4-2020

Synthesis and Characterization of Hydrophilic Ionic Liquids: Dissolution and Modification of Brown Coal (Lignite)

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Introduction

Ionic liquids (ILs) are novel organic ionic compounds with 'green' physiochemical properties, such as high thermal stability, negligible vapor pressure, tunable solvation properties,[1] and melting points <100 °C. ILs have the potential of replacing organic solvents in industrial applications.

Brown coal (lignite) is the lowest rank of coal, containing a relatively higher ratio of carbon to oxygen than anthracite (highest rank of coal). Lignite is a poor resource for energy, as the intermolecular hydrogen bonds interfere with combustion.[2] Dissolution and fragmentation of lignite removes oxygen impurities, increasing efficiency in industrial applications.

By synthesizing novel ILs we can identify the properties that will treat coal and coal derivatives, increasing the efficiency of coal consumption, ultimately producing more effective fossil fuel treatment procedures.

Objectives

Objective 1: Synthesize ILs by combining different cations and anions. Cost, ease of synthesis, and variations in physicochemical properties must be considered during synthesis. Hydrophilic ILs will be the emphasis on synthesis procedures.

Objective 2: Characterize ILs to identify physical and chemical properties that will aid in the dissolution process. The focus will be placed on water concentration, viscosity, degradation temperature, and hydrogen bond donor/acceptor properties.

Objective 3: Dissolution and characterization of coal model compounds to determine the viability of specific ILs for coal dissolution.

Objective 4: Dissolution and characterization of brown coal (lignite) using select ILs. Identification of extent of dissolution, swelling, and fragmentation will be verified via instrumental analysis of samples. Recovery of IL from coal should be possible; however, it is not the primary task for this analysis.

Methods

Synthesis of ILs were completed in three steps: Appel reaction to convert glycol to halogenated glycol, nucleophilic refluxing to produce halogenated IL, followed by anion exchange (AE) to replace halide with acetate ion.

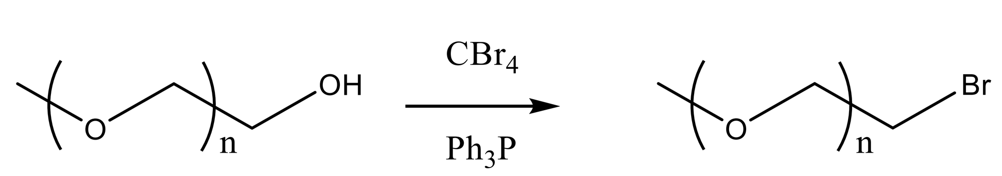
Characterization of ILs included determination of H_20 concentration, nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, thermogravimetric analysis (TGA), dynamic viscosity, and polarity and polarizability characteristics via Kamlet-Taft parameters.

Using coal model compounds to simulate lignite is an efficient method of predicting which ILs will work best with coal.

Dissolution and characterization of brown coal (lignite) using select ILs. Characterization of fragmentation and dissolution will be performed using electron microscopy, NMR, Fourier transform IR (FT-IR), and X-ray powder diffraction (XRD).

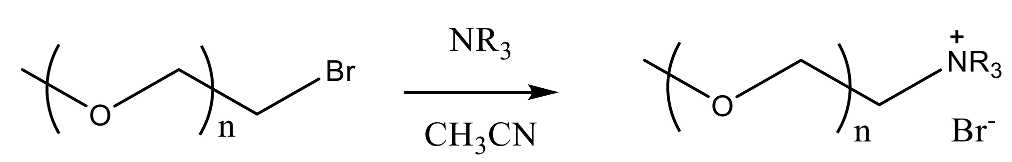
IL Synthesis

Step 1: Appel Reaction[3]



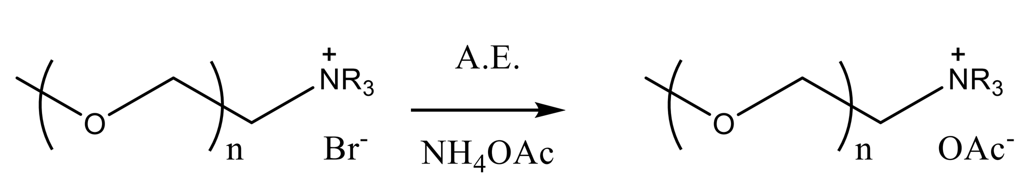
Reacting glycol with carbon tetrabromide and triphenylphosphine to produce primary alkyl halide. Reaction with 2° alcohol will invert stereochemistry.

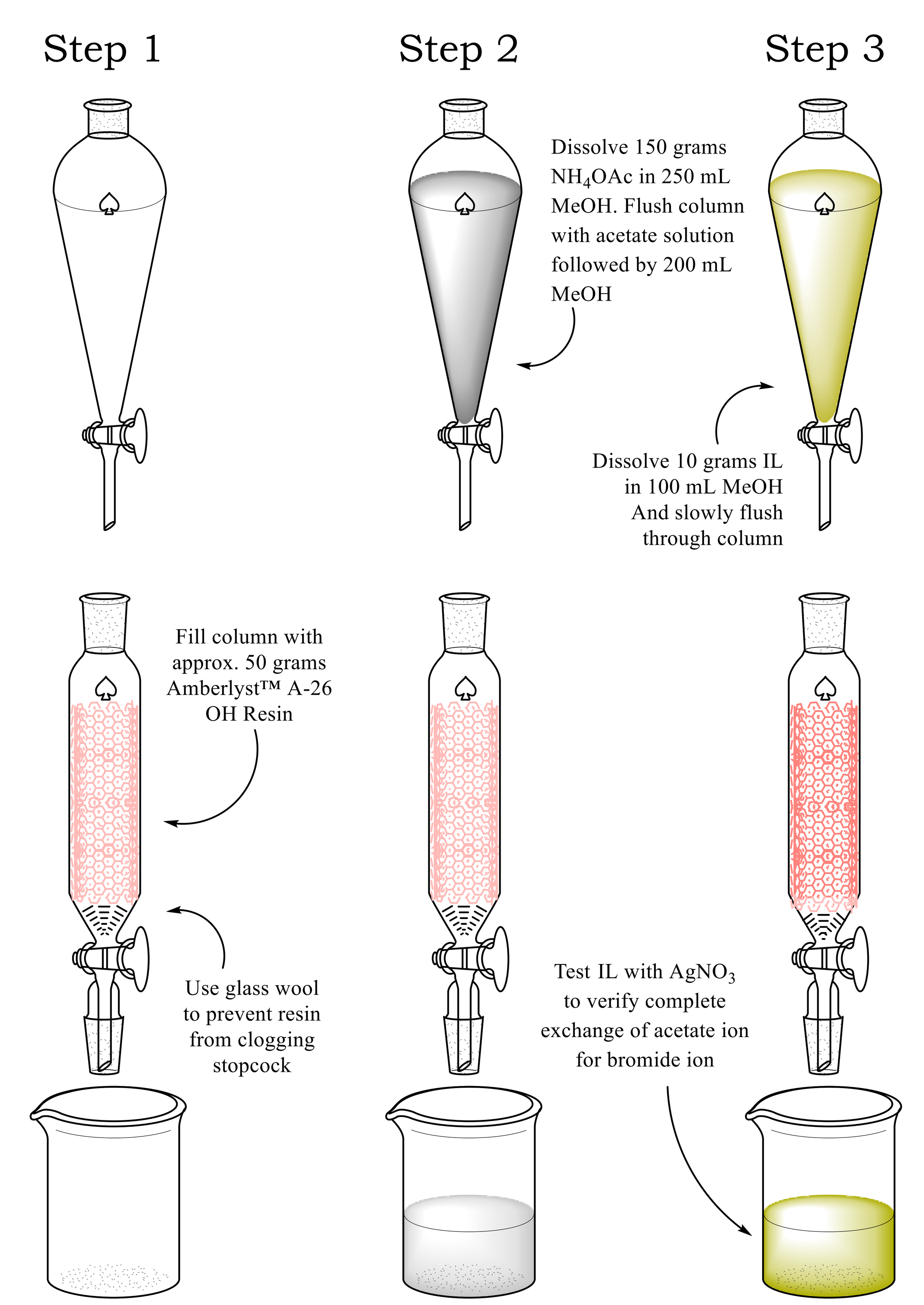
Step 2: S_N2 Reaction[4]



