



# The cloud point and the liquid-liquid equilibrium behaviors of L31/L61-K<sub>2</sub>CO<sub>3</sub>/C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub> aqueous two-phase systems at different temperatures



Baodong An<sup>a</sup>, Yanli Mao<sup>b</sup>, Wenli Zhang<sup>a,\*</sup>, Juan Han<sup>c,\*</sup>, Yun Wang<sup>a</sup>, Liang Ni<sup>a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang, 212013, China

<sup>b</sup> School of Municipal and Environmental Engineering, Henan University of Urban Construction, Pingdingshan, 467036, China

<sup>c</sup> School of Food and Biological Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang, 212013, China

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## ABSTRACT

The cloud point (CP) of triblock copolymer L31 (Mn = 1100 g mol<sup>-1</sup>) and L61 (Mn = 2100 g mol<sup>-1</sup>) solutions was determined in the absence and presence of two salting-out salts (K<sub>2</sub>CO<sub>3</sub>, C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub>) at different concentrations. The results show that the addition of K<sub>2</sub>CO<sub>3</sub> and C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub> decreases the CP of copolymer solutions and the increase in the molecular weight can also decrease the CP of copolymer solutions. The anions order to decrease the CP of L31 or L61 is as follows: CO<sub>3</sub><sup>2-</sup> > C<sub>4</sub>H<sub>4</sub>O<sub>6</sub><sup>2-</sup>. Meanwhile the liquid-liquid equilibrium (LLE) data for L31/L61-K<sub>2</sub>CO<sub>3</sub>/C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub> ATPSs was measured at three temperatures (273.15, 278.15 and 283.15) K. An increase in temperature causes an increase in the slope of the tie-line (STL) and the tie line length (TLL). A significant alteration in the biphasic area for the temperature ranging from (273.15–283.15) K is observed. The anions order to induce the phase-separation for systems containing L31 or L61 is as follows: CO<sub>3</sub><sup>2-</sup> > C<sub>4</sub>H<sub>4</sub>O<sub>6</sub><sup>2-</sup>. The two-phase region in the phase diagram also expands with the increase of the molecular weight of copolymer.

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## 1. Introduction

Aqueous two-phase systems (ATPSs) discovered in 1956 by Albertsson [1] have been adopted as a powerful separation technique which is widely applied in the separation process of phenol [2], dye molecules [3], proteins [4–6], cell organelles [7,8], membranes [9], DNA [10], antibodies [11], nanoparticles [12,13] and ions [14–19]. There are many kinds of ATPSs, such as the polymer-polymer ATPS, polymer-salt ATPS, ionic liquid ATPS and aqueous organic solvent-salt ATPS [20–22]. As one of the most widely used ATPSs in separation technique, the polymer-salt ATPS presents more advantages, such as low cost, low viscosity and a short time for phase separation. But the difficulty in isolating the target product from copolymer solutions limits its further application. However, this problem can be solved through the creation of micellar media using intelligent copolymer such as pH-sensitive copolymers or thermosensitive copolymers [23–26]. As an alternative to the limitation, ATPSs formed by arrays of ethylene oxide

(EO) and propylene oxide (PO) units, symbolized as EO-PO-EO, are excellent options for the extraction of hydrophobic solutes into the copolymer-enriched phase [27,28].

The ATPS composed of thermosensitive triblock copolymer and salt has been studied aiming to improve the separation ability and cutting the cost of copolymer recovery [28]. Because the thermosensitive triblock copolymer plays an important role in such system and one of the characteristic features of thermosensitive triblock copolymer is the behavior of CP, many works describing the origin of the CP phenomenon have been done in previous literature [29,30]. The separation ability is another characteristic feature of the thermosensitive triblock and the separation ability can be described by the LLE data, so the LLE data of ATPS containing thermosensitive triblock copolymer and salts at various temperatures was also prepared by many coworkers [29–33]. At the present time, LLE of EO-PO-EO-based (L35-salt, F68-salt, L64-salt) ATPSs have been widely reported [20,23,25,29]. However, the CP of these copolymers is usually higher than L31 and L61, and a very high CP temperature makes it difficult to recycle copolymer. As a result, we studied the behaviors of these two copolymers, L31 and L61.

In this paper, the CP of the thermosensitive triblock L31 and L61 was measured. And the influences of copolymer concentration, salt

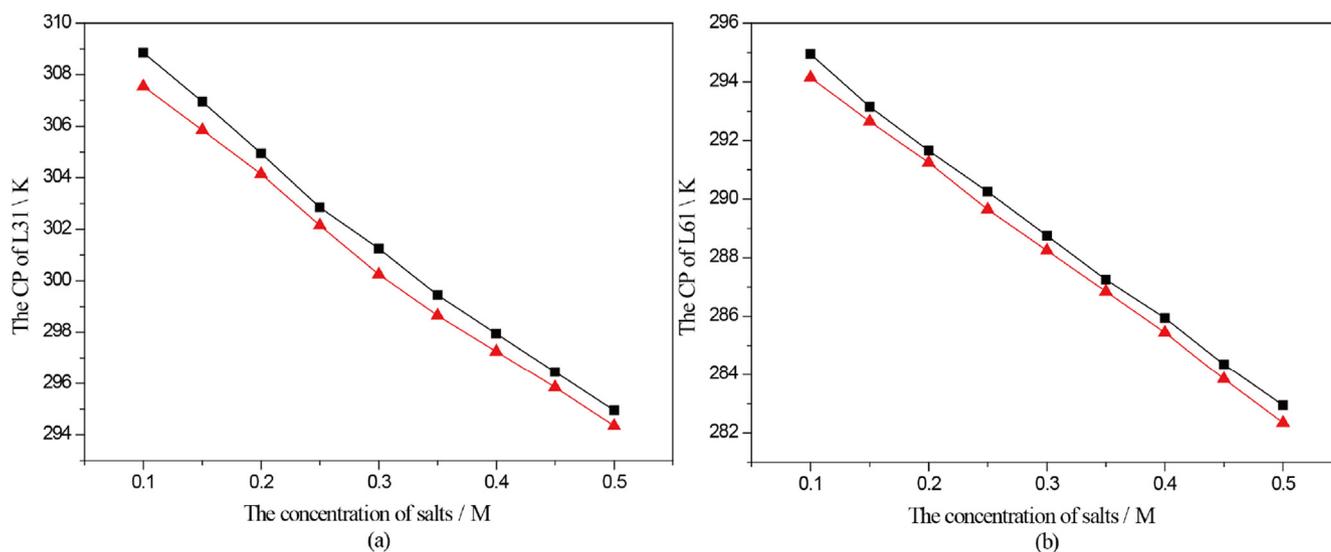
\* Corresponding authors.

E-mail addresses: [wzhang@ujs.edu.cn](mailto:wzhang@ujs.edu.cn) (W. Zhang), [hanjuan@ujs.edu.cn](mailto:hanjuan@ujs.edu.cn) (J. Han).

**Table 1**  
Purities and suppliers of chemicals used in the experiment.

Chemical	Mn/g mol <sup>-1</sup>	Source	Purification method	Final purity	Analysis method
L31	1100	Aldrich (USA)	–	–	–
L61	2100	Aldrich (USA)	–	–	–
K <sub>2</sub> CO <sub>3</sub>	138.21	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	None	0.990 (mass fraction)	GC
C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> K <sub>2</sub> ·1/2H <sub>2</sub> O	235.27	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)	None	0.990 (mass fraction)	GC

Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (L31, P(EO)<sub>2</sub>-P(PO)<sub>16</sub>-P(EO)<sub>2</sub> and L61, P(EO)<sub>3</sub>-P(PO)<sub>31</sub>-P(EO)<sub>3</sub>), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and potassium tartrate hemihydrate (C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub>).



**Fig. 1.** The effect of different salts on the CP of 1% (w/w) (a) L31, (b) L61 (▲ K<sub>2</sub>CO<sub>3</sub>, ■ C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub>) and the correlation coefficients of every system.

concentration, ions species and molecular weight on CP were discussed. Meanwhile the ATPSs formed by L31/L61 + K<sub>2</sub>CO<sub>3</sub>/C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub> were prepared, and the composition of each phase was measured. The data of LLE at (273.15, 278.15 and 283.15) K were determined for these systems and the reliability of all the tie-line experimental data was ascertained by applying the Othmer-Tobias correlation. Then, the influences of temperature, anion, and molecular weight on the LLE were evaluated. The relation between CP and phase separation was discussed.

## 2. Experimental

### 2.1. Materials

The copolymer L31 (10% EO unit) with an average molar mass (Mw) of 1100 g mol<sup>-1</sup> and the copolymer L61 (10% EO unit) with an average molar mass (Mw) of 2100 g mol<sup>-1</sup> were purchased from Aldrich (USA). The analytical grade reagents K<sub>2</sub>CO<sub>3</sub> and C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>K<sub>2</sub> were obtained from Sinopharm Chemical Reagent Co., LTD. The chemicals specifications are described in Table 1. Milli-Q II water was used to prepare all aqueous solutions.

### 2.2. Determination of CP

Solutions of surfactant with diverse concentrations were prepared by weighing appropriate amounts of copolymer and water into a glass cuvette followed by shaking until the mixture became clear. The concentrations of all the L31 or L61 solution varied from 0.1% to 8.0% (w/w). The CP was determined by visual observation of the abrupt change in the clarity of the surfactant solutions, which occurred during the increase of solution temperature. The

temperature at which the solution first became cloudy, indicating the onset of phase separation, was taken as the CP. All experiments were performed in triplicate. The CP data was given in Supporting information.

### 2.3. Preparation of ATPS and construction of phase diagrams

The ATPSs were prepared by weighing appropriate amounts of copolymer, salt and water using an analytical balance (BS-124S with an uncertainty of ±0.0001 g, Beijing Sartorius Instrument Co., Ltd., China). These systems were required to keep for about 48 h at the operation temperatures of (273.15, 278.15, and 283.15) K. The LLE state was characterized by the eventual disappearance of turbidity in both the top and bottom phases. Eventually, the liquid in each phase was collected with a syringe for analysis.

The salt concentration was confirmed by a conductivity (DDS-11A, Shanghai Dapu Instrument CO., LTD) in the mass percentage range of (0.1–0.5)% (w/w). As the previous study described [34], the conductivity of salt solution in water was the same as the conductivity in the diluted copolymer solution. The standard deviation of the salt mass percent from this method was ±0.10%. Meanwhile a

**Table 2**  
The linear relations between the CP and the concentration of salt in different systems.

System	Regression equations	Regression coefficient (R <sup>2</sup> )
L31 + K <sub>2</sub> CO <sub>3</sub>	Y = 38.82–34.83X	0.9995
L31 + C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> K <sub>2</sub>	Y = 37.53–33.37X	0.9993
L61 + K <sub>2</sub> CO <sub>3</sub>	Y = 23.92–29.33X	0.9997
L61 + C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> K <sub>2</sub>	Y = 24.54–29.60X	0.9991

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