Eutectic Ionic Liquid mixtures and its effect on CO₂ solubility and conductivity

Anna S. Ivanova,[†] Thomas Brinzer,[‡] Elliot A. Roth,[£] Victor A. Kusuma,[£] John D. Watkins,[£] Xu Zhou, ^{£,€} David Luebke,[£] David Hopkinson,[£] Newell R. Washburn,[†] Sean Garrett-Roe,^{‡*} Hunaid B. Nulwala^{†,£*}

⁺ Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213. [‡] University of Pittsburgh, Department of Chemistry, Chevron Science Center, 219 Parkman Avenue Pittsburgh, PA 15260. ^eLiquid Ion Solutions, LLC. 1817 Parkway view Drive, Pittsburgh PA 15205, ^eNational Energy Technology Laboratory, P.O. Box 10940, Pennsylvania 15129.







¹H, 300 MHz, DMSO-d₆



Measurements

Viscosity

Viscosity measurements were taken with a RheoSense microVISC viscometer, using the microVISC temperature controller to maintain the system at 50° C. Each sample was melted and filtered through hot glass wool to remove any sediment before being loaded into a 400μ L syringe. The syringe was placed into the viscometer before beginning temperature ramp to allow adequate equilibration time. Each sample was measured five consecutive times, and the average of these measurements is reported, along with error.

Density

Density measurements were obtained using a Micromeritics AccuPyc II 1340 gas pycnometer with an attached water bath to maintain a system temperature of 50°C. A 1 cm³ insert was used in the 10 cm³ sample chamber to reduce the sample size required.

Water Content

Water content was determined using a Metrohm 860 Karl Fisher (KF) Thermoprep titration unit, equipped with an 831 KF Coulometer; IL samples which had undergone KF using an oven were treated as water-free samples. Viscosity measurements were made at ambient temperatures (50 °C) using a Rheosense Inc. μ Visc unit and 400 μ L pipettes.

DSC Melting Point

Differential scanning calorimetry (DSC) was conducted using a TA Instruments Q2000 DSC equipped with a liquid nitrogen cooling accessory. A standard DSC run was conducted with a heating and cooling rate of 10°C/minute, a temperature range of -100°C to 150°C, and three cycles to ensure repeatability of the results. Tzero aluminum hermetic pans were used with a sample size of approximately 10 mg. Additionally, modulated DSC was conducted using the same instrument with a heating and cooling rate of 2°C/min, an amplitude of 0.318°C and a period of 60 seconds. No different was found between the normal DSC and Modulated DSC. A heat cool heat cycle was performed and the data was taken from the second heat. The melting point was slightly lower compared to the 10°C/min DSC run by approximately 1°C for the three samples tested confirming that the 10°C/min DSC run was sufficient for measuring the final melting point.

DSC Heat Capacity

Differential scanning calorimetry (DSC) was conducted using a TA Instruments Q2000 DSC equipped with a liquid nitrogen cooling accessory. The heat capacity measurements for the samples were measured using Tzero aluminum hermetic pans. The Q2000 instrument was calibrated for Cp analysis using water at 50°C. The heat capacity at 25° C, 50° C, and 75° C was measured using a sample size of approximately 10mg. A Quasi-isothermal method using modulated DSC with a modulated temperature of $\pm 1^{\circ}$ C, and a period of 120 seconds was used at each isothermal temperature. The temperature was kept constant for 10 minutes at each temperature for the signal to stabilize. Analysis of the DSC data was conducted using the reversing heat capacity signal and Universal Analysis 2000 software. The heat capacity reported was calculated by averaging the heat capacity over the last 2 minutes of each 10 minute isotherm at each temperature.

Conductivity

Samples were heated to 50°C for 10 minutes to melt the mixture and ensure homogeneity. The samples were withdrawn using a syringe and injected into a custom built conductivity cell. The custom built cell consisted of two 1.6 mm diameter platinum disc electrodes (BASi) in a 'face-on' configuration with a separation of 2 mm held within a PTFE tube of inner diameter 6 mm. The solution was injected through the

side wall of the cell to fill the cavity with the PTFE wall creating a seal once the syringe was removed. The entire cell was placed into a fan circulated thermostatic oven and held at 50°C for all impedance measurements. Samples were pretreated by holding at Over Current Protection (OCP) for 2 minutes before Electrochemical impedance spectroscopy (EIS) was carried out on each sample at OCP using 10, 20, and 50 mV perturbations sequentially over a frequency range of 0.1-100,000 Hz. Solution resistance was measured at the point where the plot crossed the real axis (x axis), and was converted to a conductivity by using a measured cell constant. The cell constant was found by calibration with a 1413 µS/cm conductivity standard solution over the appropriate temperature range.

TGA Thermal Stability

Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q500 with a standard furnace. The measurements were made using sample sizes of ~20 mg in platinum pans. Each sample was heated from room temperature to 900°C at 10°C/min, under a nitrogen flow of 60 mL/min. The onset, inflection, and end points were determined using TA Universal Analysis 2000 software.

