Aggregation in aqueous media of tri-block copolymers tuned by the molecular selectivity of cyclodextrins

Rosario De Lisi · Giuseppe Lazzara

Abstract The water + cyclodextrin + poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) mixtures have been investigated to explore the temperature effect on the aggregation of the copolymer in the presence of cyclodextrins (CDs). The CDs with different cavity sizes were chosen because they may include either the hydrophilic poly(ethylene oxides) block or both kinds of blocks. The differential scanning calorimetry and viscosity experiments straightforwardly evidenced that the critical micellar temperature is shifted to larger values by adding a CD which is able to include the middle poly(propylene oxide) block while it is not influenced by the presence of CD which is selective to the poly(ethylene oxide) block. The enthalpy of aggregation decreases upon the CD addition for all the investigated systems.

Keywords Critical micellar temperature · Enthalpy of aggregation · F68 · F88 · F108 · Hydroxypropyl-α-cyclodextrin · Hydroxypropyl-β-cyclodextrin · Pseudopolyrotaxanes

Introduction

Since several years we are assisting to an increasing scientific interest to the topic on the cyclodextrin (CD) + additive inclusion complex (IC) formation basically due to the large employment of the CDs in various fields [1]. The CDs are cyclic oligosaccharides consisting of glucopyranose units linked by α-1,4 glucosidic bonds. They have a truncated cone shape with a hydrophilic surface and a hydrophobic core which may incorporate hydrophobic solutes. Within this issue, several papers have been devoted to the interactions between the CD and the additives [2–15]. The presence of CD allows the increase of the critical micellar concentration of the surfactants [3, 16–18] due to the formation of surfactant + CD inclusion complexes disrupting therefore the micelles when present. The ICs composed of CD and polymers were first evidenced by Harada [19–21]. Usually, a certain number of CDs fits one polymeric molecule giving up a channel structure [22, 23]. Such complexes were synthesized following diverse routes and using various solvents [3, 24–26]. To the best of our knowledge, a very few studies on the interactions between CD and unimeric poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) are available [27–30]. Static and dynamic light scattering [29] evidenced the presence of ICs, formed by dimethylated-β-cyclodextrin (DM-β-CD) and pluronics, the size of which is significantly larger than the copolymer unimers and specific of the copolymer nature. In other investigations [27], the composition of the copolymers was tuned by properly changing the size of the PEO and/or the PPO blocks as well as that of the native and the modified cyclodextrins. Volumetric data in water [27] gave the equilibrium constant and the volume change for the IC formation as well as the IC stoichiometry. Physico-chemical studies evidenced that the native CD rings in the inclusion complex assume a channel structure [27] while the alkylated-CDs [27] decorate the copolymer forming necklace-like supramolecular structures; moreover, the included copolymer is amorphous [27, 28].

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As far we know, the influence of the CDs on the copolymer aggregation has been scarcely exploited [29, 31]. It was shown that pluronics micelles are destroyed by the presence of hydroxypropyl-β-cyclodextrin (HP-β-CD) and DM-β-CD as a consequence of the ICs formation. On this basis, it might be fascinating to explore the effect of the cavity size of the CD on the copolymer aggregation as the CD exhibits a selective behaviour towards the pluronics. Accordingly, while the native and the modified β-CDs [27, 32, 33] may fit both the EO and the PO units, the native and modified α-CDs [27–30] may incorporate only the EO units. Therefore the copolymer aggregation might be controlled by the molecular selectivity of the CD. Within this issue, we thought it would be interesting to monitor the copolymer aggregation of pluronics in the presence of hydroxypropyl-α-cyclodextrin (HP-α-CD) and HP-β-CD. For this purpose, the role of the copolymer size keeping constant the hydrophilic/hydrophobic ratio was elucidated. The studies were carried out at fixed copolymer composition by changing both the CD concentration and temperature.

