AIChE Journal

DOI10.1002/aic.17106

Promoted absorption of CO at high temperature by cuprous-based ternary deep eutectic solvents

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Abstract

Achieving efficient dissolution of carbon monoxide (CO) in the solvent is very helpful for the implementation of carbonylation reaction at ambient pressure. However, almost all of common solvents show very low solubilities of CO at high temperature. Herein, a series of cuprous-based ternary deep eutectic solvent (DES) was prepared by mixing imidazolium hydrochloride with CuCl and $ZnCl_2$. The ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ exhibited very large CO absorption capacity (0.075 mol mol^{-1}, 1 bar) even at a high temperature (353.2 K), which is superior to all of the reported absorbents. Moreover, the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ could further promote the reactive absorption of CO to conduct the aminocarbonylation reaction effortlessly at ambient pressure, and thus the targeted products benzamides were obtained in 70~97

Received: Apr 21, 2020;Revised: Sep 01, 2020;Accepted: Oct 14, 2020

yields. We believe that this finding opens a new way to design advanced solvents for efficient capture of CO at high temperature.

TOPICAL HEADING Separations: Materials, Devices and Processes

KEYWORDS carbon monoxide, absorption, high temperature, deep eutectic solvents

INTRODUCTION

Carbon monoxide (CO) as a toxic gas is serious harm to the environment and human health. It shows very high affinity with hemoglobin, which can quickly become life-threatening by reducing blood oxygen content. Also, the burning of CO has increased the CO_2 emission to cause a runaway greenhouse effect. CO is mainly present in the tail gas of many industrial processes, such as steam reforming, partial oxidation, and steelmaking process.[1,2] On the other hand, CO is an important C1 resource and raw material for a wide range of chemical productions by carbonylation process, including methanol, acetic acid, and amide, etc.[3] Therefore, research into the recovery and reuse of CO in the tail gas has received increased attention with the sustainable development of carbon resources.

Untill now, some methods have been developed for separation and purification of CO by liquid solvent absorption, such as ammoniacal cuprous chloride and aromatic $CuAlCl_4$ solution (COSORB).[4] However, these methods exhibit low capacity (e.g. 0.18

mmol CO per milliliter of $CuAlCl_4$ solution) and usually cause volatile organic compound emissions. As a kind of promising green solvents, ionic liquids (ILs) consists of organic cation and inorganic or organic ions with low melting point (e.g. below 298 K).[5,6] They have received much attention owing to their specific properties such as negligible nonvolatility, good thermal stabilities, high dissolvability, and a wide range of liquid temperatures.[7,8] Thus the unique properties of ILs provide new opportunities to capture CO.[9-11] For example, Laurenczy and co-workers reported the absorption of CO by an IL [Bmim][PF_6] with a solubility of 3.0×10^{-3} mol_{CO} mol_{IL}^{-1} at ambient condition.[9] Tao et al. proposed carbanion-functionalized ILs for highly efficient and reversible capture of CO, and the absorption capacity achieved 0.046 mol_{CO} mol_{IL}^{-1} at 293.2 K and 1 bar.[10] Subsequently, Wu et al. synthesized a cuprous IL [TEA][$CuCl_2$] for CO capture with the capacity of 0.078 mol_{CO} mol_{IL}^{-1} at 303.2 K and 1 bar.[11] These progress demonstrate that compared with traditional absorbents, tuning the cations/anions of ILs could achieve efficient capture of CO at room temperature.

As well known, ILs are composed primarily of one type of discrete anion and cation. In contrast, deep eutectic solvents (DESs) are eutectic mixtures that contain a variety of anionic and/or cationic species.[12] DESs are usually formed by the complexation of a quaternary ammonium salt with a metal halide salt or hydrogen bond donor (e.g. amide, polyol, carboxylic acid).[13] DESs not only share many properties and characteristics with

ILs, but also show several advantageous of easy preparation, non-purified, and low cost compared with ILs. Thus, DESs are widely regarded as a new class of IL analogues. Many previous studies have demonstrated the applications of DESs in the absorption of CO_2,[14] NH_3,[15,16] and H_2S.[17] Up to now, there has been less mention of using DESs for efficient absorption of CO. In addition, it is known that almost all of common solvents show very low CO solubility at a high reaction temperature. Then most industrial carbonylation processes have to be carried out at high pressure (e.g., 10~30 bar) in an effort to enhance the solubility of CO in liquid phase. Thus, it is significantly interesting to develop novel DESs absorbents with good CO solubility at high temperature.

It is validated from a previous work[18] that the addition of $ZnCl_2$ into a DES [BMIM]Cl/CuCl could activate the Cu^+ ion to enhance the capture of ethylene. This makes us aware that $ZnCl_2$ and CuCl would be helpful for efficient absorption of CO at high temperature. Herein, a series of cuprous-based ternary DESs was prepared by simply mixing imidazolium hydrochloride with CuCl and $ZnCl_2$ at different molar ratios. Then their physical properties such as density and viscosity were determined. Moreover, high-temperature absorption of CO by these ternary DESs and their thermodynamic behavior were studied in detail. In addition, the performance of the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ for reactive absorption of CO was further

investigated under ambient pressure.

EXPERIMENTAL

Materials

1-Butylimidazole hydrochloride ([BimH]Cl, ≥99%) and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl, ≥99%) were purchased from the Centre of Green Chemistry and Catalysis, LICP, CAS. Anhydrous CuCl and $ZnCl_2$ were obtained from Shanghai Adamas-Beta. CO, H_2, and N_2 with high purity (≥99.999%) were supplied from Jiangxi Huate Special Gas Co., Ltd. All the chemicals were highest purity grade and used directly without further purification.

Preparation of cuprous-based ternary DESs

Cuprous-based ternary DESs were prepared and stirred by mixing of imidazolium hydrochloride, cuprous chloride, and zinc chloride with different molar ratios (Table 1). For example, the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ was synthesized by mixing of [BimH]Cl, CuCl, and $ZnCl_2$ with a molar ratio of 1:1:1 at room temperature for 3 h. The preparation of the other two DESs [BimH]Cl-CuCl-0.8$ZnCl_2$ and [BimH]Cl-CuCl-1.2$ZnCl_2$ were according to the above-mentioned procedure excepting the molar ratio of 1:1:0.8 and 1:1:1.2. After that, DESs were dried at 353.2 K and 0.1 kPa for 12 h to remove any possible traces of water.

