

**Interactional Behavior of Polyelectrolyte Poly Sodium 4-Styrene Sulphonate (NaPSS) with  
Imidazolium based Surface Active Ionic Liquids in Aqueous Medium**

**Electronic supporting information**

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## Annexure SI

### Methods (Detailed Description)

Surface tension measurements were carried out using Kruss (Hamburg, Germany) Easy dyne tensiometer using ring detachment method at 298.15 K with an accuracy of  $\pm 0.15 \text{ mN m}^{-1}$ . A mixing time of two minutes followed by an equilibration time of 5 minutes was adopted prior to measurement. Steady-state fluorescence measurements were performed using HITACHI F-1600 Fluorescence Spectrophotometer using a 10 mm path length quartz cuvette at 298.15 K employing ANS as fluorescent probe. ANS (concentration) was excited at an excitation wavelength of 350 nm and emission spectrum was recorded in the wavelength range of 380-600 nm using an excitation and emission slit width of 2.5 nm, each. The solution was allowed to equilibrate for 5 minutes to reach the thermal equilibrium after each addition prior to measurement. Conductivity was measured at different temperatures using a digital Systronics conductivity meter model 306 with a dip-type conductivity cell having a cell constant of  $1.01 \text{ cm}^{-1}$ . Temperature of the measurement cell was controlled using an Escy IC201 thermostatic bath within the accuracy of  $\pm 0.1 \text{ K}$ . The specific conductivity of deionised double distilled water used in this study was measured to be around  $2 \mu\text{S cm}^{-1}$ . Cyclic voltammetric (CV) measurements were carried out on a PC controlled CHI660D (Austin, USA) electrochemical workstation equipped with a conventional three electrode system comprising of a working Pt electrode (2 mm in diameter), a counter Pt wire and a reference Ag/AgCl electrode. All the solutions were deoxygenated with  $\text{N}_2$  and working electrodes were polished with slurry of alumina powder. The CV measurements were carried out in the presence of 0.1 M KCl as a supporting electrolyte. In order to study the interactions between NaPSS and SAILs, successive additions of small aliquots of concentrated SAILs to TEMPO solution (2mM) containing polyelectrolyte have been carried out. The potentiometric measurements were carried out by using an Equiptronics digital potentiometer, Model EQ-602 employing the following electrochemical cell assembly:

Ag/AgCl	3M KCl	Test Solution	PVC membrane	Internal Reference Solution	3M KCl	Ag/AgCl
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The neutral ion-pair complexes of SAILs and sodium dodecylsulfate as  $C_n\text{mim}^+\text{DS}^-$  were prepared by the procedure earlier described by us [1, 2]. Equimolar aqueous solutions of ( $C_n\text{mimCl}$ ) and sodium dodecylsulfate (SDS) were mixed and after continuous stirring for a considerable time, the white precipitates of  $C_n\text{mim}^+\text{DS}^-$  were obtained. The precipitates so obtained were washed repeatedly with water to remove NaCl and recrystallized thrice from acetone. The PVC (176 mg), ion-pair (5 mg) and plasticizer (550 mg) were mixed and dissolved in minimum quantity of THF. The resulting mixture was poured in 50-mm petri dish after removing the air-bubbles. The solvent THF was allowed to evaporate at room temperature. The resulting membrane was cut to required size and attached to PVC tubes with PVC glue and equilibrated in 1mM of respective SAIL solution. The internal reference solution was 1mM SAIL in 1mM NaCl. The given composition of the components used for membrane formation represents the best system in terms of slope values, correlation coefficient, linear range and detection limit. The EMF measurements were carried out by titration method at 298.15K in the presence of 1mM NaCl solution. Turbidity measurements were performed using Systronics Digital Nepheloturbidity Meter model 132 after equilibrating the solution for 5 minutes. All the measurements were repeated thrice. Dynamic light scattering measurements were performed using a Malvern Nano-ZS Zetasizer instrument employing a He-Ne laser ( $\lambda = 632 \text{ nm}$ ) at a scattering angle of  $173^\circ$  using quartz cuvette having path length of 1 cm. The bare autocorrelation function has been analysed by cumulants fit method. The temperature of the measurement was maintained by built-in temperature controller having an accuracy of  $\pm 0.1 \text{ K}$ . Calorimetric measurements were carried out using MicroCal ITC200 microcalorimeter. The titrations were done by adding  $2 \mu\text{L}$  aliquots of stock solutions of SAILs in  $240 \mu\text{L}$  of aqueous polymer solution using Hamilton syringe. All the measurements were repeated twice. The time of addition and interval between each addition are controlled by software equipped with the instrument.

## Annexure SII.

The maximum surface excess concentration ( $\Gamma_{\max}$ ) and minimum area per molecule [3, 4] at the air-solution interface can be calculated using equation (1) and (2) as follows:

$$\frac{d\gamma}{d \ln C_T} = -nRT\Gamma_{\max} \quad (1)$$

$$A_{\min} = 10^{20} / (N_A \cdot \Gamma_{\max}) \quad (2)$$

The Gibbs free energy of adsorption ( $\Delta G^{\circ}_{\text{ads}}$ ) [5] is calculated using the equation (3)

$$\Delta G^{\circ}_{\text{ads}} = \Delta G^{\circ}_{\text{mic}} - \Pi_{\text{cmc}} / \Gamma_{\max} \quad (3)$$

## Annexure SIII

The Gibbs free energy of micelle formation,  $\Delta G_{\text{mic}}$  [6] was calculated using the equation (4)

$$\Delta G_{\text{mic}} = (1 + \beta) RT \ln X_{\text{cmc}} \quad (4)$$

Where,  $\beta$ , R, T and  $X_{\text{cmc}}$  are counter-ion binding, gas constant, temperature on Kelvin scale and  $\text{cmc}$  expressed in mole fraction. The enthalpy of micelle formation,  $\Delta H_{\text{mic}}$  was calculated by employing Gibbs-Helmholtz equation using free energy of micellization

$$\Delta H_{\text{mic}} = -RT^2 (1 + \beta) \frac{dX_{\text{cmc}}}{dT} \quad (5)$$

