

Volumetric Determination of the Hydration State in Nonionic Surfactant Solutions

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Density and sound velocity measurements were performed on water solutions of the nonionic surfactant belonging to the family of the oligooxyethylene glycol (C_iE_j), with $i = 12$ and j ranging from 5 to 8 EO units. Up to a threshold concentration, the density (ρ) and the compressibility coefficient ($\beta = \rho^{-1}c^{-2}$) measured as a function of the temperature cross the density and the compressibility coefficient of water at the temperatures (T_ρ and T_β) which depend on the surfactant. Such conditions are proper of ideal solutions; thus, our water–surfactant solutions can be analyzed in this context as ideal mixtures of the pure solvent and effective solutes. We microscopically model such effective solutes as hydrated monomers assembled in micellar aggregates. Under some assumptions on the volumetric properties of the hydrophobic micellar core, we experimentally determine the molar volume of the EO terminations at the micellar interface. By comparing these values with those obtained for solutions of water and PEG (a polymer composed by j EO units), we estimated the degree of hydration of the interfacial EO–water mixture. The compressibility $K = \beta V$ obtained from our model embodies a contribution due to the derivative of the number of the hydrated water molecules with respect to the pressure. Such derivative is characteristic of a solution in osmotic equilibrium with its solvent and, in the case of the micelles, can be rationalized on the bases of the “small system thermodynamic” theory. By comparing the compressibility of the micellar interface with that of an equivalent PEG–water solutions, we estimate the osmotic contributions for each of the investigated surfactant. The threshold concentrations, below which these solutions mix ideally, reflect an effect due to the different sizes of the solute aggregates and the solvent molecules.

1. Introduction

The nonionic surfactant belonging to the family of the oligooxyethylene glycol (C_iE_j) form in water micellar aggregates. The hydrophobic moieties (C_i) are segregated from the solvent in the micellar core region, whereas the hydrophilic terminations (E_j) are exposed to the solvent in the interfacial region.^{1,2} The surfactant solutions present a rich variety of thermodynamic phases. In the dilute and semidilute concentration ranges these mixtures are isotropic (L_1 phase), and depending on the temperature and the surfactant concentration, the aggregates can be monodisperse with a spherical shape or characterized by elongated polydisperse cylinders.^{3,4} Above the so-called lower consolute temperature a cloud curve is reached, and the solutions divide into two isotropic phases with different surfactant concentrations.⁵ At high concentration the aggregates form liquid crystal phases at low temperature⁶ and bicontinuous structures at high temperature.⁷

The average aggregate shape and size, as well as the extent of the different thermodynamic phases, depend on the volume ratio between the hydrophilic and hydrophobic terminations. As the volume of the hydrophilic moieties increases, the isotropic L_1 phase enlarges its range.⁶ Likewise, the temperature and the concentration intervals where the solution contains only mono-

disperse spherical aggregates become wider.^{3,4,8,9} From a phenomenological point of view, this simply means that the aggregates whose interface is composed of longer hydrophilic terminations can stand a wider range of thermodynamic conditions, preserving their shape and size as well as the overall solution thermodynamic phase. However, the way the hydrophobic–hydrophilic volume ratio affects the stability of the micellar dispersions is still a source of debate.

From the thermodynamic point of view, the total free energy of these surfactant solutions can be divided into three contributions: the first due to the micellar formation, the second due to the mixing of the aggregates and the solvent, and the third due to the intermicellar interactions.¹⁰ The free energy gain when a single micelle with a given shape and size self-aggregates can be evaluated by adding the free energy changes associated with a set of reversible thermodynamic transformations.¹¹ These contributions can be divided into two groups: (i) the free energy gained when the hydrophobic moiety is transferred from pure water to an oily phase; (ii) the free energy loss needed to form the aggregate interface. Therefore, the thermodynamic properties of the micelle are defined by introducing a suitable Gibbs surface function which describes the aggregate interface. The same goal can be reached on the ground of the “small system thermodynamic” theory. In this context the thermodynamic properties of the micellar core and interface are determined by averaging on a large number of aggregates of a given shape and size in equilibrium with the external solvent.^{12,13} The two approaches are equivalent; indeed, the excess properties obtained on the

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basis of the small system thermodynamic, taking as a set of independent thermodynamic variables the solvent chemical potential, the pressure, and the temperature, correspond to those obtained from the surface functions introduced by Gibbs (see ref 14, Chapter 12). In both the formulations the solution free energy is defined through the states of thermodynamical equilibrium of the three regions which characterize these nonionic micellar solutions: the aggregate interfaces, composed by the hydrophilic terminations and the hydrated water molecules, interposed between the hydrophobic oil core regions and the external water.