Experimental

Materials

Hydroxypropyl-β-cyclodextrin (HP-β-CD) with the averaged substitution degree for each glucopyranosidic unit (MS) of 0.43 is from Acros. Hydroxypropyl-α-cyclodextrin (HP-α-CD) having MS = 0.6 is an Aldrich product. The water content of the cyclodextrins was determined by thermo-gravimetric analysis. The studied block copolymers (BASF) are (ethylene oxide)$_a$-(propylene oxide)$_b$-(ethylene oxide)$_a$; they are represented in Table 1 as EO$_a$PO$_b$EO$_a$ where a and b indicate the repetitive number of the ethylene oxide (EO) and propylene oxide (PO) units, respectively. All of the mixtures were prepared by mass (± 0.01 mg). Water from reverse osmosis (Elga model Option 3) with a specific resistivity higher than 1 MΩ cm was used for the solutions preparation.

Table 1 Structure and molecular weight of tri-block copolymers used in the experiments

Structure	Abbreviation	EO/PO	M_w
EO$_{76}$PO$_{29}$EO$_{76}$	F68	4.0	8,400
EO$_{103}$PO$_{39}$EO$_{103}$	F88	4.0	11,400
EO$_{132}$PO$_{50}$EO$_{132}$	F108	4.0	14,600

Units are: EO/PO g/g; M_w g mol^{-1}

Equipment

Differential scanning calorimetry

The measurements were carried out with the micro-DSC III (SETARAM) under nitrogen flow in the 273–343 K interval with a scan rate of 0.6 K min^{-1}. The stainless steel 1 cm^3 sample cell was filled with ca. 500 mg of solution and the reference cell with the corresponding amount of water. The calibration was carried out by using naphthalene.

Viscosity

The Bohlin Visco 88 rotation viscosimeter was used. The temperature was changed from 293 to 343 K with a stability of ± 0.1 K. The apparatus gave reliable results for shear rates ranging between 200 and 1,200 s^{-1}. Under these experimental conditions, it might occur the destruction of the copolymer + cyclodextrin inclusion complexes. Nevertheless, the performed studies are reliable because we are interested to compare the temperature effect on viscosity for the various mixtures under the same shear rates. The F108 and F88 composition was set at 15 wt% and that of HP-α-CD and HP-β-CD at 9 wt%.

Results and discussion

DSC studies

The differential scanning calorimetry successfully evidenced both the inclusion of molecules into CDs and the copolymer self-assembling behavior induced by temperature [34–36]. Some examples of thermograms of the analyzed systems are illustrated in Fig. 1. As a general feature, regardless of the copolymer nature, the addition of HP-α-CD to the aqueous copolymer solution generates a decrease in the thermogram area while the addition of HP-β-CD reduces not only the area but also shifts the peak to larger temperature (T) values. From each curve one may determine: (1) the critical micellar temperature (CMT), that represents the temperature at which the copolymer starts to aggregate, as the onset of the peak; and (2) the enthalpy of micellization of copolymers (ΔH_M) that is an average value within a given range of temperature.

As concerns the behavior of the copolymer in water, the CMT and the ΔH_M values increase and decrease with the copolymer molecular weight, respectively. A similar trend was drawn for ΔH_M obtained from the dependence of the critical micellar concentration on temperature [37, 38].

