

two methods. Both methods give reasonable estimation for the system of methane, carbon dioxide and the activated carbon fiber.

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Nomenclature

B	= second virial coefficient	$[\text{m}^3 \cdot \text{mol}^{-1}]$
C	= third virial coefficient	$[\text{m}^6 \cdot \text{mol}^{-2}]$
p	= pressure	$[\text{kPa}]$
q	= amount adsorbed per kilogram of adsorbent	$[\text{mol} \cdot \text{kg}^{-1}]$
T	= temperature	$[\text{K}]$
y	= mole fraction in gas phase	$[-]$

$\langle \text{Subscript} \rangle$

i = component i

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VAPOR PRESSURES OF ISOPROPYL, *t*-BUTYL AND 2-CHLOROETHYL BENZOATES AT REDUCED PRESSURES

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Key Words: Physical Property, Vapor Pressure, Isopropyl Benzoate, *t*-Butyl Benzoate, 2-Chloroethyl Benzoate

Introduction

As few experimental data for alkyl benzoates have been published, the vapor pressures of five benzoates—methyl, ethyl, *n*-propyl, isobutyl, and *n*-butyl benzoates—were recently measured at 0.5–30 kPa.¹¹⁾

In the present work, those of three benzoates— isopropyl, *t*-butyl, and 2-chloroethyl benzoates— were measured. The results were checked by fitting a Cragoe equation.

1. Experimental

All the special-grade materials from Tokyo Kasei Co., Ltd., were used without further purification. The purity of each was determined as exceeding 99% by gas chromatographic analyses with 3 mm-I.D. and 2 m-long columns of 5% silicone SE-52 on celite for isopropyl benzoate, of 20% silicone DC-550 on celite

for *t*-butyl benzoate, and of 5% silicone SE-30 on chromosorb-W for 2-chloroethyl benzoate.

Table 1 shows the densities and refractive indexes compared with published values.^{2–4,14,15,18)}

The experimental apparatus and procedure were already described elsewhere.^{10,11)} The equilibrium still with Cottrell pump, which was of vapor circulation type, was made of Pyrex glass. The measurement and the control of pressure were carried out with a Multi-Range Model 157/100 pressure standard from Texas Instruments Inc., which had a spiral quartz Bourdon gauge and a servo-controlled valve in a vacuum line. The accuracy of the gauge was ± 0.002 kPa for the 10–34 kPa range and ± 0.001 kPa for the 0.24–10 kPa range. The variation of pressure control on operation was read from the deviation meter to be within ± 0.00003 kPa for the 1–34 kPa range and within ± 0.0004 kPa for the 0.24–1 kPa range. The lower limits of pressure control depended on the extent to which the knobs of the gain and the amplitude in the

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Table 1. Densities ρ and refractive indexes n_D of three benzoates

	T [K]	ρ [kg/m ³]		n_D [—]	
		Exptl	Lit.	Exptl	Lit.
Isopropyl benzoate	293.15	1010.1 ^{*1)}	1012.2 ¹⁸⁾	1.4950 ^{*3)}	1.4948 ²⁾ 1.4949 ³⁾
<i>t</i> -Butyl benzoate	293.15	993.46 ^{*2)}	993.3 ¹⁸⁾	1.4903 ^{*3)}	1.4910 ⁴⁾
2-Chloroethyl benzoate	293.15	1202.49 ^{*2)}		1.52094 ^{*4)}	
	288.15		1208 ¹⁵⁾		
	298.15			1.5265 ^{*3)}	1.5249 ¹⁴⁾

*1) Commercial Ostwald pycnometers (10 ml) were used with error of ± 0.2 [kg/m³].
 *2) Pycnometers (50 ml) newly made from reference to Schroeder *et al.*¹⁷⁾ were used with error of ± 0.02 [kg/m³].
 *3) An Abbe refractometer was used with error of ± 0.0002 unit.
 *4) A dipping refractometer from Carl Zeiss Jena Co. was used with error of ± 0.00002 unit.

servomechanism could be adjusted finely by hand. The limits lay in the 0.24–0.4 kPa range.