Determination of physical properties and characterization

The water content of as-prepared cuprous-based ternary DESs was measured on an instrument Mettler-Toledo DL32, and the value of water content was detected to be less than 0.05%. The densities of cuprous-based ternary DESs were recorded on an Anton Paar DMA4500 densitometer with a precision of 1×10^{-5} g cm^{-3} from 293.2-353.2 K. The viscosities of cuprous-based ternary DESs were performed on Brookfield DV II+ Pro viscometer from 313.2-353.2 K with the thermal equilibrium time about 0.5 h. Cuprous-based ternary DESs were recorded on an electrospray ionization mass spectrometry (ESI-MS) instrument (Agilent1290/maX impact) with negative ion modes. Fourier-transform infrared spectroscopy (FT-IR) spectra were carried on a NEXUS870 IR spectrometer. Raman spectra were characterized by a LabRAM HR spectrometer with an argon laser at 632 nm as an excitation source. Thermal analysis was performed on the TG (PerkinElmer Diamond TG/DTA) by heating from 298 to 1073 K at a scan rate of 10 K/min under nitrogen atmosphere with a flow rate of 50 ml/min.

Measurement of CO absorption

The schematic of absorption process is shown in Figure S1 in the Supporting Information. The apparatus for determining the solubility of CO in a cuprous-based ternary DES is very close to that reported in our previous work.[10,19] The device contains two chambers made by 316 L stainless steel. The big one is used as a gas reservoir, and

the small one is used as an equilibrium absorption cell. The volumes of these two chambers are V_1 and V_2, respectively. The pressure sensor Wideplus-8 transducers are employed to record the pressures in the two chambers with an uncertainty of 0.1 kPa by a specialized computer at 1 minute intervals. In a typical experiment, the two chambers were immersed in a water bath at 353.2 K with the accuracy of ±0.1 K. A known mass of cuprous-based ternary DES sample (*m*) was charged into the equilibrium cell, and then the whole apparatus was completely evacuated to exhaust the air, and the residual pressure was detected to be 0~0.2 kPa. CO from the cylinder was loaded into the gas reservoir to a pressure of P_1 (e.g. 260 kPa) with a flow rate of 25 ml/min. The needle valve connecting the two chambers was turned on to introduce partial CO (e.g. 110 kPa) into the equilibrium cell, and then the absorption of CO in the cuprous-based ternary DES sample was progressed with the decrease of pressure in the equilibrium cell. When the two chambers pressure remained unchanged for up to 1 h, it was conceivable to approach the absorption equilibrium. The pressure in the gas reservoir was recorded as P_1', as well as the pressure in the equilibrium cell was denoted as P_2. The amount of CO dissolved in cuprous-based ternary DES sample (*n*) was calculated using Eq. 1.

$$n = \rho_1 V_1 - \rho_1' V_1 - \rho_2 (V_2 - m/\rho_{DES}) \quad (1)$$

where ρ_1 denotes the density of CO at P_1 and T (mol·cm^{-3}), ρ_1' is the density of CO at P_1' and T, ρ_2 is the density of CO at P_2 and T (mol·cm^{-3}), and ρ_{DES} denotes the density of cuprous-based ternary DES in g cm^{-3} at a temperature of T. The density values of CO were obtained from the NIST Chemistry WebBook.[20] CO solubility was calculated and expressed as mol CO per mol DES. Each experiment was repeated three times, and the average value was taken as the experimental results. Continuous detection of CO solubilities at higher equilibrium pressures was conducted by adding more CO into the equilibrium cell to achieve another new equilibrium. In addition, CO-loaded [BimH]Cl-CuCl-1.0$ZnCl_2$ was heated to 383.2 K for desorbing CO under a vacuum of 0.1 kPa for 2 h. Then the regenerated [BimH]Cl-CuCl-1.0$ZnCl_2$ was reused again for testing the absorption of CO.

RESULTS AND DISCUSSION

Physical and thermal properties

Three cuprous-based ternary DESs ([BimH]Cl-CuCl-0.8$ZnCl_2$, [BimH]Cl-CuCl-1.0$ZnCl_2$, and [BimH]Cl-CuCl-1.2$ZnCl_2$) were easily prepared from simple mixing of imidazolium hydrochloride with CuCl and $ZnCl_2$ in quantitative yields. It is known that the densities of these three DESs are required to calculate the CO solubility by Eq. 1, as well as their viscosities are related to the absorption rate of CO.[7,21] Thus, the

viscosities and densities of these three ternary DESs at different temperatures were measured and the results are shown in Figure 1. As expected, the density value decreased linearly with the increase of temperature, while the viscosity decreased exponentially. For example, the viscosity of [BimH]Cl-CuCl-1.0$ZnCl_2$ could go down smoothly below 300 cP at 353.2 K, even though they have very high viscosity at room temperature. This characteristic endows the ternary DES with good fluidity for capture of CO at high temperature. Moreover, the effect of shear rate on the dynamic viscosities of [BimH]Cl-CuCl-1.2$ZnCl_2$, [BimH]Cl-CuCl-1.0$ZnCl_2$, and [BimH]Cl-CuCl-0.8$ZnCl_2$ were further investigated, as shown in Figure S2 in the Supporting Information. The results indicated that these three ternary DESs showed a clear trend towards non-Newtonian shear-thinning behavior, with obviously decreasing viscosity at high shear rates. The non-Newtonian behavior can be derived from the non-linear dependence of the viscosity on the shear rate.[22,23] In addition, the viscosities and densities data can be fitted by Eqs. 2 and 3, respectively. Fitting results are listed in Table S1 in the Supporting Information.

$$\rho = A_1 + A_2 T \quad (2)$$

$$\eta = \eta_0 * \exp\left(\frac{D}{T - T_0}\right) \quad (3)$$

The thermal stability of cuprous-based DESs is very crucial to capture CO at high temperature, and then thermogravimetric analysis results are shown in Figure S3 in the

Supporting Information. It is found that the decomposition temperatures for the 5 wt% (T5%) mass loss of [BimH]Cl-CuCl and [BimH]Cl-CuCl-1.0$ZnCl_2$ were 510 K and 556 K, respectively. This indicates that these two cuprous-based DES exhibit good thermal stability. Compared with the binary DES [BimH]Cl-CuCl, the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ shows high decomposition temperature because of the addition of $ZnCl_2$.

