

Supporting information for:

**Interactional Behaviour of Surface Active Ionic Liquids with Gelling Biopolymer
Agarose in Aqueous Medium**

Pankaj Bharmoria and Arvind Kumar*

†Salt & Marine Chemicals Division, CSIR-Central Salt and Marine Chemicals Research
Institute, Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar-
364002, Gujarat, India

Annexure S1.

1. Adsorption efficiency pC_{20} was calculated from surface tension vs. concentration graphs using equation 1.

$$pC_{20} = -\log C_{20} \quad (1)$$

Where C_{20} is the concentration required to reduce the surface tension of pure solvent or solution by $20 \text{ mN}\cdot\text{m}^{-1}$. A higher pC_{20} value is indicative of a higher adsorption efficiency of the surfactant at the interface and more efficiency in reducing surface tension.

2. Surface pressure at cmc, Π_{cmc} was calculated from the difference of surface tension of native solution and surface tension at cmc using equation 2.

$$\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (2)$$

where γ_0 is the surface tension of pure solvent or solution and γ_{cmc} is the surface tension of the solution at cmc. The parameter indicates the maximum reduction of surface tension caused by the dissolution of surfactant molecules and hence becomes a measure for the effectiveness of the surfactant to lower the surface tension of either pure solvent or native solution.

3. Γ_{max} is calculated following the Gibbs adsorption equation 3.

$$\Gamma_{\text{max}} = -\frac{1}{nRT} \lim_{[C] \rightarrow 0} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T \quad (3)$$

where n , R , T and $[C]$ are the number of species formed per IL molecule in solution upon ionization (it is 2 for both $[\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$ and $[\text{C}_8\text{mim}][\text{Cl}]$, the universal gas constant, absolute temperature and the molar concentration of IL in solution respectively. The parameter indicates, relative amount of surfactant adsorbed at the interface. Higher surface excess value signifies higher adsorption. Here concentration was used in place of activity, as the solutions used were fairly dilute.¹⁻³

4. A_{min} was obtained from the equation 4.

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} \quad (4)$$

Where N_A is the Avogadro number.¹⁻³ Parameter signifies the minimum area occupied by surfactant monomer at the interface. Lower value of A_{min} indicates higher adsorption of monomer at the interface.

5. The degree of counter-ion dissociation, α was calculated from the ratio of slope (S_2/S_1) of linear fragments of conductivity profiles of post-micellization(S_2) to pre-micellization (S_1) region. Parameter indicates the feasibility of micellization. Lower value of α indicates better binding of counter ion with surfactant head group thus increases the feasibility of micellization.

6. The standard Gibbs free energy of micellization ΔG_m^o was calculated using equation 5.

$$\Delta G_m^o = (2 - \alpha)RT \ln x_{cmc} \quad (5)$$

7. The standard Gibbs free energy of interfacial adsorption (ΔG_{ad}^o) was calculated using the equation 6.

$$\Delta G_{ad}^o = \Delta G_m^o - (\pi_{cmc}/\Gamma_{max}) \quad (6)$$

The parameters of equation (5) and (6) indicate feasibility of micellization in the bulk and adsorption at the interface. Higher negative value of these parameters indicates better feasibility of the process.

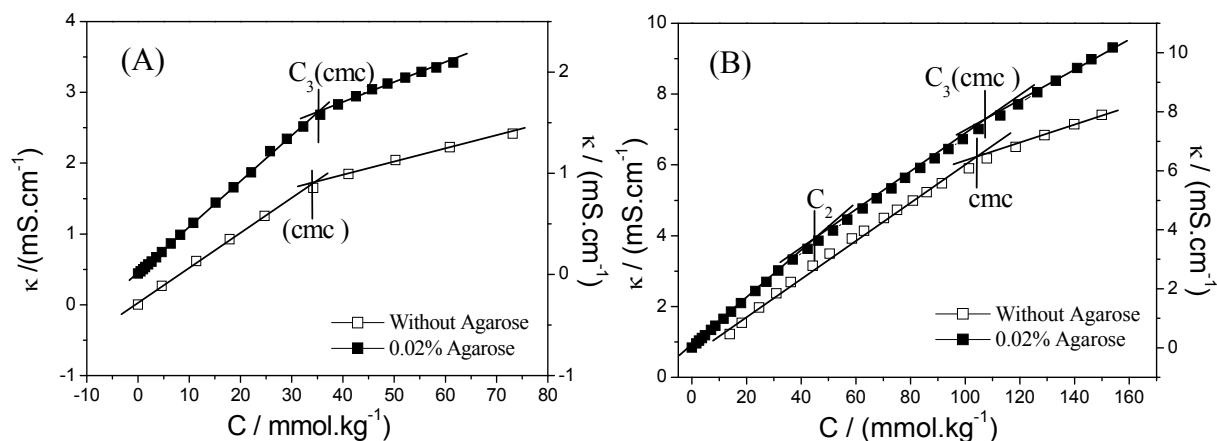


Fig. S1 Specific conductance (κ) as a function of IL concentration: (A) $[C_4mim][C_8OSO_3]$ and (B) $[C_8mim][Cl]$. Various transitions are marked with vertical line. (hollow and solid symbols correspond to left and right y-axis respectively)