The vapor pressures of isopropyl benzoate at atmospheric pressure were read by a mercury barometer of Fortin type with an error of ± 0.01 kPa.

Four mercury thermometers with immersion lines marked at the 18-cm points from their bulb ends, i.e., the set of 40–100, 100–150, 150–200 and 200–250°C graduations, were used for temperature measurements. They were calibrated at 5 K intervals with accuracies of ± 0.04 K by Watanabe Keiki Seisakusho Co., Ltd., Tokyo. The intermediate temperatures in the intervals were interpolated. After the circulation of vapor for one hour, fluctuations of the thermometers were not observed and were less than 0.02 K.

At temperatures of 436–448 K, which corresponded to 20–27.5 kPa vapor pressure of *t*-butyl benzoate, the benzoate in the still gradually acquired a brown color during the heating, but no change of temperature was observed during the 2-h heating.

At the higher temperature, 469 K, corresponding to 32.5 kPa, after the 2-h heating the benzoate was suddenly decomposed to another substance, which was distilled together with the benzoate as a vapor, and accumulated in the circulation reservoir of condensed liquid as white crystals. The substance was thought to be benzoic acid because of its 385–391 K melting point. No measurement of this benzoate at a point exceeding 448 K could be carried out.

2. Results and Discussion

The experimental results are presented in **Table 2**. The results are also plotted in **Fig. 1** including comparisons with values from the literature.^{2,4,5,7,9,12,16,18–20)}

The Chebyshev polynomial¹¹⁾ and the Cragoe,⁶⁾ Frost-Kalkwarf⁸⁾ and Antoine equations were used to fit the results.

The Chebyshev polynomial is:

Table 2. Vapor pressure of three benzoates

Isopropyl benzoate		<i>t</i> -Butyl benzoate		2-Chloroethyl benzoate	
T [K]	P [kPa]	T [K]	P [kPa]	T [K]	P [kPa]
490.75	100.39	448.05	27.500	466.20	17.500
490.65	100.28	445.21	25.000	461.76	15.000
449.81	34.000	438.25	20.000	442.80	7.500
445.74	30.000	434.30	17.500	426.47	4.000
442.85	27.500	429.86	15.000	419.50	3.000
439.73	25.000	424.50	12.500	410.03	2.000
436.46	22.500	418.32	10.000	403.70	1.500
432.80	20.000	410.53	7.500	395.32	1.000
428.81	17.500	400.14	5.000	393.38	0.900
424.25	15.000	394.66	4.000	391.06	0.800
419.01	12.500	387.90	3.000	388.53	0.700
415.47	11.000	378.86	2.000	385.80	0.600
412.81	10.000	364.92	1.000	382.46	0.500
405.13	7.500	360.66	0.800	378.81	0.400
394.86	5.000	358.25	0.700	374.22	0.300
382.70	3.000	355.55	0.600		
374.10	2.019	352.44	0.500		
368.00	1.500	348.78	0.400		
360.01	1.000	344.47	0.300		
358.31	0.919				
353.39	0.700				
347.47	0.500				
343.93	0.400				
337.35	0.261				
336.37	0.245				

$$t \ln(P) = a_0/2 + \sum a_i E_i(x) \quad (1)$$

where P kPa, $t (= T - 273.15)^\circ\text{C}$, TK , $E_1(x) = x$, $E_2(x) = 2x^2 - 1$, $E_i(x) = 2xE_{i-1}(x) - E_{i-2}(x)$, and x is a function of temperature defined as

$$x = \frac{2T - (T_{\max} + T_{\min})}{T_{\max} + T_{\min}} \quad (2)$$

where T_{\max} and T_{\min} are the maximum and minimum temperatures of the related substance, respectively.

