**Bifunctional Ionic Deep Eutectic Electrolytes for CO₂ Electroreduction**

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**ABSTRACT:** CO₂ is a low-cost monomer capable of promoting industrially scalable carboxylation reactions. Sustainable activation of CO₂ through electroreduction process (ECO₂R) can be achieved in stable electrolyte media. This study synthesized and characterized novel diethyl ammonium chloride–diethanolamine bifunctional ionic deep eutectic electrolyte (DEACl–DEA), using diethanolamine (DEA) as hydrogen bond donors (HBD) and diethyl ammonium chloride (DEACl) as hydrogen bond acceptors (HBA). The DEACl–DEA has −69.78 °C deep eutectic point and cathodic electrochemical stability limit of −1.7 V versus Ag/AgCl. In the DEACl–DEA (1:3) electrolyte, electroreduction of CO₂ to CO₂⁻ was achieved at −1.5 V versus Ag/AgCl, recording a faradaic efficiency (FE) of 94%. After 350 s of continuous CO₂ sparging, an asymptotic current response is reached, and DEACl–DEA (1:3) has an ambient CO₂ capture capacity of 52.71 mol/L. However, DEACl–DEA has a low faradaic efficiency <94% and behaves like a regular amine during the CO₂ electroreduction process when mole ratios of HBA–HBD are greater than 1:3. The electrochemical impedance spectroscopy (EIS) and COSMO-RS analyses confirmed that the bifunctional CO₂ sorption by the DEACl–DEA (1:3) electrolyte promote the ECO₂R process. According to the EIS, high CO₂ coverage on the DEACl–DEA/Ag-electrode surface induces an electrochemical double layer capacitance (EDCL) of 3.15 × 10⁻⁹ F, which is lower than the 8.76 × 10⁻⁹ F for the ordinary DEACl–DEA/Ag-electrode. COSMO-RS analysis shows that the decrease in EDCL arises due to the interaction of CO₂ non-polar sites (0.314, 0.097, and 0.779 e/nm²) with that of DEACl (0.013, 0.567 e/nm²) and DEA (0.115, 0.396 e/nm²). These results establish for the first time that a higher cathodic limit beyond the typical CO₂ reduction potential is a criterion for using any deep eutectic electrolytes for sustainable CO₂ electroreduction process.

1. INTRODUCTION

The current level of CO₂ in the atmosphere is approximately 420.57 ppm, causing a rise in global temperature because CO₂ can absorb UV-radiation from the sun and emit heat, consequently causing significant climate change.¹–⁸ Therefore, sustainable CO₂ sequestration that leaves behind a low carbon footprint and low earth temperature is desired to ameliorate climate change issues.⁹ Previous suggestions involve technologies for capture and storage of CO₂ (CCS), but the cost of desorbing and compressing CO₂ from the capture solution to a potential CO₂ electrolyzer is a major challenge.¹⁰,¹¹ Instead of the CCS, electrochemical CO₂ capture and utilization emerge to eliminate storage costs and promote the generation of platform chemicals¹²–¹⁷ and sustainable energy storage options.¹⁸–²¹

The electrochemical CO₂ reduction (ECO₂R) commonly uses CO₂ and amine solutions as inexpensive C-1 feedstock and electrolytes, respectively, to produce useful chemicals. For instance, the electroreduction of CO₂ to CO using ethylene diamine (EDA)/aqueous NaClO₄ electrolyte was reported to achieve Faradaic efficiency of 58% at the Cu electrode.²² Similarly, monoethanolamine (MEA) electrolyte was reported to facilitate the ECO₂R to CO and HCOO⁻, achieving 39.1 and 45% Faradaic efficiency, respectively. The low Faradaic efficiency is because the most captured CO₂ by MEA remained unused as free CO₂ approaches the Ag electrode in the amine electrolyte, unlike CO₂-rich carbamate species.²³ To control the ECO₂R by CO₂ adsorption or absorption, new stable electrolytes are required because the formation of proctic substances by amines can limit the process.

Deep eutectic solvents (DESs) are promising as electrolytes for ECO₂R, as they are tunable for task-specific applications.²⁴–³¹ DESs are simple to prepare, requiring only the mixing of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), avoiding any purification of side products.²² So far, there are various cheap and renewable molecules that can serve as HBA or HBD, making DESs a potential and

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sustainable media for many applications. Because the HBA and HBD are joined by hydrogen bonds for DESs formation, charge delocalization is imminent, inducing distinct physicochemical features for high CO$_2$ solubility during ECO$_2$R application. In accordance, non-amine-based DESs used as electrolyte for ECO$_2$R include choline chloride (ChCl) and urea-based DES in water (50 wt %) and ChCl and ethylene glycol (EG)-based DES over Ag electrode. These DESs electrolytes were able to facilitate CO$_2$ conversion to CO, achieving 96 and 78% Faradaic efficiency, respectively. The amine-based DESs are only common for CO$_2$ capture, but recently DESs such as methyl diethanolamine hydrochloride methyl diethanolamine (MDEAHCI-MDE) and zinc chloride ethanolamine (ZnCl-EA), have facilitated ECO$_2$R to CO and CO$_2$$^\ast$, respectively. The MDEA stores CO$_2$ in the form of bicarbonate rather than carbonate, which has a higher theoretical CO$_2$-capturing capability than MEA. Also the MDEAHCI have high CO$_2$ uptake because of the high dielectric constant and basicity. These studies affirm the viability of amine-based deep eutectic solvents as electrolytes. As the amine-based deep eutectic electrolytes are emerging as media for ECO$_2$R, the consequent effect of double-layer capacitance (EDCL) structure in CO$_2$-saturated amine-based DESs is unclear. This EDCL is important to understand the interfacial phenomena during ECO$_2$R. Since some DESs are hydrophilic, water content associated with DESs as electrolytes could potentially induce hydrogen evolution reactions during ECO$_2$R. These challenges can collectively hamper the scalable development of effective DESs media as electrolyte for CO$_2$ electroreduction.

This study investigates CO$_2$ electroreduction to CO$_2$$^\ast$ in novel diethylammonium chloride–diethanolamine (DEACI–DEA) ionic deep eutectic solvent as electrolyte. The ionic deep eutectic electrolyte was prepared from diethyl ammonium chloride (DEACI; HBA) and diethanolamine (DEA; HBD) and indexed as DEACI–DEA. The electrolyte was fully characterized to elucidate its physiochemical properties and stability that is suitable to enable understanding of interfacial phenomena during CO$_2$ saturation and electroreduction. Prior to the electroreduction process, the DEACI–DEA was vacuum dried to eliminate moisture that could induce hydrogen evolution reaction which reduces the energy efficiency of the CO$_2$ electroreduction process. Therefore, in the DEACI–DEA medium, the electroreduction of CO$_2$ to CO$_2$$^\ast$ was conducted in a membraneless electrolyzer. The corresponding current responses of CO$_2$$^\ast$ in DEACI–DEA were transformed to concentration for estimating the equivalent amount of CO$_2$ utilized during the process. The DEACI–DEA ionic deep eutectic electrolyte is unlike our previous study that used transition metal-based DESs with a pseudocapacitive attribute, in which case CO$_2$ saturation therein further increased the double layer capacitance. Instead, DEACI–DEA has a different double layer capacitance features upon CO$_2$ saturation. Therefore, electrochemical impedance spectroscopy (EIS) in the potentiostatic mode elucidated the double layer structures in the CO$_2$-saturated ionic DEACI–DEA system during the electroreduction process at the CO$_2$–DEACI–DEA/Ag electrode interface. COSMO-RS theoretical analysis further elucidates the bifunctional attribute of DEACI–DEA, forming interaction with π-orbitals of CO$_2$ through its HBA and HBD sites. The work integrated several investigations to provide insights into CO$_2$ environments as well as a simple electrochemical method for assessing the gas processing and absorption capability of potential green solvents.

2. MATERIALS AND METHODS

2.1. Materials. Ultra-pure CO$_2$ and N$_2$ gas were purchased from Gaslink SDN Malaysia. DEA and DEACI were procured from Sigma-Aldrich, Darmstadt, Germany, having 98% purity. The fittings such as electrodes include counter electrode Pt wire/5.7 cm, BASi Inc., working electrode, silver (Ag)/OD: 6 mm, ID: 3 mm, and the reference electrode of Ag/AgCl (6 mm).

2.2. Preparation of DEACI–DEA. The ionic DESs were synthesized through constant mixing of known mole ratios (1:2, 1:3, 1:4, 1:5, and 1:6) of HBA (DEACI) and HBD (DEA) components at 70 °C for 8 h using a similar method reported previously. Then, the DESs were dried and aged to observe the best mole ratio that maintained its fluidity without recrystallization.

2.3. Physicochemical Properties of DEACI–DEA. DSC-8000 PerkinElmer was used to assess the thermal behavior of the DEACI–DEA ionic DES sample. The experiments were carried out in a high-quality N$_2$ inert atmosphere of 20 mL min$^{-1}$. A sample of DEACI–DEA weighing less than 5 mg was partly encapsulated in aluminum pans to let the water evaporate freely. Multiple scans were carried out spanning the temperature range of 70–200 °C at cooling and heating speeds of 10 °C min$^{-1}$. The sample was held at 200 °C for a time after each scan to remove water. To get a stronger signal of the glass transition temperature, if present, and the melting point at the eutectic point, each sample was also held at 70 °C for 10 min.

The viscosity of DEACI–DEA ionic DESs was determined using a DVII + Pro Extra Brookfield viscometer at 25 °C for different mole ratios similar to the previous report. Typically, 10 mL of DEACI–DEA DES was poured into a cylindrical container immersed with the spindle. The spindle speed was set from the viscometer to different revolutions per minute (rpm) and corresponding shear rates (s$^{-1}$). Eventually, the viscosity of DEACI–DEA DES with different mole ratios was measured at ambient temperature throughout the process. A DM40 Mettler TOLEDO density meter was used to measure the density of DEACI–DEA ionic DESs across the temperature range of 25–90 °C in 10° steps.

2.4. Measurement of CO$_2$ Concentration in DEACI–DEA. The CO$_2$ solubility in ionic DESs was measured with the chronoamperometry module at −1.5 V versus Ag/AgCl similar to the previous procedure. In a typical experiment, an electrochemical cell of 10 mL volume was filled to 1/4 capacity with dried ionic DESs and sparged with CO$_2$ at 5 bar, as illustrated in Figure S1. The electrochemical cell contains clamped Pt wire (5.7 cm, BASi Inc.) counter electrode, a silver (Ag) (OD: 6 mm, ID: 3 mm) working electrode, and a saturated Ag/AgCl (6 mm) reference electrode. The current response for CO$_2$ was recorded on an Auto-lab Potentiostat model PGSTAT302N. The cell containing saturated CO$_2$ was surrounded with N$_2$, while the measurement process proceeded for sterilization. Therefore, Nova 2.1 software was used to control data acquisition for detecting CO$_2$ solubility in the ionic DESs. During the process, 1 SCFH continuous CO$_2$ was maintained in the electrochemical cell for a maximum of 350 s stationary current value of I$_{st}$ at 25 °C. The rates of CO$_2$ conversion through chemical absorption and dissolution are the same at I$_{st}$ following a Cottrell-like chronoa
profile with the onset of limiting currents of \( I_0 \) that are momentarily transport controlled, as given by eq 1.\(^{41}\)

Concentration \((C_0)\) of \( \text{CO}_2 \) was determined using eq 2, after substituting values of \( I_{\lim} \), \( I_0 \), \( \nu \), and an equivalent weight of \( \text{CO}_2 \).

\[
I = I_0 + (I_0 - I_{\lim})\exp\left(-\frac{A_t}{t}\right)
\]

\[
C_0 = \frac{I_t^2}{[\nu FE I_0(I_0 - I_{\lim})]}
\]

\[
I = \frac{nFAC D_{I,0.5}}{\left(n \times 0.5\right)} = \left(\frac{nFAC D_{I,0.5}}{n \times 0.5}\right) \times \left(\frac{1}{(t)^{0.5}}\right)
\]

\[
\frac{nFAC D_{I,0.5}}{n \times 0.5} = \text{slope}
\]

\[
D_b = \left(\frac{\text{slope} \times (n \times 0.5)^2}{nFAC_{\nu}}\right)
\]

\[
FE(\%) = \left(\frac{znF}{I \times t}\right) \times 100
\]

where \( I_{\lim} \) = stationary state current (mA/cm\(^2\)), \( I_{\lim} \) = limiting current (mA/cm\(^2\)), \( C_0 \) = concentration (M), \( \nu \) = volume of electrolyte (mL), \( z \) = no. of electron, \( n \) = no. of \( \text{CO}_2 \) moles obtained from Ag electrode, \( I \) = total current (mA cm\(^{-2}\)), and \( t \) = time for a sample collection from the cell (s).

2.5. COSMOS-RS Analysis of \( \text{CO}_2/\text{DEACl}−\text{DEA} \) Interaction. Using the graphical user interface of the Turbomole program version 4.0,\(^{13}\) the cut-out plane of DEACl−DEA DESs was constructed and optimized based on the Hartree–Fock level of theory and a def-SV (P) basis set. Then, utilizing density functional theory/Beck-Perdew-86 functional\(^{15}\) and zeta valence potential (def-TZVP) basis set, a single-point calculation for the ionic DESs cut-off plane was carried out. Finally, to examine \( \text{CO}_2 \) interaction with the ionic DEACl−DEA DESs, a conductor-like screening model for realistic solvents (COSMO-RS) was employed based on BP-TZVP-C30-1401-CTD parameterization in COSMOthermX19 software.\(^{43,44}\) To accurately characterize the ionic DESs, an electroneutral model was used in the COSMO-RS study. The \( \text{CO}_2 \) concentrations in ionic DESs were predicted using the solubility job function in COSMOthermX19.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties of \( \text{DEACl}−\text{DEA} \). The DSC curve for DEACl−DEA in Figure 1a shows a shift of the baseline around −56.83 °C, indicating glass transition \((T_g)\). Also, an endothermic peak was observed around −60.92 °C, indicating a melting transition. There is no exothermic peak for crystallization, indicating that DEACl−DEA is not in an amorphous state. The designation of DEACl−DEA as a glass former is made possible by the discovery of glass transition from which a glass transition temperature \((T_g)\) value may be calculated. This is indicative of a shift in the DEACl−DEA’s structure from a glass-like state to a rubber-like one, or vice versa, as shown by an increase in heat capacity. Consequently, the utilization of DEACl−DEA at the \( T_g \) for \( \text{CO}_2 \) capture application will not be viable. In Figure 1b, the eutectic point for DEACl−DEA occurs at a 1:3 mole ratio with the onset of −60.92 °C melting temperature until −68.78 °C. By heuristics, the DEACl−DEA is operable without melting up to 100 °C safe temperature, because over this temperature range (−70 to 100 °C), there is no thermal activity peak. Furthermore, following different mole ratios, DEACl−DEA have \( T_m = -68.78 \) °C lower than that of DEACl \((T_m = 232 \) °C) and DEA \((T_m = 28 \) °C). Common in the literature, the melting temperatures of some DESs are positive, but DEACl−DEA has a negative melting point similar to the zwitterionic DESs such as phenylacetic/betaine (2:1; \( T_m = -7 \) °C) and glycolic/betaine (2:1; \( T_m = -36 \) °C).\(^{46}\) The negative melting point of DEACl−DEA or the zwitterionic DESs indicates that they can melt by liberating energy at the onset of melting without the requirement of any energy inputs. The effect of HBA/HBD mole fraction on the density of DEACl−DEA is shown in Table S1. The density of all the mole fractions was found to be −1.1 g/cm\(^3\) to the nearest 1 decimal place similar to other...
typical DESs reported previously. Moreover, the viscosity of DEACI–DEA shows that there is not much variation as the shear rate increases. This result is important for the continuous sparging of CO₂ in DEACI–DEA during the ECCO₂ process. Moreover, the stability of DEACI–DEA is an important feature to notice, particularly at the cathodic potential window of −1.7 V, as shown in Figure 2c. From −1.7 to 0.9 V, there is no observable Faradaic activity, implying that the electrochemical stability window is 2.6 V versus Ag/AgCl. Usually, DESs have a low electrochemical potential window, but this result indicates the significance of cathodic limits for the prospective viability of DESs in electroreduction reactions similar to the previous report.31

3.2. Transient Current in CO₂ Saturated DEACI–DEA.

3.2.1. Limiting and Stationary Current Response. The current responses during CO₂ electroreduction in DEACI–DEA are shown in Figure 2a. In screening the CO₂ capture capacity of DESs, estimating the current response is necessary. According to Figure 2a, during continuous sparging of CO₂ in the DESs, two prominent current patterns typical of the Cottrell-like profile, are recorded; (1) a current plateau (I_o), which later declined with time, and (2) a limiting current or stationary point where there are equal rates of CO₂ capture by the DESs and CO₂ conversion to CO₂•−, through chemical absorption. The onset potential for CO₂ reduction in DESs of −1.0 and −1.5 V versus Ag/AgCl potential was adopted for CO₂ electroreduction to CO₂•− free radical similar to the previous report.31 For instance, CO₂–CoCl₂/EA had a 3.2 mA/cm²Ι₀-value and reached an Ι₀-value of 1.4 mA/cm² after 700 s for CO₂ electroreduction to CO₂•−. In comparison, CO₂–DEACI–DEA have Ι₀-values of 0.432, 0.423, 0.566, and 0.38 mA/cm² for 1:2, 1:3, 1:4, and 1:5 mole ratios, respectively. The stationary current (Ι₀-value) of 0.282, 0.267, 0.304, and 0.213 mA/cm² was reached during continuous CO₂ sparging into DEACI–DEA after 350 s. In a phenomenological sense, the swiftness in reaching a stationary state in the DEACI–DEA implies that there is high CO₂ coverage in the locality of the Ag working electrode. This current response, particularly reaching the stationary limit within 350 s, confirms the COSMO-RS suggestion of the bifunctional nature of DEACI–DEA in the physical capturing of CO₂ using its HBA (DEACI) and HBD (DEA) sites.

3.2.2. Rate-Determining Step. According to Figure 2b, the current response decreased with time during continuous sparging of CO₂ in DEACI–DEA to form the CO₂•− free radical. Consequently, the onset period of the process where t ≈ 0 and designated by Ι₀-regime diffusion, which is only high, may likely be the limiting step. In the Ι₀-regime, CO₂ consumption and conversion to CO₂•− are not equal. The Ι₀-regime reaches a stationary current value of the Ι∞-regime, where the rates of CO₂ consumption and conversion to CO₂•− are equal. The values of CO₂ diffusion in DEACI–DEA DES are 3.130 × 10⁻¹⁰, 2.822 × 10⁻¹⁰, 8.352 × 10⁻¹⁰, and 9.368 × 10⁻¹⁰ m²/s, as computed from the Cottrell constant from Figure 2b. The Cottrell constant is a collection of parameters for the CO₂–DEACI–DEA DES system and varies for each mole ratio. For instance, the Cottrell constant for 1:2, 1:3, 1:4, and 1:5 mole ratio is 3.84 ± 0.02, 3.47 ± 0.02, 5.34 ± 0.02, and 3.40 ± 0.03, respectively. These Cottrell constant values were obtained from the slope according to eq 3, which is valid only for the finite-space diffusion in the short-time domain. However, the transition from the Ι₀-regime to the Ι∞-regime is involved by long-time domain and the process may not be controlled only by the diffusion of CO₂. To confirm this observation, we investigate the short-time domain and compare it with the total time taken to reach Ι∞-regime. The slopes of I(t) versus r⁻⁰.⁵ curves in the short-time domains were extrapolated to t ≈ 0. This is the region where the short-time domain (r_d) was estimated using L/D to be 3.478 × 10⁻¹⁰, 3.859 × 10⁻¹⁰, 1.304 × 10⁻¹⁰, and 1.162 × 10⁻¹⁰ for CO₂ saturation in DEACI–DEA with mole ratios 1:2, 1:3, 1:4, and 1:5, respectively. These results are based on the CO₂ kinetic diameter of 0.330 nm⁻³ and the values of r_d < Ι₀-regime. The r_d is very short in the nanosecond scale such that the process cannot only be diffusion controlled, but other limitations such as Ohmic drops or slow interfacial charge transfer kinetics could influence or be rate controlling during the transition from the Ι₀-regime to the Ι∞-regime. As a result of using the traditional Cottrell equation to analyze transient current data,
the response of the working electrode cannot be attributed only to the diffusion control. Because Cottrell defines the current–time dependence for linear diffusion control, a linear relationship between \( i \) and \( t^{-0.5} \) otherwise known as the Cottrell plot was expected. However, the linearity spans over only a short time (see the inset in Figure 2b), after which there is deviation. The deviation from the linearity of \( i(t)/t^{0.5} \) versus \( t^{0.5} \) indicates electroreduction of CO\(_2\) because \(-1.5 \) V is within the stable cathodic potential of DEACl–DEA. Overall, CO\(_2\) diffusion, in addition to Ohmic drop or charge transfer resistance, might decide the step of CO\(_2\) electroreduction. The plot of \( i(t)/t^{0.5} \) versus \( \log(t) \) in Figure 2c shows a maximum peak due to Ohmic drop and kinetic resistive contribution to the total current response for CO\(_2\) reduction to CO\(_2\)\(^{**}\).

### 3.3. Effect of \( n(DEACl)/n(DEA) \) on CO\(_2\) Absorption and Electroreduction.

Figure 3a shows the effect of the DEACl–DEA mole ratio on CO\(_2\) physisorption. After continuous sparging of CO\(_2\) into the DEACl–DEA, an observable increase in weight was recorded. The increase in weight of DEACl–DEA was attributed to the physisorption of CO\(_2\) in the ionic media. The viscosity of DEACl–DEA also increased from 385 cP to 500 cP after sparging CO\(_2\) continuously for 350 s, but the weight was a measure for easy referencing as shown in Figure 3a. By varying the mole ratios of DEACl–DEA during the physisorption process, the mass transfer of CO\(_2\) was adjusted relative to a unique equilibration time of the absorption process. In ordinary DEA, the CO\(_2\) capacity was only 0.05 \( \mu \)mol/L at 25 °C at ambient pressure after 350 s. However, in DEACl–DEA (1:3) DES, the physisorption capacity of CO\(_2\) in the DEACl–DEA reaches up to 0.2 mol/L, minimum after 350 s of sparging (Figure 3a).

The chemisorption of CO\(_2\) by DEACl–DEA was further investigated, where \(-1.5 \) V was supplied to the media. The results in Figure 3b showed that different mole ratios of DEACl–DEA have unique CO\(_2\) chemisorption. For instance, the mole capacity of CO\(_2\) decreased from 52.7 \( \mu \)mol/L in DEACl–DEA DESs (1:3), which is the highest to 28.3 \( \mu \)mol/L in DEACl–DEA DESs (1:6). This is accompanied by the Faraday efficiency (FE\(\text{CO}_2^{**} \)) increasing from 55 (DEACl–DEA; 1:6) to 95% (DEACl–DEA; 1:3) as the electrode was negatively polarized at \(-1.5 \) V in CO\(_2\) saturated DEACl–DEA. Compared with previous studies, when MDEA used to produce MEAHCl-MDEA (1:4), the Faraday efficiency concerning producing CO was 71% at 1.1 V. These Faraday efficiencies are different for CO\(_2\) electroreduction to CO\(_2\)\(^{**}\) in DEACl–DEA (1:3) as in the present study. Structurally, MDEA is different from DEA with the methyl group and a proton in the former and latter, respectively. Moreover, DEACl and MEAHCl are also different structurally in terms of two protons and a methyl group on the amine sites of the former and latter, respectively, with consequent different interactions with CO\(_2\). Although CO\(_2\) was converted in DEACl–DEA (1:3), the result therein is better than MEAHCl-MDEA (1:4) reported previously.

### 3.4. Effect of HBA and HBD on CO\(_2\) Absorption and Electroreduction.

The effect of HBA (TEACl or DEACl) and HBD (thymol or DEA) on CO\(_2\) physisorption is shown in Figure 4a. After varying the mole fraction of HBA and HBD, TEACl–DEA was found to capture more CO\(_2\) than DEACl-thymol. Compared with the data in Figure 4a, the amount of CO\(_2\) captured by DEACl–DEA is also more than that captured by DEACl-thymol (1:4). By implication, the TEACl or DEACl
has a free amino group that can be used as an HBA to facilitate CO\(_2\) capture below its critical pressure. On the contrary, thymol contains a phenolic hydroxyl group, which is suitable as an HBD. Previous studies found that when thymol was mixed with [TETA]Cl in a 1:3 molar ratio to form TETACl-thymol DES, thymol decreased the viscosity of TETACl.\(^{49}\) Consequently, there was an improvement in the mass transfer of CO\(_2\) in the absorbent, which lowered the time required to reach equilibrium. However, they found that thymol impedes the absorption capacity of CO\(_2\), for instance, compared to ethylene glycol HBD.\(^{48}\) Using TEPACl-thymol (1:3), the mole capacity of CO\(_2\) was 1.339 mol CO\(_2\)/mol absorbent but decreased to 1.183 mol CO\(_2\)/mol absorbent upon increasing the amount of thymol to (1:7). In congruence with previous investigations, the addition of acidic components in ionic or non-ionic solvents potentially lowers the capacity of acidic gases.\(^{49,50}\) This is considering that thymol is weakly acidic due to likely deprotonation from its phenolic group.\(^{47}\) As a result, acidic attributes of thymol could decrease the capacity of CO\(_2\) in DESs.

**Figure** 4b shows the chemisorption of CO\(_2\) on TEACl–DEA through CO\(_2\) electroreduction. The primary axis is the Faradaic efficiency for CO\(_2\) electroreduction to CO\(_2\)\(^{-}\). The secondary axis shows the CO\(_2\) absorption capacity. The TEACl–DEA (1:2) electrolyte gave the best Faradaic efficiency for CO\(_2\) electroreduction to CO\(_2\)\(^{-}\) (42.5%). Also, the CO\(_2\) absorption capacity of 12.4 µmol/L was obtained due to chemisorption is best in TEACl–DEA (1:2). We established that the DEACl-thymol is not electrochemically stable as there is no observable electrochemical window. Consequently, the CO\(_2\) electroreduction in DEACl-thymol is not assured to only CO\(_2\) but also to DEACl-thymol electrolyte components such as DEACl or thymol.

### 3.5. COSMO-RS Analysis of CO\(_2\)-Ionic DESs Interaction

The COSMO-RS analysis is significant to confirm CO\(_2\) absorption by the ionic DESs, which ensures its high coverage near the surface of the working electrode. High coverage of CO\(_2\) at the surface of the electrode assures the generation of CO\(_2\)\(^{-}\) free radical.\(^{41}\) As a result, the ionic DEACl–DEA DES captures the CO\(_2\) through non-covalent interactions, and the coverage can be high at the electrode surface. Using σ-profiles, the screening charge density of the ionic DESs was used to assess their non-covalent interaction with CO\(_2\). The ionic DESs interacted with their non-covalent interaction with CO\(_2\). The respite peaks in the ionic DEACl–DEA DES’s σ-profile are shown in Figure 5a at 1.677, 0.013, and 0.567 e/\(\text{nm}^2\) at the DEACl site and 1.677, 0.115, 0.396, 1.277, and 1.730 e/\(\text{nm}^2\) at the DEA DES site. The CO\(_2\) absorption density, similar respite peaks can be seen in the σ-profile of CO\(_2\): 0.598, 0.314, 0.097, and 0.779 e/\(\text{nm}^2\). The non-polar contribution region, where \(I_p\)-values are between 1.0 and +1.0 e/\(\text{nm}^2\), is where the DEACl–DEA DES and CO\(_2\) interacting screening charge densities are located.\(^{51,52}\) As previously reported,\(^{41}\) the screening charge densities on linear-symmetric CO\(_2\)’s electron function can indicate the non-polar contribution of linear–CO\(_2\) interaction with DESs, including ionic DES. It is worth noting that the CO\(_2\) interaction with DEACl–DEA DES is not the form of energized CO\(_2\) (CO\(_2^+\) free radical) with geometry from linear to bent at ~150°.\(^{41,53}\) The interaction of CO\(_2\) with DEACl–DEA DES based on the COSMO-RS analysis occurs on their non-polar sites such as −0.013, −0.567 e/\(\text{nm}^2\) at the DEACl site and −0.314, −0.097, −0.779 e/\(\text{nm}^2\) on CO\(_2\). Moreover, the 0.115, −0.396 e/\(\text{nm}^2\) non-polar site on DEA can interact with −0.314, −0.097, −0.779 e/\(\text{nm}^2\) on CO\(_2\). The results also confirmed that the interaction of CO\(_2\) with the ionic DES occurs in the non-polar region similar to the transition metal-based DESs reported previously.\(^{41}\) The DEACl–DEA DES has bifunctional attributes as both the HBD and HBA have been indicated by COSMO-RS analysis to interact with neutral CO\(_2\). These interactions are based on the criterion of like dissolves like. This indicates that the less endothermic the enthalpy of the solution is, the more soluble CO\(_2\) is in ionic DESs, and vice versa.

**Figure** 5. COSMO-RS analysis showing (a) σ-profiles of DEACl–DEA DES and (b) σ-potential of DEACl–DEA DES.
Figure 6. (a) Sigma surface showing the interaction of DEA with CO₂, (b) sigma surface showing the interaction of DEACl with CO₂, (c) effect of pressure on COSMO-RS CO₂ solubility at DEA and DEACl sites, (d) effect of temperature on COSMO-RS CO₂ solubility at DEA and DEACl sites, (e) Nyquist plot for ordinary DEACl−DEA, and (f) Nyquist plot for CO₂ saturated DEACl−DEA.
for DEACl and DEA sites. These findings support the notion that neutral CO$_2$ absorbed via the HBA or HBD site in ionic DESs is more likely to form CO$_2$ free radicals during the CO$_2$ electroreduction process.

3.6. Mechanism of CO$_2$ Absorption and Electroreduction in DEACl–DEA. COSMO-RS sigma profile analysis (Figure 5a,b), COSMO surface (Figure 6a,b), and CO$_2$ physiosorption or solubility were used to determine and understand the bifunctional way of delivering CO$_2$ to the electrode in DEACl–DEA electrolyte (Figure 6c,d). According to the COSMO-RS study, the DEACl–DEA ionic DES can capture a considerable quantity of CO$_2$ even at low CO$_2$ partial pressures until a critical pressure of 61 and 71.7 bar is attained at the DEACl and DEA sites, respectively (see Figure 6c,d). The high capacity of CO$_2$ in DEACl–DEA DES reveals that DEACl–DEA and CO$_2$ interact not only physically but also chemically. Furthermore, as indicated in Table 1, the density, viscosity, and mass of DEACl–DEA increased following CO$_2$ absorption. This means that new interacting bonds were formed during CO$_2$ absorption, with the chemical interaction being substantially stronger than the physical relationship. On their COSMO surface, the physical interaction between CO$_2$ and DEACl–DEA is depicted in Figure 6a for DEACl and Figure 6b for the DEA site.

EIS was utilized to confirm the chemisorption of CO$_2$ by DEACl–DEA electrolyte. The Nyquist curve for impedance measurement in DEACl–DEA under −1.5 V potentiostatic control before and after CO$_2$ absorption was measured and is shown in Figure 6e and f, respectively. The difference in Nyquist plot response in DEACl–DEA before and after CO$_2$ sparging suggests changes in the interfacial double layer capacitance structure of the ionic DEACl–DEA DES with CO$_2$. The DEACl–DEA system’s Nyquist plot (Figure 6e) has a smaller semicircle than the CO$_2$–DEACl–DEA system (Figure 6f and Table 1). When regular DEACl–DEA was compared to CO$_2$–DEACl–DEA, this result indicated faster charge transfer processes with resistive-capacitive (RC) circuits.

The equivalent circuit (EC) illustrated in the insets of Figure 6e and f were used to estimate impedance parameters (see Table 1) such as capacitance in conjunction with the RC circuit of the Nyquist plot for DEACl–DEA or CO$_2$–DEACl–DEA systems. The EC was designed with two resistances $R_i$ and $R_d$ as well as a double layer capacitance inform of constant phase element. The resistance of the DEACl–DEA or CO$_2$–DEACl–DEA medium is $R_i$, and the resistance of the interfacial charge transfer necessary for CO$_2$ electroreduction to CO$_2$ free radical is $R_d$. As a result, it was discovered that the resistance ($R_i$) of DEACl–DEA media is 3815 and 12756 $\Omega$ for CO$_2$–DEACl–DEA media. The rise in medium resistance following CO$_2$ sparging in DEACl–DEA seems to indicate the media’s CO$_2$ sorption capability. According to Figure 6e, the capacitance of the DEACl–DEA medium is 8.759 nF before sparging CO$_2$, with a Faradaic charge transfer resistance of 348.6 $\Omega$. Furthermore, after sparging CO$_2$, the capacitance of the CO$_2$–DEACl–DEA medium reduced to 3.145 nF, with a}

| Table 1. EIS Characteristics for ECO$_2$R at −1.5 V Versus Ag/AgCl under Normal and CO$_2$ Saturation Conditions at Ag Electrode |
|----------------|----------------|----------------|----------------|----------------|----------------|
| S/N | ionic deep eutectic electrolyte | $R_i$ (Ohm) | $R_d$ (Ohm) | $C_d$ (nF) | $\mu$ (cP) | $\rho$ (g/cm$^3$) |
| 1  | DEACl–DEA | 3815 | 348.6 | 8.759 | 401.9 | 1.09 |
| 2  | CO$_2$–DEACl–DEA | 12,756 | 809.3 | 3.145 | 528.5 | 2.03 |

4. CONCLUSIONS

The activity of amine-based bifunctional ionic deep eutectic electrolytes for CO$_2$ electroreduction was demonstrated in this study. Because amine-based ionic deep eutectic electrolytes do not have pseudocapacitive properties, saturating them with CO$_2$ suppresses the interfacial double layer capacitance. Further investigation revealed that the types of HBD and HBA used, as well as their molar ratios, can affect CO$_2$ reduction performance. Moreover, HBA with longer chain length can reduce the Faradaic efficiency of CO$_2$ electroreduction in ionic DESs. DEACl, which has a short chain length, demonstrated 71% Faraday efficiency for CO$_2$ electroreduction to CO$_2$•−. This is in contrast to TEACl, which has a longer chain length and achieved a Faraday efficiency of 38.6% for CO$_2$ electroreduction to CO$_2$. Most importantly, the DEACl–DEA have a higher cathodic electrochemical stability limit than the typical potential required to electrochemically reduce CO$_2$, indicating that the process of reducing CO$_2$ in deep eutectic electrolyte is feasible. These findings open up the possibility of stabilizing amine via the formation of deep eutectic electrolytes for long-term CO$_2$ capture and electroreduction.
Experimental setup for CO$_2$ electroreduction in DEACl–DEA, flow properties of DEACl–DEA at ambient condition, and interfacial depition of CO$_2$ reduction in DEACl–DEA electrolyte (PDF)

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**Notes**

The authors declare no competing financial interest.

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