Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Bile Salt-Surface Active Ionic Liquid Mixtures; Mixed Micellization and Solubilization of Phenothiazine

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Evaluation of Thermodynamic Parameters

Various thermodynamic parameters have also been evaluated for the aqueous bile salt-SAIL mixtures. The standard free energy of micellization (ΔG^{o}_{m}, change in free energy accompanying the formation of 1 mole of micelles at a temperature of 298.15 K) and standard free energy of adsorption (ΔG^{o}_{ads}, work done to transfer the surfactant molecules in the monomeric form at the surface to the micellar stage through the aqueous medium at 298.15 K) have been computed using equations (1) and (2) respectively as

$$\Delta G_{m}^{0} = RT \ln X_{cmc} \tag{1}$$

$$\Delta G_{ads}^{0} = \left(\Delta G_{m}^{0}\right) - \left(\frac{\pi_{cmc}}{\tau_{max}}\right) \tag{2}$$

Where X_{cmc} is the cmc in mole fraction units. The ΔG^{o}_{m} and ΔG^{o}_{ads}values for NaC, NaDC, C_{12}mimBr and their binary mixtures are given in Table S1 below. Negative values of both ΔG^{o}_{m} and ΔG^{o}_{ads} confirm the spontaneity and feasibility of the micellization as well as adsorption phenomenon in NaC/NaDC + C_{12}mimBr mixtures. The more negative values of ΔG^{o}_{ads} relative to ΔG^{0}_{m} indicate the more spontaneity of the monolayer formation at air-water interface than the micellization phenomenon. Hence, adsorption of mixed surfactants at air-water interface is primary process whereas micellization is secondary so work needs to be done to transfer the surfactant molecules at interface to the micelles through aqueous medium. The ΔG^{o}_{m} and ΔG^{o}_{ads} values for the mixtures of NaC/NaDC with C_{12}mimBr are found to be higher in magnitude than the pure components hinting at the greater stability of the mixed micelles and the mixed monolayer respectively. As mentioned earlier, the micelles in the mixtures containing 0.4:0.6 mole fraction ratio of NaC/NaDC and C_{12}mimBr are the most stable ones. Further free energy at equilibrium (G^{s}_{min}) and excess free energy (ΔG_{ex}) have been computed using equations (3) and (4) respectively.

$$G_{min}^{s} = A_{min} \gamma_{cmc} N_{A} \tag{3}$$

$$\Delta G_{ex} = \left[X_{1}^{m} \ln f_{1}^{m} + \left(1 - X_{1}^{m}\right) \ln f_{2}^{m}\right] RT \tag{4}$$

The G^s_{min} values accounts for the synergism in mixed adsorbed monolayer formed. The G^s_{min} value for C_{12}mimBr is low but found to increase with increase in the mole fraction of bile salts, suggesting the enhanced favorable interactions in mixed monolayer of NaC/NaDC with C_{12}mimBr. Also negative values of ΔG_{ex} for the various binary mixtures of NaC/NaDC with C_{12}mimBr indicate the higher spontaneity and stability of mixed micelles, which is greater for NaDC + C_{12}mimBr mixtures.

Hence, to conclude the aqueous binary mixtures of NaC/NaDC with C_{12}mimBr exhibit strong synergistic activity both in the mixed micelles and at the mixed monolayer in comparison to their pure counter parts, owing to the presence of strong hydrophobic and electrostatic forces between the oppositely charged amphiphiles. These favorable interactions are however found to be highest in case of mixtures containing mole fraction ratios of NaC/NaDC : C_{12}mimBr to be 0.4:0.6. The size of the mixed micelles at this mixture composition is also found to be largest.

