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The association of anionic surfactants with β-cyclodextrin. An isothermal titration calorimeter study

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The association of a series of anionic surfactants ($C_nH_{2n+1}SO_4Na$, $n = 6, 8, 10, 12, 14$) with β-cyclodextrin was studied by means of the isothermal titration calorimeter (i.t.c.) at $T = 298.15$ K. For these types of inclusion complexes, the results agreed well with a 1:1 association model. Apparent values for the association constants, and changes in the standard molar Gibbs energies, enthalpies, and entropies were derived for the association process. The results indicated that the association of surfactants with β-cyclodextrin is characterized by both favourable enthalpy and favourable entropy changes. The results also demonstrated that the longer the alkyl chain of the anionic surfactant, the greater the association constant with β-cyclodextrin.

KEYWORDS: association constant; β-cyclodextrin; anionic surfactants; isothermal titration calorimeter; thermodynamic parameters

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides built up from 6, or 7, or 8 glucose units, called α-, β-, and γ-CD, respectively.[1] To a first approximation, they can be regarded as cylinders with a hydrophilic exterior and a hydrophobic interior. In an aqueous solution of a hydrophobic guest, the cyclodextrin molecule results in complexation in which no covalent bonds are formed.[1–4] Surfactants are ideal guests, which allow a systematic study of complexation with cyclodextrins, since both their hydrophobic and hydrophilic moieties can be systematically changed.[5–14] Studies on the association of anionic surfactants

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with cyclodextrins have been reported.[5–14] Unfortunately, the association constants of anionic surfactants with β-CD reported in the literature differ widely.[5–14] In this study, an isothermal titration calorimeter (i.t.c.)[15, 16] was used to measure association constants and standard molar enthalpies for the reaction of a series of anionic surfactants ($C_nH_{2n+1}SO_4Na$, $n = 6, 8, 10, 12, 14$) with β-cyclodextrin. The indirect thermodynamic parameters (enthalpy ΔH^o, association constant K_a, and stoichiometry n) were calculated using the optional ITC Bindworks program.[15, 16] The results obtained in this study were examined to obtain information about the variation of thermodynamic quantities with hydrophobic alkyl chain length of surfactants. This information can be useful both for understanding the chemistry in these reactions and estimating thermodynamic quantities.

2. Experimental

REAGENTS

The β-cyclodextrin (β-CD) was obtained from Aldrich (purity ≥ 0.99 mass fraction) and dried at 86 °C *in vacuo* for 24 h before use. Sodium alkyl sulfates ($C_nH_{2n+1}SO_4Na$, $n = 6, 8, 10, 12, 14$) were synthesized in our laboratory, and purified by recrystallization twice from ethanol.[17] The critical micelle concentrations (c.m.c.s) of the surfactants were determined by an electrical conduction method, and the values of the c.m.c.s obtained were 200 mmol $\cdot$ dm^{-3}, 140 mmol $\cdot$ dm^{-3}, 33 mmol $\cdot$ dm^{-3}, 8.7 mmol $\cdot$ dm^{-3}, and 2.4 mmol $\cdot$ dm^{-3} for $C_6H_{13}SO_4Na$, $C_8H_{17}SO_4Na$, $C_{10}H_{21}SO_4Na$, $C_{12}H_{25}SO_4Na$, and $C_{14}H_{29}SO_4Na$, respectively. The results are in agreement with the literature.[17]

ISOTHERMAL TITRATION CALORIMETER MEASUREMENTS

The experiments were performed in a Model 4200 isothermal titration calorimeter (Calorimetry Sciences Corporation, U.S.A.). All solutions were degassed by water aspiration prior to loading. The sample cell (750 μL) was filled with surfactant solution at approximately 0.1 mmol $\cdot$ dm^{-3}, and a 250 μL burette syringe was filled with β-CD solution of approximately 1.2 mmol $\cdot$ dm^{-3}. The titration consisted of 25 injections of 10 μL each at 300 second intervals. The i.t.c. uses proprietary software to set up experiments, control the calorimeter, and collect the raw heat rate data. The software ITC Dataworks is used to integrate the heat pulses and make baseline and/or blank corrections. The thermodynamic parameters (enthalpy change ΔH^o, association constant K_a, and stoichiometry n) were calculated with the optional Bindworks program.[15, 16]

