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## Unusual temperature-promoted carbon dioxide capture in deep-eutectic solvents: the synergetic interactions

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**A series of novel ethylenediamine(EDA)-based deep-eutectic solvents (DESS) gave rise to unexpectedly large carbon dioxide (CO<sub>2</sub>) capturing capacity at higher temperatures owing to the “synergetic interaction” between the donor and acceptor moieties.**

Reversible fixation-release of carbon dioxide (CO<sub>2</sub>) has attracted much attention during the last few decades due to an excessive increase in fossil fuel consumption as the main source of energy thus causing an upsurge in the CO<sub>2</sub> emissions leading to global warming. The current state-of-the-art industrial technology uses amine-based solvents in reversible CO<sub>2</sub> capture.<sup>1</sup> This methodology lingers with critical issues such as high regeneration energy, amine instability, high volatility, corrosion and high maintenance costs.<sup>2,3</sup> In order to optimize the CO<sub>2</sub> uptake, the flue gas is cooled to room temperature before absorption whereas high temperatures are required in the desorption-regeneration step. This increases the cost of the setup and hence in order to develop a solvent system that can absorb CO<sub>2</sub> directly from hot flue gas and also allows for rapid desorption is the most attractive solution but no such technologies have been introduced until now.

The last century witnessed a surge in the development of a number of “green and sustainable” alternatives to the 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 negligible vapour pressure, wide liquidus range, low flammability, high thermal stability and recyclability.<sup>4,5</sup> Blanchardt *et al.* reported for the first time the potential of ILs in the CO<sub>2</sub> capture.<sup>6</sup> Later, various ILs differing in the cation, anion and the size of alkyl chain length were applied to optimize the CO<sub>2</sub> uptake and to gain understanding about the functioning

of these neoteric media.<sup>7-10</sup> The basicity of the anion was identified as the key factor in attaining high CO<sub>2</sub> uptake and is most explored till date.<sup>11-14</sup> For example, in carbonyl-containing anion-functionalized ILs, high CO<sub>2</sub> intake was favoured by the H-bonding interactions.<sup>15</sup> Pan *et al.* reported an equimolar CO<sub>2</sub> uptake in anion-functionalized hydroxypyridine-based ILs owing to the intramolecular proton transfer.<sup>16</sup> However, the high molar uptake in ILs is attributed to a large molar mass and, thus is less impressive when converted to the gravimetric values.<sup>10,17</sup> Similarly, the task-specific ILs for CO<sub>2</sub> capture are expensive, require a long time to synthesize and are therefore rendered unsuitable in industrial applications.<sup>18</sup>

On the contrary, DESS; a new generation of solvent analogues to ILs, provide a more promising alternative in CO<sub>2</sub> capture that involve cost-effective and easy preparation, exhibiting properties similar to ILs and resulting in higher gravimetric CO<sub>2</sub> uptake.<sup>19,20</sup> 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.<sup>21-26</sup> The performance of DESS as sorbents in CO<sub>2</sub> capture relies on pairing an efficient hydrogen bond donor (HBD) with hydrogen bond acceptor (HBA) with an optimal molar ratio.<sup>27-29</sup> Later developments showed moderate to high CO<sub>2</sub> uptake for different classes of DESS.<sup>30-33</sup> We recently presented an in-depth discussion about the role of intermolecular interactions on the CO<sub>2</sub> uptake in ethylenediamine ([EDA]-), 3-amino-1-propanol ([AP]-), and polyamine-based DESS.<sup>33</sup> Unlike ILs and amine-based solvent systems where basicity is prerequisite for high CO<sub>2</sub> capture, the interplay between the hydrogen bond donor acidity ( $\alpha$ ) and hydrogen bond acceptor basicity ( $\beta$ ) governs the CO<sub>2</sub> absorption in DESS.<sup>33</sup> Additionally, the reaction conditions also influence the CO<sub>2</sub> solubility and maximum uptake takes place at low temperatures and high pressures.<sup>34</sup> In line with the current technology, flue gas passes through a cooler before traveling to the absorption tank.<sup>35</sup> Therefore, employing a medium that has low enthalpy of absorption ( $\Delta H_{abs}$ ) and can reversibly absorb CO<sub>2</sub> in the post-combustion process, at typical flue gas

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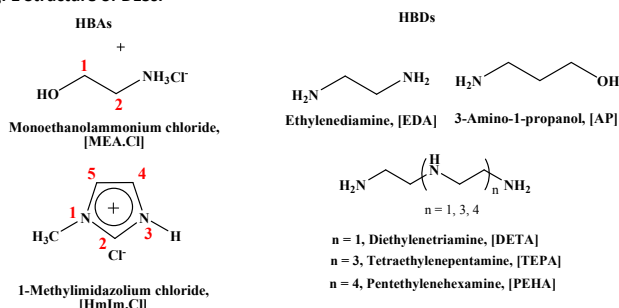
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Electronic Supplementary Information (ESI) available: Tables and figures, Synthesis and characterization of DESS, polarity, viscosity, activation energy of viscous flow and thermodynamic characterization, temperature-dependent CO<sub>2</sub> capture profiles. See DOI: 10.1039/x0xx00000x

temperatures, will eliminate the necessity of a cooler unit and extra steam (for desorption) thus bringing down the cost of the overall setup and makes the whole process more lucrative.

Herein, we synthesized DESs containing [EDA], [AP], diethylenetriamine ([DETA]), tetraethylenepentamine ([TEPA]) and pentaethylenhexamine ([PEHA]) as HBD and monoethanolammonium chloride ([MEA.Cl]) and 1-methylimidazolium chloride ([HmIm.Cl]) as their HBA counterpart (see ESI for details) and measured the CO<sub>2</sub> uptake at temperatures 298K – 328K, at ambient pressure (Table 1). The structures of different DESs are shown in Fig. 1. As depicted in Figs. 2 and 3, respectively, [EDA]- and [AP]-based DESs have opposite CO<sub>2</sub> uptake behaviour 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 negative impact of increasing temperatures upon CO<sub>2</sub> capture has been perceived in previous investigations.<sup>32,35,36</sup>

Fig. 1 Structure of DESs.



As shown in Fig. 2, gravimetric CO<sub>2</sub> uptake increases from 11.4% to 24.8% in [MEA.Cl][EDA] = 1:1 and 3.6% to 12.1% in [HmIm.Cl][EDA] = 1:1, respectively, in the temperature range 298K – 328K in 1h. The CO<sub>2</sub> capture capacity increases further upon increasing the HBA:HBD from 1:1 to 1:4. In [MEA.Cl][EDA] = 1:4, CO<sub>2</sub> uptake reaches ~36% in 1h at 328K whereas in [HmIm.Cl][EDA] = 1:4 ~34% of CO<sub>2</sub> is sorbed at 328K (ESI Fig. S1-S4). Contrary to our reports, trivedi *et al.* reported lower CO<sub>2</sub> uptake in [MEA.Cl][EDA]=1:3 at a higher temperature which is surprising to us.<sup>32</sup> The temperature-promoted CO<sub>2</sub> 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, Figs. S5 and S6).

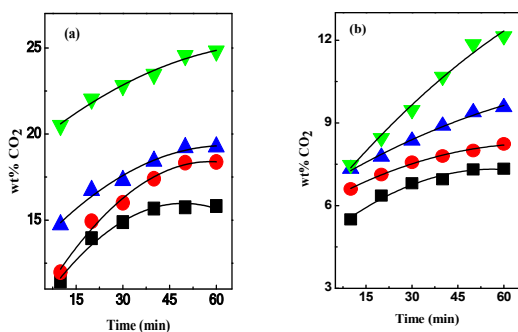


Fig. 2 CO<sub>2</sub> uptake kinetics in 1:1 (a) [MEA.Cl][EDA]- and (b) [HmIm.Cl][EDA]-based DESs at 298K (■), 308K (●), 318K (▲) and 328K (▼).

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<sub>2</sub> capture, at higher temperatures. Therefore, temperature-favoured CO<sub>2</sub> uptake in [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 = 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<sub>2</sub> 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. The  $E_{a,\eta}$  accounts for the hindrance in the diffusion of CO<sub>2</sub> by the DES. At HBA:HBD = 1:1, the [EDA]-based DESs possess lower  $E_{a,\eta}$  than [AP]-class of DESs but, at higher HBA:HBD ratios, the trend in  $E_{a,\eta}$  reverses (Table 1). The  $E_{a,\eta}$  of [DETA], [TEPA] and [PEHA]-based DESs varies between 43.2 – 60.6 kJ.mol<sup>-1</sup> despite the positive effect of temperature on CO<sub>2</sub> capture (ESI, Table S1). Thus, the positive and negative temperature effects on the CO<sub>2</sub> solubility in [EDA]- and [AP]-based DESs, respectively, might originate from the different intermolecular interactions between DES and CO<sub>2</sub>.

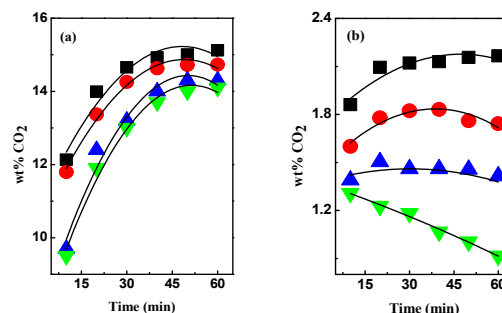


Fig. 3 CO<sub>2</sub> uptake kinetics in 1:1 (a) [MEA.Cl][AP]- and (b) [HmIm.Cl][AP]-based DESs at 298K (■), 308K (●), 318K (▲) and 328K (▼).

Table 1. Activation energy of viscous flow, thermodynamic and polarity parameters in [EDA]- and [AP]-based DESs

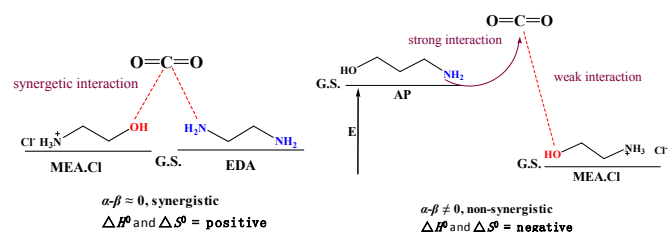
| DESs               | $E_{a,\eta}$ | $\Delta H^\circ$ | $\Delta S^\circ$ | $E_T(30)$ | $\alpha$ | $\beta$ |
|--------------------|--------------|------------------|------------------|-----------|----------|---------|
| [MEA.Cl][EDA]=1:1  | 42.7         | 11.9             | 4.3              | 59.2      | 0.948    | 0.688   |
| [MEA.Cl][EDA]=1:2  | 42.4         | 10.8             | 4.0              | 56.5      | 0.785    | 0.681   |
| [MEA.Cl][EDA]=1:3  | 42.2         | 8.0              | 3.1              | 54.6      | 0.673    | 0.658   |
| [MEA.Cl][EDA]=1:4  | 41.8         | 7.3              | 2.9              | 53.2      | 0.599    | 0.791   |
| [HmIm.Cl][EDA]=1:1 | 48.0         | 17.0             | 5.7              | 54.7      | -        | -       |
| [HmIm.Cl][EDA]=1:2 | 42.1         | 7.9              | 3.0              | 54.7      | 0.653    | 0.615   |
| [HmIm.Cl][EDA]=1:3 | 38.9         | 7.2              | 2.9              | 53.9      | 0.646    | 0.861   |
| [HmIm.Cl][EDA]=1:4 | 38.8         | 7.1              | 2.8              | 52.7      | 0.613    | 0.901   |
| [MEA.Cl][AP]=1:1   | 48.3         | -10.0            | -4.5             | 60.2      | 1.013    | 0.526   |
| [MEA.Cl][AP]=1:2   | 47.3         | -8.6             | -3.7             | 59        | 1.045    | 0.628   |
| [MEA.Cl][AP]=1:3   | 43.0         | -7.5             | -3.1             | 58        | 0.932    | 0.696   |
| [MEA.Cl][AP]=1:4   | 35.6         | -6.6             | -2.8             | 57.2      | 0.895    | 0.720   |
| [HmIm.Cl][AP]=1:1  | 49.3         | -25.2            | -12.5            | 59.2      | 1.000    | 0.631   |
| [HmIm.Cl][AP]=1:2  | 43.2         | -9.1             | -4.5             | 58.1      | 0.941    | 0.629   |
| [HmIm.Cl][AP]=1:3  | 42.7         | -8.0             | -3.6             | 57.4      | 0.910    | 0.720   |
| [HmIm.Cl][AP]=1:4  | 39.8         | -5.8             | -2.6             | 56.6      | 0.869    | 0.713   |

$E_{a,\eta}$  = kJ.mol<sup>-1</sup>,  $\Delta H^\circ$  = kJ.mol<sup>-1</sup>,  $\Delta S^\circ$  = J.K<sup>-1</sup>.mol<sup>-1</sup>,  $E_T(30)$  = kcal.mol<sup>-1</sup>, error in  $E_{a,\eta}$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $E_T(30)$  are  $\pm 0.003$ ,  $\pm 0.002$ ,  $\pm 0.001$  and 0.004, respectively.

