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TORSION–KNUDSEN EFFUSION VAPOUR-PRESSURE MEASUREMENT OF *o*, *m* AND *p*-CHLOROBIPHENYLS

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ABSTRACT

The torsion method and a coupled torsion–Knudsen effusion apparatus were used to measure the vapour pressures of *o*, *m* and *p*-chlorobiphenyls. The equations selected were: *o*-chlorobiphenyl(l), $\log P(\text{kPa}) = (10.48 \pm 0.50) - (4149 \pm 230)/T$; *m*-chlorobiphenyl(l), $\log P(\text{kPa}) = (8.68 \pm 0.47) - (3614 \pm 188)/T$; *p*-chlorobiphenyl(s), $\log P(\text{kPa}) = (9.44 \pm 0.63) - (3849 \pm 200)/T$; and *p*-chlorobiphenyl(l), $\log P(\text{kPa}) = (8.28 \pm 0.55) - (3541 \pm 250)/T$. The free energy functions, $(G^\circ_T - H^\circ_{298})/T$, for gaseous *o* and *p*-chlorobiphenyls were also estimated.

INTRODUCTION

The only vapour pressure values of *o* and *p*-chlorobiphenyls were those reported by Stull [1] and those measured by Geidarov [2] using a quartz manometer. With regard to *m*-chlorobiphenyl, no vapour data are reported in the literature except for two boiling points at 150–160°C and 87°C under pressures of 6 and 0.15 mm Hg, respectively, as reported by Beilstein [3].

As part of our program on the vaporization study of pure organic substances, vapour pressure values of *o*, *m* and *p*-chlorobiphenyls were measured using techniques based on the molecular effusion.

EXPERIMENTAL PROCEDURE AND RESULTS

Commercial *o*, *m* and *p*-chlorobiphenyls were supplied by INC Farmaceuticals.

The vapour pressures of the compounds were measured by the torsion–effusion method employing a conventional apparatus similar to that described previously [4] and by using a new apparatus in which the torsion–effusion equipment is suspended from an electrobalance. In the torsion–effusion method, at each temperature the pressure in the effusion cell can be

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determined by its torsion angle, α, from the relation [5]

$$P = \frac{2K\alpha}{a_1 l_1 f_1 + a_2 l_2 f_2}$$

where K is the torsion constant ($0.346 \pm 0.003\ 10^{-5}$ N m) of the torsion tungsten wire; a_1, a_2, l_1 and l_2 are the areas of the effusion orifices and their distances from the rotation axis, respectively; and f_1 and f_2 are the corresponding geometrical factors derived from the equation [6]

$$\frac{1}{f} = 0.0147\left(\frac{R}{r}\right)^2 + 0.3490\left(\frac{R}{r}\right) + 0.9982$$

where r and R are the radius and thickness of the effusion hole, respectively.

The vapour pressure values can also be determined by the Knudsen effusion method [7] from the rate of mass loss (dm/dt) of the sample produced from a Knudsen cell using the equation

$$P(\mathrm{kPa}) = 2.29K'\frac{\mathrm{d}m}{\mathrm{d}t}\left(\frac{T}{m}\right)^{1/2} S$$

were S and K' are the area and Clausing's factor [8] of the effusion hole of

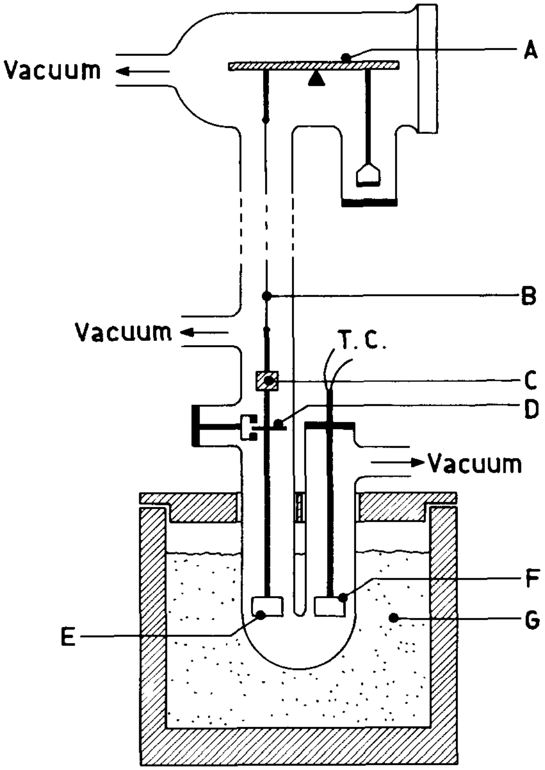

Fig. 1. Torsion–Knudsen assembly. A, Electrobalance; B, tungsten torsion wire; C, reflecting mirror; D, braking disc; E, torsion cell; F,' twin cell; G, thermostatic sand bath.

the cell, respectively, and M is the molar weight of the vapour.