The binding of Ba^{2+} to 18-crown-6 is an ideal reaction for verifying the performance of the calorimeter, and the values for the binding constant and the binding enthalpy has been very precisely determined by Wadsö and co-workers.[19] We performed a single determination under conditions very similar to those of Wadsö *et al.*, and obtained n, K_a, and ΔH^o values of 1, (5754 ± 200) dm^3 $\cdot$ mol^{-1}, and $-(31.25 \pm 0.40)$ kJ $\cdot$ mol^{-1}, respectively. The published values are $n = 1$, $K_a = (5900 \pm 200)$ dm^3 $\cdot$ mol^{-1}, and $\Delta H^o = -(31.42 \pm 0.20)$ kJ $\cdot$ mol^{-1}.[19]

The enthalpies of dilution of the titrant and surfactants were determined in separate experiments. Small dilution effects were obtained for surfactants, which were used to

correct results of the associated experiments, whereas no significant effect was found for β-CD. The dilution of the solution titrated gave no significant contribution in any of the cases. The calorimeter was frequently calibrated electrically during the course of the study.[15, 16] The calorimetric measurements were carried out at $T = 298.15$ K.

3. Results and discussion

Data from a representative titration experiment are given in figure 1. The area under each peak in figure 1 gives the heat Q for that injection. Data such as these were corrected for surfactant heats of dilution, processed on the computer, and then deconvoluted using an algorithm based on the Marquardt method.[20, 21] Results from the deconvolution of one set of data (corresponding to that in figure 1) are shown in figure 2, where the points are experimental values and the solid line is the calculated best-fit curve by least-squares deconvolution. The best values of the fitting parameters are $n = 1.03$, $K_a = 8370\ \mathrm{L \cdot mol^{-1}}$, and $\Delta H^o = -(10.9 \pm 0.24)\ \mathrm{kJ \cdot mol^{-1}}$. The standard deviation of points from the calculated line is 0.047 per cent of the total heat for association. The titration curve for the heat of association of $C_{12}H_{25}SO_4Na$ with β-CD obtained after subtracting the heat of dilution of surfactant is shown in figure 3 and represents the best-fit to the 1:1 association model. The thermodynamic parameters (enthalpy change ΔH^o, association constant K_a, and stoichiometry n) were calculated with the optional Bindworks program.[15, 16] The entropy change ΔS^o and free energy change ΔG^o of association were calculated by using the equation:

$$\Delta G^o = -RT \ln K_a = \Delta H^o - T\Delta S^o, \tag{1}$$

where R is the universal gas constant.

Table 1 lists the thermodynamic data of anionic surfactants with β-CD and the published values.[6–11] For these types of inclusion complexes, the results agree well with a 1:1 association model, consistent with the literature.[6–11] (The stoichiometric ratio for the $C_{12}H_{25}SO_4Na/\beta$-CD complex can also be obtained from the endpoint of figure 3. The other stoichiometric ratios for these complexes can be obtained in the same way.) Most of the published association constants[6, 8–10] are in disagreement with those of this work (see table 1). However, these values have not been determined at the same surfactant concentration, and this factor notably influences the association constant value.[11]

The most likely mode of complexation of ligands to cyclodextrins consists of insertion of the hydrophobic portion of the ligand into the cyclodextrin cavity with the polar group of the ligand remaining solvent exposed at the wide top end of the cavity.[1–4] In general, the complexation is non-covalent. A combination of hydrophobic effects and van der Waals forces and, in some cases, hydrogen bonding between the ligand and the cyclodextrin are involved.[1–4, 22] The resultant of all these interactions is described by the thermodynamic quantities in this study. Although, at present, it does not appear possible to obtain a rigorous, quantitative breakdown of the relative contributions of these various interactions for any specific (ligand + cyclodextrin) reaction, we believe that the following qualitative picture is useful for understanding these complexation reactions.

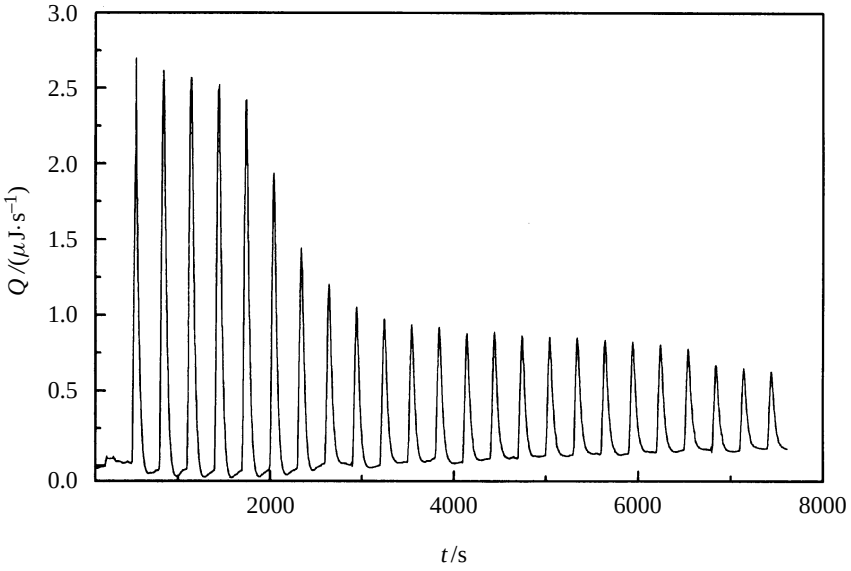

FIGURE 1. Plot of heat Q against time for the measurement of the heat produced by chemical reaction. The raw data were obtained for 25 automatic injections, each of 10 μL, of β-cyclodextrin solution into the sample cell containing $C_{12}H_{25}SO_4Na$ solution.

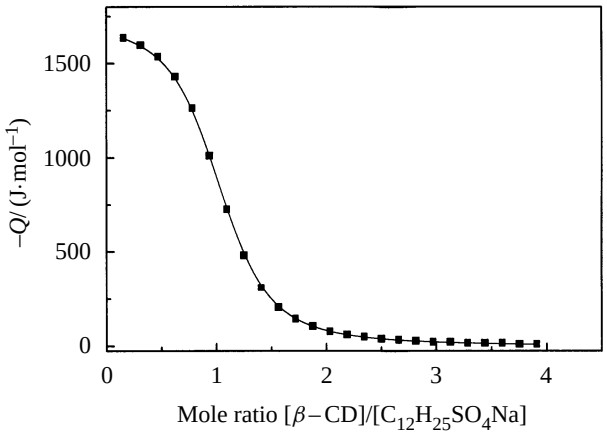

FIGURE 2. Total integral heat of association $-Q$ of $C_{12}H_{25}SO_4Na$ with β-cyclodextrin against mole ratio.

As can be seen from table 1, the inclusion complexes of surfactants with β-CD are exclusively exothermic and mostly enthalpy driven with varying positive entropic

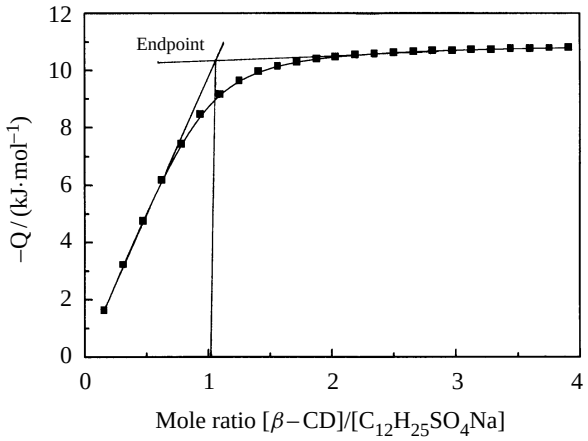

FIGURE 3. The heat of association $-Q$ of $C_{12}H_{25}SO_4Na$ with β-cyclodextrin against mole ratio.

TABLE 1. Values of the thermodynamic parameters; stoichiometry n, association constant K_a, enthalpy change ΔH^o, free energy change ΔG^o, and the entropy change ΔS^o for the association of anionic surfactants with β-CD at $T = 298.15$ K[a]

