Effect of Additives upon the Phase Transition Temperature of α,ω-(2-Hydroxyethoxy) Oligo(propylene oxide) in Aqueous Solutions

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The influence of various additives, like salts, alkohols, surfactants and water-miscible organic solvents, upon the cloud point of α, ω - (2-hydroxyethoxy) oligo(propylene oxide) in aqueous solutions was investigated for the first time. The results showed that NaH_2PO_4, NaCl, NaBr, NaI, 1-butanol, ethylene glycol and dimethylsulfoxide decreased the cloud point, while 1,2-propylene glycol, sodium dodecylsulfate, nonylphenyl ethoxylated with 9 moles of ethylene oxide and dioxane increased it. Addition of N,N-dimethylformamide practically had no influence upon the cloud point on the concentration interval investigated. The LCST of α, ω - (2-hydroxyethoxy) oligo(propylene oxide) in aqueous solution was also determined and it was found equal to 19°C.

Keywords: α, ω-(2-hydroxyethoxy) oligo(propylene oxide), thermosensitive polymers, cloud point, low critical solution temperature (LCST), additives

Water-soluble polymers displaying a soluble - insoluble transition in aqueous solution as a consequence of a temperature change have attracted a lot of attention within the last several decades due to their various applications, like vehicles for controlled delivery of drugs and bio-molecules, cell culture, flow modifiers, catalysts, smart clothing fabrication, chemical valves and sensors, etc. [1-8]. This transition is usually reversible and occurs at a certain temperature called phase-separation temperature (T_{ph}). Depending on the direction of this transition as a function of temperature, the thermoresponsive polymers can be divided into 2 classes: a) polymers with lower critical solution temperature (LCST), i.e. the polymer passes from a soluble state to an insoluble one when temperature raises over T_{ph}, and b) polymers with higher critical solution temperature (HCST) or upper critical solution temperature (UCST), i.e. polymers that precipitate out during a chilling process [1]. LCST represents the minimum value on the T_{ph} – polymer solution concentration plot, while UCST represents the maximum value on a similar plot [1].

Amongst the LCST-displaying polymers, the poly (ethylene oxide)–poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers, also known as Pluronics or Poloxamers, have been very much investigated, due to their employment in many fields, ranging from agriculture to medicine and pharmacy [9-11]. At low temperature, both PEO and PPO blocks are hydrated and water soluble, but as temperature increases their solubility decreases. PPO, being more hydrophobic, loses its water solubility below or around room temperature [12], while the PEO reported LCST is around 100°C [13]. If the polymer concentration is above a certain value, after the precipitation of the PPO block, micelles with a hydrophobic core made up of PPO and a corona of hydrated PEO blocks are formed at the critical micellar temperature (CMT) [10]. As temperature further increases, the water solubility of the PEO block keeps on decreasing, so that at a certain temperature (T_{cloud}) the copolymer as a whole becomes insoluble and the solution turns cloudy (the cloud point, CP). T_{cloud} was taken in many papers as the phase transition temperature [14,15].

Both CMT and T_{cloud} are important for various applications. They can be adjusted from the composition (ratio between the amounts of the PO and EO units) and molecular weight of the triblock copolymer [9], as well by adding various additives to the polymer solution, like salts, surfactants, urea, alcohols [10-12,16-20]. Many PEO-PPO-PEO triblock copolymers have been investigated from the point of view of the additive effect upon the CMT and/or CP of their aqueous solutions, like for example Pluronic P123 [10,18], P85 [10], L64 [11,16,17], F38 [12], F68 [12], F108 [12], F88 [12,19], F127 [18], L44 [20] etc. Both PEO and PPO blocks of these triblock copolymers posess more that 10 monomer units each.

A special case amongst the Pluronic copolymers is represented by L31, whose chain is made up of 17 PO units and 2 EO units, one at each end of the PPO block ($EOPO_{17}EO$, α,ω-(2-hydroxyethoxy) oligo(propylene oxide), and therefore it is not a true triblock copolymer. Because of its special structure, L31 may display a different behaviour in the presence of additives. Consequently, the present paper aims at investigating the influence of various organic and inorganic additives upon the CP of the L31 aqueous solutions. To the best of our knowledge, no such investigation was carried out up to now.

