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Is basicity the sole criterion for attaining high carbon dioxide capture in deep-eutectic solvents?†

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A critical analysis of the role of Hammett basicity (H_-) and aqueous basicity (pK_a) in CO_2 uptake in deep-eutectic solvents (DESS) suggests that neither H_- nor pK_a correlates with the CO_2 w/w% capacity in the studied DESS. Instead, strong “synergistic interactions” between donor and acceptor moieties satisfactorily relate to the w/w% of CO_2 in DESS.

The use of renewable energy as the primary energy supply also requires the improvement in the conservation efficiency of fossil fuels and can only be accomplished by efficient environment-friendly carbon dioxide (CO_2) capture.¹ The anthropogenic emissions of CO_2 in the atmosphere are surging day-by-day and increasing the threat of global warming.² The current state-of-the-art technology in the CO_2 capture is the use of basic amine solutions as a scrubber though this methodology is associated with several critical shortcomings such as high regeneration energy, amine volatility and corrosivity and high maintenance cost of the setup.^{3,4}

The past century has witnessed a lot of effort in quest of “green and sustainable” solvents alternative to volatile organic solvents. Among them, ionic liquids (ILs) and deep-eutectic solvents (DESS) have garnered maximum attention, as they have the potential to be utilized in various applications because of their advantageous properties such as often insignificant vapour pressure, high thermal stability, a wide liquidus range, low flammability and good recyclability.^{5,6} In the past two decades, interest emerged in testing the ability of both ILs and DESS as scrubber solvents in the acid gas (CO_2 and SO_2) sequestration.

The pioneering work of Blanchard’s *et al.* showed that CO_2 can be partitioned in the IL phase with the least contamination to the CO_2 phase.⁷ This study garnered the attention of researchers worldwide and the last decade has witnessed an upsurge in utilizing ILs in the CO_2 capture.^{8–10} As an example, use of a 60% IL–water mixture instead of aqueous mono-ethanolamine (MEA) lowered the energy costs by 16%.¹¹

Later, significant improvements in the CO_2 capture were noticed upon the introduction of a basic moiety on the cation side-chain and involving a highly basic anion.^{12–23} However, a direct correlation of CO_2 loading (w/w%) with the basicity is missing for ILs. Despite the extensive research efforts in the CO_2 capture in ILs, these coulombic solvents turn into a viscous glue and hence render regeneration very difficult.^{24,25} Furthermore, the synthesis of task-effective ILs is not cost-competitive as it requires several synthetic and purification steps compared to MEA.^{13,22,26}

Contrary to the ILs, DESS, which require a single step atom-economic process and have properties analogous to ILs, provide a promising alternative in CO_2 capture and result in a higher gravimetric uptake.²⁷ The efficiency of DESS in CO_2 capture relies on complexing an adequate hydrogen bond acceptor (HBA) with an efficient hydrogen bond donor at an optimal molar ratio.²⁸ Because of the ease in terms of property tunability, in a short span, DESS have found application in synthesis, polymerization, stabilization of biomolecules, nanotechnology, separation, extraction of various compounds and so on.^{29–33} The screening of DESS in CO_2 capture showed moderate to high CO_2 uptake in potential DESS.^{34–40} Out of several structural features of DESS, the role of HBD components was acknowledged more in attaining high gravimetric CO_2 .^{35–37}

Despite the huge success in identifying the potential media for CO_2 capture, the major discussion revolves around the acid–base interactions between the solvents and CO_2 molecules. Be it the aqueous MEA, methyldiethylamine (MDEA), ionic liquids (ILs) or deep-eutectic solvents (DESS), basicity has been the only criterion suggested for the high CO_2 uptake although it failed at some instances.⁴⁰ The activation of amino-acid ILs by the

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carboxyl group has shown the importance of the “multiple-site interactions” in multimolar CO₂ capture.⁴¹ Recently, we discussed the significance of the intermolecular interactions in guiding high CO₂ uptake in DESs.⁴² The “synergistic interaction” between the donor and acceptor moieties in DESs was observed as the controlling parameter in the temperature-dependent CO₂ capture in ethylenediamine (EDA)- and polyamine-based DESs.⁴³ Though the multiple-site-, intermolecular- and synergistic-interactions are accounted where basicity does not act as a guiding factor, their applicability, especially the synergistic interactions, which can be represented by making use of the Kamlet–Taft parameters,⁴³ has not been tested as a guiding criterion in the acid gas capture. The current work presents a critical discussion about the role of basicity and synergistic interactions in the CO₂ uptake in DESs. The Hammett basicity (*H*_–) and aqueous basicity of HBD components are applied as basicity parameters for DESs.