Surfactants	n	K_a / $dm^3 \cdot mol^{-1}$	ΔH^o / $kJ \cdot mol^{-1}$	ΔG^o / $kJ \cdot mol^{-1}$	ΔS^o / $J \cdot K \cdot mol^{-1}$
$C_6H_{13}SO_4Na$	1 ± 0.01	543 ± 29 [144 ± 37][b] [350][c]	-1.17 ± 0.05	-15.6 ± 0.1	48.4 ± 0.5
$C_8H_{17}SO_4Na$	1 ± 0.02	1210 ± 95 [343 ± 11][b] [1610][c] [565][d] [2560][e]	-3.63 ± 0.15	-17.6 ± 0.2	46.9 ± 2
$C_{10}H_{21}SO_4Na$	1 ± 0.02	3446 ± 190 [2240 ± 150][b] [5400][c] [2310][d] [8750][e]	-6.82 ± 0.2	-20.2 ± 0.30	44.8 ± 1.7
$C_{12}H_{25}SO_4Na$	1 ± 0.03	8150 ± 402 [4320 ± 670][b] [6600][c] [7230][d] [25600][e] [3630][f] [300][g]	-10.9 ± 0.24	-22.3 ± 0.1	38.2 ± 1
$C_{14}H_{29}SO_4Na$	1 ± 0.03	14561 ± 510	-18.1 ± 0.18	-23.86 ± 0.1	18.9 ± 0.9

[a] Values are the averages of three determinations; [b] n.m.r. spectroscopy;(10) [c] conductimetry(11); [d] conductance measurements;(7) [e] fluorimetric measurements (using fluorescent probes as a competitive inhibitor for association);(8) [f] conductance measurements;(6) [g] conductivity and P^{Na} measurements.(9)

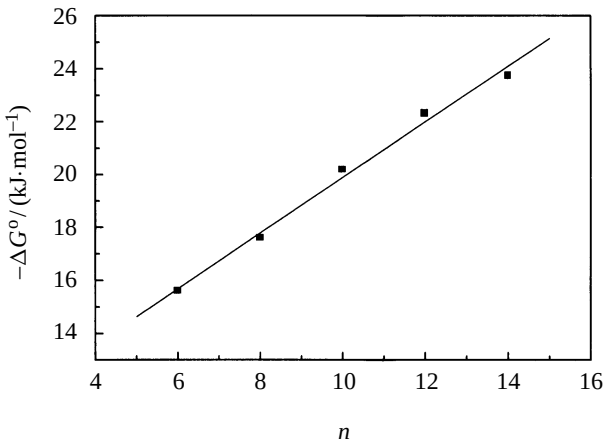

FIGURE 4. Relationship between Gibbs free energy ($-\Delta G^o$) and the number (n) of carbon atoms in the hydrocarbon tail of the surfactants.

contributions. From studies of the thermodynamics of the β-CD–surfactant interaction, we conclude that there is a significant contribution from the classical hydrophobic effect (*i.e.* a positive ΔS^o contribution)[18, 20, 21] but that this contribution is reduced by predominant binding forces characterized by negative enthalpy and entropy changes. We speculate that the latter forces may be due to van der Waals interactions and hydrogen bonding between the surfactant and β-CD. Using the simple qualitative argument that a surfactant strongly bound within the β-CD cavity has lost some freedom of motion, one expects it to have a lower entropy than if it were weakly bound within the cavity. The van der Waals and hydrophobic interactions become stronger with increasing alkyl chain length of the surfactants.[23, 24] The values of enthalpy change ($-\Delta H^o$) increase with increasing alkyl chain length of the surfactants, and this indicates that it is energetically favourable for the weak polar surfactants to be included in the β-CD cavity (inner diameter of 0.78 μm wide and a length of 0.78 μm).[1–4, 18] Obviously, the largest changes in enthalpy would be for the $C_{14}H_{33}SO_4Na$ that has the longest alkyl chain length with the highest association constant. The values of the entropy change (ΔS^o) are positive and decrease with increasing alkyl chain length of the surfactants. This indicates that the degrees of freedom of the surfactant included in the β-CD cavity become lower with increasing alkyl chain length of the surfactants. The results also indicate that $-\Delta G^o$ increases steadily with increasing alkyl chain length of the surfactants (see figure 4). The results demonstrate that the longer chain surfactants lead to a greater association constant with β-CD.

The rationalization of ΔH^o and ΔS^o values, while of interest for understanding the molecular details and driving forces involved in complex formation, is necessarily somewhat speculative, and it must be realized that other factors such as the displacement of high-energy water from within the β-CD cavity, or structural changes of the β-CD molecule may contribute to ΔH^o and ΔS^o for the surfactant binding.[18, 24–28] However, a

straightforward interpretation of ΔG^{o} for β-CD/surfactant complex formation is possible in terms of hydrophobic binding forces between the surfactant and the β-CD.

In conclusion, the experiments provide estimates of the heat and entropy of association in addition to the association constant, leading to a more complete characterization of the thermodynamics of interaction.

