

**EXPERIMENTAL AND THEORETICAL  
INVESTIGATIONS INTO CO<sub>2</sub> CAPTURE BY TASK-  
SPECIFIC DUAL FUNCTIONALIZED IONIC LIQUID  
AQUEOUS BLENDS**

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**Experimental and Theoretical Investigations into CO<sub>2</sub>  
Capture by Task-Specific Dual Functionalized Ionic Liquid  
Aqueous Blends**

*by*

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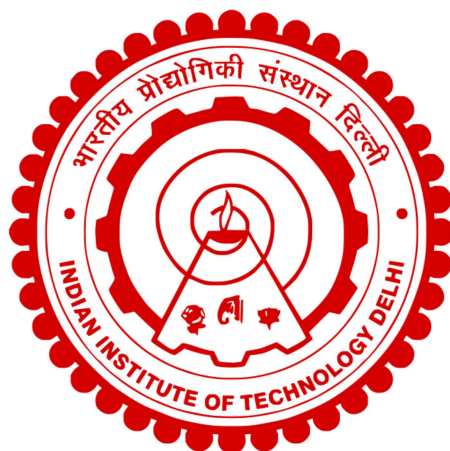
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**In fulfilment of the requirements of the degree of**

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## CERTIFICATE

This is to certify that the thesis titled " **Experimental and Theoretical Investigations into CO<sub>2</sub> Capture by Task-Specific Dual Functionalized Ionic Liquid Aqueous Blends**" being submitted by Mr. Surya Chandra Tiwari to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemical Engineering is a record of bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the requisite standard.

The work presented in this thesis is original and has not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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## ABSTRACT

Industrial flue gas effluent streams containing CO<sub>2</sub> are a significant source of air pollution. The use of benign, cost-effective solvents for CO<sub>2</sub> capture is a crucial operation not only in the process industry for separating and recovering CO<sub>2</sub> from industrial off-gas streams but also for direct air capture to purify the environment. Researchers have identified numerous solvents with high CO<sub>2</sub> capture efficiency due to their favorable chemical and physical properties, mechanisms of CO<sub>2</sub> interaction, and low energy costs for regeneration. However, alkanolamines such as Monoethanolamine (MEA), Diethanolamine (DEA), and Methyldiethanolamine (MDEA) are most commonly used for CO<sub>2</sub> capture. Despite their effectiveness, these solvents face several challenges, including limited thermal stability, formation of heat-stable salts, and high degradation rates. To overcome these issues, the development of a new type of solvent is necessary. Additionally, the design of packed column absorbers traditionally used in the industry is energy-intensive during both the absorption and solvent regeneration cycles. Therefore, this work explores the use of a coiled flow inverter as an innovative approach to reduce overall energy requirements while enhancing capture efficiency.

In this research study, task-specific dual-functionalized ionic liquids (DFILs) designed for carbon capture were synthesized, employing four different cyclic anions—azolide (Im/Py/Tz) or piperazine (Pz)—combined with a triethylenetetramine (TETA) cation. The resulting DFILs are [TETAH][Pz], [TETAH][Im], [TETAH][Py], and [TETAH][Tz], respectively. These DFILs were utilized as aqueous absorbents for CO<sub>2</sub> capture, with [TETAH][Pz] and [TETAH][Im] demonstrating the highest CO<sub>2</sub> loadings among the four. However, using an individual DFIL was found to be economically impractical for large-scale CO<sub>2</sub> capture. Consequently, a blended aqueous absorbent system was developed, combining different weight percentages of DFILs with MDEA. This approach confirmed that the [TETAH][Im]/MDEA/H<sub>2</sub>O system significantly reduces the regeneration energy for CO<sub>2</sub> desorption by approximately 33% compared to the industrial MEA system, offering a cost-effective solution for CO<sub>2</sub> absorption. A thermodynamic analysis was conducted to assess the equilibrium rate constant, heat of absorption, Gibbs free energy, and entropy for [TETAH][Im] and [DETAH][Im] blended with MDEA absorbents in CO<sub>2</sub> interaction. Kinetic studies were carried out using zwitterion and tetramolecular-based models, revealing activation energies for the [TETAH][Im] and [DETAH][Im] blended systems to be 25.61 kJ/mol

and 24.87 kJ/mol, respectively. Moreover, an economic assessment indicated that blended MDEA absorbents with [TETAH][Pz], [TETAH][Im], and [DETAH][Im] could reduce costs by approximately 45% to 26% compared to the industrial MEA (5M) absorbent. A coiled flow inverter absorber (CFI) was employed to analyze mass transfer performance, focusing on absorption rate, efficiency, and volumetric mass transfer coefficient. The findings suggest that the CFI absorber has significant potential for enhancing mass transfer performance.

