CHAPTER IV

EXPERIMENTAL

4.1 Chemicals

All pure liquids used in this work were of analytic grade from Carlo ERBA, Italy. Their purity was determined by gas-liquid chromatography to be better than 99.8 % for benzene, better than 99.5 % for cyclohexane, and better than 99.7 % for n-heptane.

Nitrogen gas was supplied by Thai Industrial Gases Public Company Limited (Thailand).

4.2 Apparatus

4.2.1 The Model DMA512P/ mPDS2000 Densitometer

The densitometer consists of the model DMA 512P and mPDS2000 unit. The model DMA512P densitometer which was manufactured by Anton Paar is designed to measure the density of liquids and gases under high pressure and high temperature.

4.2.1.1 DMA512P Specifications

Maximum temperature rating	302 °F (150 °C)
Maximum pressure rating	10,000 psi (700 bar)
Resolution	$\pm 1 \times 10^{-5}$ g/cm^3
Sample volume	2 cm^3

4.2.1.2 mPDS2000 Evaluation Unit

The mPDS2000 is a microprocessor based evaluation unit that is designed to be used with the DMA512P densitometer. It features a fully programmable, menu-driven software interface, a graphics LC display, along with several built-in inputs and outputs for various control and monitoring purposes.

4.2.2 Constant Temperature Bath

The constant temperature bath consists of automatic temperature controller; FCS-13A-R/M, thermocouple of type Pt100 that have scale range –199.9 to 850°C, and a circulating pump. The equipment is filled with distilled water.

4.2.3 Gas Chromatograph (Hewlett Packard 6890)

The operating conditions are illustrated in Table 4.1.

Table 4.1 Operating conditions of gas chromatograph.

Parameter	Condition
Detector	Flame Ionization Detector(FID)
Temperature	250 °C
Hydrogen flow	30 cm^3/min
Air flow	400 cm^3/min
Oven	
Initial temperature	40 °C
Front inlet	
Initial temperature	200 °C
Helium flow rate	5.6 cm^3/min
Back inlet (split/splitless)	
Initial temperature	150 °C
Split ratio	150:1
Split flow	332.1 cm^3/min
Column	
Capillary column	Wasson KC21
Inlet flow	2.2 cm^3/min

4.3 Experimental Section

4.3.1 Calibration of the Gas Chromatograph

The gas chromatograph was calibrated with gravimetrically prepared standard mixtures for the ternary system covering the entire composition range of interest consisting of about 6 samples including each pure component. At least two injections were made for both standard mixtures and pure components. An injection volume of 1 μl was used. The results were shown by standard curves generated by Chem Station program of Hewlett Packard.

4.3.2 DMA 512P Densitometer Operation and Calibration

Density measurements were carried out with an Anton Paar DMA 512P vibrating tube densitometer with an accuracy of $\pm$ 1x10^{-5} g/cm^{-3}. The density determination was performed by measuring the period of harmonic oscillation of a vibrating U-tube, filled with the samples. The period of oscillation can be converted to density if two apparatus constants A and B are known. The constants are determined by calibration with fluids of known density at each investigated temperature and pressure. In this work, the instrument was calibrated with benzene and nitrogen gas.

The values of A and B can then be entered into the Submenu Cell of mPDS2000. For samples whose densities are to be measured at the pressure and temperature of interest, the mPDS2000 then displays the calculated density of the fluid according to the following equation relating the period of oscillation to the fluid density:

$$\rho = Ap^2 - B \tag{4.1}$$

where p is the oscillation period in microseconds.

The constants A and B are only valid for the set of pressure and temperature where they have been determined (See Appendix E).

หอสมุดกลาง สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

4.3.3 Preparation of Samples

A sample of 50 gram was prepared for each density measurement. For pure component, it was introduced into the flask until its weigh was 50 gram with an accuracy of 0.01 gram. For a mixture, each component was introduced into the flask in series with its weigh equaled to its pre-determined weigh, so that the weighs of all components would sum up 50 gram. Sample preparation flasks were stoppered by septums to prevent evaporative composition changes. Finally, the exact composition of a mixture was determined by gas chromatograph.

