Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Ruthenium nanoparticles in ionic liquids: structural and stability effects of polar solutes

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ELECTRONIC SUPPORTING INFORMATION

Figure S1. Normalized size distribution histograms of RuNPs with $Ru_{0.1}$ (grey), $Ru_{0.2}$ (red), $Ru_{0.5}$ (blue) and Ru_1 (green).

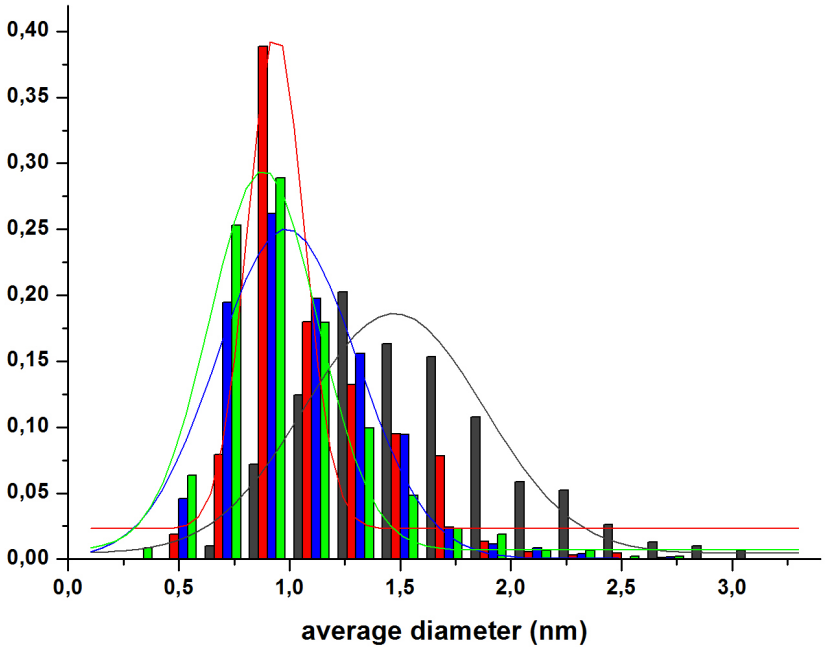


Table S1. Experimental values of surface tension of the mixture 1-octylamine+$[C_1C_4Im][NTf_2]$ at various concentration of 1-octylamine.

***T* (K)**	***γ* (mN m^{-1})**	***T* (K)**	***γ* (mN m^{-1})**
Pure $[C_1C_4Im][NTf_2]$		*c = 0.1 mM*	
297.85	33.0	300.35	32.7
303.15	32.7	302.95	32.5
308.45	32.4	307.85	32.3
313.75	32.1	312.75	32.1
319.05	31.8	317.75	31.9
323.35	31.6	322.65	31.6
c = 0.2 mM		*c = 0.4 mM*	
301.05	32.7	298.55	32.7
305.15	32.5	301.55	32.6
307.95	32.3	306.95	32.4
312.85	32.0	312.85	32.1
317.75	31.8	317.75	31.8
322.55	31.6	322.65	31.4

c = 0.8 mM	
298.95	32.5
302.95	32.1
307.85	32.0
307.85	32.0

c = 1.6 mM	
299.15	32.5
303.15	32.3
308.45	31.9
313.75	31.8
319.05	31.3
324.25	31.2

