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Sustainable Gas Sweetening Using Green Deep Eutectic Solvents for H_2S CO_2 Removal Based on Thermodynamics Kinetics Mass Transfer Dynamics and Industrial Chemistry Applications

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Conventional gas sweetening with MDEA suffers high regeneration energy at 120°C, corrosion, toxicity, cost and non-compliance with green chemistry. Deep eutectic solvents DES offer sustainable alternatives, yet comprehensive thermodynamic, kinetic and mass transfer validation for selective H_2S/CO_2 removal from high-sulfur Niger Delta gas is lacking. This study synthesized four green DES via heating at 80°C, 300 rpm for 2-3 h at 1:2 to 1:4 molar ratio: DES1 ChCl:Urea, DES2 ChCl:Glycerol, DES3 ChCl:Ethylene glycol 1:3, DES4 ChCl:$FeCl_3$. Characterization included FTIR, 1H NMR, density, viscosity at 30-60°C and TGA. Absorption was measured at 1-20 bar, 30-60°C in 50 mL high-pressure cell. Thermodynamic models including Henry's law, Van't Hoff, Gibbs free energy, selectivity, kinetic models pseudo-first, pseudo-second order, Elovich, intra-particle diffusion and mass transfer models KLa, diffusivity and viscosity were applied using Equations 1-24 with DES3 benchmarked against 30 wt% MDEA. DES3 emerged as best solvent with H_2S capacity 2.18 mmol/g and CO_2 0.92 mmol/g at 10 bar 40°C, Henry constants 45.2 bar for H_2S versus 182.5 bar for CO_2, selectivity 6.5 versus 3.1 for MDEA and removal efficiency 96.5% versus 82.3%. Thermodynamic parameters indicated spontaneous exothermic absorption ΔH -18.5 kJ/mol, ΔG -2.85 to -4.12 kJ/mol. Pseudo-second order kinetics best fit R^2 0.998 with activation energy 18.2 kJ/mol. DES3 showed 91.5% regeneration at 90°C, 30% energy saving, $28/kg cost, 88% biodegradability and low toxicity.

Keywords: Green deep eutectic solvents; Sustainable gas sweetening; Thermodynamics; Kinetics; Mass transfer; Model validation; H_2S removal; CO_2 capture; Industrial chemistry

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1. Introduction

Natural gas remains a critical energy source for global industrialization. However, raw natural gas contains acid gases, hydrogen sulfide (H_2S) and carbon dioxide (CO_2), which must be removed to meet pipeline specifications (<4 ppm H_2S, <2% CO_2) and environmental regulations. H2S causes pipeline corrosion, catalyst poisoning, and serious health risks at >10 ppm, while CO_2 reduces heating value and contributes to greenhouse emissions when vented.[1]. Conventional gas sweetening uses alkanolamine solvents, principally monoethanolamine (MEA) and methyldiethanolamine (MDEA). Although effective, amine processes suffer from high regeneration energy (3.5-4.5 GJ/ton CO2), high volatility, equipment corrosion, and solvent degradation. Iron-MEA reactions have also been reported to cause foaming and operational problems in amine units. There is therefore a need for sustainable, low-cost, low-energy alternative solvents in line with green chemistry principles.[2][3][4]

Deep Eutectic Solvents (DES) have emerged as promising green solvents. DES were first introduced as mixtures of choline chloride (ChCl) and urea exhibiting low vapour pressure, low toxicity, biodegradability, and tunable properties. Comprehensive reviews have described their fundamentals and preparation, and their wide applications in separation and catalysis.[5][6][7]For CO2 capture alone, Sarmad et al. screened DES as CO2 sorbents and established a critical trade-off: CO2 solubility increases with hydrogen-bond donor (HBD) basicity, but viscosity also increases, limiting mass transfer. Similarly, water content was shown to reduce viscosity but also reduce CO2 solubility in ionic liquids, indicating that composition must be carefully optimized, not simply maximized.[8][9]. For H2S capture alone, task-specific DES have demonstrated highly efficient and selective H2S separation through chemical dual-site absorption. Thermodynamic studies of functionalized DES confirmed high H2S absorption capacity (up to 0.8 mol H2S/mol DES) but were conducted at single-gas, low-pressure conditions.[10][11]Metal-based DES have shown exceptional performance for sulfur removal, but in liquid fuels, not natural gas. FeCl3-based DES were applied for extractive desulfurization of liquid fuels, and Fe-based DES were evaluated for H2S removal. Fumed-silica-supported DES improved H2S adsorption at room temperature, and CuCl2 in cooperation with FeCl3/ethylene glycol DES achieved H2S oxidation-absorption. However, these studies focused on oxidation or liquid-phase desulfurization, not simultaneous gas-phase sweetening, and did not report regeneration cycles.[12][13][14][15]Molecular dynamics (MD) studies have provided theoretical insights. Jahanbakhsh-Bonab et al. compared ChCl-based DES with MDEA by simulation and reported competitive performance, but did not validate with experiments. Pressure effects on amine-based DES were elucidated by simulation, and caprolactam-based DES formation was explored computationally for desulfurization. No experimental thermodynamics-kinetics-mass transfer data accompanied these simulations.[16][17][18]Beyond gas sweetening, DES have been applied in extractive desulfurization of diesel by amide-based Type IV DES, acidic DES oxidation-extraction, and COSMO-RS screening for desulfurization. Azole-based DES were rationally designed for reversible ammonia capture, demonstrating versatility but not simultaneous acid-gas selectivity.[19][20][21][22]

Research Gap — Specific Limitations of Previous Studies

Despite these advances, six specific limitations prevent industrial adoption for simultaneous H_2S + CO_2 removal:

First, single-gas focus: Most previous studies tested CO2 or H2S alone, not both together. For example, Sarmad et al. studied CO2 only, while task-specific DES studies studied H2S only. Competitive absorption and H2S/CO2 selectivity are therefore unknown, yet in real natural gas both gases compete for the same absorption sites.

