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Energetics of clouding and size effects in non-ionic surfactant mixtures: The influence of alkyl chain length and NaCl addition

J.A. Molina-Bolívar, J.M. Hierrezuelo, C. Carnero Ruiz *

Grupo de Fluidos Estructurados y Sistemas Anfifílicos, Departamento de Física Aplicada II, Escuela de Ingenierías, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain

The clouding behavior of two non-ionic mixed surfactant systems (n-dodecyl-b-D-maltoside/n-dodecyl- hexaethylene-glycol and n-decyl-b-D-maltoside/n-dodecyl-hexaethylene-glycol) was investigated over the entire composition range in pure water and in 1 M NaCl. The evolution of micellar size as a function of temperature was monitored by dynamic light scattering and a unimodal distribution pattern of aggregates consistent with a single scattering species was found. Our results confirm that an increase of temperature induces micellar growth and that clustering of micelles occurs as the temperature approaches the cloud point. It was observed that, with increasing temperature, the higher the n-dodecyl-hexaethylene-glycol content the greater the micellar growth. The presence of sugar surfactant monomers in the mixed micelle enhances the cloud point of the system. This phase behavior is sensitive to the presence of NaCl in the micellar solution which induces cloud point depression. For a certain system composition, the cloud point decreases as the alkyl chain length of the sugar-based surfactant increases. Cloud-point thermodynamics were evaluated assuming that clouding indicates the solubility limit when phase separation occurs. The micelle–solvent interactions were characterized from the compensation temperatures, which were determined from the enthalpy–entropy plots.

1. Introduction

The solubility of aqueous micellar solutions of non-ionic surfactants is strongly affected by variation in temperature. Two-phase separation occurs when the temperature is raised above a certain temperature, the so-called cloud point (CP). One of the phases is surfactant-rich, and the other is surfactant-depleted phase (aqueous phase). The onset of phase separation is accompanied by a sudden increase of scattered light, with the process being manifested by a cloudiness of the solution [1]. It is well-established that the origin of the phase separation is the reduction of the intermicellar repulsions as a result of the dehydration of the hydrophilic groups of the surfactant when the temperature is raised [2]. Above the CP, intermicellar aggregation occurs and the micelles become macroscopically large leading to a concentrated micellar phase. The analysis of the thermodynamics of the clouding phenomenon is important for the understanding of the stability of the non-ionic based system surfactants involved [3,4]. It also plays a relevant role in many chemical processes in which clouding compounds are used either alone or as mixtures for purposes of effective solubilization, reaction, separation, and product formulation. The CP depends on the surfactant structure [5,6], particularly the polyoxyethylene chain length [1], and the environmental changes may have a striking influence on this parameter [7,8]. Thus, alterations in the solvent medium produced by the presence of electrolytes induce either a decrease or an increase in the CP. It is believed this effect is due to the modification of both hydration extension and water structure in the hydration layer of micelles. Inorganic salts that induce a salting-out effect, such as chloride and sulfate, reduce the CP. On the other hand, the CP is increased by the addition of nitrate or thiocyanate which are known to cause a salting-in effect.

Nowadays, the most widespread non-ionic surfactants are the ethers derived from ethylene glycol, which are commonly called ethylene-based surfactants. They have been studied extensively because they exhibit interesting properties, mainly the fact that they are soluble not only in water but also in most organic solvents. However, toxicological studies have shown a possible repro- toxic activity [9]. Consequently, there is a need for new harmless surfactants possessing comparable physicochemical properties. The ‘‘green’’ tendency encourages the development of new environmentally friendly products that bear at least a natural polar moiety. Within this context, sugar-based compounds, such as alkylpolyglucosides, have gained some importance within the last decade. Alkylpolyglucosides can be made from renewable materials and are biodegradable. Therefore, they are very attractive candidates for technical applications in areas such as cosmetics, consumer products and industrial cleaners [10,11]. Unlike the ethylene-based surfactants, alkylpolyglucosides do not show the clouding phenomenon. This limits their use in some applications such as extraction and pre-concentration by the cloud point method [12,13].

TABLE 1
Surfactants used in the present study.

Surfactant	Abbreviation	Manufacturer	Grade	Mass fraction purity
n-Decyl-b-D-maltoside	$C_{10}G_2$	Anatrace	Anagrade	P0.99
n-Dodecyl-b-D-maltoside	$C_{12}G_2$	Calbiochem	Ultrol	0.997
n-Dodecyl-hexaethylene-glycol	$C_{12}E_6$	Sigma	BioXtra	P0.98

In most applications, mixtures of several surfactants are used because synergistic effects can improve their performance. As an example, non-ionic surfactants are often added to ionic surfactants to decrease the repulsion between head groups. This facilitates micellization and improves the solubilizing capability of the system [1]. The mixed micellar systems are also of great theoretical interest, as the structural properties of the mixed aggregates can be substantially different from those formed by the individual surfactants alone [14]. Extensive studies have been carried out on various mixed surfactant systems like ionic–ionic and ionic-non-ionic [2,14,15]. However, only limited studies in binary mixtures of ethoxylated and alkylpolyglucoside surfactants have been reported to date [15–19].

Here, we report the micellar size and clouding of mixed micelles of n-dodecyl-b-D-maltoside/n-dodecyl-hexaethylene-glycol through the whole composition range in the absence and presence of NaCl. To show the influence of the length of the hydrocarbon chain of the sugar-based surfactant, this study has been extended to the system of n-decyl-b-D-maltoside/n-dodecyl-hexaethylene- glycol. The thermodynamic parameters of clouding phenomena have been evaluated. The surfactant molecules investigated have polar groups that are very different chemically and structurally. The hexaethylene glycol group is like a short polymer chain and more flexible, unlike the rather stiff, maltoside head groups [20]. This dissimilarity causes not only different hydration states, but also different packing conformations. This will result in significant alterations in both micellar size and phase behavior of the mixed system with composition.

2. Experimental

2.1. Materials

Table 1 contains the main characteristics of the surfactant samples used in the present study. Due to their high purity grade, all these samples were used without further purification. Aqueous stock solutions of surfactants were prepared by weighing. From these, working solutions at a lower concentration (20 mM) were prepared daily. The bulk composition of these solutions is ex- pressed as the mole fraction of the ethoxylated surfactant, a_2, defined by the relationship $[C_{12}E_6]/[C_iG_2] + [C_{12}E_6]$ (with i = 10, 12), where $[C_iG_2]$ and $[C_{12}E_6]$ are the molar concentrations of the sugar-based surfactant and $C_{12}E_6$, respectively. Ultra-pure water (conductivity ~ 5.5 1S ■ m ^{1}) used in the preparation of all solutions was obtained by passing pure water from a Millipore Elix system through an ultra high quality Millipore Synergy purification system.