The DESs employed in the present work were synthesized by complexing monoethanolammonium chloride ([MEA.Cl]), tetrabutylammonium bromide ([TBAB]), and diethylenetriammonium trichloride ([DETA.Cl]) with moderate to high basicity HBDs such as ethanolamine ([EA]), diethanolamine ([DEA]), triethanolamine ([TEA]), [EDA], 3-amino-1-propanol ([AP]) and tetraethylenepentamine ([TEPA]) (see the ESI† for synthesis, entry 1) and their structures are exhibited in Fig. 1. Their characterization results and CO₂ uptake monitoring by ¹³C NMR are given in the ESI† (entries 2–6).

For all the DESs, the CO₂ uptake at saturation, Hammett basicity (*H*_–), pseudo-rate constant (*k*) and some Kamlet–Taft parameters (α and β) are shown in Table 1 and their methods are discussed in the ESI† (see entry 7). *E*_T(30) and π^* are given in Table S2 (see the ESI†). For all the DES systems, the mass of CO₂ captured was observed to fit into an exponential growth model equation proposed by Box & Lucas (see the ESI†, Fig S34).

$$w_{\text{CO}_2} = a(1 - e^{-kt}) \quad (1)$$

where *a* is the maximum amount of CO₂ absorbed in DESs and *k* is the pseudo-rate constant for the CO₂ capture. The parameter *k* does not represent the first order kinetics by any means

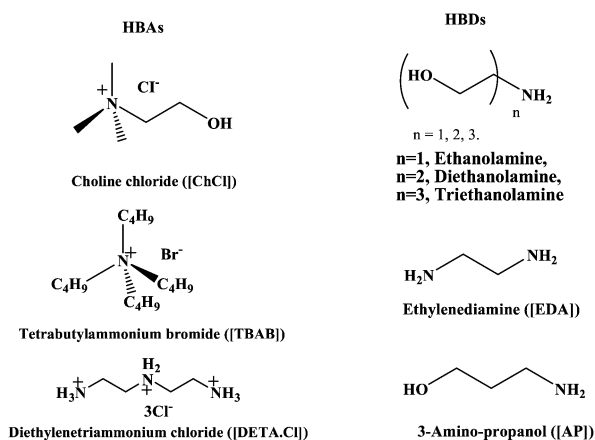


Fig. 1 Structure of DESs.

Table 1 Gravimetric CO₂ uptake, pseudo rate constant, Hammett basicity, Kamlet–Taft parameters and viscosity in different DESs

DESs	<i>k</i> (min ^{–1}) × 10 ²	CO ₂ uptake (w/w%)	<i>H</i> _–	α	β
[ChCl][EA] = 1 : 6	25.9	29.2	4.83	0.64	0.68
[ChCl][DEA] = 1 : 12	14.9	19.6	4.40	0.78	0.68
[ChCl][TEA] = 1 : 3	5.0	8.0	4.37	0.81	0.68
[TBAB][EA] = 1 : 5	15.0	19.7	4.54	0.42	0.81
[TBAB][DEA] = 1 : 2	4.1	9.6	4.43	0.45	0.78
[TBAB][TEA] = 1 : 2	3.1	2.5	4.35	0.53	0.76
[DETA.Cl][EDA] = 1 : 4	15.7	32.2	6.51	0.83	0.65
[DETA.Cl][AP] = 1 : 4	12.4	18.3	4.43	1.03	0.61
[DETA.Cl][TEPA] = 1 : 4	2.9	9.9	5.59	0.57	1.28

Errors associated with the pseudo rate constant (*k*), wt% CO₂, polarity parameters and Hammett basicity are ±0.003, ±0.004, ±0.004, and, ±0.003, respectively.