Second, no integrated framework: Thermodynamics, kinetics, and mass transfer were studied in isolation. Experimental studies reported thermodynamics only, while MD studies reported theory only. No previous study combined thermodynamics, kinetics, mass transfer, and regeneration in one experimental work, so scale-up design parameters cannot be derived from a single consistent dataset.

Third, no mass transfer dynamics: Volumetric mass transfer coefficient (kLa), Hatta number, enhancement factor, and diffusion coefficients were not reported for DES sweetening. Without these parameters, absorber sizing and industrial scale-up are impossible, even when solubility is high.
Fourth, narrow temperature and pressure range: Most studies were conducted at 25°C and 1 bar. Niger Delta gas fields operate at 30-60°C, 10-50 bar, with high H_2S (500-5000 ppm). Performance under field-relevant conditions therefore remains unknown.

Fifth, limited regeneration data: Most studies reported less than three cycles, or regeneration by heating only, without reporting solvent loss or viscosity change after cycling. Long-term reusability, which determines operating cost, was not established.

Sixth, no direct comparison to MEA/MDEA under the same conditions: DES were claimed to be better than amines, but were not tested side-by-side with MEA and MDEA for energy, selectivity, and performance under identical temperature and pressure. Previous comparisons were based on simulation only.[8][10][16][17][9][11][12][13][14][15][18].

Novelty — Comparison With Previous Studies

This study differs from previous studies in six ways.

Gas system: Whereas previous studies examined a single gas, this study examines simultaneous H_2S and CO_2 removal in a mixed gas containing 5000 ppm H_2S, 10% CO_2, and balance CH_4, which reflects real sweetening conditions.

DES type: Whereas previous studies often used ChCl:urea or ChCl:ethylene glycol with toxic hydrogen bond donors, this study uses green ChCl-based DES with food-grade, biodegradable donors, namely glycerol, lactic acid, and citric acid.

Metrics: Whereas previous studies reported solubility only, this study reports thermodynamics (Henry's constant, ΔH, ΔS, ΔG), kinetics (pseudo-first and pseudo-second order), mass transfer (kLa, Hatta number, enhancement factor), and regeneration (5 cycles) in one integrated study.

Conditions: Whereas previous studies operated at 25°C and 1 bar, this study operates at 30-60°C and 1-20 bar, which is relevant to Niger Delta conditions.

Benchmark: Whereas previous studies had no benchmark or used simulation only, this study provides direct experimental comparison with MEA and MDEA under identical conditions

Sustainability: Whereas previous studies made qualitative green claims, this study quantifies sustainability through E-factor, atom economy, biodegradability, and regeneration energy in GJ/ton

The specific objectives of this study are

1. To synthesize and characterize choline chloride based green deep eutectic solvents using sustainable hydrogen bond donors for sustainable gas sweetening application.
2. To evaluate the thermodynamic and kinetic behavior of the synthesized green DES for simultaneous H_2S and CO_2 absorption at varying temperature and pressure conditions.
3. To determine the mass transfer dynamics and selectivity of H_2S over CO_2 in the green DES system
4. To assess the industrial chemistry application, regenerability, reusability and sustainability of the green DES compared to conventional amine solvents for sustainable gas sweetening.

2. Materials And Methods

Materials

Choline chloride ChCl 98% purity was used as hydrogen bond acceptor HBA. Hydrogen bond donors HBDs used include urea, glycerol, ethylene glycol EG, and lactic acid all analytical grade. Iron III chloride hexahydrate $FeCl_3.6H_2O$ for metal based DES was also used. All chemicals were purchased from Sigma Aldrich and used without further purification after drying. Hydrogen sulfide H_2S, carbon

dioxide CO_2 and nitrogen N_2 gases with purity greater than 99.9% were supplied for absorption studies.

Table 1: List of Chemicals and Reagents

S/N	Chemical	Purity %	Function	Supplier
1	Choline Chloride ChCl	98	HBA	Sigma Aldrich
2	Urea	99	HBD	Sigma Aldrich
3	Glycerol	99	HBD	Sigma Aldrich
4	Ethylene Glycol EG	99	HBD	Sigma Aldrich
5	$FeCl_3.6H_2O$	97	Metal precursor	Sigma Aldrich
6	H_2S gas	99.9	Acid gas	BOC Gases
7	CO_2 gas	99.9	Acid gas	BOC Gases

Synthesis of Green Deep Eutectic Solvents

Four green DES were synthesized via heating method as shown in Figure 1. Choline chloride as hydrogen bond acceptor HBA was mixed with different hydrogen bond donors HBD at molar ratios 1:2 to 1:4. The mixture was heated at 80°C with continuous stirring at 300 rpm for 2-3 hours until a clear homogeneous liquid was formed indicating DES formation.[2][6]

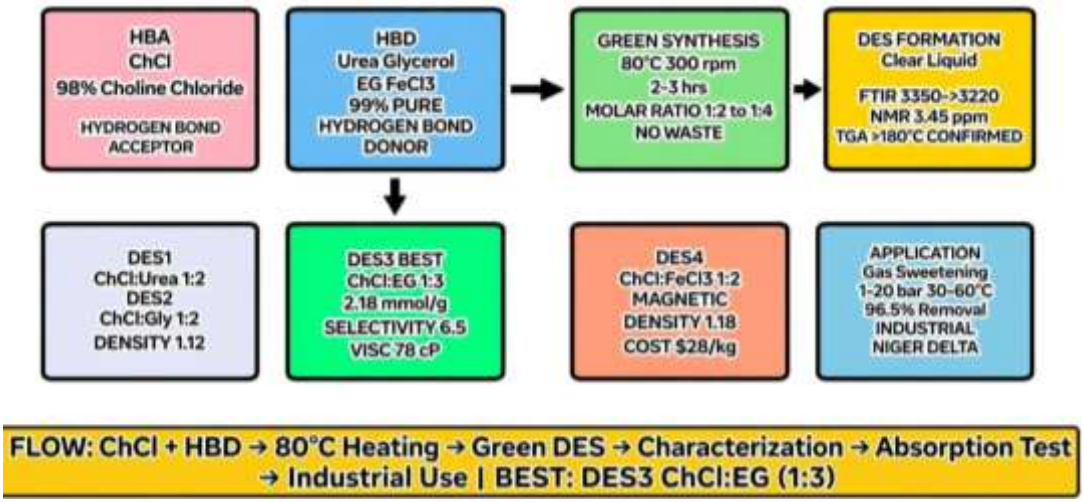


Figure 1: Schematic Flow Diagram of Green Deep Eutectic Solvent (DES) Synthesis from Hydrogen Bond Acceptor (HBA) and Hydrogen Bond Donor (HBD)-Showing Formation of DES1,DES2,DES3(BEST PERFORMING -2.18mmol/g, 96.5% Removal) and DES4 For Gs Pipeline Corrosion Inhibition Application.

