Electronic supporting information for

“The importance of solvent reorganisation in the effect of an ionic liquid on a unimolecular substitution process”

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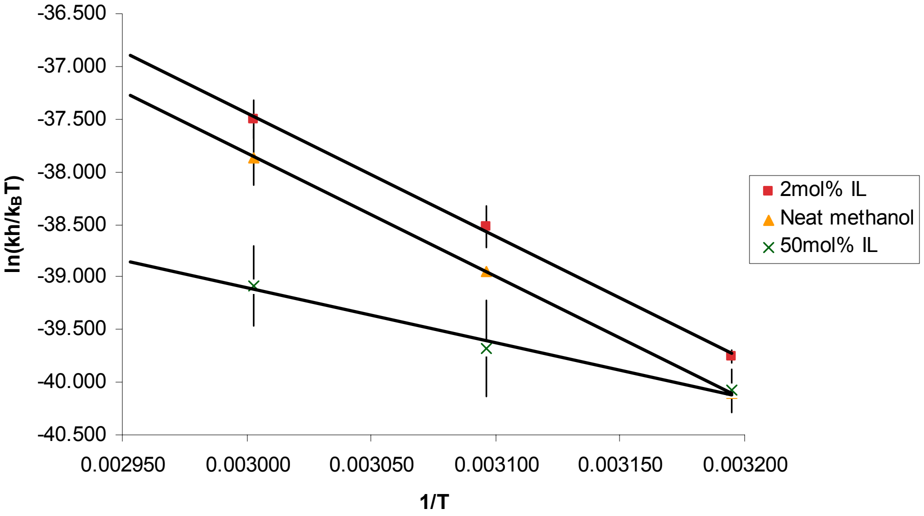
Eyring Plot from which the data presented in Table 1 is derived.

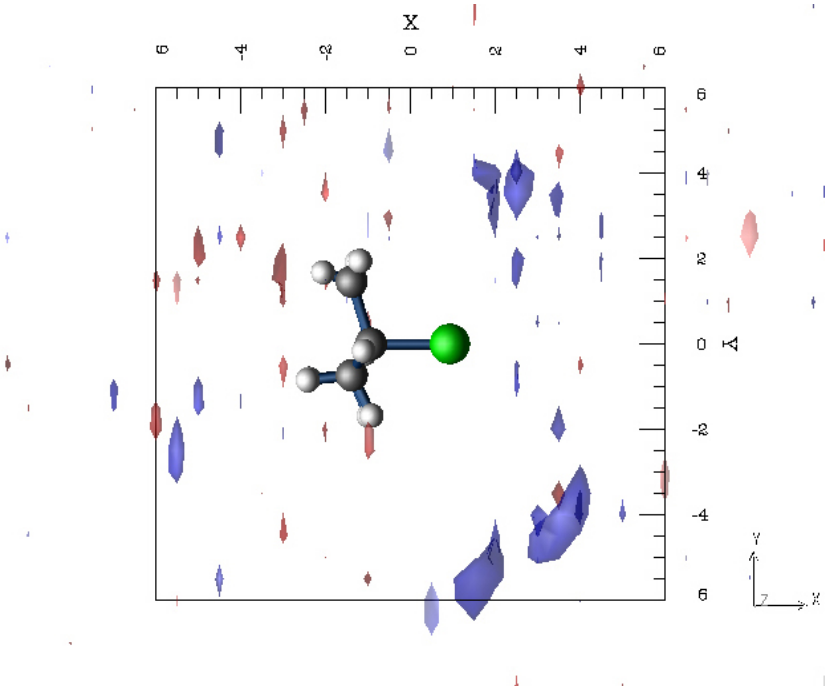


Plot of the temperature-dependent kinetic data of the methanolysis reaction shown in Scheme 1 in the presence of various amounts of the ionic liquid [Bmim][$N(CF_3SO_2)_2$], using the Eyring equation. Each point is the average of at least three, and up to six, rate constants and the error is reported as the standard deviation of the mean. The range of temperatures is limited, with the maximum constrained by the boiling point of methanol and the minimum by the slow rate of the process (*ca*. 10^{-5} s^{-1} at 313 K).

