Electronic Supplementary Information

Aggregative processes in aqueous solutions of mono- to tetra- ethylene glycol dimethyl ether at 298.15 K

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Table S1 Experimental values of density, ρ, for x_A monoglyme + $(1 - x_A)$ water at 298.15 K

x_A	ρ/kg m^{-3}	x_A	ρ/kg m^{-3}
0	997.0474	0.28000	940.498
0.01495	993.493	0.31990	932.519
0.03000	991.109	0.35999	924.968
0.04494	989.208	0.40024	918.096
0.06003	987.382	0.45008	910.492
0.07002	986.024	0.50027	903.590
0.07999	984.590	0.55970	896.266
0.09023	983.060	0.61995	889.847
0.10000	981.329	0.67999	884.039
0.11497	978.508	0.73932	878.968
0.13002	975.422	0.80056	874.075
0.15003	970.976	0.86016	869.783
0.17999	963.976	0.91059	866.516
0.21275	955.979	0.94988	864.154
0.23986	949.608	1	861.351

Table S2 Experimental values of V_m^E, u, $K_{S,m} = -(\partial V_m/\partial p)_S$ and of the excess molar quantity $K_{S,m}^E$ for x_A monoglyme + (1 − x_A) water at 298.15 K

x_A	V_m^E/cm^3 mol^{-1}	u/m s^{-1}	$K_{S,m}$/m^3 PPa^{-1} mol^{-1}	$K_{S,m}^E$/m^3 PPa^{-1} mol^{-1}
0	0	1496.687	8.09	0
0.01020	−0.0970	1530.12	8.10	−1.05
0.01993	−0.1967	1558.35	8.13	−2.01
0.02995	−0.3050	1583.10	8.20	−2.96
0.04530	−0.4739	1611.84	8.37	−4.31
0.05999	−0.6332	1639.27	8.63	−5.50
0.07503	−0.7884	1637.48	9.00	−6.59
0.09000	−0.9309	1637.52	9.46	−7.57
0.1100	−1.0995	1627.58	10.21	−8.71
0.1314	−1.2509	1608.03	11.18	−9.73
0.1611	−1.4158	1572.72	12.77	−10.85
0.1892	−1.5278	1535.88	14.51	−11.64
0.2219	−1.6133	1494.06	16.75	−12.28
0.2499	−1.6576	1460.86	18.82	−12.63
0.2800	−1.6849	1428.82	21.15	−12.87
0.3100	−1.7011	1400.73	23.56	−12.99
0.3400	−1.6991	1377.00	26.01	−13.03
0.3801	−1.6757	1349.05	29.39	−12.94
0.4201	−1.6360	1325.96	32.82	−12.75
0.4601	−1.5812	1306.30	36.30	−12.46
0.5104	−1.4922	1285.77	40.73	−12.00
0.5701	−1.3658	1264.91	46.12	−11.25
0.6447	−1.1843	1242.85	53.03	−10.06
0.7200	−0.9750	1224.00	60.20	−8.58
0.7899	−0.7494	1208.10	67.11	−6.89
0.8600	−0.5030	1193.36	74.28	−4.91
0.9300	−0.2545	1179.20	81.71	−2.61
1	0	1165.57	89.41	0

Table S3 Experimental values of V_m^E, u, $K_{S,m} = -(\partial V_m/\partial p)_S$ and of the excess molar quantity $K_{S,m}^E$ for x_A diglyme + $(1 - x_A)$ water at 298.15 K

x_A	V_m^E/cm^3 mol^{-1}	u/m s^{-1}	$K_{S,m}$/m^3 PPa^{-1} mol^{-1}	$K_{S,m}^E$/m^3 PPa^{-1} mol^{-1}
0	0	1496.687	8.09	0
0.00503	−0.0536	1520.18	8.09	−0.52
0.00999	−0.1100	1541.50	8.09	−1.03
0.01505	−0.1703	1561.32	8.12	−1.52
0.01998	−0.2306	1578.89	8.15	−1.98
0.02498	−0.2935	1594.79	8.20	−2.44
0.03001	−0.3577	1608.89	8.27	−2.88
0.03497	−0.4199	1620.86	8.35	−3.29
0.04001	−0.4824	1631.33	8.45	−3.69
0.05006	−0.6039	1646.83	8.70	−4.43
0.05497	−0.6612	1652.30	8.84	−4.77
0.05996	−0.7178	1656.10	9.00	−5.10
0.06497	−0.7729	1658.81	9.17	−5.41
0.07008	−0.8275	1660.43	9.36	−5.71
0.07505	−0.8778	1660.70	9.57	−5.99
0.08000	−0.9253	1660.04	9.78	−6.25
0.08488	−0.9701	1658.68	10.00	−6.49
0.10006	−1.0976	1650.33	10.75	−7.17
0.10999	−1.1726	1642.37	11.29	−7.56
0.11994	−1.2448	1633.08	11.86	−7.92
0.14011	−1.3768	1611.84	13.11	−8.52
0.17015	−1.5258	1578.13	15.17	−9.19
0.21003	−1.6442	1536.32	18.16	−9.76
0.25006	−1.7378	1499.97	21.34	−10.09
0.28998	−1.7863	1469.77	24.65	−10.23
0.33001	−1.7820	1444.01	28.11	−10.20
0.38009	−1.7444	1418.00	32.52	−10.02
0.44015	−1.6544	1392.57	37.96	−9.61
0.49994	−1.5218	1371.69	43.52	−9.00
0.55993	−1.3580	1354.55	49.19	−8.26
0.61999	−1.1820	1339.89	54.96	−7.39
0.68007	−1.0068	1327.10	60.80	−6.43
0.74029	−0.8381	1315.89	66.71	−5.39
0.79982	−0.6640	1306.10	72.61	−4.29
0.85953	−0.4790	1297.19	78.60	−3.09
0.91972	−0.2802	1289.18	84.68	−1.82
0.96949	−0.1093	1283.06	89.77	−0.71
1	0	1279.48	92.91	0

