Online analysis of amine concentration and CO_2 loading in MEA solutions by ATR-FTIR spectroscopy at process conditions

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INTRODUCTION

Process information regarding the CO_2 loading (mol CO_2/mol amine) and the amine concentration of aqueous amine solvents for CO_2 capture are essential for amine based carbon capture plant operation and in various experimental apparatuses studying CO_2 absorption by amines. Conventionally, these liquid analyses have been performed manually by the use of relatively time-demanding methods. Manual off-line liquid analysis does not provide input data for real-time process control and optimization. In addition, the methods used are generally labor-intensive and impractical for studies of transient conditions during dynamic changes in a process. Both from a scientific- and an operational aspect, real-time data of CO_2 loading and amine concentration during operation of experimental equipment and CO_2 capture plants would provide much useful information for process characterization and control.

Fourier Transform Infrared (FTIR) spectroscopy has substantial potential for scientific purposes and as a quantitative quality control tool for the industry. FTIR spectrometry has the advantage, compared with other methods that several compounds can be detected simultaneously, and the monitoring can be performed continuously. Recent advances in FTIR spectroscopy have allowed for rapid and accurate analysis of liquid samples in conjunction with Attenuated Total Reflectance (ATR) technology. FTIR ATR liquid analysis of CO_2 absorption in amine solutions has demonstrated that both carbamate and carbonate formation can be monitored using this technique [1]. The advantage of choosing FTIR as a quantitative technique lies in its ability to readily carry out multi-component analysis in association with multivariate analysis methods such as Partial Least Squares (PLS) regression [2].

EXPERIMENTAL SETUP

Infrared (IR) spectra were obtained on an ABB FTLA2000 Series Laboratory FTIR spectrometer using a PIKE MIRacle™ ATR cell with diamond as ATR crystal. A multi-component calibration model was obtained by PLS regression of IR spectra from ATR analysis of liquid samples of mono-ethanolamine (MEA) of different amine concentrations and CO_2 loadings, with the calibration set spanning the relevant range of concentrations. The calibration model was validated by ATR-analysis of different samples of aqueous MEA with known concentrations of amine and CO_2. A setup was constructed for extractive sampling of liquid through a temperature controlled ATR flow-cell for liquid analysis. Liquid samples of MEA in a CO_2 absorption column were continuously extracted and analyzed online by the setup during operation of the column.

RESULTS

The results presented in Figure 1 are online measurements of CO_2 loading of 30 wt% MEA in an amine absorber during operation at transient conditions. The online measurement by ATR analysis was verified by judgment sampling and subsequent off-line manual analysis. The results show that FTIR spectroscopy of liquids combined with multivariate methods such as PLS and proper pretreatment of the infrared spectra used in calibration is well suited for this purpose.

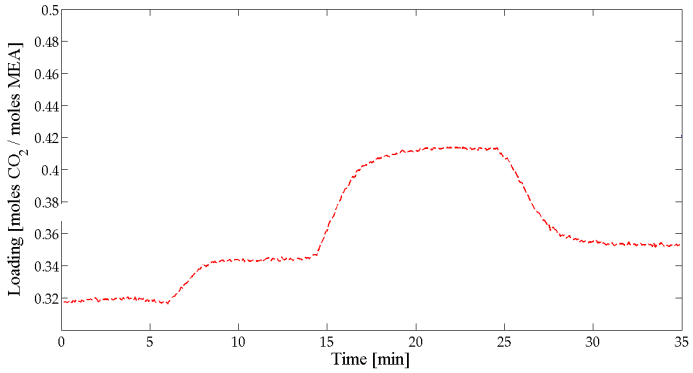

Figure 1: Example of on-line measurement of CO_2 loading of rich 30wt% MEA solvent downstream the absorption column during dynamic operation of the pilot plant.

The calibration model was expanded to involve simultaneous analysis of both CO_2 loading and amine concentration in MEA solutions. A PLS model was obtained based on a set of calibration spectra obtained from ATR measurements of liquid samples of MEA of different concentrations and CO_2 loading. Figure 2 shows results from the multivariate data analysis.

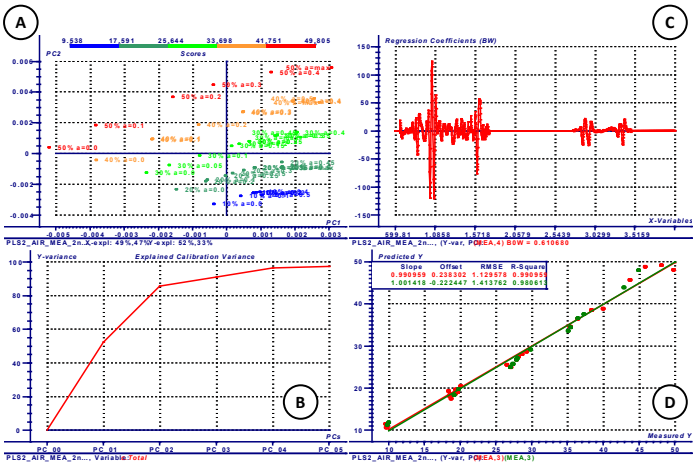

Figure 2: PLS model results: score plot (A), estimated calibration variance (B), regression coefficients (C) and measured vs predicted concentrations (D).

The score plot (Figure 2A) indicates trends in its display of information on sample relationships; both CO_2 loading and amine concentration for the different samples show a linear trendline. The regression coefficient plot (Figure 2C) indicates that the wave numbers from 679 cm^{-1} to 1786 cm^{-1} and from 2821 cm^{-1} to 3479 cm^{-1} are the most important for the prediction of CO_2 loading and MEA concentration. Root mean standard error of prediction (RMSEP) of CO_2 loading in the model is 1.01 with 4 PC components. The model with 4 PCs describes 96.4 % of the total validation variance in the data.

REFERENCES

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