



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

Duan-Jian Tao | Feng Qu | Zhang-Min Li | Yan Zhou

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi, China

Correspondence

Duan-Jian Tao, College of Chemistry and Chemical Engineering, Jiangxi Normal University at Nanchang, Jiangxi 330022, China.
Email: djtao@jxnu.edu.cn

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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 ZnCl₂. The ternary DES [BimH]Cl-CuCl-1.0ZnCl₂ 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-1.0ZnCl₂ 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 yields. We believe that this finding opens a new way to design advanced solvents for efficient capture of CO at high temperature.

KEYWORDS

absorption, carbon monoxide, deep eutectic solvents, high temperature

1 | 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 CO₂ 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.

Until now, some methods have been developed for separation and purification of CO by liquid solvent absorption, such as ammoniacal cuprous chloride and aromatic CuAlCl₄ solution (COSORB).⁴ However, these methods exhibit low capacity (e.g., 0.18 mmol CO per milliliter of CuAlCl₄ 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, Laurency and co-workers reported the absorption of CO by an IL [Bmim][PF₆] 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][CuCl₂] 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, nonpurified, 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 CO₂,¹⁴ NH₃,^{15,16} and H₂S.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 work¹⁸ that the addition of ZnCl₂ into a DES [BMIM]Cl/CuCl could activate the Cu⁺ ion to enhance the capture of ethylene. This makes us aware that ZnCl₂ 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 ZnCl₂ 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-1.0ZnCl₂ for reactive absorption of CO was further investigated under ambient pressure.

2 | EXPERIMENTAL

2.1 | 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 ZnCl₂ were obtained from Shanghai Adamas-Beta. CO, H₂, and N₂ 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.

2.2 | 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-1.0ZnCl₂ was synthesized by mixing of [BimH]Cl, CuCl, and ZnCl₂ with a molar ratio of 1:1:1 at room temperature for 3 h. The preparation of the other two DESs [BimH]Cl-CuCl-0.8ZnCl₂ and [BimH]Cl-CuCl-1.2ZnCl₂ 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.

2.3 | 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 1,073 K at a scan rate of 10 K/min under nitrogen atmosphere with a flow rate of 50 ml/min.

2.4 | 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 V₁ and V₂, 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 P₁ (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

TABLE 1 Cuprous-based ternary DES with different molar ratios

Ternary DESs	Molar ratio		
	([BimH]cl)	CuCl	ZnCl ₂
[BimH] Cl-CuCl-1.0ZnCl ₂	1	1	1
[BimH] Cl-CuCl-0.8ZnCl ₂	1	1	0.8
[BimH] Cl-CuCl-1.2ZnCl ₂	1	1	1.2

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 Equation 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 ($\text{mol}\cdot\text{cm}^{-3}$), ρ_1' is the density of CO at P_1' and T , ρ_2 is the density of CO at P_2 and T ($\text{mol}\cdot\text{cm}^{-3}$), and ρ_{DES} denotes the density of cuprous-based ternary DES in $\text{g}\cdot\text{cm}^{-3}$ 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-1.0ZnCl₂ 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-1.0ZnCl₂ was reused again for testing the absorption of CO.

3 | RESULTS AND DISCUSSION

3.1 | Physical and thermal properties

Three cuprous-based ternary DESs ([BimH]Cl-CuCl-0.8ZnCl₂, [BimH]Cl-CuCl-1.0ZnCl₂, and [BimH]Cl-CuCl-1.2ZnCl₂) were easily prepared from simple mixing of imidazolium hydrochloride with CuCl and ZnCl₂ in quantitative yields. It is known that the densities of these three DESs are required to calculate the CO solubility by Equation 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-1.0ZnCl₂ 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-1.2ZnCl₂, [BimH]Cl-CuCl-1.0ZnCl₂, and [BimH]Cl-CuCl-0.8ZnCl₂ 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 nonlinear dependence of the viscosity on the shear rate.^{22,23} In addition, the viscosities and densities data can be fitted by Equations 2 and 3, respectively. Fitting results are listed in Table S1 in the Supporting Information.

