Verification and Estimation of Evaporation Heat of 1,4-dioxane Aqueous Solution at Constant Pressure (101.325 kPa)

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Abstract

This study determined the evaporation heat of 1,4-dioxane aqueous solution, which is necessary to plan the absorption-type refrigeration cycle using the working medium developed by the authors and to establish a method of estimating it based on the existing forms of both components of 1,4-dioxane aqueous solution. Evaporation heat at constant pressure (101.325 kPa) and molar fraction dependence were measured and calculated during both the evaporation process in which the vapor-liquid composition remained constant and the process in which the composition changed, in consideration of the liquid structure of 1,4-dioxane aqueous solution. The measurements and calculation results were compared with existing evaporation heat data and led to the following results : (1) The mean difference in evaporation heat was 2.07% between the value calculated using calculation software (UNIFAC method) that simulated a certain amount of evaporation in vapor-liquid equilibrium at low pressure and the value determined by experiments. (2) The mean difference in evaporation heat was 3.35% between the value determined from total evaporation using TG-DSC and the value calculated from the approximate expression of the relation between cumulative evaporation heat of partial evaporation heat and cumulative sample evaporation. (3) The mean difference in evaporation heat between the value calculated as molar fraction means of both components of the simple mixture model and (1) or (2) was 2.55% and 3.41%, respectively. In conclusion, the evaporation heat of 1,4-dioxane aqueous solution can be estimated as molar fraction means of both components of the simple mixture model as an ideal mixture of normal liquid.

Key words : 1,4-dioxane Aqueous Solution, Evaporation Heat, Mole Fraction Dependency, Temperature Dependency, Liquid Structure of Water, Estimation

1. Introduction

The reduction of CO_2 emissions requires the recovery and effective use of low quality thermal energy of factory waste heat or the like at 100°C or less. To achieve this it is desirable to develop a thermal medium having a low boiling point at atmospheric pressure (101.325 kPa). We investigated 1,4-dioxane aqueous solution because it is compatible with water and has similar vapor-liquid composition to the azeotropic composition of $X_c = 0.625$ over a wide range

of mixture mole fractions $X_C = 0.6$ to 0.825[1] (water : primary component) and a similar boiling point to the azeotropic boiling point of about 353 K. As a thermal working fluid of low boiling point, we considered the different physical, thermal and momentum properties of 1,4-dioxane aqueous solution. Tominaga et al[2]. examined the state of existence of the two components in a 1,4-dioxane aqueous solution using Raman spectroscopic analysis and showed that monomolecular 1,4-dioxane and water are homogeneously mixed without forming a hydrogen bond in the 1,4-dioxane aqueous solution. Using the ^{17}O–NMR chemical shift method, we demonstrated that the 1,4-dioxane broke the hydrogen bond acting between water molecules and changed the liquid structure of water[3][4]. Moreover, we demonstrated that in a 1,4-dioxane aqueous solution, water takes different liquid structures depending on the mole fraction, and different forms of water are homogeneously mixed with monomolecular 1,4-dioxane independently from each other form of water without forming a bond. Next, we examined whether the monomolecular water that formed in the 1,4-dioxane aqueous solution would increase the solubility of LiBr $\cdot$ 2H$_2$O in water and investigated the solubility increase and solution mechanism. We used the pair of LiBr-1,4-dioxane aqueous solution and 1,4-dioxane solution as the working medium, and showed high eligibility for the absorption refrigerating cycle[5][6].

In order to plan and design the absorption refrigerating cycle using the developed working pair, it is necessary to understand the evaporation heat (this term is used because the liquid is a mixture) of 1,4-dioxane aqueous solution. Therefore, this study was conducted to establish an estimation method of the evaporation heat based on the state of existence of the two components in the 1,4-dioxane aqueous solution.

The evaporation latent heat of a liquid of a pure substance can be measured by an adiabatic calorimeter. It can also be calculated from the Clausius-Clapeyron equation, which is based on the equivalence relation of Gibbs free energy between vapor and liquid phases. In a mixed liquid, however, this relation is replaced by the equivalence relation of chemical potential, which is a partial quantity of Gibbs free energy corresponding to each component. Ito et al.[7] reported that the Clausius-Clapeyron relation would not hold.

In this report, considering the liquid structure of 1,4-dioxane aqueous solution, we employed evaporation processes (①, ②) during which the vapor and liquid composition is held constant and an evaporation process (③) during which the composition changes. Using these methods, we calculated or measured the evaporation heat at constant pressure (101.325 kPa) and its dependence on mole fraction. Furthermore, we compared the results with the evaporation heat data given in previous reports.

① Calculation of evaporation heat at constant pressure from low pressure vapor-liquid equilibrium characteristics by the UNIFAC method
② Measurement of evaporation heat at constant pressure from low pressure vapor-liquid equilibrium characteristics experiments
③ Measurement of evaporation heat at constant pressure using a differential scanning calorimeter (TG-DSC)

From these results, we examined the state of mixture of the two components in the vapor

and liquid phases and proposed a method for estimating the evaporation heat of a 1,4-dioxane aqueous solution at constant pressure (101.325 kPa).

2. Purpose and previous data of comparison between low pressure vapor-liquid equilibrium method and total evaporation method (TG-DSC)

Table 1 compares the features of the methods used for calculation and measurement of the evaporation heat of 1,4-dioxane at constant pressure (101.325 kPa) and summarizes the previous data.

If the evaporation heat values obtained by methods ① and ② agree with the previous data within the range of an appropriate error, the component vapores of the vaporeous phase can be considered a mixture of perfect vapores. Likewise, if this result agrees with the evaporation heat value obtained by method ③, the evaporation heat of a 1,4-dioxane aqueous solution does not depend on the mixture mole fraction. When the two components in the solution evaporate independently, the mean of the sum of the evaporation heat values of the components averaged by the solution weight is the evaporation heat of that aqueous solution. In other words, Tominaga et al.[2] and these findings[3][4] confirm that the two components independently exist in the solution without forming a hydrogen bond. These results indicate that the solution a mixture of perfect liquids.

In the previous data, documented data[8]–[12] are available on the evaporation latent heat of 1,4-dioxane as a single component, but there is insufficient documented data on 1,4-dioxane aqueous solutions.

Figure 1 shows the dependence of vapor-liquid equilibrium temperature of a 1,4-dioxane aqueous solution on mixture mole fraction (at 101.325 kPa), excerpted from the previous data. The values used in the UNIFAC method are given in **Table 1**.