The effect of the CD presence on the copolymer behavior is specific of the CD cavity size. It is intriguing that both HP-α-CD and HP-β-CD reduce the ΔH_M values (Figs. 2, 3, 4)
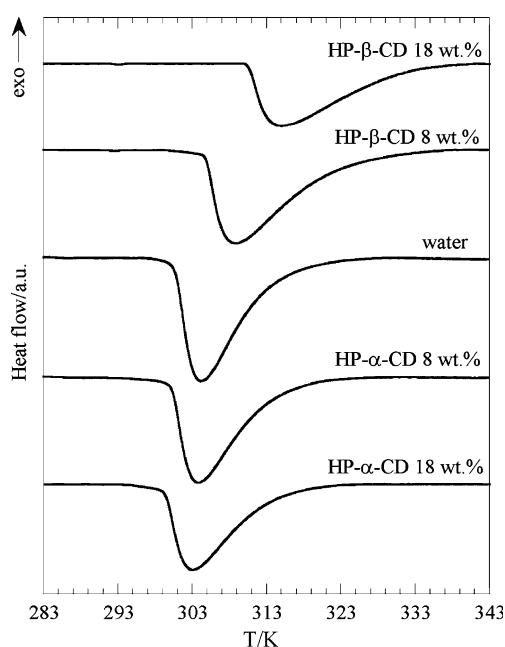
Fig. 1 DSC curves of F88 15 wt% in water and in the presence of CDs at variable concentration
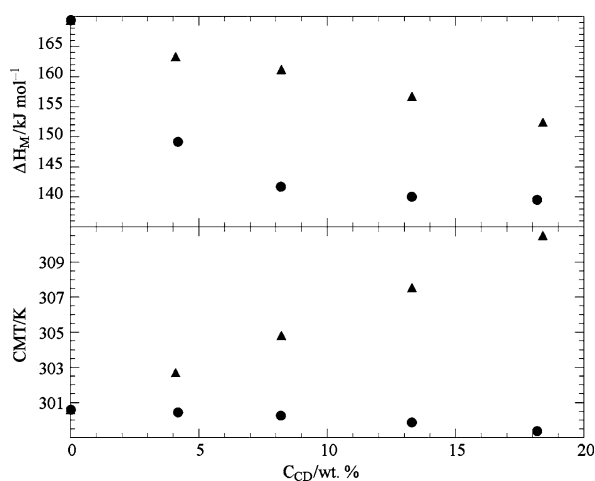

Fig. 2 Enthalpy of micellization and critical micellar temperature for the aqueous F88 15 wt% as functions of HP-α-CD (*filled circle*) and HP-β-CD (*filled triangle*) concentrations

Fig. 3 Enthalpy of micellization and critical micellar temperature for the aqueous F108 15 wt% as functions of HP-α-CD (*filled circle*) and HP-β-CD (*filled triangle*) concentrations

Fig. 4 Enthalpy of micellization and critical micellar temperature for the aqueous F68 15 wt% as functions of HP-α-CD (*filled circle*) and HP-β-CD (*filled triangle*) concentrations