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

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

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-1.0ZnCl₂ were 510 K and 556 K, respectively. This indicates that these two cuprous-based DESs exhibit good thermal stability. Compared with the binary DES [BimH]Cl-CuCl, the ternary DES [BimH]Cl-CuCl-1.0ZnCl₂ shows high decomposition temperature because of the addition of ZnCl₂.

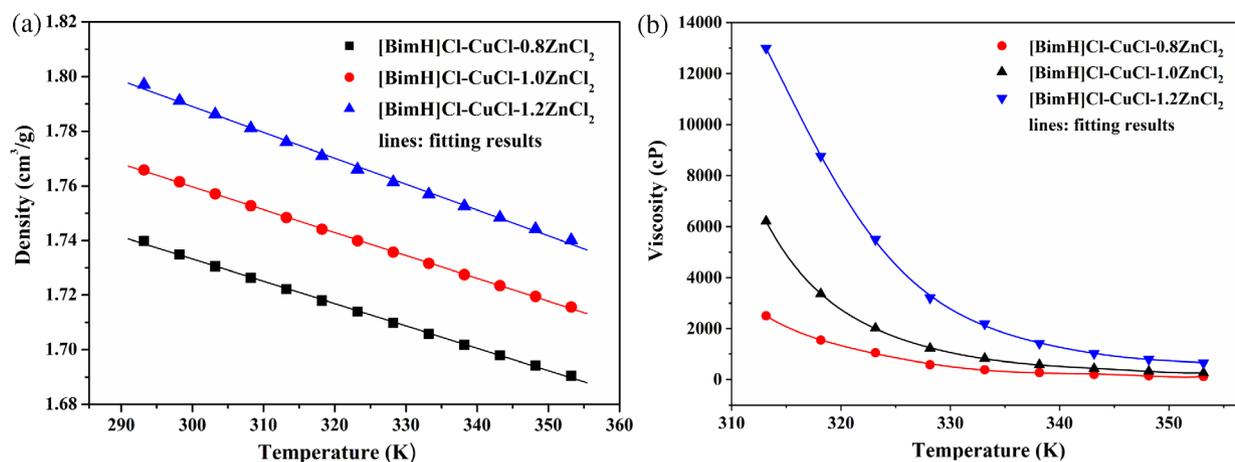


FIGURE 1 Densities (A) and viscosities (B) of cuprous-based ternary DESs at different temperatures [Color figure can be viewed at wileyonlinelibrary.com]

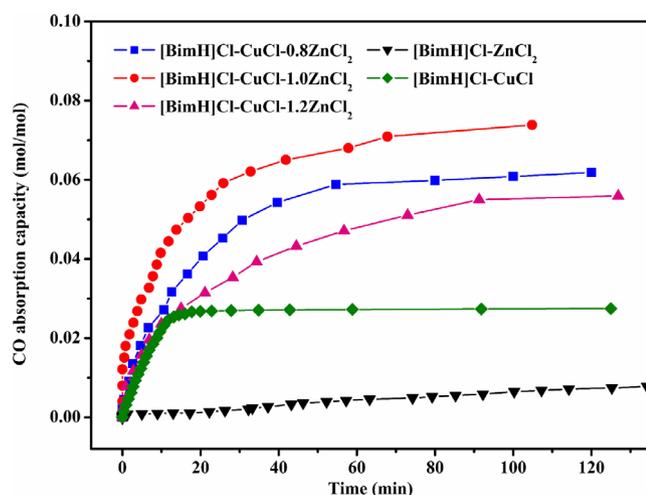


FIGURE 2 CO solubilities in various DESs at 353.2 K and 1 bar [Color figure can be viewed at wileyonlinelibrary.com]