CO absorption capacity at high temperature

To evaluate their CO capture ability, the solubilities of CO in various DESs at high temperature were measured. As seen in Figure 2, the ternary DES [BimH]Cl-CuCl-*x*$ZnCl_2$ (*x* = 0.8, 1.0, 1.2) exhibited very high CO absorption capacity at 353.2 K and 1 bar, and were obviously higher than the performance of binary DESs [BimH]Cl-CuCl and [BimH]Cl-$ZnCl_2$. For example, [BimH]Cl-CuCl showed a CO solubility of 0.0075 mol mol^{-1} at 353.2 K and 1 bar. Another ternary DES [BimH]Cl-CuCl-1.0$AlCl_3$ also exhibited the CO absorption capacity of 0.0089 mol mol^{-1}. In contranst, 0.075 mol of CO per mol of DES was obtained for [BimH]Cl-CuCl-1.0$ZnCl_2$ under the same condition. These results demonstrate that $ZnCl_2$ plays a key role in excellent CO solubility at a certain high temperature. Moreover, the additive amount of $ZnCl_2$ had also affect on the CO capacity of [BimH]Cl-CuCl-*x*$ZnCl_2$. It is found that [BimH]Cl-CuCl-1.0$ZnCl_2$ exhibited the highest CO absorption capacity compared with

[BimH]Cl-CuCl-0.8$ZnCl_2$ and [BimH]Cl-CuCl-1.2$ZnCl_2$ (Figure 2). This is because the viscosity of [BimH]Cl-CuCl-1.0$ZnCl_2$ was only 266 cP and had not changed obviously after CO absorption. On the contrary, despite the temperature of 353.2 K, [BimH]Cl-CuCl-1.2$ZnCl_2$ still had a very large viscosity of 655 cP due to the maximum additional amount of $ZnCl_2$ (Figure S4, Supporting Information). The bad fluidity of [BimH]Cl-CuCl-1.2$ZnCl_2$ caused large transfer resistances during the process of CO capture and thereby to result in a relatively low CO solubility.[24]

Moreover, the effect of pressure on the absorption of CO by [BimH]Cl-CuCl-*x*$ZnCl_2$ was further studied. As shown in Figure 3, it is obvious that the absorption of CO in [BimH]Cl-CuCl-*x*$ZnCl_2$ was physical type, as well as the solubility increased linearly with the pressure.[21,25] When the partial pressure increased from 1 to 3 bar, the CO absorption capacity of [BimH]Cl-CuCl-1.0$ZnCl_2$ improved significantly from 0.075 to 0.198 mol mol^{-1}. This result indicates that high pressure is beneficial to the capture of CO, which is good argree with the reported results from previous studies.[21,24,26] In addition, Table 2 summarizes the CO capture capacities in other absorbents reported in the references, including normal ILs and cuprous-based ILs.[9-11,21,26,27] It is found that the CO solubility in the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ was superior to most other solvents, even though the absorption temperature of the former was remarkably higher than the latter.

In addition, the solubilities of pure N_2, H_2, and CO_2 in the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ were further measured at 353.2 K and 1 bar to evaluate the ideal selectivity of CO capture (Figure 4). Compared to efficient absorption of CO, [BimH]Cl-CuCl-1.0$ZnCl_2$ showed extremely low capacities for capturing N_2, H_2, and CO_2 at 353.2 K and 1 bar. The idea selectivity S (1/1) of CO/N_2, CO/H_2, and CO/CO_2 were calculated up to 9.3, 16.6, and 15.7, respectively, which is much higher than most of the common ionic liquids such as [hmim][$CuCl_2$] and [bmim][Tf_2N].[26-28]

Promoted role of $ZnCl_2$

To clarify the role of $ZnCl_2$ for promoting absorption of CO, FT-IR and electrospray ionization mass spectrometry (ESI-MS) characterizations were performed and analyzed as shown in Figures 5. Compared with fresh DESs samples, the FT-IR spectra of CO-loaded [BimH]Cl-CuCl-1.0$ZnCl_2$ and [BimH]Cl-CuCl discovered new peaks at 2112 and 2088 cm^{-1} (Figure 5a), respectively, which was ascribed to the stretching vibration of captured CO. Compared to fresh CO (2143 cm^{-1}),[29-31] the vibrational frequency of absorbed CO was slightly red-shifted, implying the physical absorption of CO by cuprous-based DESs.[21,32]

Moreover, Figure 5b shows the ESI-MS results of the anion species of [BimH]Cl-CuCl-1.0$ZnCl_2$ and [BimH]Cl-CuCl. It is found that [BimH]Cl-CuCl had two kinds of *m*/*z* peaks at 134.86 and 232.76, which is assigned to the anion of $CuCl_2^-$ and $Cu_2Cl_3^-$,

respectively. For [BimH]Cl-CuCl-1.0$ZnCl_2$, three kinds of *m*/*z* peaks at 134.86, 170.83, and 232.76 were detected and assigned to $CuCl_2^-$, $ZnCl_3^-$, and $Cu_2Cl_3^-$, respectively.[33,34] That is to say, compared with the anion species of [BimH]Cl-CuCl, the peak of $ZnCl_3^-$ was dominant in [BimH]Cl-CuCl-1.0$ZnCl_2$ and the peak intensities of $CuCl_2^-$ and $Cu_2Cl_3^-$ became significantly weak. This finding is consistent with the previous study by Yang et al.,[18] which reveals that the Cu−Cl bond was weakened with the addition of $ZnCl_2$ and the electron transferred from a Cl^- ion of $CuCl_2^-$ to the Zn^{2+} ion. As a result, the Cu^+ ion can be activated by the weakening of the Cu−Cl bond to enhance the absorption of CO in [BimH]Cl-CuCl-1.0$ZnCl_2$ at high temperature.