IR Spectroscopy

CO₂ was loaded into each ionic liquid by exposure of a small volume of the rapidly-stirred ionic liquid to a pure CO₂ atmosphere at approximately 1 bar for 2 hours. Following this time, a 2 μ L aliquot of the sample was placed between two CaF₂ windows (2mm thickness) with a 25 μ m spacer. In the case of [C₁C₁pyrr]_{0.7}[Tf₂N], the sample was heated to ~35°C before loading, then allowed to supercool to room temperature before measuring. [C₆C₁Im][Tf₂N] was loaded at room temperature. Optical density of CO₂ dissolved in [C₆C₁Im][Tf₂N] was o.3, while that dissolved in [C₁C₁pyrr]_{0.7}[Tf₂N] was o.1. Cells were assembled under ambient conditions. Water content of the ILs after assembly was estimated using absorbance of water stretching modes seen on FTIR. Mass fractions for [C₁C₁pyrr]_{0.3}[C₁pyr]_{0.7}[Tf₂N] (0.001) and [C₆C₁Im][Tf₂N] (0.0012) were similar.

A commercial Ti:Sapphire laser source (Coherent Legend Elite) was used to pump an optical parametric amplifier (OPA) to generate mid-infrared pulses^[1]. These pulses were directed to a two-dimensional infrared (2D IR) spectrometer in a pump-probe geometry^[2]. The resulting signal was dispersed onto a 2x32 channel array MCT detector (Infrared Associates) using a single monochromator (150 line/mm grating) (Horiba iHR320).

Following spectral calibration, the spectra were globally fitted to a calculated spectrum, which was based on a third-order nonlinear response function formalism^[3] using a two point correlation function

$$c(t_2) = \frac{\delta(t_2)}{T_2} + \Delta^2 e^{-\frac{t_2}{\tau_c}}$$

where the first (Bloch) term represents molecular processes in the homogeneous (fast or motional narrowing) limit, and the second term corresponds to Kubo's ansatz for a spectral diffusive process. The resulting lineshape function

$$g(t_2) = \frac{t_2}{T_2} + \Delta^2 \tau_c^2 \left[e^{-\frac{t_2}{\tau_c}} + \frac{t_2}{\tau_c} - 1 \right]$$

was substituted into the third-order response functions to generated a calculated 2D IR spectrum that depends on the correlation time (T_c) and dephasing time (T_2) of the chromophore.

Following normalization of the 2D-IR spectra to the CO₂ antisymmetric stretch peak to remove the effects of vibrational relaxation on spectral intensity, a nonlinear least squares fitting algorithm was used to minimize the squared error between the series of calculated spectra and the experimental spectra, with parameters of homogeneous dephasing time (T_2), spectral diffusion time ($^{\tau_c}$), frequency range for spectral diffusion ($^{\Delta}$), anharmonicity, transition dipole moment for the o \rightarrow 1 and 1 \rightarrow 2 transitions, phase, and central frequency. When the value of the squared error for all spectra had converged, the fitting parameters were considered to be optimized.

In order to obtain confidence intervals for the fitting parameters, a bootstrapping procedure was employed^[4]. Briefly, the spectra were repeatedly fitted using a set of randomly selected points in the experimental and calculated spectra. The total number of data points chosen for each optimization was kept constant in order to preserve appropriate statistical weighting. The resulting parameters from 100 fits using random data points were used to generate a histogram of values for each fitting parameter, which were then analyzed to obtain confidence intervals for each parameter.

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Data

TGA Data

	%	%			Inflect.	Weight	Weight
Sample	$[C_1 pyr][Tf_2N]$	$[C_1C_1pyrr][Tf_2N]$	Onset (°C)	End (°C)	(°C)	(mg)	(%)
AI 2-18	100	0	422.22	451.49	445.37	20.52	97.61
AI 2-24a	90	10	421.41	452.46	446.34	21.04	96.64
AI 2-24b	80	20	419 .2 4	453.35	444.34	22.25	97.51
AI 2-24c	70	30	424.44	454.1	446.02	29.19	97.84
AI 2-24d	60	40	417.85	452.76	444.31	17.86	98.75
AI 2-24e	50	50	415.02	451.93	442.81	13.07	98.87
AI 2-24f	40	60	424.58	455.84	447.31	23.6	98.92
AI2-24g	30	70	425.47	457.7	448.51	22.84	99.16
AI 2-24h	20	80	429.85	461.93	452.75	21.3	99.14
AI 2-24i	10	90	428.91	462.67	453.19	16.78	99.51
AI 2-19	0	100	430.55	462.87	453.79	18.11	99.62

MDSC Data (second heat at 2°C/min)

Sample	$% [C_1 pyr] [Tf_2 N]$	$% [C_1C_1pyrr][Tf_2N]$	T _m °C (peak)	
AI 2-18	100	0	44	

AI 2-24a	90	10	38
AI 2-24b	80	20	33

Water Content Data

The water content of the three samples of most interest was measured using KF titration described in the water content section. Prior to the measurement the samples were sealed and stored in a Sanpla Dry Keeper vertical desiccator with a relative humidity of approximately 40%. The KF titration unit was checked for accuracy by measuring the water content of 4 Hydranol standards that contained a certified amount of 999ppm of water. The average measurement for the water standards was 976 ppm giving an error of approximately 2.3%. The results are shown in the Table below.

Sample	$%[C_1 pyr][Tf_2N]$	%[C ₁ C ₁ pyrr][Tf ₂ N]	ppm H2O
Al-2-24a	10	90	820 ±50
Al-2-24b	20	80	3210±50
Al-2-24C	30	70	680±50