3.2 | 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 ZnCl₂ ($x = 0.8, 1.0, 1.2$) 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-ZnCl₂. 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-1.0AlCl₃ also exhibited the CO absorption capacity of 0.0089 mol mol⁻¹. In contrast, 0.075 mol of CO per mol of DES was obtained for [BimH]Cl-CuCl-1.0ZnCl₂ under the same condition. These results demonstrate that ZnCl₂ plays a key role in excellent CO solubility at a certain high temperature. Moreover, the additive amount of ZnCl₂ had also effect on the CO capacity of [BimH]Cl-CuCl- x ZnCl₂. It is found that [BimH]Cl-CuCl-1.0ZnCl₂ exhibited the highest CO absorption capacity compared with [BimH]Cl-CuCl-0.8ZnCl₂ and [BimH]Cl-CuCl-1.2ZnCl₂ (Figure 2). This is because the viscosity of [BimH]Cl-CuCl-1.0ZnCl₂ 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-1.2ZnCl₂ still had a very large viscosity of 655 cP due to the maximum additional amount of ZnCl₂ (Figure S4, Supporting Information). The bad fluidity of [BimH]Cl-CuCl-1.2ZnCl₂ 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 ZnCl₂ was further studied. As shown in Figure 3, it is obvious that the absorption of CO in [BimH]Cl-CuCl- x ZnCl₂ 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-1.0ZnCl₂ 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 agreeing with the reported results from previous studies.^{21,24,26} In addition, Table 2

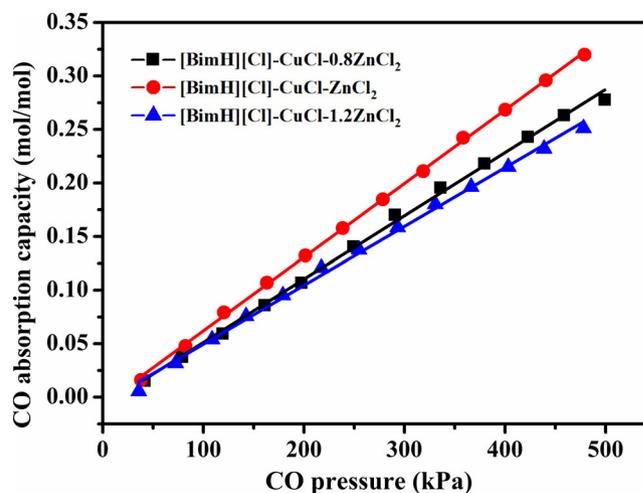


FIGURE 3 The effect of CO partial pressure on the absorption capacity of cuprous-based ternary DESs at 353.2 K [Color figure can be viewed at wileyonlinelibrary.com]

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-1.0ZnCl₂ 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 N₂, H₂, and CO₂ in the ternary DES [BimH]Cl-CuCl-1.0ZnCl₂ 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-1.0ZnCl₂ showed extremely low capacities for capturing N₂, H₂, and CO₂ at 353.2 K and 1 bar. The idea selectivity $S(1/1)$ of CO/N₂, CO/H₂, and CO/CO₂ 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][CuCl₂] and [bmim][Tf₂N].²⁶⁻²⁸

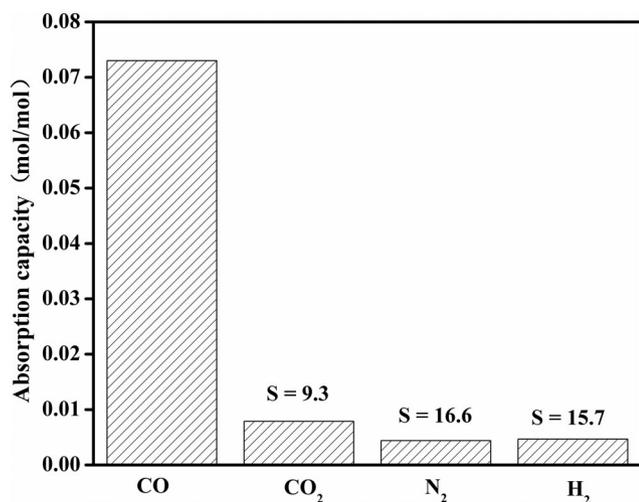
3.3 | Promoted role of ZnCl₂

To clarify the role of ZnCl₂ 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-1.0ZnCl₂ and [BimH]Cl-CuCl discovered new peaks at 2112 and 2088 cm⁻¹ (Figure 5(A)), respectively, which was ascribed to the stretching vibration of captured CO. Compared to fresh CO (2,143 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 5(B) shows the ESI-MS results of the anion species of [BimH]Cl-CuCl-1.0ZnCl₂ 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 CuCl₂⁻ and Cu₂Cl₃⁻, respectively.

