

FAST WATER-LEAN SOLVENT SCREENING USING FTIR SPECTROSCOPY: IN-SITU (IN-LINE) MONITORING USING AN ATR REACTION CELL INTEGRATED WITH ON-LINE MONITORING ATTACHED TO A LIQUID-FLOWCELL

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Abstract

This study presents a fast and precise solvent characterizing method for the screening of novel CO₂ capture systems. In this method, time-base Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy was used for in-situ monitoring of CO₂ absorption and desorption processes of non-aqueous amine systems. Different equal mole amines were used to qualify and quantify changes of the IR vibrations. The method enables identification of reaction mechanism along with full speciation. In order to confirm repeatability and representability of the screening test, a replication experiment using liquid-flow cell FTIR analysis is also presented.

Keywords: FTIR-ATR, fast solvent screening, representative sampling, non-aqueous solvents, speciation

1. Introduction

The annual increase in CO₂ emissions is the main contributor to the increase in the greenhouse gas (GHG) level causing climate changes and global warming [1]. Fossil-fuel combustion and industrial processes are the dominant triggers of anthropogenic CO₂ emissions [2]. Integration of the post-combustion CO₂ capture (PCC) to industrial point sources is an essential attempt to alleviate this phenomenon [3, 4].

Different processes are employed for CO₂ capture and separation such as distillation, absorption, adsorption, and advanced membrane filtration [5]. Aqueous amine based gas-liquid chemical absorption is the most common method currently being used in industrial plants [4, 6]. Aqueous 30% MEA solvent is the benchmark capture system and the first patented amine-based solvent system [7-9]. MEA-based solvents are most popular due to MEA's high reactivity and low cost.

However, main concerns of aqueous MEA systems are energy intensiveness, solvent corrosivity and degradation in addition to solvent emissions. Although amine based solvent development has been in focus for several decades to identify appropriate solvent systems, it is still challenging to overcome the aforementioned drawbacks. A method enabling fast screening of solvent systems is thus essential to identify promising CO₂ capture systems.

Amines are widely used for chemical absorption of CO₂. During this reaction, reversible carbonaceous products are formed. In this context, amines are an interesting group of chemical compounds which can be classified into three main groups of primary, secondary, or tertiary amines. Furthermore, amines may react differently due to

steric hindrance, cyclic structures or multiple amine functions present in one amine molecule. Aqueous, non-aqueous, water-lean, by-phasic, and ionic/eutectic amine based solvents systems are being investigated to identify the most promising capture systems.

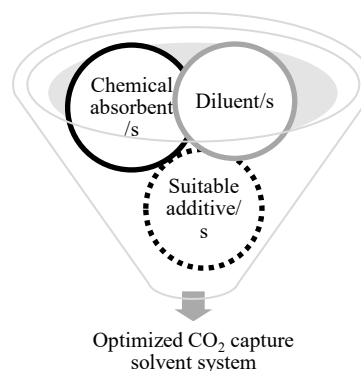


Figure 1: Amine based CO₂ capture system interpretation

Generally, an amine based CO₂ capture system is a blend of several components as shown in Figure 1. It may consist of an amine or a blend of amines to act as a chemical absorbent of CO₂. Moreover, this part is diluted with suitable diluents like water or organic solvents. Furthermore, this system may be optimized by addition of suitable additives to enhance the solvent's chemical and physical properties. Since all components may interact with each other, identifying a novel and promising CO₂ capture system is a challenging task. Therefore, combination of fast and precise chemical analytics with chemical mechanistic insight is paramount.

There are several methods currently being employed to characterize potential solvent. The wetted wall column (WWC) is a well-known apparatus for CO₂ absorption rate measurements also used in a modified version for solvent screening [10]. An atmospheric solvent screening apparatus has been developed to mimic the CO₂ absorption and desorption processes [11-13]. Solvent performance can be determined versus reference solvents by continuous monitoring of the CO₂ capture rate using non-dispersive infrared (ND-IR) CO₂ sensor [14]. The same method was used to screen strong bicarbonate-forming solvents gathering at the same time information on solvent foaming, solid precipitation, and discoloration [15]. Furthermore, Luo et.al. introduced a rapid screening apparatus for improved analysis of single and blended amine solvent systems [16]. Molecular simulations [17] or different modeling tools like soft SAFT[18], COSMO-RS [19, 20] are also used to predict reactive absorption properties of novel solvents without doing laborious experiments.

