectivity slightly. Species of solvent has a huge effect on separation performance. [Bmim][Cl]-pyridine-CuCl gives the best separation performance, e.g., in the absorption of a mixture of 50 mol% propylene and 50 mol% propane, the solubility of propylene in [Bmim][Cl]-pyridine-CuCl-2M (mass ratio of [Bmim][Cl]:pyridine, 10:1) is 0.064 mol/L at 298 K/2 bar while that of propane is 0.0105 mol/L with absorption selectivity of 6.1, which is comparable to some other ILs-Ag⁺ or ILs-Cu⁺ absorption systems. Such an absorption system can be regenerated through temperature and pressure swing and recycled without remarkable activity loss. Therefore, this new system is a good potential absorbent for separating propylene and propane.

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1. Introduction

Propylene and propane are two basic chemicals, especially the former plays an important role in many chemical syntheses and industrial processes [1]. Propylene is generally obtained together with light paraffins such as propane, by steam cracking, fluidized catalytic cracking or alkane dehydrogenation [2,3]. Due to the physicochemical similarity between propylene and propane (e.g., b.p. of propylene, 225.3 K at 1 bar while propane, 230.9 K), their separation heavily depends on low-temperature distillation, which is one of the most difficult and also the most energy-consuming separation processes in the petrochemical industry. Some alternative separation methods for the separation of propylene and propane have been studied such as absorption [4–6], adsorption [6–13] and membrane technology [14,15]. Among them, reactive

absorption of propylene with transition metal salt solution has attracted many attentions due to large propylene capacity and cost-effectiveness.

Previous researches have been focused on organic solvent or water with a transition metal salt (e.g., silver/Ag⁺ or cuprous/Cu⁺ salt), which can form complex selectively with propylene via π -bound interaction [13,15,16–22]. Some examples are aqueous AgNO₃ solution [23,24]; basic solvent composed of CuCl, aniline and DMF [3]; cuprous diketonate [25]. In these processes, volatile loss and contamination of organic solvents are problematic.

Ionic liquids (ILs) have been demonstrated to be ideal solvents for separation of propylene and propane because of their ionic and organic nature together with some desirable properties such as negligible vapor pressure, high thermal and chemical stability, nonflammability and high solvent capacity [26–28]. ILs can dissolve transition metal salt and resultant ILs-metal salt possesses the similar properties listed above. ILs can be used to control the interaction between transition metal (e.g., Ag⁺ or Cu⁺) and

* Corresponding author.

E-mail address: gryu@mail.buct.edu.cn (G. Yu).

Table 1
Solubility of propylene and propane in different absorbents.

Type	Absorbents	P (bar)	T (K)	Propylene (mol/L)	Propane (mol/L)	Selectivity	Ref.
Adsorbents	Cu-BTC tablets	150 ^a	373	5.06 ^c	3.09 ^c	1.63	[7]
	Cu-BTC powder	1	373	6.34 ^c	5.14 ^c	1.23	[8]
	Cu-BTC extrudates	1	373	2.83 ^c	1.91 ^c	1.48	[8]
	AgNO ₃ /SiO ₂	1	343	1.5	0.37	4.05	[34]
Traditional absorbents	CuNO ₃ /ethanolamine	12 ^b	308	4 ^d	–	–	[6]
	Cuprous diketonate	–	–	–	–	10	[25]
	AgBF ₄ solution	1/6	–	0.29/0.7	0.02/0.05	14.5	[29]
Pure ILs	[Bmim][Tf ₂ N]	–	323	11.22 ^e	6.26 ^e	2.048	[30]
	[Emim][Tf ₂ N]	–	323	11.45 ^e	6.51 ^e	2.010	[30]
	[Bmim][BF ₄]	1/6	298	0.08/0.42	0.02/0.15	4	[31]
	[Bmpy][BF ₄]	1/6	298	0.09/0.52	0.04/0.16	2.25	[31]
ILs-Ag ⁺ salt	[Bmim][BF ₄]-AgBF ₄ -0.25M ^f	1/6	298	0.38/0.85	0.04/0.2	9.5	[31]
	[Bmpy][BF ₄]-AgBF ₄ -0.25M	1/6	298	0.51/1.05	0.04/0.21	12.75	[31]
ILs-Cu ⁺ salt	[Bmim][Br]-CuBr-2M	1/6	298	0.13/0.57	0.01/0.075	13	[32]
	[Bmim][Br]-CuCl-2M	1/6	298	0.12/0.42	0.01/0.075	12	[32]
	[Emim][Br]-CuBr-2M	1/6	298	0.11/0.4	0.01/0.054	11	[32]
	[Emim][Br]-CuCl-2M	1/6	298	0.08/0.32	0.01/0.057	8	[32]
	[Bmim][SCN]-CuSCN-1.5M	1/6	298	0.12/0.51	0.012/0.12	10	[33]
	[Emim][SCN]-CuSCN-1.5M	1/6	298	0.09/0.42	0.011/0.085	8.181	[33]
	[Bmim][Cl]-CuCl-2M	1/6	298	0.051/0.32	0.0042/0.048	12.1	This work
	[Bmim][Cl]-pyridine-CuCl-2M	1/6	298	0.064/0.46	0.0105/0.137	6.1	This work

^a kPa.