4.3.4 Procedure

In measuring density of the samples, must previously calibrate DMA 512P with fluid standard calibration; benzene and nitrogen gas. Schematic diagram of assembling of experimental apparatus is shown in Figure 4.1.

4.3.4.1 Open valve 1 (4), valve 2 (13) and close valve 3 (14), fill cylinder (3) with hydraulic oil and then close valve 2 and open valve 3, start the vacuum pump (15) in order to pull the best possible vacuum on the closed system.

4.3.4.2 Close valve 2, valve 3 and open valve 1, use hydraulic pump to drive hydraulic oil from cylinder to attract preparing sample in the cylinder by the way inlet sample together.

4.3.4.3 Open valve 2, compress slowly hydraulic oil to fill the sample a whole system and purge air bubbles out of the system about 20 cm^3 and then close valve 2.

4.3.4.4 Set temperature of 35°C in constant temperature bath (9) and circulate around U-tube densitometer about 1 hour.

4.3.4.5 Set pressure of 1.01325 bar, then measure the period of harmonic oscillation or density of U-tube containing the sample and record the data that were shown in MPS2000.

4.3.4.6 Continue to increase the pump pressure, push piston in cylinder until the pressure of pressure gauge (12) is at 2, 5 and 10 bar, and then record the data each pressures.

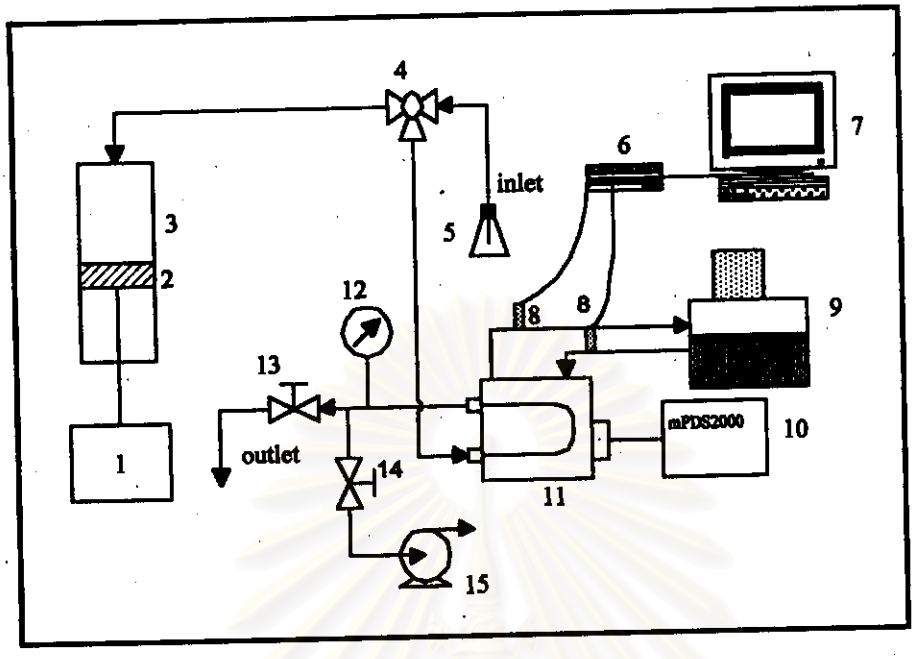
4.3.4.7 Set required temperature at 40, 45 and 50°C respectively and repeat from item 4.3.4.5 to 4.3.4.6 every temperature.

4.3.4.8 Open valve 2, use the pump to drive the whole sample from cylinder to the outlet and take immediately some sample in viol to analyze by using a Hewlett Packard 6890 gas chromatograph equipped with a flame ionization detector and then go to item 4.3.4.9.

4.3.4.9 Purge the rest of sample in system with nitrogen gas.

4.3.4.10 Change sample and repeat from item 4.3.4.1. to 4.3.4.9.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



1. Hydraulic pump
2. Piston
3. Cylinder
4. Valve 1
5. Sample inlet
6. Data acquisitor
7. Computer
8. Thermocouple type K
9. Constant temperature bath with circulating pump
10. mPDS2000 Unit
11. DMA 512P densitometer
12. Pressure gauge
13. Valve 2
14. Valve 3
15. Vacuum pump

Figure 4.1 Schematic diagram of assembling of experimental apparatus.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย