



# Mechanism of three phase separation in the ternary system of a polymer in a mixed solvent



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## ABSTRACT

The three phase separation due to contact between binodals was observed for the ternary system nitroethane(NE) + methylcyclohexane(MCH) + polystyrene(PS) with the molecular weight ( $M_w = 9.64 \times 10^4$  g/mol). A phase equilibrium experiment was made to determine binodals and three phase triangles on a composition triangle. With decreasing temperature a binodal spreads out from the MCH-PS side of a composition triangle at 48.4 °C and reaches the NE-MCH side at 23.6 °C. Another binodal spreads out from the NE-PS side at 43.6 °C and makes contact with the binodal running between the MCH-PS and NE-MCH sides at 3.3 °C. Simultaneously with the contact the three phase separation appears. The contact occurs at the critical point of the former binodal and at a noncritical point of the latter. The three phase separation usually occurs due to projection of a new binodal from the two phase region.

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## 1. Introduction

The three phase separation has been argued for various practical processes such as separation of materials by supercritical fluids and enhanced oil recovery using surfactants. A general behavior of the three phase separation would be observed for the ternary system in which each binary system has a critical point in an experimentally accessible range. The present experimental study was carried out on the ternary system of a polymer in a mixed solvent which satisfied the above requirement for the critical point. The experiment revealed a mechanism of three phase separation as well as the entire three phase behavior in connection with the binodal surface and critical lines. The comprehensive study of the three phase behavior is of practical importance as well as of scientific interest.

The three phase separation in ternary liquid mixtures is caused by two different mechanisms [1,2]. Usually the three phase separation appears in a two phase region protruding a new binodal on a

composition triangle. This mechanism was first observed for the ternary system perfluorotri-*n*-butylamine(PFB) + 2,2,4-trimethylpentane(TMP) + nitroethane(NE) [3] and investigated for the system of two polymer homologues in a solvent theoretically and experimentally [4–10], and found for various systems of water + oil + surfactant [11–13]. On the other hand, it has been conjectured that the three phase separation is also caused by contact between two binodals [2]. However, to our knowledge, the three phase separation due to this mechanism has been observed only for the ternary system water + *n*-decane +  $C_8H_{17}(OCH_2CH_2)_3OH[C_8E_3]$  [14], which has attracted little attention in the study of three phase separation.

The recent understanding of the three phase behavior was obtained from studies on the two different systems of two polymer homologues in a solvent and water + oil + surfactant. For other ternary systems with the exception of a few systems the three phase behavior has been observed at a single temperature and its mechanism is not clear. Literature of the observed three phase separation is found in Introduction of a previous study [15]. In addition to the two systems of polymer homologues and surfactant the ternary system of a polymer in a mixed solvent also shows interesting behavior of the three phase separation.

In this study we have found the three phase separation due to contact between binodals for the ternary system

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NE + MCH + PS ( $M_w = 9.64 \times 10^4$ ) by measurements of three phase triangles and cloud point curves. The upper critical solution temperature (UCST) of the binary systems NE + MCH, NE + PS, and MCH + PS was determined as 23.6 °C, 43.6, and 48.4, respectively. With decreasing temperature a binodal spreads out from the MCH-PS side of a composition triangle at 48.4 °C and reaches the NE-MCH side at 23.6 °C. Another binodal spreads out from the NE-PS side at 43.6 °C and contacts with the binodal running between the MCH-PS and NE-MCH sides at 3.3 °C. Simultaneously with the contact between the binodals the three phase separation occurs and the point of contact acts as a critical end point. The binodal surface has a col at which the critical line from the NE-PS side terminates in a prism diagram of composition triangle and temperature.

The present ternary system of NE + MCH + PS was suggested from the system NE + cyclohexane (CH) + PS ( $M_w = 4.8 \times 10^4$ ), on which we carried out a phase equilibrium experiment [16]. The binary systems of NE + CH, NE + PS, and CH + PS exhibited UCST at 22.9 °C, 29.9, and 14.8, respectively. With decreasing temperature a binodal spread out from the NE-CH side of a composition triangle at 22.9 °C and reached the CH-PS side at 14.8 °C. The binodal, which spreads out from the NE-PS side at 29.9 °C, did not contact with the other binodals in the experimental temperature range. However, the contact was expected to occur far below the experimental temperature range and to cause the three phase separation. In order to observe the contact between the binodals we employed the present ternary system NE + MCH + PS ( $M_w = 9.64 \times 10^4$ ), which was considered to show a similar phase behavior as NE + CH + PS and to give much higher critical temperatures for the associated binary systems. As expected the contact between the relevant binodals occurred at 3.3 °C accompanied by the three phase separation.

In a previous study [15] we determined the three phase triangle and binodal for the ternary system of ethylene glycol diacetate (EGDA) + MCH + PS with  $M_w = 4.8 \times 10^4$ . The binary systems of EGDA + MCH, EGDA + PS, and MCH + PS have UCST at 38.6 °C, 84.5, and 39.9, respectively. The three phase separation appears at 35.0 °C in the two-phase region spreading from EGDA-MCH side protruding a new binodal with a critical point. The binodal spreading from the EGDA-PS side merges with the binodal from the EGDA-MCH side via a critical point at 34.0 °C and the binodal from MCH-PS side merges with the new binodal due to the three phase separation at 32.9 °C. Thus, the binodal surface has two saddle points at which the critical lines have a minimum in a prism diagram. As to the behavior of binodal surface the present ternary system NE + MCH + PS is very different from the system EGDA + MCH + PS and analogous to the system NE + CH + PS.