while they play a very different role on the CMT (Figs. 2, 3, 4) which is very slightly shifted to lower values by HP-α-CD while it increases in the presence of HP-β-CD. These results reflect the important feature of the copolymer; the EO hydration as well as the PO solubility are strongly reduced with temperature raise driving the copolymer self-assembling in water. The ability of HP-β-CD to include both the EO and the PO segments disturbs the formation of micelles and, consequently, the monomer concentration required for the aggregation is reached at larger temperatures allowing an
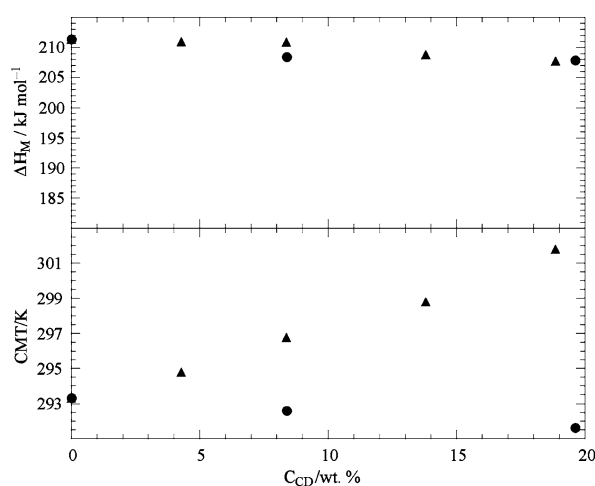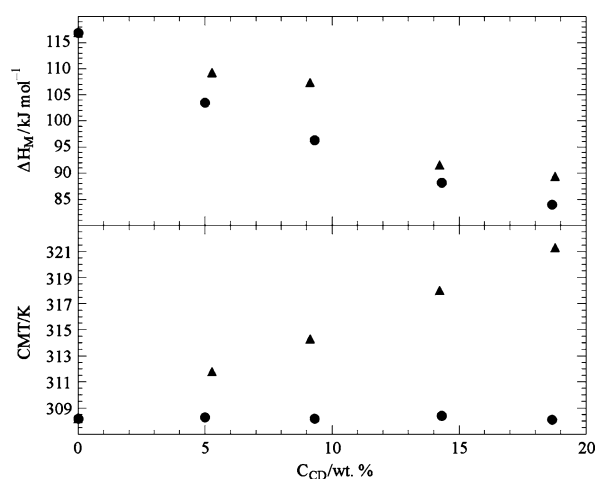
increase in the CMT. This result agrees with Cosgrove and coworkers [31] and Gaitano et al. [29] who found that modified β-CDs destroy the micellar aggregates. More striking is the behavior of HP-α-CD which slightly decreases the CMT. It has to be remembered [34] that the CMT of the copolymer in water decreases upon the addition of the solute if the latter is incorporating into the micelles. In the presence of HP-α-CD, micelles having the hydrophilic shells decorated with the CD baskets may be formed as HP-α-CD can include only the EO units.

The effects of both HP-α-CD and HP-β-CD on the aggregation process are also clearly represented by the trends of the fraction of the copolymer in the micellar state (χ_M) as a function of temperature obtained from a proper
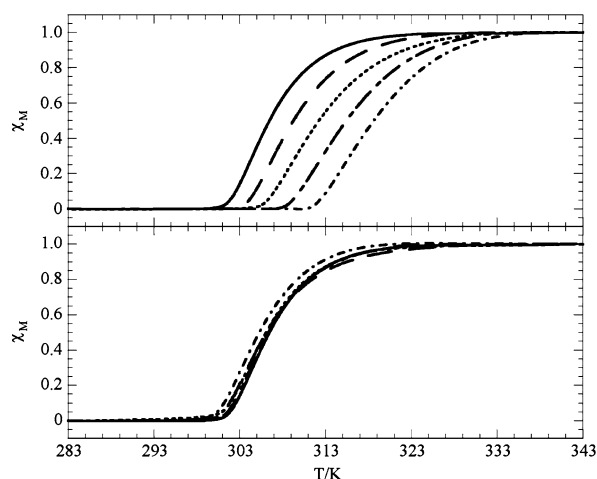
Fig. 5 Fraction of F88 15 wt% in the micellized state: in water (—) and in the presence of HP-β-CD (*top*) and HP-α-CD (*bottom*). The CD concentrations are: (– –), 4 wt%; (- - -), 9 wt%; (— -), 15 wt%; (– ·), 18 wt%

integration of the area in the thermograms. As Fig. 5 illustrates, for F88 the χ_M vs. T trend is a S-shaped curve which is moved to higher temperature upon increasing the HP-β-CD concentration. By replacing HP-β-CD with HP-α-CD, the χ_M vs. T curves (Fig. 5) are slightly moved to lower T. Similar results are observed for F68 and F108.

Whatever is the CD size, the ΔH_M decreases upon the macrocycle addition. The effect is more pronounced with the regular decrease of the copolymer size. As concerns HP-α-CD, the ΔH_M values basically refer to the same temperature as the CMT change is very small. Therefore, the ΔH_M decrease may be attributed to the lack of the desolvation contribution of the EO units which have released some water molecules during the IC formation. In the case of HP-β-CD, the temperature effect on ΔH_M has to be taken into account as the variation of CMT with the CD composition is important. Note that negative heat capacities of micellization are expected on the basis of literature data on other pluronics [39, 40]. Moreover, in agreement with our idea, the desolvation effect is somewhat less for HP-α-CD as some EO segments are already included into the CD cavity generating smaller ΔH_M endothermic values.

