Systematic Method for Screening Ionic Liquids as Extraction Solvents Exemplified by Extractive Desulfurization Process

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**MOTIVATION**

Ionic liquids (ILs) are highly promising alternatives for volatile organic solvents in liquid-liquid extraction, gas absorption, extractive distillation, etc. Application challenges include:

- A large number of ILs, various separation processes,
- Complex effects of IL molecular decision variables at different levels.

**Goal:**
Develop systematic methods for screening practically attractive IL solvents for separation processes.

**IL SCREENING: STATE OF THE ART**

**CURRENT METHODS**
- **Experimental**: Expensive and time-consuming, limited to simple laboratory experiments
- **Computational**
  - Ab initio calculation
  - Computational expensive
  - NRTL, UNIQUAC, EoS (PC-SAFT)
  - Require experimental data, molecule-specific
  - Limited predictive ability for novel systems

**UNIFIC-I**
- GC-based, limited group parameters available
- COSMO-RS model
- Independent of experiment, molecule/group profile
- Virtually applicable to any system
- Good qualitative & acceptable quantitative prediction

**Main Limitations of Previous Screening**
- Mixtures to be separated
- MW of ILs
- Physical properties: Process performance

**SYSTEMATIC METHOD FOR IL SCREENING**

- **Modified thermodynamic criteria**
  - \( \beta = n_B^0 m_B^0 \) (finite dilution, molar
  - \( S = m_B^m_m_B^S \) (mole)
  - \( S_L = m_L^m \) (mole)

- Effect of molecular weights (MWs) of ILs, effect of practical condition

- **Physical property estimation by GC models** [ref]
  - \( T_m(K) = 288.7 + \sum n_B^0 m_B^0 + \frac{\sum n_B^0 m_0 B}{\sum n_B^0 m_B^S} \) (melting point)
  - \( \ln \eta = 6.982 + \sum n_B^0 m_B^0 + \frac{\sum n_B^0 m_0 B}{\sum n_B^0 m_B^S} \) (viscosity)

- **Process simulation of IL-based processes** [ref]
  - ILs defined as pseudo-component in Aspen Plus [ref]
  - MW, \( \rho, T_m \), critical properties
  - NRTL model as the thermodynamic model parameters regressed from COSMO-RS data

- **Systematic IL screening**
  - 3 steps
  - decomposition
  - a list of top candidates

**APPLICATION – EXTRACTIVE DESULFURIZATION**

**EDS case study**
- removal of trace aromatic sulfur compounds from fuel oils
  - simulated: thiophene/naphthalene mixture (sulfur content 100 ppm)
  - Sulfolane is employed as the benchmark solvent

**Step 1:** Pre-screening by modified thermodynamic criteria

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<th>( \beta )</th>
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<td>m_B^0</td>
<td>m_B^S</td>
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**Step 2:** Further screening by \( T_m \) and \( \eta \) constraints

**Step 3:** Final selection by process simulation

**ILs:**
- Sulfolane process requires 2 distillation columns, more capital cost
- Required SF of all ILs is lower than sulfolane, less solvent needed
- IL regeneration: different dependencies of the operating pressure on the temperature, different energy cost

**ILs:** much lower energy and solvent consumption, higher fuel product recovery ratio

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**REFERENCES**