

Effect of hydroxypropylmethylcellulose on Lower Critical Solution Temperature

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The effect of hydroxypropylmethylcellulose(HPMC) with molecular weight $M_w=1.24 \times 10^6$ on the phase equilibrium behavior of solution, ethylene glycol mono-isobutyl ether (C_4E_1) in water, has been studied. For low concentrations of HPMC, the cloud point curve had a double minimum, the stable critical points disappeared and a three-phase equilibrium appeared near the lower critical solution temperature of the binary system C_4E_1 + water. These characteristic behavior is discussed from an aspect of the universal behavior of the ternary system polymer + good solvent + poor solvent.

Key words: cloud point, critical line, three phase equilibrium, lower critical solution temperature

1. INTRODUCTION

Aqueous solutions of a family of nonionic surfactants oligooxyethylene alkyl ethers denoted as C_nE_m are known to exhibit entropy-driven phase equilibrium having the lower critical solution temperature (LCST)[1]. Hydration of C_nE_m decreases with increasing temperature, which results in the deterioration of its solubility. For industrial applications of C_nE_m , we commonly encounter ternary systems containing associated polymers as the third component. Hence, the general properties of the solubility change due to the modification of the interaction between C_nE_m and the associated polymer or a redistribution of hydrated water. In this study, we measured characteristic phase equilibrium properties, the cloud point curve, the critical line and the three-phase equilibrium, of aqueous solutions of the simplest family of C_nE_m , ethylene glycol mono-isobutyl ether (C_4E_1) with a cellulose-derivative, hydroxypropylmethylcellulose (HPMC). Cellulose-derivatives such as HPMC play a role as stabilizers and absorbents in many pharmaceutical applications[2], so, the interaction with surfactants is also interesting from both pharmaceutical and biological aspects.

2. EXPERIMENT

HPMC 60SH-4000 was a gift from *Shin-Etsu*. Gel permeation chromatography showed a broad unimodal molecular weight distribution with $M_w=1.24 \times 10^6$ and $M_w/M_n=7.42$. The weight percent of methoxyl and hydroxypropoxyl groups was 28-30% and 7-12%, respectively, according to the manufacturer. The polymers were used without further purification. Reagent grade ethylene glycol mono-isobutyl ether was distilled twice just before use. No impurity was observed with vapor chromatography. Distilled water for high performance liquid chromatography was purchased from Wako Pure Chemical Ind. and used without further purification. Desired amounts of

HPMC were dispersed in water at 60°C and dissolved completely in a freezer at 4°C. Then the solution was mixed with C_4E_1 at various compositions.

Cloud point curves were measured from the transmitted light pattern of laser light and by observation of cloud particles. Critical line, the locus of the critical point and the three-phase region were determined. The critical point is the intersection of the spinodal curve and the cloud point curve, so it is identified by the observation of a spinodal ring on the cloud point curve. The cloud point temperature and the critical temperature were determined with the precision of $\pm 0.2K$ and $\pm 0.5K$, respectively. The two-phase and three-phase regions were determined by putting samples with various concentrations in a thermostated bath at different temperatures. It took more than 24 hours to reach the equilibrium state near the critical temperature.

3. RESULTS

Figure 1 shows the cloud point curves for the various overall concentration. Hereafter, we denote the weight fractions of water, C_4E_1 and HPMC as w_1 , w_2 and w_3 , respectively. The solid circles are the coexistence curve for the binary system C_4E_1 + water (no HPMC) cited from Ref. 3. The cloud point temperature determined from this study (denoted by open circles) agrees excellently with the coexistence curve. The cloud point curve for 0.1 ~ 0.7%HPMC shows a double minimum and one maximum. The double minimum is found at both sides of the critical point. The dilute branch of the cloud point curve is located roughly parallel to the binary coexistence curve but at lower temperatures and the concentrated branch agree with the binary coexistence curve. With increasing concentration of HPMC, the minimum at the concentrated branch becomes deeper, but the dilute and concentrated parts of the cloud point curves agree with the cloud point curve with 0.1%HPMC. The solid

squares show the critical line (the locus of the critical point for various compositions of HPMC) in relation to the binary coexistence curve. For the sample with HPMC weight percent less than 1.0%, no spinodal ring could be observed on the cloud point curve, i.e., a stable critical point was not observed or ends at a definite concentration of HPMC. The upper and lower limit of the three-phase region were 38 and 25.7 °C.