2.2. Methods

From dynamic light scattering measurements (DLS), performed using a Zetasizer Nano-S system (Malvern Instruments, UK), we were able to determine the z-average mutual translational diffusion coefficient of the particles in solution and consequently the average hydrodynamic radius (R_H). This instrument uses a back-scattering detection system (scattering angle h = 173°) and is fitted with a Helium-Neon laser source (633 nm and 4.0 mW). It has a built-in Peltier temperature control with accuracy of ±0.1 °C. Micellar solutions of varying compositions and at a fixed concentration (20 mM) were filtered directly into the cuvette using a membrane filter with a pore size of 0.1 μm. Prior to each measurement, the cuvette was rinsed several times with ultrapure water and then filled with filtered micellar solutions. To obtain R_H values within a temperature range, sets of experiments were performed by programming a number of automated temperature-trend measurements. The viscosity of the pure water and the NaCl solutions was automatically adjusted for the temperature. The data evaluation of DLS measurements was carried out using the CONTIN algorithm. With these experiments, we checked the size distributions obtained from the correlation functions as well as the polydispersity index (PDI) of all samples. It is notable that our results reveal a similar unimodal distribution pattern of aggregates, suggesting the presence of only single scattering species.

From the light scattering experiments, clouding was inferred by the sharp increase of scattering when the temperature was raised. Accurate cloud point values were obtained by noting the temperature at which the continuously heated solution suddenly became turbid. For this purpose, the test tubes containing the surfactant samples at a total concentration of 20 mM were placed in a transparent water bath with a heat control unit. Heating was regulated to approximately 0.5 °C ■ min^{-1} around the cloud point. At the point of clouding, the temperature was noted and heating was discontinued. The system then underwent self-cooling, and the temperature was noted at which the turbidity disappeared. The average of the two readings was taken as the CP. Cloud point determination in each sample was repeated at least two times. When good reproducibility was not found, the experiment was repeated a third time.

3. Results and discussion

3.1. Micellar size

To design optimal surfactant schemes for desired uses, it is helpful to establish structure–performance relationships based on the colloidal properties of the surfactants. In this regard, the size and shape of micelles become important, as nanostructures of mixed micelles determine their solution and rheological properties [21]. As a result, it is of interest to study the influence of temperature on micellar size. Changes with temperature of the apparent hydrodynamic radius of mixed micelles of $C_{10}G_2/C_{12}E_6$ and $C_{12}G_2/ C_{12}E_6$ in water at different mole fractions of $C_{12}E_6$ in the bulk (a_2), are shown in figures 1 and 2, respectively. In addition to the pure surfactants themselves, four mixtures covering the whole composition range were evaluated while the total surfactant concentration was maintained at 20 mM. Figures 1 and 2 reveal that pure surfactants exhibit variable

behavior depending on the temperature. Thus, while the micellar size of pure $C_{10}G_2$ and $C_{12}G_2$ remains almost constant with temperature, $C_{12}E_6$ shows dramatic growth. Indeed, no clouding is observed in micellar solutions of $C_{10}G_2$ and $C_{12}G_2$, whereas the $C_{12}E_6$ sample becomes turbid at around 52 °C, which reveals the existence of a cloud point phenomenon.

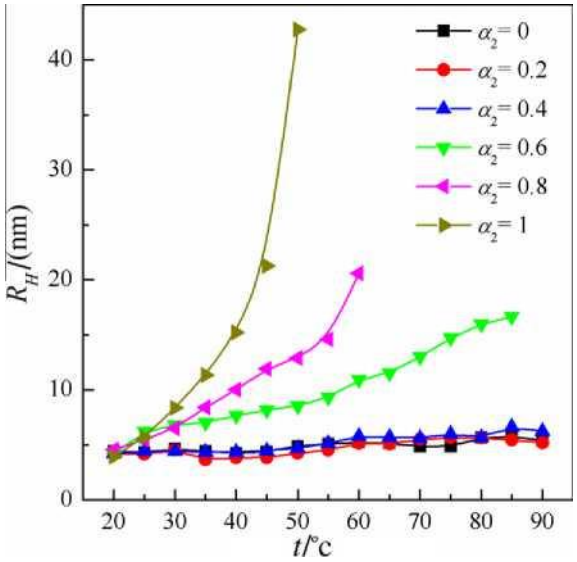

FIGURE 1. Variation of the apparent hydrodynamic radius, R_H, of $C_{10}G_2/C_{12}E_6$ mixed temperature, at different bulk compositions in the absence of micelles with electrolyte

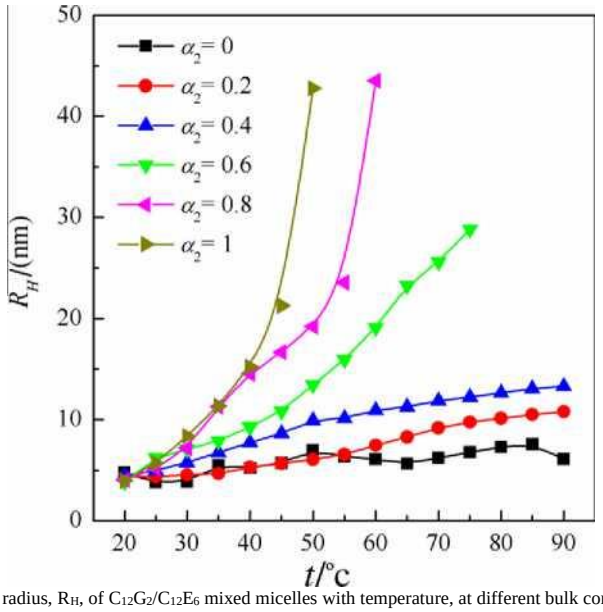

FIGURE 2. Variation of the apparent hydrodynamic radius, R_H, of $C_{12}G_2/C_{12}E_6$ mixed micelles with temperature, at different bulk compositions in the absence of electrolyte.