REFERENCES

1. Bender, M. L.; Komiyana, M. *Cyclodextrin Chemistry*. Springer-Verlag: Berlin. **1987**.
2. Fendler, J. H. *Membrane Mimetic Chemistry*. Wiley-Interscience: New York. **1982**, pp. 194–201.
3. Griffiths, D. W.; Bender, M. L. *Adv. Catal*. **1973**, 23, 209–218.
4. Cramer, E.; Saenger, W.; Spatz, H.-Ch. *J. Am. Chem. Soc.* **1967**, 89, 14–19.
5. Okubo, T.; Kitano, H.; Ise, N. *J. Phys. Chem.* **1976**, 80, 2261–2664.
6. Satake, I.; Yoshida, S.; Hayakawa, K.; Maedaand, T.; Kusumoto, Y. *Bull. Chem. Soc. Japan* **1986**, 59, 3991–3003.
7. Palepu, R.; Reinsborough, V. C. *Can. J. Chem.* **1988**, 66, 325–328.
8. Park, J. W.; Song, H. J. *J. Phys. Chem.* **1989**, 93, 6454–6459.
9. Georgos, J.; Desmettre, S. *J. Colloid Interface Sci.* **1987**, 118, 192–200.
10. Guo, Q.-X.; Li, Z. Z.; Ren, T.; Zhu, X. Q.; Liu, Y.-C. *J. Inc. Phenom.* **1994**, 17, 149–156.
11. Saint Aman, E.; Serve, D. *J. Colloid Interface Sci.* **1990**, 138, 365–375.
12. Junquera, E.; Tardajos, G.; Aicart, E. *Langmuir* **1993**, 9, 1213–1219.
13. Sasaki, K. J.; Christian, S. D.; Turker, E. E. *J. Colloid Interface Sci.* **1990**, 134, 412–416.
14. Lu, R.-H.; Hao, J.-C.; Wang, H.; Tong, L.-H. *J. Colloid Interface Sci.* **1997**, 192, 37–42.
15. Wiseman, T.; Williston, S.; Brandts, J. F.; Lin, L.-N. *Anal. Boichem.* **1989**, 179, 131–137.
16. Freire, E.; Mayorga, O.; Straume, M. *Anal. Chem.* **1990**, 62, 950–959.
17. Jerchel, D.; Becher, H.; Varahamutri, M. K. *Z. Naturforsch. Teil* **1956**, 11, 681–687.
18. Cromwell, W. C.; Bystrom, K.; Eftink, M. R. *J. Phys. Chem.* **1985**, 89, 326–332.
19. Briggner, L. E.; Wadsö, I. *J. Biochem. Biophys. Methods* **1991**, 22, 101–118.
20. *ITC Data Analysis in Origin*. MicroCal Software Inc.: MicroCal Origin, Northampton, CA. **1993**, pp. 65.
21. Berington, P. R. *Data Reduction and Error Analysis for the Physical Science*. McGraw-Hill: New York. **1969**, p. 235.
22. Rekharsky, M. V.; Mayhew, M. P.; Goldberg, R. N. *J. Phys. Chem. B* **1997**, 101, 87–100.
23. Tanford, C. *The Hydrocarbon Effect: formation micelles and biological membranes*. Wiley: New York. **1980**, p. 51.
24. Bastors, M.; Briggner, L. E.; Shehatta, I.; Wadso, I. *J. Chem. Thermodynamics* **1990**, 22, 1181–1190.
25. Inoue, Y.; Hakushi, T.; Liu, Y.; Tong, L.-H. *J. Am. Chem. Soc.* **1993**, 115, 475–481.
26. Liu, T.; Tong, L.-H.; Inoue, Y.; Hakushi, T. *J. Chem. Soc., Perkin Trans.* **1990**, 2, 1247–1252.
27. Liu, T.; Tong, L.-H.; Inoue, Y.; Hakushi, T. *J. Phys. Chem.* **1990**, 94, 2666–2672.
28. Liu, T.; Tong, L.-H.; Inoue, Y.; Hakushi, T. *J. Phys. Chem.* **1988**, 94, 2371–2374.

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Appendix

TABLE A.1. Values of the experimentally determined heats of association $-Q$ for the association of $C_6H_{13}SO_4Na$ with β-CD at $T = 298.15$ K and various mole ratios

Injection number	Mole ratio	$-Q(\mu J)$ per injection	Total $-Q(\mu J)$ measured	$-Q$ $kJ \cdot mol^{-1}$
1	0.15648	13.92851	13.92851	0.17687
2	0.31296	13.59225	27.52076	0.34947
3	0.46944	13.05439	40.57515	0.51524
4	0.62592	12.16845	52.7436	0.66976
5	0.7824	10.7232	63.47092	0.80598
6	0.93888	8.61604	72.08696	0.91539
7	1.09535	6.17007	78.25703	0.99374
8	1.25184	4.06664	82.32367	1.04538
9	1.40831	2.63104	84.95471	1.07879
10	1.56479	1.74983	86.70454	1.10101
11	1.72127	1.21511	87.91965	1.11644
12	1.87775	0.88121	88.80086	1.12763
13	2.03422	0.66229	89.46315	1.13604
14	2.19071	0.51345	89.9766	1.14256
15	2.34719	0.40871	90.38531	1.14775
16	2.50368	0.33312	90.71843	1.15198
17	2.66015	0.27562	90.99405	1.15548
18	2.81662	0.23153	91.22558	1.15842
19	2.9731	0.19766	91.42324	1.16093
20	3.1296	0.1701	91.59334	1.16309
21	3.28608	0.14883	91.74217	1.16498
22	3.44255	0.12994	91.87211	1.16663
23	3.59902	0.11498	91.98709	1.16809
24	3.75548	0.10316	92.09025	1.1694
25	3.91198	0.09214	92.18239	1.17057

TABLE A.2. Values of the experimentally determined heats of association $-Q$ for the association of $C_8H_{17}SO_4Na$ with β-CD at $T = 298.15$ K and various mole ratios

Injection number	Mole ratio	$-Q(\mu J)$ per injection	Total $-Q(\mu J)$ measured	$-Q$ / kJ · mol^{-1}
1	0.15646	43.977	43.9770	0.548
2	0.31293	42.91599	86.89229	1.08277
3	0.46939	41.21801	128.1103	1.59639
4	0.62586	38.42129	166.53159	2.07516
5	0.78232	33.86791	200.3995	2.49719
6	0.93879	27.20395	227.60345	2.83618
7	1.09524	19.48229	247.08574	3.07895
8	1.25171	12.83839	259.92413	3.23893
9	1.40817	8.30748	268.23161	3.34245
10	1.56463	5.52602	273.75763	3.41131
11	1.7211	3.83675	277.59438	3.45912
12	1.87756	2.78147	280.37585	3.49378
13	2.03402	2.09051	282.46636	3.51983
14	2.19049	1.62185	284.08821	3.54004
15	2.34696	1.29122	285.37943	3.55613
16	2.50343	1.05048	286.42991	3.56922
17	2.65988	0.86991	287.29982	3.58006
18	2.81634	0.73188	288.0317	3.58918
19	2.9728	0.62354	288.65524	3.59695
20	3.12929	0.53767	289.19291	3.60365
21	3.28575	0.46866	289.66157	3.60949
22	3.44221	0.41169	290.07326	3.61462
23	3.59866	0.36353	290.43679	3.61915
24	3.7551	0.32501	290.7618	3.6232
25	3.91159	0.29051	291.05231	3.62682

TABLE A.3. Values of the experimentally determined heats of association $-Q$ for the association of $C_{10}H_{21}SO_4Na$ with β-CD at $T = 298.15$ K and various mole ratios

Injection number	Mole ratio	$-Q(\mu J)$ per injection	Total $-Q(\mu J)$ measured	$-Q$ / kJ · mol^{-1}
1	0.15725	81.916	81.916	1.03039
2	0.31449	79.93805	161.85405	2.0359
3	0.47174	76.77633	238.63038	3.00164
4	0.62899	71.56749	310.19787	3.90186
5	0.78623	63.08643	373.2843	4.6954
6	0.94348	50.6733	423.9576	5.3328
7	1.10072	36.28037	460.24697	5.78927
8	1.25797	23.9136	484.16057	6.09007
9	1.41521	15.47387	499.63444	6.28471
10	1.57246	10.29367	509.92811	6.41419
11	1.7297	7.14705	517.07516	6.50409
12	1.88695	5.18022	522.25538	6.56925
13	2.04419	3.89391	526.14929	6.61823
14	2.20144	3.02179	529.17108	6.65624
15	2.35869	2.40488	531.57596	6.68649
16	2.51595	1.95649	533.53245	6.7111
17	2.67318	1.62021	535.15266	6.73148
18	2.83042	1.36343	536.51609	6.74863
19	2.98767	1.16229	537.67838	6.76325
20	3.14493	1.0017	538.68008	6.77585
21	3.30218	0.87211	539.55219	6.78682
22	3.45942	0.76718	540.31937	6.79647
23	3.61665	0.67734	540.99671	6.80499
24	3.77388	0.60499	541.6017	6.8126
25	3.93115	0.5414	542.1431	6.81941

TABLE A.4. Values of the experimentally determined heats of association $-Q$ for the association of $C_{12}H_{25}SO_4Na$ with β-CD at $T = 298.15$ K and various mole ratios

Injection number	Mole ratio	$-Q(\mu J)$ per injection	Total $-Q(\mu J)$ measured	$-Q$ ($kJ \cdot mol^{-1}$)
1	0.15789	125.048	125.048	1.63062
2	0.31578	122.028	247.076	3.22185
3	0.47366	177.202	364.278	4.75016
4	0.63155	109.25	473.528	6.17477
5	0.78944	96.304	569.832	7.43057
6	0.94733	77.354	647.186	8.43926
7	1.10521	55.397	702.583	9.16164
8	1.26311	36.505	739.088	9.63766
9	1.42098	23.622	762.71	9.94569
10	1.57887	15.713	778.423	10.15059
11	1.73676	10.911	789.334	10.29286
12	1.89465	7.907	797.241	10.39597
13	2.05253	5.945	803.186	10.47349
14	2.21043	4.612	807.798	10.53363
15	2.36831	3.671	811.469	10.5815
16	2.52621	2.987	814.456	10.62045
17	2.68409	2.474	816.93	10.65271
18	2.84197	2.081	819.011	10.67985
19	2.99986	1.774	820.785	10.70298
20	3.15777	1.29	822.314	10.72292
21	3.31565	1.332	823.646	10.74029
22	3.47353	1.17	824.816	10.75555
23	3.63141	1.035	825.851	10.76904
24	3.78928	0.923	826.774	10.78108
25	3.94719	0.827	827.601	10.79186

TABLE A.5. Values of the experimentally determined heats of association $-Q$ for the association of $C_{14}H_{29}SO_4Na$ with β-CD at $T = 298.15$ K and various mole ratios

Injection number	Mole ratio	$-Q(\mu J)$ per injection	Total $-Q(\mu J)$ measured	$-Q$ / kJ · mol^{-1}
1	0.15773	207.27245	207.27245	2.73627
2	0.31546	202.26538	409.53783	5.40644
3	0.4732	194.26769	603.80552	7.97103
4	0.63093	181.08644	784.89196	10.36161
5	0.78866	159.62797	944.51993	12.46891
6	0.94639	128.21748	1072.73741	14.16155
7	1.10411	91.8234	1164.56081	15.37374
8	1.26185	60.50834	1225.06915	16.17253
9	1.41958	39.15442	1264.22357	16.68942
10	1.57731	26.04512	1290.26869	17.03325
11	1.73504	18.08455	1308.35324	17.27199
12	1.89277	13.10703	1321.46027	17.44502
13	2.05049	9.85356	1331.31383	17.5751
14	2.20824	7.64469	1338.95852	17.67602
15	2.36597	6.08499	1345.04351	17.75635
16	2.52371	4.95102	1349.99453	17.82171
17	2.68143	4.10035	1354.09488	17.87584
18	2.83915	3.44966	1357.54454	17.92138
19	2.99688	2.94061	1360.48515	17.9602
20	3.15464	2.5346	1363.01975	17.99366
21	3.31237	2.20735	1365.2271	18.0228
22	3.47009	1.93996	1367.16706	18.04841
23	3.62781	1.71498	1368.88204	18.07105
24	3.78552	1.53015	1370.41219	18.09125
25	3.94328	1.37032	1371.78251	18.10934

TABLE A.6. Values of experiments for the association of anionic surfactants with β-CD for the injection numbers, mole ratios ([β-CD]/[surfactant]), and heats of association $-Q/(\mathrm{kJ \cdot mol^{-1}})$

	($C_6H_{13}SO_4Na$)		($C_8H_{17}SO_4Na$)		($C_{10}H_{21}SO_4Na$)		($C_{12}H_{25}SO_4Na$)		($C_{14}H_{29}SO_4Na$)	
Injection number	Mole ratio	$-Q$ / $\mathrm{kJ \cdot mol^{-1}}$	Mole ratio	$-Q$ / $\mathrm{kJ \cdot mol^{-1}}$	Mole ratio	$-Q$ / $\mathrm{kJ \cdot mol^{-1}}$	Mole ratio	$-Q$ / $\mathrm{kJ \cdot mol^{-1}}$	Mole ratio	$-Q$ / $\mathrm{kJ \cdot mol^{-1}}$
1	0.15648	0.17687	0.15646	0.548	0.15725	1.03039	0.15789	1.63062	0.15773	2.73627
2	0.31296	0.34947	0.31293	1.08277	0.31449	2.0359	0.31578	3.22185	0.31546	5.40644
3	0.46944	0.51524	0.46939	1.59639	0.47174	3.00164	0.47366	4.75016	0.4732	7.97103
4	0.62592	0.66976	0.62586	2.07516	0.62899	3.90186	0.63155	6.17477	0.63093	10.36161
5	0.7824	0.80598	0.78232	2.49719	0.78623	4.6954	0.78944	7.43057	0.78866	12.46891
6	0.93888	0.91539	0.93879	2.83618	0.94348	5.3328	0.94733	8.43926	0.94639	14.16155
7	1.09535	0.99374	1.09524	3.07895	1.10072	5.78927	1.10521	9.16164	1.10411	15.37374
8	1.25184	1.04538	1.25171	3.23893	1.25797	6.09007	1.26311	9.63766	1.26185	16.17253
9	1.40831	1.07879	1.40817	3.34245	1.41521	6.28471	1.42098	9.94569	1.41958	16.68942
10	1.56479	1.10101	1.56463	3.41131	1.57246	6.41419	1.57887	10.15059	1.57731	17.03325
11	1.72127	1.11644	1.7211	3.45912	1.7297	6.50409	1.73676	10.29286	1.73504	17.27199
12	1.87775	1.12763	1.87756	3.49378	1.88695	6.56925	1.89465	10.39597	1.89277	17.44502
13	2.03422	1.13604	2.03402	3.51983	2.04419	6.61823	2.05253	10.47349	2.05049	17.5751
14	2.19071	1.14256	2.19049	3.54004	2.20144	6.65624	2.21043	10.53363	2.20824	17.67602

TABLE A.6—*continued*

Injection number	($C_6H_{13}SO_4Na$) Mole ratio	$-Q$ kJ · mol^{-1}	($C_8H_{17}SO_4Na$) Mole ratio	$-Q$ kJ · mol^{-1}	($C_{10}H_{21}SO_4Na$) Mole ratio	$-Q$ kJ · mol^{-1}	($C_{12}H_{25}SO_4Na$) Mole ratio	$-Q$ kJ · mol^{-1}	($C_{14}H_{29}SO_4Na$) Mole ratio	$-Q$ kJ · mol^{-1}
15	2.34719	1.14775	2.34696	3.55613	2.35869	6.68649	2.36831	10.5815	2.36597	17.75635
16	2.50368	1.15198	2.50343	3.56922	2.51595	6.7111	2.52621	10.62045	2.52371	17.82171
17	2.66015	1.15548	2.65988	3.58006	2.67318	6.73148	2.68409	10.65271	2.68143	17.87584
18	2.81662	1.15842	2.81634	3.58918	2.83042	6.74863	2.84197	10.67985	2.83915	17.92138
19	2.9731	1.16093	2.9728	3.59695	2.98767	6.76325	2.99986	10.70298	2.99688	17.9602
20	3.1296	1.16309	3.12929	3.60365	3.14493	6.77585	3.15777	10.72292	3.15464	17.99366
21	3.28608	1.16498	3.28575	3.60949	3.30218	6.78682	3.31565	10.74029	3.31237	18.0228
22	3.44255	1.16663	3.44221	3.61462	3.45942	6.79647	3.47353	10.75555	3.47009	18.04841
23	3.59902	1.16809	3.59866	3.61915	3.61665	6.80499	3.63141	10.76904	3.62781	18.07105
24	3.75548	1.1694	3.7551	3.6232	3.77388	6.8126	3.78928	10.78108	3.78552	18.09125
25	3.91198	1.17057	3.91159	3.62682	3.93115	6.81941	3.94719	10.79186	3.94328	18.10934