

## PHASE EQUILIBRIA IN A WATER-BLOCK COPOLYMER SYSTEM

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### Abstract

Mixtures containing water and a PEO–PPO–PEO block copolymer, i.e. a polyoxyethylene–polyoxypropylene–polyoxyethylene glycol, have been investigated and the phase boundaries determined.

The phase diagram shows similarities with non-ionic surfactant systems of the *n*-alkyl-polyoxyethylene glycol family, with occurrence of different lyotropic liquid crystalline phases and of upper consolute boundaries.

Added sodium salts have a pronounced effect on the critical solution boundaries, which can be shifted upwards (downwards), depending on the counterion. A qualitative explanation of the above effects is given in terms of adsorption and/or depletion of the electrolytes at the polar-apolar interface of the aggregates formed by block copolymers.

**Keywords:** block copolymers, critical phenomena, electrolytes, liquid crystals, phase equilibria

### Introduction

Interest has been recently devoted to clarify the physico-chemical properties of systems containing block copolymers. Accordingly, theoretical and application-oriented contributions have been reported [1, 2]. The occurrence in the same molecule of regions with significantly different polarity (for instance alternate polyoxyethylene and polyoxybutylene domains) makes block copolymers quite similar to surfactants of the alkyl-polyoxyethylene glycol family [3] as the hydrophilic-lipophilic balance is concerned.

The possibility of linking polar groups to both ends of an apolar chain, and vice versa, increases the system complexity and gives rise to a complex phase behaviour in water [4], non-polar solvents [5], as well as in multi-component systems [6]. In some instances, the occurrence of different lyotropic liquid crystalline phases and solution phases has been observed in water–oil–block copolymer systems [7].

In addition to a rich polymorphic behaviour, the association features of block copolymers in solution are sensitive to the effect of temperature, pressure and ionic strength, which make such systems suitable for experimental investigation and theoretical modelling. Purpose of the present contribution is to shed light on the unusual effects played by

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simple electrolytes on the critical solution behaviour of an A–B–A block copolymer in water. The major part of the present contribution is focused, in fact, on the specificity played by selected sodium salts in controlling the occurrence and location of critical solution phenomena. Studies in this line are complementary to those dealing with the occurrence of consolute phenomena observed in alkyl-polyoxyethylene glycols [8, 9].

## Experimental

### *Materials*

The polyoxyethylene-polyoxypropylene-polyoxyethylene glycol block copolymer, hereafter referred to as A–B–A, Aldrich, was used as received. Relevant properties are: average molecular weight,  $\langle MW \rangle$ , 4.400 D, average PEO/PPO mole ratio,  $\langle \text{PEO/PPO} \rangle$ , close to 30/70, density,  $\rho$ , at 25°C, equal to 1.036 g cm<sup>3</sup> and viscosity,  $\eta$ , close to 1.200 cps, at the same temperature.

D<sub>2</sub>O, Merck, 99.5 % isotopic enrichment, was used as received. Solutions containing heavy water (about 10% of the total solvent content) were used when <sup>2</sup>H NMR investigation was required. Partial replacement of water with D<sub>2</sub>O was made on a mole fraction basis.

Water was doubly distilled, deionized through a Dowex exchange resin and degassed. Its electrical conductivity at 25°C is close to 10<sup>-6</sup> S cm<sup>-1</sup>.

Sodium acetate, sodium bromide, sodium chloride, sodium perchlorate and sodium sulphate, Aldrich, were vacuum dried prior to use.

The solutions were prepared by mass and corrected for buoyancy effects. The glass vials containing the mixtures were flame sealed and centrifuged several times. The vials were kept in a refrigerator (at 4°C) for a month.

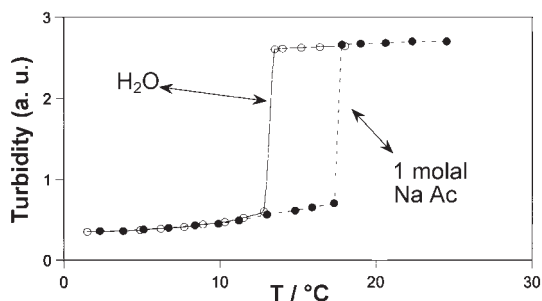
The mixtures exhibit moderate, if any, mutual miscibility at room temperature. To overcome the above drawbacks, the samples were heated in a water-methanol bath, up to the formation of an emulsion, and cooled to 5°C. The whole procedure was repeated, at least, three times.