Table S1 Thermodynamic parameters: standard free energy of micellization (ΔG^o_m), standard free energy of adsorption (ΔG^o_{ad}), surface free energy (G^s_{min}), excess free energy (ΔG_{ex}) of binary mixtures of bile salts (NaC and NaDC) with SAIL (C_{12}mimBr)

$\alpha_{BileSalts}$	ΔG^o_m (kJ mol^{-1})	ΔG^o_{ad} (kJ mol^{-1})	G^s_{min} (kJ mol^{-1})	ΔG_{ex} (kJ mol^{-1})
		NaC + C_{12}mimBr		
0.0	-21.29	-36.07	12.79	-
0.2	-26.00	-53.55	27.40	-5.53
0.4	-26.36	-52.56	25.97	-5.83
0.6	-26.14	-56.31	30.49	-5.49
0.8	-25.44	-49.89	24.52	-5.28
1.0	-20.20	-46.27	42.27	-
		NaDC + C_{12}mimBr		
0.0	-21.29	-36.07	12.79	-
0.2	-27.18	-51.05	20.02	-6.17
0.4	-27.75	-53.97	22.09	-6.33
0.6	-27.43	-54.98	22.78	-6.09

0.8	-27.00	-53.05	22.92	-5.83
1.0	-22.00	-53.73	44.05	-

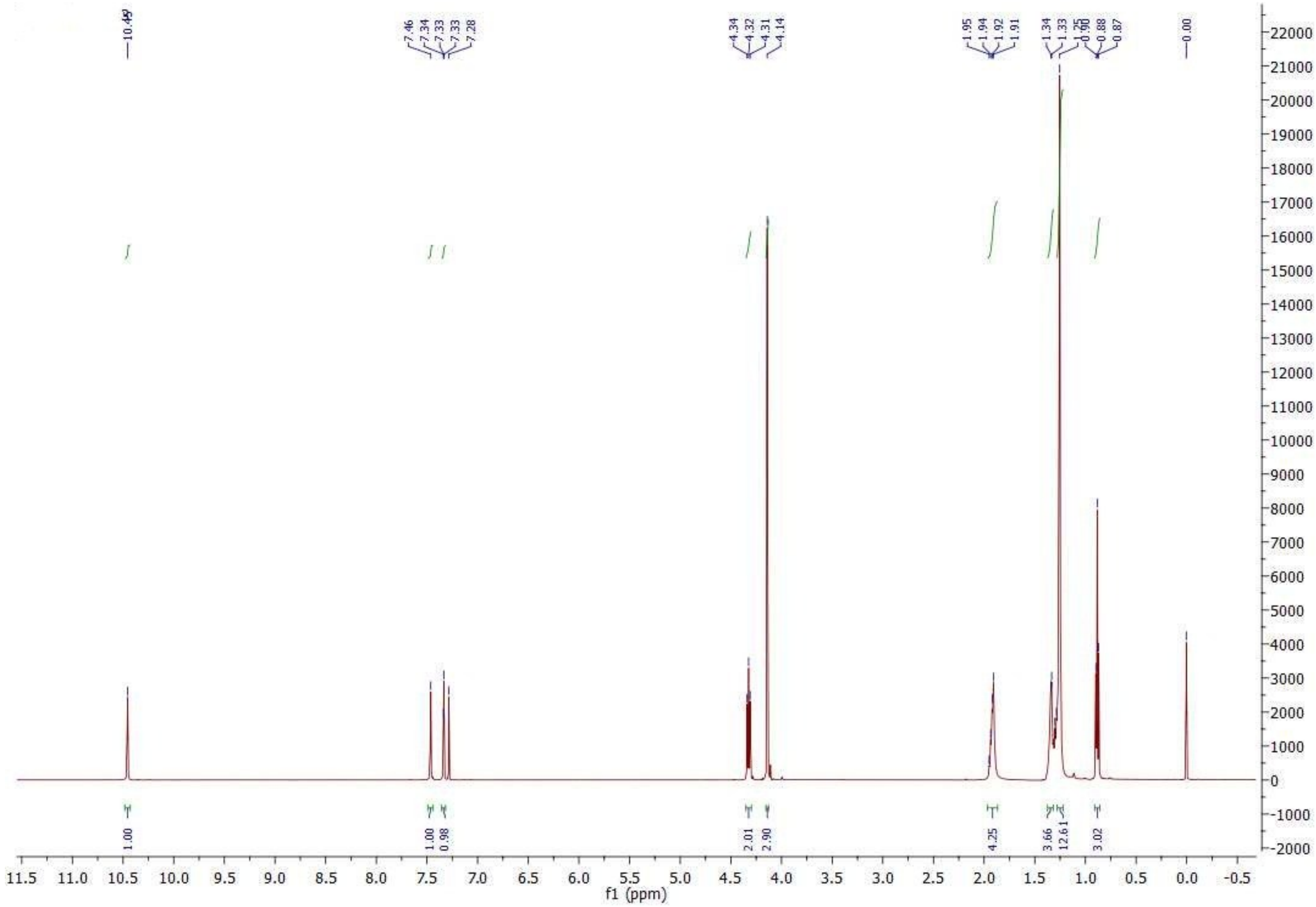
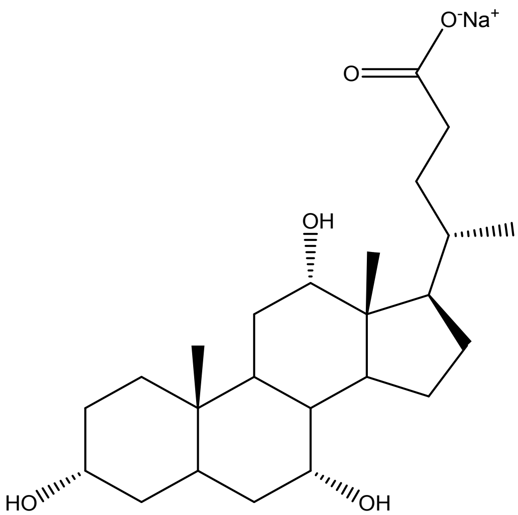


Fig. S1 ^{1}H NMR profile of 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) in $CDCl_3$

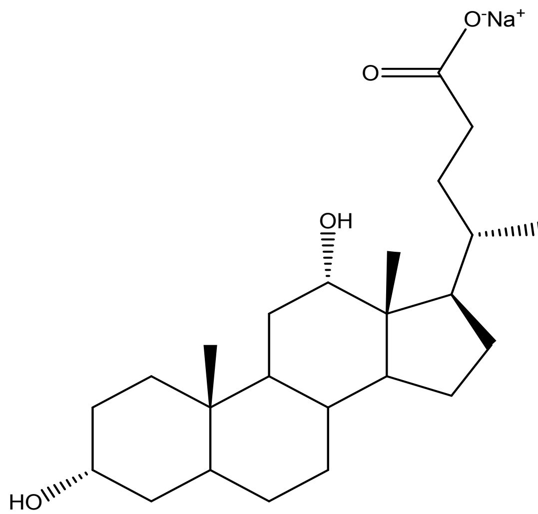
Characterization of C_{12}mimBr : ^{1}H NMR spectra of C_{12}mimBr was recorded on 500 MHz NMR in CDCl3. C_{12}mimBr contains total 31 protons and the details of chemical shift (δ) and coupling constant (J) of protons are as:

δ = 10.5 (s, 1H), δ = 7.46 (s, 1H), δ = 7.33 (t, J = 5.0 Hz, 1H), δ = 4.32 (t, J = 5.0 Hz, 2H), δ = 4.14 (s, 3H), δ = 1.91-1.94 (m, 4H), δ = 1.25-1.34 (m, 16H), δ = 0.88 (t, J = 5.0 Hz, 3H)

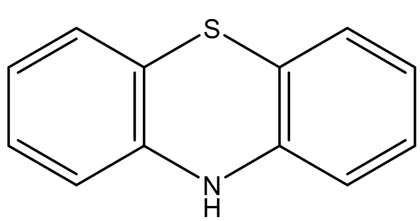
(a) 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr)



(b) Sodium Cholate (NaC)



(c) Sodium Deoxycholate (NaDC)



(d) Phenothiazine

Fig. S2 Basic structures of compounds used in present study

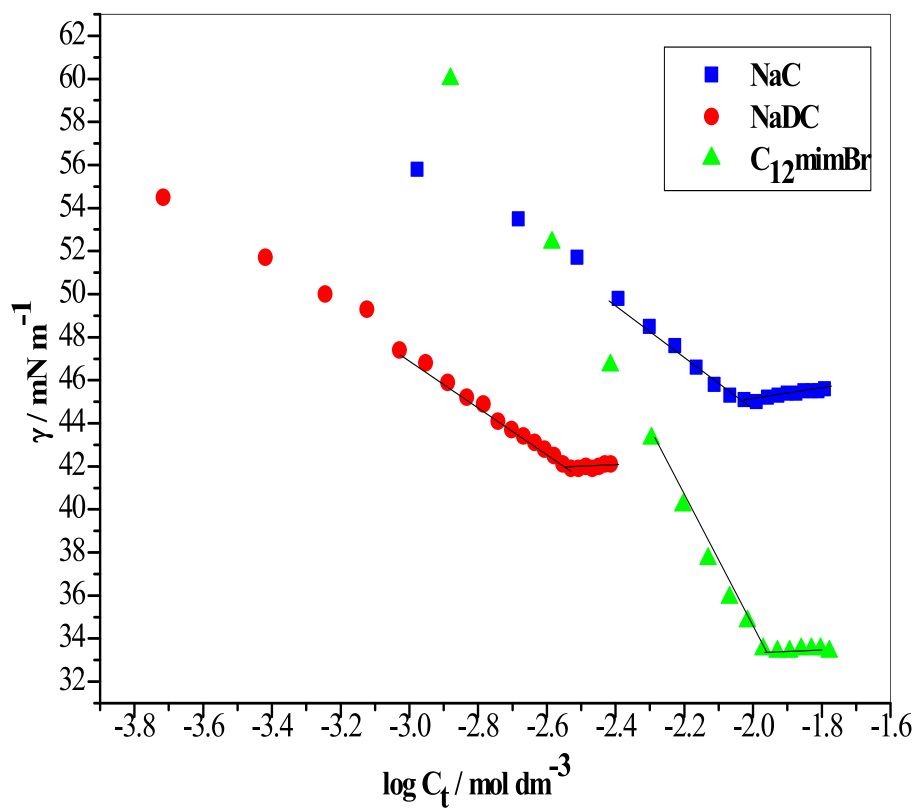


Fig. S3 Plot of surface tension (γ) *vs*. the logarithm of the total concentration (C_t) of pure amphiphiles: NaC, NaDC and C_{12}mimBr.

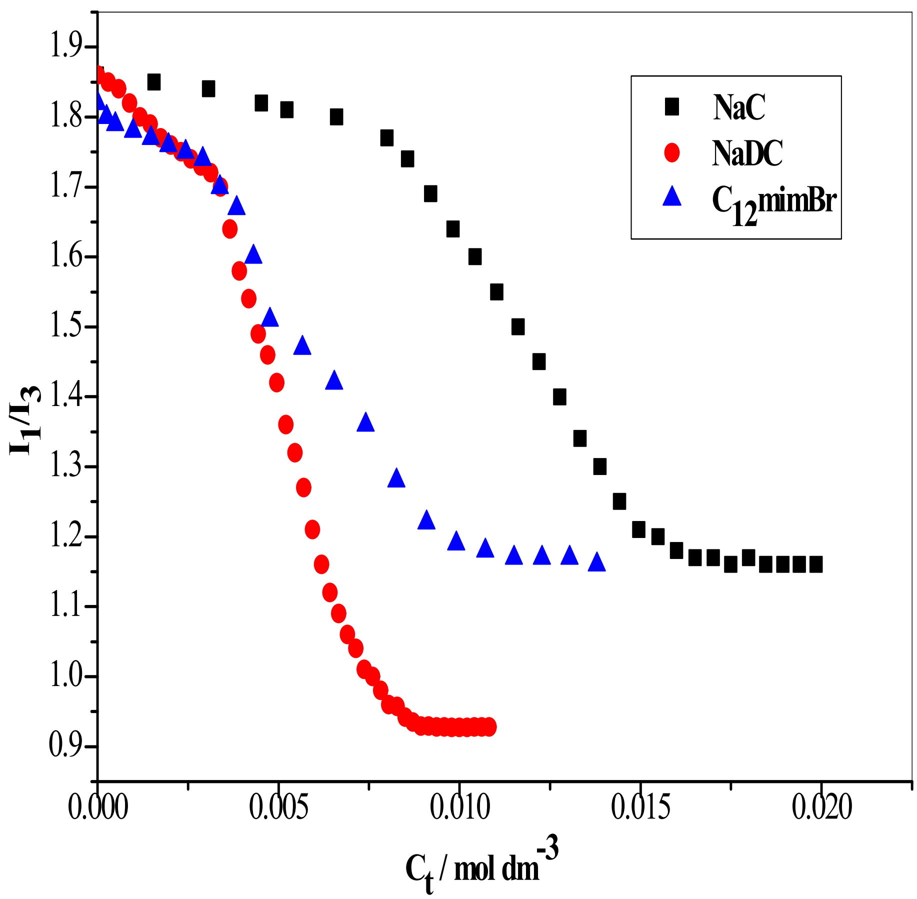


Fig. S4 Plot of pyrene intensity (I_1/I_3) ratio *vs*. the total concentration (C_t) of pure amphiphiles: NaC, NaDC and C_{12}mimBr.

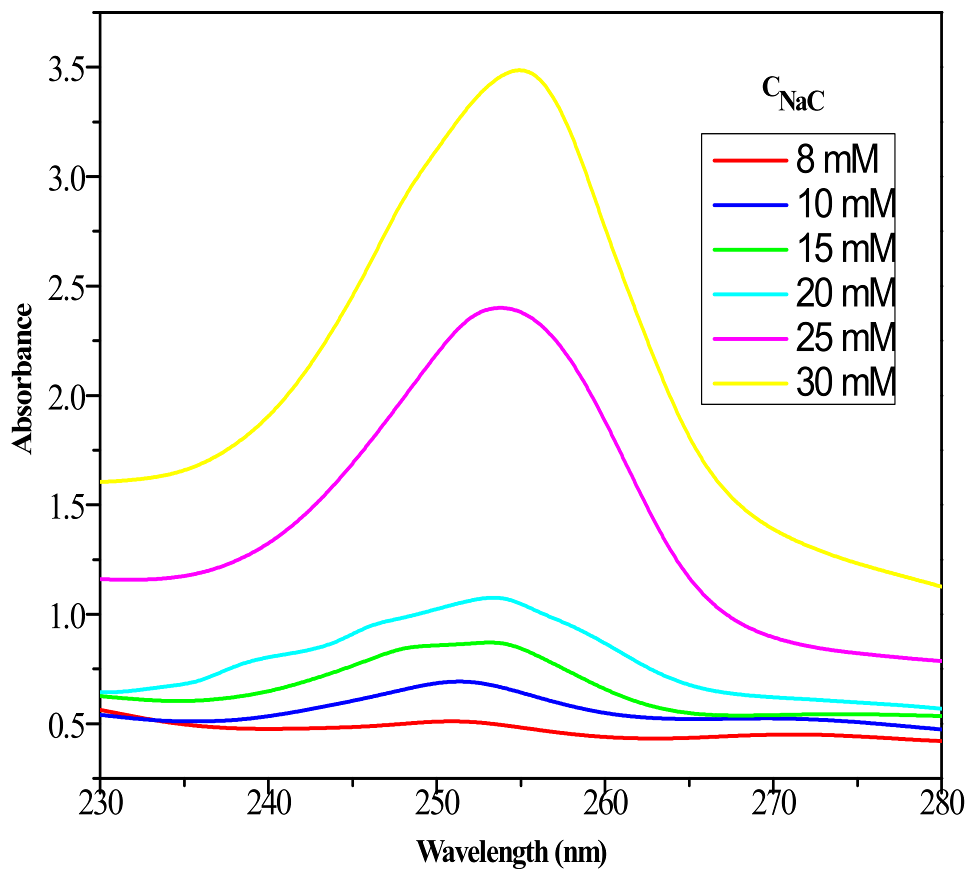


Fig. S5 UV-visible spectra of Pz loaded NaC aqueous solutions at various concentrations of NaC

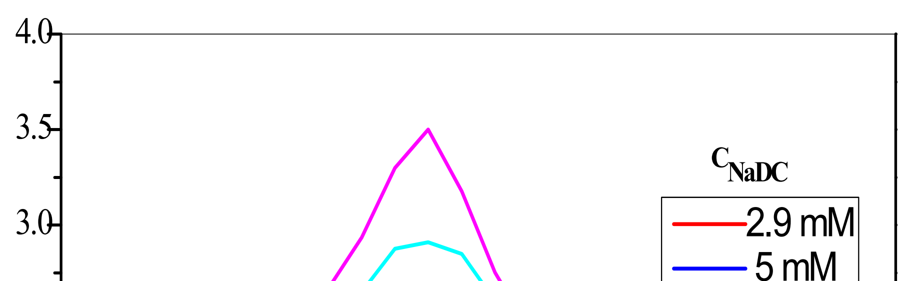


Fig. S6 UV-visible spectra of Pz loaded NaDC aqueous solutions at various concentration of NaDC

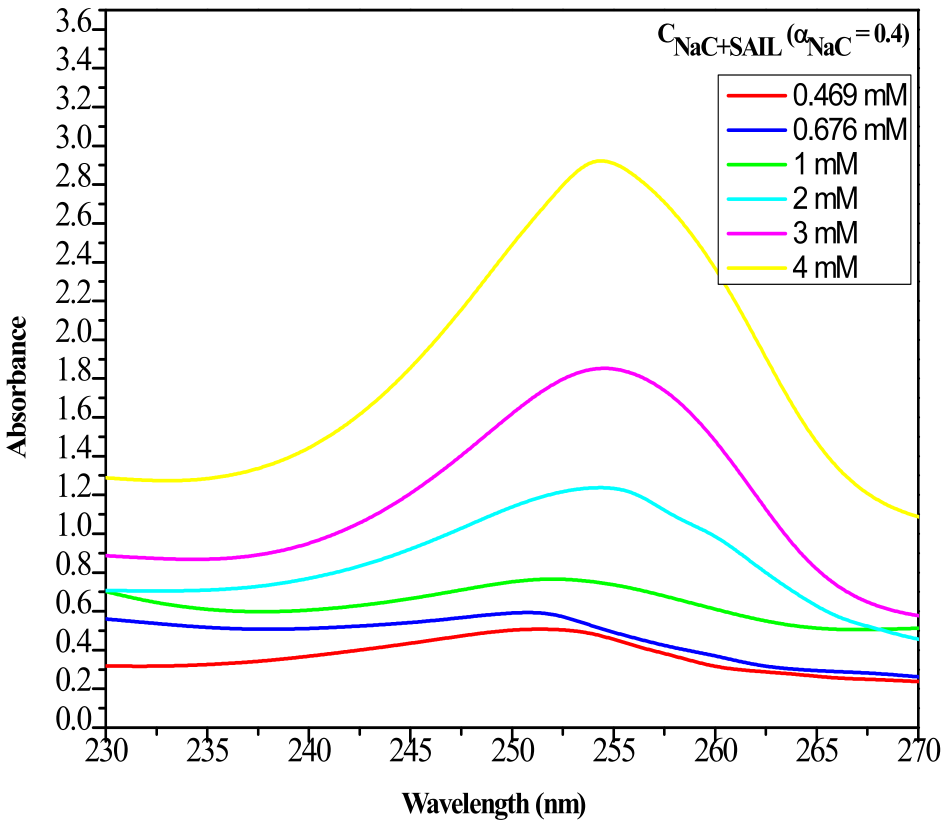


Fig. S7 UV-visible spectra of Pz loaded binary mixture of NaC+SAIL (α_{NaC} = 0.4) at various concentrations of NaC+SAIl mixture

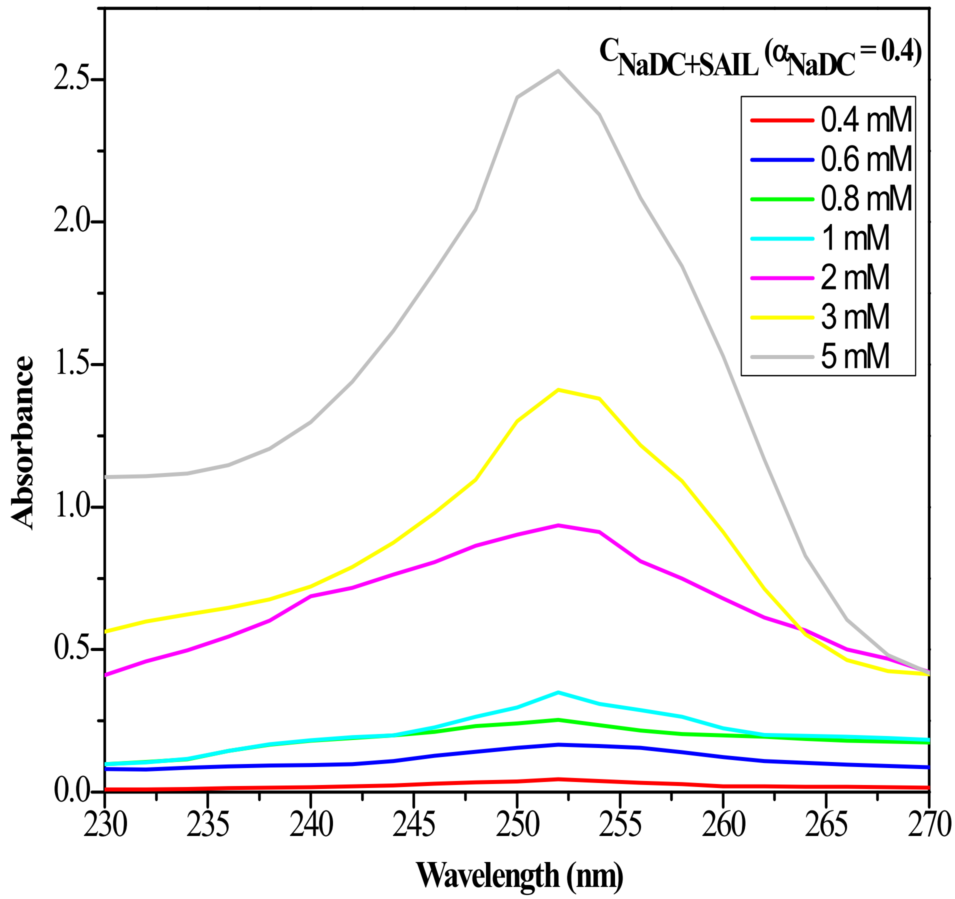


Fig. S8 UV-visible spectra of Pz loaded binary mixture of NaDC+SAIL (α_{NaDC} = 0.4) at various concentrations of NaDC+SAIL mixture