Experimental part

Materials

The L31 Pluronic® copolymer with 10 wt.% EO units and about 1100 Da molecular weight ($EOPO_{17}EO$) was obtained from Aldrich and used as received. All the other chemicals employed were of the highest purity commercially available and were used without further purification. Distilled water was employed in all experiments. The polymer solutions were prepared by loading the appropriate amounts of copolymer and

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corresponding aqueous solution into 10 mL glass vials, stirring for 2 h in an ice-water bath until homogeneous and storing overnight in the refrigerator.

Characterization

The cloud points of the polymer solutions in aqueous solvents of various compositions were determined by means of a Jasco V550 UV-VIS spectrometer, by placing about 2.5 mL solution in quartz cuvettes with 1 cm optical path. The temperature was controlled by means of a cooling-heating Peltier system attached to the UV-Vis spectrometer where the solution-filled cuvettes were introduced. The polymer solutions were magnetically stirred during the measurements. The temperature was increased in 2°C increments, the sample being allowed to equilibrate at each temperature for 5 min. The measurements were carried out at a wavelength of 600 nm. The temperature at which the transmittance decreased to 50% was taken as the cloud point (T_{cloud}).

Results and discussions

Determination of LCST

As mentioned above, LCST represents the minimum value on the T_{ph} – polymer solution concentration plot. In order to determine the LCST of the α,ω-(2-hydroxyethoxy) oligo(propylene oxide) copolymer (L31), polymer solutions of various concentrations were preparared in distilled water and their T_{cloud} was determined by measuring the solution transmittance at 600 nm as a function of temperature (fig. 1A). The thus determined T_{cloud} vs. polymer concentration plot displayed indeed a LCST-type behaviour, the minimum T_{cloud} value being equal to 19°C and corresponding to 40 wt.% polymer concentration (fig. 1B).

To determine the influence of various additives upon the thermosensitive behaviour of the L31 aqueous solutions, polymer solutions with 5 wt.% concentration were employed in order to be able to accurately determine the

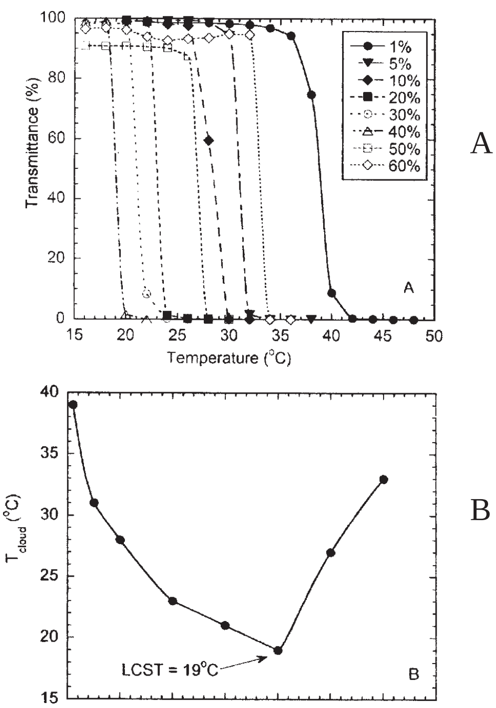

Fig. 1. Determination of the LCST of α,ω-(2-hydroxyethoxy) oligo(propylene oxide) in distilled water. A) Transmittance measurements (λ=600 nm) as a function of temperature at various polymer solution concetrations; B) T_{cloud} vs. L31 concentration plot

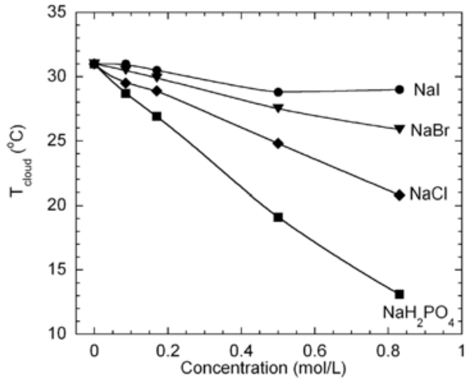

Fig. 2. Influence of salt nature and concentration upon the cloud point of the L31 aqueous solutions. Polymer concentration = 5 wt.%

change of T_{cloud} in both direction (up/down) as compared with T_{cloud} determined in distilled water (31°C).

Influence of salts

The addition of salts to the aqueous solution of thermosensitive polymers, like for example PEO-PPO-PEO triblock copolymers [12,20], poly(N-isopropylacrylamide) [21], poly(oligoethylene glycol methacrylates) [22] or polyoxazolines [23], strongly influences T_{ph}. The effect is mainly due to the anion, and its amplitude depends on the anion position within the Hofmeister series [20,21]:

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- \sim NO_3^- > I^- > SCN^-$$

The anions at the left side of the series, called kosmotropes, are well hydrated and tend to salt the polymer out of solution, thus decreasing the T_{ph}, while the anions at the right side, called chaotropes, poorly hidrated, have the opposite effect [20].

Figure 2 shows the influence of increasing concentrations of NaCl, NaBr, NaI and NaH_2PO_4 upon the T_{cloud} of the 5 wt.% L31 aqueous solutions. All these salts decreased T_{cloud}, the efect being stronger in the order NaH_2PO_4>NaCl>NaBr>NaI in agreement with the Hofmeister series, and also as the salt concentration increased.

Influence of alcohols

Alcohols are also known as affecting the CP of thermosensitive polymers [17,24] if added to the polymer aqueous solution. In the case of PEO-PPO-PEO block copolymers ($EO_{13}PO_{30}EO_{13}$), it has been reported that the addition of lower alcohols, like methanol, ethanol or 1-propanol, determined an increase of CP, while medium-chain alcohols, such as 1-butanol and 1 pentanol, more hydrophobic, depressed the CP [16]. No reports concerning the influence of 1,2-diols upon the CP of PEO-PPO-PEO block copolymers in aqueous solution could be found in literature.

Our results (fig. 3) showed that in the case of L31 aqueous solutions as well, increasing concentrations of 1-butanol (1-BuOH) determined a sharp decrease of T_{cloud}. We tested also the influence of ethylene glycol (EG) and 1,2-propylene glycol (PG). Based on the previously reported influence of monoalcohols, we would have been expected that PG, more hydrophobic, to decrease the CP, while EG, more hydrophilic to increase it. However, an opposite influence was actually observed, i.e the addition of PG increased T_{cloud}, especially at higher concentrations, while EG decreased the CP, but with a smaller slope than for 1-

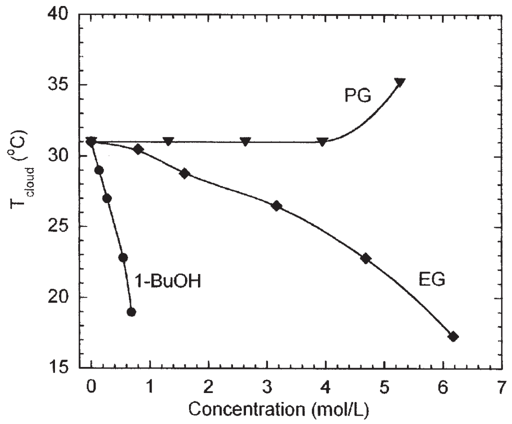

Fig. 3. Influence of alcohol nature and concentration upon the cloud point of the L31 aqueous solutions. Polymer concentration = 5 wt.%

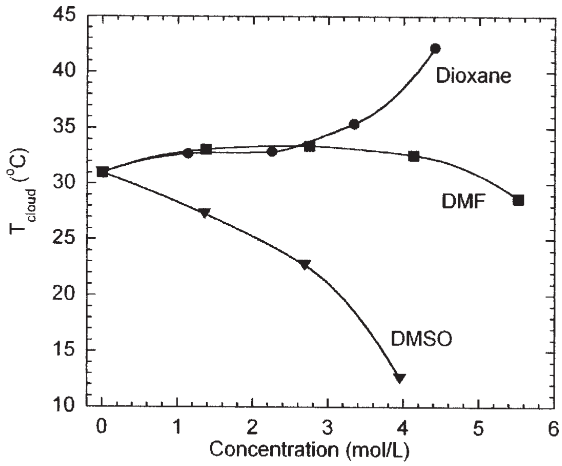

Fig. 5. Influence of the nature and concentration of the organic solvent upon the cloud point of the L31 aqueous solutions. Polymer concentration = 5 wt.%

BuOH. One should mention that L31 is immiscible with both EG and PG.