Preliminary investigation on the completion of the equilibration process was made by visual observation in white and polarised light. Additional studies were performed by optical polarising microscopy, see below. Samples at A–B–A content above 50 wt are much easier to handle and were kept at room temperature before use.

### *Methods*

<sup>2</sup>H NMR experiments were performed on a Bruker WM 300, at 46.45 MHz. Details on the apparatus set-up, on acquisition time and on the measuring procedures are reported elsewhere [10].

The recognition of anisotropic textures, as well as emulsion formation, was investigated by a CETI optical polarising microscope, equipped with a CETI hot stage, operating in the range 5–65°C with a resolution of 0.1°C. Details on the apparatus set-up have been previously given [11].



**Fig. 1** Turbidity vs. temperature plot for a 5 wt A-B-A block copolymer in water, and in 1 molal sodium acetate, dotted line. Turbidity is in arbitrary units, when the temperature is in °C. The heating rate is  $0.02^{\circ}\text{C min}^{-1}$

The thermostatic bath used to determine the critical solution boundaries operates up to  $35^{\circ}\text{C}$ , with a resolution of  $\pm 0.01^{\circ}\text{C}$ . The thermal scan speed can be varied between  $0.01$  and  $0.1^{\circ}\text{C min}^{-1}$ . The occurrence of critical solution phenomena was made visually or by using a home made turbidimeter, consisting of a copper tube, thermostatted by an electrical resistor and equipped with a red light lamp and a photomultiplier, operating in continuous mode. Turbidity vs. temperature curves were reported on a single channel Kipp & Zonen paper recorder. Details on the apparatus set-up are given elsewhere [12]. A typical turbidity vs. temperature plot is given in Fig. 1.

## Results

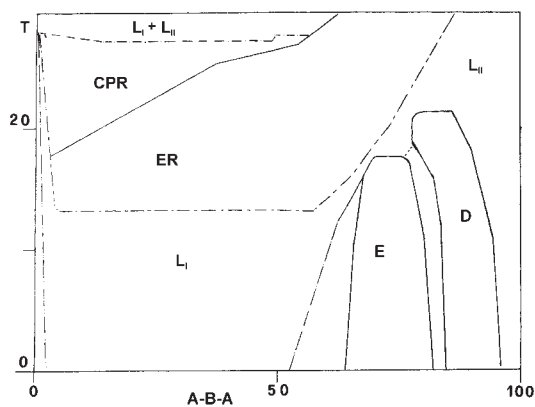
### *Phase diagram*

The phase diagram of the water-block copolymer system is reported in Fig. 2. The most significant aspect of the phase diagram is the occurrence of a wide two-phase region, at moderate temperatures, for block copolymer content up to 40 wt.

An accurate analysis of the relations between phase properties and temperature indicates that the coarse emulsion obtained on heating progressively transforms in a two-phase region at higher temperatures, through a series of non-equilibrium phases.

The driving forces controlling the phase separation process are, reasonably, the same as in water-polymer [13] and in water-non-ionic surfactant [14] systems, respectively. It is not clear, however, why the region of existence of the 'stable' emulsion region observed in the present system is so wide. In the water-dodecylhexaoxyethylene glycol system, for instance, the occurrence of an emulsion phase is a transient state. In the present system, conversely, emulsions are stable for days (weeks), provided they are kept at the proper temperature. This implies the occurrence of a slow phase separation process, which is presumably counteracted by interfacial tension and viscosity effects.

At high A-B-A content two liquid crystalline phases are observed. The former shows optical fanlike textures, Fig. 3, peculiar to hexagonal mesophases, E phase in Ekwall's terminology [15]. The second lyotropic mesophase shows mosaic optical



**Fig. 2** The phase diagram of the water/A-B-A system, as inferred by combining optical polarising microscopy, visual observation and  $^2H$ NMR. The phases denomination is, solution phase,  $L_1$ , reverse solution phase,  $L_2$ , emulsion region, ER, complex polyphasic region, CPR, two phase region,  $L_1+L_2$ , lamellar liquid crystalline,  $D$ , and hexagonal mesophase,  $E$

textures which can be assigned to a lamellar phase, ( $D$  phase). The width of the two-phase region between the liquid crystalline phases is not much different from that observed in structurally related water-surfactant systems. The same holds for the optical properties of such intermediate region.