The fact that appreciable changes in micellar size and shape may also occur as the total surfactant concentration rises hinders the comparison with previously published data. However, we can discuss some representative data. For example, Kato and Seimiya [22] have studied the effect of temperature and concentration on the hydrodynamic radius of $C_{12}E_6$. They found that below 20 °C R_H is almost unaffected by surfactant concentration, but above 20 °C there are considerable differences. At 25 °C and a surfactant concentration similar to that used for us (20 mM) R_H is between 5 and 6 nm, in excellent agreement with the value found by us (5.70 nm) at that temperature. By contrast, the study carried out by Focher et al. [23] indicates that the diffusion coefficient, and hence the hydrodynamic radius, for $C_{12}G_2$ in water is almost unaffected by surfactant concentration. They reported a value of ^3.5 nm for $C_{12}G_2$ in water, which agrees reasonably well with our value of 3.8 nm. Nevertheless, for $C_{10}G_2$ the literature data are rather scarce. Recently, Fütterer et al. [24] in an study on aggregation of an amphiphilic a oly(p-phenylene) in micellar surfactant solutions, including $C_{10}G_2$, reported a value of R_H for the micelles of this surfactant of 3.14 nm at a surfactant concentration of 2.01 wt%. This value is something lower than that found by us of 4.34 nm at 20 mM. Finally, it is important to mention here the re- sults obtained by Bäverbäck et al. [18] in a detailed study on the structure of the $C_{12}G_2/C_{12}E_6$ system by using experimental techniques such as static light scattering, SANS and SAXS. From static light scattering data, these authors concluded that pure $C_{12}G_2$ forms small globular micelles, while both pure $C_{12}E_6$ and the mixtures form micelles of much higher molar mass and elongated shape, being more favorable to the formation of elongated micelles as a greater the proportion of $C_{12}E_6$. For these latter systems, more complex models were required to describe their SANS and SAXS data. These models suggest the coexistence of spherical and spherocylindrical micelles.

According to a classical interpretation, the appearance of clouding is attributed to an almost sudden dehydration of the polyoxyethylene chain (POE) that occurs at the cloud-point temperature. This dehydration was suggested to be induced by the conformational change of the POE chain associated with the temperature rise [25]. The different behavior that was observed between these two families of non-ionic surfactants could be

attributed to considerably greater hydration, of a completely different type, of the hydroxyl groups of the sugar unit of the sugar-based surfactant compared to the hydration of the ethylene oxide based surfactant [11,26–28]. The hydration layer of the sugar head groups therefore remains almost unaffected by a temperature increase. As Drummond and co-workers [29] found on investigating the interfacial microenvironment of micelles of sugar-based surfactants, the re- gion around the head groups is highly aqueous-like, leading to effective dielectric constants of the micelle interface that are nearly twice as high as those typical of ethoxylated surfactants. The existence of a large hydrogen bond network at the surface of $C_{12}G_2$ micelles between water and the head groups, and within the head groups themselves has been recently reported [30]. Similar results have been observed for alkylmonoglucoside surfactants (i.e. $C_{10}G_1$ and C_8G_1), suggesting that this network could explain the thermal stability and cryoprotective effects of these surfactants [31,32].

With respect to figures 1 and 2, it can be seen that the micellar size of solutions containing $C_{12}E_6$ mole fractions of 0.8 and 0.6 increases continuously with temperature, followed by a steep increase at temperatures close to the cloud point. This indicates that micellar growth occurs rapidly close to this temperature. For both sugar-based surfactants, the extent of this growth is more pronounced when the relative proportion of $C_{12}E_6$ in the solution is higher. For solutions rich in the sugar-based surfactant, $a_2 = 0.4$ and 0.2, the growth occurs moderately, almost constantly in the case of the $C_{10}G_2/C_{12}E_6$ system within the temperature range investigated. From this behavior, it is reasonable to conclude that both the $C_{12}E_6$ proportion of the micellar solution and the alkyl chain length of the sugar-based surfactant, significantly influence the micellar growth process. Bäverbäck et al. [18] have recently concluded that while the structural properties of $C_{12}G_2/C_{12}E_6$ mixed micelles is dominated by $C_{12}E_6$; there is still influence by $C_{12}G_2$ as the micelles are shorter when more $C_{12}G_2$ is present.

On the other hand, dependence of the apparent hydrodynamic radius of mixed micelles on the temperature in the presence of 1 M NaCl is shown in figures 3 and 4 for the $C_{10}G_2/C_{12}E_6$ and $C_{12}G_2/C_{12}E_6$ systems, respectively. In figure 3, $C_{10}G_2/C_{12}E_6$ mixed systems with low contents of the ethoxylated surfactant show only
weak growth, which becomes more pronounced for mixtures rich in this component. However, it is apparent from figure 4 that the hydrodynamic radius of $C_{12}E_6/C_{12}G_2$ mixed micelles for $a_2 = 0.2$ increases rather slowly as the temperature increases, whereas a marked change in micellar size occurs on approaching the cloud point for the remaining solutions.

Figures 3 and 4 also show that micelles experience significant growth in the presence of the electrolyte. As previously stated, the presence of NaCl in the micellar solution reduces the amount of water linked to the micelles via hydrogen bonds, thus leading to micellar growth [33,34]. Similar trends of R_H with temperature were reported for n-octyl-b-D-thioglucoside/Triton X-100 system [34].

3.2. Cloud point thermodynamics

The clouding phenomenon is one of the most characteristic features of non-ionic ethoxylated surfactants, which is closely related to how the interaction between surfactants and water occurs. Therefore, in order to gain additional insight into these interactions, the influence of additives, such as electrolytes, on the cloud point of $C_{10}G_2/C_{12}E_6$ and $C_{12}G_2/C_{12}E_6$ mixed micelles was evaluated and analyzed. In this section, we present the results obtained investigating the effect of NaCl on the cloud-point temperature of surfactant mixtures. In figure 5, the cloud-point temperatures of surfactant mixtures in the absence and presence of NaCl, as a function of the bulk composition, are plotted. In the absence of NaCl, the cloud point values range from 51.9 °C for pure $C_{12}E_6$ to 78.2 °C for the mixture with $a_2 = 0.6$ for $C_{12}G_2$. For mixtures with $C_{10}G_2$, the cloud point increases to 91.3 °C for $a_2 = 0.6$. We found that pure $C_{12}G_2$ or $C_{10}G_2$ micellar solutions are completely miscible in water up to a temperature of 96 °C *(i.e.* no phase separation was seen). It is widely assumed that phase separation is due to the reduction of intermicellar repulsions as a result of dehydration of the solvation layer of micelles as the temperature increases. The absence of clouding for both sugar-based surfactants therefore reinforces the previous hypothesis that hydration in this micelle is much stronger than that in the micelle of $C_{12}E_6$, thus preventing a significant dehydration of the sugar moieties as the temperature increases. It is notable that no cloud-point phenomenon was seen

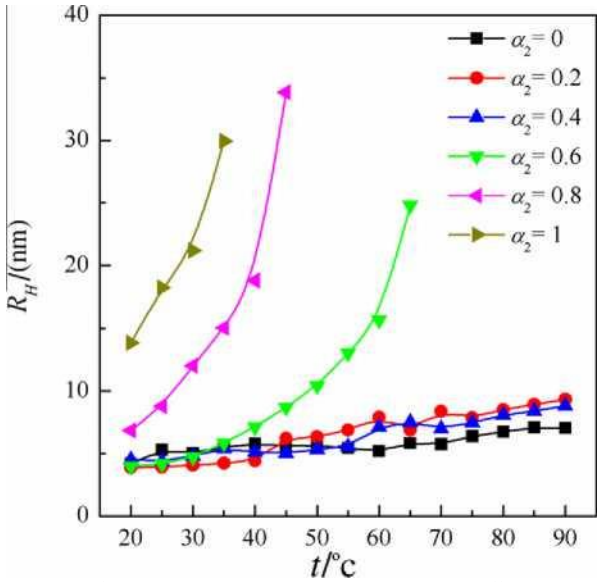

FIGURE 3. Variation of the apparent hydrodynamic radius, R_H, of $C_{10}G_2/C_{12}E_6$ mixed micelles with temperature, at different bulk compositions in 1 M NaCl.