Thermodynamic analysis

The above-mentioned data demonstrate that the capture of CO by [BimH]Cl-CuCl-*x*$ZnCl_2$ is a typical physical absorption process. It is well known that the physical absorption of a gas in a solvent usually complies with Henry's law. Thus, the Henry's law was employed for fitting the data of CO solubility:

$$H_{\mathrm{m}}(T,P) = \lim_{x_{\mathrm{CO}}\to 0} \frac{f^{\mathrm{g}}}{x_{\mathrm{CO}}} \approx \frac{P}{x_{\mathrm{CO}}} \qquad (4)$$

In Eq. 4, x_{CO} is the molality of CO absorption capacity in the DES in mol·mol^{-1}; P is the equilibrium pressure of CO in kPa; f^g is the fugacity of CO in kPa; and $H_m(T, P)$ is the Henry's law constant of CO in terms of molarity in kPa. Then, the absorption isotherms of CO in [BimH]Cl-CuCl-*x*$ZnCl_2$ were measured at temperatures from 333.2

to 353.2 K and pressures from 0 to 5.0 bar. The solubilities data and fitting linear lines correlated by Eq. 4 are shown in Figure 6. The fitting parameters of Henry's constants are also summarized in Table S2 in the Supporting Information. It is seen that the values of H_m at 333.2−353.2 K varied from 445.0 to 778.4 kPa, and all the correlation coefficients R^2 were larger than 0.99. This demonstrates that the absorption behavior of CO in the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ had a very good agreement with the Henry's law. The pressure-dependent Eq. 4 is considered to be an appreciate model for the describtion of CO absorption at high temperature.

Furthermore, the interaction between CO and the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ can be evaluated in terms of enthalpy of solution (ΔH_{sol}). Through drawing a linear fit of ln H_m with $1/T$, the value of ΔH_{sol} was calculated by Eq. 5, as shown in Figure 7. Subsequently, the Gibbs free energy change (ΔG_{sol}) and entropy change (ΔS_{sol}) were calculated by Eqs. 6 and 7, respectively.

$$\frac{\partial \ln H_m}{\partial T} = -\frac{\Delta H_{sol}}{RT^2} \quad (5)$$

$$\Delta G_{sol} = -\frac{RT \ln(H_m(T,P))}{P^0} \quad (6)$$

$$\Delta S_{sol} = \frac{\Delta H_{sol} - \Delta G_{sol}}{T} \quad (7)$$

It is found that the values of ΔH_{sol} for [BimH]Cl-CuCl-1.0$ZnCl_2$ was –22.67 kJ mol^{-1}. Also, the values of ΔG_{sol} and ΔS_{sol} were – 219.2 J mol^{-1} and –63.6 J mol^{-1} K^{-1} at 353.2 K, respectively. Thereby, the value of ΔH_{sol} for [BimH]Cl-CuCl-1.0$ZnCl_2$ was little

more than the hydrogen bonding energy range from −10 to −20 kJ mol^{-1},[35,36] again confirming the physical absorption of CO in the DES [BimH]Cl-CuCl-1.0$ZnCl_2$.

Reactive absorption of CO

Reactive absorption is a unit operation that integrates the gas absorption in liquid solutions with real-time chemical reactions in a single apparatus. Also, the carbonylation of CO is recognized as a powerful tool to produce value-added carbonyl compounds. Thus, the strategy for CO absorption and utilization at high temperature was explored for the production of benzamide using iodobenzene, amine, and CO as original materials. The detailed procedure was given in the Supporting Information. It is seen from Table 3 that the absorbent [BimH]Cl-CuCl-1.0$ZnCl_2$ could efficiently absorb CO into the liquid mixture and simultaneously promote the captured CO to react with iodobenzene and diethylamine at 373.2 K. As a result, the product N,N-diethyl benzamide was obtained with a yield of 97%, even though the reaction pressure of CO was as low as 1 bar. Moreover, the reactive absorption of CO with other secondary amines were also examined to obtain various benzamide products with excellent yields (Table S3, Supporting Information). However, compared with [BimH]Cl-CuCl-1.0$ZnCl_2$, the binary DES [BimH]Cl-CuCl and CuCl-$ZnCl_2$ displayed very low yields of N,N-diethyl benzamide because of their poor solubilities of CO. It is also indicated that previous results relied on very high pressure (5~20 bar) of CO in the absence of a

CO absorbent (Table S4, Supporting Information).[37-40] Thus, the reactive absorption of CO by [BimH]Cl-CuCl-1.0$ZnCl_2$ can dramatically decrease the pressure and efficiently promote carbonylation reaction to obtain 70~97 yields.

Recycle of [BimH]Cl-CuCl-1.0$ZnCl_2$

To evaluate the recyclability of [BimH]Cl-CuCl-1.0$ZnCl_2$ for CO absorption, the absorption-desorption cycles were run for 12 times, and the results are shown in Figure 8. It is found that the absorption of CO in [BimH][Cl]-CuCl-$ZnCl_2$ was completely reversible, and the CO absorption capacities had no obvious change during 12 cycles. In addition, the FT-IR spectra of [BimH]Cl-CuCl-$ZnCl_2$ after 12 cycles was compared with that of the original sample (Figure S5). The typical characteristic bands remained almost unchanged, indicating that [BimH]Cl-CuCl-$ZnCl_2$ is stable enough to be recycled.

CONCLUSIONS

In summary, we have successfully prepared three cuprous-based ternary DESs by mixing [BimH]Cl with CuCl and $ZnCl_2$. It is demonstrated that the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ exhibited a very high capacity of up to 0.075 mol CO per mol DES and excellent reversibility (>12 cycles) at 353.2 K and 1 bar, which is superior to many cuprous absorbents and ILs. Furthermore, the beneficial role of $ZnCl_2$ for

promoted absorption of CO at high temperature was clearly explained, in which the addition of $ZnCl_2$ could weaken the Cu−Cl bond and activate the Cu^+ ion to enhance CO absorption capacity. In addition, the ternary DES [BimH]Cl-CuCl-1.0$ZnCl_2$ could dramatically decrease the pressure and efficiently promote reactive absorption of CO to produce carbonyl compounds benzamides with 70~97 yields. The finding has great potential to achieve the efficient absorption and utilization of CO at high temperature but mild pressure.

ACKNOWLEDGMENTS

We are grateful for the financial support from the National Natural Science Foundations of China (Nos. 21566011, 31570560), the Natural Science Foundations of Jiangxi Province (No. 20192ACBL20025), and the Key Research and Development Program of Jiangxi Province (No. 20202BBGL73118).