According to two data sets of the previous data obtained from vapor-liquid equilibrium experiments, the vapor-liquid equilibrium temperature shows the same tendency in both data sets, and a high degree of agreement is seen in the neighborhood of the azeotropic composition, or $0.2 < X_c < 0.85$. If the vaporeous phase is assumed to be an ideal vapor, the calculation result by the UNIFAC method will show a different tendency from these two data sets in
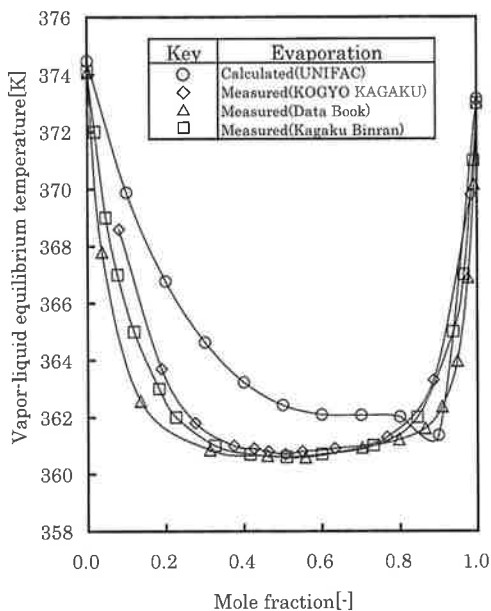

Fig. 1 Vapor-liquid equilibrium temperature of 1,4-dioxane aqueous solution on mole fraction

Table 1 Calculation and measurement methods and exiting data of evaporation heat of 1,4-dioxane aqueous solution

Method	Evaporation of a certain amount in vapor-liquid equilibrium at low pressure		Total evaporation
Calculation method Measurement method	(1) UNIFAC method	(2) Vapor-liquid equilibrium experiment	(3) Thermogravimetry-differential scanning calorimetry (TG-DSC) method
Vapor-liquid composition during process	Vapor phase: Assumed as ideal gas Liquid phas: Corrected with liquid phase activity coefficient	Keep constant by eliminating error origins to make the composition of vapor generated from a boiling liquid identical to that entering a condenser.	Vary properties other than an azeotropic point.
Items to be calculated and measured	Calculate saturation pressure versus saturation temperature at each predefined mixing molar fraction.	Measure saturation pressure versus saturation temperature at each predefined mixing molar fraction.	Measure the amount evaporated and heat consumed by evaporation at each predefined mixing molar fraction.
Calculation method for evaporation heat	Apply the Clausius-Clapeyron equation. Calculate from the gradient of a curve of saturation pressure versus saturation temperature at a predefined mixing molar fraction.	Apply the Clausius-Clapeyron equation. Calculate from the gradient of a curve of saturation pressure versus saturation temperature at a predefined mixing molar fraction.	Calculate from loss on sample weight and from heat consumed by evaporation.
Existing data	(1) Touyoujouhou system ed., Kagakukougakubenran Jouhou system PRODECE, Maruzen, p3-132~145, Tokyo, Japan (1990) P: arbitrary point, X_c; arbitrary point · Vapor phase fugacity coefficient type: Ideal gas · Liquid phase activity coefficient type: UNIFAC · Physical-properties constant: Coefficient of an Antoine vapor pressure type $\ln p^{sat}[Pa]=A-\dfrac{B}{C+T[K]}$ (see table below)	(1) Hirata, M., S. Ohe and K. Nagahama: "Denshikeisanki niyoru Kiekiheikou Data", Koudansya Scientific, pp. 745~747 (1975) P: 760,50, 100 mmHg, X_c: 12 points (2) Kogan, V.B., Fridman, V.M.Kafarov, V.V..; Hirata, M trans.: "Kiekiheikou Datebook", Koudansya Scientific, p. 290 (1974) $P=760$ mmHg, X_c: 14 points (3) Kogan, V.B., Fridman, V.M.Kafarov, V.V.; Hirata, M trans.: "Kiekiheikou Datebook", Koudansya Scientific, p. 291 (1974) $T=298$ K, X_c: 8 points (4) Nihonkagakukai ed.: Kagakubenran Kisohen 4th Ed., p. II-136, Maruzen, (1993) $P=760$ mmHg; constant, X_c; 17 points	(1) Sumika Chemical Analysis Service (2000) $X_c=0.625$

Antoine constants (Existing data, column (1) UNIFAC method):

	A[kPa,°C]	B[kPa,°C]	C[kPa,°C]	Temperature [°C]
Water	7.074	1,657.460	227.020	10,800-167,800
1,4-dioxane	6.131	1,288.500	211.000	1,850-136,850

the range $0.1 \leq X_c < 0.8$.

We compared our experimental data with these previous data.

3. Instrument and method of experiment

3.1 Test samples

Ultrapure water (full-automatic ultrapure water generator CPW-200 by Advantec Toyo) and 1,4-dioxane (by Kanto Kagaku, special grade) were used for preparing samples, and the samples were prepared in the mixture mole fraction range $X_c = 0.0$ to 1.0 with water as the primary component, at increments of 0.1. The quality of the ultrapure water is: specific resistance > 18 MΩ · cm (298 K), solubility of Na^+, Ca^{2+} and the like lower than the detection limit, and pH $= 5.8$. The same sample was used for both the vapor-liquid equilibrium and total evaporation methods.

3.2 Measuring the vapor-liquid equilibrium pressure and temperature under vapor-liquid equilibrium

3.2.1 Experimental apparatus

Figure 2 shows a schematic diagram of experimental apparatus. The experimental apparatus consists of an oil bath and a 300 ml three-port flask. The oil bath is equipped with a stirrer and thermometer and the flask is equipped with a thermometer and is installed in the bath. A stirring bar is installed in the flask and is rotated from the outside to ensure uniform temperature in the flask. The flask is connected to a condenser through a connecting pipe that is thermally insulated by an insulator. To the other ports, a vacuum pump and a mercury column manometer are connected to measure the pressure in the instrument.

3.2.2 Measuring method

Take about 200 ml of the sample prepared to the prescribed mole fraction and put it in a 300 ml three-port flask installed in an oil bath. Set the pressure in the instrument to 30.39 kPa to atmospheric pressure using the vacuum pump and a pressure regulating value and seeing the mercury column manometer connected to the instrument. Heat the sample in the oil bath to raise the liquid temperature. When the saturation temperature is reached, boiling begins and the liquid temperature remains constant. During this period, measure the temperature in the instrument and the pressure difference between the inside of the instrument
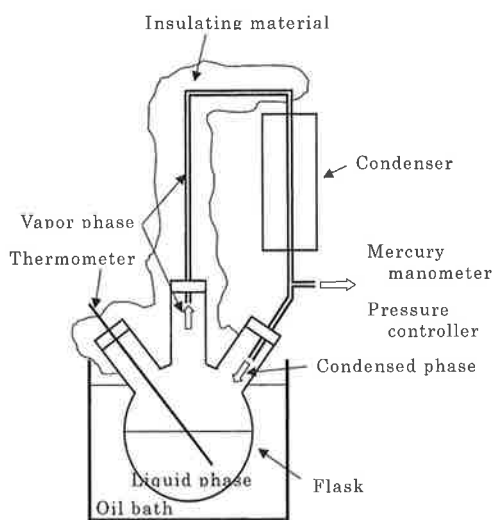

Fig. 2　Schematic diagram of experimental apparatus

and atmospheric pressure.