Table S4 Experimental values of V_m^E, u, $K_{S,m} = -(\partial V_m/\partial p)_S$ and of the excess molar quantity $K_{S,m}^E$ for x_A triglyme + (1 − x_A) water at 298.15 K

x_A	V_m^E/cm^3 mol^{-1}	u/m s^{-1}	$K_{S,m}$/m^3 PPa^{-1} mol^{-1}	$K_{S,m}^E$/m^3 PPa^{-1} mol^{-1}
0	0	1496.687	8.09	0
0.00502	−0.0623	1526.42	8.08	−0.57
0.01000	−0.1314	1553.36	8.09	−1.12
0.01501	−0.2022	1577.17	8.13	−1.64
0.02000	−0.2748	1598.79	8.18	−2.14
0.02499	−0.3487	1617.37	8.26	−2.61
0.03000	−0.4236	1633.41	8.35	−3.06
0.03500	−0.4959	1646.70	8.47	−3.46
0.03999	−0.5679	1657.49	8.61	−3.87
0.04502	−0.6396	1666.19	8.78	−4.25
0.05004	−0.7069	1672.69	8.96	−4.60
0.05501	−0.7714	1677.47	9.16	−4.93
0.05999	−0.8313	1680.44	9.38	−5.23
0.06498	−0.8897	1681.94	9.62	−5.52
0.06979	−0.9430	1682.14	9.86	−5.76
0.08001	−1.0456	1679.31	10.43	−6.27
0.09001	−1.1336	1673.18	11.04	−6.70
0.10004	−1.2138	1664.85	11.70	−7.06
0.11505	−1.3132	1649.89	12.76	−7.53
0.13008	−1.3936	1633.45	13.89	−7.90
0.14497	−1.4572	1616.56	15.09	−8.19
0.15997	−1.5045	1600.20	16.34	−8.43
0.17990	−1.5514	1579.13	18.07	−8.65
0.20002	−1.5818	1560.07	19.87	−8.82
0.22000	−1.6015	1542.89	21.70	−8.92
0.23989	−1.6107	1527.55	23.55	−8.99
0.27006	−1.6104	1506.48	26.44	−9.00
0.30988	−1.5851	1483.23	30.31	−8.90
0.36014	−1.5211	1459.57	35.30	−8.65
0.41958	−1.4265	1437.29	41.30	−8.22
0.48018	−1.3299	1418.95	47.50	−7.66
0.53991	−1.2169	1404.21	53.67	−7.01
0.60047	−1.0825	1391.61	60.01	−6.25
0.66019	−0.9367	1380.79	66.34	−5.41
0.71975	−0.7823	1371.91	72.65	−4.55
0.77937	−0.6203	1364.11	79.01	−3.64
0.84012	−0.4506	1356.83	85.56	−2.64
0.90050	−0.2786	1351.08	92.01	−1.69
0.93984	−0.1671	1347.59	96.23	−1.05
0.97084	−0.0798	1344.53	99.63	−0.47
1	0	1342.31	102.75	0

Table S5 Experimental values of V_m^E, u, $K_{S,m} = -(\partial V_m/\partial p)_S$ and of the excess molar quantity $K_{S,m}^E$ for x_A tetraglyme + $(1 - x_A)$ water at 298.15 K

