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Solution properties of octyl-β-D-glucoside. Part 2: Thermodynamics of micelle formation

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Abstract: Solution properties of octyl-β-D-glucoside have been examined in a wide temperature and concentration range, by means of freezing point depression, volumetric and calorimetric methods. Partial molal quantities and the variations consequent to micellization have been evaluated and discussed. Strong support to the hypothesis of a growth of the micellar aggregates was inferred from heat capacity findings.

Key words: Octyl glucoside – micellization – thermodynamics – activity coefficients – volumetric properties – expansibilities – calorimetry – heat capacities

Introduction

Solvent properties of alkylglucosides with respect to naturally occurring lipids have been the subject of many investigations [1–3]. Among nonionic surfactants used for biochemical purposes, their critical micelle concentrations (CMCs) are reproducible with appreciable accuracy, and they do not show head group polydispersity effects [4] or consolute phenomena [5]. In addition, their denaturant effect with respect to membrane proteins is mild and reversible [6].

A noticeable amount of experimental investigation on their biochemical uses is available, but information on physico-chemical properties is poor. Although some efforts have been made to investigate surface active properties [7–9], as well as micelle size and shape [10–12], not much is known about their thermodynamic properties, with the partial exception of volumetric investigation [12, 13].

We report here a systematic study on activity, calorimetric and volumetric data for octyl-β-D-glucoside. The volumetric findings reported here span a temperature and concentration range wider than the previously reported one and examine in deeper detail the behavior close to the CMC. The thermodynamic aspects inferred from the present investigation point to the occurrence of interesting peculiarities, due to the combined effect of hydrophobic and head group contributions to micelle formation.

Experimental

Materials

Octyl-β-D-glucoside, OG, Calbiochem, is as in previous studies [12]. Water was bidistilled, deionized and degassed: its conductivity is close to 10^{-7} ohm^{-1} cm^{-1}, at 25 °C. The solutions were prepared by weight and left to equilibrate overnight at room temperature, before each set of measurements.

Methods

Freezing point depression, ΔT, and density, ρ, were determined by Knauer and A. Paar instruments, respectively. Details on the apparatus setup and on the measuring procedures have been previously reported [14]. The accuracy on ΔT is to $\pm 1 \cdot 10^{-3}$ °C, whereas densities are to within $\pm 3 \cdot 10^{-6}$ g cm^{-3}.

Calorimetric investigations were run by 2107 LKB isothermal batch apparatus of the heat conduction type [15], equipped with gold vessels, a cooling circulator, LKB 2209, a control unit, LKB 2107-350, and a potentiometric recorder, LKB 2210, working at the required temperature; details on the apparatus set-up and on the measuring procedures are reported elsewhere [16]. The calorimetric accuracy has been tested by measuring the heat of dilution for sucrose [17]. The maximum uncertainty on integral enthalpies of dilution, $\Delta H_{i,d}$, is to within $\pm 1.0\%$ and decreases in direct proportion with molality, m.

Results

Colligative properties

The osmotic coefficients, Φ, were calculated according to [18]:

$$\Phi = [0.1278\,\Delta T/m] \times (4.207 + 2.10 \cdot 10^{-3} \Delta T)\,, \qquad (1)$$

where m is the surfactant molality. They are reported in Table 1. Each datum is the mean value obtained by five independent determinations. Activity coefficients, γ, were calculated according to [19]

$$\ln \gamma = (\Phi - 1)[1 + (1/M^0) \int dm/m]\,, \qquad (2)$$

where M^0 is the solvent molecular weight. The integral was calculated by introducing a lower limit, $m^0 = 5 \cdot 10^{-3}$ molal, in the integrand function. Values obtained by Eq. (2) are self-consistent, even if their absolute value can be systematically different from the true ones. This fact, perhaps, is not relevant to the thermodynamic analysis.

Table 1. The OG osmotic coefficients, Φ, as a function of surfactant molality, m, as inferred from freezing point depression data

$10^3\,m$	Φ	$10^3\,m$	Φ
6.1	0.9913	83.1	0.4598
9.4	1.0202	119.8	0.3215
15.2	1.0102	164.5	0.2367
20.0	1.0011	206.3	0.1927
27.5	0.9898	252.9	0.1571
36.4	0.9075	270.8	0.1480
48.8	0.7594	316.3	0.1287
61.4	0.6172	384.3	0.107

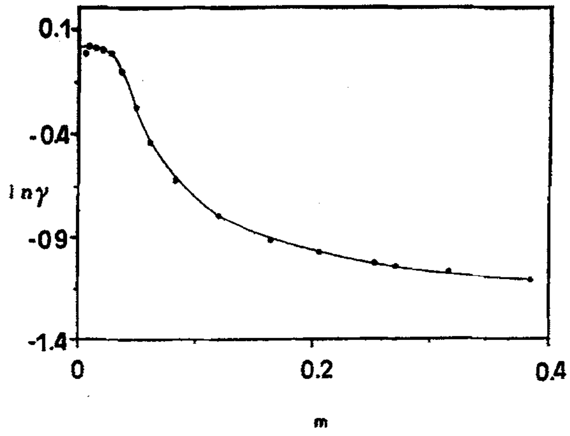

Fig. 1. Activity coefficients, γ, in logarithmic scale, inferred by freezing point depression, vs OG molality, m

The function $\ln \gamma$ vs m is reported in Fig. 1.

The activity coefficients can be higher than unity at concentrations lower than the CMC: this feature is not unusual and can be ascribed to hydrophobic solvation of molecularly disperse solutes [20–22]. Ionization effects and the presence of impurities can be ruled out.

Above the CMC, the activity coefficients sharply decrease on increasing m.

Volumetric properties

Apparent molal volumes, Φ_v, reported in Table 2, were calculated from experimental density findings according to:

$$\Phi_v = (1/\rho)[\mathrm{MW} - 10^3(\rho - \rho^0)/\rho^0 m]\,, \qquad (3)$$

where ρ and ρ^0 are the solution and solvent densities, respectively, and MW is the solute molecular weight. The accuracy on apparent molal volumes is inversely proportional to the concentration, and values at concentrations lower than $5 \cdot 10^{-3}$ molal were not reported, since the experimental uncertainty is higher than 2 cm^3 mol^{-1}. A typical plot of apparent, and partial, molal volumes versus surfactant molality is reported in

Table 2. Apparent molal volumes, Φ_v, (cm^3 mol^{-1}), of OG at 15°, 25° and 30 °C

15 °C		25 °C		30 °C	
$10^3\,m$	Φ_v	$10^3\,m$	Φ_v	$10^3\,m$	Φ_v
9.08	243.4 (± 1.3)	9.84	245.7	5.185	247.3 (2.0)
15.17	243.2	14.68	245.2 (± 1.0)	7.525	246.8
20.13	243.2	20.17	245.6	11.2	246.6 (± 1.0)
24.93	243.6	24.05	246.5 (± 0.7)	14.52	245.6
31.33	244.3 (± 0.5)	30.81	248.0	18.8	246.0 (± 0.7)
39.93	245.9	35.50	248.9	20.69	247.0
73.9	248.8	42.18	250.1	26.44	247.7
100.5	250.1	50.09	250.5	32.07	248.9 (± 0.3)
131.7	250.9 (± 0.2)	58.57	251.5	41.2	250.4
154.7	251.3	97.88	254.2	68.22	252.5 (± 0.2)
317.8	252.5	237.75	255.0	102.71	254.1
340.2	252.6	282.77	255.3	207.7	255.9
		325.93	255.5	269.69	256.2 (± 0.1)
		396.68	255.6	334.15	256.5

Values in brackets indicate the uncertainty on apparent molal volumes at a given composition