TABLE 2 A summary of CO capture capacities of different absorbents

Absorbents	Temperature (K)	CO capacity (mol mol ⁻¹)	Refs
[BimH]Cl-CuCl-1.0ZnCl ₂	353.2	0.075	This work
[BimH]Cl-CuCl-0.8ZnCl ₂	353.2	0.061	This work
[BimH]Cl-CuCl-1.2ZnCl 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 ₂ N]	303.2	1.5 × 10 ⁻³	[27]

**FIGURE 4** Absorption of CO, CO₂, N₂, and H₂ in [BimH]Cl-CuCl-1.0ZnCl₂ at 353.2 K and 1 bar

For [BimH]Cl-CuCl-1.0ZnCl₂, three kinds of m/z peaks at 134.86, 170.83, and 232.76 were detected and assigned to CuCl₂⁻, ZnCl₃⁻, and Cu₂Cl₃⁻, respectively.^{33,34} That is to say, compared with the anion species of [BimH]Cl-CuCl, the peak of ZnCl₃⁻ was dominant in [BimH]Cl-CuCl-1.0ZnCl₂ and the peak intensities of CuCl₂⁻ and Cu₂Cl₃⁻ 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 ZnCl₂ and the electron transferred from a Cl⁻ ion of CuCl₂⁻ to the Zn²⁺ 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-1.0ZnCl₂ at high temperature.

3.4 | Thermodynamic analysis

The above-mentioned data demonstrate that the capture of CO by [BimH]Cl-CuCl-xZnCl₂ 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:

$$H_m(T, P) = \lim_{x_{CO} \rightarrow 0} \frac{f_{CO}^B}{x_{CO}} \approx \frac{P}{x_{CO}} \quad (4)$$

In Equation 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_{CO}^B 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-xZnCl₂ 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 Equation 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-1.0ZnCl₂ had a very good agreement with the Henry's law. The pressure-dependent Equation 4 is considered to be an appreciate model for the description of CO absorption at high temperature.

Furthermore, the interaction between CO and the ternary DES [BimH]Cl-CuCl-1.0ZnCl₂ 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 Equation 5, as shown in Figure 7. Subsequently, the Gibbs free energy change (ΔG_{sol}) and entropy change (ΔS_{sol}) were calculated by Equations 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-1.0ZnCl₂ was -22.67 kJ mol⁻¹. Also, the values of ΔG_{sol} and ΔS_{sol} were -

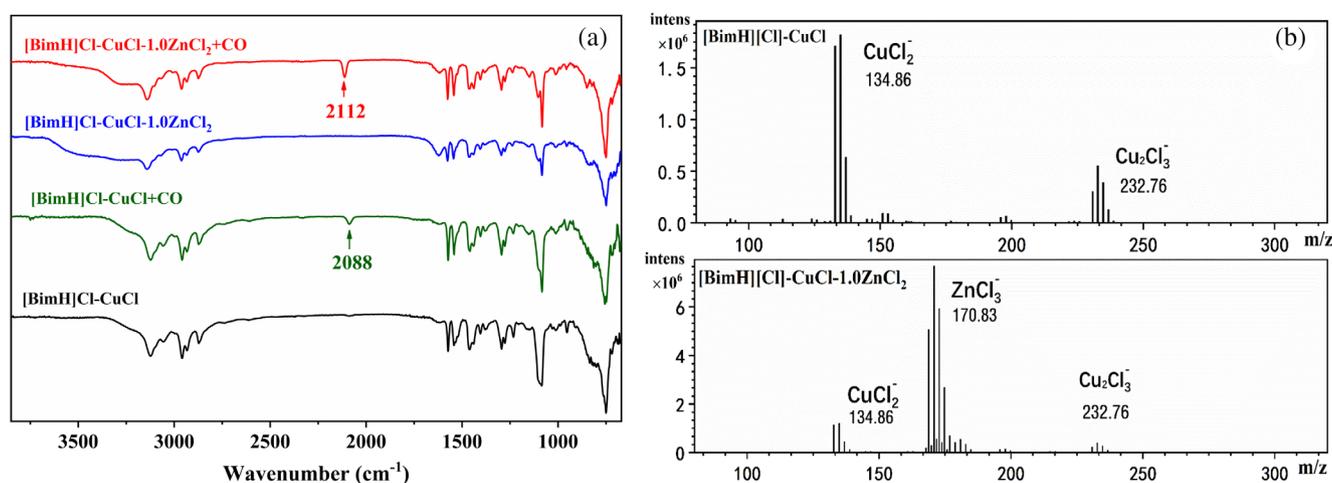


FIGURE 5 (A) FT-IR spectra of cuprous-based DESs before and after CO absorption. (B) ESI-MS analysis for anion species of cuprous-based DESs [Color figure can be viewed at wileyonlinelibrary.com]

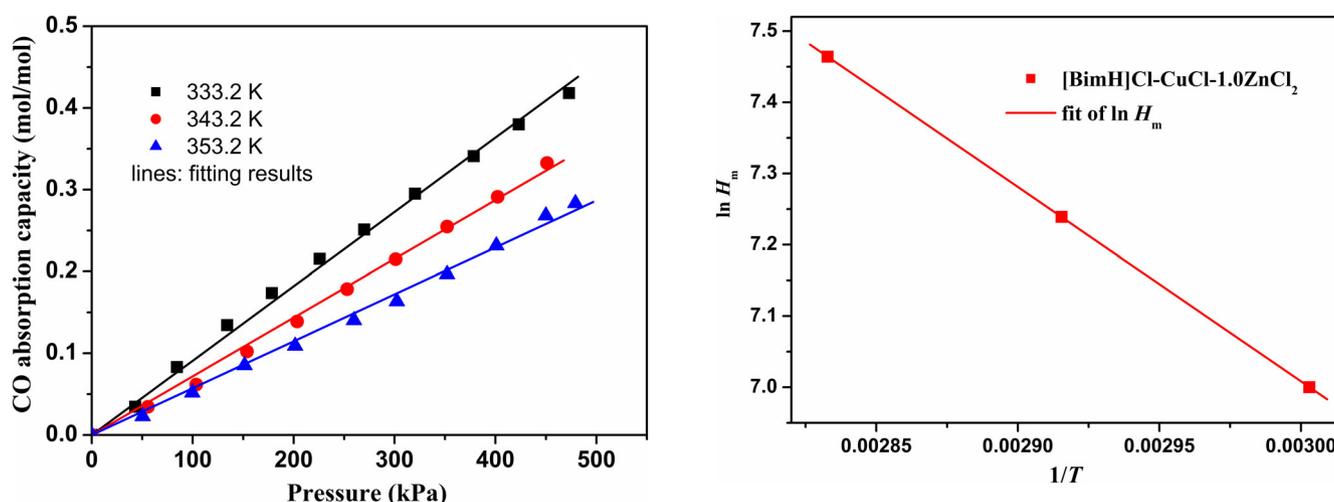


FIGURE 6 Solubilities of CO in [BimH]Cl-CuCl-1.0ZnCl₂ at different temperatures [Color figure can be viewed at wileyonlinelibrary.com]

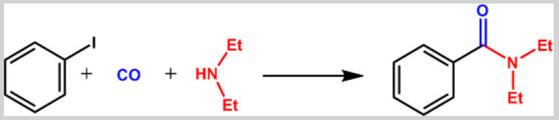
219.2 J mol⁻¹ and -63.6 J mol⁻¹ K⁻¹ at 353.2 K, respectively. Thereby, the value of ΔH_{sol} for [BimH]Cl-CuCl-1.0ZnCl₂ was little more than the hydrogen bonding energy range from -10 to -20 kJ mol⁻¹,^{35,36} again confirming the physical absorption of CO in the DES [BimH]Cl-CuCl-1.0ZnCl₂.

