Method Development for Separating Organic Carbonates Using Ion-Moderated Partition High Performance Liquid Chromatography

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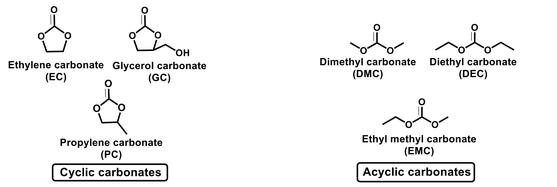
Introduction

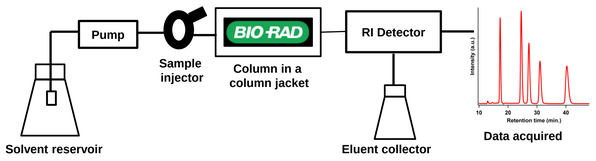
- Organic carbonates constitutes a class of compounds synthesized from CO_2 , a greenhouse gas and small bio-derived alcohols
- They are used in the production of polycarbonates, as organic solvents, fuel additives, green reagents and electrolytes in lithium ion batteries
- They are typically analyzed by destructive methods such as gas chromatography rendering them useless post analysis



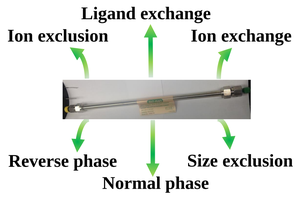
Objective

- Obtain limits of detection and quantification of standard solutions of six organic carbonates by high performance liquid chromatography (HPLC)
- Study the effect of column temperature and mobile phase flow rate on the elution of DMC and EC
- Identify the organic carbonate components of a rechargeable lithium ion battery

Ion-moderated partition chromatography



- A cation-exchange column with an exchangeable hydrogen ion (H^+) was used for the HPLC analysis in this work
- Simple, isocratic elution with 5mM sulfuric acid was conducted
- This column separates analytes by ion - moderated partition technique that includes multiple modes of interaction between the analyte and the column



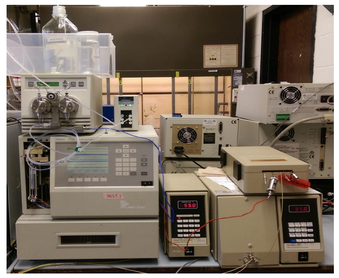
- This column is commonly used for biomass hydrosylate, fermentation broth and biological fluid analysis

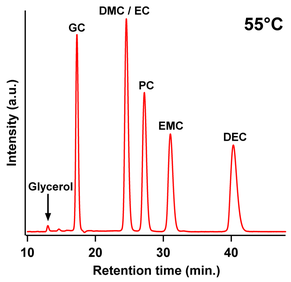
Limits of detection and quantification

Carbonate	Linear Regression	R^2	Limit of Detection (ppm)	Limit of Quantification (ppm)
DMC	y = 510,994.4x - 910.3	0.99994	7.3	24.3
EMC	y = 624,772.9x – 3853.2	0.99993	14.6	48.5
DEC	y = 690,706.5x-7,456.2	0.99912	30.8	102.7
EC	y = 700,865.9x - 1209.4	0.99999	7.5	25
PC	y = 912,036.5x - 2343.8	0.99992	8.2	27.2
GC	y = 1,114,379.2x - 1,987.6	0.99997	3.8	12.7

- Five standard solutions ranging from 50-15,000 ppm used to obtain calibration curves
- Linear relationship found for all the evaluated carbonates with $R^2 > 0.9990$

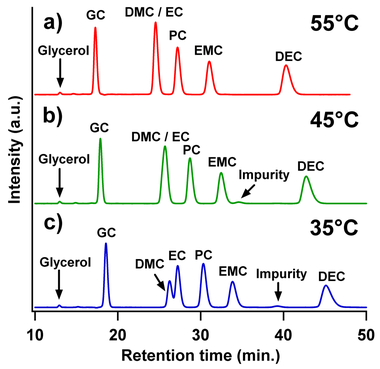
HPLC analysis





- 100mM solution mixture comprising of all six organic carbonates was analyzed by HPLC
- HPLC conditions - Column temperature: 55^0C, Refractive index (RI) detector temperature: 35^0C, mobile phase flow rate: 0.6mL.min^{-1}, injection volume: 10µL
- All carbonates except DMC and EC were baseline resolved
- Common impurity such as glycerol was also detected

Effect of temperature on the elution of DMC & EC



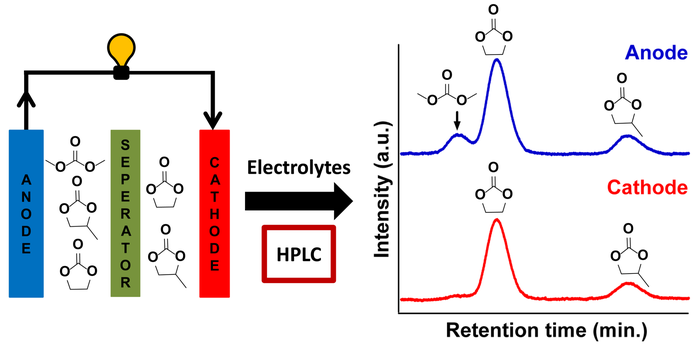
- Effect of change in column temperature on the elution of DMC and EC was evaluated at 55^0C, 45^0C and 35^0C
- Even at 35^0C, DMC and EC could not be baseline resolved
- Lowering the column temperature to 35^0C improved the capacity factor (k) for EC while that for DMC remained unchanged thus separating them
- Cyclic carbonates were hypothesized to elute via reverse phase mechanism while acyclic carbonates were separated by size exclusion mechanism

Effect of mobile phase flow rate on the elution of DMC & EC

- Effect of the flow rate on the elution of DMC & EC was evaluated at 0.6, 0.3 & 0.2mL/min
- The peak resolution (R_s) drastically improved with a decline in the flow rate but the capacity factor (k) was marginally altered

Flow Rate (mL.min^{-1})	Peak Resolution (R_s)
0.6	0.93
0.3	1.15
0.2	1.22

Identification of organic carbonates in a lithium ion battery (LIB)



- Majority of electrolytes in a LIB contain $LiPF_6$ in a solvent mixture composed of cyclic & acyclic carbonates
- The ratio of DMC:EC:PC in anode electrolyte wash was found to be 1:5:1 v/v
- The ratio of EC:PC in cathode electrolyte wash was found to be 4:1 v/v; the amount of DMC was below detection limits

Conclusion

- A novel , sensitive ion-moderated partition HPLC method was developed for organic carbonate analysis
- The method used an ion-exchange column with an isocratic mobile phase and a non-destructive detector
- This method was found to be applicable in the characterization of a commercial lithium ion battery

Acknowledgement

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