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ORIGINAL CONTRIBUTION

Effect of glycine on the surface activity and micellar properties of *N*-decanoyl-*N*-methylglucamide

C. Carnero Ruiz · J. M. Hierrezuelo ·
J. A. Molina-Bolívar

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Abstract Surface activity, micelle formation and structure of *N*-decanoyl-*N*-methylglucamide in presence of increasing glycine concentrations have been investigated. Changes in the critical micelle concentration of the surfactant with the addition of the amino acid were examined by both surface tension and pyrene 1:3 ratio methods. The observed reduction in the critical micelle concentration was attributed to the structure making action of the additive. Micelle structure parameters were obtained as a function of the glycine concentration by using light scattering and fluorescence-quenching measurements. As regard to the effect of glycine of the micelle size, it was found that both the hydrodynamic radius and the micellar aggregation number increased with the glycine concentration. However, the observed micellar growth seems to be mainly determined by the increase in the aggregation number rather than by changes in the amount of water specifically associated to the micelle. This fact is also supported by the observed trend in the micellar partial specific volume as estimated by complementary density measurements.

Keywords MEGA-10 · Glycine · Micellar properties · Surface tension · Fluorescence · Light scattering

Introduction

Amino acids, the building blocks of peptides and proteins, have a broad spectrum of applications. These substances are widely used as additives in the food industry as buffers or acid correctors, as plant growth regulators, and in the preparation of medicines, either in amino acid injection solution as nutritional infusion or as a raw material for making L-Dopa, a pharmaceutical for treating Parkinson's disease (http://www.gtamart.com/mart/products/chemical/zhitgaa.htm) [1, 2]. Glycine is the simplest amino acid and always being a prototype for larger systems. The use of glycine ranges from the food industry, where it is mainly used as nutritional supplement and food additive (http://www.gtamart.com/mart/products/chemical/zhitgaa.htm), to crop production, where it is used as a chelating agent for micronutrients and as a nitrogen fertilized [3]. When used as plant growth regulators, glycine and other amino acids are combined with various inert ingredients as surfactants, dispersants, carriers, spreader-stickers, and wetting agents [4].

On the other hand, the study of interactions between proteins and amphiphiles is of great importance from both fundamental and technological point of views [5]. However, due to the complexity of these interactions, an alternative strategy, previously used for various researchers [6–15], consists on studying the interactions in simpler systems constituted by surfactants and single model compounds, such as amino acids, which are the basic structural units of proteins. Moreover, glycine has significant influence on the aqueous system and is referred to as water structure influencing molecule [16]. In fact, the amino acids are considered to be strong structure breakers in aqueous solutions due to the presence of peripheral charges [14] and, therefore, can undergo strong electrostatic interactions with ionic species in aqueous solution. This explains that glycine interacts more strongly with ionic surfactants than with nonionic ones, as recently observed [15]. Nevertheless, the interest of nonionic surfactants resides in the fact that, due to its mild character, these substances are

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C. Carnero Ruiz (✉) · J. M. Hierrezuelo · J. A. Molina-Bolívar
Departamento de Física Aplicada II, Universidad de Málaga,
Campus de El Ejido s/n,
29071 Málaga, Spain
e-mail: ccarnero@uma.es

extensively used in many fields of technology and research, including pharmaceutical preparations, where these substances increase the stability and the dissolution rate of many active ingredients.

Among the nonionic surfactants, a relatively new class, the so-called sugar-based surfactants, is emerging due to advantages with regard to performance, health of consumers, and environmental compatibility compared to the more common ethoxylated nonionic ones [17, 18]. Since not a great deal is known about the behavior in systems involving sugar-based surfactants, relative to say ethylene oxide-based surfactants (C_iE_j), it is important to obtain an understanding on self-assembly, surface activity, and other solution properties of these molecules on the same level that we presently have for other surfactants [19]. One of the more important aspects refer to changes in the surface activity, size, and shape of the micelles induced by the presence of additives, which can affect the effectiveness of surfactants in many applications in both chemical and industrial uses [19, 20]. *N*-decanoyl-*N*-methylglucamide (MEGA-10; see Chart 1) is a representative sugar-based surfactant belonging to the group of the fatty acid glucamides, which has been used as a membrane protein solubilizer since it was synthesized by Hildreth, as this surfactant seems to maintain protein function [21]. Recently, considerable effort has been carried out in our laboratory to elucidate the solution behavior of MEGA-10 under different conditions [22–24]. In this paper, we report a study on the aggregation behavior of MEGA-10 in the presence of different concentrations of glycine. With this purpose, we have carried out measurements of surface tension, fluorescence, and light scattering. The present study is mainly focused on the effect of glycine on the surface activity and micellization of the surfactant and on the structure of the micelles formed in these media.