3.5 | 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

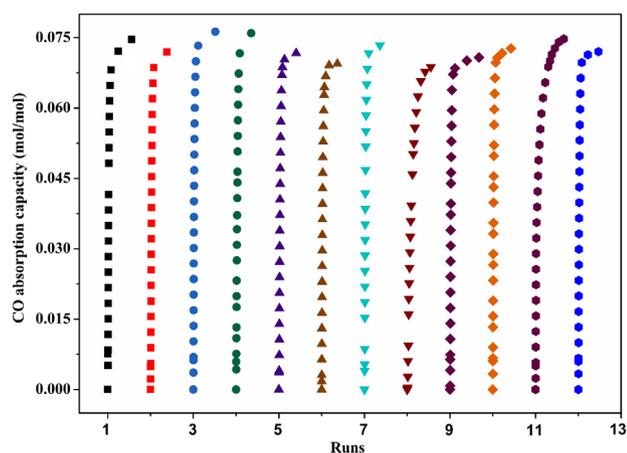
FIGURE 7 Linear fit of $\ln H_m$ and $1/T$ for CO absorption in [BimH]Cl-CuCl-1.0ZnCl₂ [Color figure can be viewed at wileyonlinelibrary.com]

original materials. The detailed procedure was given in the Supporting Information. It is seen from Table 3 that the absorbent [BimH]Cl-CuCl-1.0ZnCl₂ 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-1.0ZnCl₂, the binary DES [BimH]Cl-CuCl and CuCl-ZnCl₂ 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-1.0ZnCl₂ can dramatically decrease the pressure and efficiently promote carbonylation reaction to obtain 70–97 yields.

TABLE 3 The reactive absorption of CO promoted by different DES absorbents


Absorbent	Conv. (%)	Sel. (%)	Yield (%)
[BimH]Cl-CuCl-1.0ZnCl ₂	100	97	97
[BimH]Cl-CuCl	22	38	10
CuCl-ZnCl ₂	71	69	49
[BimH]Cl	4	83	3
—	<1	<1	<1

Note: Reaction conditions: iodobenzene (1 mmol), Et₂NH (2 mmol), absorbent (1 mmol), PdCl₂ (5 wt% based on iodobenzene), 373.2 K, 24 h, and CO (1 bar).

**FIGURE 8** Recyclability of the DES [BimH]Cl-CuCl-1.0ZnCl₂ for CO absorption [Color figure can be viewed at wileyonlinelibrary.com]

3.6 | Recycle of [BimH]Cl-CuCl-1.0ZnCl₂

To evaluate the recyclability of [BimH]Cl-CuCl-1.0ZnCl₂ 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-ZnCl₂ 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-ZnCl₂ 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-ZnCl₂ is stable enough to be recycled.

4 | CONCLUSIONS

In summary, we have successfully prepared three cuprous-based ternary DESs by mixing [BimH]Cl with CuCl and ZnCl₂. It is demonstrated

that the ternary DES [BimH]Cl-CuCl-1.0ZnCl₂ 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 ZnCl₂ for promoted absorption of CO at high temperature was clearly explained, in which the addition of ZnCl₂ could weaken the Cu-Cl bond and activate the Cu⁺ ion to enhance CO absorption capacity. In addition, the ternary DES [BimH]Cl-CuCl-1.0ZnCl₂ 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.

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ORCID

Duan-Jian Tao  <https://orcid.org/0000-0002-8835-0341>

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SUPPORTING INFORMATION

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

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