x_A	V_m^E/cm^3 mol^{-1}	u/m s^{-1}	$K_{S,m}$/m^3 PPa^{-1} mol^{-1}	$K_{S,m}^E$/m^3 PPa^{-1} mol^{-1}
0	0	1496.687	8.09	0
0.00299	−0.0430	1518.45	8.08	−0.38
0.00600	−0.0900	1539.32	8.08	−0.76
0.00900	−0.1395	1558.61	8.09	−1.13
0.01199	−0.1902	1576.59	8.11	−1.48
0.01499	−0.2413	1592.62	8.15	−1.82
0.01998	−0.3267	1616.69	8.22	−2.35
0.02501	−0.4123	1637.38	8.33	−2.86
0.02999	−0.4964	1654.09	8.47	−3.33
0.03495	−0.5790	1667.50	8.64	−3.76
0.03996	−0.6596	1678.05	8.83	−4.17
0.04499	−0.7369	1685.76	9.05	−4.54
0.05000	−0.8102	1691.08	9.30	−4.89
0.05495	−0.8787	1694.55	9.56	−5.21
0.05997	−0.9438	1695.92	9.85	−5.51
0.06493	−1.0042	1695.50	10.17	−5.78
0.06991	−1.0610	1694.04	10.49	−6.03
0.07994	−1.1633	1688.11	11.21	−6.47
0.08992	−1.2505	1679.32	11.98	−6.85
0.09984	−1.3237	1668.56	12.80	−7.16
0.10983	−1.3858	1667.38	13.66	−7.43
0.12489	−1.4612	1640.01	15.02	−7.76
0.13993	−1.5188	1622.96	16.45	−8.01
0.15969	−1.5696	1601.56	18.40	−8.25
0.17955	−1.5887	1582.25	20.44	−8.40
0.19953	−1.5963	1565.02	22.52	−8.49
0.21951	−1.5967	1549.50	24.65	−8.54
0.23934	−1.5927	1535.82	26.79	−8.55
0.26932	−1.5738	1517.52	30.08	−8.49
0.30919	−1.5295	1497.36	34.51	−8.33
0.35881	−1.4558	1477.30	40.10	−8.02
0.41878	−1.3488	1458.03	46.94	−7.52
0.47783	−1.2279	1443.02	53.75	−6.94
0.53721	−1.1052	1430.63	60.65	−6.28
0.59738	−0.9540	1420.47	67.67	−5.56
0.65639	−0.8083	1411.54	74.64	−4.77
0.71594	−0.6704	1404.21	81.64	−3.98
0.77552	−0.5190	1397.94	88.67	−3.16
0.83391	−0.3638	1393.31	95.48	−2.44
0.89314	−0.2129	1388.45	102.49	−1.58
0.93246	−0.1219	1385.23	107.19	−0.97
0.96158	−0.0631	1382.78	110.70	−0.49
0.99204	−0.0116	1381.11	114.23	−0.12
1	0	1380.56	115.18	0

Appendix S1. Summary of four-segment model equations

Water-rich segment (subscript w)

$$Q_m^E(w) = a_w(x_A - x_A^3) + b_w(x_A^2 - x_A^3) + c_w x_A^3 \quad \text{(w1s)}$$

$$dQ_m^E/dx_A(w) = a_w(1 - 3x_A^2) + b_w(2x_A - 3x_A^2) + 3c_w x_A^2 \quad \text{(w2s)}$$

$$Q_A^E(w) = a_w(1 - x_A)^2(1 + 2x_A) + 2b_w x_A(1 - x_A)^2 + c_w(3x_A^2 - 2x_A^3) \quad \text{(w3s)}$$

$$Q_W^E(w) = 2a_w x_A^3 - b_w(x_A^2 - 2x_A^3) - 2c_w x_A^3 \quad \text{(w4s)}$$

$$Q_{\phi,A}^E(w) = a_w(1 - x_A^2) + b_w(x_A - x_A^2) + c_w x_A^2 \quad \text{(w5s)}$$

$$Q_{\phi,W}^E(w) = a_w(x_A + x_A^2) + b_w x_A^2 + c_w x_A^3/(1 - x_A) \quad \text{(w6s)}$$

$$(Q_m^E)_R(w) = a_w(1 + x_A) + b_w x_A + c_w x_A^2/(1 - x_A) \quad \text{(w7s)}$$

$$d^2Q_m^E(w)/dx_A^2 = -6a_w x_A + 2b_w(1 - 3x_A) + 6c_w x_A \quad \text{(w8s)}$$

Transitional segment (eight-parameter version, subscript T)

$$\begin{aligned} Q_m^E(T) = {} & Q_m^E(w,x_1)(4f_T^3 - 3f_T^4) + Q_m^E(L,x_2)(1 - 4f_T^3 + 3f_T^4) \\ & + (x_2 - x_1)[dQ_m^E(w,x_1)/dx_A](f_T^3 - f_T^4) \\ & - (x_2 - x_1)[dQ_m^E(L,x_2)/dx_A](f_T - 3f_T^3 + 2f_T^4) - b_T(f_T^2 - 2f_T^3 + f_T^4) \end{aligned} \quad \text{(T1s)}$$

$$\begin{aligned} dQ_m^E(T)/dx_A = {} & -12[Q_m^E(w,x_1) - Q_m^E(L,x_2)](f_T^2 - f_T^3)/(x_2 - x_1) \\ & - [dQ_m^E(w,x_1)/dx_A](3f_T^2 - 4f_T^3) + [dQ_m^E(L,x_2)/dx_A](1 - 9f_T^2 + 8f_T^3) \\ & + 2b_T(f_T - 3f_T^2 + 2f_T^3)/(x_2 - x_1) \end{aligned} \quad \text{(T2s)}$$

$$\begin{aligned} Q_A^E(T) = {} & Q_m^E(w,x_1)[4f_T^3 - 3f_T^4 - 12(1 - x_A)(f_T^2 - f_T^3)/(x_2 - x_1)] \\ & + Q_m^E(L,x_2)[1 - 4f_T^3 + 3f_T^4 + 12(1 - x_A)(f_T^2 - f_T^3)/(x_2 - x_1)] \\ & + [dQ_m^E(w,x_1)/dx_A][(x_2 - x_1)(f_T^3 - f_T^4) - (1 - x_A)(3f_T^2 - 4f_T^3)] \\ & - [dQ_m^E(L,x_2)/dx_A][(x_2 - x_1)(f_T - 3f_T^3 + 2f_T^4) - (1 - x_A)(1 - 9f_T^2 + 8f_T^3)] \\ & - b_T[(f_T^2 - 2f_T^3 + f_T^4 - 2(1 - x_A)(f_T - 3f_T^2 + 2f_T^3)/(x_2 - x_1)] \end{aligned} \quad \text{(T3s)}$$

