Unusual temperature-promoted carbon dioxide capture in deep-eutectic solvents: the synergistic interactions†

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A series of novel ethylenediamine (EDA)-based deep-eutectic solvents (DESs) gave rise to unexpectedly large carbon dioxide (CO₂) capture capacities at higher temperatures owing to the "synergistic interaction" between the donor and acceptor moieties.

Reversible fixation–release of carbon dioxide (CO₂) has attracted much attention during the last few decades due to an excessive increase in the consumption of fossil fuels as the main source of energy, thus causing an upsurge in CO₂ emissions, leading to global warming. The current state-of-the-art industrial technology uses amine-based solvents in reversible CO₂ capture. This methodology has critical issues such as high regeneration energy, amine instability, high volatility, corrosion and high maintenance costs. In order to optimize the CO₂ uptake, the flue gas is cooled to room temperature before absorption, whereas high temperatures are required in the desorption–regeneration step. Both these steps increase the cost of the setup and hence developing a solvent system that can absorb CO₂ directly from hot flue gas and undergo rapid desorption is the most attractive solution but have not been introduced until now.

The last century witnessed a surge in the development of a number of "green and sustainable" alternatives to volatile solvents. Among them, ionic liquids (ILs) and deep-eutectic solvents (DESs) have been the most explored ones for various applications because of their advantageous properties such as their negligible vapour pressure, wide liquidus range, low flammability, high thermal stability and recyclability. Blanchard et al. reported for the first time the potential of ILs in CO₂ capture. Later, various ILs differing in terms of cations, anions and alkyl chain length were applied to optimize CO₂ uptake and to gain understanding about the functioning of these neoteric media. The basicity of the anion was identified as the key factor in achieving high CO₂ uptake and has been most explored to date. For example, in carbonyl-containing anion-functionalized ILs, high CO₂ intake was favoured by H-bonding interactions. Pan et al. reported an equimolar CO₂ uptake in anion-functionalized hydroxypyridine-based ILs owing to intramolecular proton transfer. However, the high molar uptake in ILs is attributed to their large molar mass and thus is less impressive when converted to the gravimetric values. Similarly, task-specific ILs for CO₂ capture are expensive and require a long time for synthesis and are therefore rendered unsuitable for industrial applications.

In contrast, DESs, a new generation of solvent analogous to ILs, provide a more promising alternative in CO₂ capture and involve cost-effective, easy preparation, exhibiting properties similar to ILs, and resulting in higher gravimetric CO₂ uptake. In a short time-span, DESs have found application in organic synthesis, polymerization, stabilization of biomolecules, nanotechnology, separation, extraction of target compounds and so on. The performance of DESs as sorbents in CO₂ capture relies on pairing an efficient hydrogen bond donor (HBD) with hydrogen bond acceptor (HBA) with an optimal molar ratio. Later developments have shown moderate to high CO₂ uptakes for different classes of DESs. We recently presented an in-depth discussion about the impact of intermolecular interactions on the CO₂ uptake in ethylenediamine ([EDA]₃), 3-amino-1-propanol ([AP]), and polyamine-based DESs. Unlike ILs and amine-based solvent systems where basicity is a prerequisite for high CO₂ capture, the interplay between the hydrogen bond donor acidity (α) and hydrogen bond acceptor basicity (β) governs the CO₂ absorption in DESs. Additionally, the reaction conditions also influence the CO₂ solubility and maximum uptake takes place at low temperatures and high pressures. In line with the current technology, flue gas passes through a cooler before traveling to the absorption tank. Therefore, employing...
a medium that has a low enthalpy of absorption ($\Delta H_{\text{abs}}$) and can reversibly absorb CO$_2$ in the post-combustion process, at typical flue gas temperatures, will eliminate the necessity of a cooler unit and extra steam (for desorption), thus bringing down the cost of the overall setup and making the whole process more lucrative.

In this study, we synthesized DESs containing [EDA], [AP], diethylenetriamine ([DETA]), tetraethylenepentamine ([TEPA]) and pentaethylenexediamine ([PEHA]) as HBDs and monoethanolammonium chloride ([MEA-Cl]) and 1-methylimidazolium chloride ([HMIM-Cl]) as their HBA counterparts (see the ESI† for details) and measured the CO$_2$ uptakes at temperatures 298 K–328 K, at ambient pressure (Table 1). The structures of the different DESs are shown in Fig. 1. As depicted in Fig. 2 and 3, respectively, the [EDA]- and [AP]-based DESs have opposite CO$_2$ uptake behaviours within the same temperature range. The [EDA]-based DESs show a positive trend in terms of temperature, while a negative temperature effect is evident for the [AP]-class of DESs. So far, only a negative impact of increasing temperatures on CO$_2$ capture has been perceived in previous investigations.$^{32,35,36}$

As shown in Fig. 2, the gravimetric CO$_2$ uptake increases from 11.4% to 24.8% in 1:1 [MEA-Cl][EDA] and 3.6% to 12.1% in 1:1 [HMIM-Cl][EDA], respectively, in the temperature range 298 K–328 K in 1 h. The CO$_2$ capture capacity increases further upon increasing the HBA : HBD ratio from 1:1 to 1:4. In 1:4 [MEA-Cl][EDA], the CO$_2$ uptake reaches ~36% in 1 h at 328 K, whereas in 1:4 [HMIM-Cl][EDA] ~34% of CO$_2$ is sorbed at 328 K (ESI,† Fig. S1–S4). Contrary to our reports, Trivedi et al. reported lower CO$_2$ uptake in 1:3 [MEA-Cl][EDA] at a higher temperature, which is surprising to us.$^{32}$ The temperature-promoted CO$_2$ uptake was not specific to the [EDA]-based DESs noted in [DETA]-, [TEPA]- and [PEHA]-based DESs; though, the efficiency was lower than in the former case (ESI,† Fig. S5 and S6).

In general, an increasing temperature results in a lower viscosity but increases the activation energy of the gas molecule at the same time. The resultant of these opposing effects directs the course of CO$_2$ capture, at higher temperatures. Therefore, the temperature-favoured CO$_2$ uptake in the [EDA]-based DESs cannot be attributed to the reduction in viscosity only. Additionally, [MEA-Cl][EDA] and [HMIM-Cl][EDA] possess low viscosity, which further decreases upon increasing the HBA : HBD ratio from 1:1 to 1:4. In the latter case, the viscosity is already low so the influence of temperature is hard to detect. To discern the impact of viscosity on CO$_2$ uptake more clearly, we calculated the activation energy of viscous flow ($E_{a,\eta}$) from the temperature-dependent viscosity data using the Arrhenius-type equation (ESI,† Fig. S7) as shown in Table 1. $E_{a,\eta}$ accounts for the hindrance in the diffusion of CO$_2$ by the DES. At HBA : HBD = 1:1, the [EDA]-based DESs possess lower $E_{a,\eta}$ than the [AP]-class of DESs but, at higher HBA : HBD ratios, the trend in $E_{a,\eta}$ reverses (Table 1). The $E_{a,\eta}$ values of the [DETA], [TEPA] and [PEHA]-based DESs vary

$$E_{a,\eta} = \text{kJ mol}^{-1}, \Delta H^* = \text{kJ mol}^{-1}, \Delta S^* = \text{J K}^{-1} \text{mol}^{-1}, E_{30}(\text{cal} \text{mol}^{-1}) \text{for} E_{a,\eta},$$

where the error in $E_{a,\eta}$, $AH^*$, $\Delta S^*$ and $E_{30}$ are ±0.003, ±0.002, ±0.001 and 0.004, respectively.
between 43.2 and 60.6 kJ mol\(^{-1}\) despite the positive effect of temperature on CO\(_2\) capture (ESI,† Table S1). Thus, the positive and negative temperature effects on the CO\(_2\) solubility in the [EDA]- and [AP]-based DESs, respectively, might originate from the different intermolecular interactions between the DESs and CO\(_2\).

To account for the impact of intermolecular interactions on the course of CO\(_2\) capture, at elevated temperatures, the thermodynamics (standard enthalpy change (\(\Delta H^\circ\)) and standard entropy change (\(\Delta S^\circ\))) of capture along with the solvent polarity parameters (\(E_I(30)\), \(\alpha\) and \(\beta\)) are discussed further to unravel the underlying mechanisms\(^{33,37}\) (see the ESI,† Fig. S8 and S9 and Table S2).