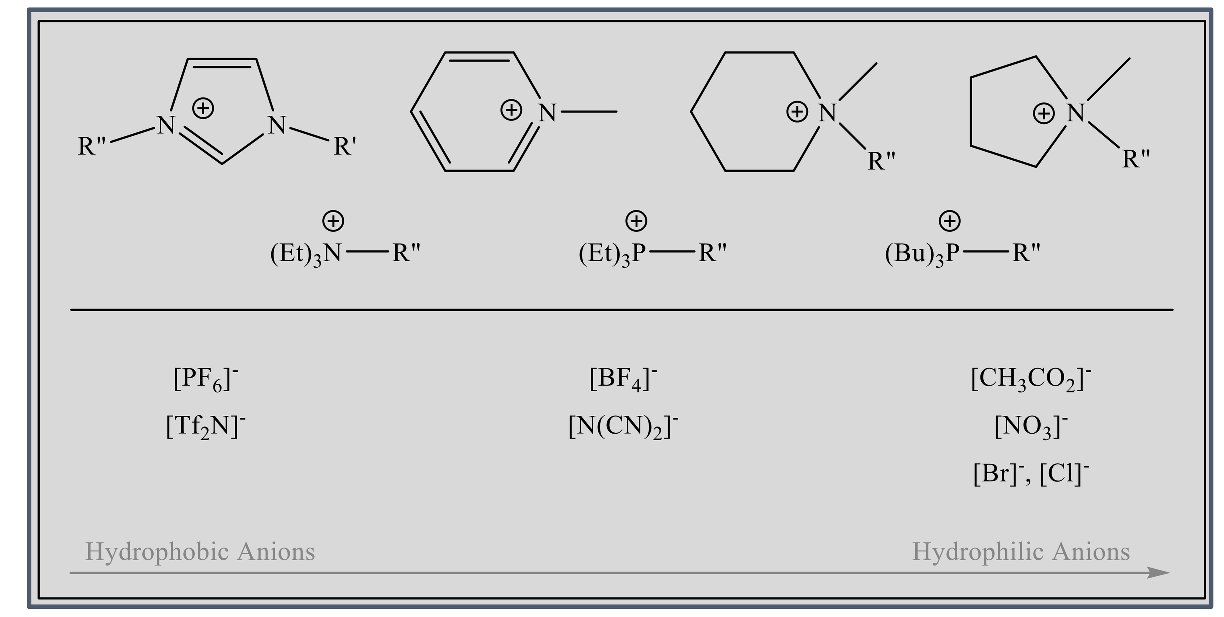
Reaction between alkyl halide and N or P containing nucleophile resulted in S_N2 reaction to produce IL. Ex: *N*-methyl imidazole and bromoethane to produce 1-ethyl-3-methylimidazolium bromide → [EMIM]Br

Step 3: Anion Exchange





Example ILs

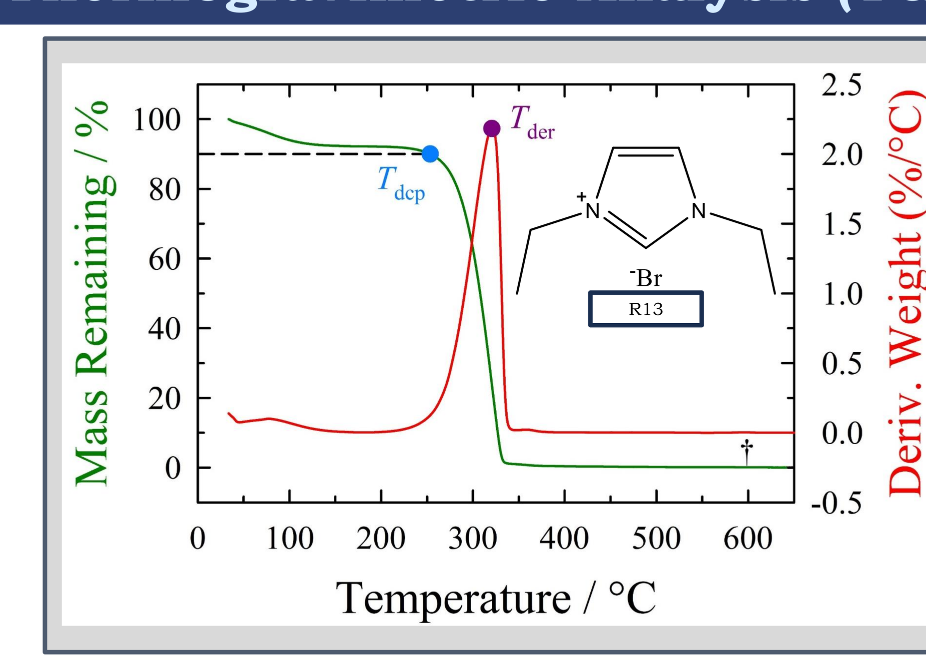


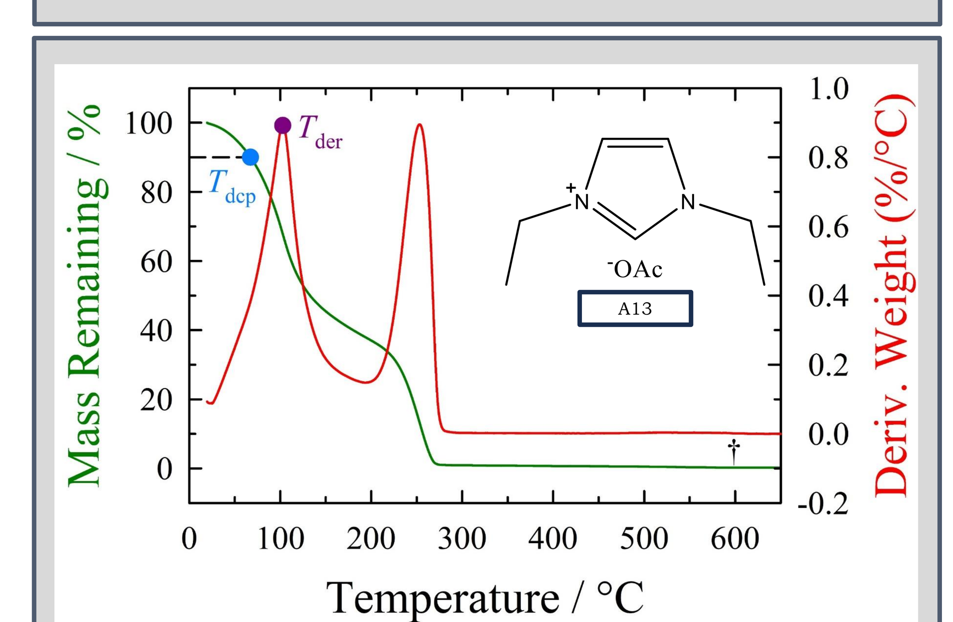
Viscosity/H_2O Concentration

Ref	Ionic Liquid	Solvent Water Content (% by mass)	Dynamic Viscosity at 30°C (mPa·s)	Ref	Ionic Liquid	Solvent Water Content (% by mass)	Dynamic Viscosity at 30°C (mPa·s)
(1)	$[BMIM][PF_6]$	0.01	205.8		$[CH_3OCH_2CH_2\text{-Me-Im}][Ac]$	0.049	44.851
(1)	$[BMIM][Tf_2N]$	0.01	41.4		$[CH_3OCH_2CH_2\text{-Et-Im}][Ac]$	0.058	36.62
(1)	$[BMIM][BF_4]$	0.03	85	(2)	$[CH_3OCH_2CH_2\text{-Et-Im}][Tf_2N]$	0.01	33.1
(1)	[BMIM][dca]	0.05	26		$[CH_3OCH_2CH_2\text{-}Et_3P][Ac]$	0.03	19.162
(2)	[BMIM][dca]	0.012	31		$[CH_3OCH_2CH_2\text{-}Et_3N][Ac]$	0.255	99.636
(2)	[BMIM][Ac]	0.0085	485		$[CH_3CH_2OCH_2CH_2\text{-}Et_3N][Ac]$	0.014	33.973
	[EMIM][Ac]	0.02	22.928		$[CH_3OCH_2CH_2\text{-}Et_3P][Ac]$	0.03	19.162
(2)	[EMIM][Ac]	0.012	17 (80°C)	(2)	$[CH_3OCH_2CH_2\text{-}Et_3P][Tf_2N]$	0.01	36
(3)	Water	---	0.890 (25°C)	(3)	$HOCH_2CH_2OH$	---	16.1 (25°C)
(3)	Glycerol	---	934 (25°C)	(3)	$HOCH_2CH_2OCH_2CH_2OH$	---	30.200 (25°C)