4. DISCUSSION

Our system contains HPMC with a unimodal molecular weight distribution, amphiphilic low-molecular weight C_4E_1 and water. HPMC is a typical associating polymer and the hydration is considered to change with varying temperature and concentration. Both binary systems HPMC-water and C_4E_1 -water have LCST at ca. 60°C and 25°C, respectively. Thus, near the room temperature, water is a good solvent for HPMC but a poor solvent for C_4E_1 . Addition of HPMC should affect the hydrated structure surrounding C_4E_1 , so it is interesting to study the change in solubility. Experiments showed that for HPMC solution, cloud point curves had a double minimum, the stable critical line truncated and extended to an unstable region, and the three-phase regions were observed near the critical temperature for the binary system C_4E_1 -water. Although HPMC has a molecular weight distribution and the system is not a simple ternary system but a quasiternary system, it is instructive to compare the experimental results with a standard solution for understanding the effect of the associated polymer on the solubility of the system C_4E_1 +water.

As we are aware, the simplest model to exhibit all the experimental characteristic phase equilibrium behavior is the homologous Flory-Huggins solution polymer I (high molecular weight) + polymer II (low molecular weight) + poor solvent.

Analytical studies of this free energy showed that the three-phase equilibrium appears if the molecular weight ratio of the two polymers r is larger than $r_1 = ca. 10$ via a heterogeneous double plait point (HDPP) [4,5]. The relative location of cloud point curve, critical line and three-phase region is very similar to the present system as shown in Fig. 1.

Since polymer I is a good solvent for polymer II, this model system can be regarded as the simplest polymer / good solvent / poor solvent system. Thus, the agreement of phase equilibrium behavior observed and calculated is reasonable. It may be suggested that the characteristic feature of the current ternary system is universal to the ternary system polymer-good solvent-poor solvent and HDPP mechanism is also applicable to various ternary systems if certain requirements for the interactions between constituent molecules are satisfied. The detail of the solubility should depend on the system, however, for example, temperature dependence of the hydration is not taken into account. It is interesting to inquire the extent of the universality of this type of solubility phenomena.

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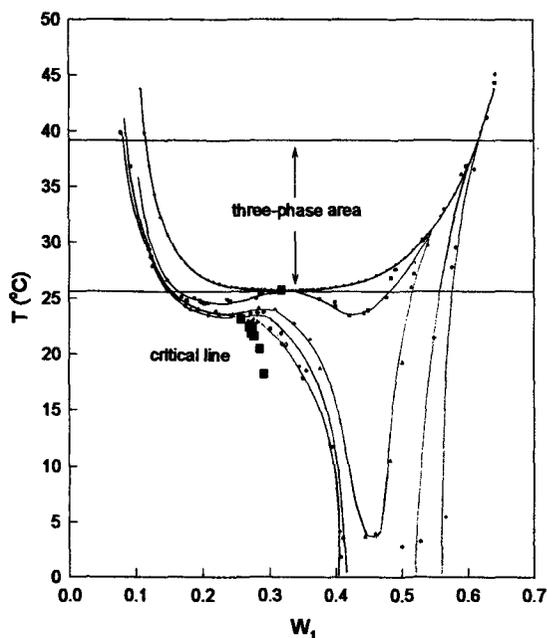


Fig.1 The locus of critical points (■) and cloud point curves for $w_2=0.001$ (□), 0.004(△), 0.007(◇), and 0.01(○) in relation to the coexistence curve for $w_2=0$ (●).

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