

Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide

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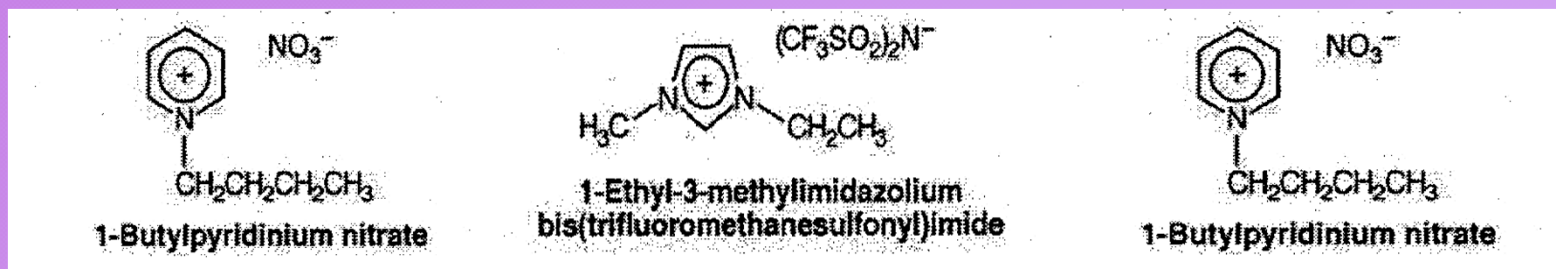
Wonyoung Choi

Introduction

- **Environmental limitation**
 - Traditional process
 - Using organic solvents
 - Volatile, toxic, flammable
 - Organic solvents violate environmental regulations
- **Alternative solvent**
 - Ionic Liquids (ILs)
 - Strong solvent that is liquid under ambient condition
 - Lack of any appreciable vapor pressure
 - Supercritical Carbon dioxide
 - Unusual properties near the critical point
 - Gas like to liquid like properties

Room Temperature Ionic Liquids

- Solutions composed entirely of ions and with melting points below room temperature.
- Structure of ILs
 - Organic cations (imidazolium, pyridinium cations)
 - Inorganic anions (Cl^- , $\text{Cl}^-/\text{AlCl}_3$, PF_6^- , BF_4^-)



Room Temperature Ionic Liquids

- Nonvolatile, nonflammable, high thermal stability
- Physical properties
 - Density : 1.1 - 1.6 gcm⁻³
 - Viscosity : tens to hundreds times that of water
 - Conductivity : order of 10⁻¹ Sm⁻¹
 - Depending on ion size, structure, degree of dissociation
- Usage
 - Chemical synthesis, catalysis, separation process, electrolytes, etc.

Using a Supercritical CO₂

- Inexpensive, nonflammable, nontoxic
 - “green solvent”
- Lack of cross-contamination
 - CO₂ is dissolved in ILs, but ILs is not dissolved in CO₂
- CO₂ is commercially viable solvent
 - coffee decaffeination
 - dry cleaning
- The solute can be separated by simple depressurization

Experimental Section

- **Solubility Measurement**

- Ionic liquid : 1-n-butyl-3-methylimidazolium - hexafluorophosphate [bmin][PF₆]
- [bmin][PF₆] should be dried and degassed (0.18wt% residual water)
 - Existence of water in ionic liquids affects the solubility of CO₂ in ionic liquids
- Measurement method
 - UV-vis spectroscopy
 - Gravimetric analysis => the solutes not exhibiting peaks in UV-vis region
- Organic solute
 - Benzene (aromatic), Hexane (aliphatic) and their substitutes

Experimental Section

- **Extraction experiments**
 - Each solute below the solubility limits dissolve in ILs
 - Experimental instrument and condition
 - ISCO 220 SX high-pressure extraction apparatus
 - At $40 \pm 1^\circ\text{C}$ and 138 ± 0.2 bar
 - Measurement the recovery of organic in solution
 - Measurement the recovery ratio with the amount of CO_2

Result

- **Solubility Measurement**
 - Solubility is affected by strong intermolecular interaction
 - Miscibility or large degree of solubility
 - Benzene family are completely miscible
 - Exception : benzene, chlorobenzene
 - Hexane family are generally immiscible
 - Exception : hexane, 2-hexane
 - Solubilities of solid solute are considerably less than those of the liquid organics