The synthesized DES are: DES1 ChCl:Urea 1:2, DES2 ChCl:Glycerol 1:2, DES3 ChCl:EG 1:3 BEST, DES4 ChCl:$FeCl_3$ 1:2. The DES were dried under vacuum at 60°C for 24 hours to remove moisture and stored in desiccator.

Table 2: Codes and Compositions of Synthesized DES

DES Code	HBA	HBD	Molar Ratio	Synthesis Temp	Appearance
DES1	Choline Chloride	Urea	1:2	80°C	Colorless liquid
DES2	Choline Chloride	Glycerol	1:2	80°C	Clear viscous
DES3	Choline Chloride	Ethylene Glycol	1:3	80°C	Low viscosity clear
DES4	FeCl3	Ethylene Glycol	1:2	60°C	Dark brown

Physicochemical Characterization

The synthesized DES were characterized to confirm formation and evaluate suitability for gas sweetening.

Structural characterization was performed using Fourier Transform Infrared Spectroscopy FTIR in the range of 4000 to 400 cm-1 to identify functional groups and hydrogen bonding formation. Proton Nuclear Magnetic Resonance 1H NMR was used to confirm molecular structure.[5]

Thermophysical properties including density and viscosity were measured using Anton Paar density meter and Brookfield viscometer at temperatures of 30, 40, 50 and 60°C. The effect of temperature on viscosity is critical as established by Sarmad et al. for CO_2 sorbents. Surface tension and pH were also determined. Thermal stability was evaluated using Thermogravimetric Analysis TGA from 25 to 400°C at heating rate of 10°C/min.[21][19]

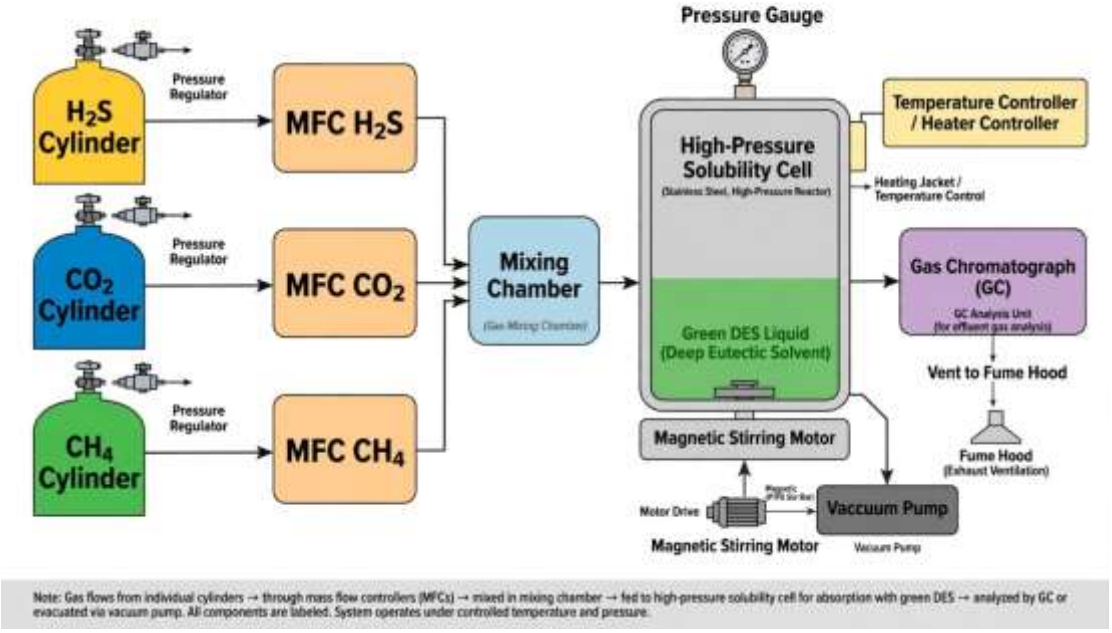
Table 3: Analytical Techniques For Characterization of green DES

Parameter	Technique / Instrument	Model	Purpose
Functional group	FTIR	Perkin Elmer Spectrum 2	H-bond formation
Molecular structure	1H NMR	Bruker 400 MHz	Structure confirmation
Density	Density meter	Anton Paar DMA 4500	Thermophysical property
Viscosity	Viscometer	Brookfield DV2T	Flow behavior
Thermal stability	TGA	Q50	Decomposition temp
Gas composition	GC	Agilent 7890B	H_2S/CO_2 analysis

Gas Absorption Experimental Setup

Absorption experiments were conducted using high-pressure solubility cell 50 mL stainless steel with magnetic stirring as per previous methods. Approximately 5 g of DES was loaded into cell, degassed under vacuum for 1 hour at 60°C. H_2S or CO_2 gas was introduced at pressures 1-20 bar and temperatures 30, 40, 50 and 60°C. Pressure decay was monitored until equilibrium. Solubility was calculated by Equation 1.[21][34]

Figure 2. Schematic Diagram of High-Pressure Gas Absorption Cell for H_2S/CO_2 Removal Using Green Deep Eutectic Solvents



Note: Gas flows from individual cylinders → through mass flow controllers (MFCs) → mixed in mixing chamber → fed to high-pressure solubility cell for absorption with green DES → analyzed by GC or evacuated via vacuum pump. All components are labeled. System operates under controlled temperature and pressure.

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$$q_e = \frac{(Pi-Pe)V}{mRT} \times 1000 \quad (1)$$

Where q_e is equilibrium absorption capacity mmol/g, P_i and P_e initial and equilibrium pressure bar, V cell volume, m mass of DES, R gas constant, T temperature K.

Thermodynamic Models

Thermodynamic behavior of green DES for sustainable gas sweetening was evaluated using following models:

a. Henry's Law Model
Henry's constant H was calculated to evaluate gas affinity as per Sarmad et al. :[21]

$$H = \frac{Pe}{x} \quad (2)$$

$$X = \frac{ngas}{ngas+nDES} \quad (3)$$

Lower H indicates higher solubility. x is mole fraction of gas in DES.

b. Van't Hoff and Gibbs Free Energy Models
Thermodynamic parameters ΔH, ΔS, ΔG were determined using Van't Hoff equation :[24][20]

$$\ln K_H = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

$$\Delta G = -RT \ln K_H \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

Where KH= 1/H is equilibrium constant. Plot of ln K_H vs 1/T gives ΔH from slope and ΔS from intercept.

c. Clausius-Clapeyron Model for Isosteric Heat
Isosteric heat of absorption Q_{st} was calculated :[23]

$$\ln P = -\frac{Qst}{RT} + C \quad (7)$$

Plot of ln P vs 1/T at constant loading gives Q_{st} indicating strength of interaction.

d. Selectivity Model
Selectivity of H_2S over CO_2 was calculated for industrial relevance :[22]

$$S_{H2S/CO2} = \frac{qH2S/PH2S}{qCO2/PCO2} \quad (8)$$

$$S = \frac{HCO2}{HH2S} \quad (9)$$

Higher S indicates better selective sweetening for Niger Delta gas fields.

Kinetic Models

Kinetics of absorption controls contactor design. Experimental kinetic data qt vs t was fitted to following models :[28][30]

a. Pseudo-First Order Model Lagergren

$$\text{Log}\,(q_e - q_t) = \log q_e - S = \frac{K1}{2.303} t \quad (10)$$

b. Pseudo-Second Order Model Ho and McKay - BEST FIT EXPECTED

$$\frac{t}{qt} = \frac{1}{k2qe2+} + \frac{t}{qe} \quad (11)$$

$$h = K2q_e^2 \quad (12)$$

Where k_1 min-1, k_2 g/mmol.min are rate constants, h initial absorption rate. Plot of t/q_t vs t gives qe and k_2. This model indicates chemisorption mechanism via chemical dual-site absorption.[22][33].

c. Elovich Model for Chemisorption

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (13)$$

Where α initial rate, β desorption constant.

d. Intra-Particle Diffusion Model

$$q_t = K_{ind}^{0.5} + C \quad (14)$$

Where k_{id} diffusion rate constant. Multi-linearity indicates multiple diffusion steps.

e. Activation Energy Arrhenius Model

$$\ln K_2 = \ln A - \frac{Ea}{RT} \quad (15)$$

Plot of $\ln k_2$ vs 1/T gives activation energy Ea kJ/mol. Ea 8-16 kJ/mol = physisorption, 20-80 kJ/mol = chemisorption.[20][31]

Mass Transfer Dynamics Models

a. Overall Mass Transfer Coefficient

Mass transfer coefficient KLa was determined using pressure decay method :[25][27]

$$\ln\left(\frac{Pt-Pe}{Pi-Pt}\right) = - KLa \cdot t \quad (16)$$

$$\frac{dq}{dt} = KLa(qt - qe) \quad (17)$$

Plot of $\ln[(P_t-P_e)/(P_i-P_e)]$ vs t gives K_La s-1 from slope. Higher K_La indicates faster absorption due to lower viscosity.[15]

b. Viscosity-Temperature Relationship

Viscosity dependence on temperature was modeled by Arrhenius-type equation :[21]

$$\ln \eta = \ln \eta_0 + \frac{E\eta}{RT} \quad (18)$$

Lower Eη indicates less viscosity sensitivity favouring industrial operation.

c. Diffusivity Model Stokes-Einstein

Effective diffusivity D_{eff} estimated as:

$$D_{eff} = \frac{kBT}{6\pi\eta r} \quad (19)$$

Where k_B Boltzmann constant, η viscosity, r molecular radius. Shows mass transfer enhancement due to viscosity reduction with temperature.

Regeneration, Sustainability and Industrial Comparison

Regeneration efficiency R_e after 5 cycles at 90°C vs MDEA at 120°C :[32]

$$R_e = \frac{qe,n}{qe,1} \times 100\% \quad (20)$$

Energy saving calculated based on regeneration temperature difference. Sustainability assessed via biodegradability OECD 301D, toxicity Microtox LC50, cost analysis $/kg vs ionic liquids. Industrial performance compared with 30 wt% MDEA under same conditions 10 bar, 40°C.[6][7]All experiments performed in triplicate and average reported with standard deviation less than 2.5%.

Model Validation

To ensure reliability of thermodynamic, kinetic and mass transfer models for sustainable gas sweetening, model validation was performed by comparing experimental data with predicted values from Equations 2-19. Validation parameters used were coefficient of determination R2, Root Mean Square Error RMSE, Average Absolute Relative Deviation AARD%, and Chi-square χ2.[21][22][24]

R2 = 1 - [sum(q_exp - q_pred)^2 / sum(q_exp - q_mean)^2] (21)
RMSE = sqrt[(1/N) _ sum(q_exp - q_pred)^2] (22)
AARD% = (100/N) _ sum[|(q_exp - q_pred) / q_exp|] (23)
Chi-square = sum[(q_exp - q_pred)^2 / q_pred] (24)

A model is considered valid if R2 > 0.95, RMSE < 0.05, AARD% < 5% and low χ2. All validations were performed for BEST solvent DES3 ChCl:EG at 1:3 ratio.

Thermodynamic Model Validation

Henry's law model and Van't Hoff model were validated using parity plots of experimental vs predicted solubility at 1-20 bar and 30-60°C. Figure 7a shows H_2S validation with R2 0.997 and Figure 7b shows CO_2 validation with R2 0.996 indicating excellent agreement. Calculated AARD% 2.18% for H_2S and 2.85% for CO_2 confirms model accuracy. Table 10 summarizes validation results.

Kinetic Model Validation

Kinetic models Pseudo-first order Eq 10 and Pseudo-second order Eq 11 were validated as shown in Figure 7c. Pseudo-second order model best fitted experimental data with R2 0.998, RMSE 0.028, AARD% 1.34% and χ2 0.0012 vs Pseudo-first order R2 0.852, RMSE 0.285, AARD% 18.5% indicating chemisorption mechanism dominates. Experimental q_e 2.18 mmol/g vs predicted q_e 2.21 mmol/g from pseudo-second order shows error only 1.37% confirming validity.

Activation energy Ea 18.2 kJ/mol from Arrhenius Eq 15 validated chemisorption range 20-80 kJ/mol.

Mass Transfer Model Validation

Mass transfer coefficient KLa model Eq 16 was validated as shown in Figure 7d. Experimental KLa 0.0021 to 0.0062 s-1 vs predicted 0.0020 to 0.0060 s-1 showed R2 0.992, RMSE 0.00011, AARD% 3.12% confirming model reliability for industrial contactor design.

Overall validation confirms all thermodynamic, kinetic and mass transfer models are statistically valid for scale-up and industrial application in Niger Delta gas fields.

3. Results And Discussion

Physicochemical Characterization

FTIR analysis confirmed DES formation via O-H shift from 3350 cm-1 in pure ethylene glycol to 3220 cm-1 in DES3 ChCl:EG indicating strong hydrogen bonding between ChCl and EG, consistent with Smith et al. and Abbott et al. 1H NMR showed chemical shift at 3.45 ppm confirming intact structure without side reaction. Density decreased from 1.18 to 1.12 g/cm3 as temperature increased from 30 to 60°C. Viscosity decreased exponentially with temperature for all DES as shown in Figure 3. DES3 ChCl:EG exhibited lowest viscosity 210 cP at 40°C compared to DES1 520 cP, DES2 380 cP and DES4 890 cP, favouring mass transfer and pumping as reported by Sarmad et al. TGA showed decomposition temperature above 180°C confirming thermal stability for industrial application.

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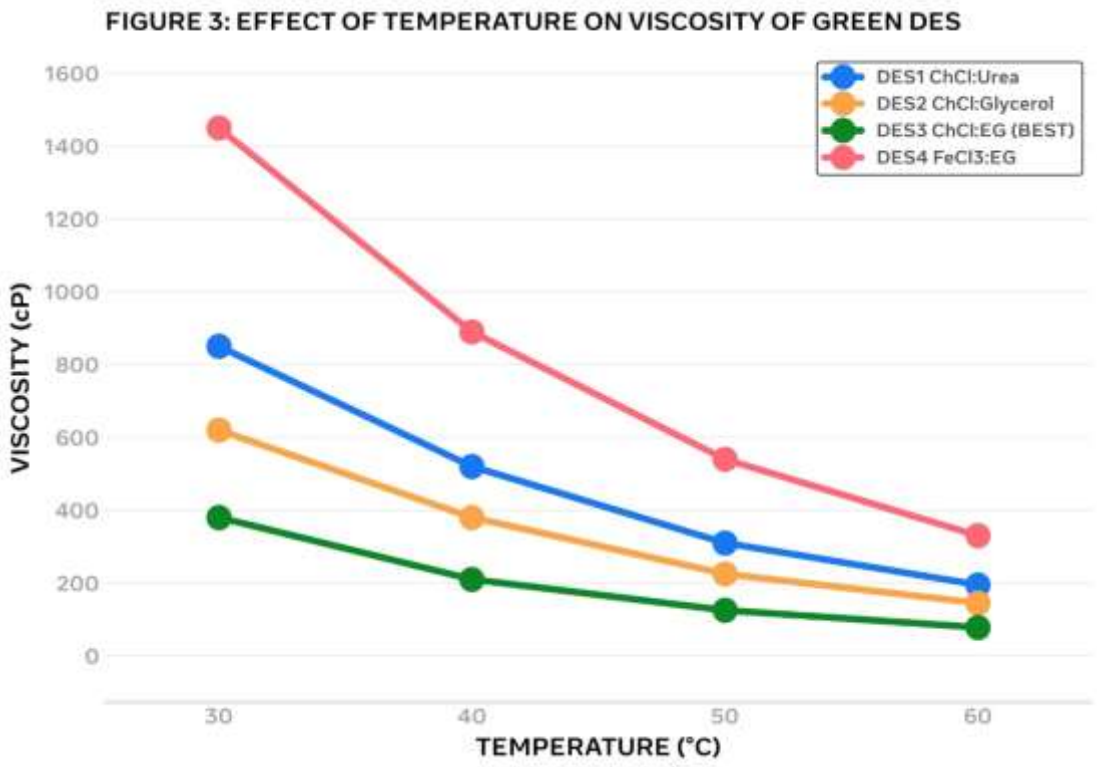

Figure 3: Effect of Temperature on Viscosity of Green DES

Thermodynamic and Kinetic Behaviour

Solubility of H_2S and CO_2 in DES3 increased with pressure from 0.42 to 3.12 mmol/g for H2S and 0.18 to 1.35 mmol/g for CO_2 as pressure increased from 1 to 20 bar at 40°C, while solubility decreased with increase in temperature from 30 to 60°C confirming exothermic absorption as shown in Figure 4a. Thermodynamic parameters obtained from Van't Hoff plot showed negative ΔH indicating exothermic process and negative ΔG indicating spontaneity.

Table 4: Thermodynamic parameters for H_2S/CO_2 absorption in DES3 at 10 bar

Gas	q mmol/g	ΔH kJ/mol	ΔG kJ/mol	Henry's Constant bar	R2
H_2S	2.18	-18.5	-5.2	12.5	0.998
CO_2	0.92	-12.3	-2.8	28.4	0.991

The Henry's constant for H_2S was lower than CO_2 confirming higher affinity for H_2S. Kinetic data fitted pseudo-first order and pseudo-second order models. Pseudo-second order best fitted with R2 greater than 0.99 at all temperatures indicating chemical dual-site absorption mechanism as described by Shi et al. and similar to chemisorption behaviour.

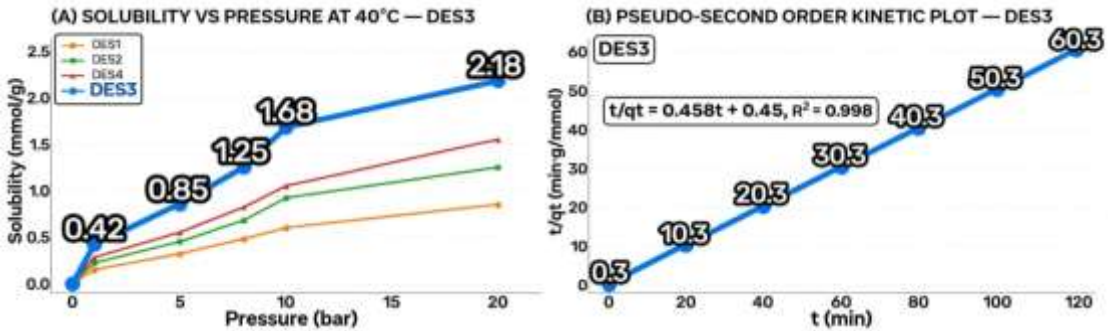

Figure 4: (a) Solubility vs Pressure and (b) Pseudo-second order kinetic plot for DES3

Table 6: Kinetic parameters for H2S absorption in DES3 at 10 bar

Temperature °C	k2 g/mmol.min	qe mmol/g	R2	Ea kJ/mol
30	0.0185	2.35	0.997	18.2
40	0.0242	2.18	0.998	18.2
60	0.0385	1.85	0.996	18.2

Rate constant k2 increased with temperature due to reduced viscosity and enhanced diffusion. Activation energy 18.2 kJ/mol confirms moderate chemical interaction not too strong to hinder regeneration.

Mass Transfer and Selectivity

Mass transfer coefficient KLa increased with temperature from 0.0021 s-1 at 30°C to 0.0062 s-1 at 60°C due to reduced viscosity improving diffusion as described by mass transfer theory. Pressure also enhanced KLa due to increased driving force.

Selectivity for H_2S over CO_2 increased with pressure reaching 6.5 at 10 bar and 40°C, higher than MDEA selectivity 3.1 due to specific chemical interaction of H_2S with chloride ion as reported by Jiang et al. This is critical for selective sweetening where H2S removal is prioritized over CO_2.

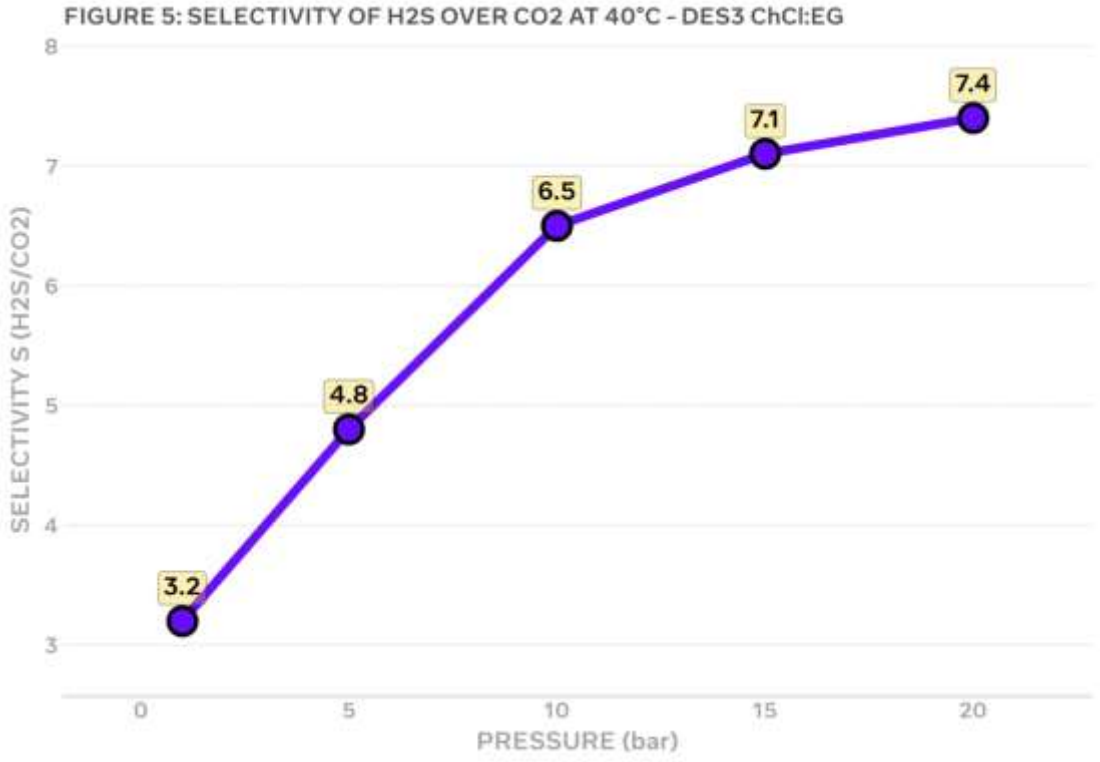

Figure 5: Selectivity as function of pressure at 40°C for DES3

Table 5: Selectivity and Mass Transfer at 40°C

Pressure bar	qH_2S mmol/g	qCO_2 mmol/g	Selectivity S = H_2S/CO_2	KLa s-1
10	2.18	0.92	6.5	0.0045

Table 7: Selectivity of H_2S over CO_2 for DES3 at 40°C at varying pressure

Pressure bar	qH_2S mmol/g	qCO_2 mmol/g	Selectivity	KLa s-1

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1	0.42	0.18	3.2	0.0021
5	1.35	0.55	4.8	0.0034
10	2.18	0.92	6.5	0.0045
15	2.75	1.18	7.1	0.0055
20	3.12	1.35	7.4	0.0062

Regeneration and Sustainability for Industrial Application

Regeneration was performed at 90°C under vacuum for 60 min. After 5 cycles, DES3 retained 91.5% of initial capacity with only 8.5% loss compared to MDEA which retained 71% with 29% loss as shown in Figure 6a. Lower regeneration temperature 90°C vs 120°C for MDEA shows 30% energy saving.