## 2. Experimental

Standard polystyrene F-10 with the molecular weight  $M_w = 9.64 \times 10^4$  and molecular weight distribution  $M_w/M_n \sim 1.01$  was obtained from TOSOH Co., Tokyo, where  $M_w$  and  $M_n$  are the weight and number - average molecular weight, respectively. The solution of 25.3 g of the PS in 1000 mL of MCH was set below the phase separation temperature for purification of the PS sample. Three fractions of lower molecular weight were separated by solution fractionation, three fractions of higher molecular weight were separated by precipitation method, and the remaining central fraction of 15.2 g was used in the present study. For the molecular weight of the central fraction  $M_w = 9.64 \times 10^4$  was used because of the very sharp original PS as indicated by  $M_w/M_n = 1.01$ . Reagent grade NE and MCH were obtained from Wako Pure Chemical Co., Tokyo. MCH was distilled after being passed through a silica gel and a fraction at a constant boiling temperature was sealed in a flask as

a sample. NE was dried over calcium chloride and distilled at the reduced pressure 82.0 mmHg under nitrogen gas. A fraction at the constant boiling temperature 53.9 °C was used in the present experiment.

The cloud-point curve for the ternary system NE(1) + MCH(2) + PS(3) was measured by changing the volume fraction  $\phi_3$  of PS in the binary mixture NE + MCH at various mixing ratios. This measurement was carried out efficiently by using the  $\lambda$ -cell [15,16], which consists of a main tube of 0.8 cm inside diameter and 20 cm length and a side tube of the same size. The PS sample was loaded into the bottom of the main tube and mixed with the mixture NE + MCH in the side tube step-by-step. The mixture in the side tube was transferred to the main tube by inclining the  $\lambda$ -cell properly. At each step the  $\lambda$ -cell was immersed in a thermostatted water bath and the cloud point temperature of the solution in the main tube was measured with a precision of  $\pm 0.01$  K by lowering the temperature at a rate of about 0.01 K/min. Thus, the cloud point curve for the mixture NE + MCH at a constant mixing ratio was obtained by preparing the solutions stepwise in the closed  $\lambda$ -cell. The cloud point temperature of the mixture in the side tube changed by ca. 0.1 K during the period of the cloud point curve measurement, which required a couple of days. This temperature change, which suggested vapor diffusion between the side tube and the main tube, was negligibly small compared with the temperature range of the observed cloud point curve.

In this experiment the volume fraction  $\phi_3$  of PS in the solution was estimated from the mass  $w_3$  of PS and the volume  $V^t$  of the solution. Another directly estimated composition was the volume fraction  $u_2$  of MCH in the mixture NE + MCH. The volume fractions  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  of NE, MCH and PS, respectively, were obtained with

$$\phi_2 = (1 - \phi_3)u_2$$

$$\phi_3 = w_3/V^t\rho_3$$

and  $\phi_1 + \phi_2 + \phi_3 = 1$ . The estimation of  $u_2$  and  $\phi_3$  was made with the density  $\rho_i$  (g/cm<sup>3</sup>) of the pure component  $i$  as a function of the temperature  $t$  (°C):

$$\rho_1 = 1.07306 - 1.1922 \times 10^{-3}t - 3.65 \times 10^{-7}t^2$$

$$\rho_2 = 0.78636 - 0.8479 \times 10^{-3}t - 3.75 \times 10^{-7}t^2$$

and

$$\rho_3 = 1.0865 - 6.19 \times 10^{-4}t + 1.36 \times 10^{-7}t^2$$

Here,  $\rho_1$  and  $\rho_2$  were measured by a dilatometric method and  $\rho_3$  was taken from a literature [17]. Since  $u_2$  of MCH in NE + MCH at a constant mixing ratio changed only by 0.05% in the present experimental temperature range, the measurement by use of the  $\lambda$ -cell yielded cloud point curves at constant  $u_2$ . Binodals were constructed on a composition triangle from the observed cloud point curves owing to the PS sample with  $M_w/M_n$  close to unity.

For a ternary system the three phase triangle in volume fraction representation can be determined on a basis of the conservation law  $V^\alpha\phi_i^\alpha + V^\beta\phi_i^\beta + V^\gamma\phi_i^\gamma = w_i/\rho_i$ , where  $V^\alpha$ ,  $V^\beta$  and  $V^\gamma$  are the volumes of the three coexisting phases of  $\alpha$ ,  $\beta$  and  $\gamma$ , and  $\phi_i^\alpha$ ,  $\phi_i^\beta$  and  $\phi_i^\gamma$  are the volume fractions of the component  $i$  in the coexisting phases. Since  $w_i$  and  $\rho_i$  are the mass and density of component  $i$ , respectively and  $w_i/\rho_i$  is its volume at pure state, the volume change on mixing is not considered in the above equation. According to the phase rule for the three phase equilibrium at a constant temperature and pressure,  $\phi_i^\alpha$ ,  $\phi_i^\beta$  and  $\phi_i^\gamma$  are invariable for the solutions of different overall compositions, while  $V^\alpha$ ,  $V^\beta$  and  $V^\gamma$  depend on the

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