Overall, this work provides systematic insights that will help researchers and engineers comprehensively understand the efficacy of absorption solvents and the development of absorbers for CO<sub>2</sub> capture.

## सारांश

औद्योगिक फ्ल्यू गैस उत्सर्जन धाराएँ जिनमें  $\text{CO}_2$  होती हैं, वायु प्रदूषण का एक महत्वपूर्ण स्रोत हैं।  $\text{CO}_2$  कैप्चर के लिए सौम्य, किफायती सॉल्वेंट्स का उपयोग न केवल औद्योगिक गैस धारा से  $\text{CO}_2$  को अलग करने और पुनः प्राप्त करने के लिए महत्वपूर्ण है, बल्कि सीधे वायु से  $\text{CO}_2$  को पकड़कर पर्यावरण को शुद्ध करने के लिए भी महत्वपूर्ण है। शोधकर्ताओं ने कई सॉल्वेंट्स की पहचान की है जिनमें  $\text{CO}_2$  कैप्चर की उच्च दक्षता होती है, जो उनके अनुकूल रासायनिक और भौतिक गुणों,  $\text{CO}_2$  इंटरैक्शन के तंत्र, और पुनरुत्थान के लिए कम ऊर्जा लागत के कारण होती है। हालांकि, मोनोएथेनॉलामाइन (MEA), डाइएथेनॉलामाइन (DEA), और मेथाइलीडाइथेनॉलामाइन (MDEA) जैसे अल्कनोलामाइन सबसे अधिक सामान्यतः  $\text{CO}_2$  कैप्चर के लिए उपयोग किए जाते हैं। उनकी प्रभावशीलता के बावजूद, इन सॉल्वेंट्स को कई चुनौतियों का सामना करना पड़ता है, जिसमें सीमित थर्मल स्थिरता, गर्मी-स्थिर लवणों का निर्माण, और उच्च अपघटन दर शामिल हैं। इन समस्याओं को दूर करने के लिए, एक नए प्रकार के सॉल्वेंट का विकास आवश्यक है। इसके अलावा, उद्योग में पारंपरिक रूप से उपयोग किए जाने वाले पैकड कॉलम एब्जॉर्बर्स का डिज़ाइन अवशोषण और सॉल्वेंट पुनरुत्थान दोनों चक्रों के दौरान ऊर्जा-गहन होता है। इसलिए, इस कार्य में ऊर्जा आवश्यकताओं को कम करते हुए कैप्चर दक्षता बढ़ाने के लिए एक नवाचारी दृष्टिकोण के रूप में एक कॉइल्ड फ्लो इन्वर्टर के उपयोग का पता लगाया गया है।

इस अनुसंधान अध्ययन में, कार्बन कैप्चर के लिए डिज़ाइन किए गए कार्य-विशिष्ट द्वि-कार्यात्मकित आयनिक तरल पदार्थ (DFILs) का संश्लेषण किया गया, जिसमें चार अलग-अलग चक्रीय एनायन—अजोलाइड (Im/Py/Tz) या पिपराजिन (Pz)—को ट्राइएथिलीनटेट्रामाइन (TETA) कैशन के साथ मिलाकर तैयार किया गया। परिणामी DFILs [TETAH][Pz], [TETAH][Im], [TETAH][Py], और [TETAH][Tz] हैं। इन DFILs का उपयोग  $\text{CO}_2$  कैप्चर के लिए जलीय एब्जॉर्बेंट्स के रूप में किया गया, जिसमें [TETAH][Pz] और [TETAH][Im] ने चारों में सबसे उच्च  $\text{CO}_2$  लोडिंग प्रदर्शित की। हालांकि, बड़े पैमाने पर  $\text{CO}_2$  कैप्चर के लिए एक व्यक्तिगत DFIL का उपयोग आर्थिक रूप से अव्यवहारिक पाया गया। परिणामस्वरूप, एक मिश्रित जलीय एब्जॉर्बेंट प्रणाली विकसित की गई, जिसमें विभिन्न वजन प्रतिशत DFILs को MDEA के साथ मिलाया गया। इस दृष्टिकोण ने पुष्टि की कि [TETAH][Im]/MDEA/ $\text{H}_2\text{O}$  प्रणाली  $\text{CO}_2$  के निर्गमन के लिए पुनरुत्थान ऊर्जा को औद्योगिक MEA प्रणाली की तुलना में लगभग 33% तक कम कर देती है, जो  $\text{CO}_2$  अवशोषण के लिए एक किफायती समाधान प्रदान करती है। एक ऊष्मागतिक विश्लेषण किया गया जिसमें

[TETAH][Im] और [DETAH][Im] को MDEA एब्जॉर्बेट्स के साथ मिश्रित कर CO<sub>2</sub> इंटरैक्शन में संतुलन दर स्थिरांक, अवशोषण की ऊष्मा, गिब्स मुक्त ऊर्जा, और एंट्रॉपी का आकलन किया गया। गतिज अध्ययन ज्विटरायन और टेट्रामोलेक्यूलर-आधारित मॉडल का उपयोग करके किए गए, जिससे [TETAH][Im] और [DETAH][Im] मिश्रित प्रणालियों के लिए सक्रियण ऊर्जा क्रमशः 25.61 kJ/mol और 24.87 kJ/mol पाई गई। इसके अतिरिक्त, एक आर्थिक आकलन ने संकेत दिया कि [TETAH][Pz], [TETAH][Im], और [DETAH][Im] के साथ मिश्रित MDEA एब्जॉर्बेट्स औद्योगिक MEA (5M) एब्जॉर्बेट की तुलना में लागत को लगभग 45% से 26% तक कम कर सकते हैं। एक कॉइल्ड फ्लो इन्वर्टर एब्जॉर्बर (CFI) का उपयोग अवशोषण दर, दक्षता, और वॉल्यूमेट्रिक मास ट्रांसफर गुणांक पर ध्यान केंद्रित करते हुए मास ट्रांसफर प्रदर्शन का विश्लेषण करने के लिए किया गया। निष्कर्ष बताते हैं कि CFI एब्जॉर्बर में मास ट्रांसफर प्रदर्शन को बढ़ाने की महत्वपूर्ण क्षमता है।

समग्र रूप से, यह कार्य व्यवस्थित अंतर्दृष्टि प्रदान करता है जो शोधकर्ताओं और इंजीनियरों को CO<sub>2</sub> कैप्चर के लिए अवशोषण सॉल्वेंट्स की प्रभावशीलता और एब्जॉर्बर्स के विकास को समझने में मदद करेगा।

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## THESIS CONTRIBUTIONS

- 1) **S.C. Tiwari**, K.K. Pant, and S. Upadhyayula, Efficient CO<sub>2</sub> Absorption in Aqueous Dual Functionalized Cyclic Ionic Liquids. *Journal of CO<sub>2</sub> Utilization*, 45 (2021), 101416. **(I.F. 7.7)**
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- 2) **S.C. Tiwari**, K.K. Pant, and S. Upadhyayula, Synthesis of new class dual functionalized ionic liquids and their performance for effective CO<sub>2</sub> capture: Properties and interaction mechanism analysis. **9th IUPAC International Conference on Green Chemistry**, Athens, Greece, September 2022.
- 3) **S.C. Tiwari**, K.K. Pant, and S. Upadhyayula, Kinetics Modelling and Thermodynamics Study of Dual Functionalized Ionic Liquid blend Methyldiethanolamine system for CO<sub>2</sub> capture. **9th International Congress on Ionic Liquids (COIL-9)**, Lyon, France, May 2023.

### Patent

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