3.3　Measuring evaporation heat by the total evaporation method (TG–DSC)

3.3.1　Differential scanning calorimeter (TG–DSC)

The TG–DSC (Thermo Gravimetry–Differential Scanning Calorimeter) used for the test is the Type 8110 made by Rigaku Denki.　This instrument is the input compensation type, which detects the temperature difference between the sample and a reference substance and measures the compensating electric energy to offset the temperature difference.

Figure 3　shows a schematic diagram of the inside of the DSC furnace.

Temperature adjustment inside the furnace is accomplished by the heater installed on the side face of the furnace, and compensating heat control is automatically regulated by the thermocouple installed in the sample holder and a compensating heater.　At this time, the required power for heat control is depicted in a DSC curve as the difference in quantity of heat. And, TG (Thermo Gravimetry) makes possible the simultaneous and quantitative detection of a change in weight due to heating or in quantity of heat and in weight accompanying a chemical reaction. For measurement of the solution, this study followed the convention of using an empty container as the reference substance ; in this case an aluminum sample container.

3.3.2　Sample container and covering method

For the sample container, we used the aluminum pan LQ with a cover for liquid samples (8580 T1X15N 30 μl made by Rigaku Denki).　We examined the effect of the pan covering method on the TG–DSC curve.

First, we examined the TG–DSC curve using an uncovered sample container.　The TG curve decreases from the beginning of measurement at a certain gradient.　The DS curve is greatly disturbed and the constant-pressure evaporation heat obtained from it is lower than the documentary value[13] by as much as 37.46%.　This is because the sample evaporation area is large and the temperature change is intense at the vapor-liquid interface, so stable sample evaporation is thought impossible.　To prevent the effect of temperature changes, we prepared a cover with a hole of 0.5 mm diameter and put it on the sample pan.　The DSC curve was sharp compared to the uncovered container, and the intense temperature change at the vapor-liquid interface was prevented.　However, the amount of evaporation heat was lower than the documentary value by 6.83%.　This is due to the fluctuations of the DSC curve, which are thought to be brought about by the leakage of the sample vapor through the gap between the peripheries of the cover and pan.　Then, we crimped the pan and cover usinvaporample
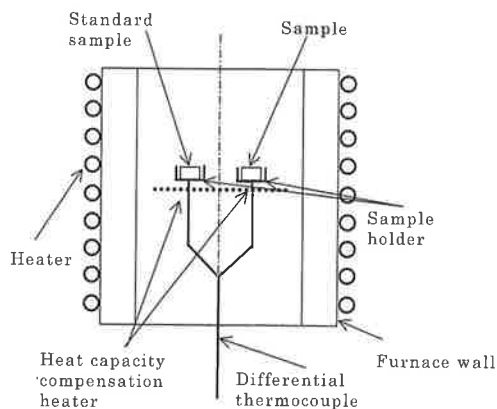

Fig. 3　Schematic diagram of the inside of the DSC furnace

sealer. The fluctuations of the DSC curve disappeared, and the amount of evaporation heat was 2,181.5 J・g^{-1}. The difference from the documentary value is -3.34%, indicating that high accuracy measurement is possible. For this reason, we carried out experiments using a pan with a crimped cover.

Figure 4 shows the TG-DSC curve for $X_c = 0.0$ and 1.0.

For the measurement, a sample container of 30 mg capacity was filled with 10 mg of the sample. The large volume container is used to avoid boiling over during measurement and a sample size of 10 mg was chosen to prevent the DSC curve from becoming broad. Fluctuation occurs with a sample size of 5 mg, making the analysis difficult.

3.3.3 Temperature program

The programmed temperature mode was

Fig. 4   TG-DSC curve for $X_c = 0.0$ and 1.0

used for the measurement of constant pressure evaporation heat. First, we held the furnace temperature at 318 K for the 5 minutes before the start of measurement to thermally soak the reference substance and sample container. This clarifies the sample loss at the start of temperature rise and the changes of the quantity of heat and reduces the measurement errors. The sample weight is about 10 mg, and the temperature difference between the reference substance and solution is slight, so a holding time of 5 minutes is sufficient for thermal soaking. 318 K is the highest attainable temperature of the instrument when the furnace is cooled by the air inside the furnace.

We set the endpoint above the boiling point of the sample (383 K) and raised the temperature at a predetermined rate until the endpoint was reached. Then, we held the temperature to the endpoint. We conducted a preliminary experiment at temperature rise rates 1, 3, 5 and 10 K・min^{-1}. For temperature rise rates >3 K・min^{-1}, the endpoint was reached before the sample had evaporated completely, and some of the compositions of the sample solution required modifications of the temperature program, making measurement under the same conditions impossible. For temperature rise rates <3 K・min^{-1}, a great deal of time is consumed until the endpoint is reached and noises are apt to interfere with the measured data. In addition, the amount of natural evaporation is larger than the amount of heated evaporation, and this lowers the measurement accuracy. Therefore, we set the temperature rise rate at 3 K・min^{-1}.

3.3.4 Amount of evaporation heat

The amount of evaporation heat is converted by peak area. The peak area must have

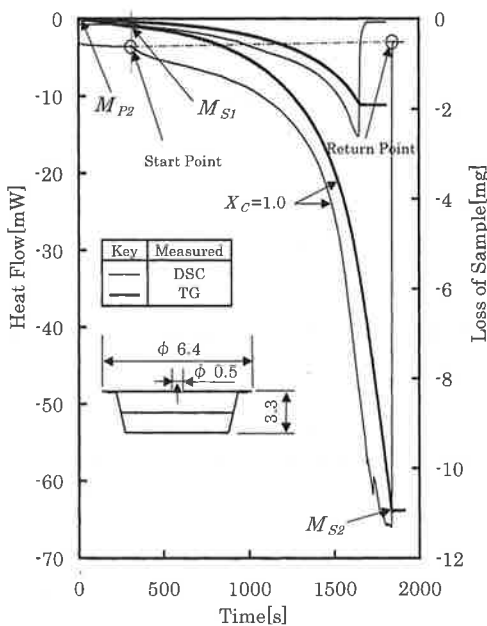reproducibility and linearity with respect to sample weight, so meticulous care is necessary in deciding how to take the peak area. There are four methods of taking the peak area. One method uses the reaction endpoint. This endpoint is the temperature at which the logarithm of temperature difference begins to have linearity with respect to sample temperature. However, the simplest method is to connect the points at which the peak curve leaves the baseline (rising point and returning point), and we employed this method because it is widely used and has reproducibility and linearity.

