Supporting Information

Surfactant and Gelation Properties of Acetylsalicylate Based Room Temperature Ionic Liquid in Aqueous Media

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NMR Spectral Data:

The NMR chemical shifts and assigned protons and carbon atoms along with MS spectral data for 1-dodecyl-1-methylpiperidinium chloride are: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.795 (3H, t, H_{19}), 1.196 (18H, m, H_{10}, H_{11}, H_{12}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}, H_{18}), 1.931 (2H, m, H_4), 2.590 (3H, s, H_7), 4.780 (2H, t, H_3,H_5), 7.880 (2H, d, H_2, H_6, H_8), 9.253 (2H, d, H_9). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (C_{19}), 19.4 (C_3C_5), 22.0 (C_4), 22.7 (C_{18}), 25.7 (C_9), 29.3 ($C_{14}C_{11}$), 29.6 ($C_{12}C_{13}C_{14}C_{15}$), 31.9 (C_{17}), 50.1 (C_7), 62.2 (C_8), 63.2 (C_2C_6). MS (m/z) = 309.5 (100 %), 31.25 (31.25 %).

The NMR chemical shifts and assigned protons and carbon atoms along with MS spectral data for 1-dodecyl-1-methylpiperidinium acetylsalicylate are ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.876 (3H, t, H_{19}), 1.312 (18H, m, H_{10}, H_{11}, H_{12}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}, H_{18}), 1.645 (2H, m, H_4),1.729 (6H, m, H_3, H_5, H_9), 2.091(3H, s, H_{13}), 3.241 (9H, m, H_2, H_6, H_7, H_8), 7.245 (1H, t, $H_{6'}$), 7.449 (1H, t, $H_{7'}$), 7.449 (2H, t, $H_{5'}$, $H_{8'}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (C_{19}), 19.4 (C_3C_5), 22.0 (C_4), 22.7 (C_{18}), 25.7 (C_9), 26.8 (C_{16}), 29.3($C_{11}C_{16}$), 29.6 ($C_{12}C_{13}C_{14}C_{15}$), 31.9 (C_{17}), 50.1 (C_7), 63.2 (C_2C_6), 120.5 ($C_{5'}$), 126 ($C_{7'}$), 129.6 ($C_{2'}$), 130 ($C_{8'}$), 134($C_{6'}$), 153.6 ($C_{3'}$), 169.0 ($C_{11'}$), 177($C_{1'}$). MS (m/z) = 447.33 (100 %), 421.4 (26.3 %) 389.33 (71.39 %), 222.0 (30.32 %)

Surface Active Parameters:

The surface active parameters namely the area per adsorbed molecule at the air/water interface, a_1^s (which measures the packing densities in terms of area occupied by molecules in a unit area on the surface), the saturation adsorption values, Γ_{max} at the air/water interface, pC_{20} (which defines the concentration of an amphiphile at which the surface tension of water is reduced by 20 mNm^{-1} and gives a measure of the adsorption efficiency at air/water interface) and the surface pressure, π_{CMC} were calculated using the equations:

$$a_1^s = 10^{26} / N_A \Gamma_m \quad (1)$$

$$\Gamma_{max} = -\frac{1}{2RT}\left(\frac{\partial \gamma}{\partial \ln C}\right) \quad (2)$$

where, R = 8.314 J mol^{-1} K^{-1}, T = absolute temperature in K, γ = surface tension values in mNm^{-1}, C = concentration in $mol.dm^{-3}$ and N = Avogadro's number. The Γ_{max} is expressed in $mol.cm^{-2}$ and area per molecule (a_1^s) at air/water interface is expressed in $Å^2$.

$$pC_{20} = - \log C_{20} \quad (3)$$

where, C is the molar concentration of surfactant and C_{20} stands for the concentration of IL required to reduce the surface tension of water by 20 mN m^{-1}.

$$\pi_{CAC} = \gamma_0 - \gamma_{CAC} \quad (4)$$

γ_0 is the surface tension of pure solvent i.e. water and γ_{CAC} is the surface tension of the solution at CAC.

Thermodynamic Parameters of Aggregation:

Gibbs free energy of aggregation, ΔG_{agg} is calculated directly from the binding constant, K_a using the relation,

$$\Delta G_{agg} = -RT \ln K_a \quad (5)$$

The change in entropy of aggregation, ΔS_{agg} is then obtained from the relation,

$$\Delta G_{agg} = \Delta H_{agg} - T\Delta S_{agg} \quad (6)$$

The thermodynamic parameters of aggregation are also calculated by describing the aggregation process in terms of mass action model, following the line of Moroi. The following relations were used for calculating various thermodynamic parameters of aggregation. The Gibbs free energy of aggregation i.e. the Gibbs free energy change per the

transfer of one mole of [C_{12}mpip][AcSa] from aqueous to the aggregation phase is given by the relation,

$$\Delta G_{agg} = (2 - \beta)\, RT \ln X_{CAC} \quad (7)$$

where, X_{CAC} is the critical aggregation concentration in mole fraction units, β represents the degree of counter ion binding namely the fraction of amphiphile ions in the aggregate neutralized by the counter anions. The values of β were calculated from (1-α), where α is the ratio of slopes of the two linear lines drawn through the pre and post aggregation regions corresponding to the specific conductance versus concentration. The enthalpy, ΔH_{agg} and entropy, ΔS_{agg} of aggregation are calculated through the relations,

$$\Delta H_a^0 = -(2 - \beta)\, RT^2 \left(d\ln X_{CAC} / dT\right) \quad (8)$$

and $$\Delta S^0_a = (\Delta H^0_a - \Delta G^0_a) / T \quad (9)$$

where $d\ln X_{CAC}/dT$ is obtained as slope of the linear plot of $\ln X_{CAC}$ vs. T.

Shape of the Micellar Aggregates from $\overline{D}_o$:

For obtaining the information about the shape of the micellar aggregates from the mean translational diffusion coefficients at zero concentration ($\overline{D}_o$), we employed Stokes law (assuming aggregates to be spherical) and Tanford formula (assuming micellar aggregates to be of oblate or prolate ellipsoids of revolution). This procedure requires the initial input values of hydrodynamic radius, R_h (spherical shape) or values of semi-major (b) and semi-minor axis (a). Considering that the micellar aggregates consists of the [C_{12}mpip][AcSa] molecules, with a fully stretched dodecyl chain, the values of b ranging from 13 to 30 Å and values of a ranging from 12 -18 Å (more than double of size of the head group [mpip]) were considered. The iteration process gives the frictional coefficient, f(t) as output. The mean difference between the experimental f(t), as obtained directly using eq 6 of the main text and

f(t) values calculated from a given set of a and b values was found to be 0.0005 and 0.015 for formulas of prolate and oblates shaped aggregates respectively. Therefore, it is assumed that the micelles of $[C_{12}mpip][AcSa]$ in water are of prolate shaped.

Rheological Measurements:

Carreau –Yasuda Model[1,2]:

The steady state shear rheology is well described the Carreau – Yasuda model, which relates the shear viscosity, η with zero shear, η_o, and infinite – shear viscosity, η_α through the relation;

$$\eta = \eta_\alpha + (\eta_o - \eta)[1 + (\dot{\gamma} / \dot{\gamma}^*)_a]^{(n-1)/a} \quad (10)$$

where η_α (= 0.0001Pa.s), is characteristics shear rate for the onset of shear thinning (=10 s^{-1}), n is the power law exponent (= 0.01) and *a* is the dimension less fitting parameter (= 1.14) that influences the speed of transition from constant shear viscosity to the power – law region.

The rheological behavior of worm-like micelles can be described well through Maxwell model with a single relaxation time, τ_R, for which the storage modulus, G'(ω), loss modulus G''(ω) and the magnitude of the complex viscosity $[\eta^*]$ are given by equations

$$G'(\omega) = G_0 (\omega^2 \tau^2_R / 1 + \omega^2 \tau^2_R) \quad (11)$$

$$G''(\omega) = G_0 (\omega\tau_R / 1 + \omega^2 \tau^2_R) \quad (12)$$

$$[\eta^*] = \frac{\sqrt{G'^2+G''^2}}{\omega} \quad (13)$$

where, G_0 is the plateau modulus of G'(ω), τ_R is the relaxation time, which is equated to 1/ ω_{co}, ω_{co} is the cross over frequency or frequency at which G'(ω) is equal to G''(ω).

