

Measurement of Vapor-Liquid Equilibria for Azeotropic systems

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Abstract

It is known that about half of the binary vapor-liquid equilibrium (VLE) data available in the literature are azeotropic systems. There are generally two types of azeotrope of isobaric binary systems: the minimum boiling azeotrope, where the boiling point is lower than that of the pure component at a specific composition, equal composition of vapor and liquid phases, and the maximum boiling azeotrope, where the boiling point is higher. In addition, in very few cases, there are the double azeotrope that have both minimum and maximum boiling points at each specific composition. In isobaric ternary VLE, there are the minimum boiling azeotrope and the saddle azeotrope.

In this study, the VLE of azeotropic systems measured using the original equilibrium stills with circulation of both the vapor and liquid phases, equipped with a Cottrell pump are shown. For some systems, VLE was measured under pressurized conditions using a pressure-resistant equilibrium still, and the azeotropic data determined based on the VLE data showed how the azeotropic data changed with pressure.

Keywords

Vapor-liquid equilibria, Azeotrope, Equilibrium still

1. Introduction

Reliable data on the phase behavior is essential for the design and operation of separation processes. An azeotrope is the mixture consists of two or more substances in which the equilibrium vapor and liquid compositions are equal and the equilibrium temperature (or pressure) is an extreme value. If the mixture of two or more liquids is an azeotropic system, it cannot be completely separated or changed to the desired composition by simple distillation. Therefore, it is important to know the accurate azeotrope data for chemical processes design.

The authors have designed several original equilibrium stills with circulation of both the

vapor and liquid phases, equipped with a Cottrell pump for accurate VLE measurements. In this study, the apparatus used for the VLE measurements are presented, and show the experimental VLE data of positive azeotrope, negative azeotrope, and double azeotrope for the binary systems. For the ternary system, the positive azeotropic system and the saddle azeotropic system are shown.

2. Experimental

2.1. Apparatus

The equipment and techniques for determining the VLE were developed in our laboratory. An all-glass liquid-vapor ebullition type equilibrium still, developed to determine accurately azeotropic data, is shown schematically in Fig. 1 [1], consists of two ebulliometers connected in series. The still consists of a liquid phase boiling vessel and a vapor phase boiling vessel equipped with the Cottrell pump and a thermometer well, respectively. The still features ability to measure boiling points of not only liquid but vapor portions also and to determine the azeotropic data from the composition at which boiling point difference is zero. Boiling flasks for liquid and vapor have a capacity of about 250 cm³ and are provided at their bottoms with magnetic stirrers to stir the liquids in the stills.

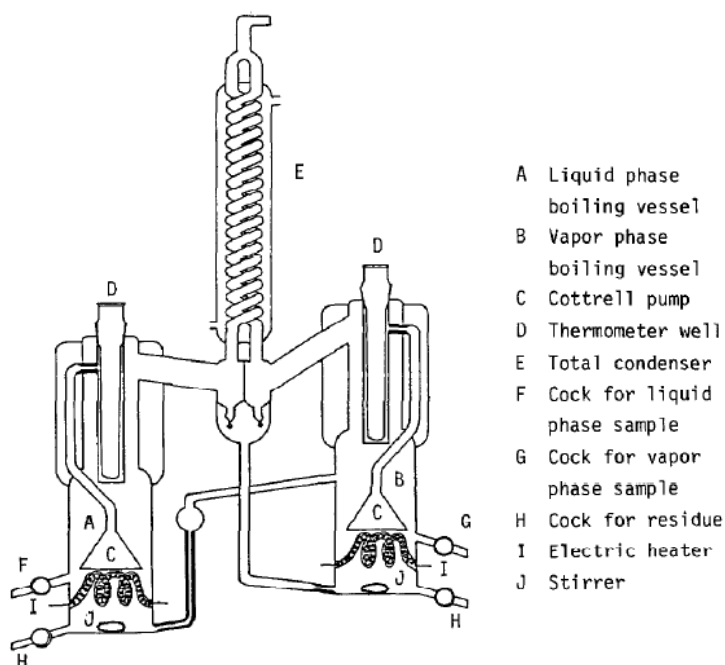


Fig. 1 Schematic diagram of liquid-vapor ebullition type equilibrium still

Several types of equilibrium stills with a provision for vapor and liquid circulation were developed. The Rogalski-Malanowski type still, shown schematically in Fig. 2 (1) [2], equipped with the Cottrell pump have a capacity of about 90 cm³ of solution. A small capacity equilibrium still was developed. The overall charge of the still was approximately 18 - 35 cm³ [3, 4]. A schematic diagram of the VLE apparatus is shown in Fig. 2 (2).