Description of computational methodology

Molecular dynamics studies were carried out using models in which the components of the mixture were treated as rigid multi-site bodies with point charges at the atomic sites to simulate the electronic distributions as determined using ab initio methods (MP2/6-311+G(3dp,2f)//B3LYP/6-31G(d)). Classical molecular dynamics simulations were carried out using DL_POLY 2.16 in an NVT-ensemble at 400 K using a Berendsen thermostat and cubic periodic boundary conditions, optimised for each system. The simulation box contained 191 of each of the components of [Mmim][PF6] and either a single tert-butyl chloride molecule or a tert-butyl cation and a chloride anion. Probability distributions shown are the average of a minimum of 600,000 timesteps of 2 fs, for a total simulation time of 1.2 ns. Visualisation of the 3D hypersurface was carried out using OpenDX.

Probability distribution for the ionic liquid about *tert*-butyl chloride

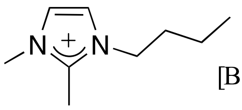


Ordering of the components of [Mmim][PF_6] about *tert*-butyl chloride. Areas in red are more likely to contain the anion while those in blue are more likely to contain the cation. Simulation time was 3.36 ns and probability hypersurface cut-offs are 0.01 (cation and anion) relative to those in Fig. 1, which are 0.014 (cation and anion), 0.080 (chloride).

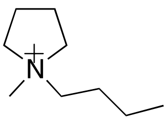
Analysis of literature data using bimolecular form of the Eyring equation

The kinetic data presented for the nucleophilic substitution of methyl *p*-nitrobenzenesulfonate with chloride anion in reference 12 was reanalysed using the bimolecular form of the Eyring equation to give the data presented below.

Solvent	**$\Delta H^{\ddagger}$ [kJ mol^{-1}]**	**$\Delta S^{\ddagger}$ [J mol^{-1} K^{-1}]**
CH_2Cl_2 ion pair	78.5 ± 2.9	-60 ± 21
CH_2Cl_2 free ion	52.8 ± 5.7	-131 ± 20
[Bm_2im][$N(CF_3SO_2)_2$]	67.8 ± 0.3	-115 ± 1
[BMPy][$N(CF_3SO_2)_2$]	65.1 ± 1.2	-120 ± 4
[Bmim][$N(CF_3SO_2)_2$]	67.7 ± 0.5	-121 ± 2
[Bmim][BF_4]	54.9 ± 5.2	-156 ± 17
[Bmim][PF_6]	69.3 ± 5.4	-109 ± 18
[Bmim][SbF_6]	65.8 ± 5.1	-127 ± 17



[Bm_2im]$^+$

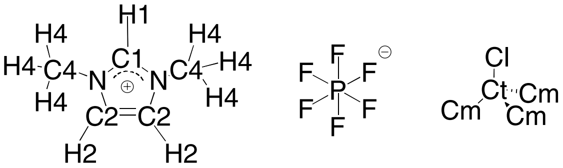


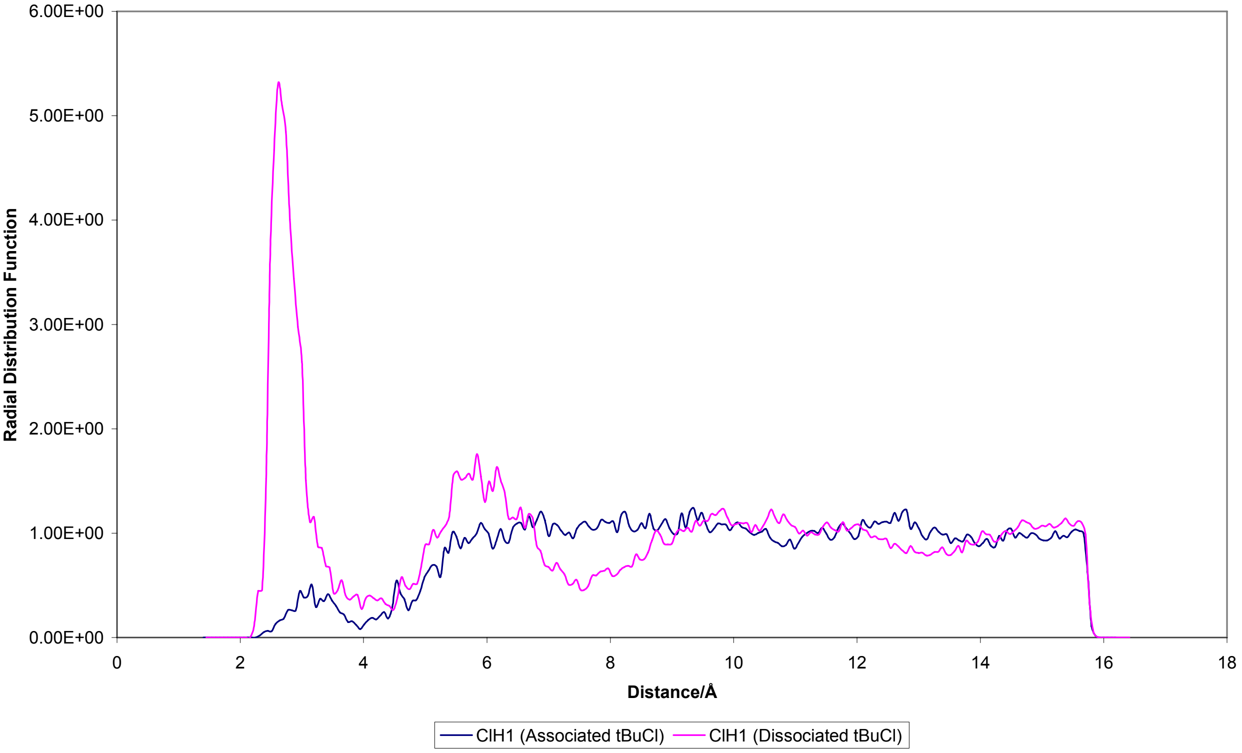
[BMPy]$^+$

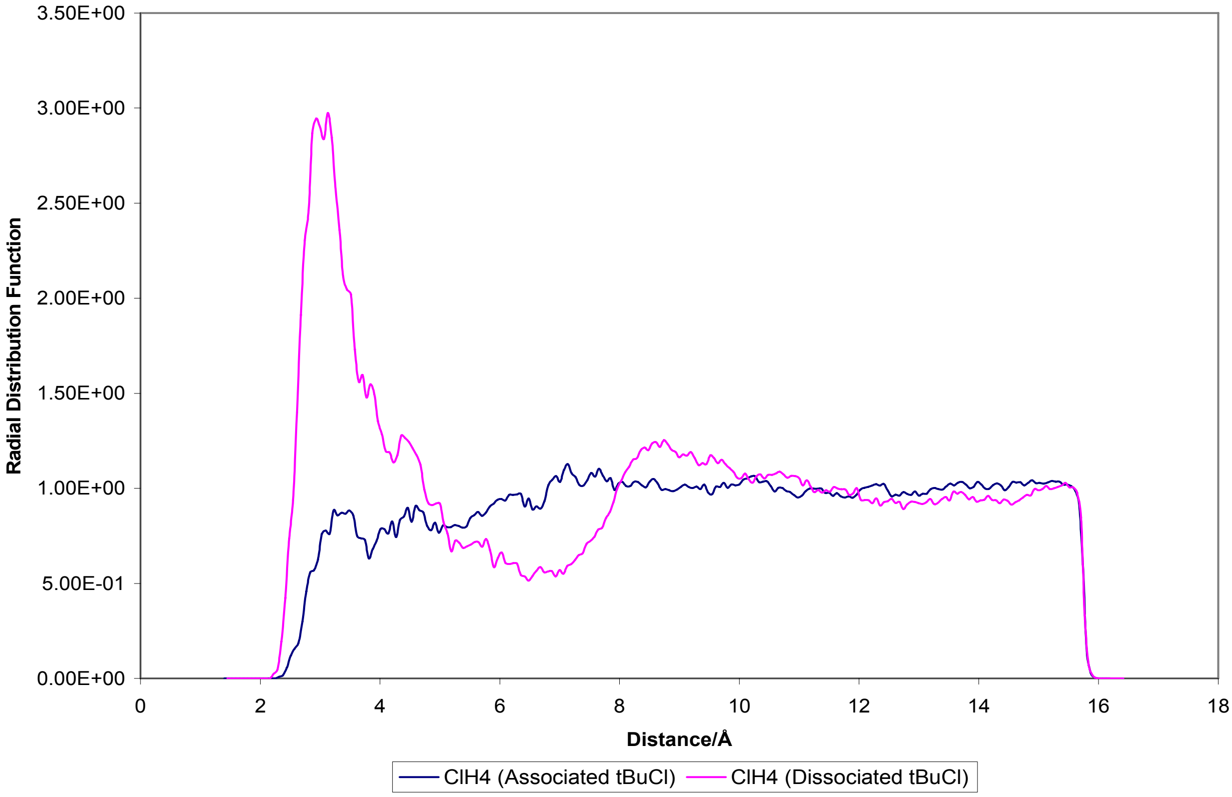
A selection of radial distribution functions illustrating:

1. Greater organisation of the ionic liquid cation around the chloride anion (H1 of cation; H4 of cation; C4 of cation – nomenclature outlined below)
2. Decreased cation organisation around the t-butyl cation (Ct of t-butyl, C4 of cation)
3. Increased organisation of anion around t-butyl cation (Ct of t-butyl/Cm of t-butyl with P of anion)

Distributions summed over 1.2 ns for dissociated species (t-Bu cation + Cl anion); 3.36 ns for associated species (t-BuCl).