Result

solute ^a	solubility (solute mole fraction)	dipole moment (Debye)	analysis method (wavelength (nm))	T _m (°C)	T _b (°C)
benzene	0.66	0	UV-vis (255, 261)	5.5	80
chlorobenzene (s) (halogen)	0.58	1.69	UV-vis (258, 271)	-45	132
phenol (alcohol)	0.69	1.45	UV-vis (273)	40	182
anisole (ether)	miscible	1.38	UV-vis (271, 278)	-37	154
aniline (amine)	miscible	1.53	UV-vis (236, 286)	-6	184
acetophenone (ketone)	miscible	3.02	UV-vis (241)	19	202
benzoic acid (s) (carboxylic acid)	0.07	1.00	UV-vis (231)	121	249
methyl benzoate (ester)	miscible	2.55	UV-vis (273)	-12	198
benzamide (s) (amide)	0.04	3.60	UV-vis (225)	128	288
benzaldehyde (aldehyde)	miscible	2.80	UV-vis (245)	-26	178
hexane	miscible	0	gravimetric	-95	69
1-chlorohexane (halogen)	0.25	1.99	gravimetric	-94	133
1-hexanol (alcohol)	0.26	1.65	gravimetric	-52	156
butyl ethyl ether (ether)	0.06	1.22	gravimetric	-124	91
cyclohexane	0.21	0	gravimetric	6.5	81
2-hexanone (ketone)	miscible	2.68	UV-vis (278)	-57	127
hexanoic acid (carboxylic acid)	0.13	1.57	UV-vis (219)	-3	202
methyl pentanoate (ester)	0.59		UV-vis (209)		128
hexanamide (s) (amide)	0.06	3.90	UV-vis (203)	100	225
1,4-butanediol	0.51	2.58	gravimetric	16	230

^a Solids are indicated by (s).

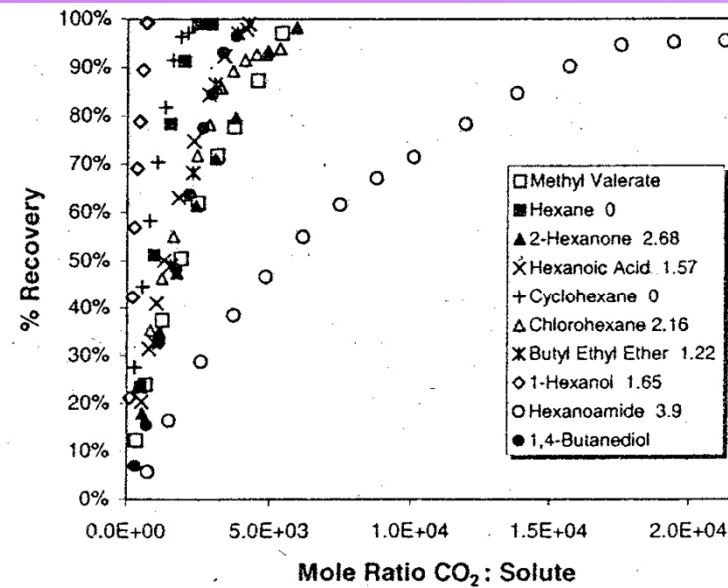
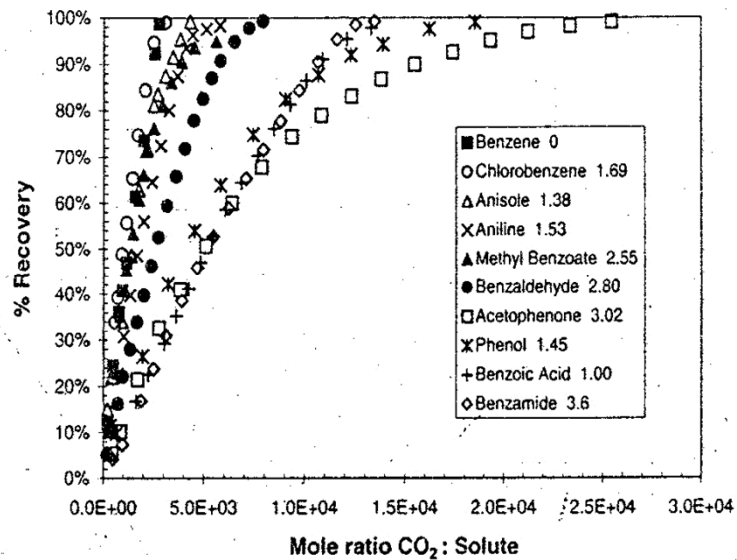
Result