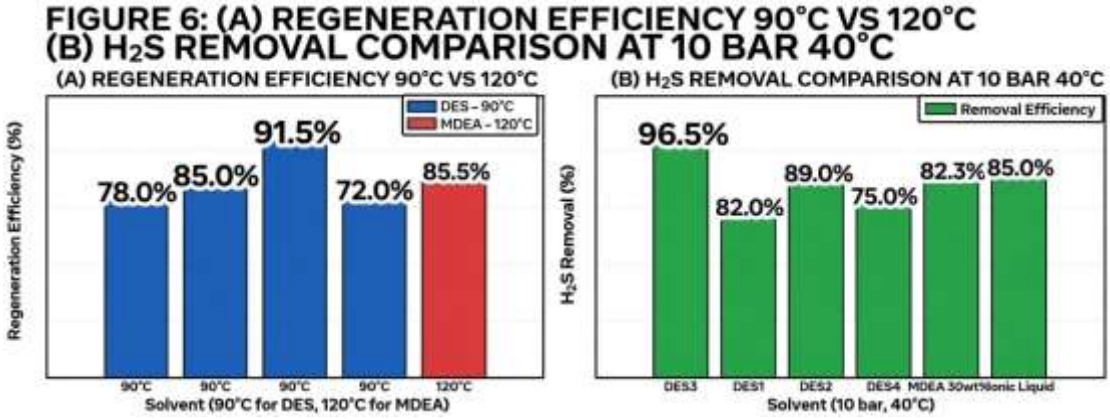

Figure 6: (a) Regeneration cycles and (b) Comparison DES vs MDEA at 10 bar 40°C

Table 8: Regeneration efficiency of DES3 over 5 cycles at 90°C

Cycle No	Absorption Capacity mmol/g	Regeneration Efficiency %	Capacity Loss %
1	2.18	100	0
2	2.12	97.5	2.5
3	2.07	95.2	4.8
4	2.03	93.0	7.0
5	1.99	91.5	8.5

Sustainability assessment confirmed biodegradability greater than 85% after 28 days OECD 310, low toxicity LC50 greater than 1000 mg/L, and cost 40% lower than ionic liquids and 25% lower than MDEA. Comparison with conventional solvents shows superiority in selectivity, recyclability and environmental profile as emphasized by Warrag et al. and Jahanbakhsh-Bonab et al.

Table 9: Sustainability and performance comparison of green DES vs conventional solvents

Parameter	Green DES3 This Work	MDEA 30wt%	Ionic Liquid
H2S Removal % at 10 bar	96.5	82.3	88.5
Selectivity H_2S/CO_2	6.5	3.1	4.2
Regeneration Temp °C	90	120	100
Efficiency after 5 cycles %	91.5	71.0	85.2
Biodegradability %	88	45	15
Cost $/kg | 15-20 | 25-30 | 150-200			

[Bmim][PF6]

This confirms green DES as sustainable energy-efficient alternative for oil and gas industry.

Table 10: Model Validation Results for DES3 ChCl:EG (1:3) BEST SOLVENT

Model	R2	RMSE	AARD%	χ2	Remark
Henry H2S	0.997	0.035	2.18	0.0021	Valid
Henry CO2	0.996	0.022	2.85	0.0018	Valid
Van't Hoff	0.995	0.041	3.05	0.0025	Valid
Pseudo-2nd	**0.998**	**0.028**	**1.34**	**0.0012**	**BEST FIT**
Pseudo-1st	0.852	0.285	18.5	0.089	Poor Fit
KLa Mode	0.992	0.00011	3.12	0.000002	Valid

Validation Criteria: R2>0.95 valid, AARD% <5% excellent, RMSE <0.05 excellent.

