

Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide

Lynnette A. Blanchard and Joan F. Brennecke

Department of Chemical Engineering, University of Notre Dame, Indiana 46556

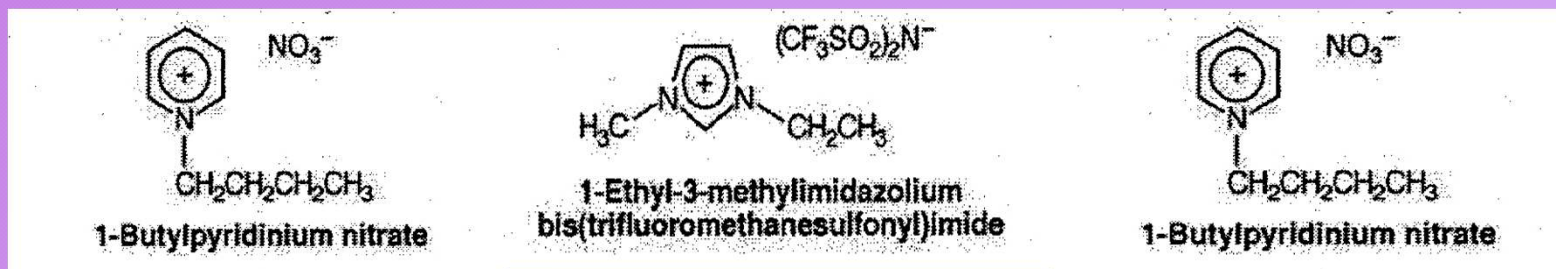
Wonyoung Choi

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).

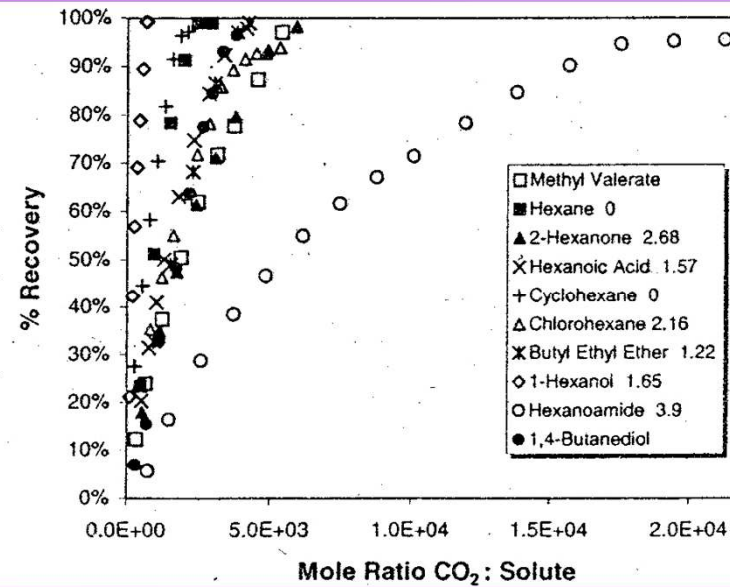
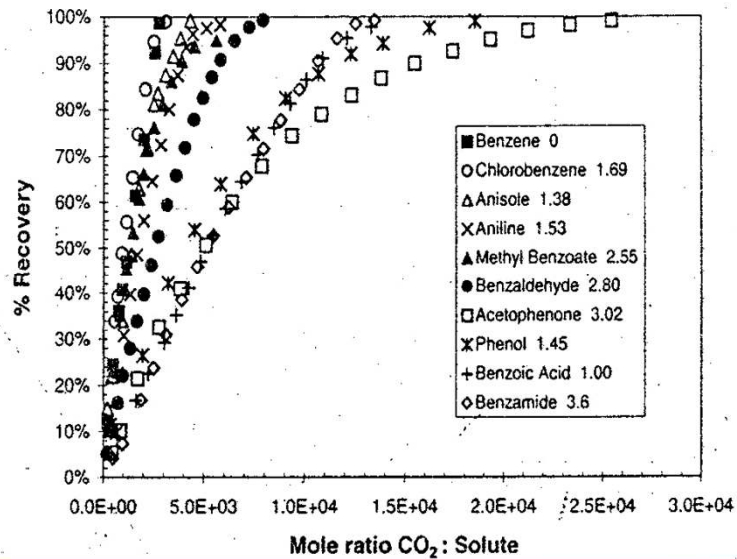
Result