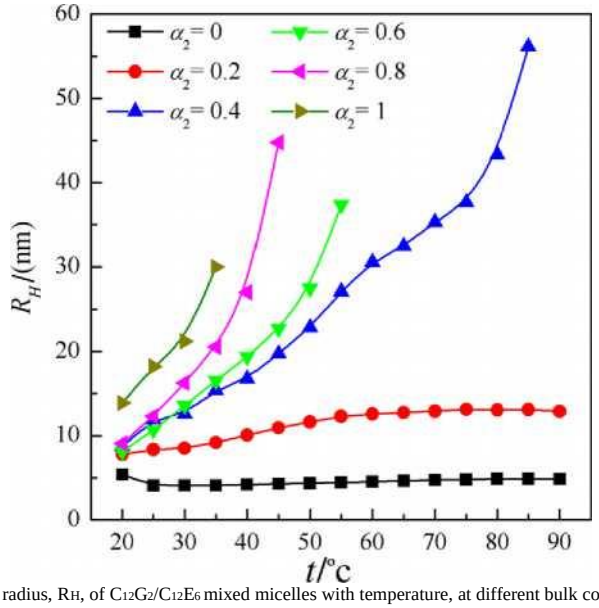

FIGURE 4. Variation of the apparent hydrodynamic radius, R_H, of $C_{12}G_2/C_{12}E_6$ mixed micelles with temperature, at different bulk compositions in 1 M NaCl.

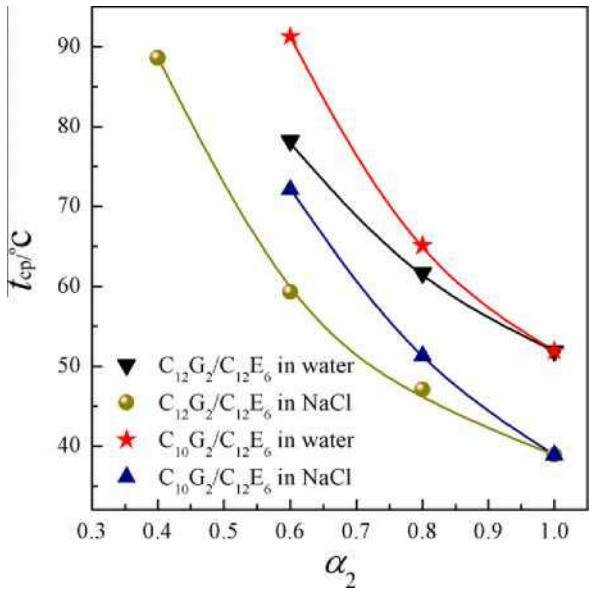

FIGURE 5. Cloud point temperature as a function of mole fraction of $C_{12}E_6$ in the bulk (a_2) in pure water and in the presence of 1 M of NaCl for both sugar-based surfactants.

for solutions with $a_2 = 0.4$ and $a_2 = 0.2$ for both sugar-based surfactants. For these micellar solutions, within the temperature range studied, the sugar moieties can interact with water molecules more favorably than with polyoxyethylene segments, which prevent any significant dehydration of the sugar moieties that compound the mixed micelle.

It is clear from figure 5 that the presence of sugar surfactant molecules in the mixed micelle enhances the cloud point of the system. Indeed, the correlation observed between the cloud point and the sugar-based surfactant content suggests that more heating would be required to dehydrate the micelle. This is due to the increased participation of sugar-based monomers in the mixed micelle, hence clouding occurs at higher temperatures. On the other hand, at a fixed value of a_2 the cloud point increases with decreasing length of the alkyl chain of the sugar-based surfactant. The change in the cloud point for $a_2 = 0.6$, which occurs with a change of two carbon atoms, is thus larger than 13 °C, which is remarkable. On the basis of the molecular structure, when two carbon atoms are added to the alkyl chain of the sugar-based surfactant, it is expected to induce a lower hydrophilicity. As a consequence, the cloud point for the $C_{12}G_2/C_{12}E_6$ system is lower than for the $C_{10}G_2/C_{12}E_6$ system at a fixed value of a_2. This result is consistent with the reported observation of polyoxyethylene alkyl ethers with the same chain length, which show reducing the cloud point values with increasing hydrophobic chain length [9].

A notable feature of figure 5 is that the cloud point of mixed micelles is extensively affected by the electrolyte for both sugar- based surfactants. Thus, the presence of NaCl in the solution induces cloud-point depression in the mixed micelles. This decrease in the cloud point represents a salting-out effect of Na^+ ions [35,36]. The cloud point shifts is a manifestation of the lowering of solvation due to water abstraction from the surfactant by the salt. The Na^+ cation acts as a water-structure maker, and as a result, the hydrophobic interactions between micelles increase with the addition of Na^+ by removing water molecules surrounding the micelles, which in turn decreases the cloud point. The salt changes the solvent

structure and/or the extent of hydration of the clouding species, which enables an easy approach of micelles towards each other, leading to the formation of larger micelles.

For purposes of comparison, we define the cloud point shift value D as the difference between the cloud point of a solution containing a surfactant mixture plus NaCl and the cloud point of a solution containing a surfactant mixture only. This parameter is a sensitive indicator of the effectiveness of NaCl in changing the cloud point of the micellar solution. For both sugar-based surfactants, the value of D increases with decreasing $C_{12}E_6$ in the micellar solution. The effect of NaCl on the cloud point is so critical, that a solution of $C_{12}G_2/C_{12}E_6$ at $a_2 = 0.4$ in water does not present any cloud-point phenomenon, which conversely appears in the presence of NaCl. When comparing the cloud-point shifts for a given value of a_2, we note that the parameter D is independent from the nature of the sugar-based surfactant. This result suggests that the presence of NaCl in the solution affects mainly the water structure around $C_{12}E_6$ monomers in the mixed micelle. All these observations are of interest in order to exploit this ability to control, to our advantage, the cloud point of a surfactant-based system. Note that by varying the micellar composition, or by adding of electrolyte, the conditions and efficiencies in applications where a phase-separation process is either required or avoided, can be optimized.

