Salts Dissolved in Salts

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Supplemental Information

Details of the computational results

Table S-1 Energy of the metathesis reaction as calculated by DFT and MP2, including the zero point energy and thermal corrections to Gibbs Free Energy (+Z) and basis set superposition error(+B) corrections. The different rows of ΔE and ΔG (kJ/mol) have been calculated from either the most stable ion pairs per complex (MIN), the less stable ion pairs (MAX) or the average Energy of the two (AVR).

	DFT	DFT+Z	DFT+Z+B	MP2	MP2+Z
MIN	-24.10	-24.81	-24.89	-0.84	-0.69
MAX	-23.67	-15.63	-14.68	-18.22	-11.05
AVR	-23.88	-20.22	-19.78	-9.53	-5.87

Derivation of equation 1

We can obtain a relationship between the concentration of contact ion pairs (C_{CIP}) and the total concentration of Kosower's complex (C_0) by using a 'double equilibrium' analysis. Using Scheme 1, with ion dissociation constants K_1 and K_2:

$$\underset{\text{CIP}}{[\text{Py}]\text{I}} \xrightleftharpoons{K_1} \underset{\text{SSIP}}{[\text{Py}]^{+}||\text{I}^{-}} \xrightleftharpoons{K_2} \underset{\text{Free ions}}{[\text{Py}]^{+}, \text{I}^{-}}$$

(Scheme 1)

Then:

$$K_1 = \frac{C_{SSIP}}{C_{CIP}} \qquad \text{(S-1)}$$

and:

$$K_2 = \frac{C_{[Py]} * C_I}{C_{SSIP}} \qquad \text{(S-2)}$$

Assuming all pyridiniums and iodides were added as 1-ethyl-4-(methoxycarbonyl)pyridinium iodide,

$$C_{[Py]} = C_I \qquad \text{(S-3)}$$

$$C_0 = C_{[Py]} + C_{SSIP} + C_{CIP} \qquad \text{(S-4)}$$

Rearranging equation (S-1):

$$C_{SSIP} = K_1 * C_{CIP} \qquad \text{(S-5)}$$

Rearranging equation (S-2):

$$C_{[Py]}^2 = K_2 * C_{SSIP} \qquad \text{(S-6)}$$

Substituting equation (S-5) into (S-6):

$$C_{[Py]}^2 = K_1 * K_2 * C_{CIP} \qquad \text{(S-7)}$$

Taking the square root of both sides of equation (S-7):

$$C_{[Py]} = K_1^{0.5} * K_2^{0.5} * C_{CIP}^{0.5} \qquad \text{(S-8)}$$

Substituting equation (S-8) and (S-5) into (S-4):

$$C_0 = K_1^{0.5} * K_2^{0.5} * C_{CIP}^{0.5} + K_1 * C_{CIP} + C_{CIP} \qquad \text{(S-9)}$$

Rearranging equation (S-9):

$$(1 + K_1)C_{CIP} + K_1^{0.5} K_2^{0.5} C_{CIP}^{0.5} - C_0 = 0 \qquad (1)$$

Derivation of equation 3

Using a simple 3D lattice model, we can determine the probability of a 1-ethyl-4-(methoxycarbonyl)pyridinium cation and an iodide anion being next to each other. We assume that each nearest neighbour pair have opposite charges. Also:

r = number of anions in the solvation shell of a cation
m_T = total number of anions in the system
m_I = total number of iodide ions in the system

The probability that any given anion in the solvation shell of a pyridinium cation is *not* an iodide would be:

$$(m_T - m_I)/m_T \qquad \text{(S-10)}$$

The probability that *none* of the r anions in the solvation shell of a pyridinium cation are an iodide would be:

$$[(m_T - m_I)/m_T]^r \qquad \text{(S-11)}$$

Therefore, the probability that at least one of the anions in the solvation shell of a pyridinium cation are an iodide would be:

$$P_{[Py]I} = 1 - [(m_T - m_I)/m_T]^r \qquad (3)$$

For r = 1 equation (3) can be derived from a simple equilibrium as well. Assuming that the ion pairing of Kosower's Dye in ionic liquids is entirely controlled by statistic, one can write:

$$K = \frac{[PyI] * [C_4mim\ OTf]}{[Py\ OTf] * [C_4mim\ I]} = 1 \qquad \text{(S-12)}$$

With
$c_{PyI} =$ the concentration of Kosower's Dye ion pairs in contact
$c_{0,PyI} =$ the initial concentration of Kosower's Dye
$c_{0,IL} =$ the initial concentration of ionic liquid
one can write

$$1 = \frac{c_{PyI} * \left(c_{0,IL} - c_{0,PyI} + c_{PyI}\right)}{\left(c_{0,PyI} - c_{PyI}\right)^2} \qquad \text{(S-13)}$$

and therefore

$$c_{PyI} = \frac{c_{0,PyI}^2}{c_{0,IL} + c_{0,PyI}} \qquad \text{(S-14)}$$

and

$$P_{[Py]I} = \frac{c_{PyI}}{c_{0,PyI}} = \frac{c_{0,PyI}}{c_{0,IL} + c_{0,PyI}} = 1 - \frac{m_T - m_I}{m_T} \qquad \text{(S-15)}$$

Therefore the statistical lattice model is identical to a chemical equilibrium description for r=1.