FT-IR spectroscopy is a versatile method for the analysis of chemical structures used in a wide range of applications. In FT-IR spectrum analysis, the bands of the functional groups and the molecular fingerprint of a chemical mixture are analyzed to give qualitative and quantitative chemical data. This is a fast and precise analysis method for efficient screening of chemicals at small sample volume. Furthermore, vibrational spectroscopy is well suited to application of multivariate calibration models to extract chemical data of species, especially for online monitoring of dynamic systems [21-23].

Chemical speciation of aqueous DEA [24] and heterocyclic amine [25] solvent systems has been performed by ATR-FTIR spectroscopic in situ monitoring. This method can be used for online monitoring of several chemical components simultaneously using Partial Least Regression (PLS-R) models [25-27].

We recently reported a novel sulfolane based non-aqueous solvent system for CO₂ capture [28]: a mixture of diisopropylamine (DIPA), sulfolane (SULF), and methanol (MeOH). Herein we report development and representativity[29]of a fast solvent screening method applied for analysis of the above-mentioned DIPA-MeOH-SULF study. The FTIR-based bulk liquid analysis was performed to confirm the fast-screening result are representative and reproducible.

2. Materials and Methods

All chemicals used in the experiments are tabulated in table 1.

Table 1 Chemical information: Name, CAS number, mole fraction purity, role, and supplier of chemicals.

Chemical name	CAS number	Mole fraction purity	Role	Supplier
Diisopropylamine (DIPA)	108-18-9	≥0.99	Amine	Sigma-Aldrich
Sulfolane (SULF)	126-33-0	≥0.99	Diluent	Sigma-Aldrich
Methanol (MeOH)	67-56-1	≥0.99	Diluent	VWR
Carbon dioxide (CO ₂)	124-38-9	0.9999	Gas	AGA Norge AS

2.1 Fast solvent screening method including solvent speciation

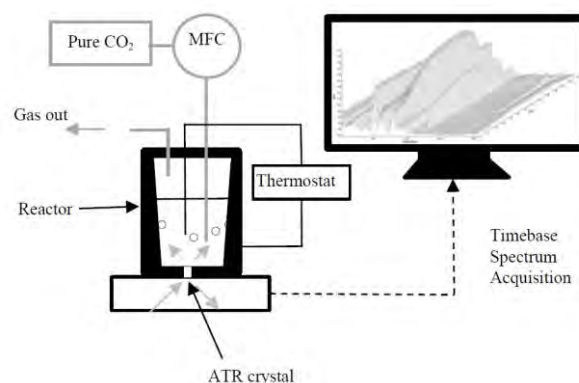


Figure 2: Schematic diagram of the experimental set-up used for the fast-screening of the non-aqueous DIPA system.

The schematic diagram of the fast-screening method is shown in Figure 2. A detailed description of the experimental procedure is given in an earlier publication [28]. The set-up (figure2) was used for screening a set of non-aqueous solvent systems as well as performance evaluation based on the spectroscopic information gathered by in-situ FTIR monitoring.

2.2 Bulk flow analysis for verifying the representativity of the screening results.

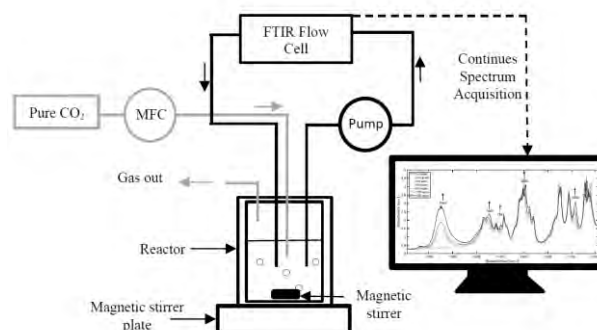


Figure 3: Schematic diagram of the experimental set-up2 for the acquisition of liquid flow cell FTIR spectra.

Since the FTIR-ATR method provides solvent composition on the surface of the ATR crystal, the representativeness of the fast-screening results for the

bulk solvent liquid needs to be assured. Hence, CO₂ absorption tests were performed using set-up2 i.e. bulk liquid-flow analysis. The schematic diagram of the set-up2 is shown in Figure 3. The reactor is a double-jacketed glass vessel with 4 inlet-outlet ports on the top. 50 ml of unloaded solution was placed inside the reactor and the solvent was mixed using a magnetic stirrer with a stirring rate of 250 rpm. Two ports were connected to the gas inlet and outlet while the other two ports were connected to the liquid flow cell inlet and outlet. To analyse the reaction liquid, the solvent was passed through a liquid-flow cell connected to a FTIR liquid sampling accessory. The liquid sampling accessory was attached to the Perkin Elmer Spectrum One FT-IR Spectrometer and the liquid passing through the sampling device was scanned at pre-determined set time. The sampling accessory is equipped with a programmable, variable-speed peristaltic pump to pass the liquid through the flow cell. The waste liquid end of the sampler was sent back to the reactor to recycle the liquid flow through the flow cell.

Prior to each experiment, a background scan of the empty flow cell was recorded. Then the sampler was turned on and unloaded CO₂ solvent started to flow through the cell. Several scans of unloaded liquid were recorded. Then, CO₂ gas was introduced into the glass reactor at a flow rate of 0.10 NL/min using a mass flow controller (MFC) from Sierra Instruments. Scans of the reaction liquid were performed timely during the CO₂ absorption reaction.

FTIR spectra were baseline corrected by Automatic Whittaker Filter method using a chemometrics software, PLS-toolbox with MATLAB® (R2019b).

3. Results and Discussion

3.1 In-situ monitoring and fast screening of a non-aqueous solvent system

In the experimental set-up1, in-situ monitoring was used to observe reaction changes during CO₂ absorption-desorption of the solvent system. The tests were performed in a reaction cell containing a diamond crystal top plate (P/N GS10507) with Golden Gate™ single reflection diamond ATR system. An inherent advantage of this system is that only small mass of solvent is needed (approx. 5g) for one screening experiment. An example of ATR-FTIR raw spectra obtained from time-based in-situ monitoring is shown in Figure 4 (a).

According to Figure 4(a), in-situ monitoring of the chemical changes in the reaction aliquot was performed in four stages. A time gap of each stage was decided during the experiment along with the appeared stack of spectra. The chemical reaction changes can be observed as ATR-FTIR spectra variations. This is a benefit of set-up1 since we can do the experiment without prior information about the time gaps of each step. It is possible to control the parameters accordingly during the experiment while observing the spectra.

Initially, a few FTIR scans were performed to check the unloaded solution. There was no evidence of premature CO₂ capture species formation or water contamination in the sample. Representative FTIR bands of mixture components were also identified.

Then CO₂ was introduced into the solvent. During this second stage, several peaks were seen to increase, decrease and shift. At the same time, several new peaks appeared according to the developing carbonaceous products. The second stage absorption step continues until the increasing band intensity is seen constant.

In the third step, the loaded solvent was observed after further CO₂ pumping. During this time all bands stayed stagnant, implying the capture products to be stable at this condition. This stage was completed after approximately 25 minutes.

In the fourth step, the temperature of the reaction cell was increased to observe the desorption reactions of the system. The reaction cell was heated up gradually and reduction of peaks were seen. Temperature for this step was kept at 58°C. At this stage, in-situ reaction monitoring is important to determine the proper desorption temperature of the new system through observation of spectra changes.

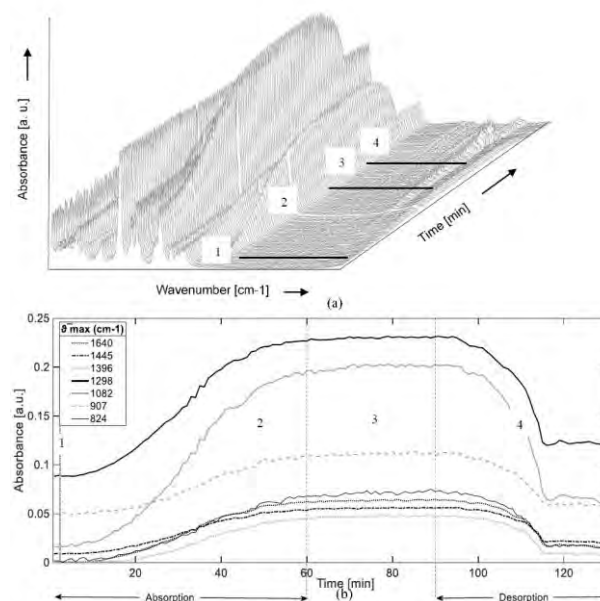


Figure 4: (a) Time-based ATR-FTIR scans (b) IR absorbance variation with time from changing IR vibrational bands; non-aqueous DIPA solvent system during the CO₂ absorption and desorption.

3.2 Full chemical speciation using time-based ATR-FTIR spectra of non-aqueous solvents

From in-situ monitoring of a reaction, plenty of chemical information about the reaction can be acquired. However, this information is available as the vibrational bands of the FTIR spectra. Vibrational band assignment of the

spectra was performed to identify the chemical species of the novel solvent system.

Spectroscopic spectra can be considered to be a multivariate output of a sample that consists of an abundance of hidden chemical information. Extracting the spectrum data would be an inexpensive method of chemical speciation. Data preprocessing tools are needed to extract qualitative and quantitative information from a specific spectrum. In this contribution, qualitative information extraction will be discussed.

Vibrational peak assignment was carried out for the changing peaks of the baseline-corrected spectra. The baseline corrected fingerprint region of the IR spectra of unloaded, loaded, and desorbed solvent are shown in Figure 5. Wavenumbers of all the increasing peaks were recognized and assigned to the relevant vibrational groups according to literature. Tabulated peak assignment information is given in Table 2. According to the peak assignment for increasing peaks, we identified the CO₂ capture product of the non-aqueous solvent system to be monomethyl carbonate (MMC) species. A proposed reaction mechanism according to the vibrational assignments has been published [28].

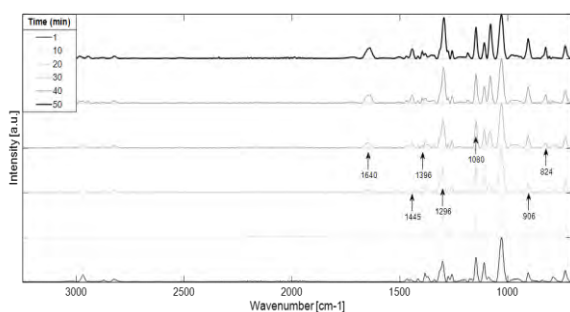


Figure 5: Increasing of the specific peak's intensities with the time during the CO₂ absorption reaction of the non-aqueous DIPA solvent system.

Therefore, in-situ monitoring by ATR-FTIR spectroscopy is a fast-screening method which is able to observe the CO₂ absorption-desorption reaction with full speciation.

Table 3. Monomethyl carbonate (MMC) peak identification of the non-aqueous DIPA system

Characteristic IR vibrational bands ν_{max} (cm ⁻¹)	MMC Peak Assignment	Reference
1640	C=O Stretching vibration	[30] [31]
1443	CH ₃ asymmetric deformation	[30] [31]
1396	CH ₃ symmetric deformation	[30] [31]
1296	O-C-O asymmetric stretching vibration	[30] [31]

1080	O-C-O symmetric stretching vibration	[30] [31]
906	CH ₃ -O stretching	[31]
824	CO ₃ deformation	[31]

However, concluding full chemical reaction speciation by in-situ monitoring in a closed system might have some uncertainties. The concerns on the non-aqueous systems could be two-fold.

1. If the system becomes heterogeneous during the absorption (e.g. phase change) the spectroscopic results will not be accurate
2. If precipitation happens on the ATR crystal the observed spectra may not represent the liquid CO₂ capture solvent.

To address the above-mentioned concerns, bulk analysis of the reaction system was conducted by using the same FTIR instrument with a different reactor set-up.

3.3 On-line bulk liquid flow monitoring of the non-aqueous solvent system to verify the fast-screening results

This experiment was conducted to check the representability of the results of the fast-screening method.

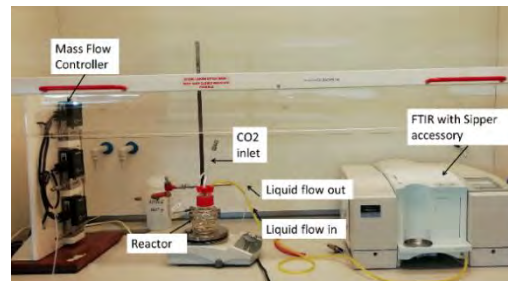


Figure 6: Laboratory arrangement of Set-up2 with a glass reactor

Precipitation on the ATR crystal may lead to analysis error, since the solvent penetration depth of the ATR measurement is very narrow, and the analysis happens at the bottom of the reaction volume. In set-up2 (shown in Figure 6), a glass reactor without an ATR crystal was used to perform the CO₂ absorption reaction. The solvent was continuously circulated through a FTIR flow cell. Therefore, the solvent system bulk was identified thus enabling verification that not solidification or precipitation occurred during the CO₂ absorption reactions.

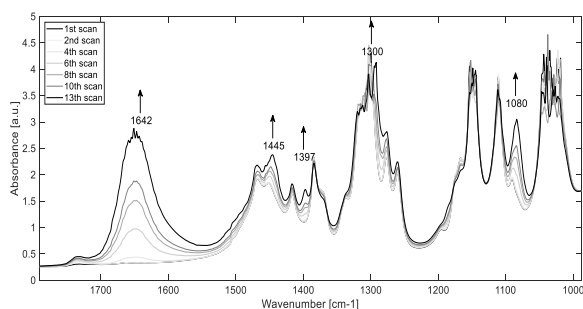


Figure 7: IR spectra obtained from liquid-flow cell measurements during CO₂ absorption experiments

All relevant MMC bands from 1000 cm⁻¹ to 1800 cm⁻¹ were identified by the liquid stream analysis using the liquid-flow cell. However, the band at 824 cm⁻¹ (MMC O-CO₂ deformation) was invisible due to the CaF₂ window material cut-off of the liquid-flow-cell. The obtained results confirmed the fast-screening speciation and showed the representativeness of the fast-screening results of the non-aqueous DIPA CO₂ absorption system.

Conclusion

From in-situ reaction monitoring using set-up1, it is shown that it was possible to obtain a fast and easy chemical characterization of non-aqueous CO₂ capture solvents. The instant observability of the reaction changes at running conditions and the possibility of inexpensive reaction mechanism identification are the main benefits of the set-up1. Furthermore, it is connected to qualitative and quantitative comparability of several solvent systems according to the IR vibrational changes.

The replication experiments using set-up2 confirm the results by addressing some concerns of set-up1. The qualitative results from set-up1 are repeatable and independent of the way of performing the FTIR analysis and the level of solvent mixing. This confirms the capture products are not a solid, gel, or high viscous liquid since the same results were obtained from liquid-flow cell measurements.

Therefore, screening set-up1 is a fast, reliable approach for identification of unknown solvent systems requiring less volume, less time, and less money as compared to traditional solvent analysis methods. Furthermore, representativeness and repeatability of the results was ensured. For non-aqueous amine systems use of an enhanced method like set-up2 is recommended.

Acknowledgements

This work was supported by the Ministry of Education and Research of the Norwegian Government.

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