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STUDY OF PHASE TRANSITION TEMPERATURE OF LIQUID MIXTURES BY A LIGHT SCATTERING TECHNIQUE

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Abstract. *Phase transition temperature of liquid mixtures was studied using the light scattering technique at a laser wavelength of 650 nanometers. The laser beam was focused on the center of a sample cell containing a liquid mixture. Two liquid mixture samples were used as methanol-cyclohexane and methanol-hexane at temperatures varying between 30 and 60 degrees Celsius with resolution of 0.10 degrees Celsius. The intensity of light scattering was measured at an angle of 0 and at 90 degrees. At the critical temperature, the liquid mixtures became opaque, with maximum intensity of light scattering at 90 degrees. Phase transition temperature was studied by two methods. The first separated the liquid mixtures and then increased the temperature to critical opalescence, defined as phase combination temperature. The second method mixed the liquid mixtures well and then decreased the temperature to critical opalescence, defined as the phase separation temperature. The liquid mixture of methanol and cyclohexane at a ratio of methanol 29% gave phase combination temperature of 46.90 degrees Celsius and phase separation temperature of 47.00 degrees Celsius. When changing the ratio of methanol to 26%, 28%, 30% and 32%, both phase combination and phase separation temperatures increased. The liquid mixture of methanol and hexane at a ratio of methanol 22% gave minimum phase combination and phase separation temperatures. When decreasing or increasing the ratio of methanol to 20%, 21%, 23% and 24%, both phase separation and phase combination temperatures increased. Phase combination and phase separation temperatures of the liquid mixtures of methanol-cyclohexane and methanol-hexane were different. The ratio of liquid mixture with the lowest critical temperature is defined as the critical composition.*
Keywords: Light scattering, Liquid mixture, Phase transition

1. **Introduction.** One of the most striking examples of light scattering discovered by Andrews in 1869 is critical opalescence [1]. As the critical temperature of a fluid is approached along the critical isochor, density fluctuations in the medium increase to greater than the wavelength of the incident beam and stay together longer. Then, independent particle approximation is no longer valid, and light intensity is scattered in all directions. Regions of liquid-like density in a fluid contain molecules moving in phase or "coherently" within them. These coherent regions in fluids near their critical temperatures behave like large spherical particles following the relationship between Mie scattering of colloids and critical opalescence. The theory of scattering from correlated particles was first developed by Ornstein and Zernike between 1914 and 1926 [2]. Many experiments have been conducted and theories postulated to explain the physics of critical point behavior. Mistura and Cohen [3] studied thermodynamic fluctuations near a critical point in binary mixtures by considering the derivatives related to density and concentration fluctuations. They identified very large density fluctuations at a liquid-liquid critical point. A general property of correlation functions of local dynamical variables was proposed based on the

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behavior of various thermodynamic derivatives near a critical point in binary mixtures, while physical quantities behave in a similar way to liquid-vapor critical phenomena. Itami and Masaki [4] studied the critical behavior of liquid alloys with mutual immiscibility under microgravity. The phenomena of two-liquid phase separations were studied using electrical resistivity measurements, both in the laboratory environment on the ground and under microgravity onboard a sounding rocket. The temperature of the samples was controlled to approach the critical temperature from the higher temperature side. Hegseth et al. [5] took in situ photographs of the samples to show the density fluctuations near the critical point of binary liquid mixtures. They used a benchtop optical microscope to form the images by applying both phase-contrast and a dark-field filter to study the mechanisms of phase separation phenomena. Direct visualized concentration fluctuations in a binary liquid (methanol and partially deuterated cyclohexane) near its consulate critical point were recorded for further study. Shirai and Amano [6] applied the potential theory to studying parameter settings of a dynamic equation for a production process with phase transition, and successfully derived the function for Ginzburg-Landau potential energy. They obtained the entropy of three states as a stable state, a state with an assumed phase transition, and a state with a phase transition.