Note: Reference (1) is (Fendt, Padmanabhan, Blanch, & Prausnitz, 2011), reference (2) is (Zhao, Kanpadee, & Jindaret, Ether-functionalized ionic liquids for nonaqueous biocatalysis: effect of different cation cores, 2019). (3) CRC handbook of chemistry and physics. (1977). *CRC Handbook of Chemistry and Physics,*

Thermogravimetric Analysis (TGA)





T_{dcp} = decomposition temperature; T_{der} = first derivative of decomposition curve[4]

Kamlet-Taft Measurements[5]

IL	$E_T(30)$	E_T^N	π*	β	α
Water	63.1	1.000	1.330	0.140	1.120
Dichloromethane	40.7	0.309	0.790	-0.010	0.040
Methanol	55.4	0.762	0.730	0.610	1.050
Acetone	42.0	0.350	0.704	0.539	0.202
$[BMIM][PF_6]$	52.4	0.669	1.032	0.207	0.634
$[BMIM][Tf_2N]$	51.6	0.644	0.984	0.243	0.617
[BMIM][OAc]	49.2	0.570	0.440	1.150	0.440

$$E_T(30) = \frac{28591}{\lambda_{RD}(nm)}$$
← Represents the energy required to go to the excited-state from the ground state (kcal/mol)

$$E_T^N = \frac{E_T(30) - 30.7}{32.4}$$
← Normalized polarity (kcal/mol)

$$\pi^* = \frac{\tilde{v}_{DENA} - 27.52}{-3.183}$$
← Provides a measure of the solvent's dipolarity/polarizability ratio

$$\beta = \frac{(1.035)\,\tilde{v}_{DENA} - \tilde{v}_{NA} + 2.64}{2.8}$$
← Provides a measure of a solvent's hydrogen-bond accepting basicity (HBA)

$$\alpha = \frac{ET(30) - 14.6\cdot(\pi^* - 0.23) - 30.321}{16.5}$$
← Provides a measure of a solvent's Hydrogen-bond donating acidity (HBD)

Conclusions and Future Work

Synthesis and characterization of 56 ILs have been completed. In agreement with the literature, imidazolium-based ILs are the most promising ILs with relatively low viscosities and strong hydrogen-bond basicity values. [BMIM][OAc] appears to have a strong likelihood of dissolving or fragmenting coal.

Objectives 3 and 4 were delayed due to the current pandemic sweeping the world. Objective 3 will include analysis of select ILs and the dissolution properties when mixed with cellulose. Cellulose comprises hydrogen bonded polymer chains that somewhat resemble the bonding network of lignite.

Objective 4 will utilize ILs that have good dissolution or fragmentation results from Objective 3. Two coal samples, one lignite and the other bituminous coal (one rank above lignite, having slightly less hydrogen bonding functional groups), will be assessed using instrumental techniques outlined in the method section.

Future work includes incorporating enzymes to assist with the degradation of lignite in conjunction with IL pretreatment and dissolution methods used in this study.

References

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Acknowledgements

Dr. Hua Zhao, research advisor and Chemistry Dept. Chair, has provided invaluable guidance and assistance in this project. ACS-PRF (#60077-ND4) funding is acknowledged, which has allowed a tremendous amount of time be spent in the lab, not to mention the purchasing of chemicals and equipment.