

Partition coefficients octanol-water of selected (-)-menthol-substituted chiral ionic liquids

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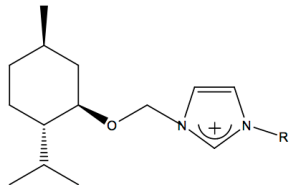
Thermodynamics of Task-Specific Materials
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Chiral ionic liquids with a natural terpene substituent

- Imidazolium-based chlorides an (1*R*,2*S*,5*R*)-(-)-menthoxymethyl substituent
- Alkyl group at N3: methyl-, butyl-, nonyl-
- Applications:
 - Chiral catalysis
 - Laccase enzyme stabilization
 - Antielectrostatic properties



Partition coefficient octanol-water

$$\log P = \log \frac{[X]_{OcOH}}{[X]_{H_2O}}$$

$$P_{thermodyn} = \frac{x_X^{OcOH}}{x_X^{H_2O}} = \frac{\gamma_X^{H_2O}}{\gamma_X^{OcOH}}$$

Infinite dilution: $x_i \approx c_i V_m^*$

$$c_X^{OcOH} V_m^{OcOH} = c_X^{H_2O} V_m^{H_2O}$$

$$P = \frac{c_X^{OcOH}}{c_X^{H_2O}} = \frac{\gamma_X^{H_2O}}{\gamma_X^{OcOH}} \frac{V_m^{H_2O}}{V_m^{OcOH}}$$

Dissociating electrolytes

$$\log P = \log \frac{[M_{v+}X_{v-}]_{OcOH}}{[M_{v+}X_{v-}]_{H_2O}}$$

$$\log D_{OW} = \log \frac{\sum([M]_{OcOH} + [X]_{OcOH})_i}{\sum([M]_{H_2O} + [X]_{OcOH})_i}$$

Non-dissociating compounds

$$\log D_{OW} = \log P$$

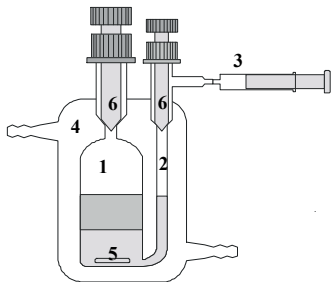
Bioconcentration factor

- Direct determination from the distribution of the compound between the living organism and water
- Indirectly from $\log P$, e.g.

$$\log K_B = \log P - 1.32$$

Mackay, D. Environ. Sci. Technol. 1982, 16, 274-278.

Experimental determination of $\log P$



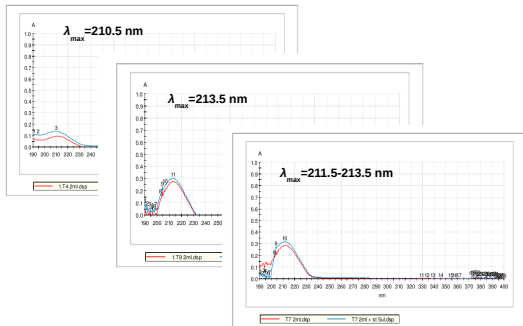
- Solvents - mutually saturated water and 1-octanol
- Equilibrium attained on stirring during 24 hours and settling overnight at 25°C

Experimental determination of log P

- Analysis by means of UV-Vis spectrophotometry
 $\lambda_{max} = 210\text{--}213\text{ nm}$
- Standard addition method

$$w_i = \frac{A_i w_s V_s}{A_{i+s} V - A_i V_0}$$

$$c_i = \frac{w_i M_i}{\rho}$$



Measurement validation using [hmim][Tf₂N]

Repeated measurements of $\log P$ with different global concentration of [hmim][Tf₂N]

- Comparison with literature data: Ropel et al. Green Chem. 7, **2005**, 83–90.
- Does the IL dissociate in aqueous phase or not?

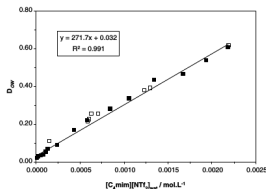


Figure 1. Experimental (■) and Ropel et al.³⁵ data (□) for octanol–water distribution coefficients at different [C₄mim][NTf₂]_c concentrations.

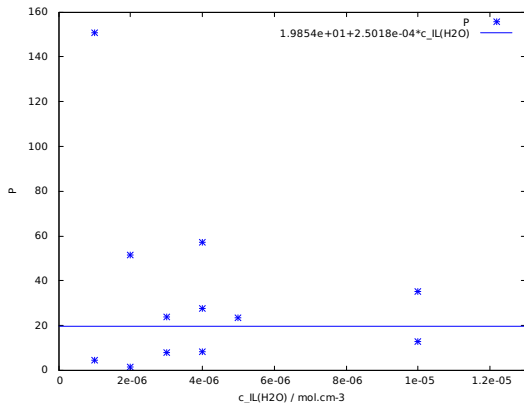
Ventura et al. J. Chem. Technol. Biotechnol. 86, **2011**, 957–963

Data analysis by means of methods based on mathematical gnostics

- Marginal analysis
- Robust regression along a gnostic influence function



log P of [hmim][Tf₂N] at 25°C as a function of concentration of IL in aqueous phase



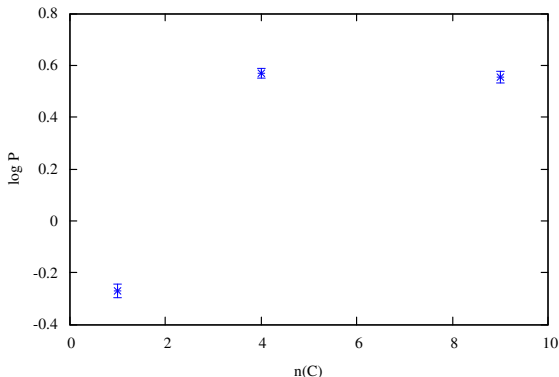
Our data
 $\log P = 1.35 \pm 0.06$

Ropel et al.
 $P = 1.42 - 1.66$

$\log P$ of the studied CILs as a function of the alkyl chain length at 25°C

Hydrophilic substances:
 $\log P < 1$

Does $\log P$ reach a constant value starting with a certain alkyl chain length?

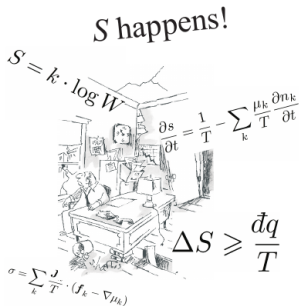


Conclusion

- Three chiral ionic liquids
1-alkyl-3-(1*R*,2*S*,5*R*)-(-)-menthoxymethylimidazolium
chlorides: methyl, butyl, and nonyl-substituted
Hydrophilic character
- Validation of $\log P$ measurements by means of [hmim][Tf₂N]
does not show a dependence of $\log P$ on the concentration of
IL in aqueous phase
Answer as to possible dissociation not obtained

What next?

- Measure $\log P$ for more members of the homologous series
- Dissociation should not be ruled out: conductivity in diluted aqueous solutions
- Solvation effects due to the presence of 1-octanol



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