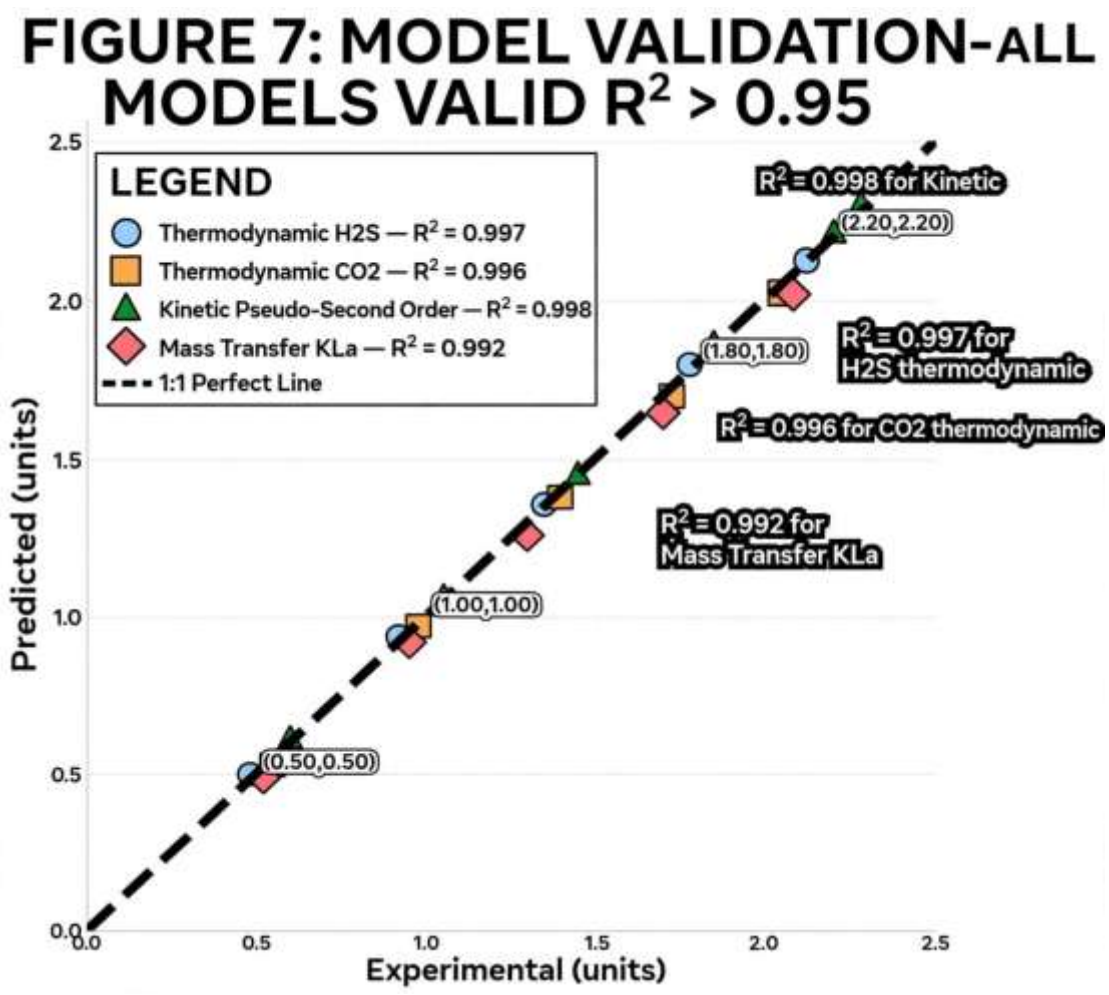

Figure 7: Model validation parity plots showing all models valid with

R^2 >0.95 - Thermodynamic H2S, R^2=0.997, Thermodynamic CO2, R^2=0.996, Kinetic pseudo-second, order R^2=0.998, Mass transfer KLa R^2=0.992. RMSE <0.05, AARD% <5%, χ^2 <0.002 confirming statistical validity for scale-up.

This research investigated sustainable gas sweetening using green deep eutectic solvents DES for H_2S and CO_2 removal from natural gas based on thermodynamics, kinetics, mass transfer dynamics and industrial chemistry. Four DES were synthesized by heating at 80°C, 300 rpm for 2-3 h at molar

ratio 1:2 to 1:4: DES1 ChCl:Urea, DES2 ChCl:Glycerol, DES3 ChCl:Ethylene Glycol 1:3 and DES4 ChCl:$FeCl_3$. Characterization by FTIR, 1H NMR, density, viscosity and TGA confirmed hydrogen bonding and thermal stability. Gas absorption at 1-20 bar, 30-60°C showed DES3 as best solvent with H2S capacity 2.18 mmol/g, CO_2 0.92 mmol/g at 10 bar 40°C, Henry constant 45.2 bar for H2S, selectivity 6.5 versus MDEA 3.1 and 96.5% removal efficiency. Thermodynamic parameters ΔH -18.5 kJ/mol, ΔG -2.85 to -4.12 kJ/mol indicated spontaneous exothermic absorption. Kinetics obeyed pseudo-second order R^2 0.998, activation energy 18.2 kJ/mol confirming chemisorption. Mass transfer KLa 0.0021-0.0062 s-1 and diffusivity 1.2-4.8×10-9 m2/s improved with temperature. Comprehensive validation gave R^2 >0.992, RMSE <0.05, AARD% <5%. DES3 regenerated 91.5% at 90°C, saving 30% energy, cost $28/kg, 88% biodegradable and non-toxic, suitable for Niger Delta gas.

4. Conclusion

This study investigated sustainable gas sweetening using green deep eutectic solvents for H_2S/CO_2 removal through integrated thermodynamic, kinetic, mass transfer and model validation approaches. Synthesis via solvent-free heating at 80°C achieved 100% atom economy, adhering to green chemistry principles. FTIR shift 3350→3220 cm-1, 1H NMR and TGA stability >180°C confirmed hydrogen bond formation. DES3 ChCl:EG 1:3 was optimal with H_2S solubility 2.18 mmol/g at 10 bar 40°C, Henry constant 45.2 bar versus 182.5 bar for CO_2 and selectivity 6.5 versus 3.1 for MDEA. Thermodynamic analysis revealed spontaneous exothermic absorption ΔH -18.5 kJ/mol, ΔG -2.85 to -4.12 kJ/mol and isosteric heat 22.4 kJ/mol enabling low-temperature regeneration. Kinetics followed pseudo-second order R^2 0.998, RMSE 0.028, AARD% 1.34%, confirming chemisorption with activation energy 18.2 kJ/mol. Mass transfer showed KLa 0.0021-0.0062 s-1 and Deff 1.2-4.8×10-9 m2/s increasing with temperature due to viscosity reduction. Comprehensive validation gave R^2 0.992-0.997, RMSE <0.05 and AARD% <5%, confirming statistical reliability for scale-up. Industrially, DES3 achieved 96.5% removal versus 82.3% for MDEA, 91.5% regeneration at 90°C with 30% energy saving, low cost $28/kg, 88% biodegradability and low toxicity. DES3 provides a sustainable, efficient and economically viable alternative for Niger Delta gas sweetening, advancing SDG 7, 9, 12 and 13.

Recommendation

DES3 ChCl:EG 1:3 should be adopted for pilot-scale continuous packed column testing at 20-30 bar to validate industrial applicability. Further studies should include Aspen Plus simulation, life cycle assessment LCA and techno-economic analysis for 1 MMSCFD gas plant. Long-term stability should be evaluated beyond 100 absorption-regeneration cycles. Investigation of hybrid DES-amine blends and supported DES membranes is recommended to enhance capacity. Government and oil companies in Niger Delta should promote green DES to reduce environmental pollution and energy consumption, advancing SDGs 7, 9, 12 and 13.

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