Thermodynamic approach to the HP-β-CD effect on the critical micellar temperature

As previously described, HP-β-CD remarkably influences the CMT of the copolymer whereas HP-α-CD slightly does in the opposite direction. In the following, a thermodynamic approach which quantitatively takes into account for the effect of HP-β-CD on the CMT of the copolymer will be proposed. In particular, one states that: (1) z molecules of HP-β-CD (CD) thread the copolymer forming a neck-lace

like structure (IC); (2) the IC is not solubilized into the micelles; and (3) the pseudo-phase transition model for the aggregation process is assumed so that the micellar phase is a segregated phase at all the temperatures.

The equilibria are given in the following

$$P_u \rightleftarrows P_M \tag{1a}$$

$$P_u + z\text{CD} \rightleftarrows \text{IC} \tag{1b}$$

where P_u is the freely dispersed copolymer in water and P_M stands for the copolymer in the micelles.

At constant pressure and in the equilibrium conditions, the chemical potential of the unimer and the copolymer in the micelles depend on temperature and concentration according to

$$RT\,d\ln x_u - S_u dT = -S_M^* dT \tag{2a}$$

where T is the absolute temperature, x_u is the mole fraction of the unimer while S_u and S_M^* are the partial molar entropies of the unimeric and micellized copolymer, respectively.

For the equilibrium 1b, one may write

$$\begin{aligned} RT\,d\ln x_u - S_u dT + zRT\,d\ln x_{CD} - zS_{CD}dT \\ = RT\,d\ln x_{IC} - S_{IC}dT \end{aligned} \tag{2b}$$

where x_{CD} and x_{IC} are the mole fractions of the cyclodextrin and the IC in the aqueous phase, respectively, while S_{CD} and S_{IC} are the corresponding partial molar entropies. Note that the activity coefficients were assumed to be unitary. By remembering that $(S_M^* - S_u) = \Delta S_M = \Delta H_M/T$ and $(S_{IC} - zS_{CD} - S_u) = \Delta S_{IC} = \Delta H_{IC}/T$ and combining Eqs. 2a and 2b one obtains

$$\int_{CMT^*}^{CMT} \frac{\Delta H_{IC} - \Delta H_M}{RT^2} dT = \int_{0}^{x_{IC}} d\ln\frac{x_{IC}}{x_{CD}^z} \tag{3}$$

where CMT* and CMT represent the critical micellar temperature in the absence and the presence of CD, respectively.

By considering the equilibrium constant for the IC formation (K_{IC}) [27] the following equation is obtained

$$\int_{CMT^*}^{CMT} \frac{\Delta H_{IC} - \Delta H_M}{RT^2} dT = \int_{x_{u,0}}^{x_{u,CD}} d\ln(K_{IC}x_u) \tag{4}$$

By integrating the latter, by assuming that both ΔH_M and ΔH_{IC} are independent of temperature, one obtains

$$\frac{(\Delta H_{IC} - \Delta H_M)(CMT - CMT^*)}{R\,CMT\,CMT^*} = \ln\frac{x_{u,CD}}{x_{u,0}} \tag{5}$$

where $x_{u,CD}$ and $x_{u,0}$ are the mole fractions of the unimer in the presence and the absence of CD, respectively, given by

$$\begin{aligned} x_{u,CD} &= m_u/(m_C + m_{CD} + 55.55) \\ x_{u,0} &= m_C/(m_C + 55.55) \end{aligned} \tag{6}$$

being m_u the molality of the unimer. Assuming that the molality of the cyclodextrin (m_{CD}) and the copolymer (m_C) are negligible with respect to the moles of water (55.55), the ratio ($x_{u,CD}/x_{u,0}$) can be written as ($1 - m_{IC}/m_C$), where m_{IC} is the molality of the IC.

Stating that $CMT \times CMT^* \approx CMT^{*2}$ and $\ln(1 - m_{IC}/m_C) \approx m_{IC}/m_C$ one obtains

$$CMT = CMT^* - \frac{RCMT^{*2}}{(\Delta H_{IC} - \Delta H_M)} \frac{\chi_1 m_{CD}}{z m_C} \qquad (7)$$

being χ_1 the fraction of the cyclodextrin involved in the IC.

As Fig. 6 shows, for all the copolymers, the fit of CMT data by means of Eq. 7 is good providing ΔH_{IC} being known ΔH_M and CMT^* (from our DSC data), the χ_1 values calculated according to the literature [27] and the z values [27] of 15, 21 and 27 for F68, F88 and F108, respectively. The ΔH_{IC} are 101 ± 2, 146 ± 2 and 182 ± 3 kJ mol^{-1} for F68, F88 and F108, respectively. These positive enthalpy changes evidence the hydrophobic desolvation occurring during the IC formation in agreement with the positive volume [27]. From the $\Delta H_{IC}/z$ ratio, one calculates the enthalpy change per mole of CD. It is intriguing that such a value is independent of the copolymer molecular weight indicating that the contribution of each CD is additive if the macromolecules possess the same hydrophilic/hydrophobic ratio.

Viscosity studies

The temperature dependence of the viscosity (η) for the aqueous copolymer solutions in the absence and the presence of HP-α-CD and HP-β-CD is illustrated in Fig. 7. The shape of the $\ln\eta$ vs. $1/T$ trends is peculiar; in the low T region, $\ln\eta$ starts to decrease with temperature, by further increasing temperature $\ln\eta$ rises reaching a maximum value thereafter it decreases.
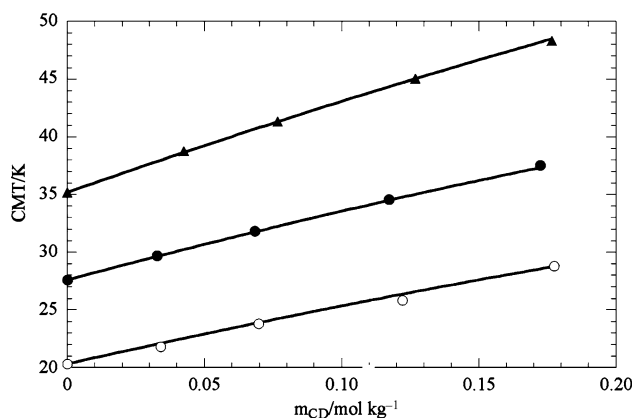

Fig. 6 Critical micellar temperatures of F108 (*open circle*), F88 (*filled circle*) and F68 (*filled triangle*) as functions of the HP-β-CD molality. Lines are the best fits according to Eq. 7
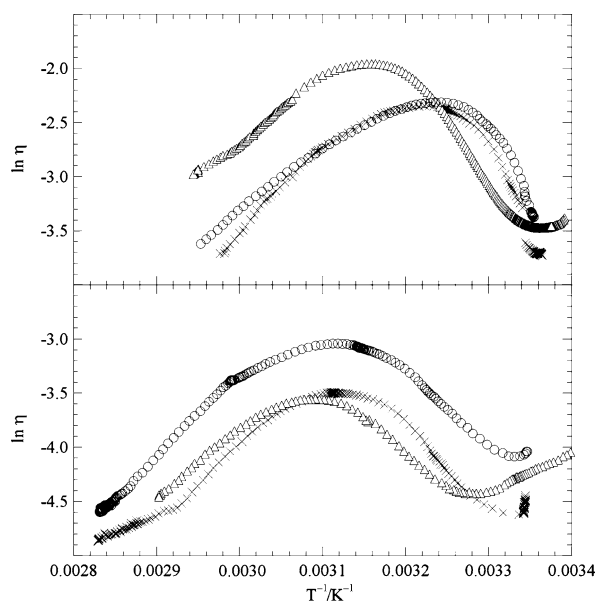

Fig. 7 Temperature dependence of viscosity for the aqueous F108 (*top*) and F88 (*bottom*) solutions (15 wt%) in the absence (*cross*) and the presence of HP-α-CD 9 wt% (*circle*) and HP-β-CD 9 wt% (*triangle*)

The data of the aqueous F88 solution can be interpreted to the light of the fraction of the aggregated copolymer as a function of temperature (Fig. 5). The small $\ln\eta$ decrease in the region below 300 K reflects the temperature effect on the solvent viscosity where the copolymer unimers are dispersed [41]; the viscosity positive temperature slope is generated by the increasing number of F88 micelles [37] while the $\ln\eta$ drop for $T > 321$ K is due to the decreasing viscosity of the solvent and/or the reduction of the hydration of the micelles [42] being that all of the copolymer is micellized.

The HP-α-CD addition to the aqueous F88 solution essentially moves the $\ln\eta$ vs. $1/T$ trend towards larger values likely due to the presence of ICs the formation of which was straightforwardly evidenced by the previous DSC as well as the literature data [27]. This suggests that the complexed copolymer does not nearly influence the CMT for the F88 aggregation. On the other hand, the parallel increase of the viscosity values may reflect the presence of larger aggregates. From literature [27] data at 298 K, we calculated that 25% of the copolymer is complexed by HP-α-CD that is an overestimated value because the IC concentration is expected to decrease with temperature based on the exothermic data for α-cyclodextrin-based molecular tube + PEO mixture [43]. Nevertheless, even under these conditions the CMT is slightly affected being 302 K.

The situation is different in the presence of HP-β-CD (Fig. 7). In fact, $\ln\eta$ decreases in a larger temperature domain and it starts to rise at a higher temperature achieving the maximum value at 325 K after which it

drops. From the $\ln\eta$ vs. $1/T$ curve, one may evaluate the CMT value of 305 K which corresponds to the free copolymer concentration of 7.7 mmol kg^{-1}. Consequently, the F88 concentration in the complexed state is 5.3 mmol kg^{-1} which is slightly larger than that (3.5 mmol kg^{-1}) computed [27] at 298 K. This small difference is likely due to the diverse temperatures. Once that the F88 aggregation starts, $\ln\eta$ assumes values even lower than those of the F88 + water mixture ascribable to a smaller amount of micelles because of the presence of ICs. As it occurs in water, η reaches the maximum value ($T = 326$ K) when F88 is likely all aggregated. Above 326 K, interactions between the free PEO units of the copolymer included into the HP-β-CD and the micelles may take place making the solution more viscous than the water + F88 mixture.

By replacing F88 with F108 alters the η magnitude but it does not the shape of $\ln\eta$ vs. $1/T$ curves. The above considerations done for F88 are still valid for F108.

Conclusions

The effect of CDs on the poly(ethylene oxides)-poly(propylene oxides)-poly(ethylene oxides) self-assembling was studied. The addition of HP-β-CD to an aqueous copolymer solution shifts the critical micellar temperature towards a higher value because HP-β-CD includes both the EO and the PO segments disturbing the copolymer aggregation. A thermodynamic model which quantitatively predicts the effect of the HP-β-CD on the CMT was proposed. HP-α-CD does not really change the CMT of the copolymer. Whatever is the macrocycle nature, the CD addition reduces the enthalpy of aggregation. The viscosity and the DSC findings are consistent with the presence of larger aggregates, in the presence of HP-α-CD, likely characterized by the hydrophilic shell decorated with the CD baskets.

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