With appropriate coupling of both methods, two simultaneous vapour pressure values of the system under study can be measured for each experimental temperature. The experimental apparatus consists of a conventional torsion–effusion apparatus, with the cell having knife-edge effusion holes in order to obtain the Knudsen conditions, suspended under vacuum from one pan of a thermobalance. Figure 1 shows a schematic representation of this apparatus. The torsion cell is heated by a thermostatic fluidised sand bath TECAM SLB-1 thermostatically maintained within ±0.2°C. The temperature of the cell was measured by a calibrated iron–copper thermocouple inserted in a cell similar to the effusion one and placed at the same level (see Fig. 1). A check of the reliability of this procedure in the temperature measurements showed that in the range 300–450 K, the temperature difference between the two cells is comparable with the sensitivity of their measurements. At each experimental temperature the rate of mass loss was determined by a RH Chan electrobalance coupled with a Philips PM 8252 recorder. The sensitivity of the electrobalance allowed determination of weight loss corresponding to pressures of about 10^{-5} kPa.

In order to test the apparatus, the vapour pressure of pure mercury as standard was measured. At each temperature the pressures derived simultaneously with both techniques agree within 5%. Moreover, the average heat of vaporization, $\Delta H_{\mathrm{T}} = 61.9 \pm 1.6$ kJ mole^{-1}, obtained by second and third-law treatment of the average vapour pressure data was in very good agreement with that selected by Hultgren et al. [9] (61.4 ± 0.1 kJ mole^{-1}).

Torsion–Knudsen effusion results

Table 1 and Fig. 2 show, for each experimental temperature, P (torsion) and P (Knudsen) values determined simultaneously by the two techniques

TABLE 1

Geometrical constants of the cells used in the torsion and in the simultaneous torsion–Knudsen methods

Cell		Orifice area × 10^4 (cm^2)		Moment arm (cm)		Correction factor
A	a_1	5.06 ± 0.03	l_1	0.85 ± 0.05	f_1^{a}	0.45
(pyrophillite)	a_2	5.06 ± 0.03	l_2	0.83 ± 0.05	f_2	0.49
B	a_1	75.4 ± 0.1	l_1	0.98 ± 0.05	S_1^{b}	0.79
(graphite)	a_2	75.4 ± 0.1	l_2	0.96 ± 0.05	S_2	0.81
C	a_1	7.07 ± 0.03	l_1	2.02 ± 0.05	S_1^{b}	0.65
(graphite)	a_2	7.07 ± 0.03	l_2	2.07 ± 0.05	S_2	0.68

[a] Freeman's factor [6].

[b] Clausing's factor [8].

TABLE 2

Vapour pressures of *o*, *m* and *p*-chlorobiphenyls measured by the torsion–Knudsen effusion method