In order to measure the VLE under pressurized conditions and to determine the trajectory of different of azeotropic points on elevated pressure, two different devise were developed. A stainless-steel VLE still with three pressure-tight glass windows as shown in Fig. 2 (3), was

used from atmospheric pressure to 0.5 MPa. The overall charge of the apparatus was about 120 cm³ [5]. The other is an all-glass pressure-resistant equilibrium still, the most recently developed device, with the volume of approximately 25 cm³ [6], which can be used for VLE measurements from atmospheric pressure to 1 MPa. The shape of the apparatus is similar to that of Fig. 2 (2), with a stainless steel pressure-resistant valve connected to the glass tube in the sampling section (I₁ and I₂).

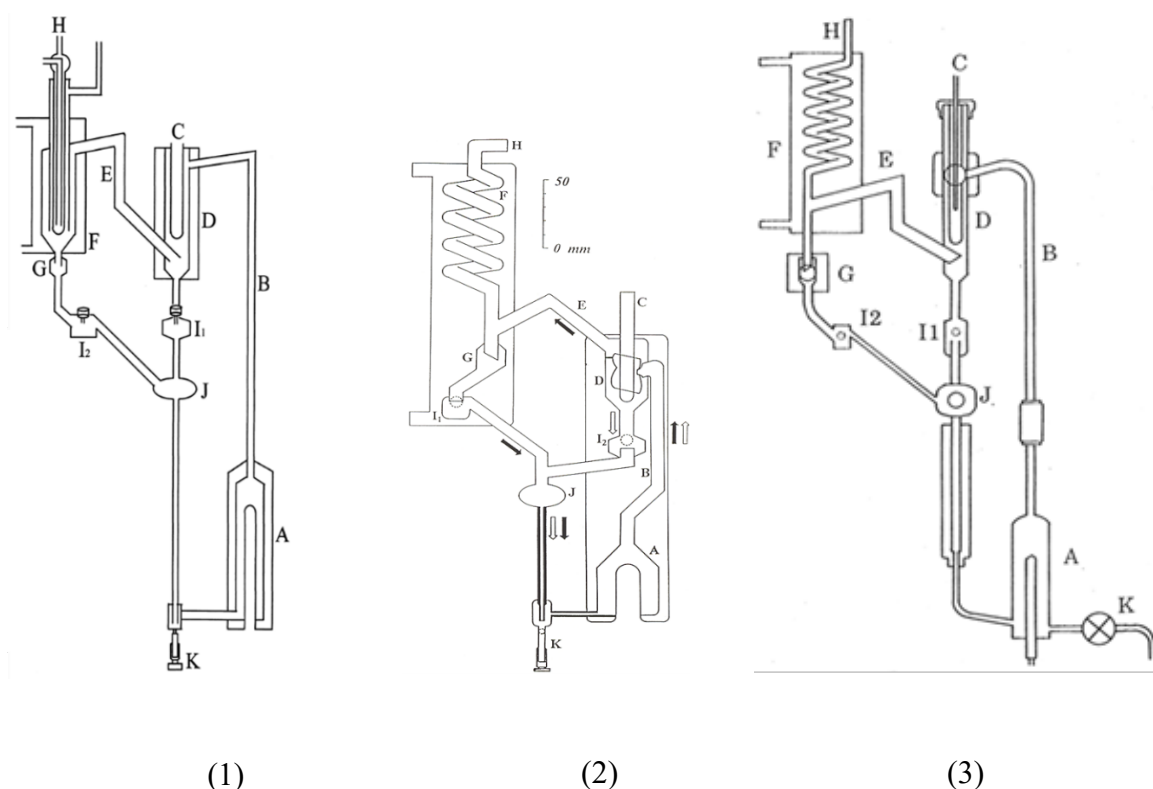


Fig. 2 Schematic diagram of the VLE apparatus. (A) Boiling flask; (B) Cottrell pump; (C) thermometer well; (D) equilibrium chamber; (E) heater for preventing partial condensation of vapor; (F) condenser; (G) drop counter; (H) to atmosphere or to pressure controller; (I₁, I₂): withdrawal of condensed vapor and liquid sample; (J) buffer for prevention of backward flow of mixing sample; (K) drain valve.

2.2. Auxiliary equipment

The temperature was measured with a calibrated quartz thermometer or platinum resistance thermometer (Pt 100 Ω). Accuracy of the equilibrium temperature measurements was estimated to be 0.03 K. The equilibrium composition of the samples were determined using a gas chromatograph equipped with a flame ionization or thermal conductivity detector and auto sampler. The relationship between the peak area and composition was determined from analysis of samples of known composition. The maximum error of liquid and vapor composition measurements is estimated to be 0.002 mole fraction.

3. Results and Discussion

3.1. Ternary positive azeotrope and positive-negative (saddle) azeotrope system

In order to determine the azeotropic data of the ternary positive azeotropic system benzene + cyclohexane + 1-propanol, the isobaric VLE of the ternary system and the constituent binary system were measured at 101.3 kPa using the proposed liquid-vapor ebullition type equilibrium still (Fig. 1). As a result, the three binary systems benzene + cyclohexane, cyclohexane + 1-propanol, and benzene + 1-propanol were all the minimum boiling azeotropic mixtures, and the azeotropic temperature for the ternary system showed the lowest temperatures. The determined azeotropic data are shown in Table 1 and the plot of the T - x for benzene + cyclohexane + 1-propanol system and the constituent binary system are shown in Fig. 3.

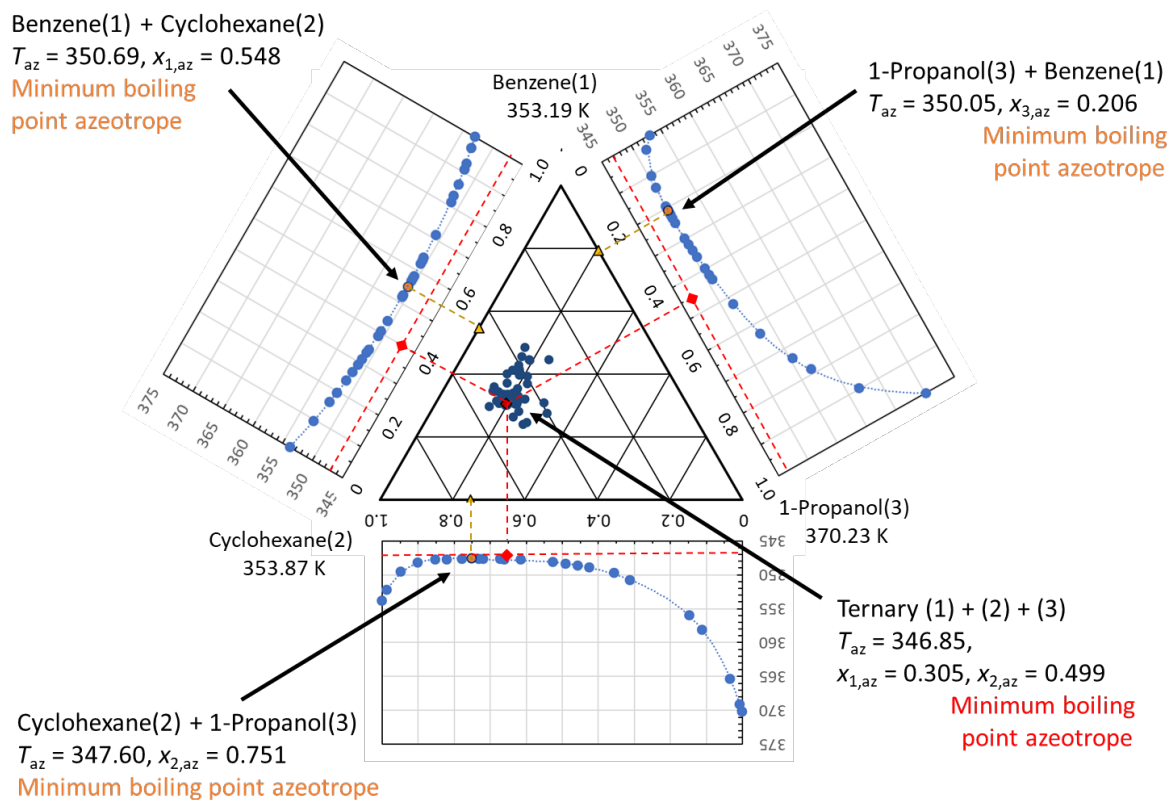


Fig. 3 Temperature–composition diagram for benzene (1) + cyclohexane (2) + 1-propanol (3) system and the constituent binary system at 101.3 kPa

The isobaric VLE of the ternary acetone + chloroform + methanol system and the constituent binary systems at 101.3 kPa were also measured using the apparatus shown in Fig. 1. The binary acetone + chloroform system was found to be the maximum boiling azeotropic mixture, while the chloroform + methanol and acetone + methanol systems were found to be the minimum boiling azeotropic mixtures. That ternary azeotrope is neither positive nor negative. The temperature of a ternary azeotrope is between the boiling points of acetone

and chloroform. This type of system is called a saddle azeotrope. The determined azeotropic data of the ternary acetone + chloroform + methanol system and the constituent binary systems are shown in Table 1 and the plot of the T - x are shown in Fig. 4 [7].

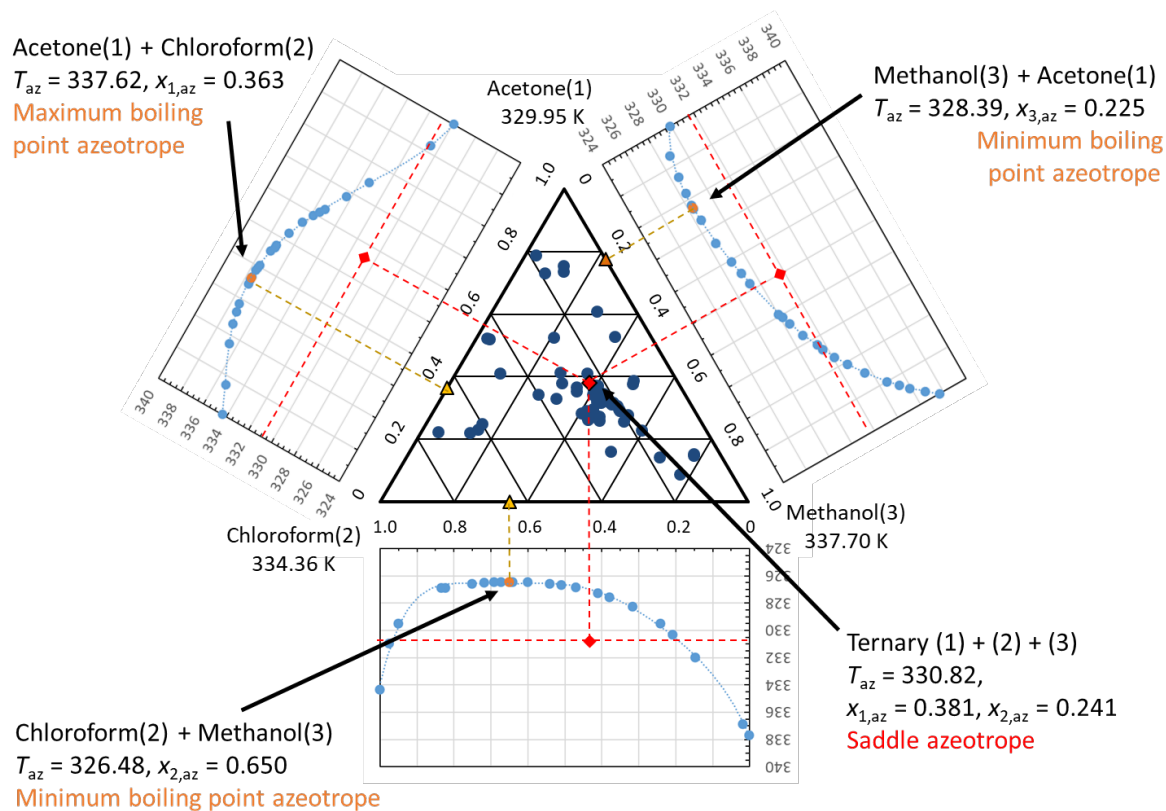


Fig. 4 Temperature–composition diagram for acetone (1) + chloroform (2) + methanol (3) system and the constituent binary system at 101.3 kPa

Table 1 Azeotropic data at 101.3 kPa determined from experimental VLE

system	T/K	x_1	x_2	x_3
benzene (1) + cyclohexane (2) + 1-propanol(3)	346.85	0.305	0.499	0.196
[binary]				
benzene (1) + cyclohexane (2)	350.69	0.548	0.452	—
cyclohexane (2) + 1-propanol (3)	347.60	—	0.751	0.249
benzene(1) + 1-propanol (3)	350.05	0.794	—	0.206
acetone (1) + chloroform (2) + methanol(3)	330.82	0.381	0.241	0.378
[binary]				
acetone (1) + chloroform (2)	337.62	0.363	0.637	—
chloroform (2) + methanol (3)	326.48	—	0.650	0.350
acetone (1) + methanol (3)	328.39	0.775	—	0.225

3.2. Binary double azeotropy

There are two types of VLE with azeotropes: those in which the azeotropic composition changes significantly with pressure and those in which it does not. For mixtures such as alcohol + water systems, the azeotropic composition does not change much as the pressure changes. A very rare example is a binary VLE system with two azeotropic points. There are double azeotropes that have both minimum and maximum boiling points at each specific composition. The dimethylamine + methanol system measured in this study is azeotropic mixture with the maximum boiling at 101.3 kPa. The second minimum boiling azeotropic point appears in the VLE at the condition of elevated pressure, around 300 kPa [5, 8]. As the pressure was further increased, the azeotropic compositions approached each other, and the pressure at which the two azeotropic compositions became one and disappeared could be determined. The azeotropic data, which were determined on the basis of the experimental VLE for dimethylamine (1) + methanol (2) system, are shown in Table 2. According to the Arrhenius plots of $\ln P$ vs. $1/T_{az}$ (Fig. 5), the azeotropic points of the dimethylamine + methanol system will be estimated to disappear at the pressure of around 0.65 MPa [5].

Table 2 Azeotropic data determined from experimental VLE for the system of dimethylamine (1) + methanol (2) at 101.3, 202.6, 300.0, 405.3 and 506.6 kPa

	maximum		minimum	
P/kPa	$x_{1,az1}$	T_{az1}/K	$x_{1,az2}$	T_{az2}/K
101.3	0.242	339.9	non	non
300.0[8]	0.25	369.9	0.985	363.8
405.3	0.259	378.8	0.954	375.5
506.6	0.282	386.2	0.863	381.3

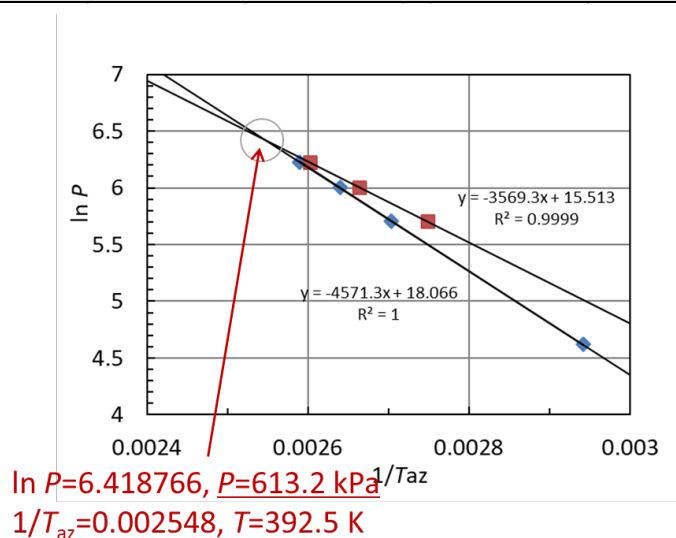


Fig. 5 Pressure dependence of azeotropic data for the diethylamine (1) + methanol (2) system: ◆ maximum temperature; ■ minimum temperature

the VLE was measured in our laboratory to determine the azeotropic data. Benzene (C_6H_6) and hexafluorobenzene (C_6F_6) have similar physical properties, as indicated by their respective chemical structures, and the mixture exhibits phase behavior similar to that of an ideal solution, but with two azeotropic points over a wide pressure range. Aucejo *et al.* [9] measured the isobaric VLE at 16.0 kPa and 120 kPa and reported the determined azeotropic data along with literature values. It is noted that the two azeotropic compositions approach each other at higher pressures, but the conditions under which the azeotropes disappear cannot be determined because VLE measurements are not possible at pressures higher than 120 kPa in glass still. It was predicted that the azeotropic point will disappear at 5 atm (415K) based on the tendency of the experimental azeotropic data. In this study, isobaric VLE at 50 kPa and 101.3 kPa were measured using a glass still, and VLE at 202.6 kPa, 303.6 kPa, and 405.2 kPa were measured using a stainless steel pressure-resistant still. The azeotropic data, which were determined on the basis of the experimental VLE for benzene (1) + hexafluorobenzene (2) system, are shown in Table 3. As the results of VLE at 405.2 kPa (Fig. 6), one consistent azeotropic temperature of 404.42 K in composition range of $x_1=0.301-0.451$. It was suggested that the azeotropic point disappears under pressure conditions above 410 kPa.

Table 3 Azeotropic data determined from experimental VLE for the system of benzene (1) + hexafluorobenzene (2) at 50.0, 101.3, 202.6, 303.9 and 405.2 kPa

P/kPa	maximum		minimum	
	$x_{1,az1}$	T_{az1}/K	$x_{1,az2}$	T_{az2}/K
50.0	0.173	333.47	0.861	331.80
101.3	0.194	353.67	0.798	352.68
202.6	0.227	377.03	0.672	376.68
303.9	0.242	392.37	0.527	392.11
405.2	$x_{1az} = 0.301-0.451, T_{az} = 404.42$			

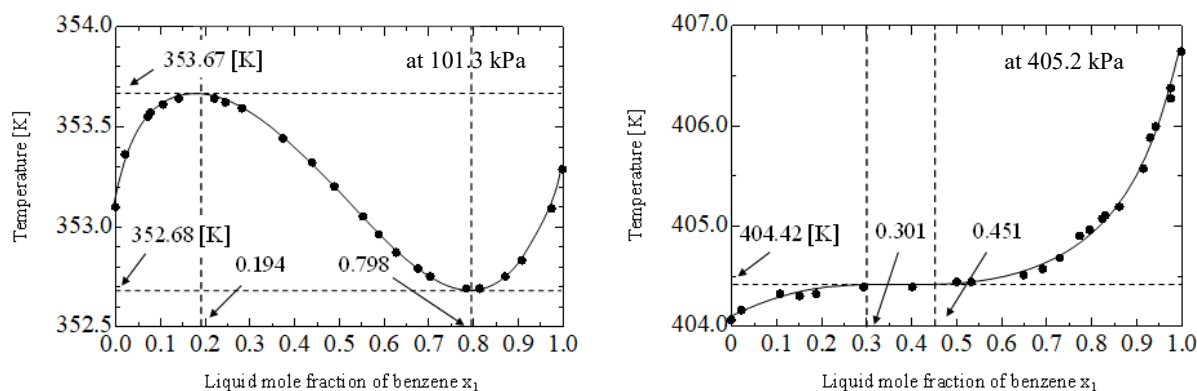


Fig. 6 Temperature - liquid composition diagram for benzene (1) + hexafluorobenzene (2) at 101.3 kPa and 405.2 kPa

4. Conclusion

Several types of stills with a provision for vapor and liquid circulation, developed in our laboratory to measuring VLE, were introduced. The azeotrope data determined based on the VLE data of azeotropic mixtures measured using these devices were shown. The azeotropic data for the minimum boiling azeotropic system, the saddle azeotropic system, and the constituent binary systems are shown for ternary systems. For the systems of double azeotrope, isobaric VLEs were measured at different pressures, and the pressure dependence of the azeotropic data is reported and the pressure conditions at which the azeotropic point disappears are shown. No isobaric VLE data and azeotropic data have been reported previously for the benzene + hexafluorobenzene system at pressures higher than 202.6 kPa.

References

- [1] Hiaki, T., Tochigi, K., Kojima, K., *Fluid Phase Equilib.* 26 (1986) 83-102.
- [2] Hiaki, T., Yamato, K., Kojima, K., *J. Chem. Eng. Data*, 37 (1992) 203-206.
- [3] Hiaki, T., Kawai, A., *Fluid Phase Equilib.* 158-160 (1999) 979-989.
- [4] Hiaki, T., Nanao, M., Urata, S., Murata, J., *Fluid Phase Equilib.* 182 (2001) 189-198.
- [5] Hiaki, T., Saida, K., Ishihara, T., Sato, T., Okada, M., Matsumoto, M., *MATEC Web of Conference* 3 (2013) 01021.
- [6] Hiaki, T., *unpublished paper*.
- [7] Hiaki, T., Kurihara, K., Kojima, K., *J. Chem. Eng. Data*, 39 (1994) 714-719.
- [8] Aucejo, A., Loras, S., Munoz, R., Wisniak, J. Segura, H., *J. Chem. Eng. Data*, 42 (1997) 1201-1207.
- [9] Aucejo, A., Monton, J. B., Munoz, R., Wisniak, J., *J. Chem. Eng. Data*, 41 (1996) 21-24.