The polynomial with four parameters is equivalent

Table 3. The percent root mean square deviations of pressure (prms)^{*1)} using Chebyshev polynomials, Frost-Kalkwarf and Antoine equations

	Chebyshev polynomials								Frost-Kalkwarf Eq.	Antoine Eq.
	3	4 ^{*2)}	5	6	7	8	9	10		
Isopropyl benzoate	5.31	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.67	1.03
<i>t</i> -Butyl benzoate	0.85	0.21	0.21	0.19	0.16	0.14	0.14	0.14	0.32	1.12
2-Chloroethyl benzoate	0.58	0.22	0.22	0.22	0.22	0.20	0.20	0.20	0.29	1.46

^{*1)} Prms was defined by $100 [\sum_i ((P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}})^2/n]^{1/2}$.

^{*2)} These values are identical with those of the Cragoe equation.

Table 4. Cragoe constants of three benzoates

	Isopropyl benzoate	<i>t</i> -Butyl benzoate	2-Chloroethyl benzoate
A_c	-2.40805	-1.33085	3.19375
B_c	-114.4181	-173.0528	-531.8495
C_c	0.484257×10^{-1}	0.383252×10^{-1}	0.414698×10^{-2}
D_c	-0.632303×10^{-4}	-0.350059×10^{-4}	0.435753×10^{-4}

to the Cragoe equation,* which is:

$$\ln(P) = A_c + B_c/t + C_c t + D_c t^2 \quad (3)$$

or

$$t \ln(P) = A_c t + B_c + C_c t^2 + D_c t^3 \quad (4)$$

The Frost-Kalkwarf equation is:

$$\ln(P) = A_f + B_f/t + C_f \ln t + D_f P/t^2 \quad (5)$$

or

$$t \ln(P) = A_f t + B_f + C_f t \ln t + D_f P/t \quad (6)$$

The Antoine equation is;

$$\ln(P) = A_a - B_a/(t + C_a) \quad (7)$$

or

$$t \ln(P) = A_a t + D_a - C_a \ln(P) \quad (8)$$

where $D_a = A_a C_a - B_a$.

As the relations between pressure and temperature in Eqs. (3), (5) and (7) are expressed as nonlinear relations, these equations with the constants, which are obtained by minimizing a linearized objective function, are feared to vary in accuracy according to the type of function selected. Here the least-square fit

* In the previous paper,¹⁰⁾ we described Eqs (3) or (4) as a Miller¹³⁾ equation, but it was found that the equation is more correctly called the Cragoe equation. However, the original Cragoe⁶⁾ equation is one having three constants A, B, and C as follows.

$$\log_{10}(P) = \frac{T - T_B}{T} \left\{ A - B \left(\frac{T - T_B}{T_B} \right) + C \left(\frac{T - T_B}{T_B} \right)^2 \right\}$$

where T [K], P [atm], and T_B [K] is the temperature at 1 atm.

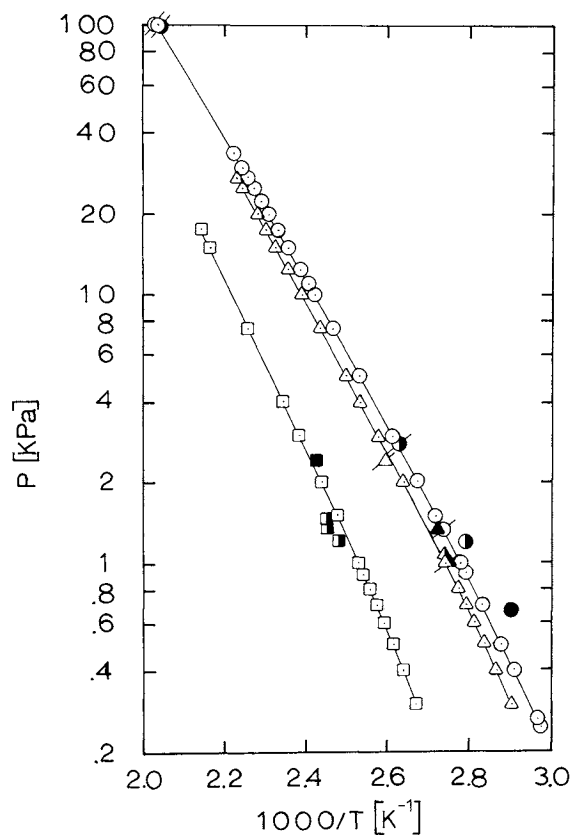


Fig. 1. Vapor pressures of three benzoates vs. $1/T$.

○, △, □ represent, isopropyl, *t*-butyl and 2-chloroethyl benzoates, respectively, in this work.

Isopropyl benzoate (○, Matsuno and Hann (1933); ●, Dorris *et al.* (1934); ○, Tommila (1942); ◐, Cohen (1944); ●, Bender (1951))

t-Butyl benzoate (▲, Pfannl (1911); △, Vavon *et al.* (1934); ◐, Cohen and Schneider (1941); ▲, Cohen (1944))

2-Chloroethyl benzoate (■, Zaki (1930); ◐, Goldfarb and Smorgonskii (1938))

All the real lines were drawn from the Cragoe equation with the constants of Table 4.

of $t \ln(P)$ was used as the function. The fit of $T \ln(P)$ was found to be far less accurate than that of $t \ln(P)$.

Table 3 shows the percent root mean square deviations of pressure (prms) using the Chebyshev polynomials with 3–10 parameters, the Frost-

Kalkwarf and Antoine equations.

For all three benzoates, the polynomial with four parameters, i.e., the Cragoe equation gives a good correlation as well.

The constants of the Cragoe equation are listed in **Table 4**. The constants of the Antoine and Frost-Kalkwarf equations are not listed, because these equations have larger errors than the Cragoe equation. The constants of the Chebyshev polynomial are not shown because the polynomial with four parameters is actually the Cragoe equation, as described above.

Conversely, the temperatures were calculated from the pressures by using the Cragoe, Frost-Kalkwarf, and Antoine equations. The mean temperature differences of the Cragoe, Frost-Kalkwarf and Antoine equations with the experimental values were taken as 0.03, 0.11 and 0.18 K, respectively, for isopropyl benzoate; 0.04, 0.05 and 0.22 K, respectively, for *t*-butyl benzoate; and 0.04, 0.05 and 0.28 K, respectively, for 2-chloroethyl benzoate.

Nomenclature

A_a, B_a, C_a	= Antoine constants defined by Eq. (7)	
D_a	= $A_a C_a - B_a$	
A_c, B_c, C_c, D_c	= Cragoe constants defined by Eq. (3)	
A_f, B_f, C_f, D_f	= Frost-Kalkwarf constants defined by Eq. (5)	
a_0, a_i	= constants of Chebyshev polynomial defined by Eq. (1)	
$E_1(x)$	= $-x$	[—]
$E_2(x)$	= $-2x^2 - 1$	[—]
$E_i(x)$	= $-2xE_{i-1}(x) - E_{i-2}(x)$	[—]
P	= pressure	[kPa]
T	= temperature	[K]

$$t = T - 273.15 \quad [^{\circ}\text{C}]$$

$$x = (2T - (T_{\max} + T_{\min})) / (T_{\max} + T_{\min}) \quad [—]$$

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KINETIC MODELING OF SIMULTANEOUS SACCHARIFICATION AND FERMENTATION OF CELLULOSE

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Key Words: Biochemical Engineering, Kinetic Modeling, Cellulose, Enzyme, Yeast, Simultaneous Saccharification Fermentation

Introduction

Cellulose is an abundant, renewable resource. However, chemical or biological treatment is required

to convert this polymeric form of glucose into useful materials. Takagi *et al.*^{1,2)} proposed an one-stage process involving the enzymatic saccharification of cellulose and simultaneous fermentation of the glucose by yeast in the one vessel (SSF). The courses of the concentration change of glucose and ethanol in

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