Substance	Run	T (K)	Torsion		Knudsen		P, ave. (kPa)
			α (degree)	P (kPa)	dm/dt (10^5) (g min^{-1})	P (kPa)	
o-Chlorobiphenyl	38.09	323	2	1.03×10^{-2}	0.36	1.73×10^{-2}	1.38×10^{-2}
	cell C	327	2.5	1.09×10^{-2}	0.40	1.92×10^{-2}	1.00×10^{-2}
		332	3	1.62×10^{-2}	0.51	2.48×10^{-2}	2.05×10^{-2}
		336	4	2.56×10^{-2}	0.75	3.69×10^{-2}	3.32×10^{-2}
	38.10	323	1.5	0.81×10^{-2}	0.27	1.28×10^{-2}	1.04×10^{-2}
	cell C	332	2.5	1.58×10^{-2}	0.47	2.29×10^{-2}	2.06×10^{-2}
		341	6	3.41×10^{-2}	1.04	5.11×10^{-2}	4.61×10^{-2}
		346	8	4.43×10^{-2}	1.32	6.55×10^{-2}	5.90×10^{-2}
		350	10	6.33×10^{-2}	1.72	8.58×10^{-2}	7.80×10^{-2}
		354	14	8.35×10^{-2}	2.30	1.15×10^{-1}	9.92×10^{-2}
		359	20	1.20×10^{-1}	3.21	1.63×10^{-1}	1.42×10^{-1}
	38.15	301	1	7.62×10^{-4}	0.43	1.50×10^{-3}	1.13×10^{-3}
	cell B	306	2	1.52×10^{-3}	0.64	2.36×10^{-3}	1.93×10^{-3}
		310	3	2.30×10^{-3}	0.93	3.42×10^{-3}	2.85×10^{-3}
		313	4	3.05×10^{-3}	1.12	4.13×10^{-3}	3.59×10^{-3}
		319	5	3.81×10^{-3}	1.38	5.17×10^{-3}	4.50×10^{-3}
		323	6	4.57×10^{-3}	1.61	6.10×10^{-3}	5.34×10^{-3}
		327	8	6.10×10^{-3}	2.56	9.69×10^{-3}	7.90×10^{-3}
m-Chlorobiphenyl	40.13	310	2	1.52×10^{-3}	0.44	2.43×10^{-3}	1.97×10^{-3}
	cell B	313	3	2.29×10^{-3}	0.65	3.62×10^{-3}	2.96×10^{-3}
		319	4	3.05×10^{-3}	0.73	4.12×10^{-3}	3.58×10^{-3}
		323	5	3.81×10^{-3}	1.10	6.23×10^{-3}	5.02×10^{-3}
		327	7	8.33×10^{-3}	1.50	8.53×10^{-3}	6.93×10^{-3}
		332	11	8.38×10^{-3}	2.23	1.29×10^{-2}	1.06×10^{-2}

		336	15	1.14×10^{-2}	3.10	1.80×10^{-2}	1.47×10^{-2}
		341	19	1.45×10^{-2}	3.87	2.25×10^{-2}	1.54×10^{-2}
		346	26	1.98×10^{-2}	5.10	3.00×10^{-2}	2.49×10^{-2}
		350	37	2.82×10^{-2}	7.40	4.32×10^{-2}	3.57×10^{-2}
	40.14	332	2	1.36×10^{-2}	0.40	1.91×10^{-2}	1.63×10^{-2}
	cell C	336	2.5	1.58×10^{-2}	0.46	2.23×10^{-2}	1.90×10^{-2}
		341	3	2.34×10^{-2}	0.58	2.90×10^{-2}	2.62×10^{-2}
		346	4	2.75×10^{-2}	0.72	3.56×10^{-2}	3.15×10^{-2}
		350	5.5	3.37×10^{-2}	0.92	4.62×10^{-2}	4.00×10^{-2}
		354	7.5	4.73×10^{-2}	1.27	6.36×10^{-2}	5.54×10^{-2}
		359	10	6.32×10^{-2}	1.68	8.49×10^{-2}	7.40×10^{-2}
p-Chlorobiphenyl	45.5	306	1	7.62×10^{-4}	0.13	6.97×10^{-4}	7.29×10^{-4}
	cell B	310	2	1.52×10^{-3}	0.16	9.02×10^{-4}	1.21×10^{-3}
		323	4	3.05×10^{-3}	0.63	3.57×10^{-3}	3.31×10^{-3}
		327	5	3.81×10^{-3}	0.86	4.90×10^{-3}	4.38×10^{-3}
		332	8	6.10×10^{-3}	1.28	7.41×10^{-3}	6.75×10^{-3}
		336	12	9.14×10^{-3}	1.79	1.04×10^{-2}	9.77×10^{-3}
		346	28	2.13×10^{-2}	3.12	1.83×10^{-2}	1.98×10^{-2}
	45.7	308	1	7.62×10^{-4}	0.16	9.17×10^{-4}	8.40×10^{-4}
	cell B	314	2	1.52×10^{-3}	0.25	1.41×10^{-3}	1.47×10^{-3}
		317	3	2.29×10^{-3}	0.30	1.72×10^{-3}	2.00×10^{-3}
		323	4	3.05×10^{-3}	0.50	2.85×10^{-3}	2.95×10^{-3}
		325	5	3.81×10^{-3}	0.78	4.44×10^{-3}	4.12×10^{-3}
		330	7	5.33×10^{-3}	1.05	6.04×10^{-3}	5.69×10^{-3}
		334	10	7.62×10^{-3}	1.46	8.43×10^{-3}	8.03×10^{-3}
		335	11	8.38×10^{-3}	1.88	1.09×10^{-2}	9.66×10^{-3}
		338	14	1.07×10^{-2}	1.90	1.08×10^{-2}	1.08×10^{-2}
		340	17	1.29×10^{-2}	2.91	1.19×10^{-2}	1.24×10^{-2}
		341	18	1.37×10^{-2}	2.59	1.29×10^{-2}	1.33×10^{-2}
		342	20	1.52×10^{-2}	2.39	1.39×10^{-2}	1.46×10^{-2}
		346	28	2.11×10^{-2}	3.17	1.86×10^{-2}	1.53×10^{-2}