The  $^2H$  quadrupole splitting,  $\Delta^2H$  (in kHz) is significantly different in the two liquid crystalline phases and increases, in either cases, in proportion to the amount of A-B-A in the mixture. Some  $^2H$  quadrupole splitting data are reported in Table 1. Significant variations in  $\Delta^2H$  values are associated to the hexagonal-lamellar phase transition.

Attempts to relate the observed quadrupole splitting to the amount of water bound at interfaces were made, according to Wennerstrom [16, 17]. The amplitude of deuterium quadrupole splitting,  $\Delta^2H$ , i.e. the distance between two adjacent quadrupolar wings occurring in the spectrum, is related to the bond order parameter of heavy



**Fig. 3** Polarising microscopy of a sample in the hexagonal liquid crystalline phase,  $E$ , at room temperature. The mixture contains about 62 A-B-A wt. The magnification of the optically anisotropic texture reported in the figure, a maltese cross, is 400

water in the given phase and to the number of water molecules bound to the polar-apolar interface. The following equation can be used

$$\Delta^2 H = \sum_{\text{H}} P_i \xi_i |S_i| \quad (1)$$

where  $P_i$  is the amount of  $^2H$  nuclei in a given environment, characterised by a peculiar quadrupole coupling constant,  $\xi_i$ , and bond-order parameter  $S_i$ , respectively.

In a two-site approximation for binding (water molecules are free or bound to the polar-apolar interface), the bond order parameter of free water is null and Eq. (1) reduces to

$$\Delta^2 H = \langle n \rangle X_A \xi_i |S_b| \quad (2)$$

where  $X_A$  is the mole fraction of the block copolymer molecule in the mixture,  $S_b$  the order parameter of bound water and  $\langle n \rangle$  the average hydration number per polar head group (two in the case of an A–B–A block copolymer). Average hydration numbers close to 10–12 have been obtained in the hexagonal mesophase and 7–8, in the lamellar one, respectively.

**Table 1** The mass percent of A–B–A block copolymer in D<sub>2</sub>O, wt, the mole fraction,  $X_{A-B-A}$ , and the deuterium quadrupole splitting,  $\Delta$ . In brackets is reported the related uncertainty. Data at 20°C

Mass/%	$X_{A-B-A}$	D/Hz
60.3	$9.60e^{-3}$	140 ( $\pm 20$ )
62.4	$1.04e^{-2}$	250 ( $\pm 20$ )
65.6	$1.18e^{-2}$	410 ( $\pm 15$ )
67.8	$1.35e^{-2}$	635 ( $\pm 15$ )
70.9	$1.55e^{-2}$	905 ( $\pm 10$ )
73.7	$1.80e^{-2}$	1215 ( $\pm 15$ )
77.1	$2.11e^{-2}$	1760 ( $\pm 10$ )

### Critical solution phenomena

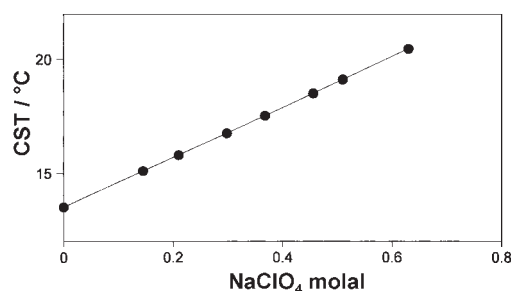
The occurrence of upper consolute boundaries extends in a significant concentration range, from about 2–3 up to 40 A–B–A wt. The shape of the critical solution curve is flat and not much dependent on the amount of A–B–A in the mixture. Comparison can be made with the water-octylpentaoxyethyleneglycol system [18], whose behaviour resembles the one depicted above.

To our knowledge, no detailed studies are reported up to now on the shape of consolute boundaries in water-block copolymer systems [19]. That's why we refer to previous models developed for alkyl polyoxyethylene glycols in water [20]. Zulauf *et al.*, for instance, demonstrated that the shape of critical boundaries is related to the interfacial curvature of the micellar aggregates coexisting in the adjacent solution

phase [18]. High aggregate interfacial curvatures (i.e. large and anisometric aggregates) imply steep and asymmetrical critical solution lines. Accordingly, the aggregates formed by A–B–A molecules should not be extremely large. In fact, the solutions below the critical solution curve are not very viscous. No critical opalescence is observed at temperature very close to the phase boundaries and the hypothesis of very large aggregates must be rejected.