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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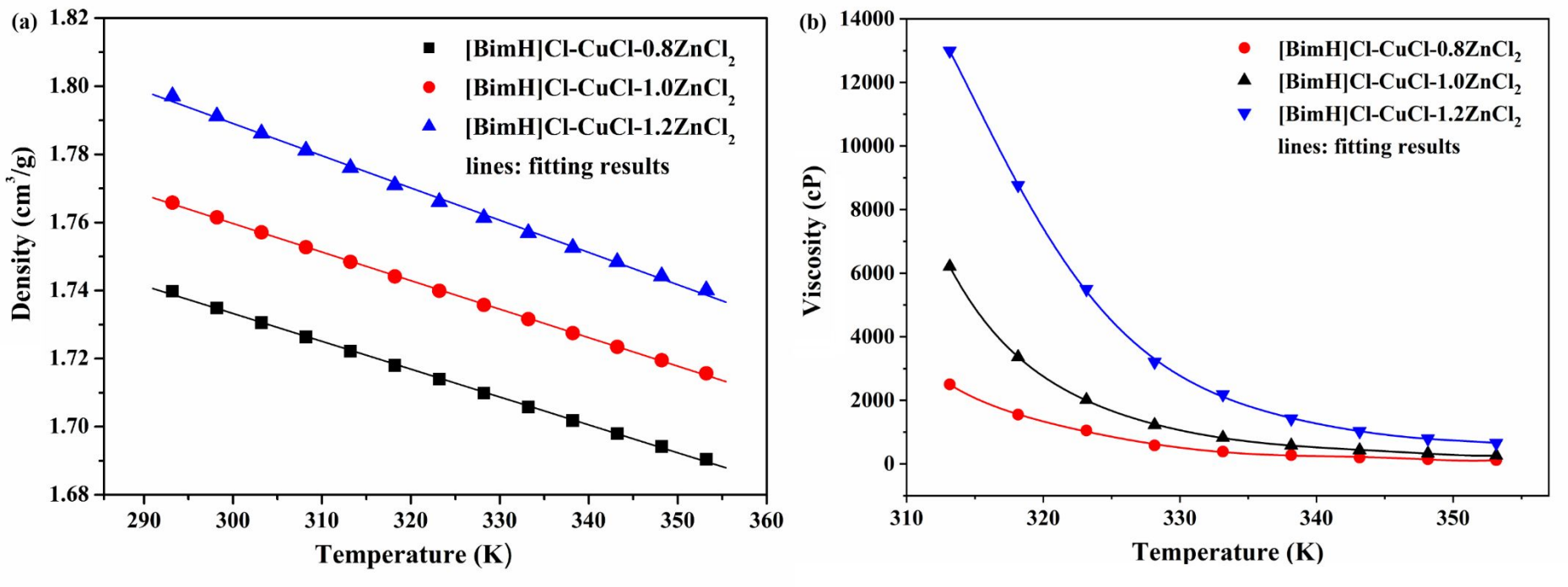


Figure 1. Densities (a) and viscosities (b) of cuprous-based ternary DESs at different temperatures.

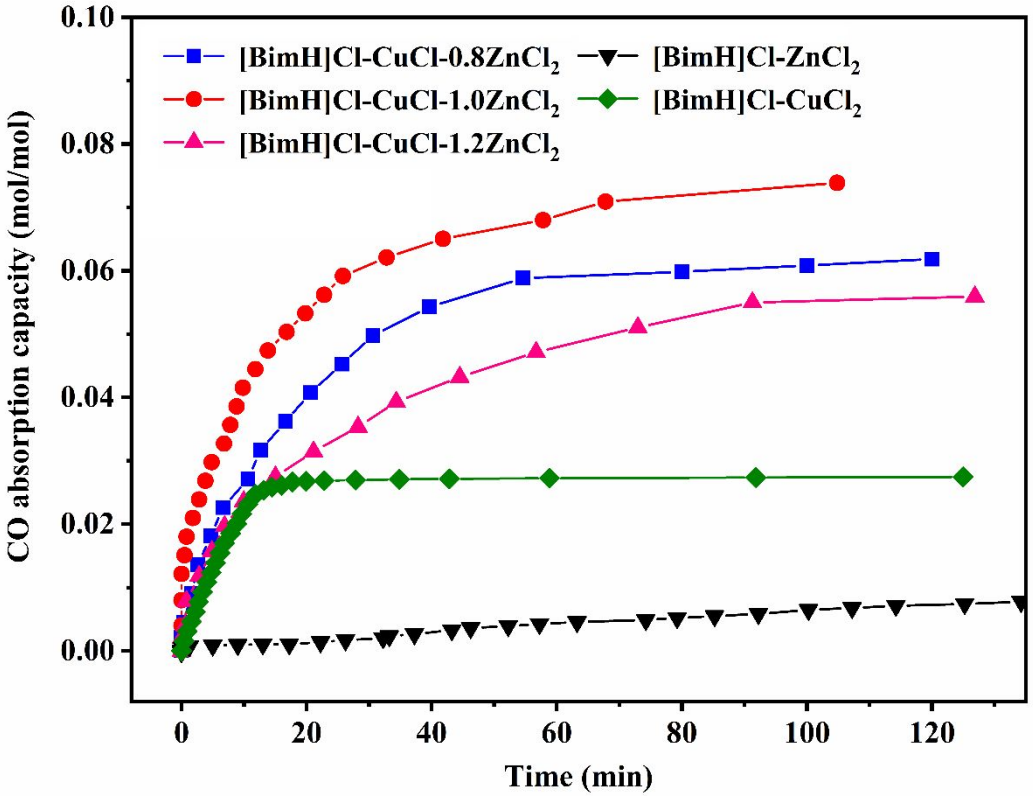


Figure 2. CO solubilities in various DESs at 353.2 K and 1 bar.