The present work is focused on the experimental determination of the volumetric properties of these three regions in the L_1 phase. We performed density (ρ) and sound velocity measurements (c) on $C_{12}E_j$ having the same hydrocarbon tail, composed of one CH_3 and 11 CH_2 units ($i = 12$) and a number of oxyethylene (CH_2-CH_2-O) terminations (indicated by EO in the rest of the work) ranging from 5 to 8. The sample preparation and the experimental methods are described in section 2. The intensive quantities ρ and β , where $\beta = \rho^{-1}c^{-2}$ is the isothermal compressibility coefficient thermodynamically defined as $\beta = -(1/v)(dv/dp)_T$, allow the determination of the molar volume $\tilde{V} = \tilde{M}/\rho$ (where \tilde{M} is the molar mass of the solution) and of the molar isothermal compressibility $\tilde{K} = \beta\tilde{V}$. It will be shown that, in a limited concentration range, these solutions can be regarded in the context of ideal mixing of the pure solvent and the hydrated solute. In this case the molar volume and compressibility of the two components result a function only of the temperature (section 3). Hence, under a sort of equivalent state hypothesis, our analysis allows us to determine the molar volume and compressibility of the oil core and of the hydrophilic terminations as well as the degree of hydration per oxyethylene unit within the interfacial region (section 4). The consistency of the obtained results is discussed in section 5, and some general conclusions are drawn in section 6.

2. Materials and Methods

The samples analyzed ($C_{12}E_{5,6,7,8}$) were purchased from Nikko Chemicals and were diluted without further purification. The concentrations of the different water solutions were stated by weighing.

The density measurements were performed with PAAR digital density meter DMA60 in combination with remote cell DMA 602, which can provide an accuracy up to $\pm 1.5 \times 10^{-6}$ g/cm³, according to the oscillating sample tube method. The external cell was thermostated by a Heto DBT 6 thermostat and a Heto CB8-30e cooling bath which guarantees a temperature stability within 0.05 °C. The PAAR instrument we used does not compensate for viscosity. Increasing the sample viscosity, the interface between the tube and the liquid surface induces an extra resonance frequency. As a result, the overall resonance frequency of the tube (that depends on the solution density) is shifted. For this reason at the highest concentrations the accuracy of our measurements reduces to $\pm 1 \times 10^{-4}$ g/cm³.¹⁵

A variable path length cell was used for the ultrasonic measurements. To matched 5 MHz fundamental crystal was used, along with a quartz delay line, in a pulsed-sound mode. The temperature of the sample was controlled by a water thermostat regulated within ± 0.1 K. The sound velocity (c) was obtained by acoustically overlapping pulses under variable-path conditions to coherent CW signal generated by a Matec pulse modulator equipment.¹⁶ The measurements were performed at

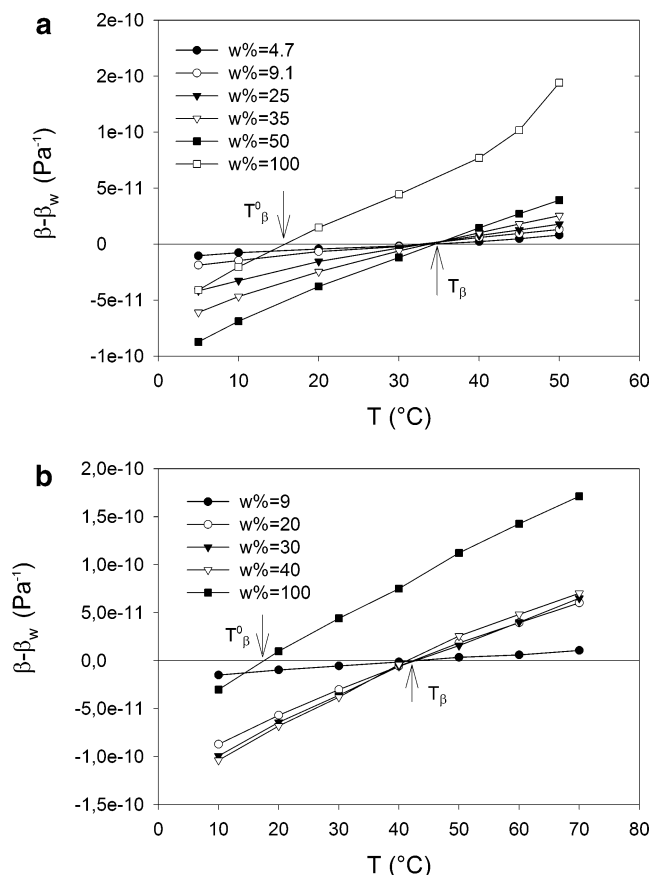


Figure 1. The quantity $\beta - \beta_w$ is plotted for the aqueous solutions of $C_{12}E_j$ with $j = 6, 8$ as a function of temperature for different concentrations: (a) $C_{12}E_6$; (b) $C_{12}E_8$.