Thermodynamic parameters associated with the clouding phenomenon can be determined from the phase-separation model. As the clouding species above the cloud point release their solvated water and separate out from the solution, the cloud point can be considered as the limit of its solubility [4,37–40]. Hence, the standard Gibbs free energy of solubilization, ΔG^0_{CP}, can be determined using the following equation:

EQ1

where X_S is the mole fraction of $C_{12}E_6$ in the solution, R is the gas constant, and T is the cloud point temperature. The standard state considered was the hypothetical standard state of unit mole fraction. The standard enthalpy (ΔH^0_{CP}) can be obtained by applying the Gibbs–Helmholtz equation to equation (1) [4,38–40]:

EQ2

According to this equation, ΔH^0_{CP} may be extracted from the slope of a plot between $\Delta G_{\wedge P}/T$ and T. Finally, once $DH°_P$ and ΔG_{0P} are known, the entropy of the clouding phenomenon (ΔS^0_{CP}) will therefore plainly be:

EQ3

Figure 6 represents the change of $\Delta G_{\wedge P}/T$ with T for all Solutions investigated. As seen in this figure, the data fit a straight line ($r > 0.998$). The derived thermodynamic functions for the phase separation are collected in tables 2 and 3 for the $C_{12}G_2/C_{12}E_6$ and the $C_{10}G_2/C_{12}E_6$ mixtures, respectively. All values of ΔG^0_{CP} in tables 2 and 3 are positive and vary within a narrow range for all of the mixed surfactant solutions. The clouding process is non-spontaneous (as it is caused by de-solvating the species using temperature). It is notable that values of ΔH^0_{CP} are slightly smaller in the presence of NaCl for a fixed mole fraction of $C_{12}E_6$, which suggests that the electrolyte favors the clouding process. Increasing the alkyl chain length of the sugar-based surfactant enhances the spontaneity of the clouding phenomenon.

The values of $T\,\Delta S^0_{CP}$ are higher than those of ΔH^0_{CP} in 2 and 3, indicating that the clouding phenomenon is entropy-driven, and the entropic term plays a dominant role in the positive free energy (ΔG^0_{CP}). The phase-separation event that occurs when a particular temperature is reached must involve a distinct change in the balance of hydrophobic and hydrophilic interactions, between the micelles and the water and between the micelles themselves with temperature. Thus, as the temperature increases, the repulsive ‘‘hydration force’’ that results from the structured water around the head groups of the surfactant molecules decreases, while the attractive forces (van der Waals and hydrophobic interactions) become increasingly important. These interactions change from repulsive to attractive, inducing an increasing size of the micellar aggregates, with the corresponding appearance of turbidity at the cloud point. It has been proposed that unfavorable interactions between hydrocarbons and water are responsible for the phase separation [5]. The loss of the solvation sphere when the temperature is raised enhances the interaction between hydrophobic moieties. This enhanced interaction provides the necessary impetus for aggregation of micelles, and phase separation is observed. In the present study, the contribution of entropy to the net interaction between micelles is higher than that of the enthalpy.

For all systems studied, the ΔH^0_{CP} values are negative and the clouding process becomes slightly more exothermic as the presence of the sugar-based surfactant in the mixed micelle increases (in the presence and in the absence of electrolyte). The net heat change of the clouding phenomenon is due to the different processes involved. Initially when the clouding process starts, the hydrated water molecules, which surround the polyoxyethylene and sugar head groups, must be released to produce free water molecules. This occurs with absorption of heat. Subsequently, association of the dehydrated micelles occurs, which involves a release of heat [41,42]. On the other hand, hydrocarbon chains would be more closely packed within the surfactant rich phase than they would be within micelles. Thus, it is likely that the hydrocarbon chains contribute to the decrease of the enthalpy when surfactants are transferred from micelles to the condensed phase [25]. In addition to these relevant contributions, other associated processes like demicellization, micellar growth, or interfacial adsorption also play a role in the energetics of the clouding phenomenon [41]. This aspect needs to be carefully assessed to decipher the true contributions of the dehydration and association phenomena. The final values of ΔH^0_{CP} and ΔS^0_{CP} depend on the relative contributions of all of these factors. The fact that the calculated ΔH^0_{CP} values are negative indicates that the net balance is exothermic. Therefore, the energy required to break the interactions between the surfactant molecules and the water surrounding them is lower than that gained by the creation of interactions between the surfactant molecules themselves, which leads to phase transition. For a given value of a_2, the exothermicity of the clouding phenomenon increased with the increase in alkyl chain length of the sugar-based surfactant (with and without electrolyte in the solution). It is probable that the heat required for the dehydration process is lower for $C_{12}G_2/C_{12}E_6$ micelles than for $C_{10}G_2/C_{12}E_6$ micelles (i.e. the cloud- point temperature is higher for $C_{10}G_2/C_{12}E_6$ mixtures than for $C_{12}G_2/C_{12}E_6$ mixtures). Our results suggest that the presence of NaCl favors the dehydration of the micellar solvation layer and, particularly, facilitates interaction between dehydrated micelles. The ΔS^0_{CP} values were found to be negative for all systems studied, becoming more negative with increasing sugar-based surfactant content. It is likely that penetration of polar groups among the dehydrated micelle aggregates made ΔH^0_{CP} negative [43].

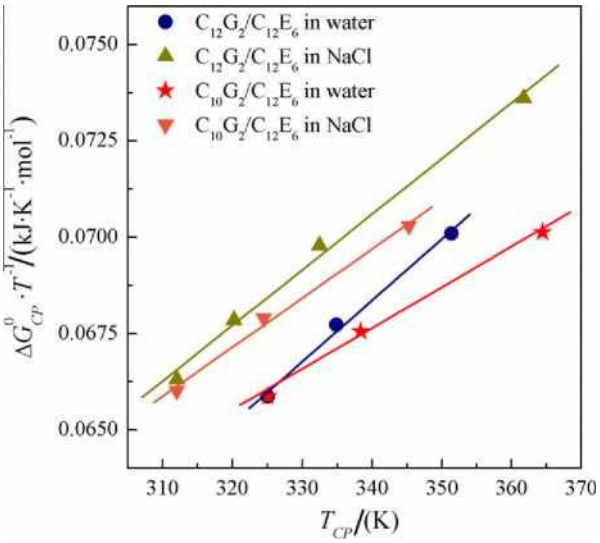

FIGURE 6. Plots of $\Delta G^0_{CP}/T$ *vs. T*, for $C_{10}G_2/C_{12}E_6$ and $C_{12}G_2/C_{12}E_6$ systems in pure water and in the presence of 1 M NaCl.

TABLE 2
Thermodynamic parameters of $C_{12}G_2/C_{12}E_6$ micelles at the cloud point in water and in the presence of 1 M NaCl.