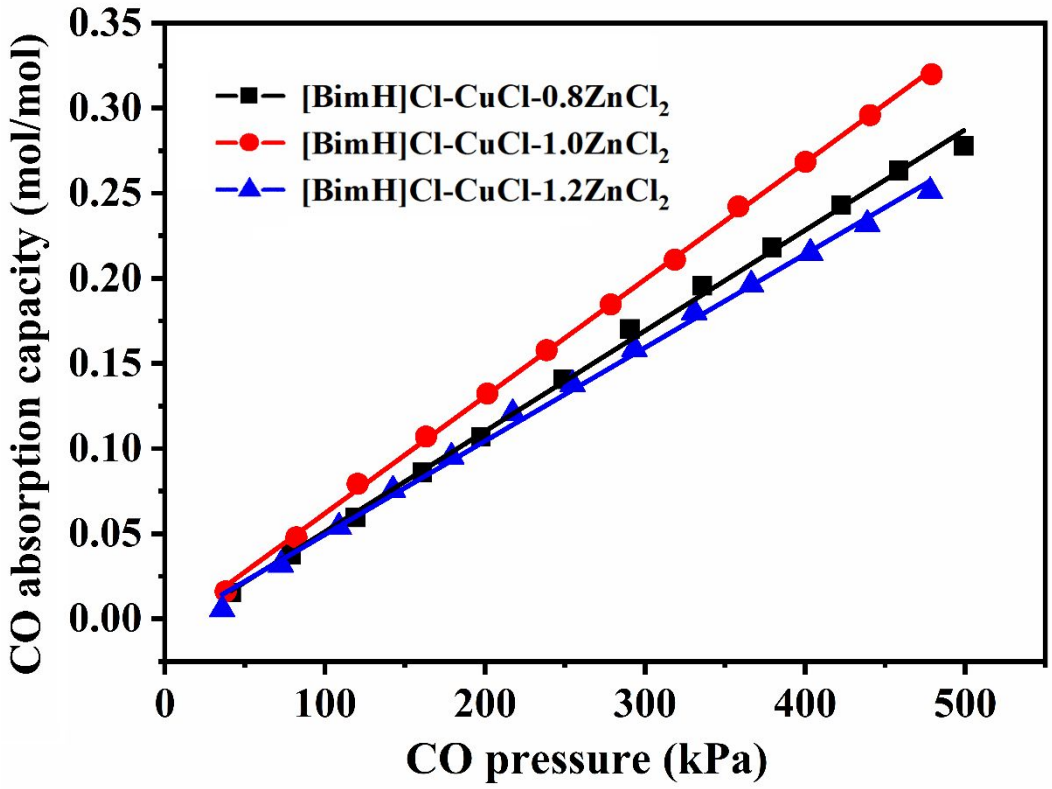


Figure 3. The effect of CO partial pressure on the absorption capacity of cuprous-based ternary DESs at 353.2 K.

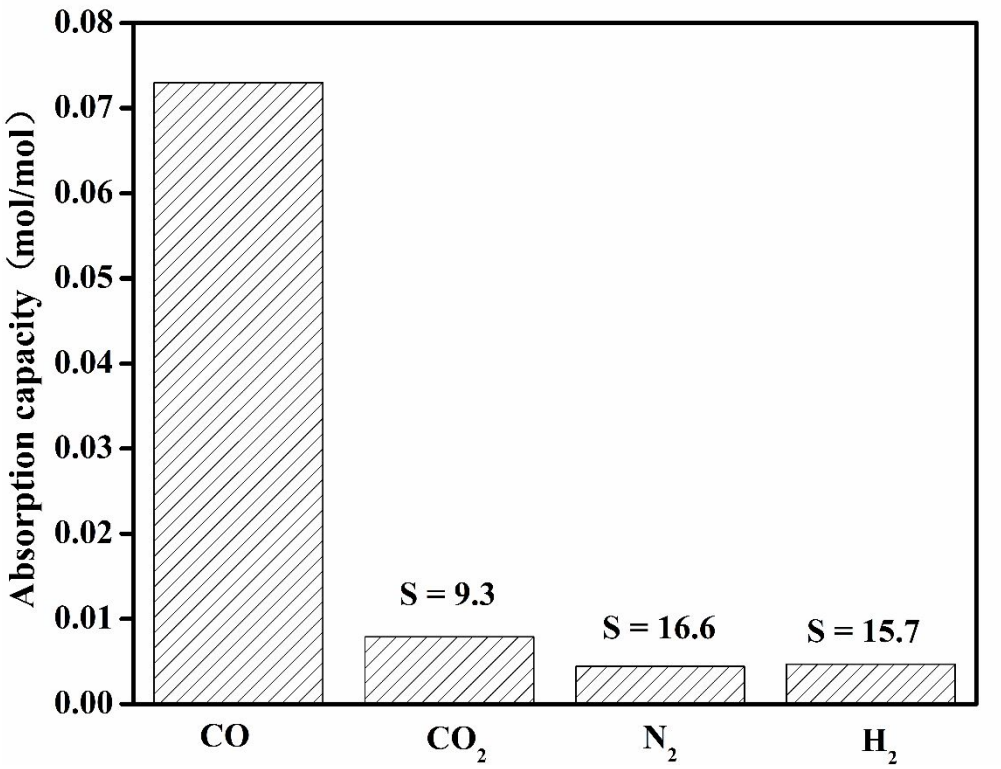


Figure 4. Absorption of CO, CO_2, N_2, and H_2 in [BimH]Cl-CuCl-1.0$ZnCl_2$ at 353.2 K and 1 bar.

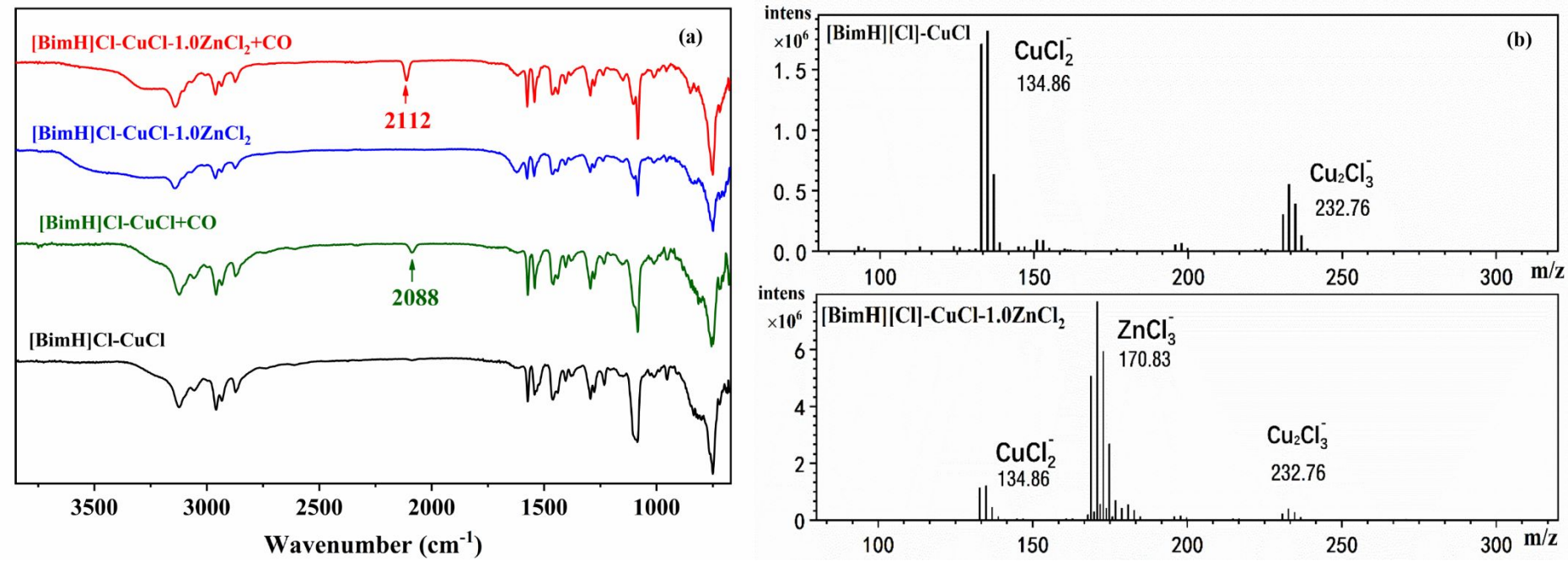


Figure 5. (a) FT-IR spectra of cuprous-based DESs before and after CO absorption. (b) ESI-MS analysis for anion species of cuprous-based DESs.

