
The Measurement of Vapor-Liquid Equilibrium Data by Headspace Gas Chromatography

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A new method for determining vapor-liquid equilibrium data, especially the relative volatility of unknown components, is explained in detail. The relative volatilities were measured by headspace gas chromatography (HSGC). This method has been used to measure physical properties such as vapor-liquid equilibria (VLE) by many researchers. Also, the experimental results for the VLE of binary systems and the activity coefficients at infinite dilution measured by HSGC are presented. Finally, the apparatus developed by Rogalski and Malanowski which have been used to measure VLE data is introduced, and compared with HSGC method.

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Introduction

The purpose of performing a distillation operation is to separate the individual components of a mixture from each other and to refine them by utilizing the vapor pressure differentials among the components. Distillation operations have been applied to bulk chemicals, such as petrochemicals, through a variety of different processes. On the contrary, in the area of fine chemicals, such as pharmaceutical preparations and agricultural chemicals, although the direct vaporization and distillation of a subject substance itself is not performed as frequently, the following common procedure is often utilized: the use of distillation in the removal/recovery of a solvent employed in a chemical reaction or an extraction process, together with the subsequent recycling of the solvent back into the process. However, if recycling is performed too frequently, impurities may accumulate in the recovered solvent, thus possibly affecting the chemical reaction and other processes in unexpected ways. It is necessary to verify the effects on the reaction results and on product quality, based upon an estimation of the final stationary composition obtained after the frequent solvent recovery operations. In the basic design of a distillation process, the binary system vapor-liquid equilibrium relationship of all the constituent com-

ponents of a system is actually a fundamental physical property of the system itself. We shall narrow the focus of this general subject down to the specific topic of low-pressure vapor-liquid equilibrium relationships, which are often discussed in relation to solvent recovery and similar processes. These processes are described in detail below.

In general, there exist an enormous number of different subject substances, each possessing any number of different individual components, thus a tremendous amount of effort is required to obtain the binary system data pertaining to even a portion of these substances. The effort required greatly increases the difficulty of responding to current market demands for increasing the speed of development of new chemical products. Furthermore, in the early stages of such development, the constituent components of some systems may have an unknown molecular structure. For these substances, the activity coefficient estimation methods, such as UNIFAC,¹⁾ cannot be applied. Therefore, a pressing need exists to develop techniques that will enable the following processes: methods for rapidly measuring the vapor-liquid equilibrium relationship in order to efficiently determine the separability of these unknown components; and methods to facilitate the obtaining of more accurate measurements for the precise design of distillation processes during the fundamental design stage.

One of the methods that can be used to easily understand the basics of the vapor-liquid equilibrium relationship is to obtain the relative volatility α using the Rayleigh equation²⁾ from the material balance obtained from a simple distillation experiment. However, while a wide composition distribution is formed within a rectifying column during actual operation, the data that can be obtained from the simple distillation experiment usually has only a narrow range of composition. As a result, in certain previous experiments, even though it was recognized that rectification separation was easy based upon the obtained α , in actual operation the expected separation could not be achieved.

The apparatus that is most commonly utilized to measure low-pressure vapor-liquid equilibrium includes the Othmer vapor-liquid equilibrium measurement apparatus,³⁾ a circulation-based type of apparatus, as well as its improved version, the Rogalski-Malanowski vapor-liquid equilibrium measurement apparatus⁴⁾ (referred to hereafter as RM measurement apparatus). As these methods of measurement incorporate the analysis of both vapor and liquid phases, a certain amount of time is required to perform the analysis (including preparation time). In addition, the amount of specimen utilized is also relatively large. For these reasons, it is desirable to develop a method that is capable of measuring vapor-liquid equilibrium in a short period of time, using only a minimal amount of specimen, with such a method being easy to automate.

The infinite dilution activity coefficient can be a useful piece of information to use when performing high purity distillation operations that must contain no more than a few ppm of impurities. In addition, by utilizing a set of infinite dilution activity coefficients for a binary system (γ_1^∞ , γ_2^∞), the 2 component parameters of an activity coefficient equation having 2 constants, such as the Wilson equation⁵⁾ can be obtained, thus enabling the expression of the vapor-liquid equilibrium relationship over the entire concentration range. Relatively speaking, γ^∞ can be easily obtained using a variety of measurement methods, including the use of an Ebulliometer⁶⁾, the gas stripping method⁷⁾ and headspace gas chromatography⁸⁾ (referred to hereafter as HSGC), which will be described later.

We have developed a method for measuring α through the use of an HSGC that can easily determine vapor-liquid equilibrium relationships and can also handle components having unknown structures. This method of measurement will be introduced here, in addition to some typical measurement results. Furthermore, the following results will also be explained within this paper: measurement results for binary vapor-liquid equilibrium relationships that require high accuracy; measurement results for γ^∞ and results of thermodynamic consistency tests conducted on the data. Lastly, we shall introduce measurement methods for the RM measurement apparatus, which we have utilized, as well as the results of actual measurements, in order to provide a comparison with the results obtained from the HSGC.

Experimental Theory

1. Relative Volatility^{9, 10)}

Both the liquid phase and the vapor phase of a system that contains components i ($= 1, \dots, n$) are analyzed using gas chromatography. In the event that a linear relationship that passes through the origin is present between the component concentration and the peak area, the liquid phase composition x_i and the vapor phase composition y_i , both of component i , can be expressed by equations (1) and (2), using the peak areas of the liquid phase and vapor phase, which are A_{xi} and A_{yi} respectively, as well as by the sensitivity ratio f_i .

$$x_i = f_i A_{xi} / \left(\sum_{i=1}^n f_i A_{xi} \right) \quad (1)$$

$$y_i = f_i A_{yi} / \left(\sum_{i=1}^n f_i A_{yi} \right) \quad (2)$$

Meanwhile, α_{ij} , which is the relative volatility of component i in relation to component j , can be expressed by equation (3).

$$\alpha_{ij} = (y_i / x_i) / (y_j / x_j) \quad (3)$$

Performing a quantitative analysis usually requires knowing f_i for A_{xi} and A_{yi} of each component, as well as having a high purity specimen of each component. Assuming that f_i is constant, regardless of the concentration, it can be simplified, as shown in equation (4), based on the results of equations (1)~(3).

$$\alpha_{ij} = (A_{yi}/A_{xi}) / (A_{yj}/A_{xj}) \quad (4)$$

In the event that equation (4) can be utilized, then α_{ij} can be obtained, even for components with completely unknown structures and molecular weights, for which a high purity specimen would normally be extremely difficult to obtain. From this point forward, this method will be referred to as the “GC area method.”

The procedures used to perform HSGC are as follows: a specimen of liquid is sealed within a pressure resistant vial. The vial is then placed in a constant temperature bath for a specific time period and allowed to reach its equilibrium state. Subsequently, its vapor phase composition is analyzed.⁸⁾ The HSGC method is utilized for the analysis of volatile organic pollutants contained within water supplies, as well as to analyze residual solvents present within chemical agents, in the fields of environmental science and in the manufacture of pharmaceutical preparations. Thus, since the vapor phase composition can be easily analyzed using the HSGC, we applied it to the GC area method. Furthermore, if high purity specimens of each component are available, the binary system vapor-liquid equilibrium relationships can be measured, as described below.

2. Vapor-Liquid Equilibrium for Binary System at Constant Temperature¹¹⁾

At lower pressures than atmospheric pressure, equation (5) can be utilized, based upon the vapor-liquid equilibrium conditions.

$$p_i/p = y_i = p_i^0 \gamma_i x_i / p \quad (i=1, 2) \quad (5)$$

In the above equation, p_i represents the partial pressure for component i , p represents the total pressure of the system, γ_i represents the liquid phase activity coefficient for component i and p_i^0 represents the saturated vapor pressure for pure component i at the system temperature. p_i is obtained from the calibration curve of the gas chromatograph, as shown in **Fig. 1**. At first, each pure component is sealed in a separate vial, then its vapor phase is analyzed using HSGC, once it has reached equilibrium condition at the measurement temperature. The measurement temperature is set to a value somewhere between the lowest setting for

the constant temperature bath (35°C) and a temperature lower than the standard boiling point of the pure component. The values for A_{yi}^0 obtained, as well as the values for p_i^0 obtained at the measured temperature, which is already known (from measurements conducted separately), are plotted to create the calibration curve for each component.

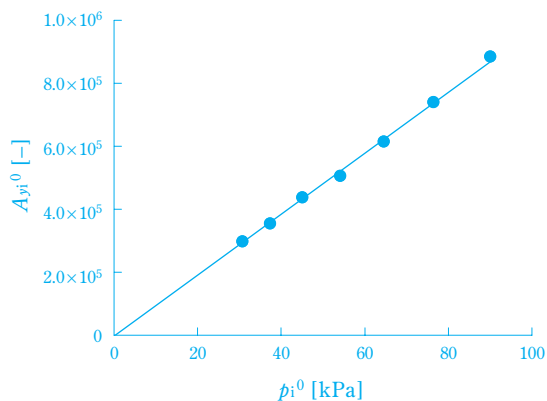


Fig. 1 A typical calibration curve of peak area vs. partial vapor pressure for a component i

To measure the binary system vapor-liquid equilibrium relationship, the vapor phase is analyzed using HSGC, once the liquid specimen, after having been adjusted to the specified composition (this will be described later), has been maintained at the measurement temperature for sufficient time to reach a equilibrium condition. Next, values are obtained for A_{yi} and p_i is then obtained for each component from the calibration curve. The total pressure p , which is the sum of all values for p_i , can be determined at the same time and y_i can be obtained from equation (5). However, as any changes in the liquid phase composition are so minimal that they can be ignored, the charge composition should be represented as x_i at the time of adjustment.

Values for vapor-liquid equilibrium data at constant temperature can be obtained from HSGC. Since distillation operations are usually conducted at a constant pressure, a constant pressure vapor-liquid equilibrium relationship is required. However, under a sufficiently low pressure, the pressure dependence of γ_i is extremely small.¹²⁾ Therefore, the actual usage will not be affected, even though the vapor-liquid equilibrium relationship at constant pressure is calculated using a parameter of the activity coefficient equation that

has been determined from the vapor-liquid equilibrium at constant temperature.

3. Infinite Dilution Activity Coefficients⁸⁾

From equation (5),

$$\gamma_i = p_i / x_i p_i^0 \quad (6)$$

The infinite dilution activity coefficient γ_i^∞ is defined by equation (7).

$$\gamma_i^\infty = \lim_{x_i \rightarrow 0} \gamma_i \quad (7)$$

The level of composition considered to be the infinite dilution area during measurement was shown by Kojima et al.¹³⁾ Both x_i and p_i are determined using the same method as that used for the vapor-liquid equilibrium measurement described in the previous section. In the event that the calibration curve is a straight line passing through the origin, as shown in Fig. 1, γ_i can be determined only from the solute A_{yi} , as shown in the equation below.

$$\gamma_i = A_{yi} / x_i A_{yi}^0 \quad (8)$$

In the above equation, A_{yi} represents the peak area of the solute i measured from the mixture of solvent and solute, and A_{yi}^0 represents the peak area of the solute i when the solute alone is maintained at the measurement temperature.

Experimental Procedures

1. Experimental Apparatus and Procedures

Fig. 2 depicts an overview of the measurement apparatus. The measurement apparatus is composed of a headspace sampler unit (Turbo Matrix HS40, manufactured by Perkin Elmer), a gas chromatograph (GC-2010, manufactured by SHIMADZU CORPORATION) ⑤; a transfer line used to connect the units together ④; and an integrator used for peak area calculation. The headspace sampler unit contains a constant temperature bath ③, which can maintain the vial ② used for the HSGC at a temperature ranging from 35–210°C, with a precision of $\pm 0.1^\circ\text{C}$ (the vial is equipped with a PTFE/Silicone upper septum having a capacity of 22cm³). The transfer line incorporates an external heating element surrounding the capillary tube,

in order to prevent vapor from condensing within the glass capillary tube itself.

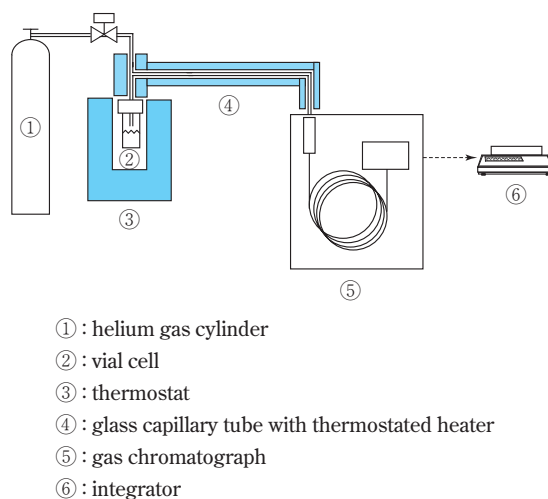


Fig. 2 Schematic diagram of experimental apparatus of HSGC

For the vapor phase measurement, a specified quantity of the specimen, which has been already adjusted, is sealed within the vial. After the vial has been maintained at the measurement temperature for a time period that will be described later, the vapor phase is allowed to accompany the carrier gas and is introduced into ⑤. The transfer line is maintained at a temperature at least 30°C higher than that of the constant temperature bath. Furthermore, in this apparatus, the carrier gas is pressurized and injected into the vial for the vapor phase collection. With this method, there is a smaller chance of the gas condensing prior to analysis, than with the syringe-based method of vapor phase collection.

As A_{xi} must be obtained for the GC area method, a preparative isolation was performed on the specimen. The isolated specimen was placed into a separate vial, then was injected into the unit ⑤ at room temperature, using a microsyringe. For the analyses of both the liquid and vapor phases, equipment having the exact same conditions was utilized, in order to ensure that a consistent f_i was obtained for each component.

All the specimens utilized were manufactured by Wako Pure Chemical Industries, Ltd., at the following purities: greater than 95% for n-hexane; greater than 98% for 2-propanol; greater than 99% for toluene and greater than 99% for acetone. Dis-

tilled water was utilized and helium was utilized as the carrier gas (having purity greater than 99.997%, manufactured by AIR WATER INC.).

2. Determining the Charge Quantity

The binary system measured in our experiment was n-hexane (1) + 2-propanol (2) ($x_1 = 0.48$). As well, the same binary system was used to determine the duration of time for which the specimen was maintained at a constant temperature. The quantities of specimen charge used in the vial were: 5, 10 and 15cm³, with vapor phase analysis being performed on each charge. From the analysis results, we confirmed that no significant differences were present among the peak areas obtained from these different charge quantities. Based on this finding, the charge quantity was set as 10cm³. Researcher Ohe¹¹⁾ had performed a previous experiment similar to ours described above, in which the quantity of charge in the vials (capacity of 26cm³) had been varied over a range of 1~20cm³. The results had also confirmed that no significant peak area differences were present. This experiment provided further corroboration for our specification of the appropriate charge quantity as 10cm³.

3. Determining the Time to Maintain the Vial at a Constant Temperature

Vapor phase analyses were performed for vials that were maintained at a constant temperature for different periods of time (10, 30 and 60 minutes). The results of analyses confirmed that no significant differences were present in the peak areas for different periods of time. Researcher Ohe had previously conducted a similar experiment in which vials were maintained at constant temperatures for different periods of time, ranging from 10~120 minutes. The results had also confirmed that no significant peak area differences were present for different periods of time. Based on these results, Researcher Ohe specified that a period of 60 minutes would be conservative. In our experiment, we selected a period of 30 minutes in order to improve measurement efficiency.

Experimental Results and Discussion

1. Relative Volatility

Table 1 shows x_1 , A and the α_{12} obtained for n-hexane (1) + 2-propanol (2) binary system at 50°C. **Fig. 3** depicts a plot of these values, together with values obtained from the literature.¹⁴⁾ From the figure, we can conclude that relative volatility can be measured accurately using HSGC.

Table 1 Relative volatilities of the binary system of n-hexane (1) + 2-propanol (2) at 50°C measured by HSGC

x_1 [-]	A_{x1} [-]	A_{y1} [-]	A_{x2} [-]	A_{y2} [-]	α_{12} [-]
0.10	8191	228295	27895	79487	9.78
0.39	27653	378740	15780	57750	3.74
0.60	37678	457694	9162	57614	1.93
0.91	48857	417703	1766	31642	0.48

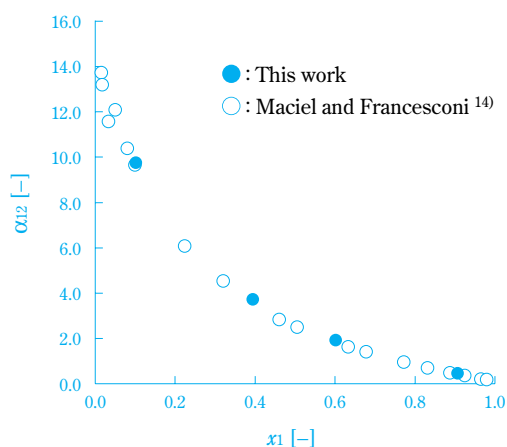


Fig. 3 Relative volatilities of the binary system, n-hexane (1)+2-propanol (2) at 50°C measured by HSGC

2. Vapor-Liquid Equilibrium for Binary System at Constant Temperature

Figs. 4 and 5, respectively, depict the results of measurements for the binary systems of: n-hexane (1) + 2-propanol (2) at 50°C, as well as n-hexane (1) + toluene (2) at 70°C. As shown in these figures, both systems correspond exactly to the values measured in the literature.^{14, 15)} Furthermore, thermodynamic consistency of the data was confirmed using the Herington method (referred to as method “A”),¹⁶⁾ as well as the method developed by Van Ness et al (referred to as method “B”).¹⁷⁾

In method “A,” thermodynamic consistency of the vapor-liquid equilibrium data at constant temperature can be confirmed by following the procedures described below (this method cannot be applied over the range from $0.95 < \gamma < 1.10$).¹⁶⁾

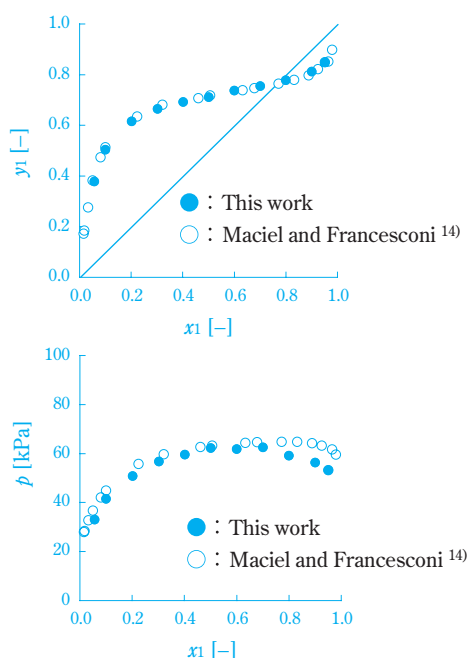


Fig. 4 Vapor-liquid equilibrium data of the binary system, n-hexane (1) + 2-propanol (2) at 50°C measured by HSGC

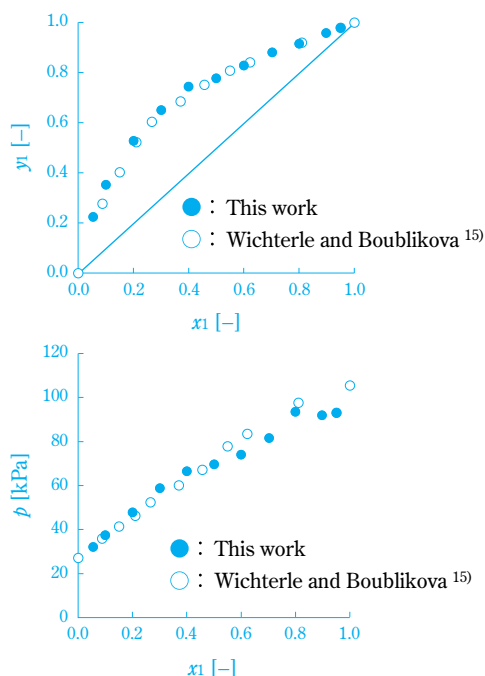


Fig. 5 Vapor-liquid equilibrium data of the binary system, n-hexane (1) + toluene (2) at 70°C measured by HSGC

- ① $\ln(\gamma_1/\gamma_2)$ is plotted for x_1 .
- ② I is calculated, as defined in equation (9), and areas $|A|$ and $|B|$ from **Fig. 6** are calculated.

$$I = \int_0^1 \ln(\gamma_1/\gamma_2) dx_1 \quad (9)$$

- ③ D is calculated, as defined in equation (10).

$$D = 100I / (|A| + |B|) \quad (10)$$

- ④ With respect to the evaluation of vapor-liquid equilibrium data at constant temperature, if $D \leq 10$, this should be considered as “good,” and if $D > 10$, this should be considered as “no good.”

In method “B”;

- ① The 2-component parameters of the activity coefficient were determined using only the pressure p vs. x_1 data, from among all the vapor-liquid equilibrium data. In this experiment, the Wilson equation was employed.
- ② The vapor composition y is obtained through the vapor-liquid equilibrium calculation, using the parameters defined.
- ③ The difference is obtained between the calculated value and the measured value for each data point, then the absolute arithmetic mean deviation Δy is obtained for all data points.
- ④ With respect to the evaluation of vapor-liquid equilibrium data at constant temperature, if $\Delta y \leq 0.01$, this should be considered as “good,” and if $\Delta y > 0.01$, this should be considered as “no good.”

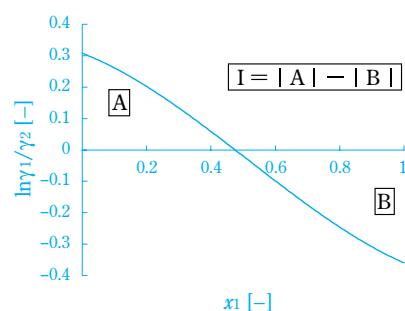


Fig. 6 Schematic description of equation (10)

Table 2 indicates the results of thermodynamic consistency testing using the two methods described above. Results were consistent for both methods, with regard to the n-hexane (1) + 2-propanol (2) binary system. As for the n-hexane

Table 2 The results of thermodynamic consistency test for the VLE data measured by HSGC

	Method A ¹⁶⁾	Method B ¹⁷⁾
n-hexane (1) + 2-propanol (2)	5.05	0.011
n-hexane (1) + toluene (2)	—	0.010

(1) + toluene (2) binary system, since this system is similar to an ideal solution, it could not be evaluated using method “A” ($\gamma_1 = 0.9\sim 1.3$). However, the results obtained from using method “B” provided a confirmation of consistency, thus we concluded that HSGC is capable of accurately measuring thermodynamic consistency.

3. Infinite Dilution Activity Coefficients

Table 3 depicts the measurement results for γ_2^∞ of the water (2) contained in acetone (1) when measured at 50°C, as well as the measurement results for γ_1^∞ of the acetone (1) contained in water (2) when measured at 50°C.

Table 3 Infinite dilution activity coefficients of the binary system, acetone (1) + water (2) at 50°C measured by HSGC

	γ^∞ [-]
1 in 2	5.60
2 in 1	8.71

As well, the relationship between the temperature and γ^∞ can be represented by equation (11).

$$h^{E\infty} = \left(\frac{\partial (\ln \gamma^\infty)}{\partial (1/T)} \right)_P \quad (11)$$

In the above equation, $h^{E\infty}$ represents the molar excess enthalpy at infinite dilution. **Fig. 7** depicts the relationship between the measured values and the values from the literature¹³⁾ for γ^∞ of the acetone (1) + water (2) system, based on equation (12).

Both γ_1^∞ and γ_2^∞ are relatively consistent.

4. Method for Determining Activity Coefficient

Equation Parameters Using γ^∞

Parameters for activity coefficient equations can be determined by using γ^∞ , such as in the Wilson equation.²⁾ An example of the application of this method to the Wilson equation is shown below. Equations (12) and (13) represent the Wilson equations for the binary system.

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right) \quad (12)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right) \quad (13)$$

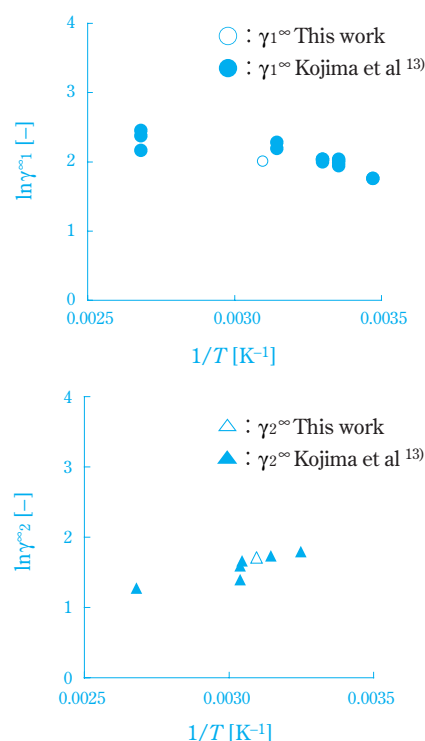


Fig. 7 Relationship between $\ln \gamma^\infty$ and $1/T$

If each of equations (12) and (13) are substituted for equation (7), then equations (14) and (15) are obtained.

$$\ln \gamma_1^\infty = 1 - \ln \Lambda_{12} - \Lambda_{21} \quad (14)$$

$$\ln \gamma_2^\infty = 1 - \ln \Lambda_{21} - \Lambda_{12} \quad (15)$$

Λ_{12} and Λ_{21} can be determined using equations (14) and (15). Using the parameter obtained from γ^∞ from the acetone (1) + water (2) system in Table 3, the vapor-liquid equilibrium for binary system was calculated for the entire area. **Table 4** depicts the parameters obtained and **Fig. 8** shows the calculated results. Thus, the use of parameters derived from γ^∞ enables us to obtain a relatively accurate vapor-liquid equilibrium relationship in a short period of time, over the entire concentration range.

Table 4 The constants of the Wilson equation for the acetone (1) + water (2) system at 50°C

	Parameter determined from γ^∞	Parameter in database ¹⁸⁾
Λ_{12}	0.2477	0.1843
Λ_{21}	0.3789	0.3905

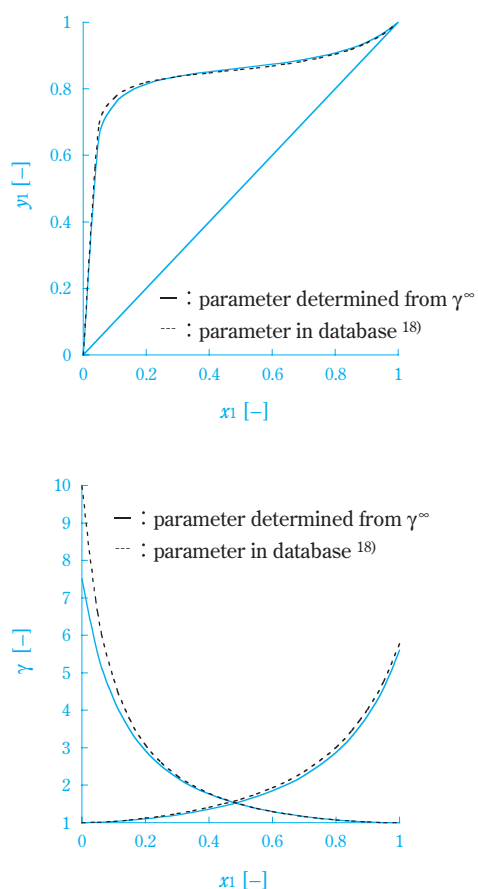


Fig. 8 Calculated results for the acetone (1) + water (2) system at 50°C

Other Experimental Apparatus~Rogalski-Malanowski Vapor-Liquid Equilibrium Experimental Apparatus⁴⁾

1. Experimental Methods

Fig. 9 depicts an overview of the apparatus. A specimen, adjusted to the specified composition, is introduced into the reboiler ① and its pressure is reduced to the measurement pressure using a vacuum pump. The specimen is stirred with the stirrer ② located within the reboiler, then is heated by the heater ③ until boiling. The boiling specimen is introduced into the vapor-liquid equilibrium chamber ④ via vapor-liquid multiphase flow and then separates into a vapor phase and a liquid phase. After separation, the vapor phase flows to the condenser ⑥ through the vapor tube ⑤ and condenses within the condenser. Lastly, the now-condensed vapor phase is introduced into the mixer ⑧ via the vapor sampling valve ⑦. The liquid phase flows into the mixing device ⑧ via the liquid sampling valve ⑨ and then mixes with the condensate in the unit. This mixture is then re-intro-

duced to the reboiler, where it is again heated to boiling by the heater and continues to circulate until it reaches equilibrium condition. After reaching equilibrium condition, sampling is performed of both the vapor and liquid phases, for the analysis of each composition. Equilibrium condition is determined when the following factors are observed: (I) temperature stability has been reached, such that the temperature indicated within the vapor-liquid equilibrium chamber does not vary by more than $\pm 0.01^\circ\text{C/hr}$; and (II) the condensation rate at the condenser outlet is stable. For reference, the temperature measurement accuracy within the vapor-liquid equilibrium chamber is $\pm 0.001^\circ\text{C}$ and the pressure measurement accuracy is $\pm 0.01\text{kPa}$.

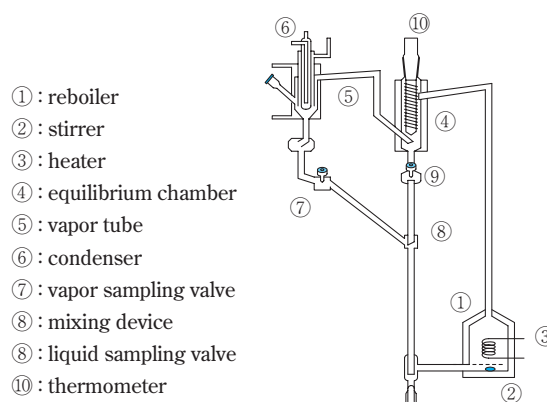


Fig. 9 Schematic diagram of experimental apparatus developed by Rogalski and Malanowski⁴⁾

2. Experimental Results

Fig. 10 depicts the measurement results for vapor-liquid equilibrium of the n-hexane (1) + 2-propanol (2) system at 101.3kPa. As indicated by the figure, the resulting values correspond well with those described in the literature.¹⁹⁾ Furthermore, the thermodynamic consistency of the measured data was confirmed via methods “A”¹⁶⁾ and “B”¹⁷⁾ as used for HSGC.

In method “A,” the thermodynamic consistency of the vapor-liquid equilibrium data at constant pressure can be verified as follows (the method cannot be applied over the range from $0.95 < \gamma < 1.10$).¹⁶⁾

- ① $\ln(\gamma_1/\gamma_2)$ is plotted for x_1 .
- ② I is calculated, as defined in equation (10), and areas $|A|$ and $|B|$ from Fig. 6 are calculated.
- ③ D is calculated, as defined in equation (11).
- ④ ΔT_{\max} ($\Delta T_{\max} > 0$) is obtained as the difference

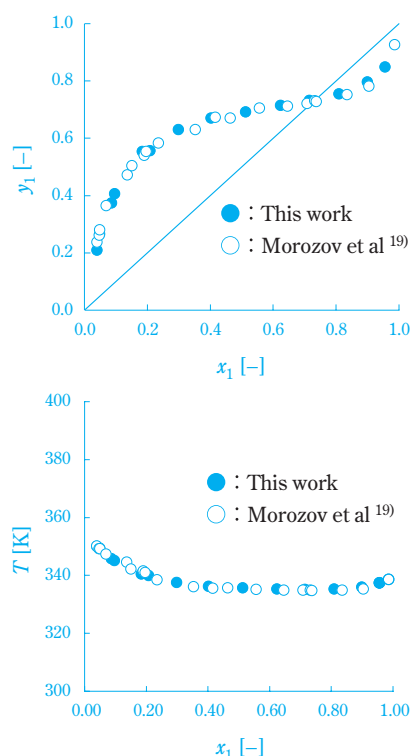


Fig. 10 Vapor - liquid equilibrium data of the binary system, n-hexane (1) + 2-propanol (2) at 101.3kPa measured by the apparatus developed by Rogalski and Malanowski ⁴⁾

between the maximum boiling point and the minimum boiling point of the system. T_{\min} is then obtained, the lowest boiling point of the system. Finally J is calculated, as defined in equation (16).

$$J = 150\Delta T_{\max} / T_{\min} \quad (16)$$

- ⑤ With respect to the evaluation of vapor-liquid equilibrium data at constant pressure, if $D \cdot J \leq$

10, this should be considered as “good,” and if $D \cdot J > 10$, this should be considered as “no good.”

In method “B,” the 2-component parameters of the activity coefficient equation were determined using only the temperature T vs. x_1 data, from among all the vapor-liquid equilibrium data. All other procedures are the same as those used for the vapor-liquid equilibrium at constant temperature.

Table 5 contains the results. As both methods provided results that demonstrate thermodynamic consistency, we therefore concluded that the RM measurement apparatus is capable of accurately measuring thermodynamic consistency.

Table 5 The results of the thermodynamic consistency test for VLE data measured by the apparatus developed by Rogalski and Malanowski ⁴⁾

	Method A ¹⁶⁾	Method B ¹⁷⁾
n-hexane (1) + 2-propanol (2)	8.73	0.007

3. Comparison between HSGC Method and RM Method

The Process & Production Tech. Center of Sumitomo Chemical Co., Ltd. owns both the RM experimental apparatus and the HSGC equipment described in this paper, using them as a means to measure vapor-liquid equilibrium relationships. **Table 6** summarizes the advantages and shortcomings of each method of measurement. As is obvious from the table, the method using HSGC required shorter experimental times and smaller

Table 6 A comparison of HSGC and the apparatus developed by Rogalski and Malanowski ⁴⁾

	HSGC (VLE)	HSGC (γ^∞)	RM
Sample volume ^{*)}	400 cm ³ (including the volume used to produce the calibration curve)	250 cm ³ (including the volume used to produce the calibration curve)	800 cm ³
Measurement time ^{*)}	3 days	2 days	2 weeks (including the analysis time)
VLE type	constant temperature only	constant temperature only	—
Vapor pressure data of pure component	needed	not needed in the case that the calibration curve pass through the origin	not needed
Automation	easy	easy	difficult
Measurement accuracy	temperature : $\pm 0.1^\circ\text{C}$	temperature : $\pm 0.1^\circ\text{C}$	temperature : $\pm 0.001^\circ\text{C}$ pressure : $\pm 0.01\text{kPa}$

*) In the case of the measurement of 10 points

quantities of specimen, as compared to that required by the RM experimental apparatus. However, the RM experimental apparatus has a broader range of application and is capable of greater accuracy than the HSGC equipment.

Conclusion

In this paper, we have primarily described the methods used to measure vapor-liquid equilibrium data using headspace gas chromatography (HSGC). HSGC is particularly useful in obtaining the relative volatility of components for which the molecular structure is unknown. An understanding of the relative volatility of components enables us to understand the behavior of impurities within a recycling system and helps to solidify the framework of the processes used in the early stages of product development. For these reasons, it is expected that the use of HSGC will lead to direct increases in the speed of product development. Furthermore, HSGC is capable of performing highly accurate and thermodynamically consistent measurements of both binary system vapor-liquid equilibrium data and infinite dilution activity coefficients, both of which are required for the effective design of dilution processes. Thus, we conclude that HSGC is an extremely effective method of vapor-liquid equilibrium measurement.

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References

- 1) R. L. J. Fredenslund and J. M. Prausnitz, *AIChE J.*, **21**, 1086 (1975)
- 2) The Society of Chemical Engineers, Japan "Kagaku-Kougaku-Binran", Sixth Edition, Maruzene, 525 (1999)
- 3) D. F. Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928)
- 4) M. Rogalski and S. Malanowski, *Fluid Phase Equilibria*, **5**, 97 (1980).
- 5) G. M. Wilson, *J. Am. Chem. Soc.*, **86**, 127 (1964)
- 6) M. F. Gautreaux and J. Coates, *AIChE J.*, **1**, 496 (1955)
- 7) J. C. Leroi, J. C. Masson, H. Renon, J. F. Fabrics and H. Sannier, *Ind. Eng. Chem. Process Des. Dev.*, **16**, 139 (1977)
- 8) P. G. Whitehead and S. I. Sandler, *Fluid Phase Equilibria*, 157, 111 (1999)
- 9) H. Narahara and M. Yamamoto, "Japanese Patent", 014721 (2003)
- 10) H. Narahara and M. Yamamoto, "Japanese Patent", 021624 (2003)
- 11) S. Ohe, "Bunri-Gijutsu", 27, 2 (1997)
- 12) J. M. Prausnitz, R. N. Lichtenthaler and E. G. Azevedo, "Molecular Thermodynamics of Fluid Phase Equilibria", Third Edition, Prentice-Hall (1999)
- 13) K. Kojima, S. Zhang and T. Hiaki, *Fluid Phase Equilibria*, **131**, 145 (1997)
- 14) M. R. W. Maciel and A. Z. Francesconi, *J. Chem. Thermodyn.*, **20**, 539 (1988)
- 15) I. Wichterle and L. Boublikova, *Ind. Eng. Chem., Fundam.*, **8**, 585 (1969)
- 16) E. F. G. Herington, *J. Inst. Petrol.*, **37**, 457 (1951)
- 17) M. M. Abbott and H. C. Van Ness, *AIChE J.*, **21**, 62 (1975)
- 18) J. Gmehling, U. Onken and W. Arlt, DECHEMA Chemistry Data Series, 1, 190 (1981)
- 19) A. V. Morozov, A. G. Sarkisov and V. B. Turovsky, *Viniti*, **78**, 103 (1978)

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