[NaCl]/M	a_2	ΔG_{CP}/(kJ - mol^{-1})^a	$-\Delta H_{CP}$/(kJ - mol^{-1})^b	$-T\Delta S_C$ /(kJ - mol^{-1})^c
0	1	21.4	16.9	38.3
	0.8	22.7	17.9	40.6
	0.6	24.6	19.8	44.4
1	1	20.6	13.7	34.3
	0.8	21.7	14.4	36.1
	0.6	23.3	15.5	38.8
	0.4	26.6	18.3	44.9

Uncertainty limits ^{a}±0.1 kJ - mol^{-1}, ^{b}±1.0 kJ - mol^{-1}, and ^{c}±1.0 kJ - mol^{-1}.

TABLE 3
Thermodynamic parameters of $C_{10}G_2/C_{12}E_6$ micelles at cloud point in water and in the presence of 1 M NaCl.

[NaCl]/M	a_2	ΔG_{CP} /(kJ - mol^{-1})^a	$-\Delta H_{CP}$ /(kJ - mol^{-1})^b	$-T\Delta S_C$ /(kJ - mol^{-1})^c
01		21.4	11.6	33.0
	0.8	22.9	12.6	35.5
	0.6	25.6	14.6	40.2
11		20.6	12.7	33.3
	0.8	22.0	13.7	35.7
	0.6	24.3	15.5	39.8

Uncertainty limits ^{a}±0.1 kJ - mol^{-1}, ^{b}±1.0 kJ - mol^{-1} and ^{c}±1.0 kJ - mol^{-1}.

The values of $T\Delta S^0_{CP}$ increased with the increase in alkyl chain length of the sugar-based surfactant. The negative values of ΔH^0_{CP} and $T\Delta S^0_{CP}$ show that heat was released during the clouding phenomenon, with overall ordering of the micellar solution.

Figure 7 provides a graphical indication on the functional relationship between ΔH^0_{CP} and the cloud-point temperature. A good linear relationship was obtained between the variables ($r > 0.9998$). The gradient of the plot ($d\Delta H^0_{CP}/dT$), which is clearly negative, is a measure of the heat capacity change between the initial and final states of the system (ΔC_{CP}) [44,45]. The linearity of the plot suggests that ΔC^0_{CP} is independent of temperature. The computed values for ΔC_{CP} from linear regression analysis are collated in table 4. A negative heat capacity change points toward the loss of the solvating water structure on micelle aggregation [45,46]. In protein biochemistry thermal protein unfolding is commonly observed to be accompanied by an increase in heat capacity between the initial and final states of the system. This is customarily attributed to the exposure of hydrophobic residues along the polypeptide chain to the aqueous solvent [47]. In the same way, a decrease in heat capacity would consequently indicate a decrease in the exposure of hydrophobic residues of micelles to the water, which would certainly be expected given the clouding phenomenon.

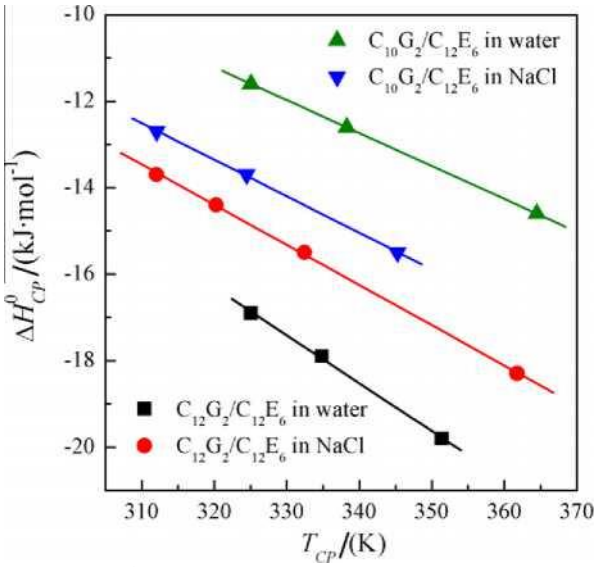

FIGURE 7. Enthalpy change as a function of cloud point temperature for $C_{10}G_2$/ $C_{12}E_6$ and $C_{12}G_2/C_{12}E_6$ systems in pure water and in the presence of 1 M NaCl.

TABLE 4
Valúes of **D**C_{CP}, T_C and DH '$_{CP}$ for the mixtures $C_{12}G_2/C_{12}E_6$ and $C_{10}G_2/C_{12}E_6$ with and without the electrolyte.

	$C_{12}G_2/C_{12}E_6$		$C_{10}G_2/C_{12}E_6$	
	Water	1 M NaCl	Water	1 M NaCl
- DC_{CP} /(kJ ■ K^{-1} - mol^{-1})	0.111± 0.004	0.093±0.002	0.076±0.001	0.084±0.002
T_C/(K)	339±4	324±6	351 ±8	331 ±4
DHC_P/(kJ ■)	23±2	22±3	24±3	23±2

The discovery and importance of the so-called ''extrathermodynamic'' relationships have attracted the interest of many researchers toward the comprehension of their physicochemical origin and functional implications [48]. One of these extrathermodynamic relationships is the enthalpy–entropy compensation. A linear relationship is known to exist between enthalpy change and entropy change for many processes involving small molecules in an aqueous solution, such as protein denaturation [49], micellization of surfactants [3], complexation [50], and oxidation and reduction reactions [51]. Although a unified view is yet to be reached, it appears that enthalpy–entropy compensations for solution processes are related to solvent reorganizations effects [52–54]. This conclusion has general validity, which is independent of the solution properties. However, in hydrogen-bonding solvents, such as water, the effects of solvent reorganization are more pronounced [55]. As the cloud point phenomenon is due to the reduction of intermicellar repulsions as a result of the dehydration process that occurs in the external layer of the micelles when the temperature is increased, it is of interest to examine the enthalpy–entropy relationship of this phenomenon. A generally-accepted thermodynamic model divides any solution reaction into a nominal process, *i.e.* the chemical event, and an environmental process which describes the associated reorganization of solvent molecules [56]. According to this working scheme, DH^0_{CP} can be written in the form:

EQ4

The slope T_C is called the compensation temperature, as it corresponds to the particular temperature at which the process is purely enthalpy-driven ($DG_{CP} = DH_{CP}$). The compensation temperature can be interpreted as a characteristic of solute-solvent interactions, i.e. proposed as a measure of the ''dehydration'' part of the clouding process [25,41]. The compensation temperature may be regarded as a measure of the strength of the surfactant–water interactions. Larger values of T_C indicate more energy is required to induce the release of a certain number of water molecules. On the other hand, the intersection of the compensation plot, DH^*_{CP}, indicates the enthalpy effect occurs in the condition of zero entropy change, and therefore characterizes the surfactant–surfactant interactions, i.e. it is considered as an index of the ''chemical'' part of the clouding process [25,57]. Thus, the enthalpy effect mainly arises from the energetic net balance between the interactions among the alkyl chains of the surfactants in the condensed and micellar phases.

