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Real-time monitoring of room-temperature ionic liquid purity through optical diode-based sensing

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ABSTRACT

Room-temperature ionic liquids (RTILs) are promising for use in many industries due to their unique properties, including wide electrochemical windows, low vapor pressures, high ionic conductivities, and chemical and thermal stability. All of these properties require high RTIL purity, and achieving this high purity is a major driver of RTIL manufacturing costs. Continuous flow processes to synthesize highly pure RTILs at a reduced cost have been developed, but due to exothermic synthesis reactions and temperature dependent reaction rates, these processes require real-time control. An ultraviolet LED based optical sensor has been designed to measure RTIL purity at millisecond sampling rates using a liquid flow cell. The sensor is demonstrated by measuring 1-methylimidazole (MIM) concentration in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]). Sensor results are compared against spectroscopic measurements with good agreement.

1. Introduction

Room temperature ionic liquids (RTILs) are a class of chemicals which are liquids at or below room temperature and are composed entirely of ion pairs. These RTILs have desirable properties as green solvents due to their low vapor pressure [1–4]. RTILs are also stable across a wide range of temperatures and possess a wide electrochemical window, making RTILs a promising class of electrolytes [5–7]. The properties of RTILs are highly dependent on purity. For example, the electrochemical window of [EMIM][TFSI] has been shown to be dependent on the water content of the sample [7,8]. Residual precursors and byproducts of RTIL synthesis can lead to electrode corrosion and other performance degradation mechanisms. For example, synthesis of the [EMIM]-cation typically begins with MIM, whose redox stability limit is within the electrochemical window of [EMIM][TFSI]. Currently, most RTILs are produced through batch processes. After the synthesis reaction is complete, the product must be separated from impurities, adding to the cost of RTILs. Due to the low vapor pressure of ionic liquids, purification through a distillation process is not feasible, and considerable effort is spent in purifying ionic liquids through filtration or recrystallization processes [9,10].

Continuous flow synthesis processes have recently been developed that have the potential to significantly reduce costs – making more industrial RTIL applications feasible [9,11]. In a continuous flow process, it is desirable to monitor the purity of the finished product in real time as the product exits the production line to ensure product quality and process control. Synthesis of quaternary amine cations pose particular challenges due to the exothermic reaction and requirement that the precursors' stoichiometry be precisely controlled. Any deviation from a 1:1 stoichiometry of tertiary amine and quaternizing agent will result in an excess of one reactant that may be difficult to remove from the product RTIL. By monitoring the purity of the finished product, it is possible to determine if the synthesis process is proceeding within normal operating conditions [9,11]. Currently, methods for determining the purity of RTILs such as ion chromatography tend to be expensive and ex situ [12,13]. An in situ sensor which is capable of determining the purity of the RTIL in real time would allow the production process to be self monitoring.

The ultraviolet absorption spectrum provides a unique identifier for ionic liquids and their chemical precursors. Previously, it was shown that by using UV spectroscopy, it was possible to detect the presence of impurities in ionic liquids by analyzing the absorption spectrum of each constituent [14]. The aim of the work reported here is to apply these findings to the problem of sensing impurities in real time. The time response and non-intrusive nature of optical

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sensors make them ideal for monitoring chemical processes. For example, optical sensors are commonly used to measure the presence of analytes in samples [15–17]. Although spectroscopic methods have been used before to characterize RTILs [18], to the best of the authors' knowledge this sensor is the first spectroscopic device designed for process control in the production of RTILs.

1.1. Absorbance in liquid samples

The LED sensor operates on the principle of optical absorption. As described by the Beer–Lambert law, at certain optical wavelengths, light is absorbed as it passes through a sample:

$$-\ln\left(\frac{I_\lambda}{I_{0,\lambda}}\right)=\sigma_\lambda X_i nL \tag{1}$$

where I_λ is the intensity of light at wavelength λ exiting the sample, $I_{0,\lambda}$ is the intensity of light at wavelength λ incident on the sample, σ_λ is the molar absorption cross-section or molar absorptivity (m^2/mol), X_i is the mole fraction of species i, n is the total molar concentration of the sample, and L is the pathlength the light travels through the sample. The absorption cross-section, σ_λ, is a wavelength-dependent material property of the sample that is measured in an optical cell of known path length and material concentration using a spectrometer. Fig. 1 shows the measured UV absorption spectra of [EMIM][TFSI] and MIM at ambient conditions. From these spectra, it can be seen that MIM has an absorption peak near 275 nm, while [EMIM][TFSI] has an absorption peak near 265 nm. Between 275 nm and 300 nm, the absorption cross-section of MIM is greater than that of [EMIM][TFSI]. At wavelengths longer than 340 nm, neither MIM nor [EMIM][TFSI] absorbs light. The sensor described in this work utilizes these spectral properties to determine the presence of MIM in [EMIM][TFSI].