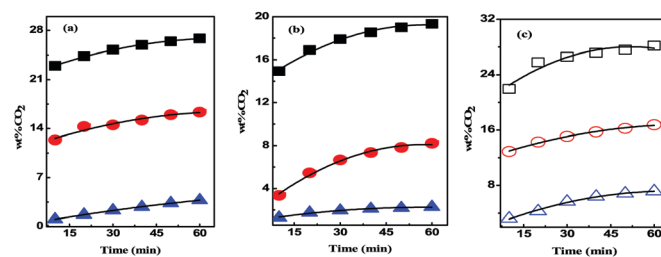


Fig. 2 CO₂ uptake in (a) [ChCl]- and (b) [TBAB]-based DESs containing HBDs [EA] (■), [DEA] (●) and [TEA] (▲) whereas (c) in [DETA.Cl]-class of DESs comprising [EDA] (□), [AP] (○) and [TEPA] (△) as HBDs.

but affords an idea about how slow or fast CO₂ capture in different DESs is. The larger value of *k* results in higher CO₂ w/w%. The goodness of fit of eqn (1) in different DESs is shown in the ESI† (Table S3).

For convenience, the dependence of CO₂ uptake on the structural parameters of DESs is analyzed in terms of the change in HBD and HBA components. The influence of different HBDs on the CO₂ uptake incorporated with similar HBAs is demonstrated in Fig. 2.

In [ChCl]- and [TBAB]-classes of DESs, CO₂ wt% lowers with the decreasing basicity of HBD from [EA] to [DEA] to [TEA] as shown in Fig. 2(a) and (b). The large difference in the CO₂ absorption isotherms in [ChCl]- and [TBAB]-based DESs indicates the influence of HBDs on CO₂ capture. Furthermore, the Hammett basicity (*k*) of DESs and aqueous basicity (*pK*_a) of HBD components were noted as guiding factors in CO₂ loading (w/w%) in [ChCl]- and [TBAB]-based DESs.

$$[\text{ChCl}][\text{EA}] (4.83) > [\text{ChCl}][\text{DEA}] (4.40) > [\text{ChCl}][\text{TEA}] (4.37).$$

$$[\text{EA}] (9.45) > [\text{DEA}] (8.88) > [\text{TEA}] (7.77).$$

The above ordering of DESs in terms of *H*_– and *pK*_a though justifies the role of basicity in CO₂ w/w% in [ChCl]- and [TBAB]-based DESs; but, the decrease in the CO₂ w/w% to 1/4th and 1/8th upon moving from [EA] to [TEA] in [ChCl]- and [TBAB]-classes of DESs despite a small change in the *H*_– and *pK*_a values



suggests that basicity alone cannot be responsible for the sharp decrease in CO₂ wt%.

The above inference becomes more evident when discussing the CO₂ uptake results in [DETA.Cl]-based DESs with [EDA], [AP] and [TEPA] as HBDs (Fig. 2(c)). In the [DETA.Cl]-class of DESs, the CO₂ loading (w/w%) does not follow the order of H_- or pK_a as shown below.

$$[\text{DETA.Cl}][\text{EDA}] (6.51) > [\text{DETA.Cl}][\text{TEPA}] (5.59) > [\text{DETA.Cl}][\text{AP}] (4.43).$$

$$[\text{EDA}] (10.71) > [\text{TEPA}] (9.81) > [\text{AP}] (4.09).$$

As the above arrangements of DESs in terms of H_- or pK_a do not correspond with CO₂ wt%, the basicity appears ineffective here. Furthermore, nearly two-fold higher CO₂ uptake is noted in [DETA.Cl][AP] = 1 : 4 than in [DETA.Cl][TEPA] = 1 : 4 despite the lower H_- or $1/2pK_a$ value of the former. These observations confirm that high CO₂ uptake in these DESs is controlled neither by H_- nor pK_a and seems to be guided by a rather complex interaction between the HBD and HBA components.

