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Measurement of Vapor-Phase Compressibility Factors of Monocarboxylic Acids Using a Flow-Type Apparatus and Their Association Constants

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The vapor-phase compressibility factors of several monocarboxylic acids (formic acid, acetic acid, propionic acid, *n*-butyric acid, isobutyric acid, and valeric acid) were measured by a flow-type apparatus at saturated vapor pressure from 30 °C to 150 °C. The vapor-phase association constants for monocarboxylic acids were evaluated from the compressibility factors obtained. They can be expressed in $\ln K = -149/R + 58\,500/RT$ for formic acid and $\ln K = -136/R + 58\,500/RT$ for other acids, where K is the association constant, T is the temperature in K, and R is the gas constant in $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$.

Introduction

The vapor-phase behavior at sufficiently low pressure can be treated as ideal in general. However, carboxylic acid vapors deviate appreciably from ideal gas behavior. The strong nonideality is caused by the formation of dimers. The vapor-phase association affects physical properties of mixtures containing carboxylic acids. For example, *PVT*, heat of vaporization, and vapor−liquid equilibria are significantly affected.

Curtiss and Blander (1988) reviewed the methods of determination for vapor-phase association constants. A popular method is the determination from vapor density or *PVT* data. In this work, therefore, the vapor-phase association constants were evaluated from compressibility factors for formic acid, acetic acid, propionic acid, *n*-butyric acid, isobutyric acid, and valeric acid. The compressibility factors were measured using a flow-type apparatus developed in the present work.

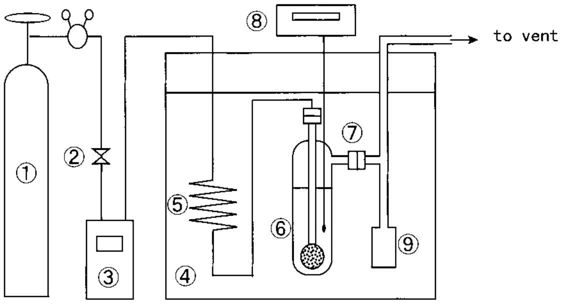

Figure 1. Schematic diagram of flow type apparatus: (1) carrier gas cylinder; (2) mass flow controller; (3) flow meter; (4) constant-temperature bath; (5) preheating coil; (6) equilibrium cell; (7) connecter; (8) thermometer; (9) trap for condensate.

Table 1. Antoine Constants for Monocarboxylic Acids (Ambrose and Ghiassee, 1987)[a]

	A	*B*	*C*
formic acid	15.405 60	3894.764	13.0
acetic acid	15.192 34	3654.622	45.392
propionic acid	15.296 86	3670.949	70.545
n-butyric acid	15.096 74	3599.963	93.307
isobutyric acid	15.311 43	3695.332	82.0
valeric acid	15.255 55	3811.202	101.0

[a] $\ln (p^{s}/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C]$.

Experimental Section

Equipment and Procedures. A flow-type apparatus was constructed to measure the compressibility factor. The schematic diagram of the apparatus is shown in Figure 1. The volume of the equilibrium cell is 30 cm^3, which was constructed according to Noda et al. (1983). A known amount of carboxylic acid was charged into the equilibrium cell, which was positioned in a constant-temperature bath. After the temperature of sample reached that of the liquid bath, helium gas was flowed into the cell. Helium gas was slowly passed (about 30 mL/min) through liquid solvent to establish equilibrium. Before the measurement, the flow rate was changed in 15−45 mL/min. The other experimental conditions such as the depth of liquid in the equilibrium cell and the measurement time were also changed to ascertain the equilibrium condition. The experimental result did not depend on the flow rate and experimental conditions changed. As a result, the flow rate of helium was controlled to be about 30 mL/min throughout the experiment. The temperature decrease due to the evaporation of liquid was within 0.2 °C. Therefore, the temperature of water bath was adjusted to be slightly above the desired temperature. After a few hours, helium gas was stopped, the equilibrium cell was taken off and weighed by a balance, and the lost mass of carboxylic acid was determined. Since the mass of the equilibrium cell was measured directly by a balance, no loss of liquid sample was considered. The total volume of helium was measured by a flow meter at atmospheric pressure, π, and the experimental

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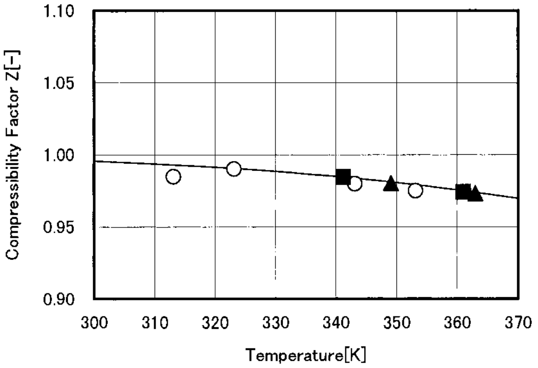

Figure 2. Compressibility factors of toluene: (○) present work; (—) correlation of Tsonopoulos (1974); (▲) Andon et al. (1957) cited from Dymond and Smith (1980); (■) Scott et al. (1962) cited from Dymond and Smith (1980).

Table 2. Compressibility Factors and Association Constants of Monocarboxylic Acids at Saturated Vapor Pressures

T/K	p^s/kPa	Z	K
	Formic Acid		
303.2	7.26	0.571	168
313.2	11.35	0.576	93.6
323.2	17.25	0.585	48.9
333.2	25.54	0.596	25.9
343.2	36.92	0.604	15.3
	Acetic Acid		
313.2	4.68	0.551	521
323.2	7.65	0.569	171
343.2	18.51	0.579	53.7
353.2	27.59	0.586	30.3
363.2	40.09	0.595	16.9
	Propionic Acid		
323.2	2.15	0.611	225
343.2	6.24	0.627	59.2
363.2	15.66	0.638	17.9
383.2	34.94	0.664	5.99
	n-Butyric Acid		
343.2	1.99	0.687	75.0
363.2	5.79	0.706	21.4
383.2	14.53	0.720	7.27
403.2	32.40	0.741	2.69
	Isobutyric Acid		
343.2	3.19	0.647	83.9
363.2	8.74	0.657	26.4
373.2	13.73	0.664	15.3
393.2	31.03	0.676	5.75
	Valeric Acid		
363.2	2.05	0.793	23.7
383.2	5.74	0.805	7.45
403.2	14.04	0.807	3.00
423.2	30.72	0.801	1.45

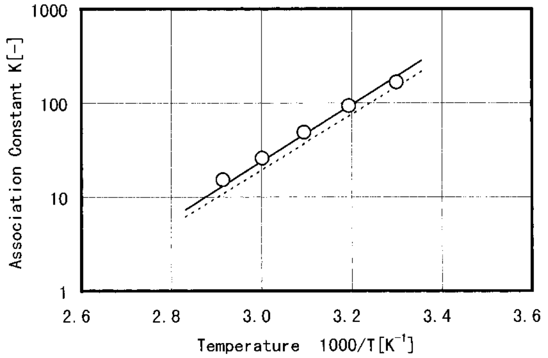

Figure 3. Association constants of formic acids: (○) present work; (—) Barton and Hsu (1969); (---) Jasperson et al. (1989). The results by Coolidge (1928) and Taylor and Bruton (1952) (not shown) are almost the same as those of Barton and Hsu.

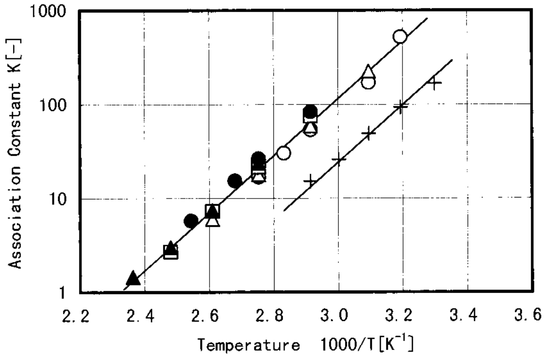

Figure 4. Association constants of monocarboxylic acids: (+) formic acid; (○) acetic acid; (△) propionic acid; (□) *n*-butyric acid; (●) isobutyric acid; (▲) valeric acid; (—) calculated by eq 7 (case 3).

temperature, *T*, and then converted to the total amount of helium, n_1[mol], by means of calculations based on the ideal gas law. The total amount of acid, n_2[mol], carried with helium can be obtained from the lost mass of acid and the appropriate molecular mass. In this experiment, a Pt-resistance thermometer, a mass flow meter, and an electric balance were used, and their accuracies were believed to be 0.05 °C, 0.2 mL/min, and 0.001 g, respectively.

In the experiment, we have a gaseous mixture containing helium (n_1) and acid (n_2), which shows the total volume *V* under atmospheric pressure and the experimental temperature. If we assume that helium is inert (ideal gas) and has no interaction with acid, the following equation is valid:

$$\pi = p_1 + p_2 \tag{1}$$

where p_1 and p_2 denote the pressures of pure helium and pure acid, the amounts of which are n_1 and n_2, respectively, under *V* and *T*.

Since pure helium can be treated as ideal, the volume is given as

$$V = \frac{n_1 RT}{p_1} \tag{2}$$

The pressure p_2 of the acid in eq 1 can be approximated by the saturated vapor pressure of the pure acid, p_2^s, at the experimental temperature on the basis of the assumptions that helium is ideal and has no interaction with the acid, that helium is insoluble in the liquid phase, and that the Poynting effect is negligible because π is atmospheric pressure and sufficiently low. Then the compressibility factor of pure acid can be obtained from eqs 1 and 2 as follows.

$$Z_2 = \frac{p_2 V}{n_2 RT} = \frac{n_1}{n_2} \frac{{p_2}^s}{\pi - {p_2}^s} \tag{3}$$

Thus, the compressibility factor of pure acid can be evaluated from the total amount of helium charged, the lost mass of acid during the experiment, atmospheric pressure, and vapor pressure of pure acid at the experimental temperature.

Materials. All chemicals used in this measurement were of guaranteed reagent grade. The purities of acetic acid, propionic acid, *n*-butyric acid, and isobutyric acid were examined by gas chromatography with a thermal conductivity detector and are more than 99.7%. They were used

Table 3. Entropy and Enthalpy for Vapor-Phase Association of Monocarboxylic Acids

	case 1			case 2			case 3		
	ΔS/ $J\cdot mol^{-1}\cdot K^{-1}$	ΔH/ $kJ\cdot mol^{-1}$	dev.[a]/%	ΔS/ $J\cdot mol^{-1}\cdot K^{-1}$	ΔH/ $kJ\cdot mol^{-1}$	dev.[a]/%	ΔS/ $J\cdot mol^{-1}\cdot K^{-1}$	ΔH/ $kJ\cdot mol^{-1}$	dev.[a]/%
formic acid	−128.3	−51.8	2.5	−155.6	−60.5	12.8	−149.0	−58.5	9.3
acetic acid	−156.7	−65.3	10.2	−143.3	−60.5	9.9	−136.0	−58.5	21.0
propionic acid	−146.1	−61.8	0.8	−142.8	−60.5	3.4	−136.0	−58.5	11.5
n-butyric acid	−149.9	−63.8	1.2	−141.6	−60.5	4.5	−136.0	−58.5	7.7
isobutyric acid	−138.4	−60.1	0.2	−139.5	−60.5	0.8	−136.0	−58.5	21.6
valeric acid	−147.1	−63.0	5.5	−140.7	−60.5	6.0	−136.0	−58.5	5.7

[a] dev. = $(100/n)\,\sum^{n}|K(\mathrm{exp}) - K(\mathrm{calc})|/K(\mathrm{exp})$, n = number of data points.

without any further purification. Valeric acid was purified by vacuum distillation, and its purity was more than 99.0%. Formic acid was purified by fractional freezing, and its purify was more than 99.7%. The chief impurity in each chemical was water. The purity of helium was reported by the supplier to be higher than 99.995%.

Results and Discussion

Compressibility Factor. The compressibility factors of several monocarboxylic acids under saturated vapor pressure were calculated with eq 3. The saturated vapor pressures were given by the Antoine equation whose parameters are presented in Table 1. The compressibility factors obtained are summarized in Table 2. These data are the averaged values of several data points at a given temperature. An error analysis with the maximum error estimated in each measurement shows 1.6% error. Further, experimental reproducibility indicates that the experimental error is within 3%. As shown in Figure 2, the compressibility factors of toluene, obtained to check the reliability of this experiment, coincide with Z values obtained by using the second virial coefficient data and also the correlation of Tsonopoulos (1974). Tsonopoulos has reported a generalized correlation method for the second virial coefficient. The second virial coefficients of toluene were converted to the compressibility factors at the saturated vapor pressures.

Association Constants. If only monomers and dimers are present in vapor phase and they are an ideal gas mixture, the compressibility factor and the saturated vapor pressure are expressed by the following equations (Jasperson et al., 1989)

$$Z = \frac{p_{\mathrm{m}} + p_{\mathrm{d}}}{p_{\mathrm{m}} + 2p_{\mathrm{d}}} \tag{4}$$

and

$$p^{\mathrm{s}} = p_{\mathrm{m}} + p_{\mathrm{d}} \tag{5}$$

where p^{s}, p_{m}, and p_{d} are the vapor pressure of acid (total pressure), monomer (partial pressure), and dimer (partial pressure), respectively. Jasperson et al. (1989) and Malijevska (1983) discussed the nonidealty of a monomer and dimer gaseous mixture. On the basis of their discussion, the error caused by the nonidealty was estimated within 2%. The quantities p_{m} and p_{d} can be obtained with eqs 4 and 5 using experimental Z and p^{s} data. The association constant, K, can be calculated with the following equation (Jasperson et al., 1989)

$$K \cong \frac{p_{\mathrm{d}}}{{p_{\mathrm{m}}}^{2}} \tag{6}$$

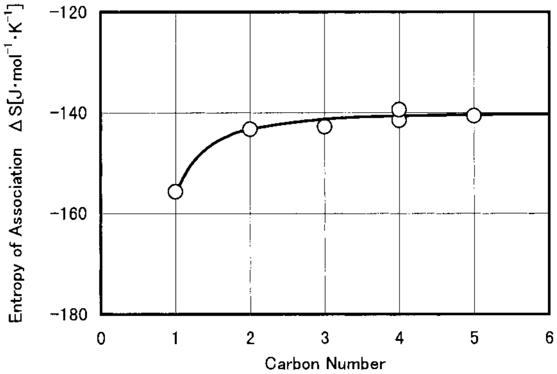

Figure 5. Entropy of association vs carbon number ($\Delta H = -60.5$ $kJ\cdot mol^{-1}$): (○) present work; (—) smoothed line.

where the fugacities of monomers and dimers are approximated by partial pressures and are reduced by the standard fugacity. The association constants are presented in Table 2 and Figures 3 and 4. In Figure 3, the association constants of formic acid are compared with the literature values. The present results are in good agreement with the literature (Barton and Hsu, 1969; Coolidge, 1928; Taylor and Bruton, 1952; Jasperson et al., 1989). Figure 4 shows the temperature dependence of association constants. It is found that the association constants can be represented by the following equation

$$\ln K = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

The values of ΔS and ΔH for each acid are shown in Table 3 (case 1). As shown in Figure 4, the slopes ($-\Delta H/R$) are almost the same. Therefore, ΔS for each acid was evaluated using constant ΔH (-60.5 $kJ\cdot mol^{-1}$) and is shown in Table 3 (case 2). Further, the relation between ΔS and the carbon number of the acid is illustrated in Figure 5. As indicated, ΔS is almost independent except for formic acid. Therefore, the association constants of other acids were recorrelated by assuming ΔS and ΔH are constants. The results are given in Table 3 (case 3). It is noted that the error of compressibility factor calculated is 2% though the error in the association constant is 20%.

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