5 MHz; the accuracy of the absolute sound velocity data (at fixed frequency) is estimated to be ± 0.2 m s⁻¹.

3. Thermodynamic Background and Experimental Results

The densities of $C_{12}E_j$ aqueous solutions as a function of temperature and surfactant concentration have been already reported for $j = 5-8$ in a previous work of the authors.¹⁷ The results show that, up to a threshold concentration whose value depends on the surfactant, the densities of the solution, ρ , measured as a function of the temperature, cross the density of water, ρ_w , nearly at the same temperature (T_ρ) for all the concentrations. In the case of 5 EO units per monomer the crossing temperature is 14 ± 1 °C, up to 25 wt %. For 6 EO units the crossing temperature is 37 ± 3 °C, up to 35 wt %. For 7 EO units $T_\rho = 53 \pm 3$ °C at least up to 30%. Finally, for 8 EO units the crossing temperature is obtained by extrapolating the experimental densities above the lower consolute temperature (present at about 80 °C), and $T_\rho = 86 \pm 3$ °C up to 40%. Above these threshold concentrations the crossing temperatures decrease monotonically down to a minimum values (T_ρ^0), eventually out of the experimental accessible range, at which the densities of the pure surfactant coincide with that of water.

A similar behavior is observed for the compressibility coefficients, in this case the crossing temperatures (T_β) are found at 34 ± 1 and 40 ± 1 °C for 6 and 8 EO units in the same concentration ranges indicated for the relative densities (see Figure 1a,b). For concentrations higher than the thresholds, the crossing temperatures decrease monotonically down to minimum

values (T_β^0) corresponding to the temperatures at which the compressibility coefficients of both the pure components coincide.

The presence of the crossing temperatures T_ρ and T_β is remarkable since it indicates that, in the given concentration ranges, the density and compressibility coefficient of the solute and of the solvent depend only on temperature and behave ideally. Indeed, both the density and the compressibility coefficient of a solution can be defined, at any concentration, by a linear combination of the contributions due to the solvent and to the solute weighed by the relative volume fraction (see Appendix). In general, these quantities depend on the solution concentration, but for ideal mixing they do not. In this case the solution density can be written as $\rho(\phi, T) = \rho_w(T) + \phi[\rho_s(T) - \rho_w(T)]$, and at a given temperature (T_ρ), it will be equal to the density of the solvent for all the concentrations. An equivalent equation holds for the compressibility coefficient (see Appendix), and at $T = T_\beta$, it will be equal to that of the solvent.

In the case of ideal mixing the values of T_ρ and T_β coincide with T_ρ^0 and T_β^0 . The values of the T_ρ^0 's are obtained by extrapolating the trend of the pure water density and those of the pure surfactant to the crossing conditions, which occur at -25 , -10 , 4 , and 22 °C, for 5, 6, 7, and 8 EO units, respectively. Similarly, by comparing the adiabatic compressibility coefficients of the pure components, the crossing temperatures T_β^0 's results to be 16 and 18 °C for C₁₂E₆ and C₁₂E₈, respectively.

The values of T_ρ 's and T_β 's experimentally determined do not agree with the values calculated assuming an ideal mixing of the pure species. Nevertheless, up to the threshold concentrations of each surfactant, the density and the compressibility coefficients of these solutions can be considered an ideal mixing of specific reference states for the water and for the surfactant. Since the solution densities cross that of the pure solvent, the solvent reference state must coincide with the pure solvent phase. Thus, the solute reference state must contain all the excess properties of the real solution with respect to the mixing of the pure components. This condition is the basic statement in the dilute solution theory that will represent the guide line for our experimental analysis.

In the following, we will proceed with the data analysis by considering the molar volume and the molar compressibility of the solution, instead of the density and the compressibility coefficient. These quantities are given by the linear combination of the molar volume and molar compressibility of the solute and of the solvent, weighed by the relative mole fraction (see Appendix). The concentration in mole fraction can be easily determined by weighing the solute and the solvent during the sample preparation, whereas the evaluation of the solute molar volume is model dependent (see below).

In the framework of the dilute solution theory, the general equation for the solution molar volume is given by¹⁸

$$\tilde{V} = \frac{\tilde{M}}{\rho} = (1 - x)\tilde{V}_w^0 + x\phi_V \quad (1)$$

and for the molar compressibility¹⁹

$$\tilde{K} = \beta\tilde{V} = (1 - x)\tilde{K}_w^0 + x\phi_K \quad (2)$$

where x is the monomeric concentration in mole fraction and $\tilde{M} = (1 - x)\tilde{M}_w + x\tilde{M}_s$ is the solution molar mass. The quantities ϕ_V and ϕ_K are respectively the so-called apparent molar volume and compressibility of the effective solute. The term *apparent* is used to indicate that these quantities reflect all the excess properties of the solution and could not correspond to the real

solute properties, whose evaluation requires a specific thermodynamic model for ϕ_V and ϕ_K . This explains why we have chosen to work with properties weighed by the relative mole fractions since in this case the concentration is unambiguously determinable experimentally. The quantities \tilde{V}_w^0 and \tilde{K}_w^0 are the molar volume and compressibility of the pure solvent. As expected from the previous remarks, the experimental values of ϕ_V and ϕ_K are nearly independent of the concentration in the given ranges for each sample. The results we obtained agree with previous data from the literature.²⁰