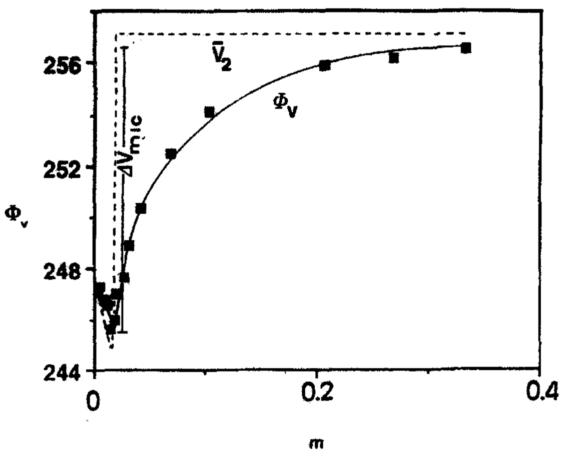

Fig. 2. Apparent molal volumes, Φ_v, (cm^3 mol^{-1}), and partial molal volumes, $\bar{V}_2$, dotted line, as a function of OG molality, at 15 °C. The volume change upon micelle formation, ΔV_{mic}, is indicated by a bar

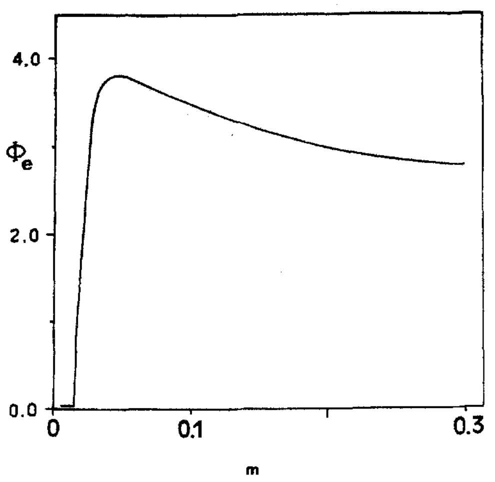

Fig. 3. Apparent molal expansibilities, $10^3\Phi_e$, (cm^3 mol^{-1} K^{-1}), as a function of surfactant molality, m, in the range 15–25 °C

Fig. 2. Partial molal volumes, $\bar{V}_2$, were calculated according to

$$\bar{V}_2 = [\partial(m\Phi_v)/\partial m]_{T,P} \,. \qquad (4)$$

The volume change upon micellization, ΔV_{mic}, inferred by the steep discontinuity in $\bar{V}_2$ values at the CMC, is nearly constant, or slightly decreases on increasing the temperature. Its value is noticeably sensitive to the data fitting: in the premicellar region, the difference between volumes calculated by assuming a linear, or quadratic, composition dependence of $\bar{V}_2$ values can be as high as 7 cm^3. The $\bar{V}_2$ values approach the corresponding Φ_v ones at high concentrations.

Apparent molal expansibilities, Φ_e, were calculated by deriving the apparent molal volumes with respect to T. Were CMCs independent of temperature, a saw-tooth function should be observed: the reported trend, Fig. 3, indicates the occurrence of relaxation displacement contributions, which are related to the thermal shift of

Table 3. Integral enthalpies of dilution, $\Delta H_{i,d}$ (Joules mol^{-1}) and OG molality before and after dilution, m_i and m_f, respectively

25 °C			30 °C		
$\Delta H_{i,d}$	$10^3\,m_i$	$10^3\,m_f$	$\Delta H_{i,d}$	$10^3\,m_i$	$10^3\,m_f$
−88.98	22.08	11.00	−194.6	20.80	10.38
−196.4	24.05	11.98	−756.8	27.33	13.62
−529.9	30.81	15.34	−923.5	28.86	14.38
−893.1	31.82	15.84	−1227	31.20	15.54
−1029	35.50	17.66	−3408	56.24	27.91
−2247	44.46	22.16	−2725	62.97	31.22
−2872	58.57	29.04	−2630	64.22	31.84
−2348	64.23	31.82	−1683	74.09	36.65
−2209	83.41	41.22	−1305	114.34	56.28
−2016	90.32	44.59	−1100	151.54	74.09
−1128	130.88	64.23	−1058	163.82	81.57
−949.7	185.47	90.31	−1015	177.31	84.12
−906.9	237.75	114.92	−943.5	194.13	91.15
−813.1	282.77	135.82	−798.7	213.62	103.61
−717.1	325.93	155.59	−691.8	251.19	121.30
			−523.7	335.07	159.72
			−344.6	455.60	213.62

The maximum uncertainty on $\Delta H_{i,d}$ is ±1%, on concentrations ±0.3%.