Experimental

Materials

The samples of MEGA-10, glycine, fluorescence probe pyrene, and quencher cetylpyridinium chloride (CPyC) were purchased from Sigma Chemical Co. Due to their high purity, all these compounds were used as received.

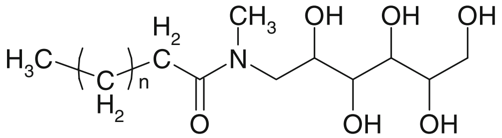

Chart 1 Molecular structure of *N*-decanoyl-*N*-methylglucamide, n=7 (MEGA-10)

Stock solutions of MEGA-10 were prepared in water, whereas that of pyrene was prepared in absolute ethanol. These solutions were stored at 4 °C. Working solutions were used immediately after preparation. Ultra pure water (resistivity ×18 MΩ·cm) for the preparation of the solutions was obtained by passing deionized water through an ultra high quality polishing system (UHQ-PS, ELGA). All chemicals used were of analytical grade quality.

Surface tension measurements

The equilibrium surface tension measurements of solutions of MEGA-10 were carried out with a Sigma 701 (KSV) tensiometer using the Du Nouy ring technique at a constant temperature (30.0±0.1 °C). The ring was cleaned with distilled water and acetone and finally flamed. The surface tension measurements were automatically corrected by the software supplied by the manufacturer. Each series of measurements was started with a concentrated solution of surfactant, and successive diluted solutions were obtained by adding either pure water or glycine solutions to a jacketed vessel, by which temperature was maintained constant with a circulating water bath. After each dilution, the resultant surfactant solution was stabilized at 30 °C for at least 15 min before carrying out the measurement. The surface tension values were accurate within ±0.1 mN m^{-1}.

Fluorescence measurements

Fluorescence measurements were recorded on a FluoroMax-2 (Horiba JOBIN YBON) spectrofluorometer in the “S” mode with bandpasses for excitation and emission monochromators of 1.05 nm, and fitted with a 150 W xenon lamp and 1×1 cm quartz cells. This apparatus is equipped with a thermostated cell housing that allowed temperature control to ±0.1 °C.

To obtain the critical micelle concentration (cmc) of the surfactant, fluorescence emission spectra of MEGA-10 solutions containing around 1 μM pyrene and fixed glycine concentrations were recorded between 360 and 500 nm using an excitation wavelength of 335 nm. From these spectra the intensities I_1 and I_3 were measured at the wavelengths corresponding to the first and third vibronic band located near 373 and 384 nm. The ratio I_1/I_3 is the so-called pyrene 1:3 ratio index.

The micellar aggregation numbers (N_{agg}) were obtained by the static quenching method using pyrene as a probe and CPyC as a quencher. In this case, stock solutions containing pyrene and MEGA-10 were prepared in several media of different glycine concentration. Working solutions of lower concentration (1 μM in pyrene and 30 mM in MEGA-10) were prepared by adding appropriate volumes of quencher solutions. These solutions were sonicated at least for 30 min at 40 °C and then stabilized at 30 °C for 2 h. Fluorescence spectra of these solutions were recorded by using an excitation wavelength of 335 nm at a constant temperature (30.0±0.1 °C). Triplicate experiments were carried out for each glycine composition. The errors in N_{agg}, in terms of the standard deviation of three individual determinations, are estimated to be less than 3%.

Density measurements

To determine the effect of glycine on the partial specific volume of micellar MEGA-10, we carried out density measurements with an Anton Paar DMA 58 density meter. This apparatus determines the density value by placing the sample in a U-shaped tube and measuring its period of oscillation. The instrument has an accuracy of $\pm 10^5$ g/cm^3, and it was calibrated with air and water. The temperature was controlled within ±0.01 °C. The partial specific volume, υ, of micellar MEGA-10 was determined from [25]

$$\upsilon = \frac{1}{\rho_0}\left(1 - \frac{\mathrm{d}\rho}{\mathrm{d}c}\right) \tag{1}$$

where ρ_0 and ρ are the densities of the solvent and micellar solutions, respectively, and c is the surfactant concentration in gram per milliliter.