2. Experimental methods

Due to the differences in spectral properties between MIM and [EMIM][TFSI] seen in Fig. 1, the presence of MIM may be detected in a sample by changes in absorption at wavelengths between 275 nm and 300 nm. In order to measure the differences in absorption between [EMIM][TFSI] and MIM, a custom LED array with wavelengths selected to measure the spectral features of [EMIM][TFSI] and MIM was obtained from Sensor Electronic Technologies Inc. A diagram of the array may be seen in Fig. 2.

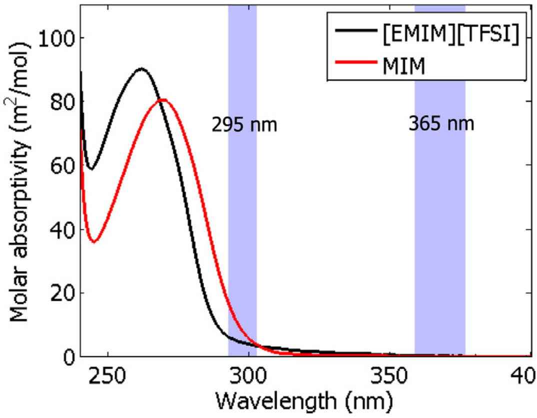

Fig. 1. Absorbance of [EMIM][TFSI] and MIM. The full-width half-maximum range of the 295 nm LED channel is shown as the shaded area on the left. The shaded area on the right is the full-width half-maximum of the 365 nm channel. Data were previously collected and presented as described in [14].

2.1. Sensor construction and testing

The LED array contained nine separate diodes: four diodes which emitted at a peak wavelength of 295 nm (9.7 nm full-width half-maximum), four diodes which emitted at a peak wavelength of 320 nm (10.4 nm full-width half-maximum), and as a single 365 nm diode (18.1 nm full-width half-maximum). The LED array was housed in a 12 pin TO-8 package. This package was soldered to a custom printed circuit board which was designed to fit into a standard 1 in. optical mount. The LED was driven by a 0–12 V logic circuit with appropriate current limiting resistors to protect the diodes in the array. The 295 nm diodes were used to detect increased absorbance due to the presence of MIM. While a larger difference in absorbance is seen at about 270 nm, inexpensive diodes at this wavelength are not yet commercially available. The 365 nm diode has been selected to provide a reference for the transmission through the RTIL. The 320 nm diodes are used for detecting a second impurity which is specific to the proprietary synthesis process developed by Boulder Ionics.

The RTIL flowed through a 2.5 mm path length flow cell (FIA Labs SMA-Z-2.5 #79048) constructed from PEEK and fitted with a pair of fused silica windows to allow transmission of ultraviolet light. Light was focused through the cell's windows by means of a series of free space optics mounted on ThorLab's 30 mm cage mount components, as shown in Fig. 2. The light transmitted through the RTIL was measured by a ThorLabs PDA10A amplified photodetector (measurement detector). An uncoated UV fused silica window directed a portion of the LED light to a second PDA10A to monitor the output of the LED (reference detector). The purpose of the reference detector was to measure and correct for variation in the output intensity of the LED. Detector output signals were filtered with 50 Hz RC low pass filters ($R = 330\,\Omega$, $C = 10\,\mu F$) and read by a National Instruments PCI-MIO-16E-1 data acquisition card.

[EMIM][TFSI] (trade name Iolyte P1) was obtained from Boulder Ionics Corp. Total halide content was less than 100 ppm and water content was less than 20 ppm. The [EMIM][TFSI] was used without further purification. MIM was also obtained from Boulder Ionics. All samples were stored and prepared in a dry nitrogen environment. Samples of [EMIM][TFSI] with known MIM concentrations were created in a controlled atmosphere glovebox with low oxygen and low humidity. Quantities of MIM were weighed using a digital balance and added to samples of pure [EMIM][TFSI]. Separate 2 mL samples were prepared in syringes and injected through the flow cell while sensor readings were recorded. Each sample was discarded after passing through the sensor to prevent contamination. Only steady-state readings were retained to avoid erroneous readings due to mixing of samples in the flow cell.

2.2. Determination of MIM concentration

Accurate MIM concentration measurements require correcting for background noise, fluctuation is LED output, and for changes in optical transmission through the cell. Background subtraction removes the small DC offset due to ambient light striking the detectors. This is accomplished by subtracting the voltage reading from each detector when all LED wavelengths are off. Fluctuations in the intensity of the LED are removed by taking the ratio of the measurement detector signal, I_M, over the reference detector signal, I_R: I_M/I_R. Taking this ratio in real-time corrects for transient fluctuations in LED output as well as intensity drift over time. These corrections can be represented in the Beer–Lambert law (Eq. (1)) as:

$$-\ln\left(\frac{I_M^{295} I_{0,R}^{295}}{I_{0,M}^{295} I_R^{295}}\right)=\sigma^{295} X_{MIM} nL \tag{2}$$