CMCs [23]. In nonionic surfactant solutions the relaxational contribution to Φ_c should be regularly dependent on temperature, provided this is far from the consolute boundaries.

Calorimetric properties

Integral enthalpies of dilution, $\Delta H_{i,d}$, are reported in Table 3. In the premicellar region they were fitted according to [24]:

$$\Delta H_{i,d} = \Phi_{L,f} - \Phi_{L,i} = (m_f - m_i)[A_L + B_L(m_f + m_i) + \ldots] , \qquad (5)$$

where $\Phi_{L,f}$ and $\Phi_{L,i}$ indicate the apparent molal enthalpies at m_f and m_i, respectively, and A_L and B_L are proper constants, which depend on temperature. Such constants are reported in Table 4. Higher terms in the power series equation are immaterial and were omitted. The resulting accuracy on fitting is to ±1.5%.

Table 4. The A_L and B_L coefficients of Eq. (6), for data in the premicellar region of OG, at 25 and 30 °C

T (°C)	A_L (J mol^2 Kg^{-1})	B_L (J mol^3 Kg^{-1})
25	$-1.351 \cdot 10^5$	$3.668 \cdot 10^6$
30	$-2.702 \cdot 10^5$	$1.104 \cdot 10^7$

Apparent molal enthalpies at concentrations higher than the CMC were obtained by a best-fit procedure based on a combined use of experimental $\Delta H_{i,d}$ and calculated Φ_L values, relative to both premicellar and micellar regions, up to convergence. The trend of partial molal enthalpies, $L_2 = (\partial[\Phi_L m]/\partial m)_{T,P}$ as well as the related apparent molal ones, at 30 °C, is reported in Fig. 4.

Heat capacities, ΔC, were obtained from the partial molal enthalpies, according to the relation [25]

$$\Delta C = \Delta L_2 / \Delta T \, . \qquad (6)$$

The heat capacities *) in Eq. (6) were calculated by assuming linearity in the function $C_p(T)$ [26]. In the premicellar region, combination of Eqs. (5) and (6) gives:

$$\Delta C = [(m_f - m_i)/\Delta T][(A_{L,T'} - A_{L,T^o}) + (B_{L,T'} - B_{L,T^o})(m_f + m_i)] , \qquad (7)$$

where the superscripts indicate different temperatures. Above the CMC, heat capacities were calculated by iterative use of analytical and graphical methods up to convergence. The best fit of the ΔC function is reported in Fig. 5. ΔC values exhibit a steep maximum in close proximity of the CMC and a significant positive slope at higher concentrations, which goes parallel to the trend of specific heats observed in some selected surfactant systems [25–27]. When enthalpic contributions to micelle formation are null, ΔC_{mic} can be obtained by extrapolation to the CMC of ΔC values relative to premicellar and micellar regions, respectively. When ΔH_{mic} is $\neq 0$, heat capacities go through a steep maximum at the CMC and the aforementioned data fitting procedure no longer holds [25b].

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*) The partial molal heat capacity is the limit of the function in Eq. (6), when $\Delta T \approx 0$. For thermodynamic consistency, we define ΔC values in terms of unspecified head capacities

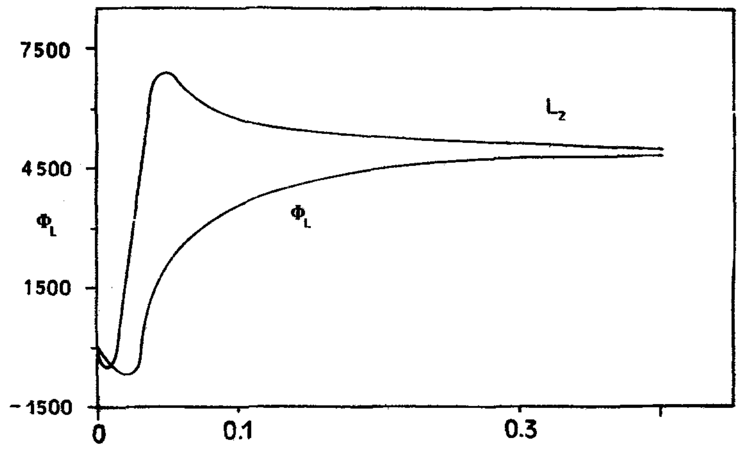

Fig. 4. Partial molal enthalpies, L_2, (Joules-mol^{-1}), and apparent molal ones, Φ_L, vs OG molality, at 30 °C

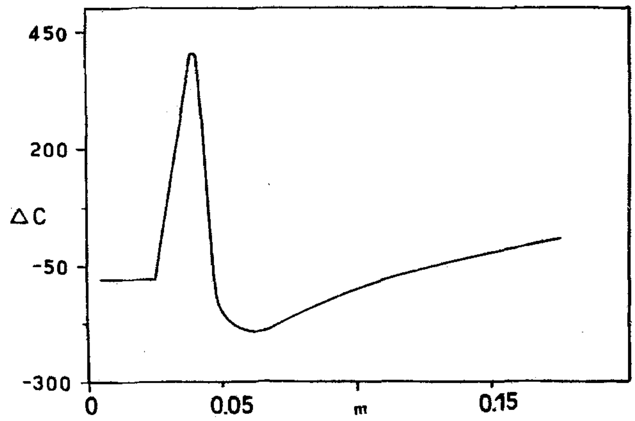

Fig. 5. Molal heat capacities, ΔC, (Joules mol^{-1} K^{-1}), as a function of OG molality, m, at 27.5 °C

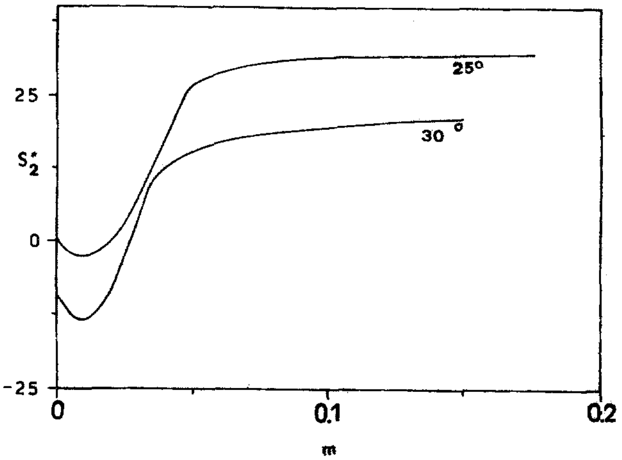

Fig. 6. Nonideal entropies, S_2^*, (Joules mol^{-1} deg^{-1}), vs. surfactant molality, at 25 and 30 °C. The latter function is shifted 10 J/(K mol) units downward

Nonideal partial molal entropies, S_2^*, were calculated according to

$$S_2^* = (L_2 - G_2^*)/T\,, \tag{8}$$

where $G_2^* = RT \ln\gamma$ is the Gibbs energy. The temperature dependence of γ values in Eq. (8) was calculated according to classical procedures [28]. The $S_2^*(m)$ function is reported in Fig. 6.

Discussion

Thermodynamic properties of association colloids have been widely investigated, particular interest being focused on enthalpies of dilution and apparent molal volumes of medium chain ionic surfactants. Recently, studies on selected nonionic surfactants, as octyltetraoxyethylene glycols [29], alkyldimethylamine oxides [23], and alkylsulphobetaines [24] have been reported too.

Some thermodynamic properties for micelle formation of OG are reported in Table 5. They refer to different temperatures and contain information on the forces controlling the process. CMCs decrease on increasing T. Even if CMC data in Table 5 refer to values obtained by different methods and some discrepancies between them can be observed [30], the errors are not

Table 5. The critical micellar concentration of OG, CMC, the volume change upon micelle formation, ΔV_{mic}, the enthalpy of micelle formation, ΔH_{mic}, the heat capacity change, ΔC_{mic}, and the expansibility change, $\Delta \Phi_{\mathrm{e,mic}}$, consequent to micelle formation

T (°C)	10^3 CMC (mol K^{-1})	$\Delta V_{\mathrm{mic}}{}^{\mathrm{a}}$ ($\mathrm{cm}^3\,\mathrm{mol}^{-1}$)	ΔH_{mic} ($\mathrm{kJ\,mol}^{-1}$)	ΔC_{mic} ($\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$)	$\Delta \Phi_{\mathrm{e,mic}}$ ($\mathrm{cm}^3\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$)
0	39^{b})	(11.9)	–	–	–
15	30	9.9 ± 1.5	–	–	–
25^{c}	24	8.5 ± 1.5	6.4 ± 0.5	–	0.16 ± 0.05
27.5	(23)	(8.0)	(6.2)	480 ± 30	(0.15)*)
30^{c}	21	7.5 ± 1.2	6.0 ± 0.5	–	0.13 ± 0.03

*) Data obtained by interpolation

a) Obtained by iterative use of Eq. (8), up to convergence

b) From freezing point depression

c) CMC values obtained from partial molal volumes

large and the trend of CMCs versus T is as expected. The different thermodynamic functions shall be discussed separately.

Volumetric and expansibility findings

For reasons discussed above, the volume change upon micelle formation, ΔV_{mic}, is subject to large uncertainties. The accuracy is dependent on the behavior of Φ_{v}'s below and above the CMC, respectively, and an attempt to define ΔV_{mic} in proper terms is model dependent (see Experimental section).

Comparison between experimental and calculated ΔV_{mic} data can be made by using apparent molal expansibilities, Φ_{e}. They were rationalized by assuming that the apparent molal volumes above the CMC are due to a mass averaged contribution due to molecularly disperse and micellar surfactant, respectively. Taking into account the thermal shift of either CMCs and ΔH_{mic}, the volume change can be obtained (see the Appendix), according to:

$$\begin{aligned}\Phi_{\mathrm{e}} &= (\partial V_{\mathrm{m}}/\partial T) + (\mathrm{CMC}^*/m)\\ &\quad\times[(\partial V_1/\partial T) - (\partial V_{\mathrm{m}}/\partial T)\\ &\quad+ \Delta H^*_{\mathrm{mic}}\Delta V_{\mathrm{mic}}/RT^2]\,, \qquad (9)\end{aligned}$$

where CMC* and $\Delta H^*_{\mathrm{mic}}$ are the critical micellar concentration and the enthalpy of micelle formation at a temperature T^*, V_1 and V_{m} the partial molal volumes of molecular and micellar surfactant, respectively. $\Delta V_{\mathrm{mic}} = V^0_{\mathrm{m}} - V^0_1$, is the volume change upon micelle formation *).

Φ_{e} values in Eq. (9) are modulated from either enthalpic and volumetric contributions and proper combination of their experimental and computed values allows to get the volume changes for micelle formation, ΔV_{mic}, reported in Table 5. They are comparable with those for other octyl chain surfactants [23, 24].

Use of apparent molal volumes to estimate number average micelle aggregation numbers, $\langle n \rangle$, discussed elsewhere [12], gives values close to 40 monomers of OG per micelle. These are not very far from those inferred from colligative properties, see below.

Enthalpic behavior

Apparent and partial molal enthalpies give positive ΔH_{mic} values, Table 5. At 25 °C, ΔH_{mic} is between that of the homologous sulfobetaine [24] and that of octyl tetraoxyethylene glycol [29]. Calorimetric investigation on octylthioglucoside micelle formation supports the aforementioned trend [31].

The glucosidic head group controls, to a minor extent, the enthalpic contribution to micelle formation, which is mainly ascribed to interactions of the hydrophobic groups with water [32]. To evaluate the head group contribution to ΔH_{mic}, we remind that the enthalpy of transfer from water to a micellar environment is close to

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*) ΔV_{mic} in Eq. (9), the volume change upon micelle formation at $m = 0$, is generally different from the value calculated at the CMC. When $V_1 = V_1^* + A_{\mathrm{s}}m$, the difference between the two values is A_{s}CMC

500 J mol^{-1} per methylene unit [33]. The enthalpy change for partial disruption of the glucoside solvation shell, released during the micellization process, results to be positive. Its estimated contribution to ΔH_{mic} results to be about 2 KJ mol^{-1}, close in modulus to the glucoside standard solvation enthalpy, $\Delta H^0_{\mathrm{solv}}$ [34, 35].

Heat capacities

In Fig. 6 is reported the heat capacity trend. Due to the small temperature difference between the two sets of measurements, we assumed a linear dependence of $C_p s$ on T, which allows us to make use of Eq. (6). The change in heat capacity at the CMC is about 500 J K^{-1} mol^{-1}, in agreement with findings relative to the partial molal capacities values, C_p, of nonionic octyl chain surfactants [23, 29].

Should micelle-micelle interactions become more and more pronounced on increasing C_m, $\approx C$ − CMC, as a consequence of changes in the aggregate shape, the system free energy should decrease further. This feature should be concomitant to variations in the $C_p(m)$ function, which, being a second derivate with respect to the Gibbs energy, is extremely sensitive to fine changes in the solution structure.

Quirion and Desnoyers found that the function $C_p(m)$ in the system water-cetyltrimethylammonium bromide-butoxyethanol [36] increases above the CMC. In addition, Kameyama [11] and some of us [12] observed that OG micelles become progressively anisometric on increasing the amount of surfactant in micellar form. Thus, changes in heat capacities at moderately high surfactant content are presumably related to small and continuous changes in micelle size and shape. The concentration at which micellar growth becomes effective is assumed to be the minimum point of the function, $(\partial \Delta C(m)/\partial(m)) = 0$, Fig. 5.

Activity coefficients

The activity coefficients of surfactant molecules drastically decrease at concentrations above the CMC and level off at high concentrations. Such decay has been rationalized by assuming micelle formation to be a chemical equilibrium between molecular and micellar surfactant, characterized by an equilibrium constant, K_{mic}. The basic requirement of the equilibrium model, developed independently by several authors [14, 21–23], is the monodispersity constraint, according to which only monomers and micelles containing n surfactant units do exist. It is possible to get number average aggregation numbers by plotting the data according to [14]:

$$\ln K_{\mathrm{mic}} + n \ln C_T[(\gamma)_{\mathrm{mic}} - (\gamma)_1] = (n-1)\ln(\gamma)_{\mathrm{mic}} + \ln C_T(\gamma)_1 \,, \qquad (10)$$

which has been derived from the Gibbs energy of micelle formation, calculated according to the mass action law:

$$\Delta G^0_{\mathrm{mic},n} = -(RT/n)\ln K_{\mathrm{mic}} \,. \qquad (11)$$

The aggregation numbers obtained in this way are in the range 30–40, which is quite low compared to values inferred from ultracentrifugation and/or light-scattering methods [10, 11]. We remind, however, that numbers obtained by Eqs. (10, 11) are number average values, whereas those from ultracentrifugation and light-scattering are related to z-average and weight average values, respectively.

Appendix

In a two-site approximation, the apparent molal volume of the surfactant molecule can be defined as:

$$\Phi_v = \alpha V^0_1 + (1-\alpha) V^0_m \,,$$

where V^0_1 is the limiting apparent molal volume in molecular form, α is the ratio between molecular and overall surfactant molality, and V^0_m the apparent molal volume of micellar surfactant. When the surfactant content exceeds the CMC, the concentration of molecular surfactant can be rewritten as:

$$\alpha = (\mathrm{CMC}/m) = (1/m)\exp(\Delta G^0_{\mathrm{mic}}/RT) \,.$$

Taking into account the effect of temperature on CMC and Φ_v and rewriting $\Delta G^0_{\mathrm{mic}}$ in terms of its enthalpic and entropic contributions, the expansibility for data above the CMC becomes:

$$\Phi_e = (\partial V_m/\partial T) + (\mathrm{CMC}^*/m)[(\partial V_1/\partial T) - (\partial V_m/\partial T) + \Delta H^*_{\mathrm{mic}} \Delta V_{\mathrm{mic}}/RT^2]$$

where CMC*, ΔV_{mic} and $\Delta H^{*}_{\mathrm{mic}}$ are values at a given temperature.

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