To account for the impact of intermolecular interactions on the course of CO<sub>2</sub> capture, at elevated temperatures, thermodynamics (standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ )) of capture along with the solvent polarity parameters ( $E_T(30)$ ,  $\alpha$  and  $\beta$ ) are discussed further to unravel the underlying mechanisms.<sup>33,37</sup> (see ESI, Figs. S8 and S9 and Table S2)

As shown in Table 1, a positive  $\Delta H^\circ$  for [EDA]-based DESs indicates an endothermic nature of CO<sub>2</sub> uptake while a negative  $\Delta H^\circ$  for [AP]-based DESs signals that the process is exothermic. The standard entropy change ( $\Delta S^\circ$ ) is positive for [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<sub>2</sub> uptake becomes more spontaneous ( $-T\Delta S^\circ > \Delta H^\circ$ ) in [MEA.Cl][EDA] and [HMIm.Cl][EDA] than the [MEA.Cl][AP] and [HMIm.Cl][AP] as the temperature rises. A shift in HBA:HBD from 1:1 to 1:4 lowers  $\Delta H^\circ$  and  $\Delta S^\circ$  in the [EDA]-based DESs and thus renders CO<sub>2</sub> uptake more spontaneous. In the [AP]-class of DESs with an increase of HBA:HBD ratio,  $\Delta H^\circ$  and  $\Delta S^\circ$  become less negative and thus spontaneous and result in higher CO<sub>2</sub> 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<sub>2</sub> spontaneously as the temperature increases (ESI Table S1). More importantly, a very small value of  $\Delta H^\circ$  for [EDA]-based DESs makes regeneration of the absorbent energy-saving which is a key factor in practical applications.<sup>38</sup>

The nature of DES-CO<sub>2</sub> interactions was then investigated in terms of the Kamlet-Taft parameters  $\alpha$  and  $\beta$  which measure donor and acceptor strength, respectively (ESI, Table S2 and Fig. S10). The positive effect of CO<sub>2</sub> uptake indicates "synergetic/synergistic interaction" of the donor and acceptor sites in the [EDA]-based DESs. The synergistic action is widely acknowledged in catalysis and polarity measurements of binary systems.<sup>39,40</sup> The "hyperpolarity" in the binary mixture of ILs was observed when the donor ( $\alpha$ ) and acceptor ( $\beta$ ) strengths become similar and favour synergetic interaction.<sup>41</sup> In other words, for synergetic 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 HBA and HBD in a DES and lower the probability for synergetic interactions (Scheme 1). The synergy in the DES results in weak interactions which is reflected in the low polarity ( $E_T(30)$ ) and  $\Delta H^\circ$  and  $\Delta S^\circ$  values.



Scheme 1. Representation of synergetic and non-synergetic interaction and thermodynamic criteria in DESs.

As shown in Table 1, the relative  $\alpha$ - $\beta$  for [MEA.Cl][EDA] is lower than [MEA.Cl][AP] and [HMIm.Cl][AP] at 1:1. The small  $\alpha$ - $\beta$

suggests alignment of the donor and acceptor energy levels for synergetic interactions. At higher HBA:HBD ratios, in [EDA]-based DESs, relative  $\alpha$ - $\beta$  nears zero and renders the synergetic interactions more feasible. Lowering in the  $\Delta H^\circ$  and  $\Delta S^\circ$  further support this trend. Similarly, the  $\alpha$ - $\beta$  trend in [HMIm.Cl][EDA]-class of DESs also indicates synergetic interactions, at different molar ratios. The relative  $\alpha$ - $\beta$  for [AP]-class of DESs is comparatively large and hence result 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 synergetic interactions (Scheme 1). Thus, the greater CO<sub>2</sub> uptake in [AP]-class of DESs, at higher HBA:HBD ratios, is due to the reduced viscosity.

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

In summary, we for the first time have reported the temperature-promoted CO<sub>2</sub> capture in the novel [EDA]-based DESs. The positive effect of temperature on CO<sub>2</sub> capture arises from the synergetic interactions between the donor and acceptor moieties. Synergetic interactions in DESs are caused by the small  $\alpha$ - $\beta$  and  $E_T(30)$  and positive  $\Delta H^\circ$  and  $\Delta S^\circ$ . Lower CO<sub>2</sub> 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 evolve as an excellent substitute for the amine-based technology in a CO<sub>2</sub> capture plant.

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## Conflicts of interest

There are no conflicts to declare.

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