4. Dependence of constant pressure evaporation heat on mole fraction under low pressure vapor-liquid equilibrium

4.1 Constant pressure evaporation heat, $L_{Ds}X_C$, obtained by low pressure vapor-liquid equilibrium computation software (UNIFAC)

We used low pressure vapor-liquid equilibrium computation software[1] to compute the evaporation heat of water-1,4-dioxane mixtures from a generalized equation of vapor-liquid equilibrium temperature and pressure and comparatively examined the dependence of the computed values of evaporation heat on mole fraction.

Finding the evaporation heat of a mixed solution is complex, and Ito et al.[7] reported that the equation would not hold. To find the evaporation heat of a mixture solution, the Clausius-Clapeyron equation[8][14] must be applied. This equation is derived by thermodynamic analysis of the phase equilibrium of a mixed solution. Except for azeotropic mixtures, the pressure and temperature changes during evaporation. Therefore, the evaporation heat of a mixed solution must be found as either isobaric or isothermal evaporation heat[8][15].

The Clausius-Clapeyron equation (for an ideal vapor in vaporeous phase) takes the form of Eq. (1).

$$\frac{d(\ln p)}{dT} = \frac{\Delta H_{m,vap}}{RT^2} \quad\cdots\cdots\cdots (1)$$

Therefore,

$$\ln p = -\frac{\Delta H_{m,vap}}{R} \cdot \frac{1}{T} + C \quad\cdots\cdots (2)$$

We computed the vapor-liquid equilibrium temperature T and vapor-liquid equilibrium pressure p using low pressure vapor-liquid computation software[1], and **Figure 5** shows the reciprocal, $1/T$, of temperature T in relation to the natural logarithm, $\ln p$, of pressure p.

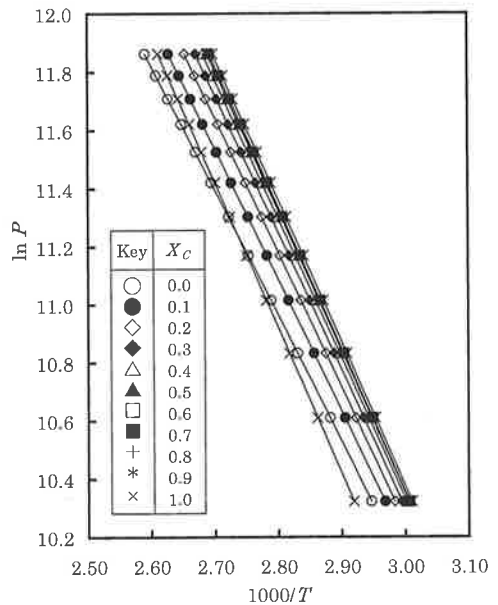| Key	X_C
○	0.0
●	0.1
◇	0.2
◆	0.3
△	0.4
▲	0.5
□	0.6
■	0.7
+	0.8
*	0.9
×	1.0

Fig. 5　Relation between $\ln p$ and $1000/T$

From Eq. (2), the gradient A of $1/T$ with respect to $\ln p$ is in the relation of Eq. (3).

$$-\frac{\Delta H_{m,vap}}{R} = -A \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

Therefore, the constant pressure evaporation heat, $L_{Ds}(X_c)$, takes the form of Eq. (4)

$$L_{Ds}(X_c) = \Delta H_{m,vap} = AR \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (4)$$

That is, it can be expressed as the product of $1/T$, the gradient A of $\ln p$ and the vapor constant R.

We calculated the constant pressure evaporation heat, $L_{Ds}(X_c)$ (marked by circles), from the vapor-liquid equilibrium pressure and temperature computed by low pressure vapor-liquid equilibrium computation software[1], and **Figure 6** shows the constant pressure evaporation heat in dependence on mole fraction.

As a tendency of the dependence of $L_{Ds}(X_c)$ on mole fraction, the constant pressure evaporation heat rapidly drops to around $X_c = 0.8$ as the amount of added 1,4-dioxane increases, that is, as the mole fraction X_c decreases. Past that point, it gradually decreases to $L_{Ds}(X_c = 0.0)$.

4.2 Constant pressure evaporation heat, $L_{Hm}(X_c)$, obtained by low pressure vapor-liquid equilibrium experiment

We measured the vapor-liquid equilibrium temperature and pressure of a water-1,4-dioxane mixed liquid using a vapor-liquid equilibrium experiment and calculated the constant pressure evaporation heat, $L_{Hm}(X_c)$, from these measured values. Then, we conducted a comparative examination on the dependence of the constant pressure evaporation heat on mole fraction.

Figure 6 shows the dependence of $L_{Hm}(X_c)$ (marked by triangles) on mole fraction.

The dependence of $L_{Hm}(X_c)$ on mole fraction shows a similar tendency to $L_{Ds}(X_c)$, that is, the constant pressure evaporation heat rapidly drops to around $X_c = 0.8$ as the amount of added 1,4-dioxane increases. Past that point, it gradually decreases to $L_{Hm}(X_c = 0.0)$.

Table 2 shows the difference between $L_{Ds}(X_c)$ and $L_{Hm}(X_c)$.

For $L_{Ds}(X_c)$, the dispersion is large over 0. $0 \le X_c \le 0.6$ but it is small in the interval $0.6 < X_c$, and its maximum is 3.71% (at $X_c = 0.0$), its
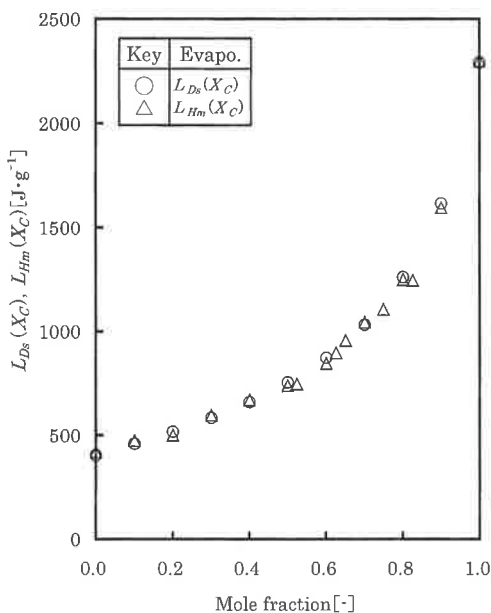