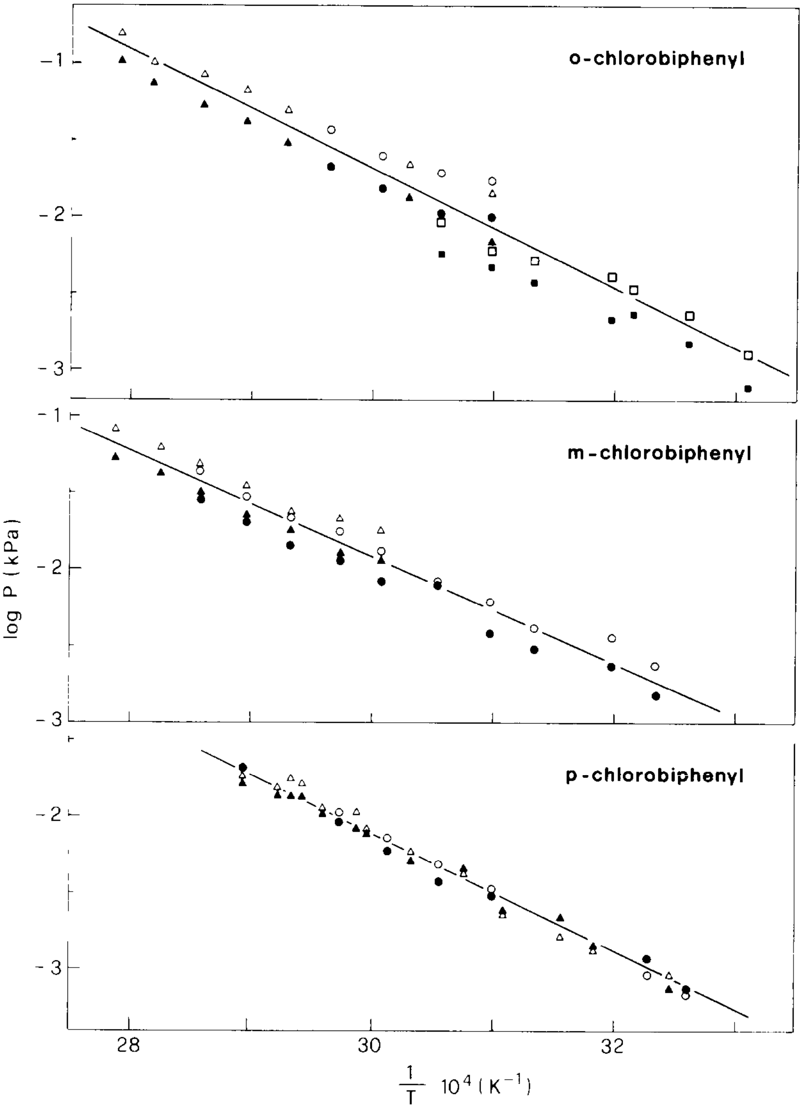

Fig. 2. Vapour pressure of *o*, *m* and *p*-chlorobiphenyls by the torsion–Knudsen effusion method. ▲, ■, ●, Torsion data; △, □, ○, Knudsen data; ———, equations obtained by elaborating the average data.

over liquid *o* and *m*-chlorobiphenyls and solid *p*-chlorobiphenyl. The geometrical constants of the graphite cells are reported in Table 2. In particular, to avoid the overflow of *m*-chlorobiphenyl from the cell owing to its wettability, a teflon liner was employed. The pressures obtained by the Knudsen method have been calculated assuming that the compounds vaporize congruently as monomeric gas. At each temperature an average of the two vapour pressure values was derived and, from the least-squares treatment of these data for each compound, the following equations were calculated

o-chlorobiphenyl$_{(l)}$, $\log P(\mathrm{kPa}) = (9.99 \pm 0.33) - (3893 \pm 108)/T$ (306–359 K) (1)

m-chlorobiphenyl$_{(l)}$, $\log P(\mathrm{kPa}) = (8.45 \pm 0.26) - (3458 \pm 87)/T$ (310–359 K) (2)

p-chlorobiphenyl$_{(s)}$, $\log P(\mathrm{kPa}) = (9.44 \pm 0.13) - (3849 \pm 36)/T$ (306–346 K) (3)

where the errors quoted are the standard deviations.

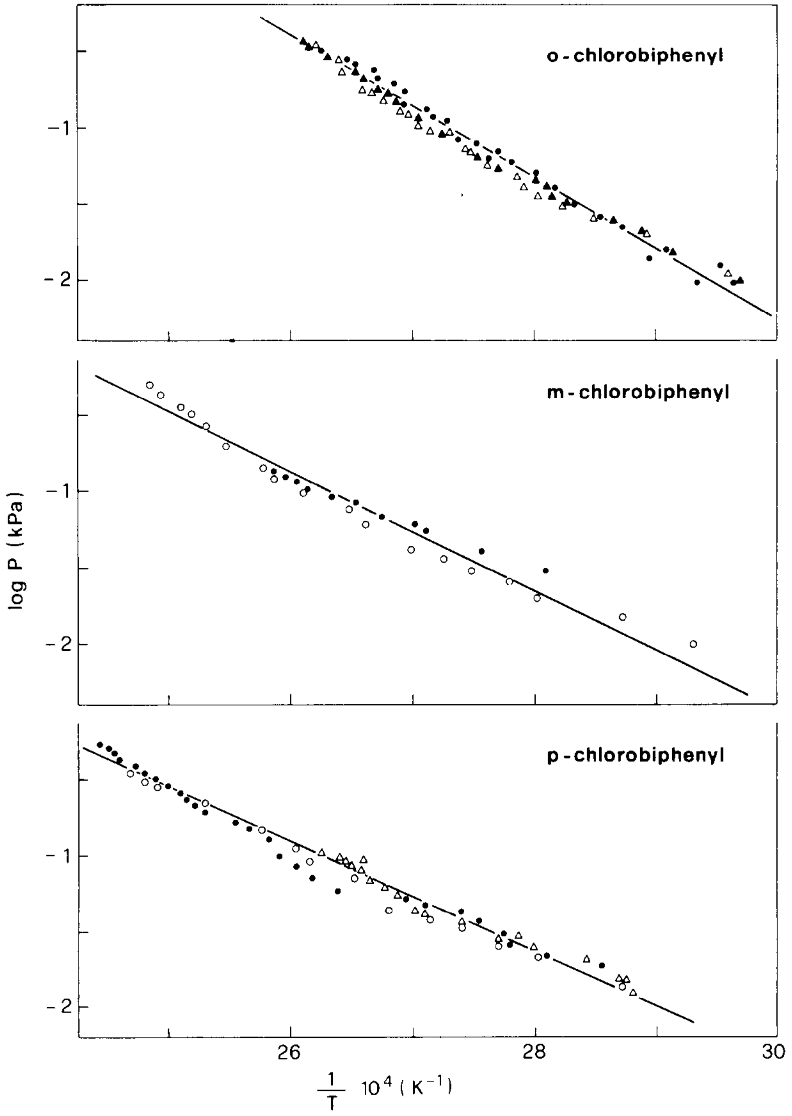

Fig. 3. Vapour pressure of o, m and p-chlorobiphenyls measured by the torsion method.