c = 2.4 mM	
304.05	32.2
308.45	32.0
313.85	31.7
319.05	31.5
323.25	31.2

c = 2.9 mM	
298.45	32.4
303.45	32.2
308.55	32.0
312.85	31.7
319.35	31.4

c = 3.9 mM	
298.35	32.3
303.25	32.1
308.55	31.9
314.85	31.6

c = 7.5 mM	
298.45	31.4
303.45	31.3
308.75	31.2
313.95	31.1

c = 10.8 mM	
297.85	31.1
303.25	31.0
308.55	31.1
313.95	31.1

c = 16.8 mM	
297.75	30.9
303.15	30.8
308.45	30.8
313.85	30.7

c = 28.8 mM	
297.75	30.6
303.15	30.4
308.45	30.2
313.85	30.1

c = 37.7 mM	
297.95	30.6
303.15	30.4
308.55	30.2
313.85	30.3

c = 49.5 mM	
300.55	30.4
303.15	30.2
308.45	30.0
313.75	29.8

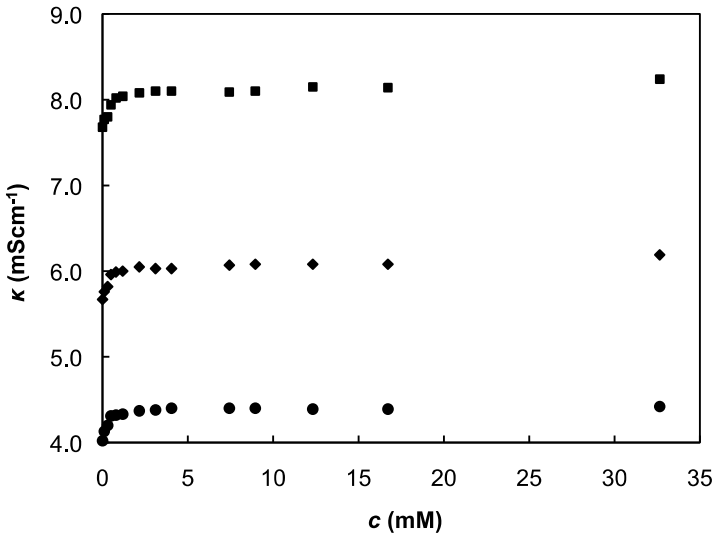
c = 78.1 mM	
298.15	30.3

c = 104.9 mM	
298.15	29.8

Table S2. Experimental values of eletrolytic conductivity of the mixture 1-octylamine+$[C_1C_4Im][NTf_2]$ at various concentrations of 1-octylamine at 298.15 K, 308.15 K and 318.15 K.

	κ (mS cm^{-1})		
c **(mM)**	**298.15 K**	**308.15 K**	**318.15 K**
0.0	4.02	5.67	7.68
0.1	4.13	5.76	7.77
0.3	4.20	5.82	7.80
0.5	4.31	5.96	7.94
0.8	4.32	5.99	8.02
1.2	4.33	6.00	8.04
2.2	4.37	6.05	8.08
3.1	4.38	6.03	8.10
4.0	4.40	6.03	8.10
7.4	4.40	6.07	8.09
9.0	4.40	6.08	8.10
12.3	4.39	6.08	8.15
16.7	4.39	6.08	8.14
32.7	4.42	6.19	8.24

Figure S2. Variation of eletrolytic conductivity with concentration of 1-octylamine in $[C_1C_4Im][NTf_2]$ at three temperatures: (●) 298.15 K, (♦) 308.15 K and (□) 318.15 K.



Isothermal titration calorimetry: Treatment of the experimental data

When the solute (1-octylamine, OA) is injected to solvent (ionic liquid, IL) at constant temperature and pressure area of the observed peak, Q_{OA}^{i} in each injection corresponds to its partial excess molar enthalpy, $\overline{H}_{OA}^{E}$ (Equation 1, where Δn_{OA} denotes quantity of 1-octylamine per injection, calculated from the injected volumes and its density). The uncertainty on the partial excess molar enthalpy was estimated to be 2 %. By fitting the experimental data to the Equation 2 parameters A_{i} were obtained. Enthalpy of mixing, $\Delta_{mix}H$ was obtained from Redlich-Kister equation (Equation 3), where, x_{OA} corresponds to the mole fraction of 1-octylamine and $x_{IL} = 1\text{-}x_{\mathrm{IL}}$ to the mole fraction of ionic liquid. In these calculations, heat due to evaporation of OA from IL solution is assumed to be negligible. Hence, no correction for the vapor pressure of the solute was made.

$$\overline{H}_{OA}^{E} = \frac{Q_{OA}^{i}}{\Delta n_{OA}} \tag{1}$$

$$\overline{H}_{OA}^{E} = \left(\frac{\partial \left(n_{IL} + n_{OA} \right) \Delta_{mix} H}{\partial n_{OA}} \right)_{n_{IL},p,T} = \left(x_{OA} - 1 \right)^{2} \left(x_{OA} \sum_{i=0}^{n} -2iA_{i} \left(1 - 2x_{OA} \right)^{-1+i} + \sum_{i=0}^{n} A_{i} \left(1 - 2x_{OA} \right)^{i} \right) \tag{2}$$

$$\Delta_{mix} H = \left(1 - x_{OA} \right) x_{OA} \sum_{i=0}^{n} A_{i} \left(1 - 2x_{OA} \right)^{i} = \left(1 - x_{IL} \right) x_{IL} \sum_{i=0}^{n} A_{i} \left(2x_{IL} - 1 \right)^{i} \tag{3}$$

Figure S3. Experimentally determined values of partial molar excess enthalpy of 1-octylamine (OA) measured by isothermal titration calorimetry at 303.15 K; x_{OA} is molar fraction of OA in the mixture with $[C_1C_4Im][NTf_2]$.

a) Pure OA was injected into pure IL to cover concentration range form $0.1 \leq x_{OA} \leq 0.4$.

b) OA solution in IL ($x_{OA} = 0.04$, $c_{OA} = 149.4$ mM) was injected into pure IL to cover concentration range form $0 \leq x_{OA} \leq 0.02$.

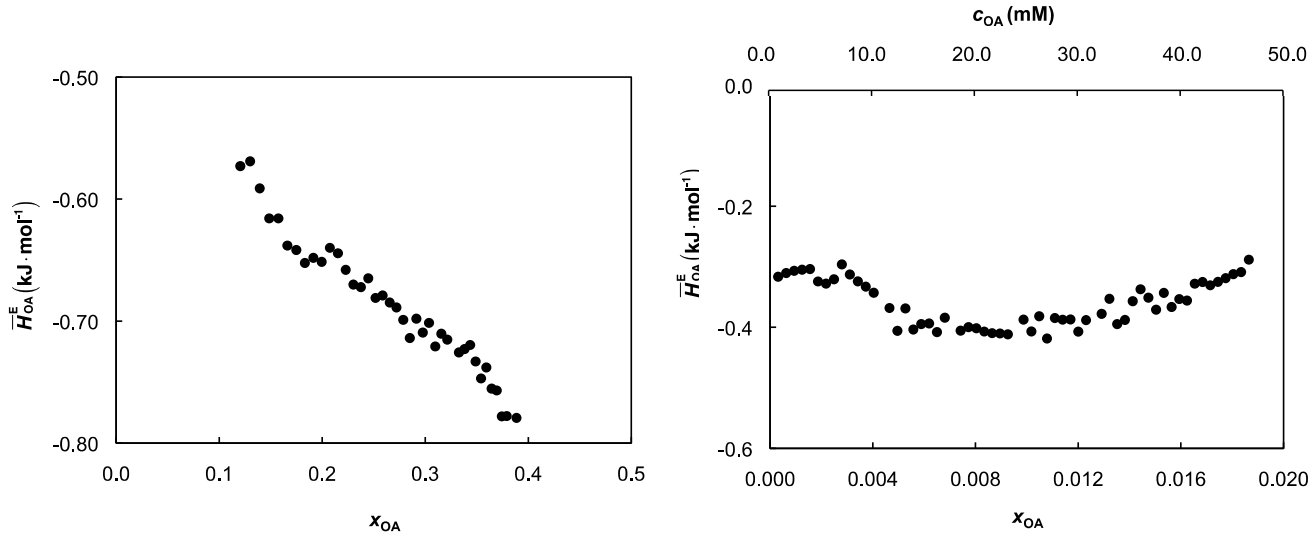


Figure S4. Site-site radial distribution functions between selected atomic sites in $[C_1C_4Im][NTf_2]$ and 1-octylamine: a) non-polar interaction sites in 1-octylamine, and b) polar interaction sites in 1-octylamine. Atomic sites are labeled as indicated in Figure 11.