Fig. 6　Evaporation heat of 1,4-dioxane aqueous solution on mole fraction

Table 2 Difference between $L_{Ds}(X_c)$ and $L_{Hm}(X_c)$

X_c	$L_{Ds}(X_c)$	$L_{Hm}(X_c)$	Difference (%)
0.000	402.667	417.87	-3.71
0.100	459.623	474.95	-3.28
0.200	518.393	501.39	3.33
0.300	584.938	597.11	-2.06
0.400	661.026	670.57	-1.43
0.500	755.956	740.52	2.06
0.524		747.65	
0.600	874.188	846.74	3.19
0.625		897.99	
0.639			
0.650		956.94	
0.700	1,032.913	1,045.43	-1.20
0.749		1,107.64	
0.800	1,263.111	1,251.17	0.95
0.825		1,247.23	
0.900	1,616.977	1,596.23	1.29
1.000	2,292.411	2,298.85	-0.28
mean	—	—	2.07

minimum is 0.28% (at $X_c = 1.0$), and its mean is 2.07%.

Because $L_{Ds}(X_c)$ obtained by method ①, or the UNIFAC method, almost agrees with L_{Hm} (X_c) obtained by method ②, or the vapor-liquid equilibrium experiment, the component vapores of the vaporeous phase of the water-1,4-dioxane mixed liquid are thought to be a mixture of perfect vapores.

5. Dependence of constant pressure evaporation heat on mole fraction, according to total evaporation method (TG-DSC)

5.1 Constant pressure evaporation heat $L_m(X_c)$ by TG-DSC

We measured the weight, Mp_1, of an empty sample container first. We prepared water-1,4-dioxane mixed liquids to different values of mole fraction and took about 10 mg of each mixed liquid using a micropipette. We dropped the sample into the sample container uniformly and evenly to obtain the best thermal contact between the sample and sample container. Then, we measured the weight, Mp_2, of the sample container filled with the sample using the TG (described in **Figure 4**). The difference between the filled and empty sample containers was

taken as the apparent sample weight $M_1 (= Mp_2 - Mp_1)$. This apparent weight was entered in the TG–DSC as the measured sample weight. The apparent amount of evaporation heat, $L_1(X_c)$ [J · g^{-1}], obtained by the DSC was computed using M_l. However, the temperature rise process was entered after holding at 318 K for 5 minutes to make the sample temperature equal to the furnace temperature. As a loss of weight $(Ms_1 - Ms_2)$ occurred due to evaporation during this period (described in **Figure 4**), the remainder after the subtraction of this loss was taken as the true sample weight M_t.

Therefore, the true constant pressure evaporation heat L_t is represented by Eq. (5) and this value was taken as the product of the experimentally obtained apparent constant pressure evaporation heat L_l and the quotient of the apparent sample weight M_l divided by the true sample weight M_t. This product was taken as the constant pressure evaporation heat, $L_m(X_c)$, obtained in the programmed temperature mode.

$$L_m(X_c) = L_t = L_l \cdot \frac{M_l}{M_t} = L_l \cdot \frac{(Mp_2 - Mp_1)}{(Ms_1 - Ms_2)} \quad \cdots\cdots\cdots\cdots\cdots (5)$$

Figure 7 shows the constant pressure evaporation heat $L_m(X_c)$ (marked by circles) obtained in the programmed temperature mode, in dependence of mole fraction.

The dependence of $L_m(X_c)$ on mole fraction is like $L_{Ds}(X_c)$. That is, as the amount of added 1,4-dioxane increases, namely, as the mole fraction X_c decreases, the evaporation heat drops to around $X_c = 0.8$. Past that point, the evaporation heat gradually decreases to $L_m(X_c = 0.0)$.

Table 3 shows the difference between $L_m(X_c)$ and $L_{Ds}(X_c)$.

We compared the difference in the dependence on mole fraction between $L_m(X_c)$ and $L_{Ds}(X_c)$ with the difference between $L_{Ds}(X_c)$ and $L_{Hm}(X_c)$. For each value of mole fraction, the former on the whole had a larger degree of scattering than the latter, that is, it took a maximum of 10.82% (at $X_c = 0.0$) and a minimum of 2.02% (at $X_c = 0.1$) and its mean was 5.88%.

For the measurement of constant pressure evaporation heat by TG–DSC, reproducibility is expected to be poor unless conditions are favorable. The scattering is thought to be caused by the following factors. The sample container must be tight to avoid the influence of evaporation. The experiment must be conducted under an N_2 atmosphere to avoid the
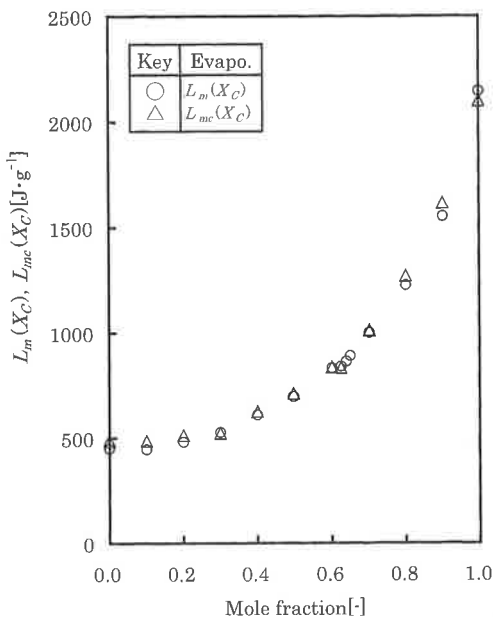

Fig. 7   Evaporation heat of 1,4–dioxane aqueous solution on mole fraction

Table 3   Difference of $L_m(X_C)$ from $L_{Ds}(X_C)$ and $L_{mc}(X_C)$

X_C	$X_m(X_C)$	$L_{Ds}(X_C)$	$Difference$ (%)	$L_{mc}(X_C)$	$Difference$ (%)
0.000	448.705	402.667	10.82	486.70	−8.12
0.100	450.440	459.623	−2.02	491.00	−8.62
0.200	486.603	518.393	−6.33	517.30	−6.12
0.300	531.782	584.938	−9.52	528.20	0.68
0.400	614.427	661.026	−7.31	629.70	−2.46
0.500	697.965	755.956	−7.98	712.30	−2.03
0.524					
0.600	836.070	874.188	−4.46	840.100	−0.48
0.625	844.774			838.100	0.79
0.639	869.262				
0.650	895.198				
0.700	999.446	1,032.913	−3.29	1,010.800	−1.13
0.749					
0.800	1,230.528	1,263.111	−2.61	1,274.600	−3.52
0.825					
0.900	1,557.316	1,616.977	−3.76	1,620.400	−3.97
1.000	2,146.629	2,292.411	−6.57	2,098.900	2.25
mean	—	—	5.88	—	3.35

influence of oxidation heat.   The sample container and instrument must be clean to avoid the influence of heat loss that may be brought about by a poor contact state or stain on the outer or bottom surface of the container.   The tightness (covering) of the container, in particular, has a large influence on the results.   According to a preliminary experiment, the most stable data gathering is possible with a cover with a hole 0.5 mm in diameter.   By crimping this cover on the pan, measurement was performed with high reliability.