Light scattering measurements

A Zetasizer Nano-S instrument (Malvern Instrument, UK) was used to perform the light scattering measurements. This apparatus, which uses the backscattering detection (scattering angle $\theta = 173°$) and an avalanche photodiode detector, is equipped with a Helium-Neon laser source (wavelength 633 nm; power 4.0 mW), and a thermostated sample chamber controlled by a thermoelectric Peltier. All the light scattering measurements were made at 30.0±0.1 °C.

Dynamic light scattering measurements were made to obtain the translational diffusion coefficients and the associated hydrodynamic radius of micelles. For dilute solutions, where the intermicellar interactions can be considered absent, the apparent diffusion coefficient (D_c) varies linearly with the surfactant concentration, c, by [26, 27]

$$D_c = D_0[1 + k_D(c - \mathrm{cmc})] \tag{2}$$

where k_D is a constant related to the second virial coefficient. The actual diffusion coefficient at infinite dilution, D_0, can be calculated by extrapolation of the apparent diffusion coefficient to zero concentration. Once the D_0 value is determined, the micelar hydrodynamic radius (R_{H}) may be obtained using the Stokes–Einstein relation

$$R_{\mathrm{H}} = \frac{k_B T}{6\pi\,\eta_0\,D_0} \tag{3}$$

where $k_B T$ is the thermal energy factor and η_0 is the solvent viscosity. These viscosity values were obtained with an automated microviscometer AMVn (Anton Paar). The measuring principle of this apparatus is based on Stoke's law. The apparatus determines the falling time of a small steel ball between a fixed distance into a Peltier-thermostated capillary. For each sample, the runtime was recorded at least four times and the temperature was 30.0±0.01 °C.

In the static light scattering (SLS) experiments the Rayleigh ratio, R_θ, of the sample solutions was determined by using toluene as a standard according to the relationship:

$$R_\theta = \frac{I_\theta}{I_{\mathrm{tol}}}\,R_{\mathrm{tol}} \tag{4}$$

where I_θ and I_{tol} are the scattered intensity of the sample solution and the toluene, respectively, and R_{tol} is the Rayleigh ratio of toluene. This value was assumed to be 1.3523×10^{-3} m^{-1} at 633 nm. The excess scattering ratio of the micelles is given by ΔR_θ, which represents the difference in the Rayleigh ratio between the micellar solution and the solvent solution in the absence of micelles, $\Delta R_\theta = R_\theta - R_\theta^0$. The analysis of SLS data were based on the relation [25, 28]

$$\Delta R_\theta = K\,M_w(c - \mathrm{cmc}) \tag{5}$$

which can be used in the case of dilute solutions of weakly interacting spherical particles. In Eq. 5, M_w is the average molecular weight of the micelles and K is an optical constant directly related to the refractive index increment of the micellar solution [25, 28]. The refractive index values of the solvent and micellar solutions were measured using a digital Abbe refractometer (WYA-1S).

Results and discussion

Surface activity and micelle formation

In order to examine the effect of the glycine addition on the cmc of the surfactant, we have employed two well-established procedures: that based on surface tension measurements [29] and the pyrene 1:3 ratio method [30]. The surface tension curves as a function of the MEGA-10 concentration are shown in Fig. 1. Plots in Fig. 1 show a typical behavior, namely, the surface tension decreases as the surfactant concentration increases, reaching marked changing points from which the surface tension remains roughly constant. The cmc values, as obtained from these

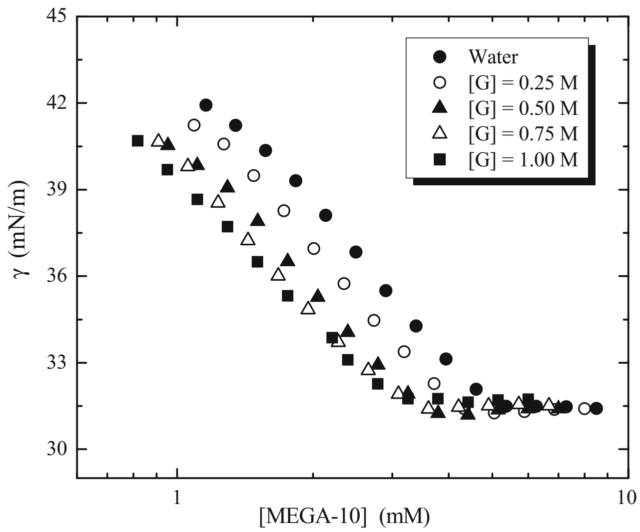

Fig. 1 Surface tension isotherms of MEGA-10 at different glycine concentrations

changing points, are listed in Table 1. Figure 2 shows the variations of the pyrene 1:3 ratio index with the total MEGA-10 concentration for various glycine concentrations. All plots in Fig. 2 show a typical sigmoidal decrease as the surfactant concentration increases. Below the cmc, the pyrene 1:3 ratio value corresponds to a polar environment; as the surfactant concentration increases, the pyrene 1:3 ratio decreases rapidly, indicating that pyrene is sensing a more hydrophobic environment. Above the cmc, the pyrene 1:3 ratio reaches a roughly constant value because of the incorporation of the probe into the hydrophobic region of the micelles. From plots in Fig. 2, the cmc values were determined by using the data treatment previously developed in our laboratory [31]. The values obtained by this last method are also listed in Table 1. It can be seen that the pyrene 1:3 ratio method provides cmc values systematically higher than those obtained by surface tension measurements. This is an expected result because the use of methods based on molecular probes requires the formation of aggregates where that molecule can be incorporated. In any case, it is to be noted that the cmc values that we have obtained in pure water at 30.0 °C agree reasonably well with previously reported values by Ray et al. [32] by using isothermal titration calorimetry (ITC; 5.65 mM) and surface tension measurements (5.95 mM), although they are lower than those obtained by light scattering measurements [33] (6.6 mM) and by ITC [34] (6.29 mM). It is also observed in Table 1 that the cmc of MEGA-10 decreases with the glycine concentration. Similar effects have been previously observed in both ionic [9, 13] and nonionic [6, 10, 11, 14] surfactants.

Another aspect to be noted in Fig. 2 is the fact that the pyrene 1:3 ratio index in the post-micellar region is almost constant (around 1.16) regardless the glycine concentration. This result indicates that the probe resides in a relatively hydrophobic micellar microenvironment, in which the local polarity is not affected by the presence of glycine in the medium. This behavior agrees with recent observations attained by other authors in the case of several common (ionic and nonionic) surfactants [15] and by ourselves in a fluorescence study of the self-assembly properties of *n*-octyl-β-D-thioglucoside in the presence of glycine [11].

The parameters of adsorption of the surfactant at the air–liquid interface were determined from the adsorption isotherm by using the usual procedure. The surfactant surface excess concentration at the interface, Γ_{max}, which represents a measurement of the effectiveness of the adsorption of the surfactant, was calculated using the Gibbs adsorption isotherm equation [29]:

$$\Gamma_{\max} = -\frac{1}{2.303\,RT}\left[\frac{\partial\gamma}{\partial\,\log c}\right]_{T,P} \tag{6}$$

in which γ is the corrected surface tension, c is the surfactant concentration, and R and T have their usual meaning. Note that to determine the derivative of the surface tension on the log c in Eq. 9 only surface tension values of the linear region in the vicinity of the cmc were used. The minimum area occupied by the surfactant

Table 1 Effect of glycine addition on micellization and adsorption parameters of MEGA-10 at 30 °C

[Glycine] (M)	cmc[a] (mM)	$-\Delta G^0_{mic}$ (kJ.mol^{-1})	$\Gamma_{max}\times 10^3$ (mmol/m^2)	A_{min} (Å^2/molécula)	Π_{cmc} (mN/m)	$-\Delta G^0_{ads}$ (kJ/mol)
0.00	4.9 (5.5)	23.5	3.16	52.54	39.53	36.0
0.25	4.1 (5.2)	24.0	3.13	53.04	40.15	36.8
0.50	3.4 (4.7)	24.4	3.09	53.73	40.35	37.5
0.75	3.1 (4.2)	24.7	2.95	56.28	40.41	38.4
1.00	2.8 (3.7)	24.9	2.85	58.26	40.51	39.1

[a] Within parenthesis are the cmc values as obtained by the pyrene 1:3 ratio method

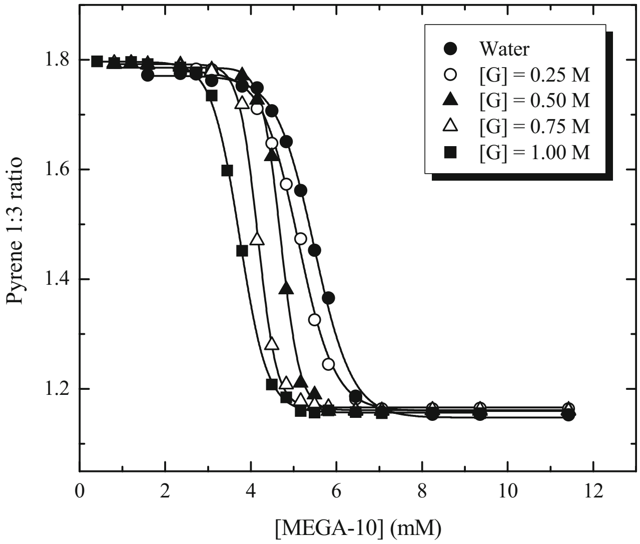

Fig. 2 Plots of the pyrene 1:3 ratio versus total concentration of MEGA-10 at different glycine concentrations

molecule at the air-liquid interface, $A_{\min}$, was then determined by the equation