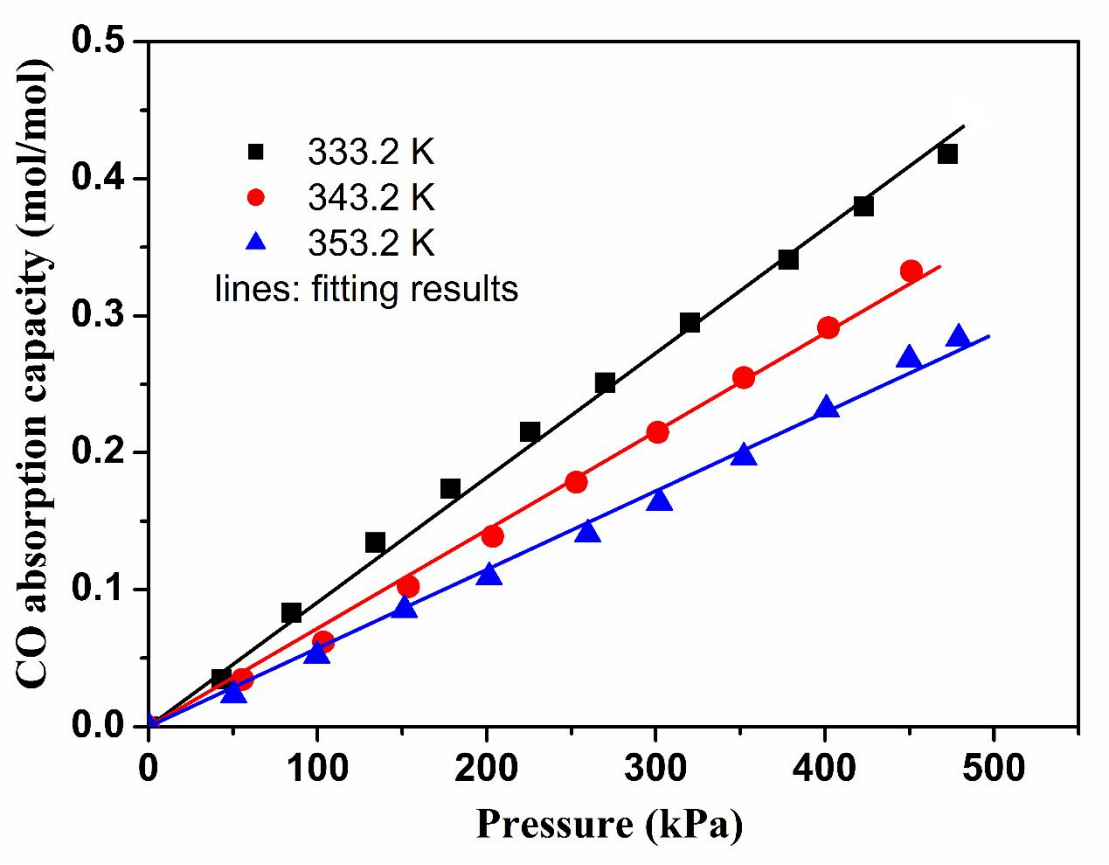


Figure 6. Solubilities of CO in [BimH]Cl-CuCl-1.0$ZnCl_2$ at different temperatures.

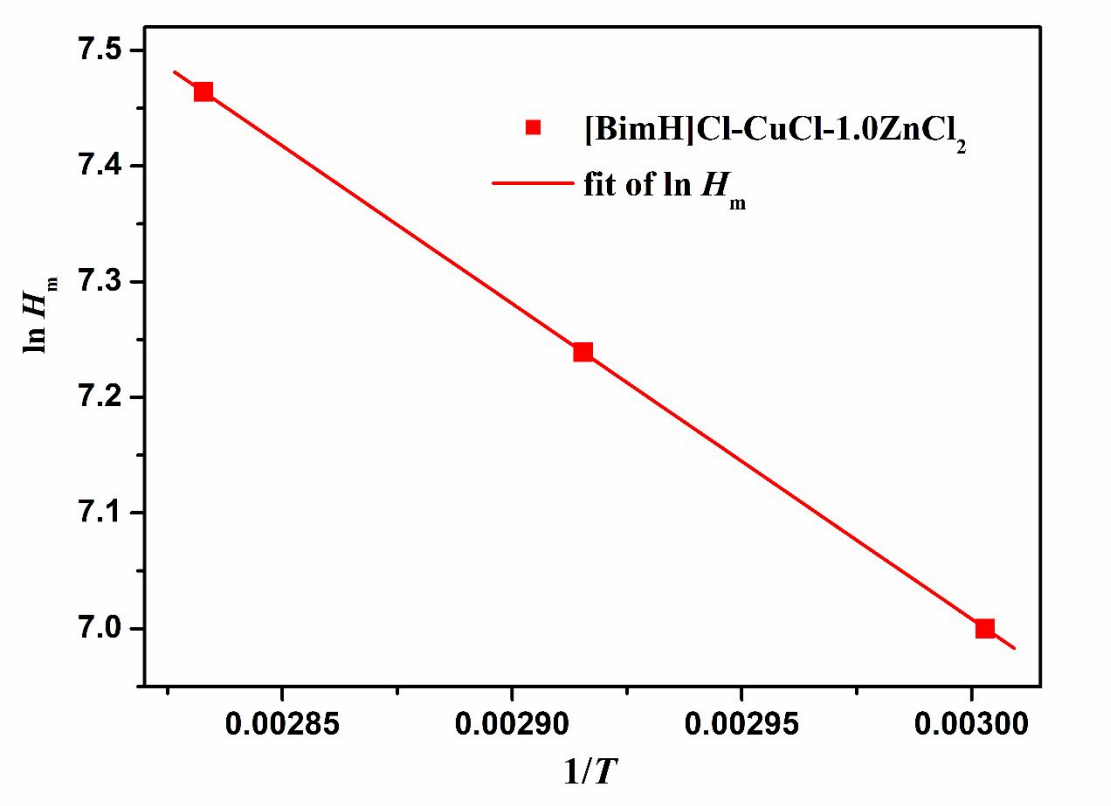


Figure 7. Linear fit of ln H_m and 1/T for CO absorption in [BimH]Cl-CuCl-1.0ZnCl$_2$.

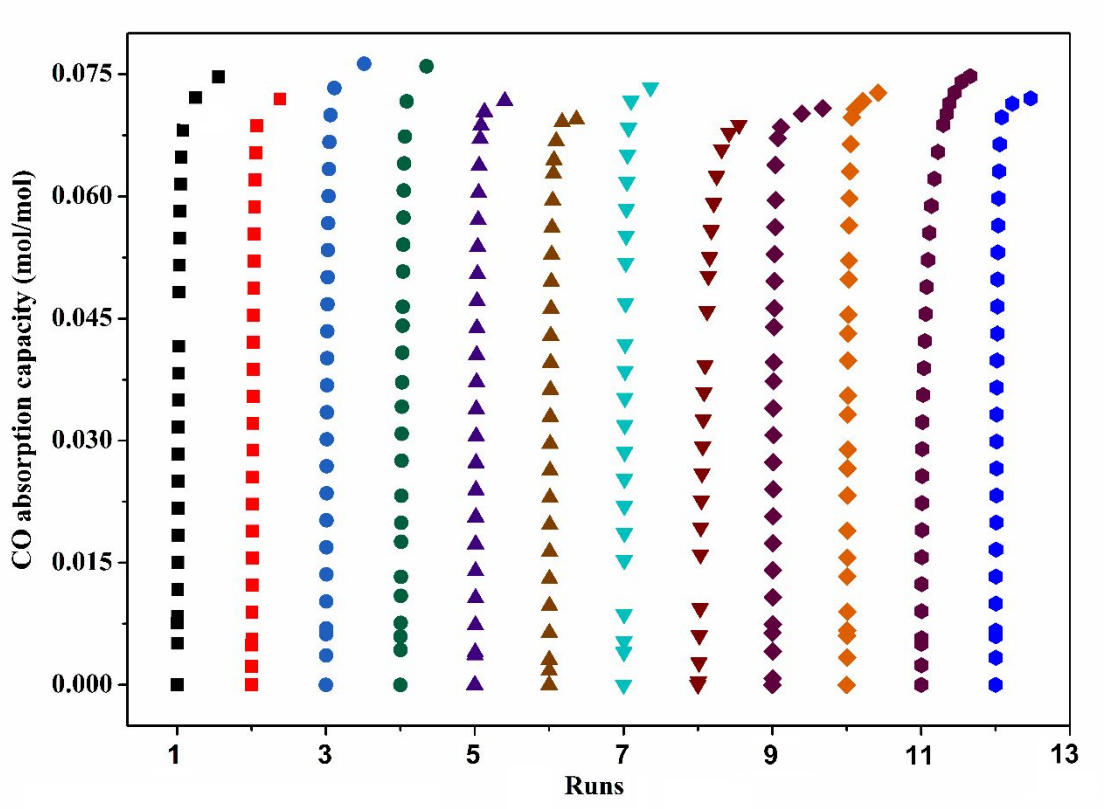


Figure 8. Recyclability of the DES [BimH]Cl-CuCl-1.0$ZnCl_2$ for CO absorption.

Table 1. Cuprous-based ternary DES with different molar ratios.

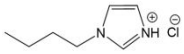
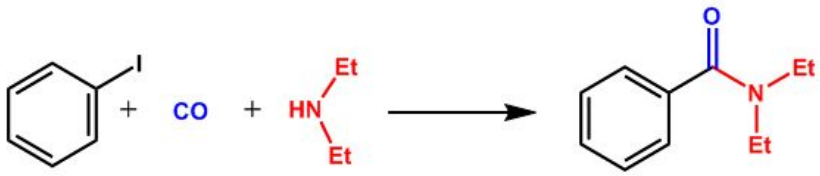
Ternary DESs	Molar ratio		
	 ([BimH]Cl)	CuCl	$ZnCl_2$
[BimH]Cl-CuCl-1.0$ZnCl_2$	1	1	1
[BimH]Cl-CuCl-0.8$ZnCl_2$	1	1	0.8
[BimH]Cl-CuCl-1.2$ZnCl_2$	1	1	1.2

Table 2. A summary of CO capture capacities of different absorbents.

Absorbents	Temperature (K)	CO Capacity (mol mol^{-1})	Refs
[BimH]Cl-CuCl-1.0$ZnCl_2$	353.2	0.075	This work
[BimH]Cl-CuCl-0.8$ZnCl_2$	353.2	0.061	This work
[BimH]Cl-CuCl-1.2$ZnCl_2$	353.2	0.056	This work
[BimH]Cl-CuCl	353.2	0.027	This work
[BimH]Cl-$ZnCl_2$	353.2	0.006	This work
[Bmim][PF_6]	295.2	3.0×10^{-3}	[9]
[P_{4448}][Pen]	323.2	0.052	[10]
[TEA][$CuCl_2$]	303.2	0.078	[11]
[EimH][$CuCl_2$]	323.2	0.033	[21]
[hmim][$CuCl_2$]	303.2	0.020	[26]
[Bmim][Tf_2N]	303.2	1.5×10^{-3}	[27]

Table 3. The reactive absorpiton of CO promoted by different DES absorbents.



Absorbent	Conv. (%)	Sel. (%)	Yield (%)
[BimH]Cl-CuCl-1.0$ZnCl_2$	100	97	97
[BimH]Cl-CuCl	22	38	10
CuCl-$ZnCl_2$	71	69	49
[BimH]Cl	4	83	3
–	<1	<1	<1

Reaction conditions: iodobenzene (1 mmol), Et_2NH (2 mmol), absorbent (1 mmol), $PdCl_2$ (5 wt% based on iodobenzene), 373.2 K, 24 h, and CO (1 bar).