- **Extraction**

- All organic solutes exhibit a greater than 95% recovery
(Several organic solutes accomplish greater than 98% recovery)

- Solid solutes at room temperature require the largest CO₂ for 95% solute recovery

Result



Discussion

- **Solubility**

- The compounds most similar to [bmim][PF₆] will have the highest solubility
 - Measurement of the retention time
 - Solvent / Solute interaction
- Benzene-based compounds are several times greater than those of their hexane-based
 - The high solubility in some molten salts can be attributed to liquid clathrate formation
- The solubility of the solids in the IL are lower than those of the organic liquids

Discussion

- For solid / liquid equilibrium, the solubility of solids in [bmim][PF₆] can be used to determine their activity coefficients in the IL-rich liquid phase.

$$\gamma = \exp \left[\frac{H_{fus} - \Delta C_p T_m}{RT_m} \left(\frac{T - T_m}{T} \right) - \frac{\Delta C_p}{R} \ln \left(\frac{T_m}{T} \right) - \ln x \right]$$

Assumption : the solubility of the liquid in the solid is negligible

- It may be possible to model the phase behavior of organic / IL mixtures with conventional excess Gibbs free energy models
- Another approach would be to start with Debye-Huckel model

Discussion

- Extraction Studies

- Numerous type of organic can all be extracted
- Analyzing the results in terms of thermodynamics