As shown in Table 1, a positive \(\Delta H^\circ\) for the [EDA]-based DESs indicates an endothermic nature of CO\(_2\) uptake, while a negative \(\Delta H^\circ\) for the [AP]-based DESs signals that the process is exothermic. The standard entropy change (\(\Delta S^\circ\)) is positive for the [EDA]-class and negative for the [AP]-class of DESs. Following the spontaneity criteria (\(\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\)), it is evident that the CO\(_2\) uptake becomes more spontaneous (\(-\Delta S^\circ > \Delta H^\circ\)) in [MEA Cl][EDA] and [HMIM Cl][EDA] than [MEA Cl][AP] and [HMIM Cl][AP] as the temperature increases. A shift in HBA : HBD from 1 : 1 to 1 : 4 increases \(\Delta H^\circ\) and \(\Delta S^\circ\) in the [EDA]-based DESs and thus renders CO\(_2\) uptake more spontaneous. In the [AP]-class of DESs with an increase of the HBA : HBD ratio, \(\Delta H^\circ\) and \(\Delta S^\circ\) become negative and thus spontaneous and result in higher CO\(_2\) uptake. The [DETA]-, [TEPA]- and [PEHA]-based DESs have positive \(\Delta H^\circ\) and \(\Delta S^\circ\) akin to the [EDA]-class of DESs and hence dissolve CO\(_2\) spontaneously as the temperature increases (ESI,† Table S1). More importantly, a very small value of \(\Delta H^\circ\) for the [EDA]-based DESs makes regeneration of the absorbent energy-saving, which is a key factor in practical applications.\(^{38}\)

The nature of DES–CO\(_2\) interactions was then investigated in terms of the Kamlè-Taft parameters \(\alpha\) and \(\beta\), which measure donor and acceptor strengths, respectively (ESI,† Table S2 and Fig. S10). The positive effect of CO\(_2\) uptake indicates “synergistic interaction” of the donor and acceptor sites in the [EDA]-based DESs. The synergistic action is widely acknowledged in catalysis and polymerizations of binary systems.\(^{39,40}\) “Hyperpolarity” was observed in a binary mixture of ILs when the donor (\(\alpha\)) and acceptor (\(\beta\)) strengths become similar and favor synergistic interaction.\(^{41}\) In other words, for synergistic interaction, the relative difference between the donor and acceptor (\(\alpha - \beta\)) should be zero. If \(\alpha - \beta \neq 0\), the system will have acidic/basic characteristics depending on the relative differences in the values of \(\alpha\) and \(\beta\). This will cause an energy difference in the HBA and HBD in a DES and lower the probability for synergistic interactions (Scheme 1). The synergy in the DES results in weak interactions, which is reflected in the low polarity (\(E_I(30)\)) and \(\Delta H^\circ\) and \(\Delta S^\circ\) values.

As shown in Table 1, the relative \(\alpha - \beta\) for [MEA Cl][EDA] is lower than those of [MEA Cl][AP] and [HMIM Cl][AP] at 1 : 1. The small \(\alpha - \beta\) suggests alignment of the donor and acceptor energy levels for synergistic interactions. At higher HBA : HBD ratios, in the [EDA]-based DESs, relative \(\alpha - \beta\) nears zero and renders the synergistic interactions more feasible. Decreases in the \(\Delta H^\circ\) and \(\Delta S^\circ\) further support this trend. Similarly, the \(\alpha - \beta\) trend in the [HMIm Cl][EDA]-class of DESs also indicates synergistic interactions at different molar ratios. The relative \(\alpha - \beta\) for the [AP]-class of DESs is comparatively large and hence results in negative \(\Delta H^\circ\) and \(\Delta S^\circ\) (Table 1). The large \(\alpha - \beta\) gives rise to differences in the ground state energy of the donor and acceptor and forbids synergistic interactions (Scheme 1). Thus, the greater CO\(_2\) uptake in the [AP]-class of DESs, at higher HBA : HBD ratios, is due to their reduced viscosity.

The [DETA]-, [TEPA]- and [PEHA]-based DESs possess large \(\alpha - \beta\) but have positive \(\Delta H^\circ\) and \(\Delta S^\circ\), which suggests the possibility of synergistic interactions. The large in \(\alpha - \beta\) difference is caused by the multiple amine groups in the HBds.

In summary, we, for the first time, have reported temperature-promoted CO\(_2\) capture in novel [EDA]-based DESs. The positive effect of temperature on CO\(_2\) capture arises from the synergistic interactions between the donor and acceptor moieties. The synergistic interactions in DESs are caused by small \(\alpha - \beta\) and \(E_I(30)\) and positive \(\Delta H^\circ\) and \(\Delta S^\circ\). Lower CO\(_2\) uptake in the [AP]-class of DESs, at elevated temperatures, is due to the large \(\alpha - \beta\) and negative \(\Delta H^\circ\) and \(\Delta S^\circ\). Very low \(\Delta H^\circ\) indicates quick regeneration of the [EDA]-based DESs and hence these DESs evolve as excellent substitutes for the amine-based technology in a CO\(_2\) capture plant.

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Conflicts of interest
There are no conflicts to declare.

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