Then the entropy of micelle formation,  $\Delta S_{\text{mic}}$  is obtained as:

$$\Delta S_{\text{mic}} = \frac{\Delta H_{\text{mic}} - \Delta G_{\text{mic}}}{T} \quad (6)$$

Table S1 Interfacial parameters *i.e.* surface tension at *cmc* ( $\gamma_{cmc}$ ), effective surface tension reduction ( $\Pi_{cmc}$ ), surface excess ( $\Gamma_{max}$ ), minimum area per molecule ( $A_{min}$ ), Gibbs free energy of adsorption ( $\Delta G^{\circ}_{ads}$ ) of SAILs in the absence and presence of polyelectrolyte NaPSS (0.002 and 0.005%) at 298.15K.

NaPSS %	$\gamma_{cmc}$ (mN m <sup>-1</sup> )	$\pi_{cmc}$ (mN m <sup>-1</sup> )	$\Gamma_{max} \times 10^6$ (mol m <sup>-2</sup> )	$A_{min}$ (nm <sup>2</sup> )	$\Delta G^{\circ}_{ads}$ kJ mol <sup>-1</sup>
[C <sub>10</sub> mim][Cl]					
0.000	31.4	41.4	1.41	1.18	-58.2
0.002	33.9	38.9	0.91	1.83	-71.0
0.005	32.3	40.5	0.92	1.81	-70.1
[C <sub>12</sub> mim][Cl]					
0.000	30.9	41.9	2.08	0.80	-54.6
0.002	34.2	38.7	2.09	0.79	-51.0
0.005	32.5	40.3	2.22	0.75	-49.6
[C <sub>14</sub> mim][Cl]					
0.000	30.2	42.7	2.27	0.73	-59.5
0.002	28.5	44.3	2.29	0.72	-57.8
0.005	27.2	45.6	2.42	0.69	-56.7

The error estimate in interfacial parameters  $\gamma_{cmc}$ ,  $\pi_{cmc}$ ,  $\Gamma_{max}$ ,  $A_{min}$  and  $\Delta G^{\circ}_{ads}$  are  $\pm 0.10$  mN m<sup>-1</sup>,  $\pm 0.10$  mN m<sup>-1</sup>,  $\pm 0.05$  mol m<sup>-2</sup>,  $\pm 0.05$  nm<sup>2</sup> and  $\pm 0.15$  kJ mol<sup>-1</sup> respectively.

Table S2 Critical micelle concentration ( $cmc$ ), counter-ion binding ( $\beta$ ), Gibbs free energy of micellization ( $\Delta G_m$ ), enthalpy of micellization ( $\Delta H_m$ ) and entropy of micellization ( $\Delta S_m$ ) of SAILs in aqueous solution at different temperatures.

T (K)	$cmc$ (mmol $dm^{-3}$ )	$\beta$	$\Delta G_m$ (kJ mol $^{-1}$ )	$\Delta H_m$ (kJ mol $^{-1}$ )	$T\Delta S_m$ (kJ mol $^{-1}$ )
[C <sub>10</sub> mim][Cl]					
298.15	33.5	0.57	-28.84	-5.79	23.05
303.15	34.8	0.54	-28.62	-5.87	22.75
308.15	35.4	0.51	-28.46	-5.95	22.51
313.15	36.2	0.49	-28.45	-6.06	22.39
[C <sub>12</sub> mim][Cl]					
298.15	12.1	0.65	-34.48	-8.73	25.75
303.15	13.0	0.63	-34.34	-8.92	25.42
308.15	13.1	0.60	-34.23	-9.04	25.18
313.15	13.6	0.57	-33.98	-9.17	24.81
[C <sub>14</sub> mim][Cl]					
298.15	2.8	0.66	-40.71	-15.88	24.83
303.15	3.0	0.61	-39.86	-15.92	23.94
308.15	3.2	0.57	-39.25	-16.04	23.21
313.15	3.4	0.52	-38.38	-16.04	22.34

The error estimate in  $cmc$ ,  $\beta$ ,  $\Delta G_m$ ,  $\Delta H_m$  and  $\Delta S_m$  are  $\pm 0.10$  mmol  $dm^{-3}$ ,  $\pm 0.02$ ,  $\pm 0.05$  kJ mol $^{-1}$ ,  $\pm 0.07$  kJ mol $^{-1}$  and  $\pm 0.13$  kJ mol $^{-1}$  respectively.

Table S3 Critical aggregation concentration (*cac*), critical micelle concentration (*cmc*), counterion binding ( $\beta$ ), Gibbs free energy of micellization ( $\Delta G_m$ ), enthalpy of micellization ( $\Delta H_m$ ) and entropy of micellization ( $\Delta S_m$ ) of SAILs in 0.002% NaPSS solution at different temperatures.

0.002% NaPSS	T (K)	<i>cac</i> (mmol dm <sup>-3</sup> )	<i>cmc</i> (mmol dm <sup>-3</sup> )	$\beta$	$\Delta G_m$ (kJ mol <sup>-1</sup> )	$\Delta H_m$ (kJ mol <sup>-1</sup> )	T $\Delta S_m$ (kJ mol <sup>-1</sup> )
[C <sub>10</sub> mim][Cl]							
	298.15	3.20	35.5	0.54	-28.07	-6.20	21.87
	303.15	3.70	36.5	0.49	-27.51	-6.21	21.31
	308.15	4.00	37.3	0.42	-26.57	-6.11	20.46
	313.15	4.50	38.6	0.41	-26.69	-6.27	20.42
[C <sub>12</sub> mim][Cl]							
	298.15	1.23	12.9	0.57	-32.56	-10.24	22.31
	303.15	1.37	13.2	0.53	-32.17	-10.32	21.85
	308.15	1.50	14.1	0.50	-31.81	-10.45	21.35
	313.15	1.58	14.7	0.46	-31.32	-10.51	20.82
[C <sub>14</sub> mim][Cl]							
	298.15	0.30	3.00	0.58	-38.44	-13.74	24.70
	303.15	0.32	3.30	0.55	-38.01	-13.93	24.27
	308.15	0.42	3.40	0.52	-37.77	-14.12	23.65
	313.15	0.45	3.70	0.49	-37.35	-14.29	23.06

The error estimate in *cac*, *cmc*,  $\beta$ ,  $\Delta G_m$ ,  $\Delta H_m$  and  $\Delta S_m$  are  $\pm 0.05$  mmol dm<sup>-3</sup>,  $\pm 0.10$  mmol dm<sup>-3</sup>,  $\pm 0.02$ ,  $\pm 0.05$  kJ mol<sup>-1</sup>,  $\pm 0.07$  kJ mol<sup>-1</sup> and  $\pm 0.13$  kJ mol<sup>-1</sup> respectively.

Table S4 Critical aggregation concentration (*cac*), critical micelle concentration (*cmc*), counter-ion binding ( $\beta$ ), Gibbs free energy of micellization ( $\Delta G_m$ ), enthalpy of micellization ( $\Delta H_m$ ) and entropy of micellization ( $\Delta S_m$ ) of SAILs in 0.005% NaPSS solution at different temperatures.

0.005% NaPSS	T (K)	<i>cac</i> (mmol dm <sup>-3</sup> )	<i>cmc</i> (mmol dm <sup>-3</sup> )	$\beta$	$\Delta G_m$ (kJ mol <sup>-1</sup> )	$\Delta H_m$ (kJ mol <sup>-1</sup> )	T $\Delta S_m$ (kJ mol <sup>-1</sup> )
[C <sub>10</sub> mim][Cl]							
	298.15	3.50	37.4	0.43	-25.88	-7.81	18.07
	303.15	3.90	38.1	0.41	-25.88	-7.96	17.92
	308.15	4.20	39.8	0.39	-25.78	-8.11	17.67
	313.15	4.80	41.7	0.31	-24.53	-7.89	17.63
[C <sub>12</sub> mim][Cl]							
	298.15	1.30	13.1	0.52	-31.41	-11.76	19.65
	303.15	1.46	13.4	0.48	-31.06	-11.84	19.22
	308.15	1.54	14.2	0.46	-30.93	-12.07	18.86
	313.15	1.62	14.9	0.42	-30.29	-12.12	18.17
[C <sub>14</sub> mim][Cl]							
	298.15	0.46	3.1	0.56	-37.86	-15.40	22.46
	303.15	0.50	3.4	0.53	-37.40	-15.62	21.78
	308.15	0.52	3.6	0.47	-36.31	-15.50	20.81
	313.15	0.54	3.8	0.43	-35.69	-15.57	20.12

The error estimate in *cac*, *cmc*,  $\beta$ ,  $\Delta G_m$ ,  $\Delta H_m$  and  $\Delta S_m$  are  $\pm 0.05$  mmol dm<sup>-3</sup>,  $\pm 0.10$  mmol dm<sup>-3</sup>,  $\pm 0.02$ ,  $\pm 0.05$  kJ mol<sup>-1</sup>,  $\pm 0.07$  kJ mol<sup>-1</sup> and  $\pm 0.13$  kJ mol<sup>-1</sup> respectively.



Table S5 Inter-micellar interaction parameter ( $k_d$ ), self-diffusion coefficient ( $D_m^0$ ) and diffusion coefficient ( $D_m$ ) of SAILs in the absence and presence of polyelectrolyte NaPSS (0.002 and 0.005%).

System	$k_d$ ( $M^{-1}$ )	$D_m^0$ ( $10^5 \text{ cm}^2 \text{ s}^{-1}$ )	$D_m$ ( $10^5 \text{ cm}^2 \text{ s}^{-1}$ )
[C <sub>10</sub> mim][Cl]	2.55	3.57	2.84
[C <sub>10</sub> mim][Cl]+NaPSS (0.002%)	1.88	2.77	3.19
[C <sub>10</sub> mim][Cl]+NaPSS (0.005%)	1.95	2.80	3.09
[C <sub>12</sub> mim][Cl]	5.26	3.45	2.97
[C <sub>12</sub> mim][Cl]+NaPSS (0.002%)	5.21	2.99	3.13
[C <sub>12</sub> mim][Cl]+NaPSS (0.005%)	6.41	2.74	2.64
[C <sub>14</sub> mim][Cl]	9.98	2.66	3.31
[C <sub>14</sub> mim][Cl]+NaPSS (0.002%)	15.2	2.64	3.06
[C <sub>14</sub> mim][Cl]+NaPSS (0.005%)	13.8	2.62	3.26

The error estimate in  $k_d$ ,  $D_m^0$  and  $D_m$  are  $\pm 0.01 \text{ M}^{-1}$ ,  $\pm 0.02 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$  and  $\pm 0.03 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$  respectively.

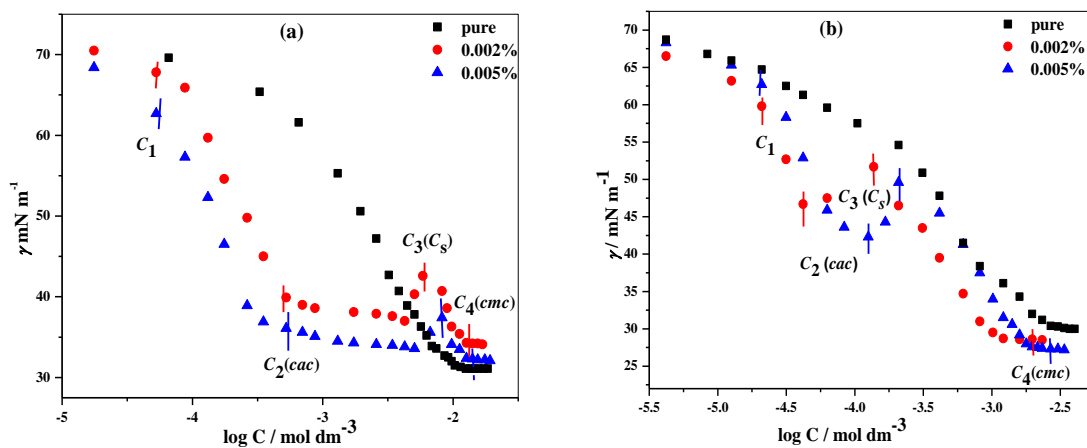


Fig. S1 Variation of surface tension ( $\gamma$ ) as a function of logarithm of concentration of SAILs at 0.002 and 0.005% concentrations of NaPSS for (a)  $[C_{12}\text{mim}][\text{Cl}]$  and (b)  $[C_{14}\text{mim}][\text{Cl}]$ .

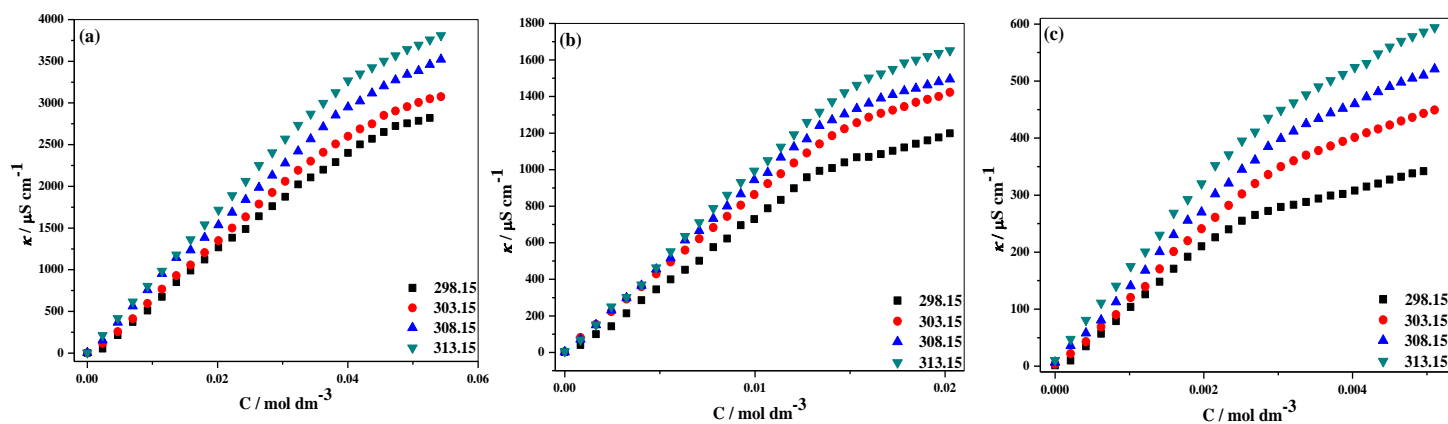


Fig.S2 Variation of specific conductivity ( $\kappa$ ) as a function of concentration of concentration of SAILs in aqueous solution at different temperatures (a)  $[C_{10}\text{mim}][\text{Cl}]$  (b)  $[C_{12}\text{mim}][\text{Cl}]$  (c)  $[C_{14}\text{mim}][\text{Cl}]$ .

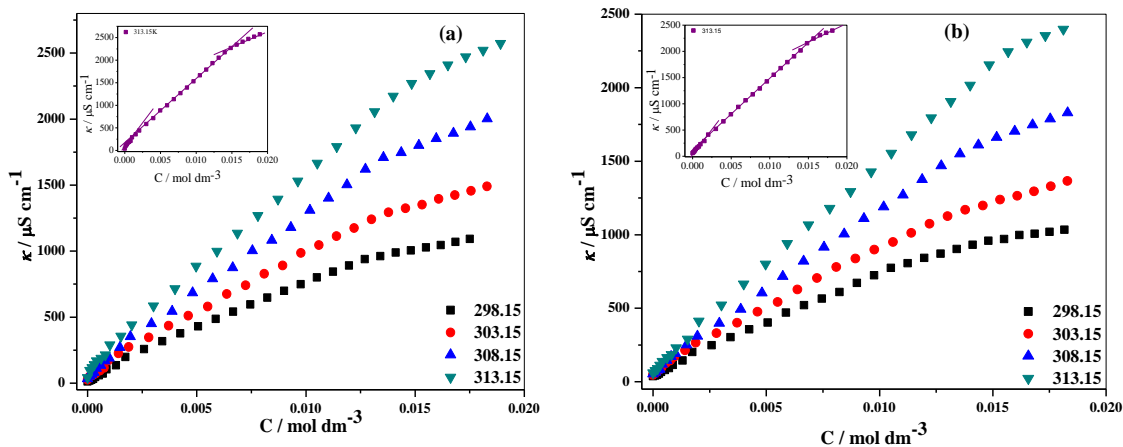


Fig.S3 Variation of specific conductivity ( $\kappa$ ) as a function of concentration of  $[C_{12}mim][Cl]$  in the presence of (a) 0.002% ; and (b) 0.005% NaPSS at different temperatures.

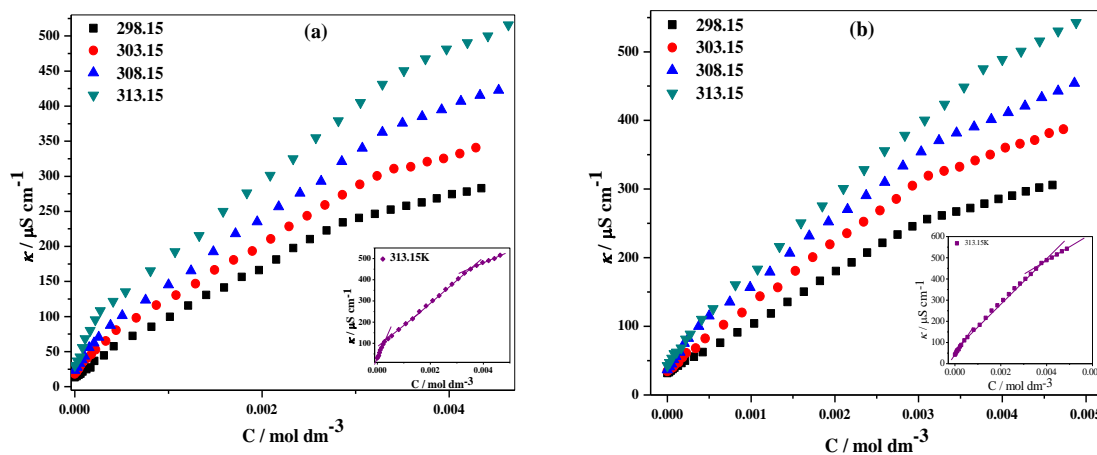


Fig. S4 Variation of specific conductivity ( $\kappa$ ) as a function of concentration of  $[C_{14}mim][Cl]$  in the presence of (a) 0.002% ; and (b) 0.005% NaPSS at different temperatures.

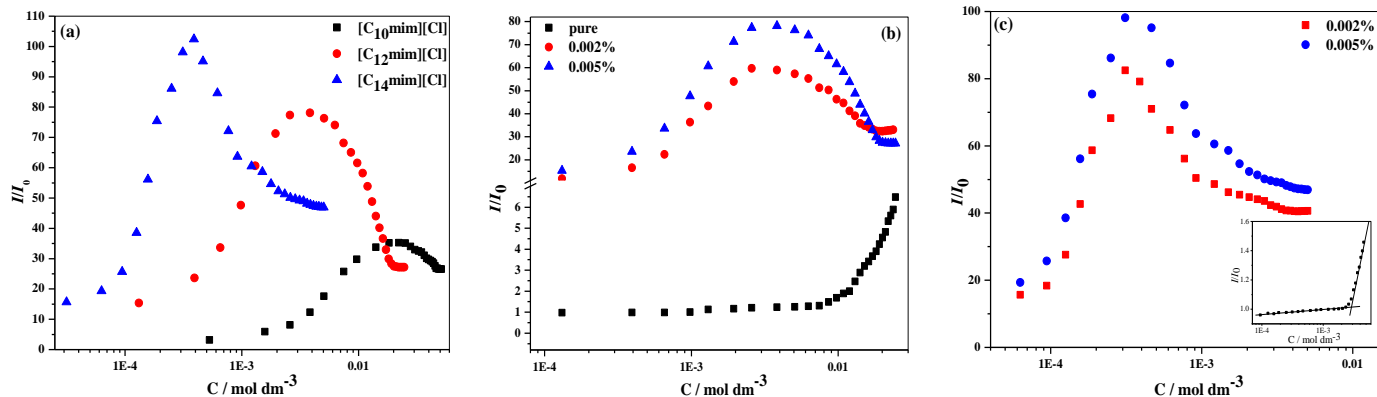


Fig.S5(a) Fluorescence intensity of ANS in 0.005% NaPSS solution as a function of concentration of SAILs. (b) and (c) represents fluorescence intensity of ANS in aqueous and aqueous NaPSS solutions at 0.002 and 0.005% concentrations as a function of concentration of  $[C_{12}mim][Cl]$  and  $[C_{14}mim][Cl]$ .

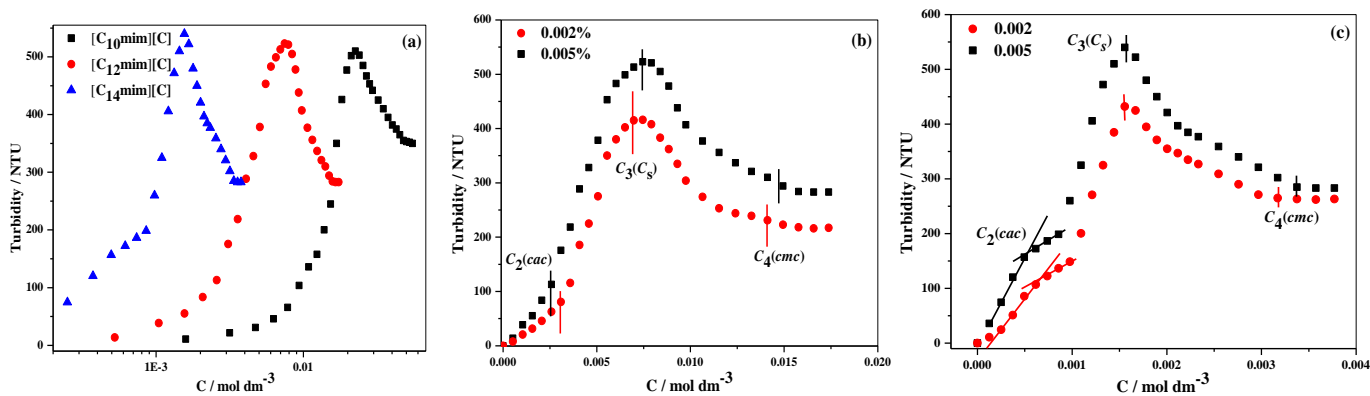


Fig.S6. Variation of turbidity versus concentration of (a) three SAILs in polyelectrolyte (NaPSS) solution at a concentration of 0.005%; (b) and (c) Variation of turbidity versus concentration of  $[C_{12}mim][Cl]$  and  $[C_{14}mim][Cl]$  at 0.002 and 0.005% concentrations of NaPSS.

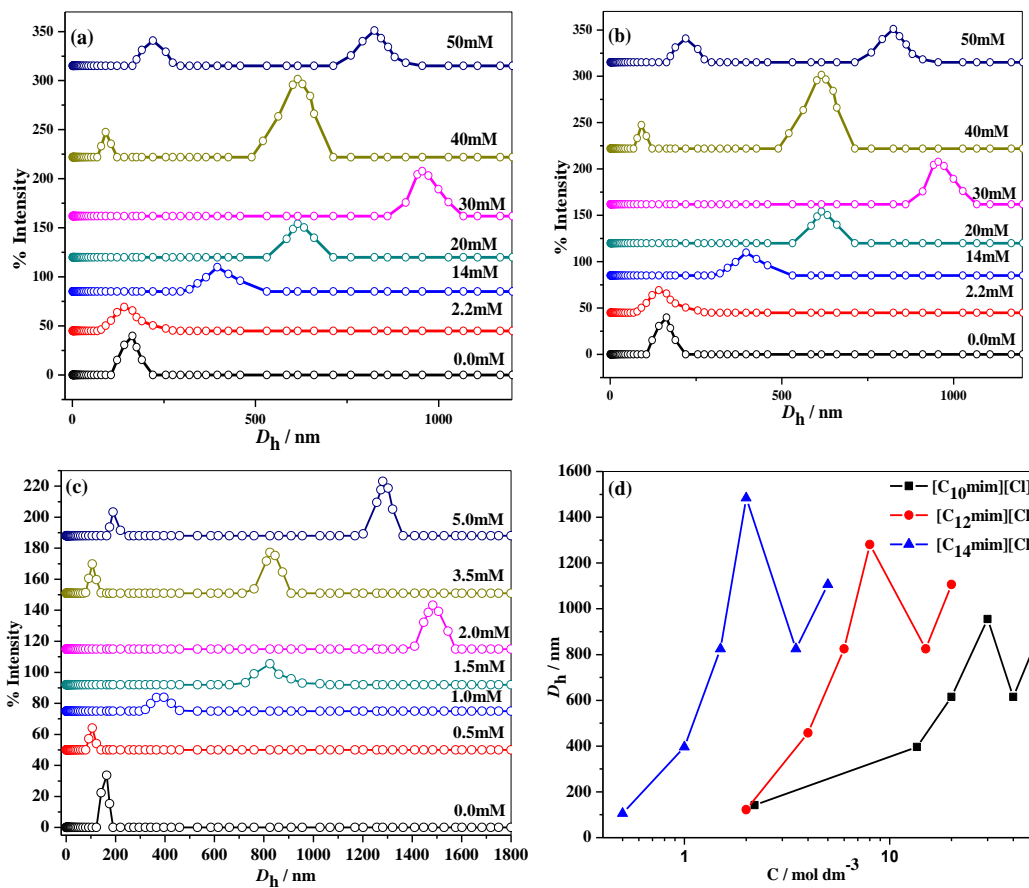


Fig.S7.Size distribution for 0.005% concentrations of NaPSS in the presence of increasing concentrations of (a)  $[C_{10}mim][Cl]$ , (b)  $[C_{12}mim][Cl]$  and (c)  $[C_{14}mim][Cl]$ . (d) Variation of hydrodynamic diameter ( $D_h$ ) as a function of concentration of SAILs in 0.005% NaPSS.

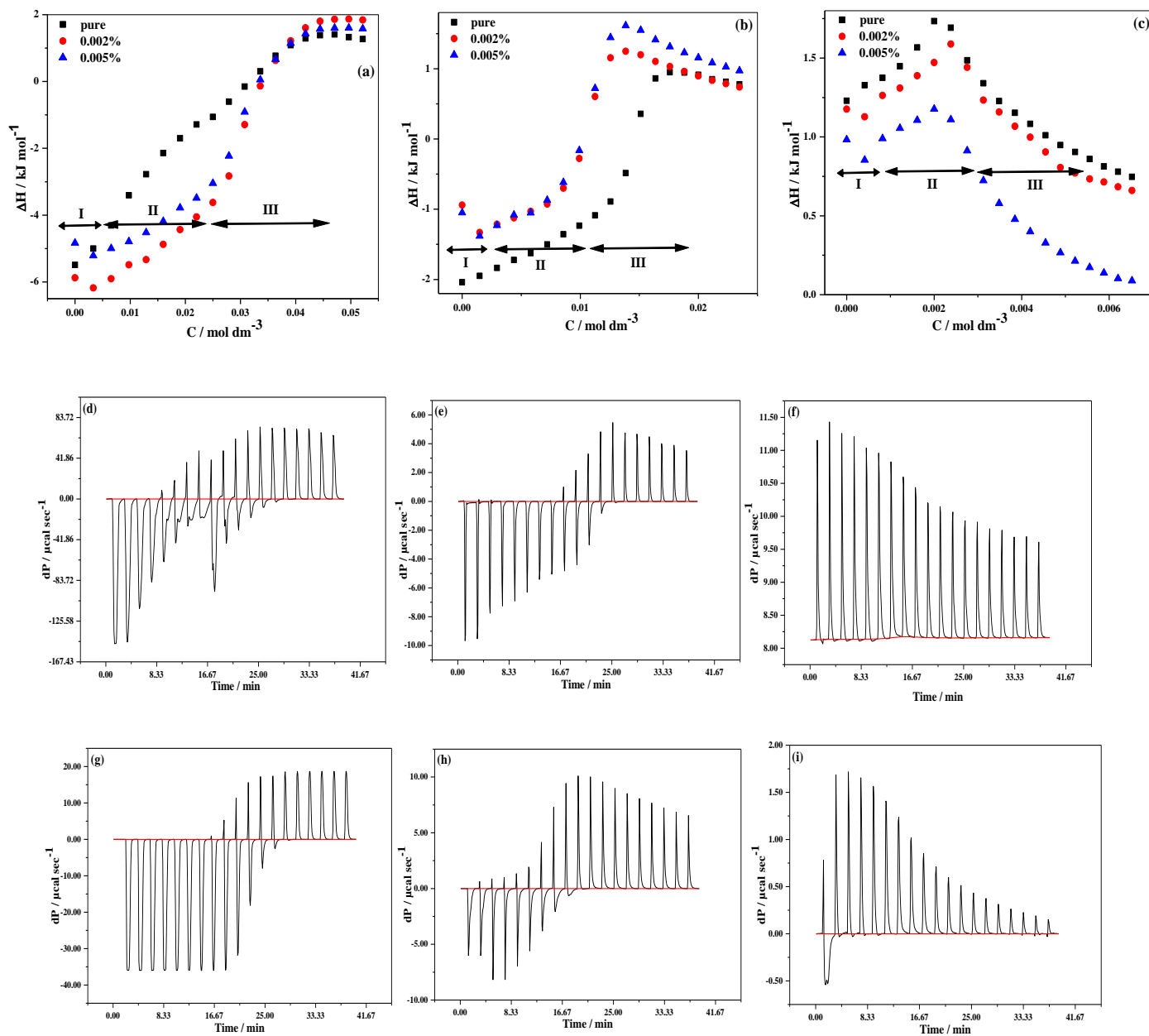


Fig.S8. Calorimetric profiles of SAILs as a function of concentration of (a)  $[\text{C}_{10}\text{mim}][\text{Cl}]$ ; (b)  $[\text{C}_{12}\text{mim}][\text{Cl}]$  and (c)  $[\text{C}_{14}\text{mim}][\text{Cl}]$  in the absence and presence of polyelectrolyte, NaPSS (0.002 and 0.005%) at 298.15K. Variation of differential power ( $dP$ ) versus time for aqueous solution of (d)  $[\text{C}_{10}\text{mim}][\text{Cl}]$  (e)  $[\text{C}_{12}\text{mim}][\text{Cl}]$  (f)  $[\text{C}_{14}\text{mim}][\text{Cl}]$  and for the interaction of NaPSS with SAILs at a concentration of 0.005% (g)  $[\text{C}_{10}\text{mim}][\text{Cl}]$  (h)  $[\text{C}_{12}\text{mim}][\text{Cl}]$  (i)  $[\text{C}_{14}\text{mim}][\text{Cl}]$ .

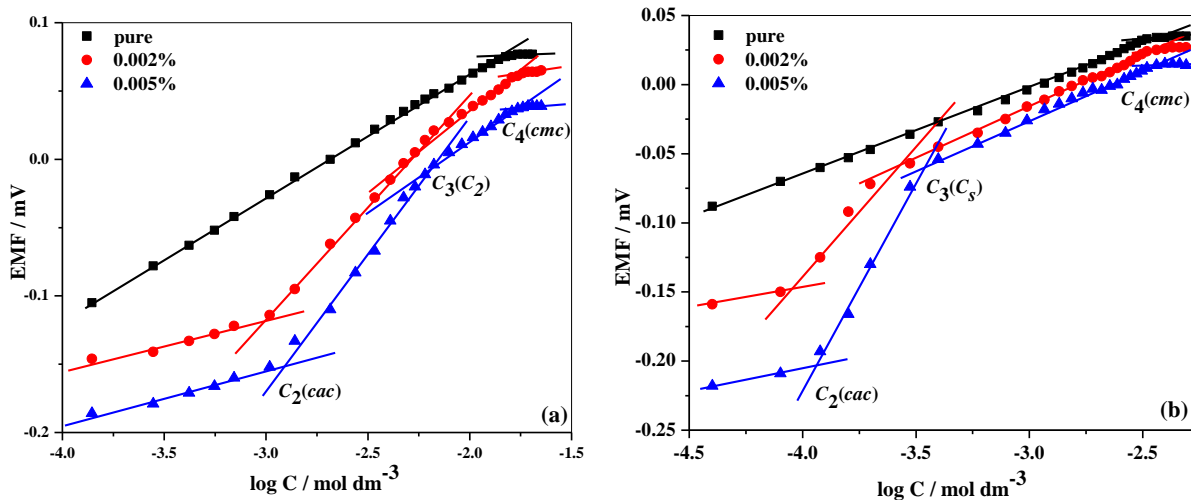


Fig.S9 (a) EMF as a function of logarithm of concentration of SAILs in the absence and presence of 0.002 and 0.005% NaPSS for (a) [C<sub>12</sub>mim][Cl] and (b) [C<sub>14</sub>mim][Cl].

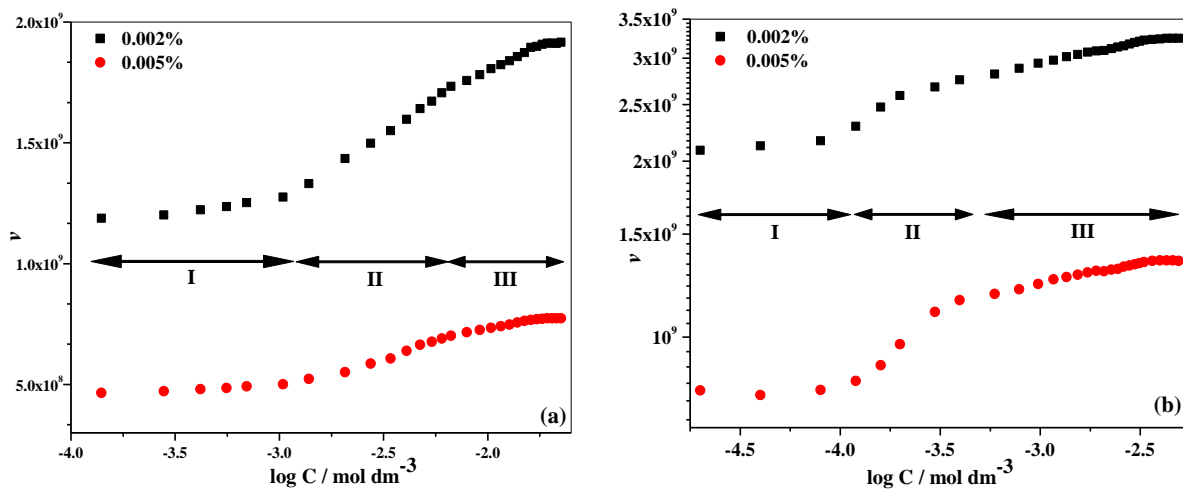


Fig.S10 Binding isotherms of  $\nu$  versus logarithm of concentration of SAILs in the presence of 0.002 and 0.005% NaPSS for (a) [C<sub>12</sub>mim][Cl] and (b) [C<sub>14</sub>mim][Cl].

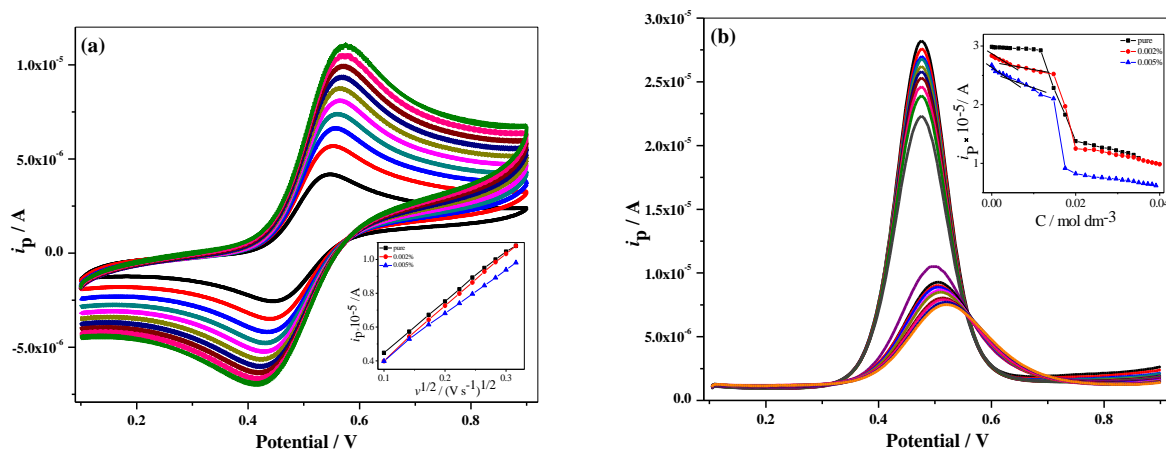


Fig.S11 (a) Reversible cyclic voltammograms of TEMPO in supporting electrolyte KCl in micellar solution of  $[C_{12}mim][Cl]$  at different scan rates in the presence of 0.005% NaPSS. [Inset of plot shows the variation of  $i_p$  (A) versus  $v^{1/2}$  for TEMPO ion in aqueous  $[C_{12}mim][Cl]$  solution and in the presence of NaPSS (b) Differential pulse voltammograms (DPV) of TEMPO (2mM) in supporting electrolyte KCl (0.1 M) for varying concentrations of  $[C_{12}mim][Cl]$  in the presence of 0.005% NaPSS [Inset of plot shows the variation of  $i_p$  as a function of  $[C_{12}mim][Cl]$  in aqueous and aqueous NaPSS solution (0.002 and 0.005%).

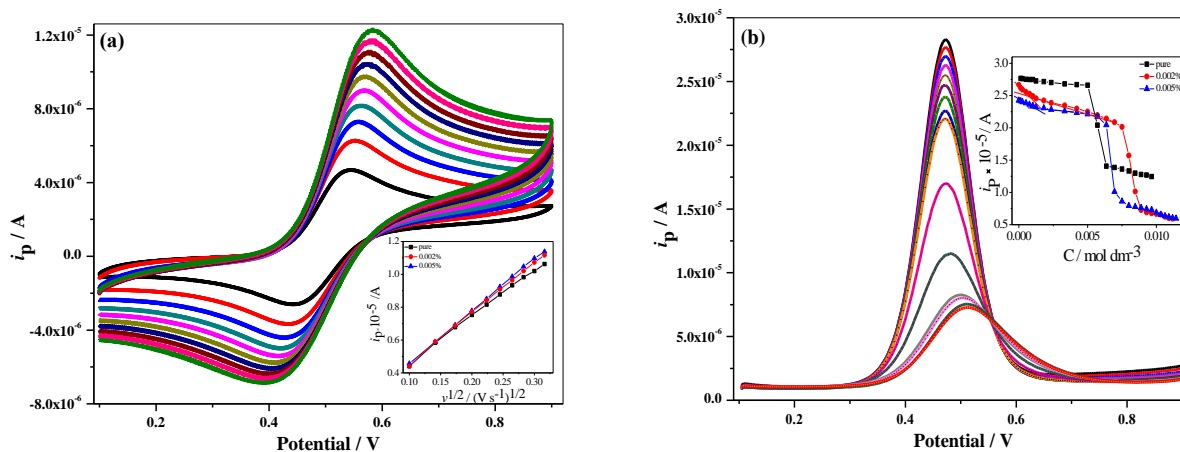


Fig.S12 (a) Reversible cyclic voltammograms TEMPO (2 mM) in supporting electrolyte KCl (0.1 M) in micellar solution of  $[C_{14}mim][Cl]$  at different scan rates in the presence of 0.005% NaPSS [Inset of plot shows the variation of  $i_p$  (A) versus  $v^{1/2}$  ( $V s^{-1}$ )<sup>1/2</sup> for TEMPO ion in aqueous  $[C_{12}mim][Cl]$  solution and in the presence of NaPSS (b) Differential pulse voltammograms (DPV) of TEMPO (2mM) in supporting electrolyte KCl (0.1 M) for varying concentrations of  $[C_{14}mim][Cl]$  in the presence of 0.005% NaPSS [Inset of plot shows the variation of  $i_p$  as a function of  $[C_{14}mim][Cl]$  in aqueous and aqueous NaPSS solution (0.002 and 0.005%).



## References

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