- **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

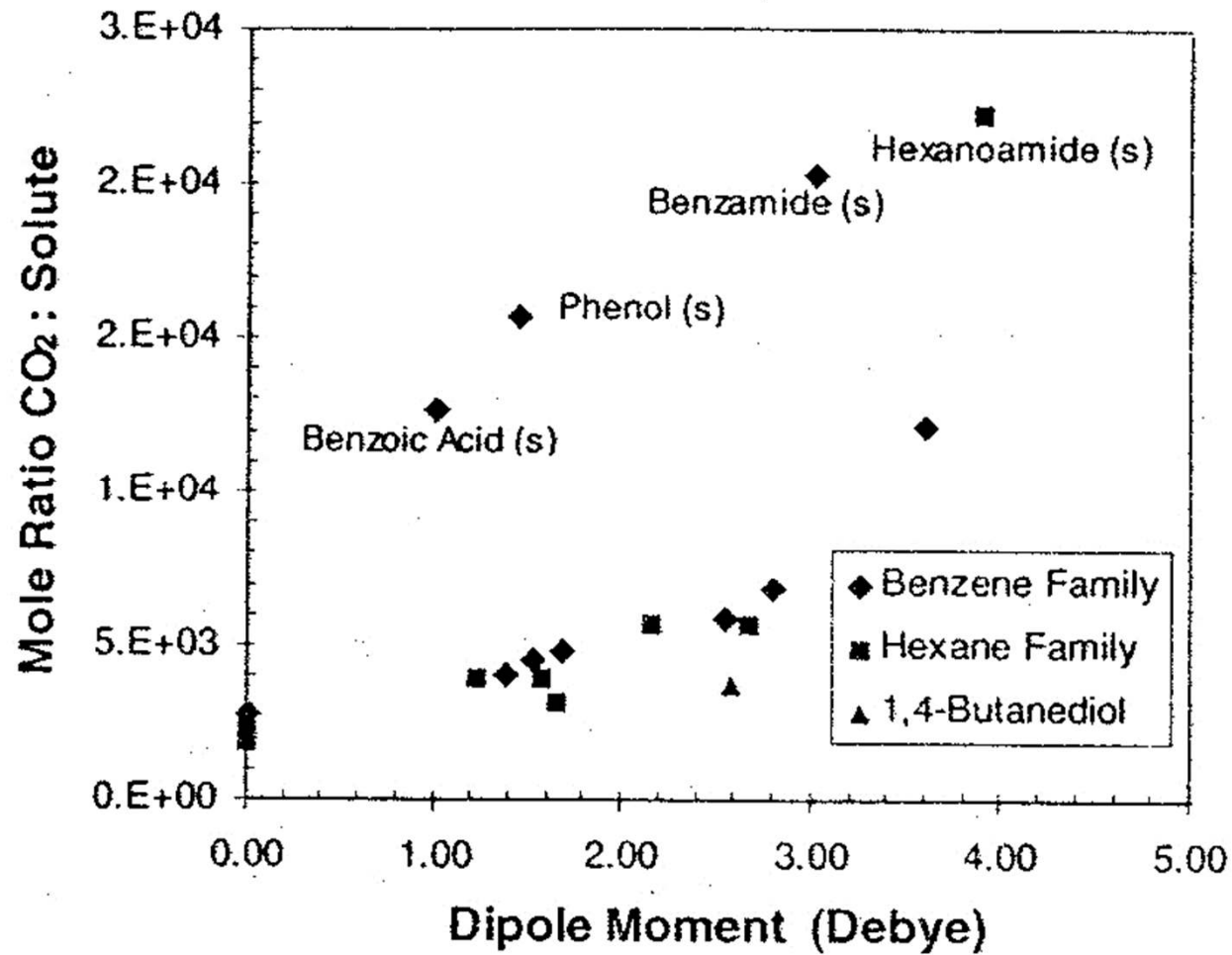
– Supercritical phase

- 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