Torsion effusion results

Figure 3 shows the vapour pressure values over liquid *o*, *m* and *p*-chlorobiphenyls as measured by a conventional torsion apparatus. The geometrical constants of the pyrophillite cells are reported in Table 2. In these experiments, for each compound all the measured vapour pressures are treated by the least-squares method and their temperature dependences are given by the equations

$$o\text{-chlorobiphenyl}_{(1)},\ \log P(\mathrm{kPa}) = (10.98 \pm 0.15) - (4406 \pm 54)/T \quad (337\text{–}383\ \mathrm{K}) \qquad (4)$$

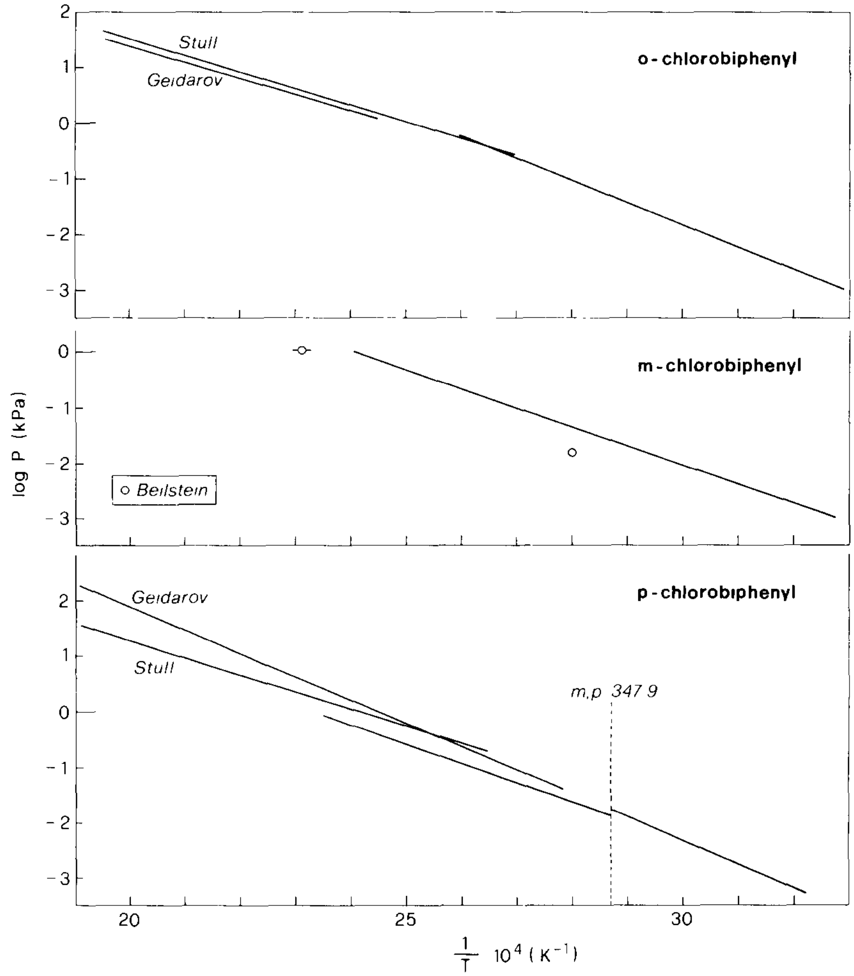

Fig. 4. Comparison of the vapour pressure data for *o*, *m* and *p*-chlorobiphenyls obtained here and in the literature.

TABLE 3

Free energy functions (f.e.f.) at 298 K of gaseous *o* and *p*-chlorobiphenyls

Liquid *o*-chlorobiphenyl				Solid *p*-chlorobiphenyl				Liquid *p*-chlorobiphenyl			
T (K)	P^{a} (kPa)	−(f.e.f.) (s) (J mole^{-1} K^{-1})	−(f.e.f.) (g) (J mole^{-1} K^{-1})	T (K)	P^{b} (kPa)	−(f.e.f.) (s) (J mole^{-1} K^{-1})	−(f.e.f.) (g) (J mole^{-1} K^{-1})	T (K)	P^{c} (kPa)	−(f.e.f.) (s) (J mole^{-1} K^{-1})	−(f.e.f.) (g) (J mole^{-1} K^{-1})
304.8	7.37×10^{-4}	304	4698	300	4.07×10^{-4}	258	412	347.9(l)	1.26×10^{-2}	260	408
320	3.27×10^{-3}	307	5148	320	2.58×10^{-3}	259	413	360	2.77×10^{-2}	264	411
340	1.89×10^{-2}	311	5164	340	1.31×10^{-2}	259	412	380	9.15×10^{-2}	272	417
360	9.01×10^{-2}	316	5186	347.9(s)	2.32×10^{-2}	260	413	400	2.68×10^{-1}	277	422
380	3.64×10^{-1}	320	5207								

[a] Calculated from eqn. (7).

[b] Calculated from eqn. (3).

[c] Calculated from eqn. (6).

m-chlorobiphenyl$_{(l)}$, $\log P(\mathrm{kPa}) = (8.91 \pm 0.28) - (3771 \pm 104)/T$
(341–402 K) (5)

p-chlorobiphenyl$_{(l)}$, $\log P(\mathrm{kPa}) = (8.28 \pm 0.12) - (3541 \pm 123)/T$
(348–409 K) (6)

where the associated errors are standard deviations.

CONCLUSIONS

The vapour pressures of *o*, *m* and *p*-chlorobiphenyls were determined by the torsion and the simultaneous torsion–Knudsen methods. From the results obtained the pressure–temperature equations selected were

o-chlorobiphenyl$_{(l)}$, $\log P(\mathrm{kPa}) = (10.48 \pm 0.50) - (4149 \pm 230)/T$ (7)

m-chlorobiphenyl$_{(l)}$, $\log P(\mathrm{kPa}) = (8.68 \pm 0.47) - (3614 \pm 188)/T$ (8)

p-chlorobiphenyl$_{(s)}$, $\log P(\mathrm{kPa}) = (9.44 \pm 0.63) - (3849 \pm 200)/T$ (3)

p-chlorobiphenyl$_{(l)}$, $\log P(\mathrm{kPa}) = (8.28 \pm 0.55) - (3541 \pm 250)/T$ (6)

The errors quoted were estimated taking into account the uncertainties in the temperature measurements (± 1.5°C) and in the calibration factors. Even if the number of pressure points obtained by the torsion–Knudsen method is smaller than those derived by the torsion method, their values are more reliable, so that the selected slopes and intercepts of *o* and *m*-chlorobiphenyls were evaluated as the average of the corresponding values of eqns. (1) and (4), and (2) and (5), respectively. Figure 4 shows our results compared with those found in literature: the comparison shows a substantial agreement of the data. With regard to *o*-chlorobiphenyl, our slope is higher than those proposed by Stull [1] and by Geidarov [2], while our *p*-chlorobiphenyl torsion results seem to be slightly lower than the literature and our torsion–Knudsen data.

From the slopes of the selected pressure–temperature equations, the second-law vaporization enthalpies of the compounds studied were derived: $\Delta H^\circ_{342}(o)_{(l)} = 79.4 \pm 4.4$, $\Delta H^\circ_{356}(m)_{(l)} = 69.2 \pm 3.6$, $\Delta H^\circ_{378}(p)_{(l)} = 67.8 \pm 3.8$ and $\Delta H^\circ_{326}(p)_{(s)} = 73.7 \pm 4.8$ kJ mole^{-1}.

Considering that the free energy functions, $(G^\circ_T - H^\circ_{298})/T$, of solid *o* and *p*-chlorobiphenyls can be evaluated from thermodynamic data reported in literature, the vapour pressure data of these compounds are treated by the third law in order to estimate the corresponding free energy functions of gaseous compounds by using the equation

$$\frac{G^\circ_T - H^\circ_{298(g)}}{T} = -R\ln P - \frac{\Delta H^\circ_{298}}{T} + \frac{G^\circ_T + H^\circ_{298(s)}}{T}$$

The standard vaporization enthalpies of both compounds. $\Delta H^\circ_{298}(o) = 93.9$ and $\Delta H^\circ_{298}(p) = 77.4$ kJ mole^{-1} were obtained using only the corresponding heats of fusion, 14.51 [10] and 13.32 [11] kJ mole^{-1} for *o* and *p*-chlorobiphenyls, respectively. The value for *p*-chlorobiphenyl is the average of two data derived from eqns. (3) and (6).

The entropies and the enthalpic functions used for the solid free energy functions calculations have been obtained by extrapolating the literature data [10,11]. The free energy functions so calculated are reported in Table 3.

The gaseous free energy functions of *o*-chlorobiphenyl are higher than those calculated for the gaseous *p*-chlorobiphenyl and this is essentially due to the difference of the values of S°_T and the standard sublimation enthalpies of the two compounds.

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