The apparent properties ϕ_V and ϕ_K represent a way to describe the experimental results on the ground of ideal mixing, where the ideality is recovered by defining an effective reference state for the surfactant. By looking at Figure 1, it can be seen that T_β increases with the water content, going from T_β^0 (absence of water) up to the indicated crossing temperature, T_β , which remains constant down to zero surfactant concentration. The same occurs to T_ρ . Phenomenologically this means that, in the presence of enough water, the micellar interfaces become fully hydrated and represent an effective solute that mixes ideally with water. Hence, we modeled these solutions as mixtures of pure water and hydrated surfactant aggregates. This is not a new concept since it is widely accepted that hydration has a fundamental role in the thermodynamic equilibrium of nonionic micellar solutions.^{5,21–25}

Formally this model implies that, during the solubilization, some of the solvent molecules become part of the hydrated solute, belonging no longer to the bulk solvent region. In general, these molecules will possess different volume V_w^h and compressibility K_w^h compared with those of the external solvent region. Hence, by taking into account the number of the hydrated solvent molecules per surfactant, indicated by h in the rest of the article, the molar volume of the solution can be written as

$$\tilde{V} = (1 - x - hx)\tilde{V}_w^0 + x\tilde{V}_s^h \quad (3)$$

where \tilde{V}_s^h is the molar volume of the hydrated solute. This is given by

$$\tilde{V}_s^h = \tilde{V}_s + h\tilde{V}_w^h = \tilde{V}_t + \tilde{V}_h + h\tilde{V}_w^h \quad (4)$$

where \tilde{V}_s is the molar volume of the surfactant monomer alone, given by the sum of molar volumes of the oily tail, \tilde{V}_t , and of the hydrophilic termination, \tilde{V}_h . By equating the right-hand sides of eqs 1 and 3, the apparent molar volume of the hydrated surfactant results:

$$\phi_V = \tilde{V}_s^h - h\tilde{V}_w^0 = \tilde{V}_s \left(1 + h \frac{\tilde{V}_w^h - \tilde{V}_w^0}{\tilde{V}_s} \right) \quad (5)$$

The molar compressibility is defined as the opposite of the derivative of the molar volume (3) with respect to the pressure. The resulting equation is:

$$\tilde{K} = (1 - x)\tilde{K}_w^0 + x \left[(\tilde{K}_t + \tilde{K}_h) + h(\tilde{K}_w^h + \tilde{K}_w^0) - \left(\frac{\partial h}{\partial p} \right)_T \times (\tilde{V}_w^h + \tilde{V}_w^0) \right] \quad (6)$$

The apparent molar compressibility ϕ_K is obtained by comparing (2) with (6):

$$\phi_K = (\tilde{K}_t + \tilde{K}_h) + h(\tilde{K}_w^h - \tilde{K}_w^0) - \left(\frac{\partial h}{\partial p} \right)_T (\tilde{V}_w^h - \tilde{V}_w^0) \quad (7)$$

The second term in the bracket of eq 5 is generally negligible. Indeed, the quantity \tilde{V}_s , which can be evaluated from the density of the pure surfactant in their liquid state, ranges from 400 cm³/mol for C₁₂E₅ to 540 cm³/mol for C₁₂E₈. These values have to be compared with the difference $\tilde{V}_w^h - \tilde{V}_w^0$, where the water molar volume is about 18 cm³/mol. A rough estimation of the above difference can be obtained evaluating the apparent molar volume of water from measurements in solution at high surfactant concentration, where the water plays the role of the solute. Indeed, even in this range of concentrations, the oily tails and the EO terminations segregate in separated regions,¹⁷ and the water is only in contact with the EO hydrophilic units. Hence, the apparent molar volume of water will ultimately reflect the local interaction with the neighbor EO terminations, i.e., an environment similar to that seen by the water molecules embedded within the micellar interface. The value we found is about 10% lower than the one observed in the bulk water. Similar considerations can be made in the case of the second term in eq 7 since the compressibility is given by the volume times the compressibility coefficient, and the compressibility coefficients measured in water and pure surfactant are very close.

In conclusion, the quantities ϕ_V and ϕ_K represent the experimental molar volume and compressibility of the solute that include all the excess properties of the solution. In the concentration ranges where the crossing temperature are given by T_ρ and T_β , ϕ_V and ϕ_K do not depend on surfactant concentration. Furthermore, for each surfactant, ϕ_V depends only on the temperature since it is nearly independent of the degree of hydration (h). On the other hand, ϕ_K still contains a term associated with derivative of the number of hydrated solvent molecules h with respect to the pressure.

4. Data Analysis

Since we have shown that the solvent reference state can be assumed equivalent to a bulk water phase, the subsequent data analysis reduces to the determination of the local composition, molar volume, and compressibility of the two regions that compose the micellar aggregates: the oil core and the interface.

We begin with the analysis of the molar volumes, considering first the hydrophobic moiety. The presence of water in the oil core region is extremely unlikely since it is hydrophobic. Thus, it must contain only oily tails, although its local density and the exact location of its interface must be defined. In the above-mentioned thermodynamic model which describes the micellar formation,¹¹ the interface of the oil core was assumed smooth and the density of the confined tails equivalent to that of a bulk oily phase, at the same temperature and pressure of the solution. This assumption implies that the hydrophilic interface compensates for any extra pressure carried on the oily region by the solvent. The roughness of the micellar interface was taken into account by excluding the ending CH₂ from the oil core region, thus by moving inward the location of the smooth interface. The excluded CH₂ group was then considered part of the interfacial region, i.e., part of the EO–water mixture covering the micellar interface. This definition of the hydrocarbon core region is supported by molecular dynamic simulations²⁶ and experimental evidence.¹⁷ As a consequence, the EO unit are identified with a more symmetric structure whose base and termination are the CH₂–O–CH₂ and CH₂–O–H units, respectively. Therefore, following these theoretical and experimental indications, the volume per monomer of the hydrophobic termination was set equal to the mass of CH₃(CH₂)₁₀ divided

by the dodecane density. This represents a sort of equivalent state hypothesis between the oil core and a similar bulk oily phase.

Once the value of \tilde{V}_l is known, the hydrated volume per polar head can be obtained, since the hydration water molecules represent a small correction to the total monomer volume $\tilde{V}_h = \phi_V - \tilde{V}_l$ (see eq 5 and the comments thereafter). Thus, we can define the molar volume per EO unit $v_{EO}(j, T) = \tilde{V}_h^j(T)/j$. The error on this quantity is related to the fluctuation of T_ρ with the concentration, and thus it can be estimated from the standard deviation of the volumes around T_ρ . The maximum error results of about 3% for all the surfactant species.

However, since the explicit contribution of the degree of hydration to ϕ_V is negligible, we cannot make any direct determination of h . Nevertheless, its value can be still obtained by comparing the changes of the volumetric properties of the EO terminations with those of a suitable reference system. The most obvious reference system for the EO–water mixtures are the solutions of poly(oxyethylene glycol) (PEG) and water, a polymer composed by j units equivalent to the EO. Likewise the solutions of nonionic micelles in water, the driving mechanism which determines the overall thermodynamic state in the PEG–water solutions is associated with the hydration state too.^{27,28}

Let us consider now the volumetric properties of the PEG–water solutions in the high concentration range, corresponding to the concentrations typical of the micellar interface (see below for the experimental confirmation). An equation equivalent to (5) can be used to determine the apparent molar volume of PEG in water from density measurements (V_{PEG}^j). For concentrated polymer solutions the second term in the equation is still negligible and $\phi_V \approx \tilde{V}_{PEG}^j(R_w, T)$, where $R_w = (1 - x)/(j'x)$ is the number of water molecules per PEG unit and x is the polymer mole fraction. Thus, the molar volume of the PEG unit is given by $v_{PEG}(j', R_w, T) = \tilde{V}_{PEG}^j(R_w, T)/j'$. The experimental results for $v_{PEG}(j', R_w, T)$, in the case of PEG200,²⁹ PEG400,³⁰ and PEG600,³¹ indicate that (i) at a given degree of polymerization, the temperature dependence of v_{PEG} shifts to lower values at increased water concentrations, with no intersection between curves at different concentrations; and (ii) by increasing the degree of polymerization, the previous curves shift downward with no intersections at the same water content and the same temperature (at least for the considered polymers). Thus, for a given temperature, the knowledge of v_{PEG} uniquely defines the water content, R_w , and the degree of polymerization j' of the PEG–water solution (these consideration will be part of a future article). In other words, the extension and conformation of a given oxyrane group (which determine its volume) depend uniquely on the number of the surrounding water molecules.

On the basis of the previous experimental evidences, we can suppose that, at a given temperature, equivalent volumes for the EO and PEG unit must pertain to a polymer chain with the same degree of polymerization and the same degree of hydration, that is, $v_{EO}(j, T) = v_{PEG}(j' = j, jR_w = h, T)$. This hypothesis is supported by the equivalence, at all the investigated temperatures, between the apparent molar volumes of water experimentally determined in concentrated polymer and in concentrated surfactant solutions. Hence, we can define the interfacial water content by singling out the concentration of the PEG–water solution at which $v_{PEG}(j' = j, jR_w, T)$ matches the experimental $v_{EO}(j, T)$. The apparent molar volumes per PEG unit as a function of the water content (R_w) and at a temperature of 20 °C are reported in Figure 2, with lines and symbols, for

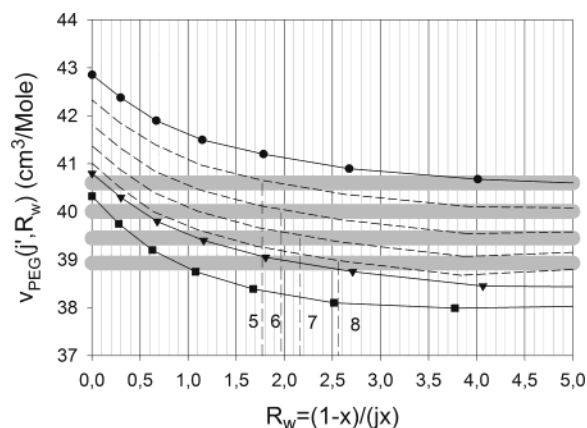


Figure 2. Apparent molar volumes are shown as a function of the hydration number per PEG units $R_w = (1 - x)/(j'x)$. Lines and symbols: $j' = 4.1$ (circles); $j' = 8.7$ (triangles); $j' = 13.2$ (squares). The dotted lines correspond to the extrapolated values for $j' = 5, 6, 7$, and 8 . The horizontal stripes are the values of the molar volume of the EO units obtained with our analysis for the micellar solutions, the thickness being the error on these determinations.