5.2   Constant pressure evaporation heat, $L_{mc}(X_C)$, by TG-DSC considering the composition change in the evaporation process

In Section 5.1, we computed the constant pressure evaporation heat $L_m(X_C)$ from the amount of heat required for total evaporation of a sample of about 10 mg in the above-mentioned programmed temperature mode without considering the changes in sample composition in the evaporation process.   In the process to complete evaporation of the entire sample, however, the composition of both the vaporeous and liquid phases is thought to change.

Thus, we took the accumulated amount of evaporation heat by adding up the partial

amount of evaporation heat by TG-DSC of every evaporated 1 mg of the sample after the start of the temperature rise and likewise the accumulated amount of sample evaporation and considered the relation between the two accumulated amounts.

By comparing and examining the changes in the relation between the accumulated amount of evaporation heat and accumulated amount of sample evaporation obtained by adding up their respective partial amounts by TG-DSC of 1mg of the sample, it is possible to track the changes in composition of the liquid.

Figure 8-1 shows the relation between the accumulated amount of evaporation heat and accumulated amount of sample evaporation and its linear (first order) approximate equation $y_{1(Xc)}$ for water and 1,4-dioxane as single-component compositions ($X_C = 1.0$ and 0.0) and a water-1,4-dioxane mixed liquid of the azeotropic composition ($X_C = 0.625$).

The two pure components and the liquid of the azeotropic composition remain in constant composition during the evaporation process in both the vaporeous and liquid phases. Therefore, the accumulated amount of evaporation heat and the accumulated amount of sample evaporation show a rectilinear relation. The correlation coefficient $r(-1 \leq r \leq 1)$ is expressed as Eq. (6) and it is used as an index to indicate the degree of linear relation between two variables.

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - y)^2}} \quad \cdots\cdots\cdots (6)$$

Our two variables show very high degrees of correlation of $r = 0.9996$ ($X_C = 1.0$), 0.9989 ($X_C = 0.625$) and 0.9956 ($X_C = 0.0$). The evaporation latent heat of the single-component liquids and the azeotropic mixed liquid is calculated from the gradient of their respective lines. Peak area can be converted into the amount of evaporation heat, whose reproducibility and linearity with respect to sample weight was confirmed in this way.

Figure 8-2 shows the relation between the accumulated amount of evaporation heat and accumulated amount of sample evaporation and its polynomial (second order) approximate equation $y_{2(Xc)}$ at $X_C = 0.3$, 0.5, 0.7 and 0.9 where the composition is thought to change in both the vaporeous and liquid phases in the process of total evaporation of the sample. In the relation between the accumulated amount
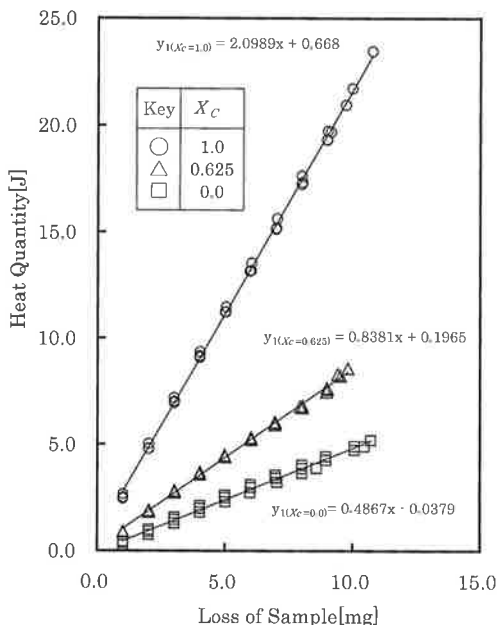

Fig. 8-1　Relation between the accumulated amount of evaporation heat and accumulated amount of sample evaporation

Equations on figure:

$y_{2(Xc=0.9)} = 0.0683x^2 + 0.9022x + 0.2879$
$y_{1(Xc=0.9)} = 1.6204x - 1.089$

$y_{2(Xc=0.7)} = 0.0192x^2 + 0.7997x + 0.0697$
$y_{1(Xc=0.7)} = 1.0108x - 0.3531$

Key	X_C
○	0.9
△	0.7
□	0.5
◇	0.3

Key	Eq.
-----	y_1
——	y_2

$y_{2(Xc=0.5)} = -0.0241x^2 + 0.9406x - 0.3887$
$y_{1(Xc=0.5)} = 0.7123x + 0.0106$

$y_{2(Xc=0.3)} = -0.0157x^2 + 0.6696x - 0.2064$
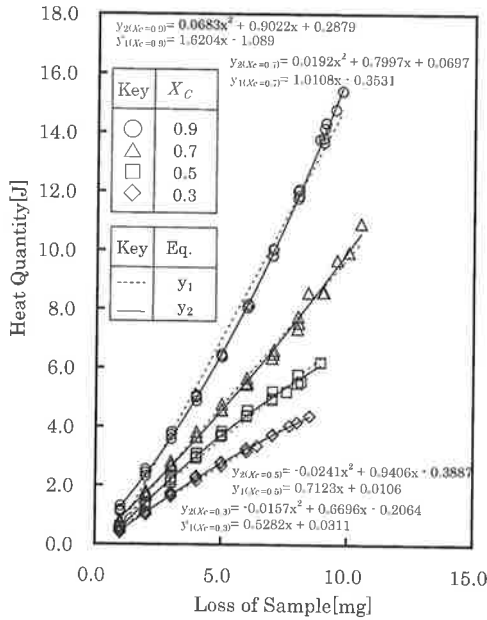$y_{1(Xc=0.3)} = 0.5282x + 0.0311$

Fig. 8-2 Relation between the accumulated amount of evaporation heat and accumulated amount of sample evaporation

of evaporation heat and accumulated amount of sample evaporation, some degree of deviation from a straight line is seen compared with **Figure 8-1**. With the azeotropic composition being the point of division, the curve is convex upwards at $X_C = 0.3$ and 0.5 and convex downwards at $X_C = 0.7$ and 0.9, indicating different changes in composition of the vaporeous and liquid phases in the evaporation process. That is, at $X_C < 0.625$, 1,4-dioxane evaporates at a higher proportion than the initial composition of the liquid in the early stage of evaporation because of its abundance. In the later stage, water becomes abundant by that amount and evaporates at a higher proportion. Therefore, the curve takes upward convex form. On the other hand, at $X_C > 0.625$, water is abundant and evaporates at a higher proportion than the initial composition in the early stage but 1,4-dioxane evaporates at a higher proportion in the later stage. Therefore, the curve is convex downwards. If the measured results are approximated by the straight line $y_{1(x_c)}$ (also shown in **Figure 8-2**), the correlation coefficient becomes $r = 0.9971$ ($X_C = 0.3$), 0.9959 ($X_C = 0.5$), 0.9969 ($X_c = 0.7$) and 0.9948 ($X_C = 0.9$), indicating a very high degree of correlation. In other words, evaporation takes place in similar composition to the liquid composition irrespective of X_C. Therefore, we approximated the results at each value of X_C by the straight line $y_{1(x_c)}$ and found the constant pressure evaporation heat $L_{mc}(X_C)$ from the gradient of these lines.

Figure 7 also shows the calculated values $L_{mc}(X_C)$ of evaporation heat in the programmed temperature mode in dependence on mole fraction.

Table 3 shows the difference between $L_{mc}(X_C)$ and $L_m(X_C)$.

The dependence of $L_{mc}(X_C)$ on mole fraction is similar as $L_m(X_C)$, that is, the difference from the $L_m(X_C)$ is 8.62% at maximum ($X_C = 0.1$), 0.48% at minimum ($X_C = 0.6$) and 3.35% on average, so the two are judged to have similar dependence. The difference from $L_{Ds}(X_C)$ also shows the same behavior, so it is thought that the two components in the liquid are mixed into a perfect liquid.

Therefore, the constant pressure evaporation heat of a 1,4-dioxane aqueous solution can be computed from the constant pressure evaporation latent heat of the two components as their mean averaged with a mole fraction weight.

6. Estimation of constant pressure evaporation heat of 1,4-dioxane by simple mixture model

We proposed a simple mixture model for evaporation heat estimation and represented it by the most simplified generalized equation. We then estimated the evaporation heat using this model and compared and examined it with the computed results.

In the simple mixture model, the evaporation latent heat of the single components of water and 1,4-dioxane does not change by mixing and there is no interaction between the two components (a mixture of normal liquids). That is, water and 1,4-dioxane are mixed but exist independently of each other. The fact that the two components exist independently of each other in mixture is already evident from previous studies[3][4].

With the simple mixture model, the evaporation heat $L_S(X_C)$ of any water-1,4-dioxane mixed liquid can be represented by Eq. (7), and its value can be found from the literary values of evaporation latent heat of the two components, or $L_W = 2258.7$ J·g^{-1} [8] and $L_D = 413.0$ J·g^{-1} [8], as their mean averaged with a mole fraction weight.

$$L_s(X_C) = \frac{M_W X_C L_W + M_D (1-X_C) L_D}{M_W X_C + M_D (1-X_C)} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (7)$$

Figure 9 shows the calculated values $L_S(X_C)$ (marked by squares) of evaporation latent heat by the simple mixture model in dependence on mole fraction and also shows $L_{DS}(X_C)$ (marked by circles) and $L_m(X_C)$ (marked by diamonds). Literary values[8] (including reference values[16]) $L_b(X_C)$ (marked by triangles) of evaporation latent heat of water and 1,4-dioxane as a single component are also shown.

Table 4 shows the differences of $L_S(X_C)$ from $L_{DS}(X_C)$, $L_m(X_C)$, and $L_b(X_C)$.

The dependence of $L_S(X_C)$ on mole fraction shows an average value with respect to $L_{DS}(X_C)$ and $L_m(X_C)$ and is plotted near the center for each value of mole fraction. At each value of X_C except $X_C = 0.0$, $L_m(X_C)$ shows a lower value than $L_{DS}(X_C)$. The difference from $L_{DS}(X_C)$ is 4.10% at maximum ($X_C = 0.4$), 0.49% at minimum ($X_C = 0.9$) and 2.55% on average, and the difference from $L_m(X_C)$ is 8.29% at maximum ($X_C = 0.0$), 0.79% at minimum ($X_C = 0.1$) and 3.41% on average.

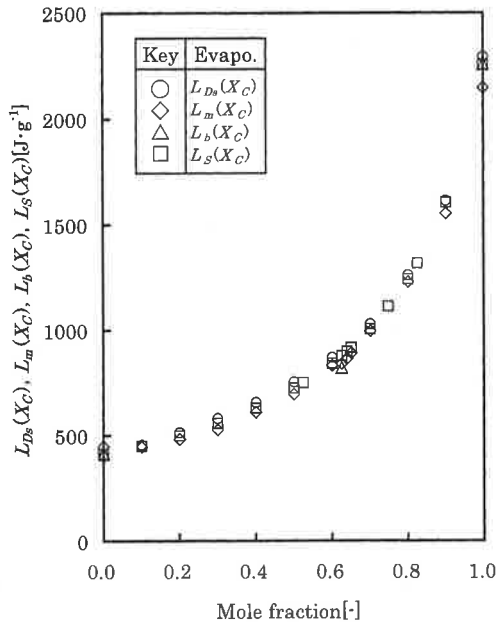At $X_C = 0.0$, the two show a difference with a large degree of scattering. The documen-