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} \tag{7}$$

where N_A is Avogadro's number. The standard free energy of adsorption, $\Delta G^0_{\mathrm{ads}}$, was calculated by the equation [29, 35]

$$\Delta G^0_{\mathrm{ads}} = \Delta G^0_{\mathrm{mic}} - \frac{\Pi_{\mathrm{cmc}}}{\Gamma_{\max}} \tag{8}$$

where the standard state for the surface phase is defined as a hypothetical surface covered with a monolayer of surfactant at its closest packing but at a surface pressure equal to zero [29]. $\Delta G^0_{\mathrm{mic}}$ is the standard free energy of micellization, given by [29, 36]:

$$\Delta G^0_{\mathrm{mic}} = RT \ln x_{\mathrm{cmc}} \tag{9}$$

in which x_{cmc} is the cmc in the molar fraction scale, and Π_{cmc} stands for the surface pressure, that is

$$\Pi_{\mathrm{cmc}} = \gamma_0 - \gamma_{\mathrm{cmc}} \tag{10}$$

where γ_0 and γ_{cmc} are the surface tension of the system solvent and of the micellar solution at the cmc, respectively. The values obtained for all these parameters are listed in Table 1. From data in Table 1, it is seen that $\Gamma_{\max}$ decreases monotonically as the concentration of glycine increases, indicating that the adsorption of the surfactant is less effective in the presence of glycine. Of course, $A_{\min}$ shows a reverse trend. Also, the surface pressure Π_{cmc} increases slightly with the glycine concentration, but this increase is probably due to the increase of γ_0 with the presence of the additive [37] rather than to an increase of the surface activity of the surfactant. Finally, it is observed (see Table 1) that $\Delta G^0_{\mathrm{ads}}$ is negative and becomes more negative as the glycine concentration increases. In addition, it is apparent that $\Delta G^0_{\mathrm{ads}}$ values are more negative than the corresponding $\Delta G^0_{\mathrm{mic}}$ values, indicating that the adsorption of the surfactant at the air–liquid interface is more favorable than micellization, so that when the micelles are formed, work must be done to transfer the surfactant monomer from the saturated interface to the micelle. Our results suggest that the presence of glycine slightly inhibits the tendency of the surfactant to adsorb at the air–liquid interface. This effect is similar to that observed in a recent study carried out in our laboratory on the effect of NaCl on the physicochemical properties of MEGA-10 [38]. In fact, Matubayasi et al. [37] have established that the surface behavior of glycine is analogous to that of a simple salt that dissociates completely into a cation and an anion. On the other hand, it must be remarked that previous studies carried out by Rakshit and coworkers [10, 14] with conventional polyoxyethylene (POE) nonionic surfactants shown an opposite trend. The aforementioned authors explained their observations on the basis of dehydration of the surfactant induced by glycine addition, which was supported by a lower cloud point in the presence of the additive [10]. This different surface behavior of MEGA-10 compared to that of POE-based surfactants is probably determined by the nature of its head group, which is mainly characterized by a minor flexibility and major hydrogen bonding possibilities [38].

From the present study, it can be concluded that the addition of glycine favors the micellar formation of MEGA-10 and slightly decreases its surface activity. With regard to the micellization process, it must be considered that when a third component is present in the system, the micellization of the surfactant can be modified by two different mechanisms: (1) through specific interactions with the surfactant molecules or (2) by changing the solvent nature [36]. Since our data do not reveal any specific interaction between glycine and MEGA-10, it seems reasonable to assume that the effect of the additive on the solution behavior of the surfactant occurs in the context of changes in the solvent properties. Our results suggest that glycine acts as a structure making agent, i.e., the addition of glycine enhances the structure of the water in such a way that the introduction of a monomeric surfactant molecule will require an additional amount of work to overcome the added structural energy, and, as a consequence, the surfactant will undergo a "salting out" effect resulting in a decrease in the cmc. In other words, the effect of glycine on the surface activity and micellization of MEGA-10 is similar to that of a simple electrolyte. It must be noticed that the same conclusion was drawn from a recent study on the effects of several amino acids (including glycine) on the cmc and surface activity of cetyltrimethylammonium bromide (CTAB) [13].

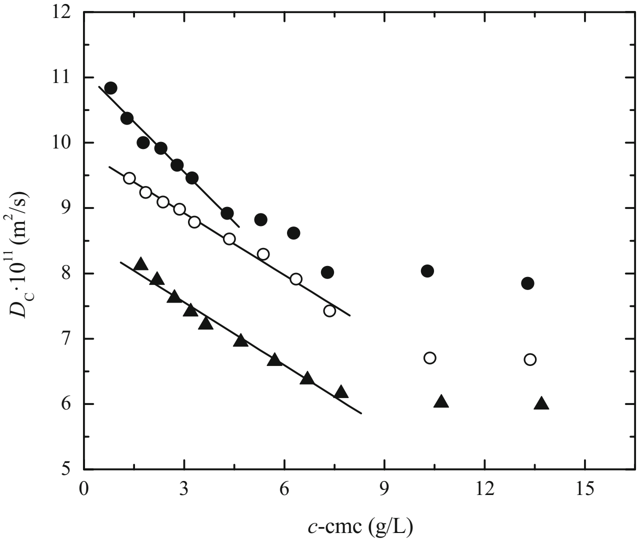

Fig. 3 Apparent diffusion coefficients D_c versus surfactant concentration at 30 °C in: (*filled circle*) water, (*empty circle*) 0.5 M glycine, and (*filled triangle*) 1 M glycine. *Solid lines* are the best fit of data to Eq. 2

Micellar size

From a structural point of view, micelles are mainly characterized by two parameters: the hydrodynamic radius and the mean aggregation number. In order to study the influence of the glycine addition on these parameters, light scattering and fluorescence static quenching measurements were carried out. Figure 3 shows the apparent diffusion coefficient, D_c, of MEGA-10 micelles as a function of surfactant concentration in water and at different glycine concentrations. Plots in Fig. 3 show two characteristic aspects. First, it is observed a weak dependence of D_c with surfactant concentration, indicating that the intermicellar interactions are negligible, as expected for nonionic micelles. Second, at a fixed micellar concentration, D_c values decrease with increasing surfactant concentration, which is mainly due to an increase in micellar size. Moreover, it is also observed in Fig. 3 that all plots show two different regions: at low surfactant concentration, D_c linearly decreases with glycine concentration, but above a certain concentration, which depends on the glycine concentration, the D_c values remain roughly constant. For these reasons, we have restricted our data treatment to the concentration range in which D_c was a linear function of the surfactant concentration; therefore, Eq. 2 was applied. From linear regression analysis of these data, the diffusion coefficients at infinite dilution, D_0, were obtained, and subsequently, the micelle R_H were determined according to Eq. 3 for each glycine concentration. The values obtained for D_0 and R_H are listed in Table 2. Data in Table 2 indicate a decrease in D_0 and moderate increase in R_H with increasing glycine concentration. This result can be interpreted in the sense that glycine induces micellar growth, which can be due to an increase in the micellar aggregation number, and/or an increase in hydration. It must be mentioned that the tendency observed here for D_0 and R_H is opposite to that recently reported by Rakshit and coworkers [14] for the POE-based surfactant nonaoxyethylene-*n*-dodecylether ($C_{12}E_9$). In the case of $C_{12}E_9$, it was found that in the presence of glycine, the micelles have higher aggregation numbers and smaller hydrodynamic radii, suggesting that the presence of the additive causes some dehydration in $C_{12}E_9$ micelles. Again, this different behavior can be attributed to the properties of the hydrophilic sugar group, which is strongly hydrated [39], and it seems that it can retain its hydration status in an easier way than POE-based surfactants.

As mentioned, one of the most important parameters characterizing the structure of micelles is the mean micellar aggregation number (N_{agg}). To analyze the effect of glycine addition on the mean aggregation number of MEGA-10 micelles, we have used two different methods: the static quenching method and that based on static light scattering measurements. The quenching static method was proposed originally by Turro and Yekta [40] and is based on the quenching of a fluorescence probe by a known concentration of quencher. Quenching experiments by using pyrene as a luminescence probe and CPyC as a quencher were carried out. This donor–quencher pair has been found to be suitable for determining the aggregation number of ionic and nonionic micelles and has been successively applied to

Table 2 Actual diffusion coefficients (D_0), solvent viscosities (η_0), partial specific volumes (υ), and other structural parameters of MEGA-10 micelles as a function of glycine concentration at 30 °C