In this study, the phase transition temperature was determined by slowly cooling homogeneous mixtures of different compositions until phase separation occurred, or slowly heating the out of phase liquid mixtures until phase combination occurred. The thermodynamic quantity ΔF_{th} of the free energy of mixing can be determined as follows. Let ϕ_A and ϕ_B be the volume fractions of the two liquid species. If there are N_A molecules of liquid species A, each in a volume Ω_A and N_B molecules of species B, each occupying a volume Ω_B, where α is an interaction parameter and not of interest here, k is the Boltzman constant and T is the absolute temperature, then the thermodynamic quantity of the free energy of mixing can be written as Equation (1) [7].

$$\Delta F_{th} = kT(N_A \ln \phi_A + N_B \ln \phi_B) + \frac{\alpha}{2} \frac{N_A \Omega_A N_B \Omega_B}{N_A \Omega_A + N_B \Omega_B} \tag{1}$$

Most previous studies investigated the phase transition temperature of liquid mixtures by starting at a temperature above the critical point and cooling until phase separation occurred [3-5,8-10]. In the case of no external force field, the critical temperature of both the phase combination and phase separation processes can be the same. At the critical point of the phase transition process, the system becomes very sensitive to external free energy of any form, including the gravitational field [4,11]. Free energy of the gravitational field may affect the phase combination temperature and phase separation temperature of mixtures.

Previous research by Dangudom [12] from our Optical Research Group of the Department of Physics, Faculty of Science, Naresuan University, who studied the magnetic field effect on phase separation process in a liquid mixture, found that slow and accurate changes are required to control the temperature near the critical point. In the research, only the phase separation temperature was studied. The phase combination temperature was not measured in detail in the experiments because it was difficult to stabilize the system. Our research group developed a liquid temperature control system for light scattering measurements that has been registered as intellectual property in Thailand under Petty Patent No. 12466. This can be used to set up a system to study the phenomenon of phase transition in liquid mixtures. This research determined the phase transition temperature, phase combination temperature and phase separation temperature of binary liquid mixtures using the light scattering technique. The experimental samples consist of five different compositions of methanol-cyclohexane and methanol-hexane.

2. **Materials and Methods.** The light scattering measurements were performed on a vibration-free optical table using a laser wavelength of 650 nm. The laser beam was focused on the center of the sample cell that contained a liquid mixture placed in the middle of a temperature-controlled heating chamber, capable of keeping a sample at a predetermined temperature within 0.01 degrees of accuracy, utilizing the resistance bridge temperature controller scheme. The light detection assembly included a photodiode and pinhole, with a pre-amplifier circuit used as a light detection device. The signal from the light detector assembly was recorded into the data acquisition system consisting of a digital multimeter connected to a computer. Two liquid mixture samples were used as methanol-cyclohexane and methanol-hexane at temperatures varying between 30°C and 60°C with a resolution of 0.10°C. The intensity of light scattering was measured at 0° and 90°. The experimental setup is shown in Figure 1. Two methods were used to study phase transition temperature. The first separated the liquid mixture and then increased the temperature to critical opalescence, defined as phase combination temperature. The second mixed the liquid mixtures well and then decreased the temperature to critical opalescence, defined as phase separation temperature.

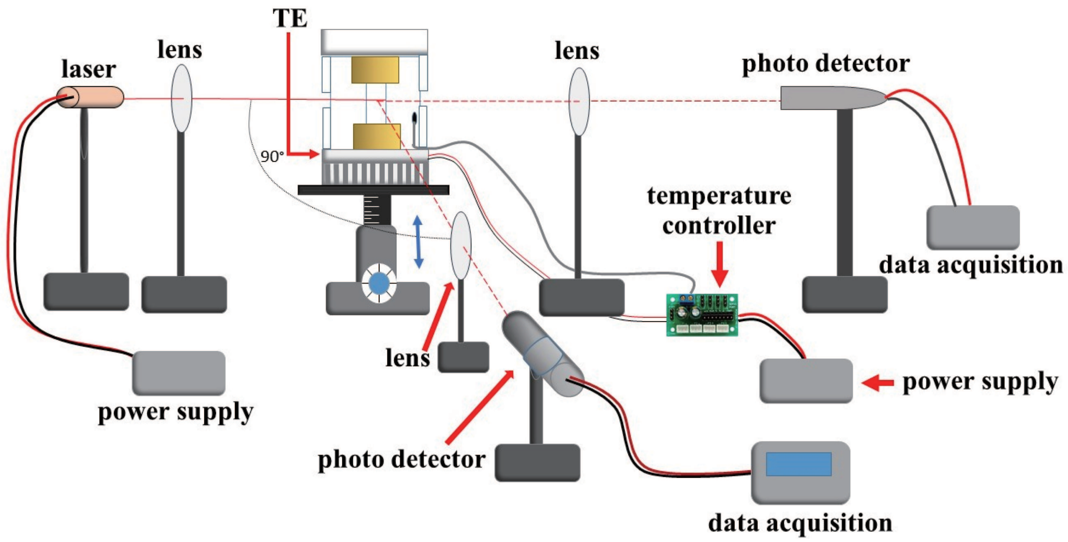

FIGURE 1. Experimental setup

The system is very sensitive at the critical point of the phase change process and temperature control must be precise. We used the bridge circuit shown in Figure 2 to control the temperature, connected to a 30 V DC supply. A transistor was used to amplify the temperature control signal using 15 V DC to power the heating coil. The thermistor (R_{th}) temperature sensor was connected as one of four resistances of the bridge circuit to control the heating coil current (I_c).

Temperature change must be performed slowly so that the system has time to attain thermodynamic equilibrium. In this experiment, temperature control was tested at 55.00°C by starting at 55.50°C. The system reached equilibrium after 1 hour, as shown in Figure 3. The temperature change was made in 0.10°C increments, with a 1-hour wait before measurement of light scattering by the liquid mixture.

3. **Main Results.** This experiment examined the phase transition phenomenon where light intensity is scattered in all directions causing opacity in a liquid mixture. Figure 4(a) shows a liquid mixture of methanol/cyclohexane starting from the homogeneous phase at above the critical temperature of 50.00°C. After cooling to near the critical point, the liquid mixture became opaque as shown in Figures 4(b)-4(e). When the temperature fell below the critical temperature, the liquid mixture separated, as shown in Figures 4(f)