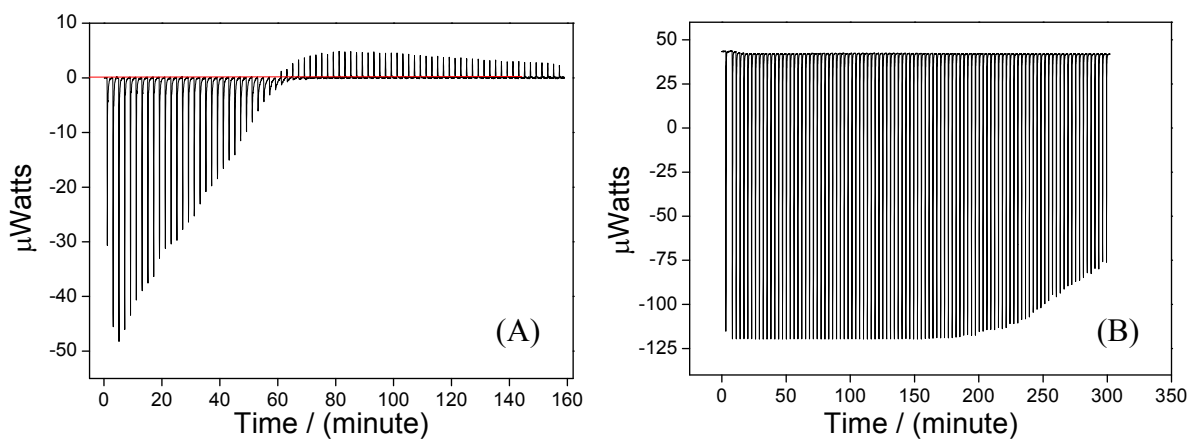


Fig. S2 Differential power plots of interaction of *Ag* with (A) $C_4mim][C_8OSO_3]$ (B) $[C_8mim][Cl]$

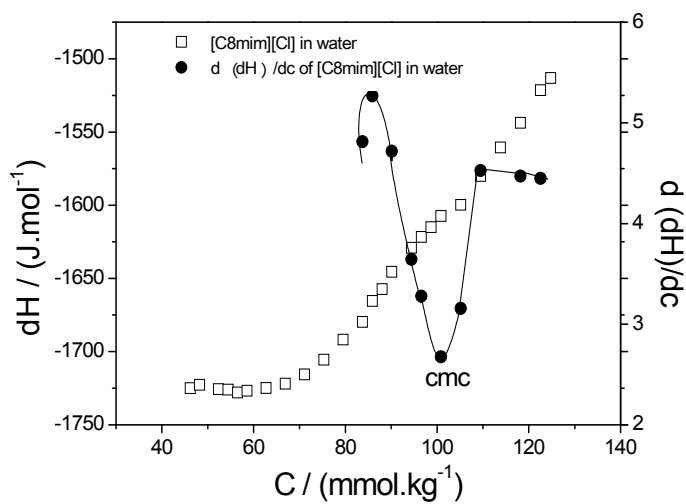


Fig. S3 ITC thermogram of $[C_8mim][Cl]$ dilution in water.
Derivative of thermogram showing transition at cmc.

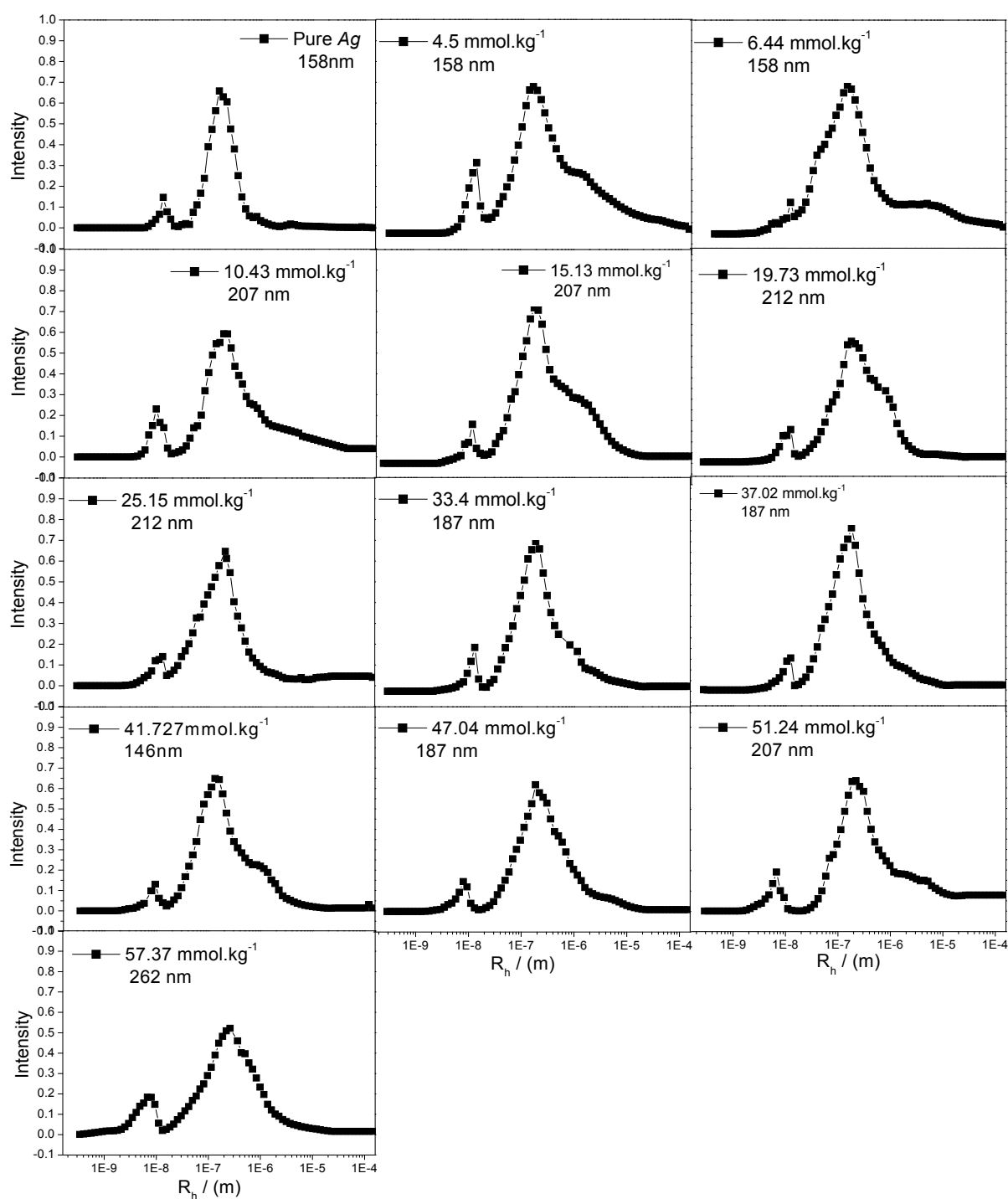


Fig. S4 Hydrodynamic Radii (R_h) distributions plotted against normalized intensity of $Ag-[C_4mim][C_8SO_3]$ complexes at various concentrations of $[C_4mim][C_8SO_3]$ in 0.02% agarose solution.

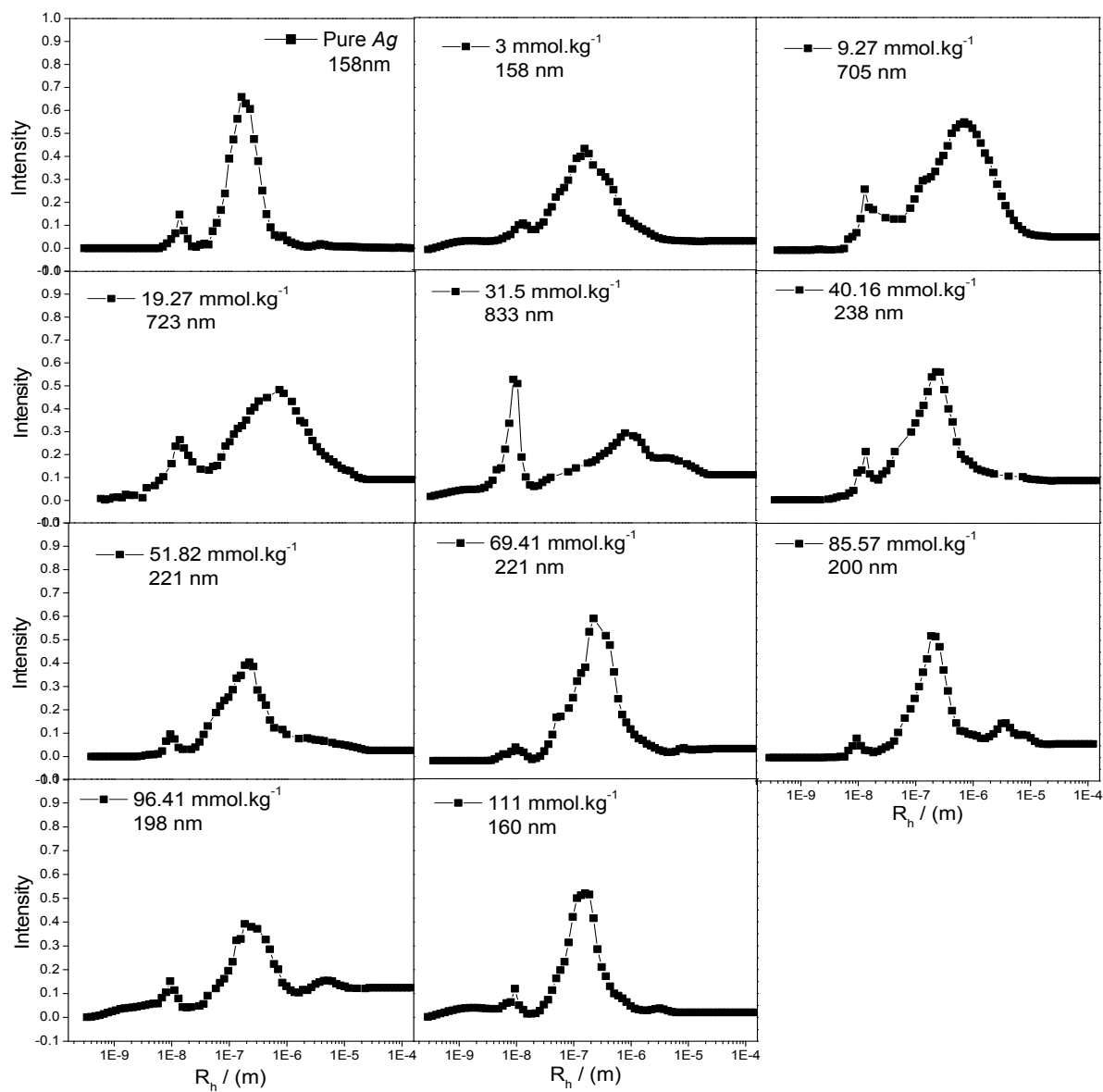


Fig. S5 Hydrodynamic Radii (R_h) distributions plotted against normalized intensity of $\text{Ag}-[\text{C}_8\text{mim}][\text{Cl}]$ complexes at various concentrations of $[\text{C}_8\text{mim}][\text{Cl}]$ in 0.02% agarose solution.

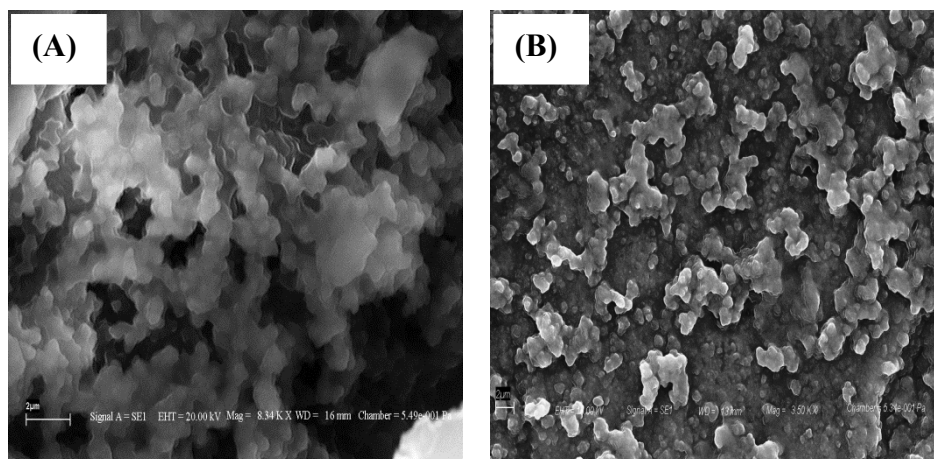


Fig. S6 SEM micrographs of (A) Native *Ag* (B) *Ag*-[C₄mim][C₈OSO₃] complex, and (C) *Ag*-[C₈mim][Cl] complex (bar in images correspond to 2 μm).

References:

1. Chakraborty, T.; Chakraborty, I.; Ghosh, S. *Langmuir* **2006**, *22*, 9905.
2. Chakraborty, T.; Chakraborty, I.; Moulik, S. P.; Ghosh, S. *J. Phys. Chem. B* **2007**, *111*, 2736.
3. Mitra, D.; Bhattacharya, S. C.; Moulik, S. P. *J. Phys. Chem. B* **2008**, *112*, 6609.