Figure 8 shows the relationship between DH^0_{CP} and DS^0_{CP} that was obtained for the mixtures $C_{12}G_2/C_{12}E_6$ and $C_{10}G_2/C_{12}E_6$, with and without electrolyte. A good linear relationship holds for these parameters ($r > 0.999$). The valúes of T_C and DH_{CP} obtained from the plots in figure 8 are listed in table 4. Our T_C values for clouding in the presence of NaCl are lower than those for surfactant mixtures in water, thus indicating that less energy is required to induce clouding in the presence of salt. This variation in T_C is due to a difference in the water–surfactant interaction mode in a medium with and without electrolyte. As can be seen in table 4, the alkyl chain length has an influence on the clouding process, i.e. the T_C

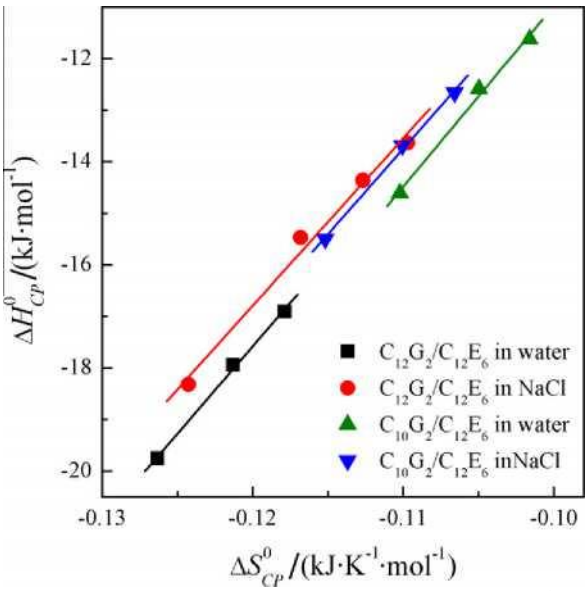

FIGURE 8. Enthalpy entropy compensation plots for $C_{10}G_2/C_{12}E_6$ and $C_{12}G_2/C_{12}E_6$ systems in pure water and in the presence of 1 M NaCl.

is higher for the $C_{10}G_2/C_{12}E_6$ mixture than for the $C_{12}G_2/C_{12}E_6$ system. This indicates that stronger surfactant-water interactions are present in the $C_{10}G_2/C_{12}E_6$ micelle compared to $C_{12}G_2/C_{12}E_6$ micelle. As the length of the alkyl chain is increased, the sugar-based surfactant molecules become less hydrophilic. The calculated DH^*_{CP} values were found to be positive for all the experimental conditions studied. These values clearly indicate that DH^*_{CP} is barely affected by the presence of the electrolyte or by the increase in the length of the alkyl chain of the sugar-based surfactant. The quantity DH^*_{CP} could be considered to be a measure of the enthalpic interaction of surfactant molecules associated with the clouding process [25]. In this sense, it seems reasonable to conclude that the presence of NaCl does not significantly affect these interactions in our mixed system.

4. Conclusions

In this work, we have used dynamic light scattering to study the temperature-induced micellar growth of the mixtures $C_{10}G_2/C_{12}E_6$ and $C_{12}G_2/C_{12}E_6$. For systems with high $C_{12}E_6$ content, a drastic increase of the apparent micellar hydrodynamic size was observed when micellar solution conditions approached the cloud-point temperature. This micellar growth is less dramatic when the relative proportion of $C_{12}E_6$ in the solution is lower. A significant change in the cloud point was observed with variation in the $C_{12}E_6$ bulk composition of both sugar-based surfactants. The cloud point of mixed micelles was found to increase with an increasing content of sugar surfactant in the micelle. At a fixed value of the proportion of $C_{12}E_6$, the cloud point increases with decreasing length of the alkyl chain of the sugar-based surfactant. On the other hand, the addition of NaCl to a micellar solution decreases the cloud point of the micelles, suggesting that the presence of electrolyte produces a remarkable alteration of the hydration layer of micelles. An interesting observation is that the cloud point shift induced by NaCl is independent from the nature of the sugar-based surfactant. In addition, the thermodynamic analysis of the cloud point process was analyzed. It was found that the clouding process is exothermic in nature for these mixed micellar systems, which was verified by the negative value of DH^0_{CP}. The process is more exothermic as the presence of the sugar-based surfactant in the mixed micelle increases (with or without NaCl in the solution). The negative values of DS^0_{CP} indicate that the association of micelles in the clouding phenomenon is entropically unfavorable. A linear relationship was found between the enthalpy and the entropy values for all the systems, i.e. the enthalpy-entropy compensation holds for the clouding phenomenon. The decrease in the compensation temperature with an increasing NaCl concentration is attributed to the fact that the presence of the electrolyte in the medium significantly alters the micellar hydration layer. The calculated compensation temperature is higher for the $C_{10}G_2/C_{12}E_6$ mixtures than for the $C_{12}G_2/C_{12}E_6$ system, suggesting that a less strong surfactant–water interaction exists in the latter. It was found from the enthalpy–temperature plots that the change in heat capacity of clouding phenomenon is negative, indicating the important role played by dehydration in this thermodynamic process.