Influence of surfactants

Surfactants are known to increase the cloud point of the thermosensitive polymer aqueous solutions because of their ability to solubilize the polymer hydrophobic domains that form as temperature increases [17,24]. Two surfactants were tested within the present work: an anionic one, namely sodium dodecyl sulfate (SDS) with the hydrophilic/lipophilic balance (HLB) equal to 40, and a nonionic one, namely nonylphenyl ethoxylated with 9 moles of EO (NPE-9, HLB = 12.9). The results showed that T_{cloud} increased with surfactant concentration in the case of both surfactants employed, as expected (fig. 4). The effect was more prominent in the case of SDS, possibly because of its higher water compatibility, as indicated by its larger HLB, that would allow for an easier solubilization of the polymer hydrophobic domains.

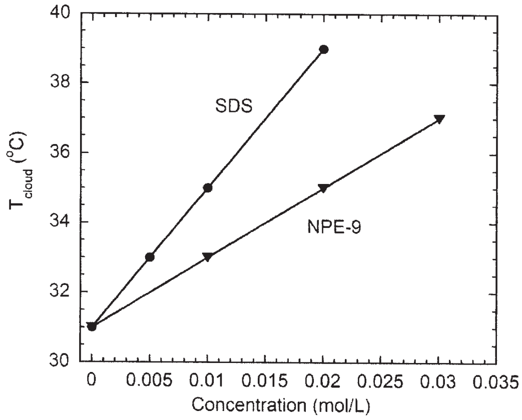

Fig. 4. Influence of surfactant nature and concentration upon the cloud point of the L31 aqueous solutions. Polymer concentration = 5 wt.%

Influence of water-miscible organic solvents

In order to test the influence of organic solvents upon the cloud point of the L31 aqueous solution, three water-miscible solvents were selected: dioxane, N,N-dimethyl formamide (DMF) and dimethylsulfoxide (DMSO). No reports concerning the influence of such solvents upon the cloud point of the PEO-PPO-PEO block copolymers in aqueous solutions could be found in literature. Dioxane, DMF and DMSO, in addition to their water miscibility, dissolve very well the polymer. Despite these similarities, the three solvents behaved very different from the point of view of their effect upon the cloud point. As one can see from figure 5, the addition of DMF practically did not affect T_{cloud} on the concentration interval investigated, while DMSO strongly decreased the cloud point, and dioxane increased T_{cloud} especially at higher concentrations. The effect of DMSO may be explained by its ability to structure water [25], thus supporting the dehydration of the polymer chains and their hydrophobic association, while the opposite effect of dioxane upon T_{cloud} may be rationalized through the capability of this solvent to break the water structure [26], thus allowing a better hydration of the polymer. Regarding DMF behaviour, we do not have a clear explanation at this time. DMF forms a 1:1 hydrate [27], and based on this property one would have been expected to behave similarly to DMSO as far as the influence upon T_{cloud} is concerned. However, it seems that this process is not a real structuration of water, as its influence on the cloud point is very little.

Conclusions

The influence of various additives, like salts, alcohols, surfactants and water-miscible organic solvents, upon the cloud point of α,ω-(2-hydroxyethoxy) oligo(propylene oxide) in aqueous solutions was investigated. It was noticed that the effect of the salts employed occurred in agreement with the predictions of the Hofmeister anion series, while that of DMSO and dioxane could be explained through the structuring and destructuring, respectively, of water. Consistent with the predictions was also the T_{cloud} increase by surfactant addition, and its decrease in the presence of 1-butanol. Less understood at this time are the increase of the cloud point by PG as long as EG decreases it, and the relative independence of T_{cloud} on DMF concentration.

The LCST of α,ω-(2-hydroxyethoxy) oligo(propylene oxide) in aqueous solution was also determined and it was found equal to 19°C.

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