Supplementary Section

A detailed assessment on the interaction of sodium alginate with a surfaceactive ionic liquid and a conventional surfactant: a multitechnique

approach

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Table S1. Fitting parameters and lifetimes (τ_1 , τ_2 and $\langle \tau \rangle$) for different time resolved decay plots calculated using IBH DAS-6 software by nonlinear least square iterative method in presence of two different surfactants with their different concentrations in presence and absence of 0.005% (w/v) NaAlg.

| [NaAlg] = 0.005% (w/v) | | | | | | | |
|-----------------------------|----------------|----------------|----------|---------|---------------------|------|--|
| [C ₁₆ MImCl]/ mM | a ₁ | a_2 | $	au_1$ | $	au_2$ | <τ> | χ2 | |
| 0 | | | 123.5 | | 123.5 | 1.05 | |
| 0.012 | 13.5 | 86.5 | 32.57 | 124.8 | 112.3 | 1.06 | |
| 0.036 | 16.9 | 83.0 | 36.07 | 124.8 | 109.8 | 1.01 | |
| 0.073 | 23.1 | 76.9 | 39.14 | 120.6 | 101.8 | 0.99 | |
| 0.121 | 34.4 | 65.6 | 64.38 | 163.9 | 129.6 | 0.99 | |
| 0.211 | 35.2 | 64.8 | 75.76 | 192.3 | 151.3 | 1.01 | |
| 0.318 | 30.4 | 69.6 | 70.39 | 180.6 | 147.1 | 1.13 | |
| 0.469 | 29.7 | 70.3 | 69.44 | 170.9 | 140.7 | 1.08 | |
| 0.668 | 37.6 | 62.3 | 74.51 | 180.5 | 140.6 | 1.03 | |
| 0.943 | 27.9 | 72.0 | 67.64 | 161.9 | 135.5 | 0.95 | |
| 1.310 | 11.1 | 88.9 | 52.62 | 163.8 | 151.5 | 1.06 | |
| 1.756 | 17.1 | 82.9 | 83.42 | 184.7 | 167.4 | 1.06 | |
| 2.939 | 4.38 | 95.6 | 55.35 | 170.4 | 165.4 | 1.03 | |
| 3.690 | 9.17 | 90.8 | 81.80 | 175.3 | 166.7 | 0.99 | |
| 4.510 | 3.18 | 96.8 | 40.71 | 170.3 | 166.2 | 1.02 | |
| 5.353 | 6.96 | 93.0 | 82.24 | 174.1 | 167.7 | 1.02 | |
| [NaAlg] = 0.005% (w/v) | | | | | | | |
| $[C_{16}TPB]/mM$ | a ₁ | a ₂ | τ_1 | $	au_2$ | $	au_{\mathrm{av}}$ | χ2 | |
| 0 | | | 123.5 | | 123.5 | 1.05 | |
| 0.005 | 6.80 | 93.2 | 16.89 | 125.9 | 118.5 | 1.03 | |
| 0.017 | 20.6 | 79.4 | 21.50 | 123.3 | 102.3 | 1.01 | |
| 0.032 | 37.6 | 62.4 | 27.43 | 118.8 | 84.38 | 1.01 | |
| 0.058 | 52.2 | 47.8 | 29.65 | 113.3 | 69.65 | 1.05 | |
| 0.097 | 65.8 | 34.2 | 32.04 | 106.3 | 57.47 | 1.05 | |
| 0.146 | 71.3 | 28.7 | 32.11 | 82.93 | 46.72 | 1.12 | |
| 0.232 | 74.1 | 25.9 | 33.14 | 71.71 | 43.15 | 1.14 | |

| 0.338 | 74.9 | 25.0 | 32.05 | 70.67 | 41.72 | 0.95 |
|-------|------|------|-------|-------|-------|------|
| 0.446 | 80.3 | 19.7 | 32.14 | 54.52 | 36.54 | 1.06 |
| 0.555 | 53.9 | 46.1 | 25.80 | 47.49 | 35.79 | 1.09 |
| 0.695 | 74.4 | 25.6 | 27.72 | 54.82 | 34.65 | 1.06 |
| 0.852 | 24.2 | 75.8 | 18.55 | 35.59 | 31.46 | 1.16 |
| 1.025 | 79.0 | 20.9 | 26.81 | 64.89 | 34.79 | 1.03 |
| 1.220 | 11.4 | 88.6 | 17.47 | 31.60 | 29.98 | 0.97 |
| 1.424 | 74.1 | 25.9 | 26.31 | 42.58 | 30.52 | 1.05 |
| 1.707 | 8.98 | 91.0 | 10.27 | 30.57 | 28.75 | 1.09 |
| 1.965 | 11.9 | 88.0 | 12.61 | 31.34 | 29.09 | 1.11 |
| 2.274 | 12.5 | 87.5 | 19.99 | 29.84 | 28.60 | 1.08 |

Table S2. Coefficients of A, B_1 and B_2 values derived from the fitting of $Y = A + B_1^*X + B_2^*X^2$ of γ vs. log [surfactant] plots given in Fig. S3.

| [NaAlg] | C ₁₆ TPB | | | C ₁₆ MImCl | | |
|---------|---------------------|----------------|----------------|-----------------------|-------|----------------|
| % w/v | А | B ₁ | B ₂ | А | B_1 | B ₂ |
| 0 | 30.4 | -8.67 | 1.16 | 34.8 | -19.8 | -3.94 |
| 0.001 | 41.8 | 7.78 | 5.12 | 37.5 | -7.55 | -0.004 |
| 0.005 | 43.2 | -1.06 | 3.00 | 39.9 | -16.6 | -1.72 |
| 0.01 | 61.9 | 7.49 | 4.86 | 50.8 | -15.6 | -2.53 |

Fig. S1. Plot of reduced viscosity (cm³/gm) vs. concentration of alginate (gm/ml) at 298.15 K at a fixed NaCl concentration (0.1 M) $^{\#}$



Intrinsic viscosity $[\eta]$ of a polyelectrolyte can be determined in salt medium using Huggins equation:

$$\frac{\eta_{sp}}{C_P} = [\eta] + k_H [\eta]^2 C_P$$

where, η_{sp} is the specific viscosity and C_P is the concentration of NaAlg (gm/ml). k_H is the

Huggins constant. $\frac{\eta_{sp}}{C_p}$, termed as reduced viscosity in cm³/g unit. A stock NaAlg solution was prepared in 0.1 M NaCl solution and progressively added to a 0.1 M NaCl solution taken in an ubbelohde viscometer fitted in a thermostatic water bath at 298.15 K and flow times were measured in triplicate after each addition of stock NaAlg. Reduced viscosity vs. concentration of alginate was plotted (shown in above). Intrinsic viscosity determined for NaAlg is 235 cm³/gm at 298.15 K and 0.01 M NaCl medium. Average viscometric molecular weight (^{M}v) of NaAlg was determined using Mark–Houwink equation: [η] = K $^{M}v^{\alpha}$

K and α are constants and characteristic of the medium, temperature and polymer. K and α values are taken from Clementi *et. al.* [41], and Masuelli M. A. *et al.* [42]. K = 0.0023 cm³ /gm , $\alpha = 0.984$.

Fig.S2. Plot of % Intensity vs. hydrodynamic diameter of pure NaAlg (0.01% w/v) and with varying the concentrations of C_{16} MImCl (A) and C_{16} TPB (B) added to it. Concentrations of surfactants have been shown at the bottom of each plot. PDI values are given within a bracket beside each figure caption.



Free NaAlg 0.01% (PDI = 0.668)







NaAlg 0.01% + 0.30 mM C₁₆MImCl (PDI = 0.221)



NaAlg 0.01% + 1.42 mM C₁₆MImCl (PDI = 0.470)



NaAlg 0.01% + 3.32 mM C₁₆MImCl (0.490)





NaAlg $0.01\% + 0.05 \text{ mM C}_{16}$ TPB (PDI = 0.184)



NaAlg $0.01\% + 0.18 \text{ mM C}_{16}$ TPB (PDI = 0.186)







NaAlg 0.01% + 1.95 mM C16TPB (PDI = 0.150)



NaAlg 0.01% + 2.33 mM C16TPB (PDI = 0.181)

Fig. S3. γ with corresponding log[surfactant] values up to cmc /C_m* and fitted them with second order polynomials [a: free C₁₆MImCl, b: free C₁₆TPB, c: C₁₆MImCl + 0.001% (w/v) NaAlg, d: C₁₆MImCl + 0.005% (w/v) NaAlg, e: C₁₆MImCl + 0.01% (w/v) NaAlg, f: C₁₆TPB + 0.001% (w/v) NaAlg, g: C₁₆TPB + 0.005% (w/v) NaAlg, h: C₁₆TPB + 0.01% (w/v) NaAlg]



Fig. S4. ln (I_0/I) vs. [CPC] in presence of two different surfactants in presence and absence of NaAlg with varying wt %. Surfactant concentrations have been fixed to ~ 10 mM for each system showing in the legend.