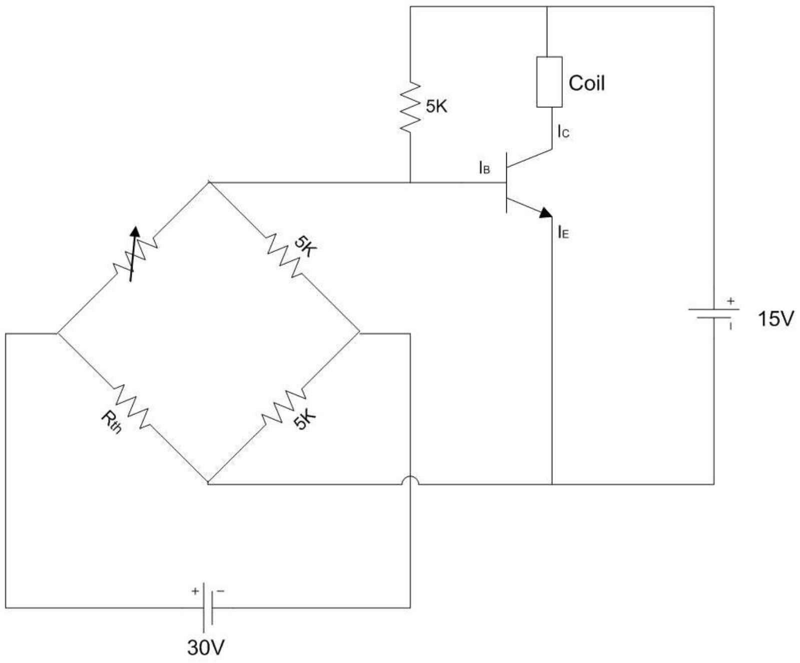

Figure 2. Temperature control circuit

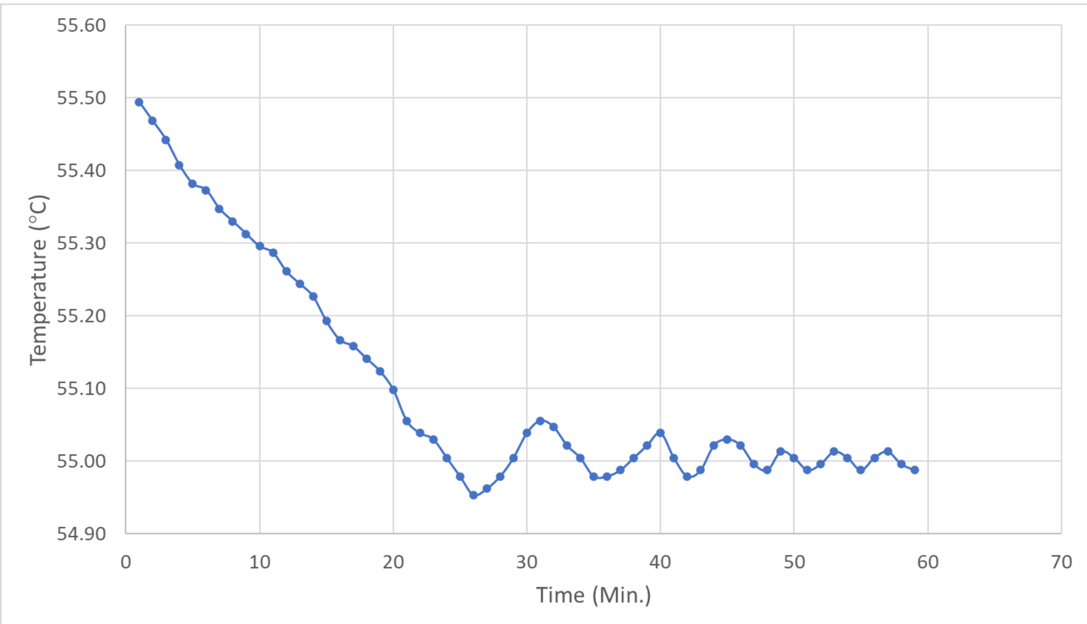

Figure 3. Temperature control at 55.00°C, starting at 55.50°C

and 4(g). When a 650 nm laser beam was shone through the liquid mixture, light was scattered at the critical point, as shown in Figure 5(a). The phase change resulted in a strong fluctuation of scattered light, as shown in Figures 5(b) and 5(c). When the two liquids completely separated, light transmittance was restored, as shown in Figure 5(d).

At phase transition temperatures, liquid mixtures show high-density fluctuation with maximum intensity of light scattering at 90° and minimum at 0°. Results showed that phase transition temperatures for phase combination and phase separation were different. For a concentration of 29% methanol/cyclohexane, phase combination and phase separation are shown in Figure 6 and Figure 7, respectively, while for a concentration of 22% methanol/hexane, phase combination and phase separation are shown in Figure 8 and Figure 9, respectively.

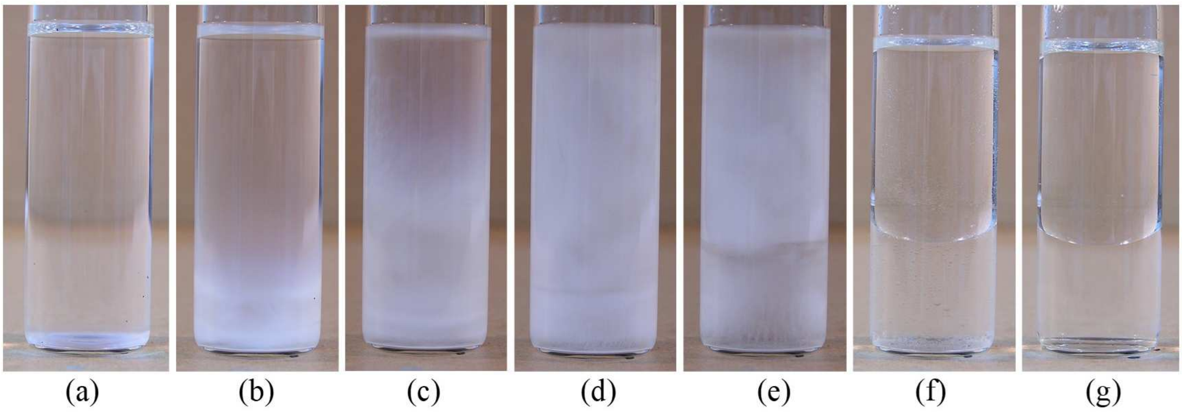

Figure 4. Density fluctuations in a liquid mixture

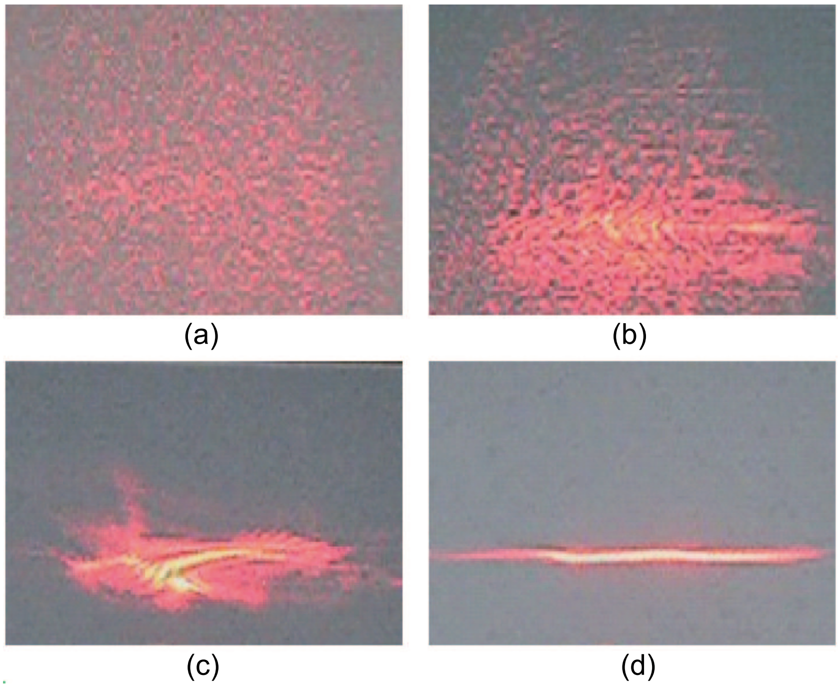

Figure 5. Light scattering by a liquid mixture

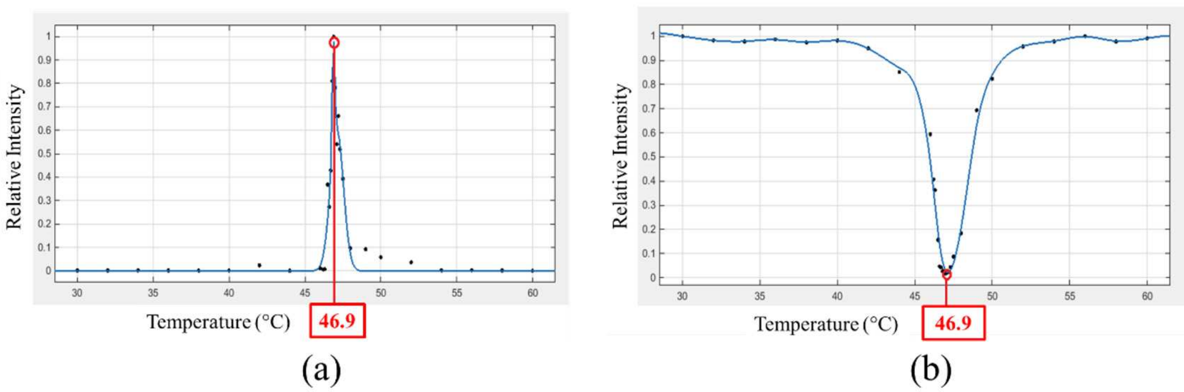

Figure 6. Phase combination of 29% methanol/cyclohexane at (a) 90° and (b) 0°

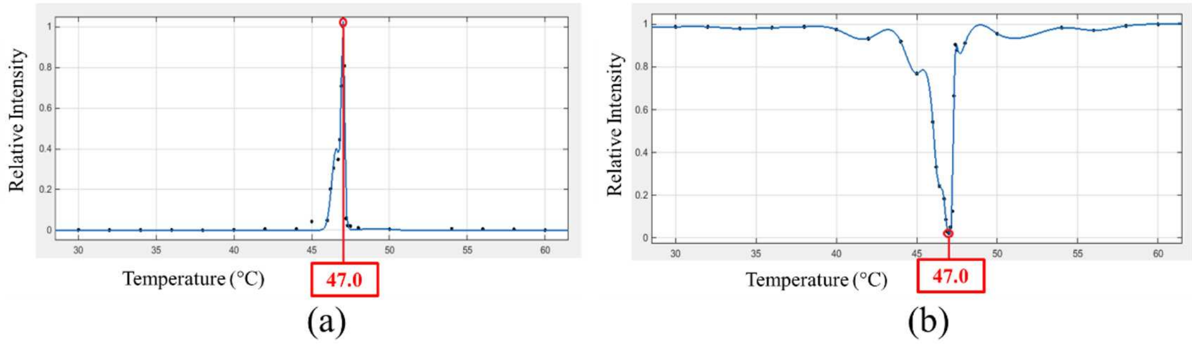

FIGURE 7. Phase separation of 29% methanol/cyclohexane at (a) 90° and (b) 0°

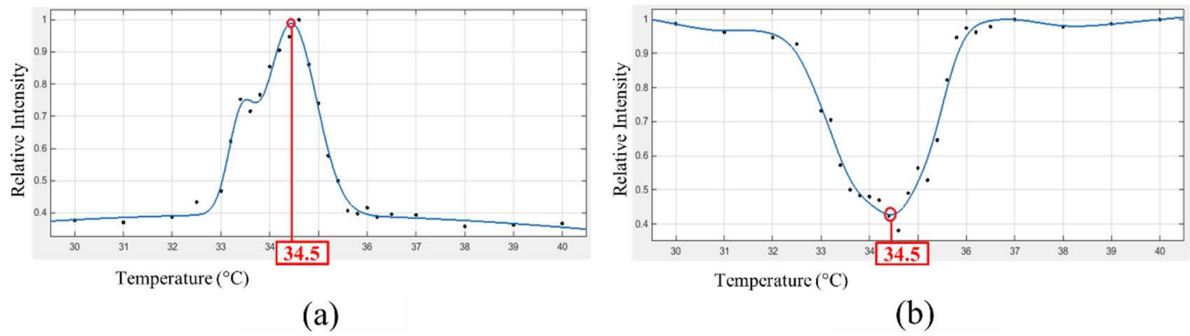

FIGURE 8. Phase combination of 22% methanol/hexane at (a) 90° and (b) 0°

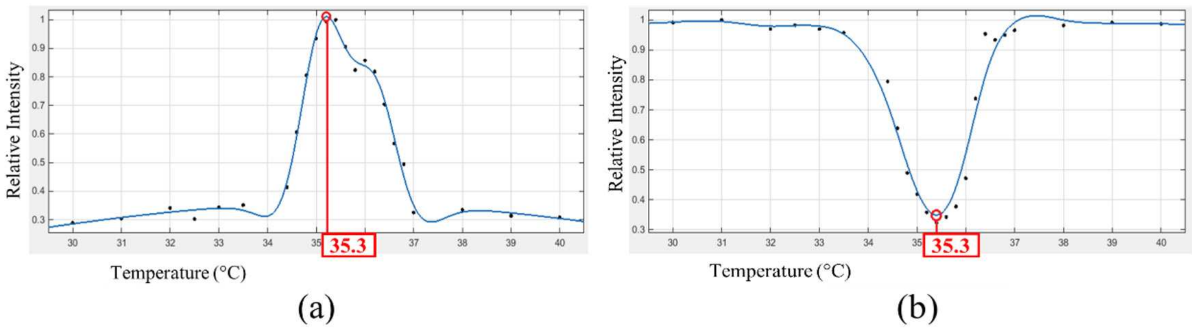

FIGURE 9. Phase separation of 22% methanol/hexane at (a) 90° and (b) 0°

The liquid mixture between methanol and cyclohexane at methanol ratio 29% gave phase combination temperature of 46.90°C and phase separation temperature of 47.00°C. When changing the methanol ratio to 26%, 28%, 30% and 32%, phase combination and phase separation temperatures increased as shown in Figure 10. The liquid mixture between methanol and hexane at methanol ratio 22% gave phase combination temperature of 34.50°C and phase separation temperature of 35.30°C. When changing the methanol ratio to 20%, 21%, 23% and 24%, phase combination and phase separation temperatures increased as shown in Figure 11.

4. **Conclusions.** This phase transition temperature study of liquid mixtures by light scattering technique determined two cases of critical temperature of phase transition processes. Phase combination and phase separation temperatures of liquid mixtures methanol-cyclohexane and methanol-hexane were different depending on the type and ratio of the liquid mixtures. Results showed that the ratio of liquid mixture affected phase separation and phase combination temperatures. The ratio of liquid mixture with

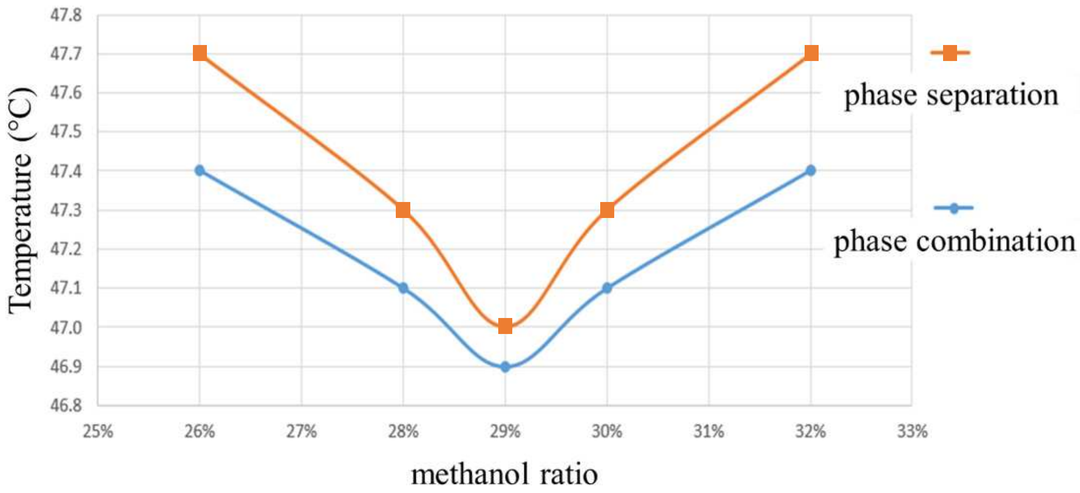

Figure 10. Phase transition of methanol/cyclohexane

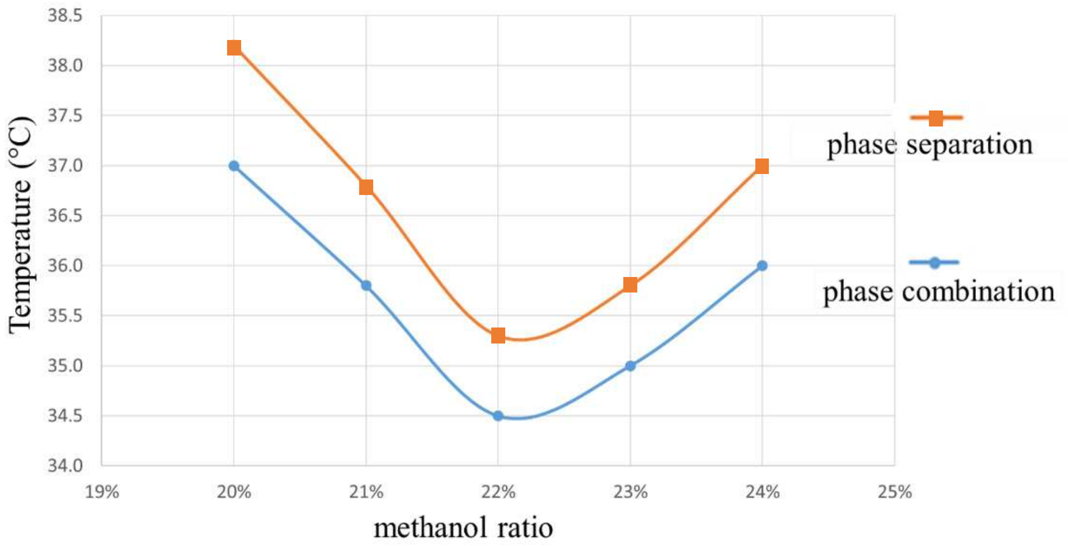

Figure 11. Phase transition of methanol/hexane

the lowest critical temperature is defined as the critical composition. Differences in phase separation and phase combination temperatures of methanol-cyclohexane were 0.10°C-0.30°C, while those of methanol-hexane were 0.80°C-1.20°C. The two liquid mixtures were similar because the ratios near the critical composition had the least differences in phase separation and phase combination temperatures, and their tendency to differ increased at ratios dissimilar from the critical composition. At the critical point of the phase transition process, the system becomes very sensitive to external forces of any form, including the gravitational field. The free energy of the liquid mixture is represented as the thermodynamic quantity, ΔF_{th} of the free energy in Equation (1) and the free energy of gravity. In the case of no external force field, the critical temperature of both the phase combination and phase separation processes can be the same. In the future, we plan to study the effects of external electric fields, magnetic fields and gravitational fields on phase separation and phase combination temperatures of liquid mixtures.

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