[Glycine] (M)	$D_0 \cdot 10^{11}$ (m^2 s^{-1})	η_0 (mPas)	R_H (nm)	M_w (Da)	N_{agg}[a]	υ (mL g^{-1})	R_0 (nm)
0	11.09	0.800	2.5	25514	73 (76±1)	0.881	2.1
0.5	9.87	0.856	2.6	28659	82 (85±1)	0.884	2.2
1.0	8.52	0.920	2.8	32154	92 (94±2)	0.869	2.2

[a] Within parenthesis are the N_{agg} as obtained by the static quenching method (mean value ± standard deviation from three individual determinations).

the determination of mean aggregation numbers of numerous micellar systems [41]. The quenching experiments were analyzed by using the following equation [40]

$$\ln\frac{I_0}{I} = \frac{N_{agg}}{c - \mathrm{cmc}}[\mathrm{Q}] \tag{11}$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, N_{agg} is the mean aggregation number, c is the total surfactant concentration, and [Q] is the quencher concentration. Figure 4 shows representative quenching plots in micellar solutions of the MEGA-10 at different glycine concentrations (data at 0.50 and 0.75 M glycine are omitted in Fig. 4 for clarity). Solid lines in Fig. 4 represent the best fit of experimental data to Eq. 11. In all these quenching experiments we found an acceptable linear behavior (r>0.99). From the linear regression analysis of the experimental quenching data the values of N_{agg} that we have obtained in presence of glycine (0, 0.25, 0.50, 0.75, and 1 M) are 76±1, 80±1, 85±1, 88±1, and 94±2, respectively. First of all, it is to be noted that the N_{agg} value that we have obtained in pure water agrees well with that reported by Okawauchi et al. [33] and by ourselves through the static light scattering technique (see Table 2). We have also employed this last technique to determine the N_{agg} values of MEGA-10 at some glycine concentrations. Our static light scattering data were treated according to Eq. 5 as described in the "Experimental Section." Figure 5 shows some representative plots of the excess scattering ratio, ΔR_θ, against the surfactant concentration for MEGA-10 solutions at different glycine concentrations. From linear regression analysis of data in Fig. 5, the micellar molecular weights (M_w) and, subsequently, the N_{agg} values were estimated. The corresponding data are also listed in Table 2. With regard to plots in Fig. 5, it must be remarked that in all the cases, a good linearity (r>0.99) was observed. This behavior indicates the absence of intermicellar interactions and also that the micellar molecular weight is independent of the surfactant concentration over the considered range. In addition, it must be pointed out that the N_{agg} values that we have obtained by both methods are in excellent agreement (see Table 2). Our results indicate that N_{agg} values increase with glycine concentration, showing a similar tendency to that observed for the hydrodynamic radius. This suggests that the observed micellar growth is due to increase of N_{agg} rather than to changes in the micellar solvation status. To elucidate this point, we have performed density measurements to determine the partial specific volume, υ, of MEGA-10 micelles. The micellar partial specific volume represents the volume occupied per gram of dry micelle. It is well known that nonionic micelles can incorporate water into its structure through two different mechanisms [42]: (1) water bound by hydrogen bonding, the so-called thermodynamic interaction, and (2) the osmotic flux and mechanical entrapment of water within the mesh of hydrated head groups that comprise the outer shell of the micelles, the so-called physical interaction. Only the first mechanism contributes to proper micellar solvation; therefore, the partial specific volume is affected by solvent molecules with a significant thermodynamic interaction with surfactant molecules via hydrogen bonds. Water mechanically trapped is hydrodynamic in nature and do not contribute to proper solvation, but these water molecules diffuse together with the micelle and do contribute to their hydrodynamic properties. Therefore, a change in the micellar solvation

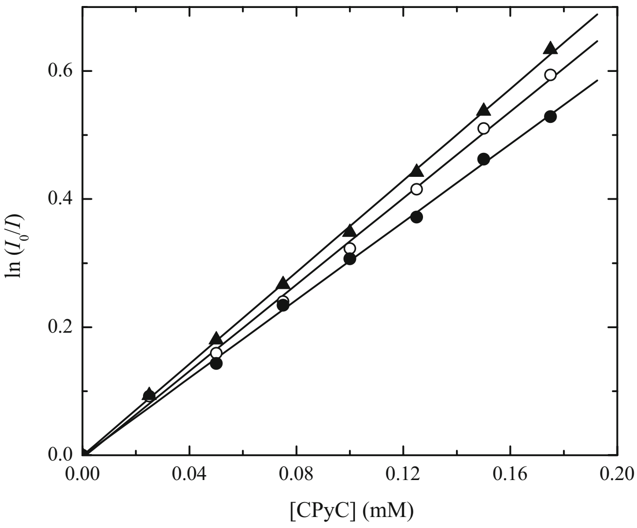

Fig. 4 Quenching plots of pyrene fluorescence in MEGA-10 micellar solutions at different glycine concentrations: (*filled circle*) water, (*empty circle*) 0.5 M glycine, and (*filled triangle*) 1 M glycine. *Solid lines* are the best fit of data to Eq. 11

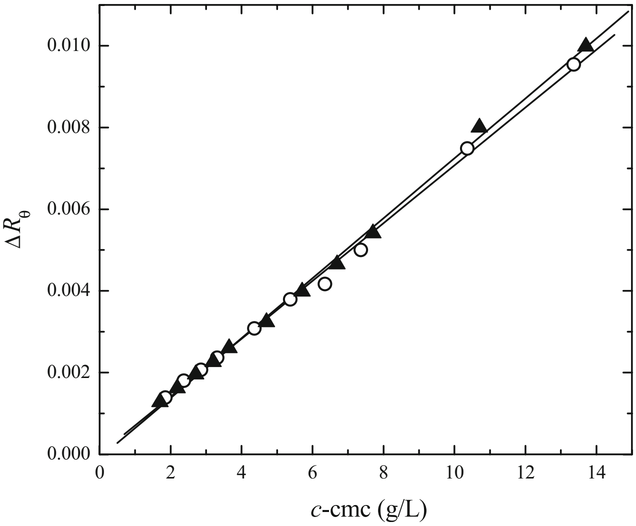

Fig. 5 Excess scattering ratios (ΔR_θ) versus surfactant concentration of MEGA-10 at different glycine concentrations: (*empty circle*) 0.5 M, (*filled triangle*) 1 M

should be reflected in a variation of υ [43]. The density of MEGA-10 solutions of varying concentrations of glycine was determined at 30 °C. Plots of density of MEGA-10 micellar solutions as a function of surfactant concentration (not presented) showed a good linear dependence ($r >$ 0.999). From these plots and by using Eq. 1, we obtained the υ values listed in Table 2. As can be seen, the micellar partial specific volume of MEGA-10 decreases around 1.4% for 1 M glycine. It is evident that this decrease is of little significance, and we think it is essentially determined by the increase in the solvent density, ρ_0, rather than to changes in the hydration micellar. Probably, this behavior stem from the strength of the hydrogen bonds between the hydroxy groups of the sugar unit and water, which prevents any significant changes of hydration of the head group when the conditions of the medium are modified. It is important to remark that this result is consistent with the fact that the micellar pyrene 1:3 ratio index does not experiment significant changes with the glycine concentration (see Fig. 2), indicating that the micellar micropolarity is not affected by the presence of glycine in the medium. Data of υ were used to determine the so-called dry micellar volume, V_0, by means of the equation [43]

$$V_0 = \frac{\upsilon M_w}{N_A} \qquad (12)$$

and hence, by assuming a spherical geometry for MEGA-10 micelles, we obtained the dry micellar radius values, R_0, listed in Table 2. It is observed that R_0 slightly increases in presence of glycine. Note that the hydrodynamic volume, as determined by R_H, contains all the solvent molecules that accompany the micelle in its diffusion movement, including both the water molecules thermodynamically interacting and those physically trapped with the micelle. Our data show that the hydrodynamic volume of MEGA-10 increases by around 40% when the system contains 1 M glycine, whereas the aggregation number increases by approximately 26%. This means that the micellar growth of MEGA-10 induced by the presence of glycine is mainly due to the increase of the aggregation number.

Conclusions

The effect of glycine on the surface activity and micellar properties of MEGA-10 has been studied. It was observed that the addition of the amino acid results in a moderate decrease of the surface activity and a significant micellar stabilization. It was established that the action mechanism of glycine on the physicochemical properties of MEGA-10 is similar to that of a simple electrolyte. The micelle size of MEGA-10 increased with the glycine concentration, which was attributed to an increase in the micellar aggregation number. Although the amount of water thermodynamically interacting with the micelle seems to be not affected by the presence of the additive, the whole micellar solvation is significantly enhanced with the glycine addition. In this context, our data suggest that MEGA-10 behaves more similarly to a conventional surfactant such as CTAB [13] than to a POE-based surfactant such as $C_{12}E_9$ [14].

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