Fig. 9 Evaporation heat of 1,4-dioxane aqueous solution on mole fraction

Table 4 Difference of $L_s(X_c)$ from $L_{Ds}(X_c)$, $L_m(X_c)$, and $L_b(X_c)$

X_c	$L_s(X_c)$	$L_{Ds}(X_c)$	Difference (%)	$L_m(X_c)$	Difference (%)	$L_b(X_c)$	Difference (%)
0.000	413.000	402.667	2.53	448.705	-8.29	413.000	0.00
0.100	454.015	459.623	-1.23	450.440	0.79		
0.200	502.789	518.393	-3.06	486.603	3.27		
0.300	561.754	584.938	-4.04	531.782	5.48		
0.400	634.479	661.026	-4.10	614.427	3.21		
0.500	726.414	755.956	-3.99	697.965	3.99		
0.524	752.211						
0.600	846.330	874.188	-3.24	836.070	1.22		
0.625	882.237			844.774	4.34	826.000	6.58
0.639	903.614			869.262	3.88		
0.650	921.101			895.198	2.85		
0.700	1,009.293	1,032.913	-2.31	999.446	0.98		
0.749	1,112.560						
0.800	1,243.553	1,263.111	-1.56	1,230.528	1.05		
0.825	1,319.059						
0.900	1,609.003	1,616.977	-0.49	1,557.316	3.26		
1.000	2,258.700	2,292.411	-1.48	2,146.629	5.09	2,258.700	0.00
mean	—	—	2.55	—	3.41	—	—

tary value of 1,4-dioxane ($X_c = 0.0$) is $L_D = 413.0$ J $\cdot$ g^{-1} [8], 425.5 J $\cdot$ g^{-1} [11] and 450.0 J $\cdot$ g^{-1} [17], that is, the reference value itself shows a large degree of scattering and a deviation of 8.61% from the mean. These values are not definite as a general documentary value, and the difference from $L_s(X_c = 0.0)$ varies largely from 1.55% ($L_m(X_c = 0.0) = 450.0$ J $\cdot$ g^{-1} [17]) to 5.68% ($L_m(X_c = 0.0) = 413.0$ J $\cdot$ g^{-1} [8]) depending on the method of taking the value of $L_b(X_c = 0.0)$. On the other hand, the documentary value of water is almost constant, such as $L_w = 2255.9$ J $\cdot$ g^{-1} [11], 2256.9 J $\cdot$ g^{-1} [10], 2257.0 J $\cdot$ g^{-1} [13], and 2258.7 J $\cdot$ g^{-1} [8].

Thus, we proposed the value of $L_s(X_c)$, and the validity of this value as an estimate of evaporation heat of a 1,4-dioxane aqueous solution can be verified with the same degree of confidence as $L_{Ds}(X_c)$ used in the literature.

7. Conclusions

We computed and measured the constant pressure evaporation heat of 1,4-dioxane aqueous solutions in dependence on mole fraction and compared the results with the evaporation heat

data in the previous reports.　Conclusions are as follows :

1) We computed and measured the vapor-liquid equilibrium pressure and temperature by vapor-liquid equilibrium computation software and a vapor-liquid equilibrium experiment and then calculated the evaporation heat ($L_{Ds}(X_C)$, $L_{Hm}(X_C)$) from these obtained values of pressure and temperature.　The mean difference between the two was 2.07%.

2) We computed the evaporation heat $L_{Ds}(X_C)$ by vapor-liquid equilibrium computation software and measured the evaporation heat $L_m(X_C)$ by a differential scanning calorimeter (TG-DSC).　The mean difference between the two was 5.88%.

3) We measured the evaporation heat $L_m(X_C)$ from total evaporation by TG-DSC and calculated the evaporation heat $L_{mc}(X_C)$ by an approximation equation representing the relation between the accumulated amount of evaporation heat obtained by adding up the partial amount of evaporation heat and the accumulated amount of sample evaporation obtained likewise.　The mean difference between the two was 3.35%.

4) We used a simple mixture model to calculate the evaporation heat $L_s(X_C)$ as the mean averaged with a mole fraction weight of the two components.　The mean difference with $L_{Ds}(X_C)$ was 2.55% and the mean difference with $L_m(X_C)$ was 3.41%.

5) The evaporation heat of a 1,4-dioxane aqueous solution is a physical quantity. Assuming that the solution is an ideal mixed liquid of normal liquids, this value can be estimated by the simple mixture model as the mean averaged with the mole fraction weightof the two components.

Nomenclature

A : Gradient　　　　　　　　　　　　　　　　　　　　　　　　　　　　[atm・K]

C : Integration constant　　　　　　　　　　　　　　　　　　　　　　　[-]

$L(X_C)$: Evaporation heat of water-1,4-dioxane mixed liquid　　　　　　[J・g^{-1}]

$L_b(X_C)$: Documentary or reference value of evaporation heat　　　　　[J・g^{-1}]

L_D : Evaporation latent heat of 1,4-dioxane as a single component　　[J・g^{-1}]

$L_{Ds}(X_C)$: Calculated evaporation heat of water-1,4-dioxane mixed liquid, calculated from the vapor-liquid equilibrium pressure and temperature obtained by vapor-liquid equilibrium computation software (UNIFAC)　　　　　　　　　　　　　　　[J・g^{-1}]

$L_{Hm}(X_C)$: Calculated evaporation heat of water-1,4-dioxane mixed liquid, calculated from the vapor-liquid equilibrium pressure and temperature measured by vapor-liquid equilibrium experiment　　　　　　　　　　　　　　　　　　　　　　　　　[J・g^{-1}]

$L_1(X_C)$: Apparent evaporation heat by TG-DSC in programmed temperature mode　[J・g^{-1}]

$L_m(X_C)$: Measured evaporation heat of water-1,4-dioxane mixed liquid by TG-DSC in programmed temperature mode　　　　　　　　　　　　　　　　　　　　　　[J・g^{-1}]

$L_{mc}(X_C)$: Calculated evaporation heat by TG-DSC in programmed temperature mode

　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　[J・g^{-1}]

L_t : True evaporation heat by TG-DSC in programmed temperature mode　[J・g^{-1}]

L_W : Evaporation latent heat of water as a single component $[J \cdot g^{-1}]$

M_{s1} : Weight of sample container filled with a sample before temperature rise $[g]$

M_{s2} : Weight of sample container filled with a sample after the start of temperature rise $[g]$

M_D : Mass of one mol of 1,4-dioxane $[g \cdot mol^{-1}]$

M_1 : Apparent measured sample weight by TG-DSC in programmed temperature mode $[g]$

M_{p1} : Weight of empty sample container $[g]$

M_{p2} : Weight of sample container filled with a sample $[g]$

M_t : True measured sample weight by TG-DSC in programmed temperature mode $[g]$

M_W : Mass of one mol of water $[g \cdot mol^{-1}]$

p : Vapor-liquid equilibrium pressure $[Pa]$

r : Correlation coefficient $[-]$

R : Vapor constant $[J \cdot K^{-1} mol^{-1}]$

T : Vapor-liquid equilibrium temperature $[K]$

X_c : Mixture mole fraction of water taken as the primary component of liquid phase composition $[-]$

$y_{1(X_c)}$: Linear (first order) approximation equation representing the relation between accumulated amount of evaporation heat and accumulated amount of sample evaporation $[-]$

$y_{2(X_c)}$: Polynomial (second order) approximation equation representing the relation between accumulated amount of evaporation heat and accumulated amount of sample evaporation $[-]$

$\Delta H_{m,vap}$: Molar evaporation heat $[J \cdot mol^{-1}]$

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