$$\begin{aligned} Q_W^E(T) = {} & Q_m^E(w,x_1)[4f_T^3 - 3f_T^4 + 12x_A(f_T^2 - f_T^3)/(x_2 - x_1)] \\ & + Q_m^E(L,x_2)[1 - 4f_T^3 + 3f_T^4 - 12x_A(f_T^2 - f_T^3)/(x_2 - x_1)] \\ & + [dQ_m^E(w,x_1)/dx_A][(x_2 - x_1)(f_T^3 - f_T^4) + x_A(3f_T^2 - 4f_T^3)] \\ & - [dQ_m^E(L,x_2)/dx_A][(x_2 - x_1)(f_T - 3f_T^3 + 2f_T^4) + x_A(1 - 9f_T^2 + 8f_T^3)] \\ & - b_T[f_T^2 - 2f_T^3 + f_T^4 + 2x_A(f_T - 3f_T^2 + 2f_T^3)/(x_2 - x_1)] \end{aligned} \quad \text{(T4s)}$$

$$Q_{\phi,\mathrm{A}}{}^{\mathrm{E}}(\mathrm{T}) = \{Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)(4f_{\mathrm{T}}{}^3 - 3f_{\mathrm{T}}{}^4) + Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)(1 - 4f_{\mathrm{T}}{}^3 + 3f_{\mathrm{T}}{}^4) + (x_2 - x_1)[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}}{}^3 - f_{\mathrm{T}}{}^4) - (x_2 - x_1)[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}} - 3f_{\mathrm{T}}{}^3 + 2f_{\mathrm{T}}{}^4) - b_{\mathrm{T}}(f_{\mathrm{T}}{}^2 - 2f_{\mathrm{T}}{}^3 + f_{\mathrm{T}}{}^4)\}/x_{\mathrm{A}} \quad \text{(T5s)}$$

$$Q_{\phi,\mathrm{W}}{}^{\mathrm{E}}(\mathrm{T}) = \{Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)(4f_{\mathrm{T}}{}^3 - 3f_{\mathrm{T}}{}^4) + Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)(1 - 4f_{\mathrm{T}}{}^3 + 3f_{\mathrm{T}}{}^4) + (x_2 - x_1)[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}}{}^3 - f_{\mathrm{T}}{}^4) - (x_2 - x_1)[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}} - 3f_{\mathrm{T}}{}^3 + 2f_{\mathrm{T}}{}^4) - b_{\mathrm{T}}(f_{\mathrm{T}}{}^2 - 2f_{\mathrm{T}}{}^3 + f_{\mathrm{T}}{}^4)\}/(1 - x_{\mathrm{A}}) \quad \text{(T6s)}$$

$$(Q_{\mathrm{m}}{}^{\mathrm{E}})_{\mathrm{R}}(\mathrm{T}) = \{Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)(4f_{\mathrm{T}}{}^3 - 3f_{\mathrm{T}}{}^4) + Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)(1 - 4f_{\mathrm{T}}{}^3 + 3f_{\mathrm{T}}{}^4) + (x_2 - x_1)[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}}{}^3 - f_{\mathrm{T}}{}^4) - (x_2 - x_1)[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}} - 3f_{\mathrm{T}}{}^3 + 2f_{\mathrm{T}}{}^4) - b_{\mathrm{T}}(f_{\mathrm{T}}{}^2 - 2f_{\mathrm{T}}{}^3 + f_{\mathrm{T}}{}^4)\}/[x_{\mathrm{A}}(1 - x_{\mathrm{A}})] \quad \text{(T7s)}$$

$$\mathrm{d}^2Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{T})/\mathrm{d}x_{\mathrm{A}}{}^2 = 12[Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1) - Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)](2f_{\mathrm{T}} - 3f_{\mathrm{T}}{}^2)/(x_2 - x_1)^2 + 6[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}} - 2f_{\mathrm{T}}{}^2)/(x_2 - x_1) + 6[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)/\mathrm{d}x_{\mathrm{A}}](3f_{\mathrm{T}} - 4f_{\mathrm{T}}{}^2)/(x_2 - x_1) - 2b_{\mathrm{T}}[1 - 6f_{\mathrm{T}} + 6f_{\mathrm{T}}{}^2]/(x_2 - x_1)^2 \quad \text{(T8s)}$$

where:

$f_{\mathrm{T}} = (x_2 - x_{\mathrm{A}})/(x_2 - x_1)$

$Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1) = a_{\mathrm{w}}(x_1 - x_1{}^3) + b_{\mathrm{w}}(x_1{}^2 - x_1{}^3) + c_{\mathrm{w}}x_1{}^3$

$\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)/\mathrm{d}x_{\mathrm{A}} = a_{\mathrm{w}}(1 - 3x_1{}^2) + b_{\mathrm{w}}(2x_1 - 3x_1{}^2) + 3c_{\mathrm{w}}x_1{}^2$

$Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2) = q_{\mathrm{A}}x_2 + q_{\mathrm{W}}(1 - x_2) + b_{\mathrm{L}}x_2\,(1 - x_2)$

$\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)/\mathrm{d}x_{\mathrm{A}} = q_{\mathrm{A}} - q_{\mathrm{W}} + b_{\mathrm{L}}(1 - 2x_2)$

Transitional segment (nine-parameter version, subscript T)

$$Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{T}) = Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1)f_{\mathrm{T}}{}^4 + Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)(1 - f_{\mathrm{T}}{}^4) - (x_2 - x_1)[\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{T}} - f_{\mathrm{T}}{}^4) - b_{\mathrm{T}}(f_{\mathrm{T}}{}^2 - f_{\mathrm{T}}{}^4) - c_{\mathrm{T}}(f_{\mathrm{T}}{}^3 - f_{\mathrm{T}}{}^4) \quad \text{(T1a)}$$

$$\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{T})/\mathrm{d}x_{\mathrm{A}} = -\,4[Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{w},x_1) - Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)]f_{\mathrm{T}}{}^3/(x_2 - x_1) + [\mathrm{d}Q_{\mathrm{m}}{}^{\mathrm{E}}(\mathrm{L},x_2)/\mathrm{d}x_{\mathrm{A}}](1 - 4f_{\mathrm{T}}{}^3)$$

$$+ [2b_T(f_T - 2f_T^3) + c_T(3f_T^2 - 4f_T^3)]/(x_2 - x_1) \quad \text{(T2a)}$$

$$\begin{aligned} Q_A^E(T) = {} & Q_m^E(w,x_1)[f_T^4 - 4(1 - x_A)f_T^3/(x_2 - x_1)] \\ & + Q_m^E(L,x_2)[1 - f_T^4 + 4(1 - x_A)f_T^3/(x_2 - x_1)] \\ & - [dQ_m^E(L,x_2)/dx_A][(x_2 - x_1)(f_T - f_T^4) - (1 - x_A)(1 - 4f_T^3)] \\ & - b_T[f_T^2 - f_T^4 - 2(1 - x_A)(f_T - 2f_T^3)/(x_2 - x_1)] \\ & - c_T[f_T^3 - f_T^4 - (1 - x_A)(3f_T^2 - 4f_T^3)/(x_2 - x_1)] \end{aligned} \quad \text{(T3a)}$$

$$\begin{aligned} Q_W^E(T) = {} & Q_m^E(w,x_1)[f_T^4 + 4x_Af_T^3/(x_2 - x_1)] + Q_m^E(L,x_2)[1 - f_T^4 - 4x_Af_T^3/(x_2 - x_1)] \\ & - [dQ_m^E(L,x_2)/dx_A][(x_2 - x_1)(f_T - f_T^4) + x_A(1 - 4f_T^3)] \\ & - b_T[f_T^2 - f_T^4 + 2x_A(f_T - 2f_T^3)/(x_2 - x_1)] \\ & - c_T[f_T^3 - f_T^4 + x_A(3f_T^2 - 4f_T^3)/(x_2 - x_1)] \end{aligned} \quad \text{(T4a)}$$

The apparent excess molar properties are:

$$\begin{aligned} Q_{\phi,A}^E(T) = {} & \{Q_m^E(w,x_1)f_T^4 + Q_m^E(L,x_2)(1 - f_T^4) - (x_2 - x_1)[dQ_m^E(L,x_2)/dx_A](f_T - f_T^4) \\ & - b_T(f_T^2 - f_T^4) - c_T(f_T^3 - f_T^4)\}/x_A \end{aligned} \quad \text{(T5a)}$$

$$\begin{aligned} Q_{\phi,W}^E(T) = {} & \{Q_m^E(w,x_1)f_T^4 + Q_m^E(L,x_2)(1 - f_T^4) - (x_2 - x_1)[dQ_m^E(L,x_2)/dx_A](f_T - f_T^4) \\ & - b_T(f_T^2 - f_T^4) - c_T(f_T^3 - f_T^4)\}/(1 - x_A) \end{aligned} \quad \text{(T6a)}$$

The reduced excess molar properties are given by:

$$\begin{aligned} (Q_m^E)_R(T) = {} & \{Q_m^E(w,x_1)f_T^4 + Q_m^E(L,x_2)(1 - f_T^4) - (x_2 - x_1)[dQ_m^E(L,x_2)/dx_A](f_T - f_T^4) \\ & - b_T(f_T^2 - f_T^4) - c_T(f_T^3 - f_T^4)\}/[x_A(1 - x_A)] \end{aligned} \quad \text{(T7a)}$$

$$\begin{aligned} d^2Q_m^E(T)/dx_A^2 = {} & 12[Q_m^E(w,x_1) - Q_m^E(L,x_2)]f_T^2/(x_2 - x_1)^2 \\ & + 12[dQ_m^E(L,x_2)/dx_A]f_T^2/(x_2 - x_1) \\ & - [2b_T(1 - 6f_T^2) + 6c_T(f_T - 2f_T^2)]/(x_2 - x_1)^2 \end{aligned} \quad \text{(T8a)}$$

Pseudolamellar segment (subscript L)

$$Q_m^E(L) = q_Ax_A + q_W(1 - x_A) + b_Lx_A(1 - x_A) \quad \text{(L1s)}$$

$$dQ_m^E(L)/dx_A = q_A - q_W + b_L(1 - 2x_A) \quad \text{(L2s)}$$

$$Q_A^E(L) = q_A + b_L(1 - x_A)^2 \quad \text{(L3s)}$$

$$Q_W^E(L) = q_W + b_L x_A^2 \quad \text{(L4s)}$$

$$Q_{\phi,\mathrm{A}}^{\mathrm{E}}(\mathrm{L}) = q_{\mathrm{A}} + q_{\mathrm{W}}(1 - x_{\mathrm{A}})/x_{\mathrm{A}} + b_{\mathrm{L}}(1 - x_{\mathrm{A}}) \quad \text{(L5s)}$$

$$Q_{\phi,\mathrm{W}}^{\mathrm{E}}(\mathrm{L}) = q_{\mathrm{A}}x_{\mathrm{A}}/(1 - x_{\mathrm{A}}) + q_{\mathrm{W}} + b_{\mathrm{L}}x_{\mathrm{A}} \quad \text{(L6s)}$$

$$(Q_{\mathrm{m}}^{\mathrm{E}})_{\mathrm{R}}(\mathrm{L}) = q_{\mathrm{A}}/(1 - x_{\mathrm{A}}) + q_{\mathrm{W}}/x_{\mathrm{A}} + b_{\mathrm{L}} \quad \text{(L7s)}$$

$$\mathrm{d}^2Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L})/\mathrm{d}x_{\mathrm{A}}^2 = -\,2b_{\mathrm{L}} \quad \text{(L8s)}$$

Amphiphile-rich segment (subscript a)

$$Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{a}) = a_{\mathrm{a}}x_{\mathrm{W}}(1 - 2f_{\mathrm{a}} + f_{\mathrm{a}}^2) + [\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}]x_{\mathrm{W}}(f_{\mathrm{a}} - f_{\mathrm{a}}^2) + Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)(3f_{\mathrm{a}}^2 - 2f_{\mathrm{a}}^3) \quad \text{(a1s)}$$

$$\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{a})/\mathrm{d}x_{\mathrm{A}} = -\,a_{\mathrm{a}}(1 - 4f_{\mathrm{a}} + 3f_{\mathrm{a}}^2) - [\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}](2f_{\mathrm{a}} - 3f_{\mathrm{a}}^2) - 6Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)(f_{\mathrm{a}} - f_{\mathrm{a}}^2)/(1 - x_3) \quad \text{(a2s)}$$

$$Q_{\mathrm{A}}^{\mathrm{E}}(\mathrm{a}) = 2a_{\mathrm{a}}x_{\mathrm{w}}(f_{\mathrm{a}} - f_{\mathrm{a}}^2) - [\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}]x_{\mathrm{W}}(f_{\mathrm{a}} - 2f_{\mathrm{a}}^2) - Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)(3f_{\mathrm{a}}^2 - 4f_{\mathrm{a}}^3) \quad \text{(a3s)}$$

$$Q_{\mathrm{W}}^{\mathrm{E}}(\mathrm{a}) = a_{\mathrm{a}}[1 - 4f_{\mathrm{a}} + 3f_{\mathrm{a}}^2 + 2x_{\mathrm{W}}(f_{\mathrm{a}} - f_{\mathrm{a}}^2)] + [\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}][2f_{\mathrm{a}} - 3f_{\mathrm{a}}^2 - x_{\mathrm{W}}(f_{\mathrm{a}} - 2f_{\mathrm{a}}^2)] - Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)[3f_{\mathrm{a}}^2 - 4f_{\mathrm{a}}^3 - 6(f_{\mathrm{a}} - f_{\mathrm{a}}^2)/(1 - x_3)] \quad \text{(a4s)}$$

$$Q_{\phi,\mathrm{A}}^{\mathrm{E}}(\mathrm{a}) = a_{\mathrm{a}}x_{\mathrm{W}}(1 - 2f_{\mathrm{a}} + f_{\mathrm{a}}^2)/(1 - x_{\mathrm{W}}) + [\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}]x_{\mathrm{W}}(f_{\mathrm{a}} - f_{\mathrm{a}}^2)/(1 - x_{\mathrm{W}}) + Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)(3f_{\mathrm{a}}^2 - 2f_{\mathrm{a}}^3)/(1 - x_{\mathrm{W}}) \quad \text{(a5s)}$$

$$Q_{\phi,\mathrm{W}}^{\mathrm{E}}(\mathrm{a}) = a_{\mathrm{a}}(1 - 2f_{\mathrm{a}} + f_{\mathrm{a}}^2) + [\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{a}} - f_{\mathrm{a}}^2) + Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)(3f_{\mathrm{a}}^2 - 2f_{\mathrm{a}}^3)/x_{\mathrm{W}} \quad \text{(a6s)}$$

$$(Q_{\mathrm{m}}^{\mathrm{E}})_{\mathrm{R}}(\mathrm{a}) = a_{\mathrm{a}}(1 - 2f_{\mathrm{a}} + f_{\mathrm{a}}^2)/(1 - x_{\mathrm{W}}) + [\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}](f_{\mathrm{a}} - f_{\mathrm{a}}^2)/(1 - x_{\mathrm{W}}) + Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)(3f_{\mathrm{a}}^2 - 2f_{\mathrm{a}}^3)/[x_{\mathrm{W}}(1 - x_{\mathrm{W}})] \quad \text{(a7s)}$$

$$\mathrm{d}^2Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{a})/\mathrm{d}x_{\mathrm{A}}^2 = -\,2a_{\mathrm{a}}(2 - 3f_{\mathrm{a}})/(1 - x_3) + 2[\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}}](1 - 3f_{\mathrm{a}})/(1 - x_3) + 6Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)[1 - 2f_{\mathrm{a}}]/(1 - x_3)^2 \quad \text{(a8s)}$$

where:

$f_{\mathrm{a}} = x_{\mathrm{W}}/(1 - x_3)$

$Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3) = q_{\mathrm{A}}x_3 + q_{\mathrm{W}}(1 - x_3) + b_{\mathrm{L}}x_3(1 - x_3)$

$\mathrm{d}Q_{\mathrm{m}}^{\mathrm{E}}(\mathrm{L},x_3)/\mathrm{d}x_{\mathrm{A}} = q_{\mathrm{A}} - q_{\mathrm{W}} + b_{\mathrm{L}}(1 - 2x_3)$

Appendix S2. Equations of the single-association ideal mass-action model grafted into the four-segment model scheme

Various suggestions have been put forward to describe quasi-chemical equilibria involving aggregates that are formed by amphiphile molecules in aqueous environment.

A model in which there were two types of amphiphile hydrates, hydrophilic and hydrophobic was described. The two types of hydration water were treated as being in equilibrium with each other and with the bulk water.[42,43]

Another mass-action model in which the amphiphile monomers are in equilibrium with oligomeric amphiphile clusters was proposed.[44] This model has proved to be useful in several respects, even for species which are obviously non-micelle forming.

The basic equilibrium is represented by:

$$n\mathrm{A} \Leftrightarrow \mathrm{A}_n$$

where n is the aggregation number of the oligomer.

We can write an equilibrium constant expression of the type:

$$K = \alpha_n/\alpha_1^{\,n} \qquad \text{(A2. 1)}$$

where α_n and α_1 are the respective activities of the (n-mer) oligomer and the amphiphile monomer.

At some amphiphile mole fraction x_A, a large fraction, f, of the amphiphile molecules remains in the monomeric state. We may chose to represent the two activities by:

$$\alpha_n = x_\mathrm{A}\,(1 - f)/n \qquad \text{(A2. 2)}$$

and

$$\alpha_1 = x_\mathrm{A}\,f \qquad \text{(A2. 3)}$$

This treats each of the hydrated solute species as though ideal. It gives:

$$K = x_\mathrm{A}\,(1 - f)\,n^{-1}/(x_\mathrm{A}\,f)^n \qquad \text{(A2. 4)}$$

From eqn. (A2. 4), we can derive:

$$\Delta G_n^{\mathrm{o}}/RT = -\ln K = n \ln f - \ln(1 - f) + (n - 1)\ln x_\mathrm{A} + \ln n \qquad \text{(A2. 5)}$$

where ΔG_n^{o} is the standard Gibbs energy for the formation of one mole of micelles, from the monomeric molecules. The standard states of both monomer and micelle are Henry's law states; that is to say unit mole fractions but enthalpies corresponding to a totally solvent (aqueous) environment.

It turns out that it is more convenient to work with ΔG_1°, which is the same quantity *per* mole of monomers.

$$\Delta G_1^{\circ}/RT = \ln f - n^{-1} \ln (1 - f) - [(n - 1)/n] \ln x_A + n^{-1} \ln n \qquad \text{(A2. 6)}$$

Equation (A2. 6) provides us with a means of determining the monomer fraction, f, for a given combination of x_A, $\Delta G_1^{\circ}/RT$ and n. Solving this equation for f is by no means a simple exercise, calling for some type of successive approximation technique.

Having obtained values of f for each of the mole fractions, x_A, for which data points are available, it is possible to analyse the excess apparent, excess reduced and excess molar property data.

The simplest analytic equation is:

$$Q_{\phi,A}^{E} = f\, a_{mono} + (1 - f)\, a_{mic} \qquad \text{(A2. 7)}$$

where a_{mono} and a_{mic} are the apparent excess molar properties of the monomer and micellar aggregate, at infinite dilution, respectively. In the latter case, the molar value is per unit of amphiphile. In other notation, $a_{mic} = a_n/n$.

This equation does not have sufficient flexibility for all of the data sets that we have had occasion to analyse, with this type of model. As it stands, the model ignores all types of solute–solute interaction other than those giving rise to cluster formation. The simplest of the solute–solute interactions require terms that are quadratic in mole fraction for Q_m^E. We have chosen to expand eqn. (A2. 7) in the form:

$$Q_{\phi,A}^{E} = f\, a_{mono} + (1 - f)\, a_{mic} + bf^2\, x_A \qquad \text{(A2. 8)}$$

This equation is not totally satisfactory but it shows about as much flexibility as the vast majority of data sets could warrant.

It is possible to incorporate this version of the mass action model into the four-segment model scheme. Eqn. (A2. 8) replaces the original water-rich segment eqn. (w5s) in Appendix S1:

$$Q_{\phi,A}^{E}(\mathrm{w}) = a_w(1 - x_A^2) + b_w\, (x_A - x_A^2) + c_w\, x_A^2 \qquad \text{(w5s)}$$

The new water-rich segment extends up to a new version of the segment junction x_1.

The remaining equations are:

$$Q_m^{E}(\mathrm{ma}) = [f\, a_{mono} + (1 - f)\, a_{mic}]\, x_A + b\, f^2\, x_A^2 \qquad \text{(ma1)}$$

$$\mathrm{d}Q_m^{E}(\mathrm{ma})/\mathrm{d}x_A = f\, a_{mono} + (1 - f)\, a_{mic} + 2\, b\, f^2\, x_A$$
$$+\, x_A\, (a_{mono} - a_{mic})\, \mathrm{d}f/\mathrm{d}x_A + 2\, b\, f\, x_A^2\, \mathrm{d}f/\mathrm{d}x_A$$

We can obtain an expression for $\mathrm{d}f/\mathrm{d}x_\mathrm{A}$ from:

$$\Delta G_1^{\mathrm{o}}/RT = \ln f - n^{-1} \ln (1 - f) + [(n - 1)/n] \ln x_\mathrm{A} + n^{-1} \ln n$$

$$0 = \mathrm{d} \ln f/\mathrm{d}x_\mathrm{A} - n^{-1} \mathrm{d} \ln (1 - f)/\mathrm{d}x_\mathrm{A} + [(n - 1)/n] \mathrm{d} \ln x_\mathrm{A}/\mathrm{d}x_\mathrm{A}$$

$$0 = f^{-1} \mathrm{d}f/\mathrm{d}x_\mathrm{A} + n^{-1} (1 - f)^{-1} \mathrm{d}f/\mathrm{d}x_\mathrm{A} + [(n - 1)/n] x_\mathrm{A}^{-1}$$

$$\mathrm{d}f/\mathrm{d}x_\mathrm{A} = - [(n - 1)/n] x_\mathrm{A}^{-1}/[f^{-1} + n^{-1}(1 - f)^{-1}]$$

$$= - [(n - 1)/n] [n f(1 - f)] x_\mathrm{A}^{-1} [n - (n - 1) f]^{-1}$$

$$= - (n - 1) f(1 - f) x_\mathrm{A}^{-1} [n - (n - 1) f]^{-1}$$

$$\mathrm{d}Q_\mathrm{m}^{\mathrm{E}}(\mathrm{ma})/\mathrm{d}x_\mathrm{A} = f a_\mathrm{mono} + (1 - f) a_\mathrm{mic} + 2 b f^2 x_\mathrm{A} - (a_\mathrm{mono} - a_\mathrm{mic} + 2 b f x_\mathrm{A}) (n - 1) f (1 - f)/[n - (n - 1) f] \quad \text{(ma2)}$$

Since

$$Q_\mathrm{A}^{\mathrm{E}} = Q_\mathrm{m}^{\mathrm{E}} + (1 - x_\mathrm{A}) \mathrm{d}Q_\mathrm{m}^{\mathrm{E}}/\mathrm{d}x_\mathrm{A}$$

$$Q_\mathrm{A}^{\mathrm{E}}(\mathrm{ma}) = f a_\mathrm{mono} + (1 - f) a_\mathrm{mic} + 2 b f^2 x_\mathrm{A} - b f^2 x_\mathrm{A}^2 - (1 - x_\mathrm{A}) (a_\mathrm{mono} - a_\mathrm{mic} + 2 b f x_\mathrm{A}) (n - 1) f (1 - f)/[n - (n - 1) f] \quad \text{(ma3)}$$

Since

$$Q_\mathrm{W}^{\mathrm{E}} = Q_\mathrm{m}^{\mathrm{E}} - x_\mathrm{A} \mathrm{d}Q_\mathrm{m}^{\mathrm{E}}/\mathrm{d}x_\mathrm{A}$$

$$\mathrm{Q}_\mathrm{W}^{\mathrm{E}}(\mathrm{ma}) = - b f^2 x_\mathrm{A}^2 - x_\mathrm{A} (a_\mathrm{mono} - a_\mathrm{mic} + 2 b f x_\mathrm{A}) (n - 1) f (1 - f)/[n - (n - 1) f] \quad \text{(ma4)}$$

The apparent molar excess properties are given by:

$$Q_{\phi,\mathrm{A}}^{\mathrm{E}}(\mathrm{ma}) = f a_\mathrm{mono} + (1 - f) a_\mathrm{mic} + b f^2 x_\mathrm{A} \quad \text{(ma5)}$$

$$Q_{\phi,\mathrm{W}}^{\mathrm{E}}(\mathrm{ma}) = [f a_\mathrm{mono} + (1 - f) a_\mathrm{mic}] x_\mathrm{A}/(1 - x_\mathrm{A}) + b f^2 x_\mathrm{A}^2/(1 - x_\mathrm{A}) \quad \text{(ma6)}$$

The reduced excess molar properties are given by:

$$(Q_\mathrm{m}^{\mathrm{E}})_\mathrm{R}(\mathrm{ma}) = [f a_\mathrm{mono} + (1 - f) a_\mathrm{mic}]/(1 - x_\mathrm{A}) + b f^2 x_\mathrm{A}/(1 - x_\mathrm{A}) \quad \text{(ma7)}$$