

## Vapor Pressure Determination for Individual Polychlorinated biphenyls and Commercial Fluids using the Knudsen Effusion Method

Katsuhiko Nakajoh<sup>1</sup>, Etsuro Shibata<sup>2</sup>, Tomohiro Todoroki<sup>3</sup>, Atsushi Ohara<sup>1</sup>,  
Katsushi Nishizawa<sup>1</sup>, Takashi Nakamura<sup>2</sup>

<sup>1</sup>PCB Detoxification Promotion Division□Industrial Power Systems and Services Company□Toshiba Corporation□Kawasaki

<sup>2</sup>Institute of Multidisciplinary Research for Advanced Materials (IMRAM)□Tohoku University, Sendai

<sup>3</sup>Environmental Technology Laboratory□Corporate Research & Development Center□Toshiba Corporation□Kawasaki

### Introduction

To understand and model the behaviour of polychlorinated biphenyls (PCBs) in the atmosphere, it is necessary to know the accurate vapor pressures of individual PCB congeners and commercial fluid PCBs, which are mixtures of numerous congeners. For developing suitable models, knowledge of the liquid phase vapor pressures as a function of temperature and experimental data at various temperatures are particularly important.

Experimental vapor pressures have been determined for a large number of PCB congeners<sup>1-5)</sup>, but usually only at a single temperature (e.g. 293 K or 298 K). Therefore, the required vapor pressures are often lacking, or are in some cases questionable.

In this study, we measured the vapor pressure of commercial Kanechlor fluids (Kanechlor300 and Kanechlor500) and 6 PCB congeners (major dichlorobiphenyls and trichlorobiphenyls) in Kanechlor300 using the Knudsen effusion method over a temperature range of 273 K to 368 K. Our focus here is on low vapor pressure solid or liquid at various temperatures. At room temperature, commercial PCB mixtures are liquids whereas most of the pure congeners are crystalline solids. To estimate the liquid phase vapor pressure (subcooled liquid,  $P_L$ ) of the congeners, we also measured their melting points and enthalpies of fusion using a modulated differential scanning calorimeter (modulated DSC). The thermodynamic parameters (enthalpies and entropies) of sublimation and vaporization were derived from the temperature dependence of the vapor pressure. From the thermodynamic correlation, we checked the reasonableness of our experimental vapor pressure data.

## Methods and Materials

**Materials:** We used the following chemicals for the vapor pressure determinations: Kanechlor300 (lot no.0617), Kanechlor500 (lot no.0712), 2,2'-dichlorobiphenyl (IUPAC no.4), 2,4'-dichlorobiphenyl (IUPAC no.8), 4,4'-dichlorobiphenyls (IUPAC no.15), 2,2',5-trichlorobiphenyl (IUPAC no.18), 2,4,4'-trichlorobiphenyl (IUPAC no.28), 2,4',5-trichlorobiphenyl (IUPAC no.31). All the chemicals were purchased from GL Science, Inc.

**Knudsen Effusion Method:** The Knudsen effusion method is a dynamic technique based on the rate of escape of vapor molecules through an orifice into vacuum. We have described the apparatus and procedure for the Knudsen effusion method in a separate report.<sup>6)</sup> The apparatus is especially designed for vapor pressure measurement of POPs, which are low-volatility chemicals. Due to the high toxicity and high cost of the PCBs, the sample amount used in each experiment has to be as small as possible, and so the size of the Knudsen effusion cell should also be as small as feasible. In this study, we have two types of aluminum effusion cell. One (Cell-A), used for the PCB congener, is a cylinder of internal diameter of 4.4mm, depth of 4.6mm and wall thickness of 0.1mm. The other (Cell-B), used for the commercial fluid PCBs, is a cylinder with internal diameter of 8mm, depth of 4mm and wall thickness of 0.1mm. There is an effusion hole coaxially located at the lid of the cell. The following orifice diameters were used: 0.15mm (Cell-A), 0.2mm (Cell-B-1) 0.3mm (Cell-B-2), 0.4mm (Cell-B-3).

The theoretical background of the method is the kinetic theory of gases, from which Knudsen derived an expression for the slow isothermal flow of vapors through orifices. The mass loss  $\Delta m$  of the sample in a specified period of time  $t$  is related to the vapor pressure near the orifice,  $p_k$  by

$$p_k = \{ \Delta m / A_o K_C t \} (2\pi R T / M)^{1/2} \quad (1)$$

where  $A_o$  is the area of the effusion orifice,  $M$  is the molecular weight of the effusing vapor,  $T$  is the absolute temperature,  $R$  is the gas constant, and  $K_C$  is the Clausing probability factor of the orifice, which is cited in the literature.<sup>7)</sup>

The Knudsen cell, because of the continuous loss of vapor thorough the orifice, is not really an equilibrium pressure  $p_{eq}$ . Therefore, the vapor pressure  $p_k$  calculated from the rate of effusion may be less than the equilibrium pressure  $p_{eq}$ . For a Knudsen cell in which height equals diameter, Whitman and Motzfeldt have shown that  $p_{eq}$  and  $p_k$  are related to through the equation:

$$p_{eq} = p_k [1 + K_C A_o / (\alpha A_s)] \quad (2)$$

where  $A_o$  is the area of the cross-section of the cell, and  $\alpha$  is the condensation coefficient, which is a characteristic of the particular compound. For typical Knudsen cell dimensions,  $A_o / A_s \ll 0.01$  and for  $\alpha \approx 1$  the experimental error is great enough to mask the difference between  $p_{eq}$  and  $p_k$ . This study thereby employed equation (1) to evaluate vapor pressure of sample.

The vaporization, or sublimation enthalpy and entropy of the sample can be obtained using the Clausius-Clapeyron equation (3).

$$\ln p = -(\Delta H_{vap}/R) / T + \Delta S_{vap}/R \quad (3)$$

**DSC Methods:** We determined the melting point ( $T_m$ ), enthalpies ( $\Delta H_{fus}$ ) and entropies ( $\Delta S_{fus}$ ) of fusion for PCB congeners using a modulated DSC (TA Instruments heat flux calorimeter, model DSC 2920) in an Ar flow at a rate of 40ml/min. Sample of about 10 mg were hermetically sealed in aluminum pans. The heating rate was 1 K/min. from 298 K-523 K. Conversion of the vapor pressure of the crystalline solid ( $P_S$ ) to that of the (subcooled) liquid state ( $P_L$ ) is possible using equation (4)

$$\ln(P_S / P_L) = -(\Delta S_{fus} / R) [(T_m / T) - 1] \quad (4)$$

where  $\Delta S_{fus}$  is entropy of fusion. Because melting is a reversible isothermal process,  $\Delta S_{fus}$  can be calculated from  $\Delta H_{fus}$  using  $\Delta S_{fus} = \Delta H_{fus} / T_m$ .

**GC/MS-SIM Analysis:** For quantification and identification of the PCB congeners, we performed GC-MS analyses using a HP 6890 series gas chromatograph with an HT8-PCB column (60 m, 0.25mm i.d., 0.33 $\mu$ m film thickness, SGE) and an AutoSpec Ultima mass spectrometer (Micromass).

## Results and Discussion

**Vapor pressure of commercial PCBs:** The experimental results of vapor pressure, enthalpy and entropy for Kanechlors obtained for individual cell and overall are given in Table1. Our results show no significant variation of  $p$  and reproducible result with different orifice size, which might mean the Knudsen cells employed in this study are suitable in order to obtain the accurate and stable data.

In Fig.1 we compare the experimental vapor pressures for the Kanechlors used in this study with literature values.<sup>8)</sup>

Table 1: Vaporization enthalpies and entropies of commercial PCBs.

Commercial PCBs	Knudsen Cell	Temperature range (T/K)	$\ln(p/\text{Pa}) = a - b \square (K/T)$		Correlation coefficient	$\Delta S_{vap}(T)$ $\text{J} \square \text{mol}^{-1} \square \text{K}^{-1}$	$\Delta H_{vap}(T)$ $\text{kJ} \square \text{mol}^{-1}$
			$a$	$b$			
Kanechlor 300	Cell-B-1	308 – 328	25.39 $\pm$ 0.61	8.4362 $\pm$ 0.194	0.9981	211.09	70.13 $\pm$ 1.61
	Cell-B-2	308 – 348	24.62 $\pm$ 0.38	8.1934 $\pm$ 0.124	0.9984	204.69	68.12 $\pm$ 1.03
	Cell-B-3	273 – 333	25.61 $\pm$ 0.60	8.5167 $\pm$ 0.181	0.9951	212.92	70.81 $\pm$ 1.51
	overall	273 – 348	25.14 $\pm$ 0.42	8.3715 $\pm$ 0.129	0.9972	209.01	69.60 $\pm$ 1.07
Kanechlor 500	Cell-B-1	333 – 368	23.71 $\pm$ 0.19	8.6423 $\pm$ 0.065	0.9996	197.04	71.85 $\pm$ 0.54
	Cell-B-2	308 – 353	23.85 $\pm$ 0.35	8.7030 $\pm$ 0.116	0.9986	198.29	72.36 $\pm$ 0.96
	Cell-B-3	298 – 343	23.65 $\pm$ 0.60	8.6371 $\pm$ 0.191	0.9962	196.63	71.81 $\pm$ 1.59
	overall	298 – 368	23.79 $\pm$ 0.22	8.6759 $\pm$ 0.072	0.9991	197.79	72.13 $\pm$ 0.60

The experimental vapor pressures for Kanechlor300 and Kanechlor500 are in good agreement with literature values<sup>2)</sup> of Aroclor 1242 and Aroclor 1254 (Aroclor 1242 and Aroclor 1254 correspond to KC300 and KC500, respectively) which were calculated using the vapor pressures of the individual PCB congener assuming Raoult's Law. The temperature dependence of the vapor pressures of the Kanechlors is linear ( $r^2=0.9972$ - $0.9991$ ), even though these materials are mixtures of PCB congeners. This suggests that the vapor pressures of Kanechlor300 and 500 in the experimental temperature range are largely dominated by a few of the more volatile PCB congeners.

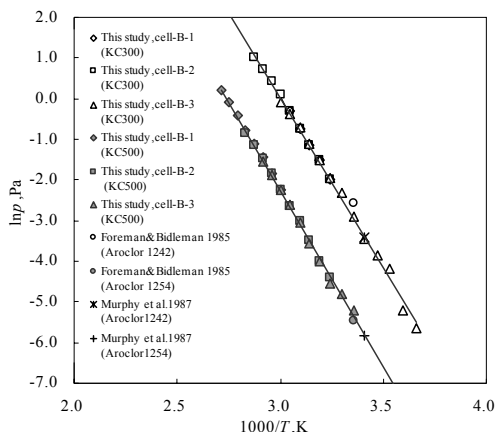


Fig.1: Vapor pressures of commercial PCB mixtures.

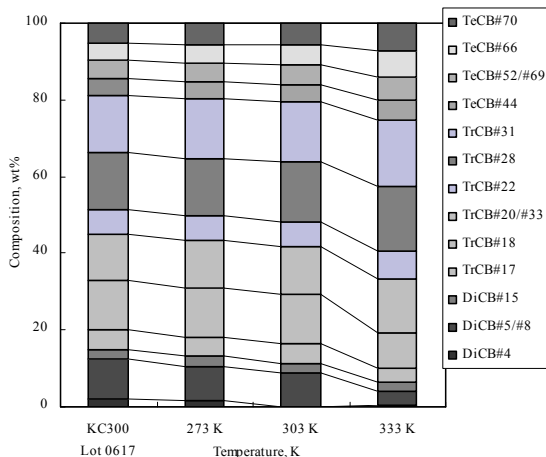


Fig.2: Relative composition of the major PCB congeners remaining in KC300 after vaporization at various temperatures.

Fig.2 shows the major PCB components of Kanechlor300 and the change in the composition of the remaining liquid KC300 after the vaporization at several temperatures in the region from 273K to 333K. The time of vaporization at each temperature was fixed for 10 hr. In this temperature range, vaporization of the dichlorobiphenyls and the trichlorobiphenyls are predominant. These components are most likely to be enriched in gaseous PCB emissions at ambient temperature.

**Vapor pressures of PCB congeners:** To convert from  $P_S$  to  $P_L$ , we determined  $T_m$  and  $\Delta H_{fus}$  from the modulated DSC data. The entropy of fusion ( $\Delta S_{fus}$ ) and vapor pressure ( $P_S$  and  $P_L$ ) results are given in Table 2 for the major PCB congeners, which are crystalline solid at room temperature.

The experimental vapor pressures for 3 dichlorobiphenyls and 3 trichlorobiphenyls as function of temperature are shown in Fig.3 and Fig.4, respectively. For comparison, the data reported in the literatures<sup>1)-3), 9), 10)</sup> are plotted together in Figs. 3 and 4. For #8 (as subcooled liquid and solid), #15 (as subcooled liquid and solid), and #31 (as subcooled liquid), the experimental vapor pressure results of this study are reasonable agreement with the literature values.

The vapor pressures of the dichlorobiphenyls decreased in the order #4 > #8 > #15, and the vapor pressures of trichlorobiphenyls decreased in the order #18 > #28, #31. We note that within homologous series, the greater is the number of ortho chlorine substituents, the higher is the vapor pressure, due to the “ortho-effect”.<sup>1)</sup> The subcooled liquid data, which we converted from the solid vapor pressures measured in this study, fall on a line extrapolated from the liquid phase vapor pressure data ( $r^2=0.9982-0.9993$ ). This suggests that the experimental vapor pressure data for solid and liquid determined in this study are reasonable. From their temperature dependencies of Eq.3, the vaporization enthalpies of the congeners were derived and shown in Table 2.

Table 2: Entropy of fusion and vapor pressure results of major PCB congeners in Kanechlor 300.

PCBs (Congener No.)	$\Delta H_{\text{fus}}$ $\text{kJ mol}^{-1}$	$\Delta S_{\text{fus}}$ $\text{J mol}^{-1} \text{K}^{-1}$	$P_S(298 \text{ K})^*$ Pa	$P_L(298 \text{ K})$ Pa	$\Delta H_{\text{vap}}(T)$ $\text{kJ mol}^{-1}$
2,2'-DiCB (#4)	16.6	50.0	0.22	0.42	71.46±2.17 (313 to 328 K)
2,4'-DiCB (#8)	18.0	56.8	0.11	0.17	75.75±1.47 (303 to 320 K)
4,4'-DiCB (#15)	22.8	54.2	0.0032	0.047	79.17±1.15 (328 to 358 K)
2,2',5-TriCB (#18)	16.9	53.5	0.062	0.092	76.25±1.18 (303 to 333 K)
2,4,4'-TriCB (#28)	18.7	56.8	0.017	0.033	79.44±0.86 (313 to 343 K)
2,4',5-TriCB (#31)	19.8	58.9	0.012	0.026	83.57±1.40 (318 to 353 K)

\* Extrapolated values.

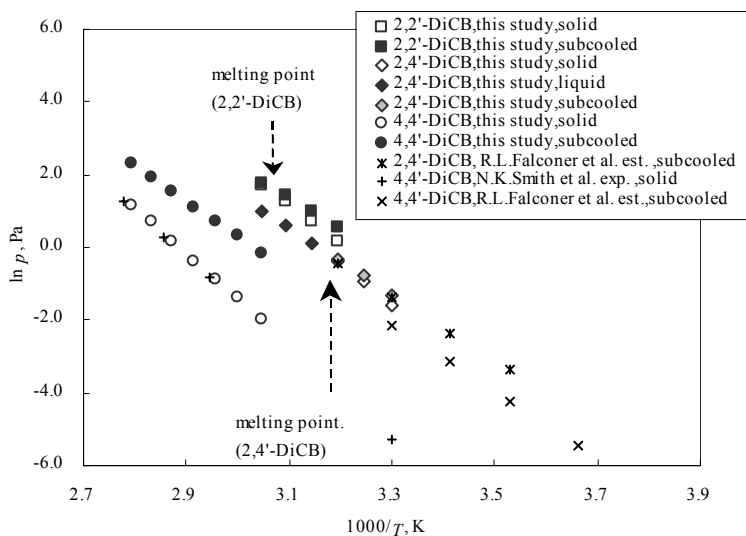


Fig.3: Vapor pressures of 2,2'-, 2,4'-, 4,4'-dichlorobiphenyls obtained in this study and the literatures.

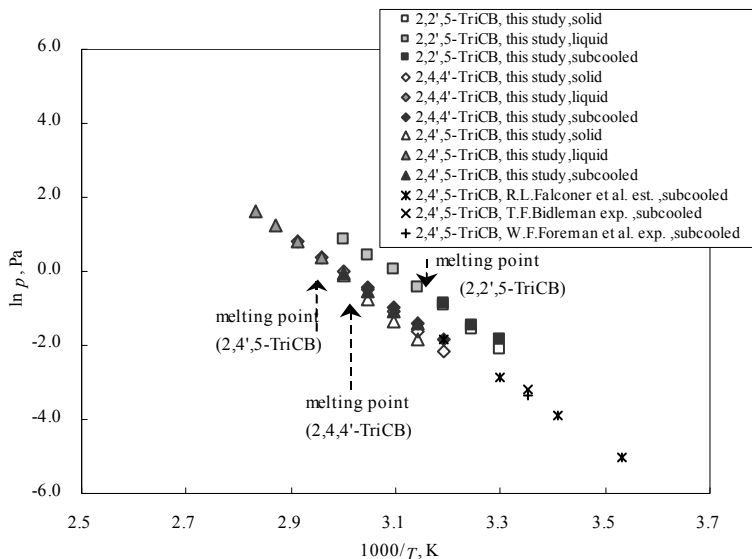


Fig.4: Comparison of the vapor pressure data for 2,2',5-, 2,4,4'-, 2,4',5-trichlorobiphenyls obtained in this study and the literature.

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