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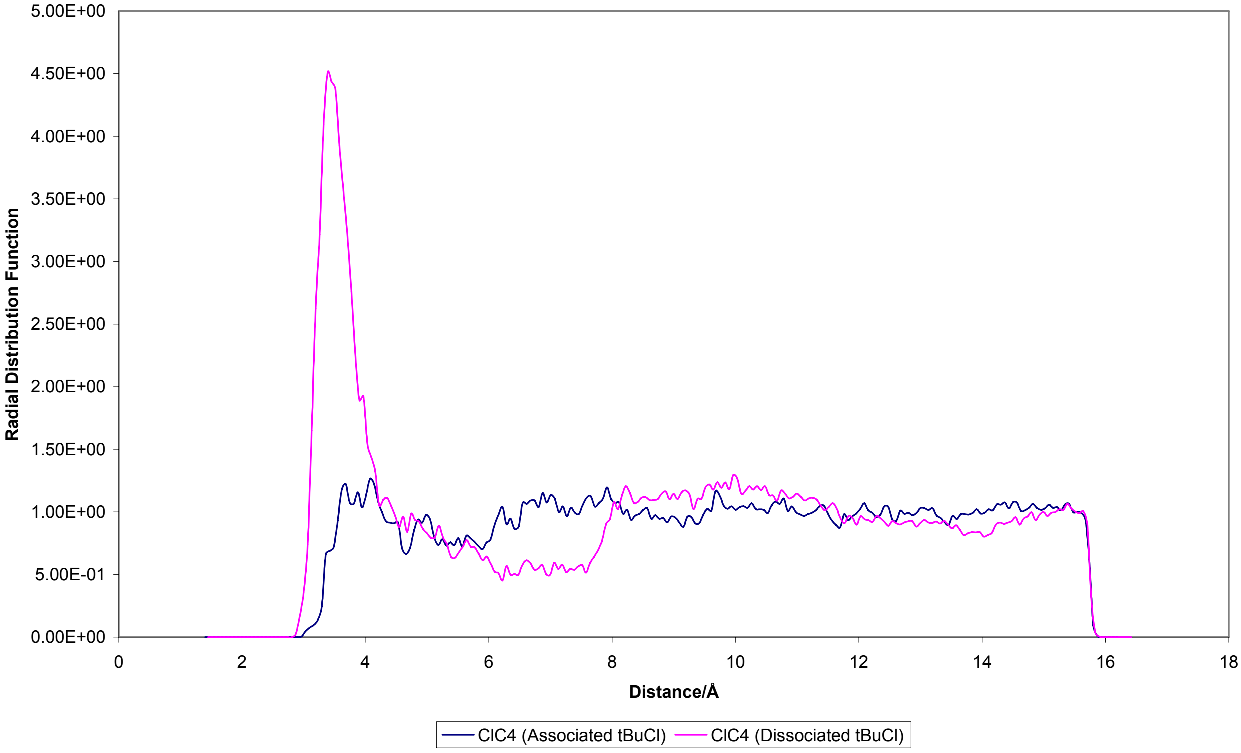
1.00E+00
5.00E-01
0.00E+00
Radial Distribution Function
0
2
4
6
8
10
12
14
16
18
Distance/Å
ClH4 (Associated tBuCl)
ClH4 (Dissociated tBuCl)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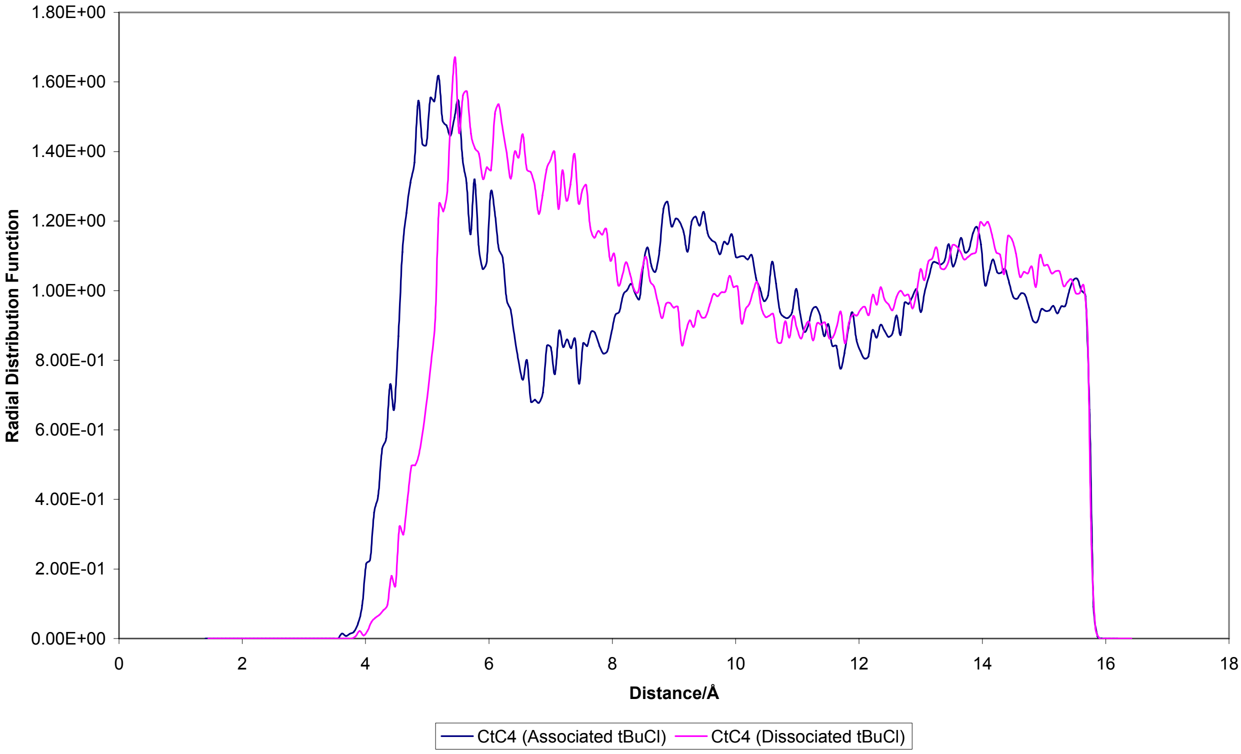
1.00E+00
5.00E-01
0.00E+00
Radial Distribution Function
0
2
4
6
8
10
12
14
16
18
Distance/Å
ClC4 (Associated tBuCl)
ClC4 (Dissociated tBuCl)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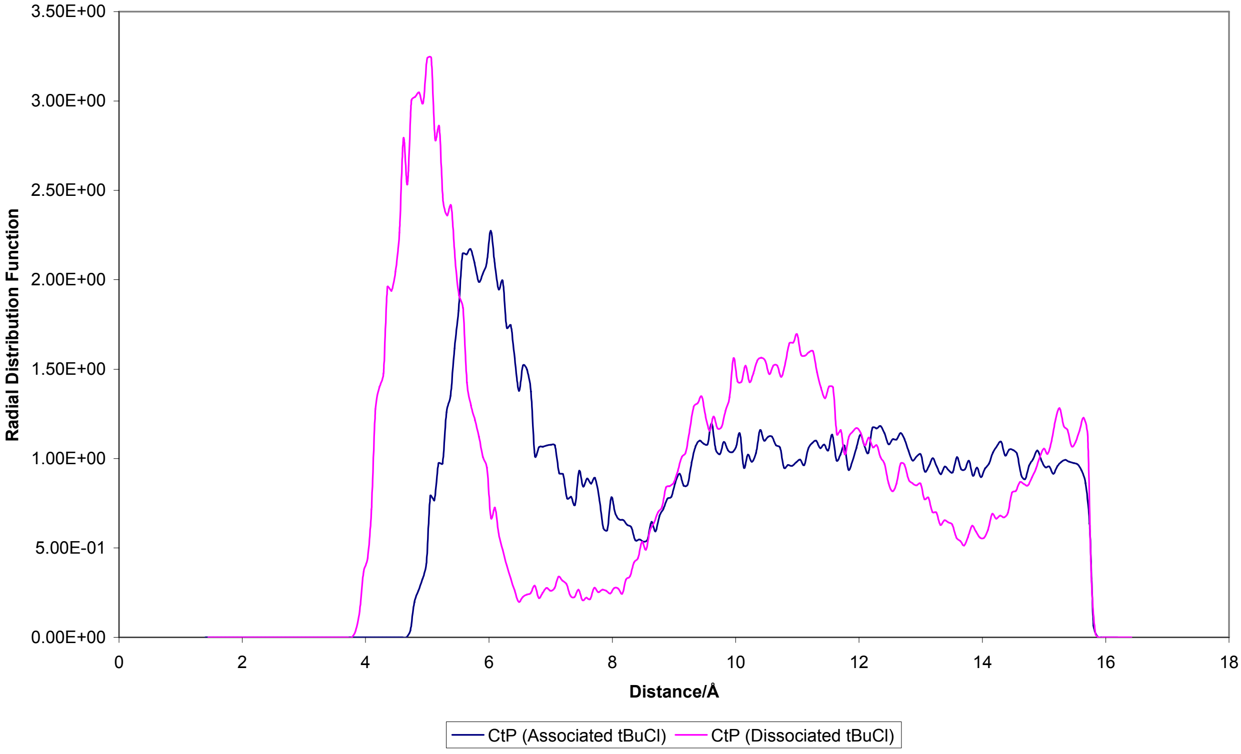
2.00E-01
0.00E+00
Radial Distribution Function
0
2
4
6
8
10
12
14
16
18
Distance/Å
CtC4 (Associated tBuCl)
