Electronic Supplementary Material (ESI) for Faraday Discussions.

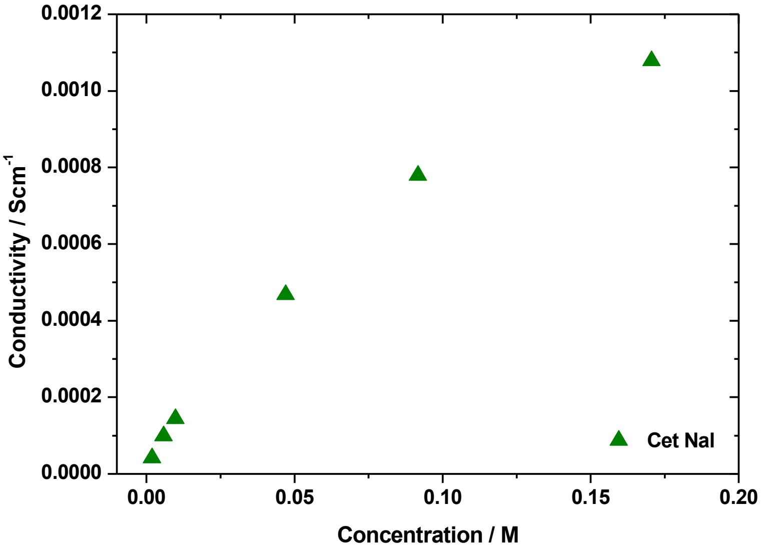
Supplementary Information to accompany:

New Dimensions in Salt-Solvent mixtures: A 4th Evolution of Ionic Liquids

Douglas R. MacFarlane[a], Alison Chong[a], Maria Forsyth[b], Mega Kar[a], R. Vijayaraghavan[a],
Anthony Somers[b] and Jennifer M. Pringle[b]

[a]School of Chemistry and the Australian Centre of Excellence for Electromaterials Science,
Monash University, Clayton Vic 3800, Australia
[b] Institute for Frontier Materials and the Australian Centre for Electromaterials Science,
Deakin University, Melbourne, Australia

Figure S1. Conductivity of cetrimonium nalidixate in water



The free energy of dissolution of a salt in a liquid solvent

The free energy of dissolution of a salt in a liquid solvent, ΔG_s, at any temperature below the melting point, T_m, of the salt can be considered, in principle, in terms of a thermal cycle Figure S2 that relates ΔG_s to other measurable parameters. These can be accessed using differential scanning calorimetry and isothermal calorimetry or similar as long as the temperature range is within the stability limits of the components involved. The analysis allows the consideration of the effect of mixing at a lower temperature, T_1, when mixing or dissolution is known to be spontaneous to some degree at some higher temperature, $T_{2,}$ above the melting point of the salt.

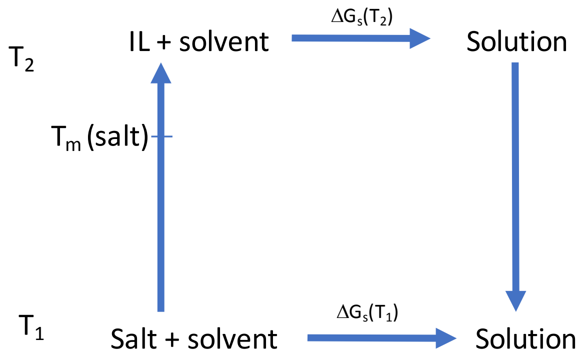


Figure S2. Thermochemical cycle comparing the dissolution of a crystalline salt in a solvent with dissolution of the liquid phase of the same salt.

The analysis is as follows, where the Δ indicate the change from salt + solvent to solution:

Recognising that at constant pressure:

$$\frac{dG}{dT} = -S = -\int_{T_1}^{T_2} C_P(T)dlnT$$

then ΔG_s at one temperature can be related to ΔG_s at some other temperature via:

$$\Delta G_s(T_1) = \Delta G_s(T_2) + \int_{T_1}^{T_2} d\Delta G_s$$

$$= \Delta G_s(T_2) - \int_{T_1}^{T_2} \Delta S(T)dT$$

$$= \Delta G_s(T_2) - \int_{T_1}^{T_2} [\int_{T_1}^{T_2} \Delta C_P(T)dlnT\ ]\ dT$$

$$= \Delta G_s(T_2) - [\int_{T_1}^{T_2} [\int_{T_1}^{T_2} C_P^{solution}(T)dlnT]\ dT - [\int_{T_1}^{T_2} [\int_{T_1}^{T_2} C_P^{solute}(T)dlnT]\ dT - [\int_{T_1}^{T_2} [\int_{T_1}^{T_2} C_P^{solvent}(T)dlnT]\ dT\ ]$$

(note that the free energy of melting of the salt at its melting point does not appear because it is zero by definition).

Each of these quantities is in principle accessible by measuring the heat capacities as a function of temperature between a higher temperature T$_2$ where the two liquids are assumed to be miscible ($\Delta G_s(T_2)$ is negative) to a lower temperature T$_1$ where the solute is below its melting point. The integrals can be carried out numerically and this would most directly be done by calculating $\Delta C_P(T)$ from the individually measured $C_P(T)$ data.