Moreover, the HBA's comparison shows higher CO₂ loading in [ChCl]- than in [TBAB]-based DESs despite the similar HBD components (Fig. 3). The large difference in the CO₂ uptake capacity of [ChCl] and [TBAB] could be partially due to the steric repulsion caused by the long butyl chain present in the [TBAB] and partly to the higher molar ratio of the HBD components. A crossover point is noticed in the case of [TEA] owing to the viscosity variation during the CO₂ capture (Fig. 3(c)).³¹ Given these observations, it can be conferred that along with the basicity of HBD components, the structural and electronic features of HBAs also play an important role in the CO₂ capture.

In DESs, both the donor and acceptor lose their identity and result in a new continuum with a different set of solvation properties. Therefore, the inclusion of the solvation properties of DESs, which arises due to the complex donor-acceptor interactions, in the current discussion might help in identifying the governing factors which control the CO₂ capture.

The solvation behaviors of DESs and ILs have been perceived in terms of the electronic transition energy ($E_T(30)$) and Kamlet-Taft parameters, which comprise of hydrogen bond donor acidity (α), hydrogen bond acceptor basicity (β) and the polarity index (π^*).³⁵ The details about the polarity parameters are discussed in the ESI† (see entry 7).

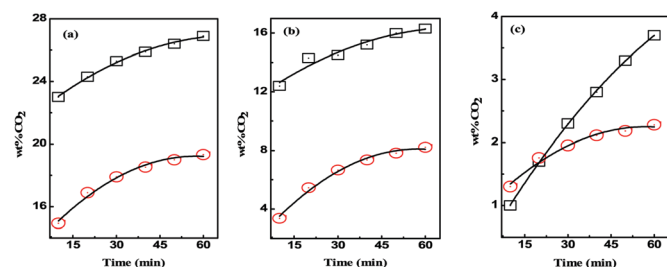


Fig. 3 CO₂ uptake in [ChCl] – (□) and [TBAB] – (○) based DESs containing (a) [EA], (b) [DEA] and (c) [TEA] as HBDs.

The Kamlet-Taft parameters (α and β) for different DESs are shown in Table 1. The correlation of polarity parameters with the CO₂ uptake data for [TBAB]-based DESs is exhibited in Fig. 4. As shown in Fig. 4(a), high CO₂ uptake is favored in less polar DESs. An inverse trend between π^* and $E_T(30)$ for the [TBAB]-class of DESs is due to the high β value (Fig. 4(a) and (c)). The $E_T(30)$ increases upon increasing the number of ethanolic (–CH₂–CH₂–OH) moieties in the HBD component. The trend of CO₂ against α and β indicates that higher CO₂ uptake can be achieved in DESs by complexing less acidic and strongly basic moieties (Fig. 4(b)). Contrary to [ChCl]- and [DETA.Cl]-classes of DESs, [TBAB]-based DESs possess lower $E_T(30)$, smaller α but higher β . The [ChCl]-based DESs have higher $E_T(30)$ but comparable α and β values than the [TBAB]-class of DESs. Though the trend of $E_T(30)$, α and β against the CO₂ uptake is similar in [ChCl]- and [TBAB]-based DESs, higher CO₂ wt% is noted in [ChCl]-based DESs than in the [TBAB]-class of DESs with identical HBDs. However, none of these polarity parameters correlate with the CO₂ w/w% in all DESs.

A temperature-promoted CO₂ capture study in ethylenediamine (EDA)-based DESs showed that rather than the hydrogen bond donor basicity (β), comparable α and β values correlate well with the CO₂ w/w%.⁴³ The comparable α and β cause “synergism” in the DES and result in higher CO₂ w/w%. Synergistic interaction is noted as a thermodynamically controlled phenomenon and takes place under the positive set of enthalpy (ΔH°) and entropy (ΔS°) changes.⁴³ In an ideal case, for maximum synergistic interaction $|\alpha - \beta| = 0$. In a previous study, a near-zero $|\alpha - \beta| \approx 0$ is linked with the high CO₂ uptake in DESs.⁴³ The synergistic action is widely acknowledged in catalysis and polarity measurements of binary systems.^{43,44}

Synergistic interaction was noted operative in the DESs employed for CO₂ capture. [ChCl][EA] = 1 : 6 showed higher CO₂ uptake (29.2 wt%) than [TBAB][EA] = 1 : 3 (19.7 wt%) because of the equivalent α (0.64) and β (0.68) values in the former than the latter. Likewise, [ChCl][DEA] = 1 : 12 has similar α and β and hence possesses higher CO₂ uptake (19.6 wt%) than [TBAB][DEA] = 1 : 2 (9.6 wt%) for which $\beta \gg \alpha$. Analogously, higher CO₂ uptake in [ChCl][TEA] = 1 : 3 in comparison with [TBAB][TEA] = 1 : 2 can be ascribed to the nearly lower $|\alpha - \beta|$ values.

In the [DETA.Cl]-class of DESs, the strongest synergistic interaction prevailed in [DETA.Cl][EDA] = 1 : 4 and resulted in 32.2 wt% CO₂ owing to the comparable but higher α and β

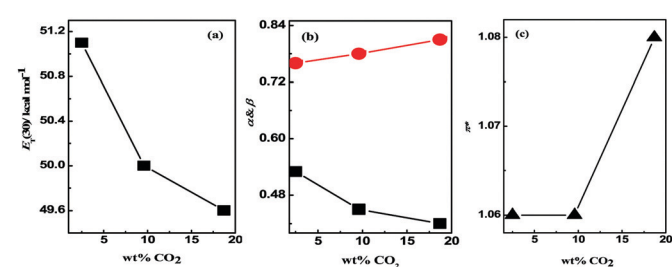


Fig. 4 A correlation between the CO₂ uptake (wt%) and (a) $E_T(30)$, (b) α (■) and β (●) and (c) π^* (▲) in [TBAB]-based DESs.



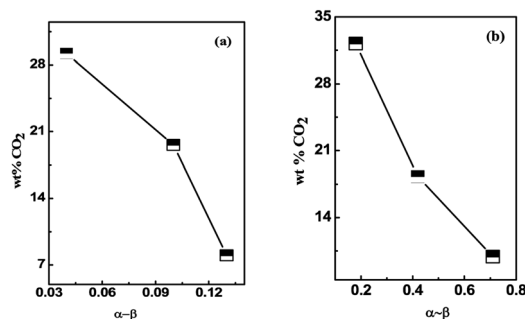


Fig. 5 A correlation between CO₂ wt% and $|\alpha - \beta|$ in (a) [ChCl]- and (b) [DETA.Cl]-based DESs.

values. [DETA.Cl][AP] = 1:4 and [DETA.Cl][TEPA] = 1:4 have higher $|\alpha - \beta|$ and hence 18.3 wt% and 9.9 wt% of CO₂ were obtained, respectively. The greater $|\alpha - \beta|$ causes an energy difference between the donor and acceptor moieties and disfavor high CO₂ capture, whereas, the comparable α and β values bring the donor and acceptor together for optimum CO₂ w/w%. Fig. 5 exhibits the dependence of CO₂ wt% on $|\alpha - \beta|$ in [ChCl]- and [DETA.Cl]-based DESs.

The above discussion delineates the importance of synergistic interaction in high CO₂ capture in DESs. The synergistic interaction becomes important in cases where a direct correlation of basicity or acidity with the observation is not feasible. The CO₂ uptake analysis in [TBAB]-, [ChCl]- and [DETA.Cl]-based DESs represents one such case, where CO₂ uptake resulting in the studied DESs can be explained based on the $|\alpha - \beta|$ values.

In conclusion, we have discussed the importance of the synergistic interaction upon CO₂ capture in various classes of DESs. The above investigation demonstrates that neither the high Hammett basicity H_- nor pK_a results in high CO₂ capture as noted in the case of [DETA.Cl][TEPA] = 1:4 (H_- = 5.59 and β = 1.28). Alternatively, comparable α and β values in a DES establish synergistic interactions and favour high CO₂ uptake. We believe that this study will motivate researchers to explore other important factors such as multiple-site- and intermolecular-interactions which will help in developing the understanding of acidic gas capture and conversion to useful products.

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Conflicts of interest

There are no conflicts to declare.

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