Kinetic Models for Drug Release[3]:

There exists several models based on different mathematical functions to describe the drug dissolution profiles. Depending upon the suitable function selected to express the release data, the dissolution or release profiles are evaluated in terms of the model parameters.

Zero-order model.

The zero order rate describes the systems where the drug release rate is independent of its concentration.

$$Q_t = Q_O + K_O \quad (14)$$

In this equation Q_t is the cumulative amount of drug released at time t, Q_0 is the initial amount of drug, at t=0 and K_0 is the corresponding release rate constant expressed in units of concentration / time, t. This relationship can be used to describe the drug dissolution from matrix tablets with low soluble drugs.

First order model.

The first order rate describes the release from system where it is concentration dependent:

$$\text{Log } Q_t = \text{Log } Q_O - \frac{K_1}{2.303} t \quad (15)$$

where, Q_0 is the initial concentration of drug, Q_t is the cumulative amount of drug released at time t and K_1 is first order constant expressed in units of time, t. This relationship is used for describing the drug dissolution from various dosage forms containing water soluble drugs in porous matrices.

Hixson Crowell model.

The Hixson Crowell cube root law describes the release from systems where there is a change in surface area and diameter of particles,

$$Q_o^{1/3} - Q_t^{1/3} = K_{HC}t \quad (16)$$

where, Q_t is the amount of drug released in time t, Q_0 is the initial amount of the drug in the micelle and K_{HC} is the rate constant. This expression is applicable for dosage forms such as tablets, where the dissolution occurs in planes that are parallel to the drug surface.

Higuchi model.

Higuchi described the release of drugs from insoluble matrix as a square root of time dependent process based on Fickian diffusion,

$$Q_t = K_H t^{1/2} \quad (17)$$

where, K_H is the constant reflecting the design variables of the system. Hence drug release rate is proportional to the reciprocal of the square root of time. This model is usually used to describe the drug dissolution from matrix tablets with water soluble drugs.

Koresmeyer- Peppas model.

$$Q_t = K_M t^n \quad (18)$$

where. Q_t is the amount of drug released in time t n is diffusion release exponent K_M is the constant reflecting the design variables of the system. In this model the values of n characterizes the release mechanism of drugs: $0.45 \leq n$ – Fickian diffusion, $0.45 < n < 0.89$ to non – Fickian transport, n – 0.89 – relaxational transport, $n > 0.89$ super case transport.

Ritger and Peppas model.

Ritger and Pepass have described a general of release of a solute mathematically in the form of a below given simple equation considering that the matrix systems themselves are non-swellable,

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(n+1)^2} \exp\left\{ - \frac{(2n+1)^2 \, D\pi^2}{l^2} \, t \right\} \qquad (19)$$

where M_t/M_∞ is the fractional amount of drug released, l is the thickness of the hydrogel matrix, t is the time, D_{drug} is the drug diffusion coefficient for diffusion in one dimensional x – direction. M_t is the mass of the drug released at time, 't' and M_∞ is the mass of the drug released at infinite time. The above equation can be simplified to a linear one just by taking only the first term in the summation series:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\frac{8}{\pi^2} - \frac{D\,\pi^2}{l^2}\, t \qquad (20)$$

So, by plotting ln (1- M_t/M_∞) against t, D_{drug} can be determined from the slope value ($-D\pi^2/l^2$). We have fitted our experimental data on fractional drug released to eq. 20 and determined the slope values through a linear regression based on least squares method.

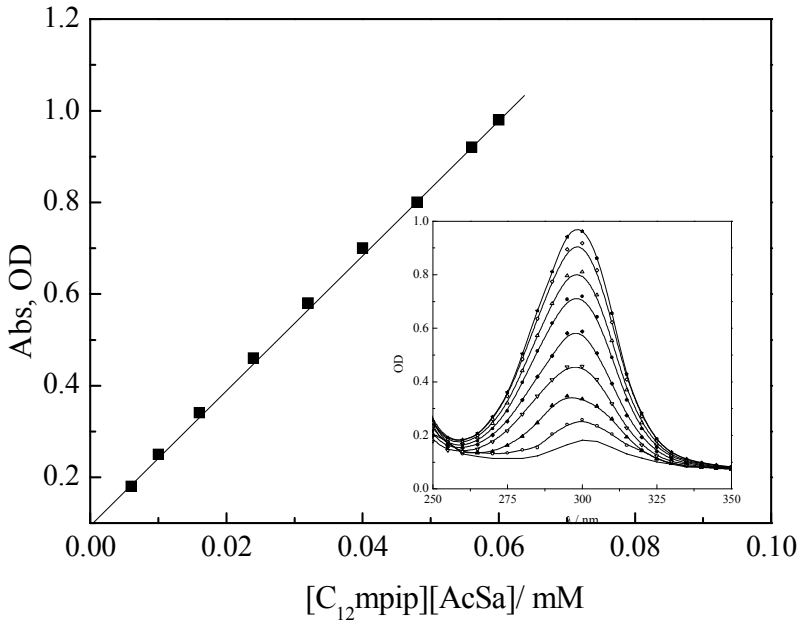

Figure S1. Calibration plot of absorption vs [[C_{12}mpip][AcSa]] in aqueous solution (abs. measured at λ_{max} = 230 nm)