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References

[1] K. Holmber, B. Jönsson, B. Kronberg, B. Lindman, Surfactants and Polymers in Aqueous Solution, second ed., John Wiley & Sons Ltd., Chichester, 2003. pp. 97– 118.
[2] K. Glenn, A. van Bommel, S. Bhattacharya, R. Palepu, Colloid Polym. Sci. 283 (2005) 845–853.
[3] M.H. Alimohammadi, S. Javadian, H. Gharibi, A.R. Tehrani-Bagha, M.R. Alavijeh, K. Kakaei, J. Chem. Thermodyn. 44 (2012) 107–115.
[4] C. Batigöc, H. Akbas, M. Boz, J. Chem. Thermodyn. 43 (2011) 1800–1803.
[5] L.A.M. Rupert, J. Colloid Interf. Sci. 153 (1992) 92–105.
[6] K. Shigeta, U. Ollson, H. Kuneisa, Langmuir 17 (2001) 4717–4723.
[7] N. Pandit, T. Trygstad, S. Croy, M. Bohórquez, C. Kotch, J. Colloid Interf. Sci. 222 (2000) 213–220.
[8] S. Kumar, D. Sharma, Z.A. Khan, Kabir-ud-Din, Langmuir 19 (2003) 3539–3541.
[9] H. Tani, T. Kamidate, H. Watanabe, Anal. Sci. 14 (1998) 875–888.
[10] C. Stubenrauch, Curr. Opin. Colloid Interf. Sci. 6 (2001) 160–170.
[11] J.A. Molina-Bolívar, C. Carnero Ruiz, in: C. Carnero Ruiz (Ed.), Sugar-Based Surfactants: Fundamentals and Applications, CRC Press, Boca Raton, 2009, pp. 61–104.
[12] J.L. Li, B.H. Chen, J. Colloid Interf. Sci. 263 (2003) 625–632.
[13] Z. Wang, F. Zhao, D. Li, Colloids Surf. A 216 (2003) 207–214.
[14] M. Abe, K. Ogino, in: K. Ogino, M. Abe (Eds.), Mixed Surfactant System, Marcel Dekker, New York, 1993, pp. 1–21.
[15] C. Carnero Ruiz, in: C. Carnero Ruiz (Ed.), Sugar-Based Surfactants: Fundamentals and Applications, CRC Press, Boca Raton, 2009, pp. 413–461. and references herein.
[16] S.R. Patil, N. Buchavzov, E. Carey, C. Stubenrauch, Soft Matter 4 (2008) 840– 848.
[17] C. Stubenrauch, R.M. Claesson, M. Rutland, E. Manev, I. Johansson, J.S. Pedersen, D. Langenvin, D. Blunk, C.D. Bain, Adv. Colloid Interf. Sci. 155 (2010) 5–18.
[18] P. Bäverbäck, C.L.P. Oliveira, V.S. Garamus, I. Varga, P.M. Claesson, J.S. Pedersen, Langmuir 25 (2009) 7296–7303.
[19] C. Carnero Ruiz, J.A. Molina-Bolívar, J. Colloid Interf. Sci. 361 (2011) 178–185.
[20] C.M. Persson, U.R.M. Kjellin, J.C. Eriksson, Langmuir 19 (2003) 8152–8160.
[21] J.T. Petkov, I.M. Tucker, in: V.M. Starov (Ed.), Nanoscience: Colloidal and Interfacial Aspects, CRC Press, Boca Raton, 2010, pp. 1131–1171.
[22] T. Kato, T. Seimiya, J. Phys. Chem. 90 (1986) 3159–3167.
[23] B. Focher, G. Savelli, G. Torri, G. Vecchio, D.C. McKenzie, D.F. Nicoli, C.A. Bunton, Chem. Phys. Lett. 158 (1989) 491–494.
[24] T. Fütterer, T. Hellweg, G.H. Findenegg, J. Frahn, A.D. Schlüter, Macromolecules 38 (2005) 7443–7450.
[25] T. Inoue, H. Ohmura, D. Murata, J. Colloid Interf. Sci. 258 (2003) 374–383.
[26] J.A. Molina-Bolívar, J. Aguiar, J.M. Peula-García, C. Carnero Ruiz, J. Phys. Chem. B 108 (2004) 12813–12820.
[27] E. Tyrode, C.M. Johnson, A. Kumpulainen, M.W. Rutland, P.M. Claesson, J. Am. Chem. Soc. 127 (2005) 16848–16859.
[28] E. Tyrode, C.M. Johson, M.W. Rutland, P.M. Claesson, J. Phys. Chem. C 111 (2007) 11642–11652.
[29] G.G. Warr, C.J. Drummond, F. Grieser, B.W. Ninham, D.F. Evans, J. Phys. Chem. 90 (1986) 4581–4586.
[30] S. Abel, F.Y. Dupradeau, E.P. Raman, A.D. MacKerell, M. Marchi, J. Phys. Chem. B 115 (2011) 487–499.
[31] A.R. van Buuren, H.J.C. Berendsen, Langmuir 10 (1994) 1703–1713.
[32] T.T. Chong, R. Hashim, R.A. Bryce, J. Phys. Chem. B 110 (2006) 4978–4984.
[33] J.A. Molina-Bolívar, J.M. Hierrezuelo, C. Carnero Ruiz, J. Phys. Chem. B 110 (2006) 12089–12095.
[34] J.A. Molina-Bolívar, C. Carnero Ruiz, Fluid Phase Equilib. 327 (2012) 58–64.
[35] H. Schott, J. Am. Oil Chem. Soc. 65 (1988) 1658–1663.
[36] H. Schott, J. Colloid Interf. Sci. 189 (1997) 117–122.
[37] P.R. Majhi, K. Mukherjee, S.P. Moulik, S. Sen, N.P. Sahu, Langmuir 15 (1999) 6624–6630.
[38] Md.S. Alam, Kabir-ud-Din, A.B. Mandal, Colloids Surf. B 76 (2010) 577–584.
[39] Md.S. Alam, A. Mandal, A.B. Mandal, J. Chem. Eng. Data 56 (2011) 1540–1546.
[40] Md.S. Alam, D. Samanta, A.B. Mandal, Colloids Surf. B 92 (2012) 203–208.
[41] A. van Bommel, R.M. Palepu, Colloids Surf. A 233 (2004) 109–115.
[42] M. Prasad, S.P. Moulik, D. Chisholm, R. Palepu, J. Oleo Sci. 52 (2003) 523–534.
[43] B. Naskar, S. Ghosh, S.P. Moulik, Langmuir 28 (2012) 7134–7146.
[44] B.Z. Chowdhry, M.J. Snowden, S.A. Leharne, Eur. Polym. J. 35 (1999) 273–278.
[45] I. Paterson, J. Armstrong, B. Chowdhry, S. Leharne, Langmuir 13 (1997) 2219– 2226.
[46] J. Armstrong, B. Chowdhry, R. OBrien, A. Beezer, J. Mitchell, S. Leharne, J. Phys. Chem. 99 (1995) 4590–4598.
[47] P. Privalov, Crit. Rev. Biochem. Mol. Biol. 25 (1992) 281–306.
[48] Q. Zhang, Z. Gao, F. Xu, S. Tai, J. Colloid Interf. Sci. 371 (2012) 73–81.

[49] R. Lumry, in: G.K. Ackers, M.L. Johnson (Eds.), Methods in Enzymology, vol. 259, Academic Press, New York, 1995, pp. 628–720.
[50] P. Bustamante, S. Romero, A. Pena, B. Escalera, A. Reillo, J. Pharm. Sci. 87 (1998) 1590–1596.
[51] P. Irwin, J. Brouillette, A. Giampa, K. Hicks, A. Gehring, S.I. Tu, Carbohydr. Res. 322 (1999) 67–76.
[52] G. Battistuzzi, M. Bellei, M. Borsari, G.W. Canters, E. Waals, L.J.C. Jeuken, A. Ranieri, M. Sola, Biochemistry 42 (2003) 9214–9220.
[53] L. Liu, Q.X. Guo, Chem. Rev. 101 (2001) 673–695.
[54] P. Strazewski, J. Am. Chem. Soc. 124 (2002) 3546–3554.
[55] E. Grunwald, C. Steel, J. Am. Chem. Soc. 117 (1995) 5687–5692.
[56] R. Lumry, S. Rajender, Biopolymers 9 (1970) 1125–1132.
[57] S.Y. Lin, C.C. Huang, L.J. Chen, J. Phys. Chem. B 102 (1998) 4350–4356.

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