- Distribution coefficient

$$K = \frac{y}{x}$$

- Modeled with an equation of state

$$K = \frac{\varphi_{liq}}{\varphi_{SCF}}$$

- Modeled with an activity coefficient

$$K = \frac{\gamma_{sat} \exp \int_{p_2^s}^p \frac{v_2^s}{RT} dp}{\varphi P}$$

Discussion

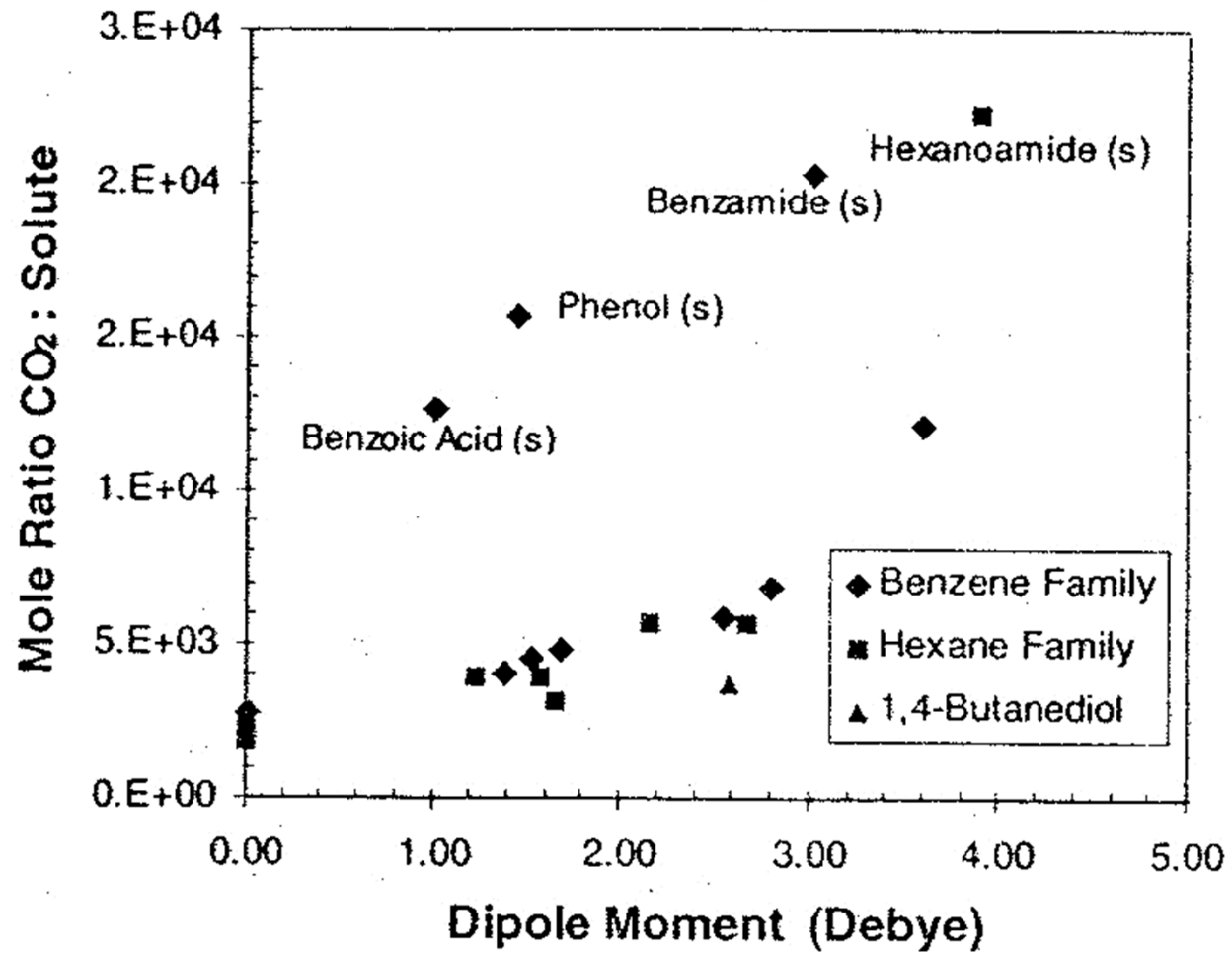
– Supercritical phase

- The fugacity coefficient can be estimated with a simple equation of state like Peng-Robinson
- From the experiment, measured solubility of solutes in CO₂ indicates fugacity coefficients can be very small numbers

– Liquid phase

- At 138 bar, CO₂ is dissolved in IL as high as 0.85mole fraction
- And combined with the Solute-IL solubility measurements
- It has the trends of distribution coefficients
 - High volatility and low polarity will favor the solubility of a solute - larger y value
 - High polarity and aromaticity will favor solute solubility in the IL-rich liquid phase - larger x value

Discussion



Discussion

- Another measurement of the ease of extraction of compounds
 - Phase behavior of the organic solute-CO₂ binary systems
 - A measure of affinity for CO₂ is determined at low pressure
 - Compounds in which CO₂ readily dissolves at low pressures have greater attraction for CO₂

Table 3. CO₂-Liquid Organic Solute Binary Phase Behavior

binary system	pressure ^a (bar)	mole ratio CO ₂ :solute for 95% recovery
CO ₂ -hexane ¹⁶	54.1	2.34E+03
CO ₂ -benzene ¹⁶	59.6	2.75E+03
CO ₂ -anisole ¹⁷	60.8	4.00E+03
CO ₂ -cyclohexane ¹⁸	64.8	1.84E+03
CO ₂ -chlorobenzene ¹⁹	66.7	4.77E+03
CO ₂ -methyl benzoate ²⁰	71.0	5.87E+03
CO ₂ -acetophenone ²¹	75.4	2.03E+04
CO ₂ -benzaldehyde ¹⁹	77.8	6.85E+03

^a Pressure required to dissolve 70 mol % CO₂ in the liquid phase at 40 °C.

Conclusion

- CO₂ can completely extract a wide array of organic solutes from an ionic liquid.
- Using hexane, benzene roots and their substitute, a correlation relating dipole moment to the amount of CO₂ necessary for solute recovery has been established.
- Intermolecular interaction between the organics and [bmim][PF₆] do not limit the degree to which a solute can be separated from the IL.
- Overall, ionic liquids and scCO₂ offer not only a new avenue for reactions and separations but have the additional asset of environmental sustainability