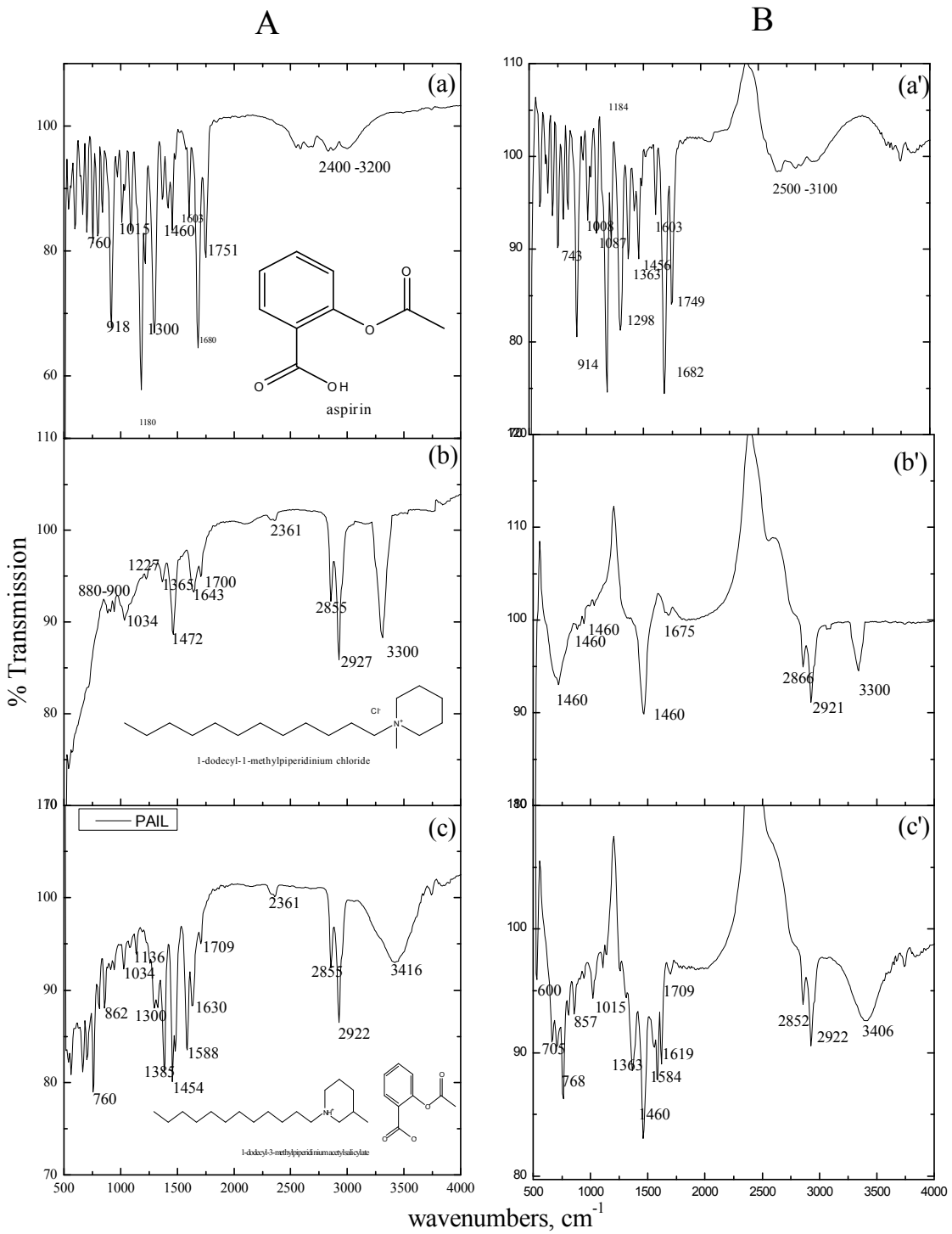

Figure S2. ATR-FTIR spectra of acetylsalicylic acid (a)(a'), $[C_{12}mpip][Cl]$ (b)(b'), $[C_{12}mpip][AcSa]$ (c)(c') in pure state (A) and in D_2O solutions (B).

Table S1. Assignment of ATR-FTIR spectral features for $[C_{12}mpip][Cl]$, Acetylsalicylic acid and $[C_{12}mpip][AcSa]$

Functional Group	Frequency, cm^{-1}					
	Acetylsalicylic acid		$[C_{12}mpip][Cl]$		$[C_{12}mpip][AcSa]$	
	Pure	in D_2O	Pure	in D_2O	Pure	in D_2O
C–H alkane	–	–	2900 – 2850	2900 – 2850	2900 – 2850	2900 – 2850
C–H bend aromatic	768	743	–	–	760	768
–OH of carboxylic acid	2400 – 3200	2500 – 3000	–	–	–	–
–C=O stretch	1680	1680	–	–	1710	1710
C=C stretch	1603	1603	–	–	1588	1588
–NH, stretch	–	–	3300	3300	3000–3650	3000–3650

Table S2. Zero shear viscosities of $[C_{12}mpip][AcSa]$ + SS mixture solutions prepared by mixing equimolar concentrations (in mM) at 298.15 K

	η_o Pa.s			
$X_{[C12mpip][AcSa]}$	100	200	400	600
1	0.004	0.002	0.001	0.001
0.9	0.045	0.003	0.001	0.001
0.8	0.373	0.003	0.001	0.001
0.7	0.355	0.003	0.010	0.011
0.6	0.040	0.003	0.043	0.015
0.5	0.013	581.4	0.677	0.016
0.4	0.348	1262.2	1.185	0.017
0.3	2.973	574.2	0.594	0.011
0.2	5.740	0.555	0.011	0.002
0.1	2.857	0.050	0.008	0.001
0	0.010	0.010	0.008	0.001

Table S3. Summary of constants for various models tried for drug anion release data

T °C	Zero Order Release model		First Order Release model		Hixson-Crowell release model		Higuchi Release model		Koresmeyer Peppas model			Ritger and Peppss model	
	r^2	K_o	r^2	K_1	r^2	K_{HC}	r^2	K_H	r^2	n	K_m	r^2	K
20	0.993	-0.108	0.882	0.813	0.988	-0.002	0.933	-2.55	0.923	0.1	0.43	0.975	0.03
37	0.92	-0.13	0.978	0.827	0.941	-0.002	0.986	-3.07	0.705	0.08	2.08	0.972	-0.05

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(1) Bird R. B.; Armstrong R. C.; Hassager O.; Dynamics of Polymeric Liquids, John Wiley and Sons, New York **1987.**

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