Colloidal Systems of Surface Active Ionic Liquids and Sodium Carboxymethyl Cellulose: Physicochemical Investigations and Preparation of Magnetic Nano-composites

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Supporting Information

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Annexure S1.

Details of methods used for various experiments: Interfacial behaviour of colloidal systems of NaCMC and different SAILs was investigated by using KRÜSS (Hamburg, Germany) Easy Dyne tensiometer by ring method using a platinum ring. Before each measurement, concentrated stock solution of respective SAILs was added to an aqueous solution of NaCMC and stirred for 3-4 min for complete solubilisation. The resultant solutions were kept for at least 5 min for equilibration. The temperature during experiment was controlled using a Julabo water thermostat within ±0.1 K. Measurements were performed in triplicate with an uncertainty of ± 0.15 mN m⁻¹. Specific conductance (κ) was measured employing a digital conductivity meter (Systronics 308) using a cell of unit cell constant. The temperature of measurement cell was controlled with a water thermostat within ± 0.1 K. Measurements were performed in triplicate with an uncertainty of less than 1%. Turbidity measurements were performed on Oakton T-100 Handheld Turbidity Meter from Cole-Parmer. The instrument uses infrared LED light source for measurements with an accuracy of 0.01 NTU. Zeta-potential (ζ-potential) and dynamic light scattering (DLS) measurements were performed on light scattering apparatus (Zeta-sizer, Nano-series, Nano-ZS) from Malvern Instruments, equipped with a built-in temperature controller having an accuracy of ±0.1 K using a path length of 1 cm employing a quartz cuvette. Aqueous solutions of NaCMC were filtered using a membrane filter having a pore size of 450 nm before addition of SAILs in order to eliminate chances of any possible contamination caused by dust particles. An average of 10 measurements was considered as experimental data. Scanning electron microscopy (SEM) measurements were performed using Zeiss Ultra 55-Limited edition scanning electron microscope. The samples for SEM measurements were prepared by placing a drop of colloidal suspension containing NaCMC-SAIL complexes at different concentrations of investigated SAILs on a cleaned glass surface and were dried for 24 hours in air. The samples were coated with silver in vacuum environment before measurement. Steady-state fluorescence measurements were performed using a Perkin Elmer LS-55 spectrophotometer using a quartz cuvette of path length 1 cm. Pyrene was used as polarity probe considering the sensitivity of ratio (I₁/I₃) of its first (I₁ at 373 nm) to third vibronic peak (I₃ at 384 nm) towards polarity of region surrounding pyrene. Fluorescence spectra were recorded in wavelength range 350–550 nm an excitation wavelength of 334 nm keeping
excitation and emission slit widths of 3 nm, each. The concentration of pyrene used was kept as 2 µM to avoid excimer formation. SAIL-NaCMC-Zinc ferrite (ZnFe$_2$O$_4$) nano-composites were prepared by doping already reported ZnFe$_2$O$_4$ nanoparticles (NPs)$^{62,63}$ into colloidal suspensions of NaCMC and SAILs at fixed concentration of respective SAILs. For example, 10 mg of ZnFe$_2$O$_4$ NPs were added to NaCMC-SAIL colloidal systems (160 ml) keeping concentration of respective SAIL at 1 mM. The samples were stirred vigorously for 2 hours to ensure complete homogenization. The prepared nano-composites were characterized using SHIMADZU MAXima 7000 powder X-ray Diffractometer, which is provided with Cu K$_\alpha$ radiation of wavelength 1.541Å in 20 range of 20°-70° using a step size of 0.02°. Shape and size of nano-composites was evaluated by transmission electron microscopy (TEM) using a JEM-2100 transmission electron microscope (TEM) at a working voltage of 200 kV without staining the sample. For obtaining TEM image, a drop of freshly prepared colloidal dispersion of NaCMC-SAIL or NaCMC-SAIL-Zinc ferrite (ZnFe$_2$O$_4$) nano-composites in colloidal form was placed on a carbon coated copper grid (300 mesh) and the residual solution was blotted off. The sample of pure ZnFe$_2$O$_4$ for TEM measurements was prepared by dispersing ZnFe$_2$O$_4$ NPs in ethanol followed by sonication prior to drop cast. The prepared samples were dried in air at room temperature for 24 h before measurements. Similarly, Magnetic studies of prepared nano-composites were carried out at 298.15 K in the applied magnetic field of -18 to +18 kOe using Microsense EV-90 vibrating sample magnetometer (VSM).

Annexure S2.

1. $\Gamma_{\text{max}}$ is calculated following the Gibbs adsorption equation:$^{1,2}$

$$\Gamma_{\text{max}} = -\frac{1}{2.303 nRT} \left( \frac{d\gamma}{d \log C} \right)_T$$

Where $n$, $R$, $T$, and $[C]$ is the number of species formed per molecule of ionic liquid surfactant (ILS) in solution upon ionization (it is 2 for investigated ILSs), the universal gas constant, absolute temperature and the molar concentration of ILS in solution, respectively.

2. $A_{\text{min}}$ was obtained from the relation:

$$A_{\text{min}} = 10^{23}/N_A \Gamma_{\text{max}}$$

where $N_A$ is the Avogadro’s number.
3. \( \Delta G^o_{ads} \) is calculated from the equation:

\[
\Delta G^o_{ads} = \Delta G^o_{mic} - \frac{\pi_{cmc}}{\Gamma}
\]

where \( \pi_{cmc} \) is the surface pressure at the saturated air-solution interface and is calculated as:

\[
\pi_{cmc} = \gamma_0 - \gamma_{cmc}
\]

where \( \gamma_0 \) the surface tension of the aqueous solution with/without NaCMC and \( \gamma_{cmc} \) corresponds to surface tension of solutions of SAILs aqueous solution at \( cmc \) with and without NaCMC respectively.\(^1,2\)

4. \( \Delta G^o_m \) is calculated from the equation:

\[
\Delta G^o_m = (1+\beta)RT \ln X_{cmc}
\]

Where \( R \) is universal gas constant, \( T \) is absolute temperature, \( X_{cmc} \) is \( cmc \) in mole fraction and \( \beta \) is degree of counterion binding, which is obtained using the ratio of slopes \( (1-S_2/S_1) \) where \( S_1 \) and \( S_2 \) are the slopes of pre and post micellar region respectively (i.e. before and after the \( cmc \)) of \( \kappa \) vs \( C \) plots.

**Table S1:** The comparison of various transitions obtained in the previous and present investigated biopolymer systems in the presence of SAIL-1, SAIL-2, SAIL-3. Note the values given in the tabular form are average values of transition obtained from various techniques.*Four transitions were obtained only in case of BSA.\(^3\)
**Figure S1(A,B):** (A) Hydrodynamic ($D_h$) diameter of colloidal complexes of NaCMC-SAILs in the presence of NaCMC as a function of concentration of SAIL (B) Bimodal distribution of particle size of NaCMC in 0.01% aqueous solution.

**Figure S2(A-C):** Scanning electron micrographs (SEM) of SAIL-2 in NaCMC (0.01%) solution at different transitions as (A) near $C_1$ (0.59 mmol L$^{-1}$); (B) $C_2$ (1.20 mmol L$^{-1}$); (C) $C_3$(cmc) (5.93 mmol L$^{-1}$).

**Figure S3(A-C):** Scanning electron micrographs (SEM) of SAIL-3 in NaCMC (0.01%) solution at different transitions as (A) $C_1$ (0.59 mmol L$^{-1}$); (B) Below $C_2$ = (1.20 mmol L$^{-1}$); (C) Near $C_3$(cmc) (5.93 mmol L$^{-1}$).
Figure S4(A-D): SAED pattern from transmission electron microscopy (TEM) of (A) Bare zinc ferrites (ZnFe$_2$O$_4$) NPs; the NPs encapsulated in SAIL-3 (B) $C_1$ (1mM); (C) $C_2$ (1.7mM); (D) $C_3_{(cmc)}$ (6.7mM).

Figure S5(A,B): (A) XRD pattern and (B) Hysteresis loop of Zinc ferrite ZnFe$_2$O$_4$ NPs, ZF; CM-1; CM-2; CM-3, composite of ZF with complexes of SAIL-1, SAIL-2 and SAIL-3 NaCMC respectively at 1.0mM.
Figure S6(A-B): (A) Hysteresis pattern of zinc ferrites NPs and its composites as; ZF, zinc ferrite; composite with SAIL-3 at near C1 (1 mM), CM-1; at C2 (1.7 mM), CM-2; at C3(cm)(6.7 mM) CM-3 in smaller range (B) Hysteresis pattern of only CM-3 for sake of clarity at 298.15K.

References: