Supporting Information

Micellization and adsorption behaviour of bile salt systems

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Surface excess and minimum area per molecule of the single and mixed bile salt systems

To calculate the amount of surfactant adsorbed per unit area at the air/aqueous solution interface for different systems, the Gibb's adsorption equation[1] has been utilized. For a binary and ternary combinations, Gibb's surface excess of surfactant relative to a zero excess of water per unit area of surfactant is given by the equation

$$d\gamma = \sum \Gamma_i RTd \ln a_i \qquad (1)$$

where γ, Γ_i and a_i denote surface tension, surface excess (adsorption density) and the activity of ith component in the mixed film respectively. For a constant composition of the ionic surfactant mixtures having concentration C_1 of any one of the components, the equation[2] is

$$\Gamma = -\frac{1}{2.303RT}\left(\frac{d\gamma}{d\log C_1 + d\log \gamma_{\pm}}\right) \qquad (2)$$

The maximum adsorption denisty (Γ_{max}) and the minimum area per surface active component (A_{min}) in angstrom units can be found from the relations

$$\Gamma_{max} = -\frac{1}{2.303RT}\lim_{C_1 \longrightarrow cmc}\left(\frac{d\gamma}{d\log C_1}\right) \qquad (3)$$

$$A_{min} = \frac{10^{18}}{N\Gamma_{max}^{tot}} \qquad (4)$$

where N is the Avogadro's number. Since dilute solutions of the surfactants were used, the dlog $\gamma_{\pm}$ term was not considered in calculations.

Thermodynamics of micelle formation and adsorption at air/aqueous solution interface

The free energy of micellization per mole of monomer unit, ΔG^o_m, can be calculated by the equation,[1, 3]

$$\Delta G_m^o = (1+f)RT \ln cmc \qquad (5)$$

where f is the fraction of counterions bound to the micelles and is determined as described in above section. The standard free energy of adsorption,[1, 4] ΔG^o_{ad}, can be calculated using ΔG^o_m by the relation

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

where π_{cmc} is the surface pressure at cmc ($\pi_{cmc} = \gamma_{cmc} - \gamma_o$, γ_o and γ_{cmc} being surface tension of water and that of a given surfactant system at its cmc respectively).

For a complete thermodynamic analysis ΔH^o_m is required along with ΔG^o_m. The temperature effect on cmc can be used to estimate ΔH^o_m assuming aggregation number as well as the counterion binding to be independent of temperature. ΔG_m^0 can be obtained from the equation

$$\Delta G = -RT \ln CMC \qquad (7)$$

where, R is the Universal Gas constant and T is the absolute temperature.

$$\Delta H_m^0 = -RT^2 \frac{d \ln CMC}{dT} \qquad (8)$$

where $\frac{d \ln CMC}{dT}$ at each temperature can be calculated using the plot of $\ln CMC$ versus T and represents change in logarithm of cmc as a result of a small increment in temperature. Therefore, the entropy of micellization, ΔS^{o}_{m} follows from the Gibb's relationship

$$\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0 \qquad (9)$$

Table 1s

Critical micelle concentration, cmc, degree of counterion binding, *f*, maximum surface excess, Γ_{Max}, minimum area per molecule, A_{min}, and I_1/I_3 values of pure bile salts at different temperatures.

System	T (°C)	f	cmc (mM) (S.T)	cmc (mM) (Cond)	$\Gamma_{Max}/10^{-6}$ (mol m^{-2})	A_{min} (nm^2)	I_1/I_3
NaC	10	0.06	10.8	12.5	2.45	0.68	0.86
	20	0.08	7.78	8.25	2.58	0.64	0.88
	30	0.09	5.89	7.35	2.27	0.73	0.92
	40	0.08	6.10	7.50	2.45	0.68	0.96
NaTC	10	0.09	6.79	7.92	1.64	1.01	0.94
	20	0.06	6.68	7.30	1.78	0.93	0.94
	30	0.07	6.14	6.81	1.61	1.03	0.97
	40	0.09	6.36	7.20	1.88	0.88	1.01
NaDC	10	0.12	4.65	5.82	1.19	1.40	0.70
	20	0.16	3.80	5.36	1.13	1.47	0.69
	30	0.18	3.02	4.05	1.17	1.42	0.71
	40	0.18	3.16	4.32	1.25	1.33	0.73
NaTDC	10	0.11	2.01	2.21	3.30	0.50	0.71
	20	0.1	1.88	2.62	3.17	0.52	0.71
	30	0.09	2.43	2.90	3.26	0.51	0.72
	40	0.08	2.88	3.50	2.82	0.59	0.75

S.T. Stands for Surface Tension and Cond. for Conductance. The aggregation number of all the bile salts was found to be between 5-17 at 20 °C and found to be slightly temperature dependent. Error in the measurement of cmc was < 0.5%.

Table 2s

Critical micelle concentration, C_{mix} (experimental) and $^{ideal}C_{mix}$, maximum surface excess, Γ_{Max}, minimum area per molecule, A_{min} (experimental) and $^{ideal}A_{min}$ and I_1/I_3 values for equimolar binary bile salt systems at different temperatures.

System	T (°C)	C_{mix} (mM)	$^{ideal}C_{mix}$ (mM)	$\Gamma_{Max}/10^{-6}$ (mol m^{-2})	A_{min} (nm^2)	$^{ideal}A_{min}$ (nm^2)	I_1/I_3
NaDC-NaTC	10	5.95	5.52	1.26	1.32	1.20	0.72
	20	3.92	4.84	1.37	1.21	1.20	0.75
	30	4.75	4.05	1.56	1.06	1.23	0.76
	40	4.83	4.22	1.16	1.43	1.11	0.79
NaTC-NaTDC	10	2.77	3.10	2.26	0.74	0.76	0.75
	20	1.73	2.93	2.73	0.61	0.73	0.77
	30	1.59	3.48	2.80	0.59	0.77	0.78
	40	2.29	3.96	2.08	0.80	0.74	0.81
NaTDC-NaDC	10	2.96	2.81	2.13	0.78	0.95	0.70
	20	2.92	2.52	2.19	0.76	1.00	0.72
	30	2.63	2.69	1.59	1.04	0.96	0.73
	40	2.29	3.01	1.47	1.13	0.96	0.74
NaC-NaDC	10	4.40	6.50	1.37	1.21	1.04	0.71
	20	3.72	5.11	1.48	1.12	1.06	0.73
	30	3.96	3.99	1.60	1.04	1.08	0.75
	40	4.97	4.16	1.35	1.23	1.00	0.77
NaC-NaTC	10	9.22	8.32	1.77	0.94	0.85	0.88
	20	8.95	7.19	2.14	0.78	0.79	0.91
	30	8.00	6.01	2.73	0.61	0.88	0.93
	40	6.68	6.23	2.00	0.83	0.78	0.97
NaC-NaTDC	10	2.96	3.39	2.48	0.67	0.59	0.73
	20	2.75	3.03	2.54	0.65	0.58	0.76
	30	1.97	3.44	2.41	0.69	0.62	0.77
	40	2.60	3.91	2.54	0.65	0.63	0.80

Table 3s

Critical micelle concentration, C_{mix} (experimental) and $^{ideal}C_{mix}$, maximum surface excess, Γ_{Max}, minimum area per molecule, A_{min} (experimental) and $^{ideal}A_{min}$ and I_1/I_3 values for equimolar ternary bile salt systems at different temperatures.

System	T (°C)	C_{mix} (mM)	$^{ideal}C_{mix}$ (mM)	Γ_{Max} /10^{-6} (mol m^{-2})	A_{min} (nm^2)	$^{ideal}A_{min}$ (nm^2)	I_1/I_3
NaTC-NaDC-NaTDC	10	3.85	3.31	1.58	1.05	0.97	0.72
	20	3.32	3.56	1.83	0.91	0.97	0.75
	30	3.20	3.36	1.85	0.90	0.99	0.76
	40	2.65	3.53	1.83	0.91	0.93	0.77
NaTC-NaDC-NaC	10	6.25	5.99	1.97	0.84	1.03	0.75
	20	6.03	5.54	2.09	0.79	1.01	0.79
	30	5.20	4.52	2.07	0.80	1.06	0.81
	40	4.74	4.19	1.42	1.17	0.96	0.83
NaTDC-NaDC-NaC	10	4.15	3.73	1.63	1.02	0.86	0.72
	20	3.51	3.65	1.79	0.93	0.88	0.74
	30	3.32	3.33	1.73	0.96	0.89	0.76
	40	2.96	3.43	1.82	0.91	0.86	0.78
NaTC-NaTDC-NaC	10	1.50	3.83	2.43	0.68	0.73	0.78
	20	1.49	4.24	2.80	0.59	0.70	0.81
	30	1.47	4.10	2.53	0.66	0.76	0.83
	40	1.17	4.02	2.73	0.61	0.72	0.85

Table 4s

ΔG^o_m, ΔH^o_m, ΔS^o_m, ΔG^o_{ad} and π_{cmc} values for pure and equimolar binary and ternary bile salt systems at different temperatures.

System	T (°C)	ΔG^o_m (kJ mol^{-1})	ΔH^o_m (kJ mol^{-1})	ΔS^o_m (JK^{-1}mol^{-1})	π_{cmc} (mN/m)	ΔG^o_{ad} (kJmol^{-1})
NaC	10	-10.7	21.6	114.1	29.4	-22.7
	20	-11.8	21.6	113.9	30.6	-23.7
	30	-12.9	8.3	73.4	31.8	-27.0
	40	-13.3	-2.9	33.2	33.9	-27.1
NaTC	10	-11.8	1.1	45.2	27.8	-28.7
	20	-12.2	3.6	53.9	24.3	-25.9
	30	-12.8	1.9	48.6	27.1	-29.7
	40	-13.2	-2.9	32.7	24.0	-25.9
NaDC	10	-12.6	13.4	91.8	27.7	-35.9
	20	-13.6	15.4	98.8	26.8	-37.3
	30	-14.6	7.1	71.5	26.2	-37.0
	40	-15.0	-3.8	35.9	25.9	-35.7
NaTDC	10	-14.6	4.3	66.8	27.6	-23.0
	20	-15.3	-6.9	28.8	27.3	-23.9
	30	-15.2	-16.3	-3.9	27.0	-23.5
	40	-15.2	-14.0	4.0	23.7	-23.6
NaDC-NaTC	10	-12.1	27.8	140.9	28.8	-34.9
	20	-13.5	8.0	73.5	28.4	-34.2
	30	-13.5	-8.0	18.1	27.7	-31.2
	40	-13.9	-1.4	10.0	27.4	-37.5
NaTC-NaTDC	10	-13.9	31.5	130.0	29.3	-26.8
	20	-15.5	19.9	120.8	27.8	-25.7
	30	-16.2	-10.7	18.2	26.2	-25.6
	40	-15.8	-29.8	-44.7	27.4	-29.0
NaTDC-NaDC	10	-13.7	1.1	52.2	28.7	-27.2
	20	-14.2	4.3	63.1	29.5	-27.7
	30	-15.0	9.2	79.8	28.3	-32.8
	40	-15.8	11.3	86.5	25.7	-33.3

NaC-NaDC	10	-12.8	11.0	84.1	29.8	-34.5
	20	-13.6	3.7	59.1	28.7	-33.0
	30	-13.9	-11.0	9.7	29.1	-32.1
	40	-13.8	-18.4	-14.6	28.4	-34.8
NaC-NaTC	10	-11.0	2.0	42.8	29.2	-27.5
	20	-11.5	5.1	56.5	30.4	-25.7
	30	-12.2	11.2	77.0	29.9	-23.1
	40	-13.0	14.6	88.4	27.4	-26.7
NaC-NaTDC	10	-13.7	4.9	65.7	29.7	-25.7
	20	-14.4	14.6	98.9	29.3	-25.9
	30	-15.7	2.2	59.0	28.0	-27.3
	40	-15.5	-22.7	23.1	27.3	-26.2
NaTC-NaDC-NaTDC	10	-13.1	10.0	81.5	29.6	-31.9
	20	-13.9	6.7	70.2	28.5	-29.5
	30	-14.5	8.5	75.9	27.7	-29.4
	40	-15.4	15.2	97.9	26.9	-30.1
NaTC-NaDC-NaC	10	-11.9	2.4	56.9	29.9	-27.1
	20	-12.5	6.6	61.4	29.0	-26.3
	30	-13.3	9.2	65.6	28.2	-26.9
	40	-13.9	7.6	59.7	27.1	-33.0
NaTDC-NaDC-NaC	10	-12.9	11.1	84.7	29.9	-31.3
	20	-13.8	8.0	74.2	29.8	-30.4
	30	-14.4	6.5	68.8	29.1	-31.2
	40	-15.2	9.1	77.5	27.3	-30.1
NaTC-NaTDC-NaC	10	-15.3	0.2	54.6	28.7	-27.1
	20	-15.9	0.6	56.1	28.1	-25.9
	30	-16.4	9.3	84.7	28.1	-27.6
	40	-17.6	18.6	115.6	24.0	-26.4

Table 5s

Micellar mole fraction, X_1, interaction parameter, β, activity coefficients, g_1 and g_2 of two components for equimolar ternary bile salt systems according to Rubingh's pseudobinary treatment at different temperatures.

System	T (°C)	X_1	β	g_1	g_2
NaTDC-(NaTC-NaDC)	10	0.188	1.86	3.408	1.068
	20	0.303	0.92	1.567	1.089
	30	0.233	1.03	1.828	1.057
	40	0.246	0.39	1.250	1.024
NaTC-(NaDC-NaTDC)	10	0.147	0.72	1.690	1.016
	20	0.223	-0.49	0.743	0.976
	30	0.186	-0.10	0.933	0.996
	40	0.213	-0.41	0.777	0.982
NaDC-(NaTC-NaTDC)	10	0.0824	1.44	3.3584	1.01
	20	0.131	1.06	2.224	1.018
	30	0.142	1.24	2.481	1.025
	40	0.239	0.27	1.170	1.016
NaTC-(NaDC-NaC)	10	0.344	0.67	1.336	1.083
	20	0.056	1.89	5.400	1.006
	30	0.141	0.94	1.997	1.019
	40	0.454	-0.66	0.822	0.873
NaC-(NaDC-NaTC)	10	0.268	-0.61	0.722	0.957
	20	0.036	2.08	6.914	1.003
	30	0.131	1.07	2.245	1.019
	40	0.454	-0.52	0.856	0.898
NaDC-(NaC-NaTC)	10	0.668	0.05	1.005	1.022
	20	0.539	-0.09	0.981	0.974

	30	0.571	0.03	1.006	1.010
	40	0.513	-0.12	0.973	0.970
NaDC-(NaTDC-NaC)	10	0.076	1.59	3.892	1.009
	20	0.171	0.86	1.800	1.025
	30	0.206	0.35	1.602	1.023
	40	0.257	0.35	1.214	1.024
NaTDC-(NaDC-NaC)	10	0.551	1.11	1.251	1.401
	20	0.426	0.50	1.180	1.095
	30	0.442	0.00	1.000	1.000
	40	0.477	-1.20	0.719	0.761
NaC-(NaDC-NaTDC)	10	0.071	0.69	1.807	1.003
	20	0.188	-0.34	0.800	0.988
	30	0.164	0.19	1.145	1.005
	40	0.320	-0.63	0.748	0.938
NaTDC-(NaTC-NaC)	10	0.630	-3.82	0.592	0.220
	20	0.549	-4.64	0.389	0.247
	30	0.535	-4.65	0.367	0.264
	40	0.510	-5.52	0.266	0.238
NaC-(NaTDC-NaTC)	10	0.351	-4.80	0.132	0.554
	20	0.280	-2.85	0.228	0.799
	30	0.272	-2.23	0.307	0.848
	40	0.425	-4.50	0.226	0.444
NaTC-(NaTDC-NaC)	10	0.434	-4.27	0.255	0.448
	20	0.370	-4.05	0.201	0.574
	30	0.321	-3.01	0.249	0.734
	40	0.435	-4.86	0.212	0.399

Subscript 1 refers to Bile Salt Component Outside Parentheses while 2 for Two Bile Salts in Parentheses Treated as Single Component.

Table 6s

Micellar mole fraction, X_1, interaction parameter, β, activity coefficients, g_1 and g_2 of two components for equimolar binary bile salt systems according to Rubingh's formulation at different temperatures.

System	T (°C)	X_1	β	g_1	g_2
NaDC-NaTC	10	0.610	0.31	1.049	1.124
	20	0.596	-0.90	0.864	0.726
	30	0.749	0.77	1.050	1.544
	40	0.729	0.64	1.048	1.405
NaTC-NaTDC	10	0.278	-0.60	0.733	0.955
	20	0.397	-3.08	0.326	0.616
	30	0.418	-3.46	0.309	0.546
	40	0.410	-2.36	0.440	0.673
NaTDC:NaDC	10	0.724	0.28	1.021	1.156
	20	0.740	0.71	1.006	1.017
	30	0.544	-0.16	0.968	0.954
	40	0.515	-1.10	0.771	0.747
NaC-NaDC	10	0.388	-1.71	0.526	0.773
	20	0.394	-1.36	0.607	0.809
	30	0.341	-0.03	0.986	0.996
	40	0.256	0.84	1.593	1.057
NaC-NaTC	10	0.358	0.43	1.194	1.057
	20	0.432	0.89	1.330	1.180
	30	0.524	1.14	1.296	1.369
	40	0.512	0.28	1.070	1.077
NaC-NaTDC	10	0.228	-0.84	0.605	0.957
	20	0.244	-0.56	0.549	0.873

30	0.406	-2.51	0.412	0.662
40	0.401	-1.76	0.532	0.753

Subscript 1 refers to First Bile Salt in Each System.

Table 7s

Critical micelle concentration: C_{mix} (experimental), $^{ideal}C_{mix}$ and $^{RH}C_{mix}$, micellar mole fraction, X_i, activity coefficients, g_I, for equimolar ternary bile salt systems according to Rubingh-Holland treatment at different temperatures.

System	T (°C)	C_{mix} (mM) (S.T)	$^{ideal}C_{mix}$ (mM)	$^{RH}C_{mix}$ (mM)	X_1	X_2	X_3	g_1	g_2	g
NaTC(1):NaDC(2):NaTDC(3)	10	3.85	3.31	3.46	0.225	0.183	0.591	0.986	1.355	0.9
	20	3.32	3.56	2.24	0.342	0.146	0.511	0.325	1.343	0.6
	30	3.20	3.36	2.16	0.362	0.102	0.536	0.325	2.334	0.5
	40	2.65	3.53	2.59	0.248	0.269	0.483	0.651	1.017	0.6
NaTC(1):NaDC(2):NaC(3)	10	6.25	5.99	4.80	0.299	0.364	0.337	1.030	0.945	0.4
	20	6.03	5.54	4.41	0.224	0.526	0.251	0.985	0.735	0.7
	30	5.20	4.52	5.18	0.146	0.573	0.281	1.933	0.997	1.0
	40	4.74	4.19	5.88	0.244	0.525	0.232	1.502	1.181	1.7
NaTDC(1):NaDC(2):NaC(3)	10	4.15	3.73	3.33	0.529	0.256	0.215	1.043	0.933	0.4
	20	3.51	3.65	2.95	0.456	0.282	0.262	0.924	0.918	0.4
	30	3.32	3.33	2.42	0.490	0.195	0.315	0.659	1.373	0.4
	40	2.96	3.43	2.79	0.480	0.313	0.206	0.672	0.938	0.9
NaTC(1):NaTDC(2):NaC(3)	10	1.50	3.83	3.22	0.260	0.544	0.196	0.798	0.982	0.5
	20	1.49	4.24	2.39	0.341	0.574	0.084	0.350	0.595	1.2
	30	1.47	4.10	2.04	0.298	0.546	0.156	0.372	0.497	0.7
	40	1.17	4.02	2.82	0.282	0.522	0.197	0.623	0.626	1.0

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