CtC4 (Dissociated tBuCl)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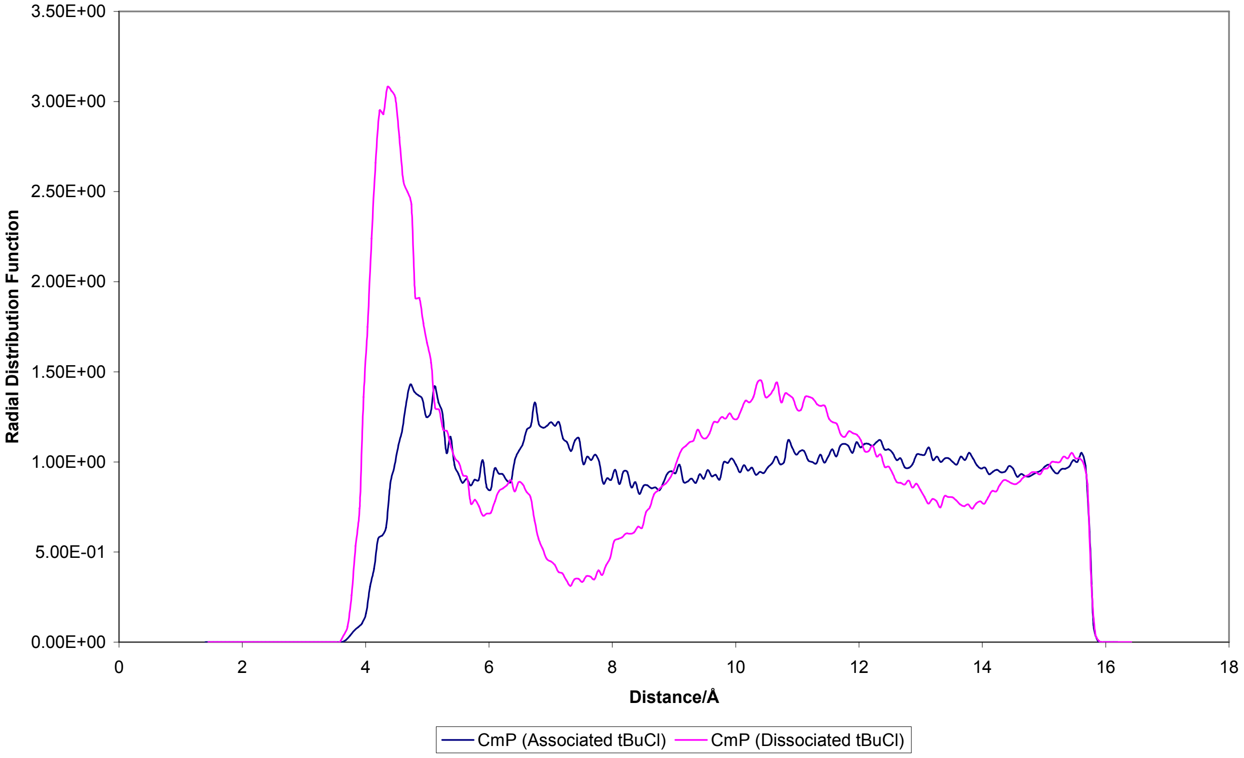
Radial Distribution Function
0
2
4
6
8
10
12
14
16
18
Distance/Å
CtP (Associated tBuCl)
CtP (Dissociated tBuCl)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5.00E-01
0.00E+00
Radial Distribution Function
0
2
4
6
8
10
12
14
16
18
Distance/Å
CmP (Associated tBuCl)
CmP (Dissociated tBuCl)