#### *Effect of added electrolytes*

Addition of neutral electrolytes has a significant effect on the location of the critical solution curve. Let us consider, for instance, the effect played by progressive amounts of sodium perchlorate on the critical solution temperature of a 5 wt water–A–B–A mixture, Fig. 4. There a regular shift of the consolute boundaries to high temperature is evident. This implies that the phase transition is driven by the solvent ionic strength, for a given salt.



**Fig. 4** Dependence of the critical solution temperature (CST), in °C, of an aqueous mixture containing 7.5 A–B–A wt on the molality of added sodium perchlorate. The uncertainty on CST is about 0.03°C. The line is a guide to the eye

**Table 2** Effect of added sodium salt on the critical solution temperature, CST, in °C, of a 5 wt A–B–A block copolymer in water. Data refer to 1 mole of added salt, with the exception of sodium sulphate (0.33 molal)

Medium	CST/°C
No salt	+13.5
1 molal NaCH <sub>3</sub> COO	+17.8 (+4.3)
1 molal NaBr	+10.5 (–3.0)
1 molal NaCl	+11.5 (–2.0)
1 molal NaClO <sub>4</sub>	+24.5 (+11.0)
0.33 molal Na <sub>2</sub> SO <sub>4</sub> *	+01.3 (–12.2)

\*The above solution is isotonic to 1 molal 1-1 electrolytes

However, the phase boundaries change if different electrolytes, having the sodium ion in common, are compared. Let us consider, for instance the role played by addition of sodium acetate, sodium bromide, sodium chloride, sodium perchlorate and sodium sulphate, respectively, on the occurrence of critical solution phenomena of a 5 wt A–B–A mixture. Accordingly, 1 molal sodium acetate and perchlorate shift the critical solution boundaries upwards, when all other salts shift them in the reverse direction, Table 2.

## Discussion

Mixtures of water and A–B–A block copolymers form different phases, depending on composition. This is because the aggregation of block copolymers and the resulting segregation into polar/apolar domains obeys the hydrophobic effect and is responsible for their polymorphic behaviour [21]. The reasons for such a behaviour imply the formation of (quasi) micelle aggregates, with a distinct separation into polar and non polar regions. The latter region is rich in the more lipophilic component, PPO in the present case.

Critical solution phenomena are due to modifications in the conformational state of the polymer chain segments. A strong temperature dependence of the polymer dipole moment, which progressively reduces on increasing  $T$ , is expected also in the present case. As in bulk polyoxyethylene glycol's, a decrease of the dipole moment of PEO chains implies a decreased solubility in water. In other words, the polymer chains become more hydrophobic on increasing the temperature, up to phase separation.

The nucleation of an oily phase from water is controlled by addition of electrolytes, which distribute between the water pool and the polar-apolar interface, depending on their molecular polarizability. This effect is quite general and has been observed in counterion specificity effects on the solubility of ionic polymers [22], in micelle formation of ionic surfactants [23], in controlling the region of existence of balanced microemulsions [24], in bubble coalescence [25], etc. All the above cases imply the adsorption-depletion of ions from a given polar–apolar interface.

These effects are well known since many years. A relevant example is the Hofmeister series [26]. A complete physico-chemical rationalisation of the above effect is a formidable task. Most hypotheses so far carried out imply that electrostatic effects play an ancillary role in the overall system stability. Accordingly contributions due to ion polarizability can be dominant with respect to purely electrostatic ones, even at low electrolyte content. Theories developed on this purpose are, unfortunately, qualitative [27].

Craig *et al.* nicely explained the above effects and showed that neutral electrolytes can have a positive (or negative) effect on the observed properties, for instance will increase or reduce bubble coalescence [25]. The same holds to be true for the occurrence of critical solution phenomena, as can be observed in Table 1. Accordingly, a polarizability scale for anions can be drawn from experiments. Similar results can be obtained when dealing with the effect of cations (which is, however, much weaker).

The effect of electrolytes on the micellar to liquid crystalline phase transition is much less significant than the one reported above. This is presumably due to a signifi-

cant interface permittivity [28, 29], which reduces the above mentioned polarizability contributions. The partition of ions between the water pool and interfaces in lyotropic phases (where the dielectric permittivity of the interface region is close to 40 [28]) is significantly different compared to that of water–oil systems (dielectric constant of about 2). Thus, the polarizability contribution and the significant effects reported for the latter case, shall be largely dominant when the dielectric constant of the two coexisting media are largely different.

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