^b atm.

^c mol/kg.

^d L/L.

^e g/g.

^f [Bmim]BF₄-AgBF₄-0.25M, 0.25M means Ag⁺ concentration is 0.25 mol/L.

counteranion (X[−]) in ILs-metal salt system. The addition of ILs can make the transition metal cation chemically more active in forming transition metals-olefin complex [29–33]. Recently, it was observed the solubility of propylene in ILs-Ag⁺ salt or ILs-Cu⁺ salt is much higher than that in pure ILs and is comparable to that in aqueous-Ag⁺. Some previous solubility results of propylene and propane in ILs and ILs-metal salt are summarized in Table 1.

Compared with Ag⁺ salt, Cu⁺ salt is much cheaper. In our previous study, we prepared a series of ILs-Cu⁺ salt (e.g., [Emim][Br]-CuBr, [Bmim][Br]-CuBr [32], [Bmim][SCN]-CuSCN, [Bmim][SCN]-CuSCN [33]) and investigated the separation capability for propylene from propane, which showed comparable or higher absorption capability and selectivity than ILs-Ag⁺ salt [29,30]. In this work, a new absorption system is prepared, [Bmim][Cl]-organic solvent-CuCl, where organic solvent is pyridine, N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP). The addition of organic solvent is expected to lower the viscosity of absorption system and enhance mass/heat transfer in absorption process. We determine experimentally the solubility of propylene, propane, or their mixture in [Bmim][Cl]-CuCl and [Bmim][Cl]-organic solvent-CuCl at 1–7 bar and 298–318 K, and investigate a variety of factors such as temperature, pressure, Cu⁺ concentration and organic solvent species. This work will show such an IL-solvent-Cu⁺ salt absorption system is one new class of preferable reactive absorbents for separation of propylene and propane.

2. Experimental section

2.1. Chemicals

Propylene (99.5v%) and propane (99.5v%) were purchased from Sinopec Beijing Yanshan Co. Ltd. N-methylimidazole (A.R.) was purchased from Shanghai Senhao Fine Chemicals Co. Ltd. 1-chlorobutane (≥98%) was purchased from Beijing Yili Fine Chemicals Co. Ltd. DMF (≥99%), NMP (≥99%) and pyridine (≥99%) were purchased from Beijing Beihua Fine Chemicals Co.

Ltd. Cuprous chloride (≥99%) was supplied by Tianjin Fuchen Chemical Reagents Factory. Nitrogen gas (≥98.5%) was supplied by Beijing Yuandong Weiye Gas Factory.

2.2. Preparation of absorbent

[Bmim][Cl] is prepared first, and the synthesis schematic is as follows [35]. 46.285 g (0.5 mol) of 1-methylimidazole and 45.16 g (0.55 mol) of *n*-butylchloride are added to a dry round-bottom flask under nitrogen atmosphere, and react at 353 K for 48 h. The resultant pale yellow, viscous liquid is washed with ethyl acetate, and the remained ethyl acetate is removed by rotary evaporation. The crude ILs is put into refrigerator for 8 h and the final white crystal of [Bmim][Cl] is obtained. [Bmim][Cl]-CuCl is prepared by mixing [Bmim][Cl] and CuCl under nitrogen atmosphere at 348 K for 4 h. The synthesis procedure for [Bmim][Cl]-organic solvent-CuCl is similar to that for [Bmim][Cl]-CuCl. We take [Bmim][Cl]-pyridine-CuCl as example, and the synthesis procedure is as follows. [Bmim][Cl] and pyridine with different mass ration are added to a dry round-bottom flask under nitrogen atmosphere at first, and then we put CuCl into flask and make them react at 348 K for 4 h.

2.3. Apparatus and measurement

A diagram of the equipments used for determining gas solubility into absorbent is given in Fig. 1. The equipment consists of a stainless steel gas buffer reservoir (196.7 ml) and a stainless steel absorption chamber (112.3 ml) with magnetic stirring. Both tanks are put into a thermostatic water bath to control temperature. The temperature is monitored by K-type thermocouple TS404 (Beijing Tiantai Tech. Co. Ltd) with an accuracy of 0.1 K; the pressure is measured by pressure transducer TS200-T1 (Beijing Tiantai Tech. Co. Ltd) with an accuracy of 0.001 bar. Temperature and pressure are recorded by a paperless recorder TS606 (Beijing Tiantai Tech. Co. Ltd). Before the absorption experiment, the seal

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