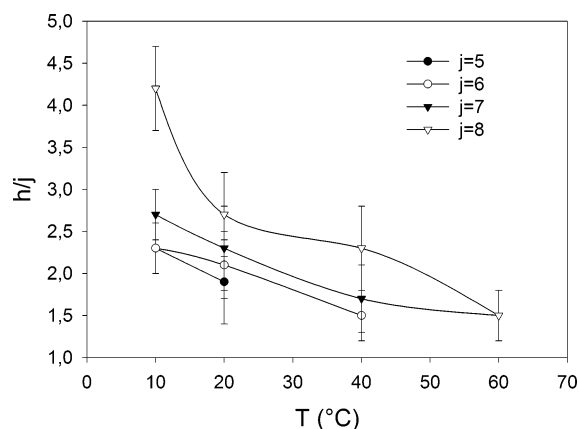


Figure 3. Hydration numbers per EO units h/j as a function of temperature are shown for the different surfactant solutions. These values of h/j correspond to the concentrations at which the EO and the PEG molar volumes cross in Figure 2.

PEG200 ($j' = 4.1^{29}$), PEG400 ($j' = 8.7^{30}$), and PEG600 ($j' = 13.2^{31}$). The dotted lines are the values interpolated at $j' = 5, 6, 7$, and 8 PEG units. In the same figure the horizontal stripes correspond to the values of the molar volumes per EO units at the same temperature, the thickness being the errors in their determination. The crosses between the molar volumes of EO and PEG, with the same degree of polymerization, identify the hydration state of the EO–water mixtures at the micellar interface $h = jR_w$. The hydration numbers per EO unit (h/j) as a function of temperature, obtained through this comparison, are shown in Figure 3. It is evident that the evaluated degree of hydrations correspond to high polymer concentrations. For these concentrations the error introduced neglecting the second term in eq 5 when used to determine ν_{PEG} , i.e., the ratio $j'R_w(V_w^h - V_w^0)/V_{\text{PEG}}$, is about 10%.

A similar procedure can be used to evaluate the interfacial contribution to the compressibility. As we already mentioned, also in this case the second term in the square bracket of eq 6 is negligible, and the molar compressibility per EO unit is approximately given by

$$k_{\text{EO}} \cong \frac{\phi_K - \tilde{K}_t}{j} = \frac{\tilde{K}_h}{j} \left[1 - \left(\frac{\partial h}{\partial p} \right)_{S,x} \frac{\tilde{V}_w^h - \tilde{V}_w^0}{\tilde{K}_h} \right] \quad (8)$$

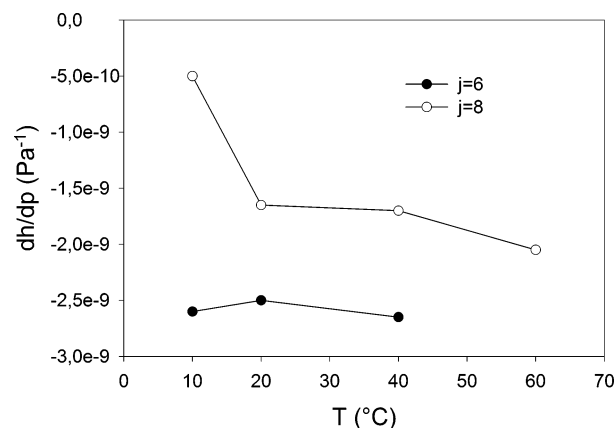


Figure 4. Values of dh/dp for the two surfactant C_{12}E_6 and C_{12}E_8 are reported as a function of the temperature.

A comparison can be made also in this case between the values of the compressibility obtained in the surfactant solutions and those in PEG–water solutions. The consistency of this approach is supported again by the equivalence within few percent of the apparent compressibility of water in PEG_j and in C_{12}E_j concentrated solutions for all the investigated temperatures. Hence, we can still suppose that $k_{\text{EO}}(j, T) = k_{\text{PEG}}(j' = j, jR_w = h, T)$, where h is again the degree of hydration per monomer at the micellar interface.

Remarkably, if we use the values of h determined from the volumetric analysis to evaluate the compressibility, the obtained numerical results are systematically higher than those experimentally observed in the corresponding PEG–water solutions. These discrepancies can be explained with the following considerations: (i) in the PEG–water solutions the polymer concentration is high so that no free water molecules are available; (ii) in the micellar solutions the aggregate interfaces are in contact with a bulk solvent region, and the hydration water molecules exchange with those in the bulk phase. As a consequence, the derivative of the hydration number h with respect to the pressure must be very different in the two cases. Thus, the depletion of the compressibility present at the micellar interface can be assigned to the second term in eq 8. The values of this contribution for each surfactant can be easily obtained by taking the difference between the compressibility in PEG–water solution,^{29,31} at the given degree of hydration (h), and that of the EO–water mixture, experimentally determined with our procedure. The results are reported in Figure 4.

5. Discussion

The density and compressibility coefficient of the investigated nonionic surfactant cross the correspondent curves of the water at given temperatures up to defined threshold concentrations. In our analysis these concentrations can be considered the upper limits for the ideal mixing of hydrated micelles in water. On increasing the surfactant concentration, the reference chemical potential of the hydrated solute and/or of the solvent does not correspond anymore to those of the fully hydrated solute and of the pure solvent. Thereafter, the solute and/or the solvent density and compressibility coefficient begin to depend on the surfactant concentration, and the crossing temperatures decrease. This occurs mainly because, when the number of the monomers in solution increases, the total area of the solute–solvent interface grows. Thus, above a given extent, on one side the available water molecules are not enough to fully hydrate the solutes and/or, on the other, the residual solvent molecules out of the interface, do not correspond any more to a pure solvent

phase at the same temperature and pressure of the solution. This threshold for the total interfacial area of the solutes depends on the area per monomer or, equivalently, on the relative hydration number h ; both these quantities reflect the shape and size of the aggregates. Consequently, the range where ideality is fulfilled depends on the relative size of the solute aggregate and of the solvent molecule. This consideration simply means that the surfactant solutions are composed of mesoscopic solutes (the micellar aggregates) in microscopic solvent (the water) and hence pertain to the category of the athermal solutions where the solute size defines their main features.¹⁸

As far as the degree of hydration is concerned, our determination is set up using an equivalent state hypothesis concerning the volumetric properties of the EO at the micellar interface and those of PEG polymers in water. Such hypothesis was already used to determine the hydration numbers per EO unit (h/j) at the micellar interface. These analysis give a wide variety of numbers for the $C_{12}E_j$ surfactant: chemical trapped reactant on $C_{12}E_6$ gives 4.2 at $T = 20\text{ }^\circ\text{C}$ and 3.5 at $T = 40\text{ }^\circ\text{C}$;³² dielectric constant increment on $C_{12}E_6$ gives 10 at $T = 10\text{ }^\circ\text{C}$ and 4 at $T = 45\text{ }^\circ\text{C}$, whereas on $C_{12}E_8$ gives 12 at $T = 10\text{ }^\circ\text{C}$ and about 1 at $T = 45\text{ }^\circ\text{C}$.³³ Without using any comparison with PEG–water solutions, other techniques give indirect evaluations of the hydration numbers: micellar self-diffusion on $C_{12}E_8$ gives 5 at $T = 5\text{ }^\circ\text{C}$ and 3 at $T = 45\text{ }^\circ\text{C}$;²² small-angle neutron scattering combined with quasi-elastic neutron scattering gives about 1.5 at $T = 11\text{ }^\circ\text{C}$ and 0.5 at $T = 32\text{ }^\circ\text{C}$ for $C_{12}E_6$, whereas for $C_{12}E_8$ gets 2.5 at $T = 30\text{ }^\circ\text{C}$ and 0.6 at $T = 60\text{ }^\circ\text{C}$.³ Some authors suggested that the hydration number depends on the distance from the oil core region, ranging from 2.8 in the inner layers to 14 in the outer ones for $C_{12}E_8$.³⁴ Hence, each technique gives a specific value for the degree of hydration which depends on the probed interfacial region and on the sensibility of the method used. Our results, reported in Figure 3, fall within the range of the previous data, lying between the results from chemical trapped reactant and those from neutron analysis. The data analysis assigns all the solution excess properties to the interfacial region under the assumption that the oil core and the external solvent properties are equivalent to the corresponding bulk phase. The reliability of our determination is based on the statement that the contribution due to the hydration water molecules to the solution excess volume is negligible for both the molar volumes, $v_{\text{PEG}}(R_w, j', T)$ and $v_{\text{EO}}(j, T)$. This condition is well-fulfilled in our experiments.

It is noticeable that the excess properties derived with the Gibbs surface function correspond to those obtained in the framework of the “small system thermodynamics” when the set of independent variables is the chemical potential of the exchangeable particles, the external pressure, and temperature.¹⁴ These variables, in the limit of ordinary thermodynamics, pertain to solutions in osmotic equilibrium with its solvent. At this particular equilibrium, a pressure difference between the regions containing the solvent and the solution exists. This pressure difference is the osmotic pressure acting on the semipermeable membrane between the two regions, and its value determines the solution concentration. The compressibility we obtain assuming the proposed model for the excess volume contains the derivative of the hydration number with respect to the pressure. In other words, the local EO–water composition at the micellar interface depends on the pressure; likewise, the concentration of a solution in osmotic equilibrium with its solvent depends on the osmotic pressure. Hence, in the framework of the small system thermodynamics, the EO–water mixture can be considered in osmotic equilibrium with the

external bulk solvent. This osmotic equilibrium is set through an ideal membrane dividing the interface from the solvent region, whose origin is due to the formation of aggregates with given shape and size. Since a micelle can exchange monomers and solvent molecules with the external region, this ideal membrane must be considered permeable both to the solvent molecules and to the monomers.

6. Conclusion

Going back to the initial question concerning the interfacial adaptation against the solvent condition, it has been shown that the mean features of these micellar solutions can be fully described under the constraints pertaining to an osmotic equilibrium. In our analysis these constraints were set in such a way that the oil core region possesses the same density of a corresponding oily phase. Thus, the properties of the interfacial region in our model are a function of the degree of hydration h and the osmotic term in k_{EO} ; these quantities take into account all the remaining excess contributions with respect to the ideal mixing of the pure components. Furthermore, we have shown that these solutions can be considered ideal mixtures of the pure solvent and the hydrated aggregates up to threshold concentrations, which depend on the surfactant. These thresholds reflect a size effect due to the mesoscopic dimension of the solute. Recently a theoretical work pointed out the relevance of the size in the case of hydrophobic mesoscopic solute in water.³⁵ Also in this case the thermodynamic state of the hydration shell depends on the solute size.

The proposed analysis gives an unexplored view for the equilibrium conditions in surfactant solutions based on osmotic constraints. This approach can bring to new and interesting interpretations on many of the aspects concerning the detergency properties of these surfactant solutions. Besides, it can be useful also in the analysis of solutions containing polymers and biomaterial, since the osmotic pressure that the solvent exercises on the solute can be one of the main factors in generating the solute folding properties.

Appendix

The density ρ of a solution is defined as the ratio between the total mass of the components and the total volume of the solution. At a given temperature and pressure, this quantity can be written, for any concentration, as a linear combination of the densities of the components weighed by the relative volume fractions. Indeed, for a binary solution we have

$$\rho = \frac{M}{V} = \frac{n_1 \tilde{M}_1 + n_2 \tilde{M}_2}{V} = \frac{n_1 \tilde{V}_1}{V} \frac{\tilde{M}_1}{\tilde{V}_1} + \frac{n_2 \tilde{V}_2}{V} \frac{\tilde{M}_2}{\tilde{V}_2} = (1 - \phi) \rho_1 + \phi \rho_2 \quad (9)$$

where the n_i 's are the number of moles of the species i and \tilde{M}_i 's are the relative molar masses. The \tilde{V}_i can be identified with the partial molar volume or with molar volume of the two components. Thus, $\phi = n_2 \tilde{V}_2 / V$ is the volume fraction of the solute. In general, the \tilde{V}_i 's are a function of temperature, pressure, and the solution concentration. Thus, in the previous expression the density of the solvent and of the solute, ρ_1 and ρ_2 , depend also on the solution concentration. But in the case of ideal mixing the \tilde{V}_i 's correspond to the volumes of the pure components at all the concentration; hence, ρ_1 and ρ_2 do not depend on concentration.

With the same notation the molar volume of a solution can be obtained as a linear combination of the \tilde{V}_i 's weighed by the

relative mole fraction. Indeed, for a two components solution it is given by

$$\tilde{V} = \frac{n_1 \tilde{V}_1 + n_2 \tilde{V}_2}{n_1 + n_2} = (1-x)\tilde{V}_1 + x\tilde{V}_2 \quad (10)$$

where $x = n_2/(n_1 + n_2)$ is the mole fraction of the solute.

The compressibility coefficient β can be easily obtained by using the previous expression for the volume:

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) = -\frac{1}{V} \left(\frac{\partial}{\partial P} \right) (n_1 \tilde{V}_1 + n_2 \tilde{V}_2) = -\frac{n_1 \tilde{V}_1}{V} \frac{1}{\tilde{V}_1} \left(\frac{\partial \tilde{V}_1}{\partial P} \right) - \frac{n_2 \tilde{V}_2}{V} \frac{1}{\tilde{V}_2} \left(\frac{\partial \tilde{V}_2}{\partial P} \right) = (1-\phi)\beta_1 + \phi\beta_2 \quad (11)$$

Thus, it can be written as a linear combination of the compressibility coefficients of the two components weighed by the relative volume fractions.

The molar compressibility K of a solution is given by

$$\tilde{K} = - \left(\frac{\partial (n_1 \tilde{V}_1 + n_2 \tilde{V}_2)}{\partial P} \right) = -(1-x) \left(\frac{\partial \tilde{V}_1}{\partial P} \right) - x \left(\frac{\partial \tilde{V}_2}{\partial P} \right) = (1-x)\tilde{K}_1 + x\tilde{K}_2 \quad (12)$$

and it results to be a linear combination of the compressibility of the two components weighed by the relative mole fractions.

References and Notes

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