Table IV. Hypersonic Velocity and Dynamic Isentropic Compressibility for 60% (v/v) Benzonitrile in Carbon Tetrachloride

T, K	ω_s, GHz	C_s, ms^{-1}	χ_s, GPa
300.3	5.49	1300	0.463
303.9	5.42	1313	0.476
306.9	5.33	1293	0.493
319.1	5.27	1284	0.507
322.7	5.15	1256	0.532
326.9	5.13	1253	0.537
332.1	5.02	1228	0.562
339.1	4.90	1202	0.592
345.1	4.81	1182	0.616

Table V. Index of Refraction (n) for Solutions of Benzonitrile in Carbon Tetrachloride

	n			
T, K	100% [a]	90% [a]	80% [a]	60% [a]
295.5	1.5276			
295.7		1.5221	1.5165	
295.9				1.5040
306.9	1.5226	1.5170	1.5115	1.4985
317.1	1.5178	1.5124	1.5063	1.4933
326.9	1.5139	1.5084	1.5025	1.4895
337.1	1.5093	1.5040	1.4972	1.4840
344.1	1.5064			
343.9		1.4995	1.4940	1.4805

[a] Concentration given as volume percent benzonitrile in carbon tetrachloride.

quency shift of the digitized data.

The hypersonic velocity, C_s, was calculated with eq 1

$$C_s = 2\pi\omega_s/\mathrm{q} \qquad (1)$$

where q is the scattering wave vector, given by

$$\mathrm{q} = (4\pi n/\lambda)\sin(\theta/2) \qquad (2)$$

and where n is the refractive index, λ is the wavelength of the incident light, and θ is the scattering angle which for our measurements was 90°. The refractive indices were measured in our laboratory as a function of temperature and are given in Table V. A thousand data points were taken over two spectral orders. All the spectra were fitted to a Lorenztian line shape by using a Simplex fitting routine from which the ω_s values were obtained.

The dynamic isentropic compressibility, χ_s, was calculated with

$$\chi_s = C_s^{-2}\rho^{-1} \qquad (3)$$

where ρ is the density. Values for the density were measured in our laboratory to complement values in the literature (*3*). The refractive indices and densities were interpolated to the spectral temperature. From the uncertainty in the reported values of density and refractive indices the error is less than 1% and does not contribute significantly to the error in the reported velocity. The major source of error is in the uncertainty in the FSR (±2%) which produces systematic error in all data sets.

The values of the speed of sound as measured by ultrasonic absorption as reported in the literature are 1378 and 1428 ms^{-1} at 308 and 293 K, respectively (*4*, *5*). The reported values for the hypersonic velocity are greater than the ultrasonic values due to a relaxation processs in the hypersonic frequency region. A discussion of the relaxation mechanism has been given (*6*). Relaxation always gives rise to positive dispersion; therefore, we should expect that the hypersonic velocity should be greater than the ultrasonic velocity. This is in agreement with the observed results. The reported compressibility is the dynamic compressibility; that is, it also contains the contribution due to the shear modulus. In the hypersonic frequency region the shear modulus is, in general, not negligible.

Registry No. Benzonitrile, 100-47-0; carbon tetrachloride, 56-23-5.

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Vapor Pressures for Biphenyl, 4-Chlorobiphenyl, 2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl, and Decachlorobiphenyl

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Vapor pressures were determined by using a gas saturation technique for biphenyl, 4-chlorobiphenyl, 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, and decachlorobiphenyl over the temperature ranges of 5.2–24.7, 4.2–24.9, 29.0–61.2, and 50.7–89.8 °C, respectively. Vapor pressures (in pascals ± standard deviation) at 25 °C were extrapolated or interpolated from the measured values, and these values are as follows: biphenyl, 1.19 ± 0.03; 4-chlorobiphenyl, 0.175 ± 0.006; 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, (2.90 ± 0.20) $\times 10^{-5}$; and decachlorobiphenyl, (5.30 ± 0.31) $\times 10^{-8}$.

Introduction

In understanding and modeling the dynamics of polychlorinated biphenyls (PCBs) in the environment, one needs physical and chemical properties such as aqueous solubilities, vapor pressures, and melting points. Currently, vapor pressure data for the very highly chlorinated PCB congeners do not exist. In this report, vapor pressures determined by a gas saturation technique are reported for two highly chlorinated PCB congeners (2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl and decachlorobiphenyl) and for 4-chlorobiphenyl and biphenyl.

Experimental Section

Compounds and Reagents. The 4-chlorobiphenyl and decachlorobiphenyl were obtained from Aldrich Chemical Co., Milwaukee, WI. The biphenyl and 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl were obtained from Ultra Scientific, Hope, RI. All compounds were used as received and had purities of 99% or greater. Fisher Scientific, Itasca, IL, pesticide-grade solvents

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Table I. Vapor Pressures, Clapeyron Coefficients, and Average Enthalpies of Sublimation (ΔH_s) for Biphenyl, 4-Chlorobiphenyl, 2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl, and Decachlorobiphenyl

	vapor press.,[b] Pa				$\log P = A - B/T$[c]			ΔH_s,[d]
temp,[a] °C	$\bar{x}$	S	$100(S/\bar{x})$	n	A	B	r^2	kcal/mol
				Biphenyl				
5.2	1.06×10^{-1}	2.05×10^{-3}	1.9	6	14.840 ± 0.0006	4402.1 ± 1.8	1.000	20.1 ± 0.01
14.9	3.61×10^{-1}	9.73×10^{-3}	2.7	10				
24.7	1.15×10^{0}	3.23×10^{-2}	2.8	6				
				4-Chlorobiphenyl				
4.2	1.11×10^{-2}	2.35×10^{-4}	2.1	6	15.188 ± 0.083	4754.1 ± 24.0	1.000	21.7 ± 0.11
15.0	4.93×10^{-2}	2.35×10^{-3}	4.8	10				
24.9	1.72×10^{-1}	4.52×10^{-3}	2.6	7				
				2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl				
29.0	4.95×10^{-5}	4.56×10^{-6}	9.2	8	13.262 ± 0.856	5307.3 ± 271.7	0.995	24.3 ± 1.24
39.9	2.24×10^{-4}	1.95×10^{-5}	8.7	15				
50.0	5.83×10^{-4}	3.12×10^{-5}	5.4	8				
61.2	2.65×10^{-3}	1.09×10^{-4}	4.1	8				
				Decachlorobiphenyl				
50.7	2.69×10^{-6}	1.80×10^{-7}	6.7	7	14.049 ± 0.536	6358.0 ± 185.5	0.997	29.1 ± 0.85
64.9	1.68×10^{-5}	9.73×10^{-7}	5.8	7				
72.3	4.00×10^{-5}	2.93×10^{-6}	7.3	6				
80.5	1.43×10^{-4}	5.27×10^{-6}	3.7	6				
85.2	1.88×10^{-4}	1.08×10^{-5}	5.8	8				
89.8	3.36×10^{-4}	1.91×10^{-5}	5.7	7				

[a] All temperatures have an uncertainty of ±0.1 °C. [b] $\bar{x}$ = mean; S = standard deviation; n = number of determinations. [c] In pascals and kelvin. A and B ± standard deviations; r^2 = correlation coefficient of the regression. [d] ΔH_s ± standard deviation.

and Florisil absorbent (100–200 mesh) were used. Compressed air purified by using molecular sieve and Drierite traps served as the air source.

Apparatus. The gas saturation apparatus consisted of the following components: a generator column for saturating the air with the analyte, an adsorbent trap for collecting the analyte from the air, and a device for measuring the volume of air passed through the generator column.

The generator columns were constructed in the manner of Sonnefeld et al. (*1*). The columns consisted of a tube, either stainless steel (508 × 6 mm) or Pyrex (508 × 6 mm), packed with glass beads (80/120 mesh). The beads were coated with the analyte prior to packing the columns at a loading of 2.48%, 3.13%, 0.428%, and 3.13% (w/w) for biphenyl, 4-chlorobiphenyl, 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, and decachlorobiphenyl, respectively.

In this investigation, the generator columns had similar physical dimensions and percentage loading of the analyte on the glass beads to the columns of Sonnefeld et al. (*1*). We observed a flow rate range where the vapor density was independent of flow, 1–16 mL/min; this range is similar to the range reported by Sonnefeld et al. (*1*), 1–18 mL/min. All reported vapor pressures were measured in this range of flow rates, and each reported vapor pressure was determined by using two or more flow rates. In addition, a total of four or five different flow rates was used if all temperatures are considered.

The adsorbent trap, consisting of 500 mg of 3% deactivated (w/w) Florisil (100–200 mesh) packed in 6-mm Pyrex tubing, was similar to traps described by Giam et al. (*2*) and Westcott et al. (*3*) for vapor collection. The traps were connected to the generator column by using 1.59-mm stainless steel tubing and Swagelok fittings.

The collection and elution efficiency of the Florisil vapor trap was evaluated by placing in a gas chromatograph injection port a glass tube (450 × 6 mm) which contained a Florisil trap at the downstream end. A spike of the compound was vaporized in the heated injection port (ca. 250 °C), and the vaporized spike was collected from the air passing through the injection port tube apparatus by the Florisil trap. The collected spike was eluted from the Florisil trap and quantified as described in the Procedure section. All compounds had combined collection and elution efficiencies of 99% or greater.

The volume of air passed through the system was measured by collecting the air in an inverted volumetric flask filled with water. The volume of gas passing through the generator column was calculated from the temperatures and pressures at the end of the generator column and at the volumetric flask by using the method of Thomson (*4*).

The generator column, switching valve, stainless steel tubing, and part of the Florisil trap were temperature controlled to ±0.1 °C by using a water bath. All temperature measurements were made with thermometers corrected to ASTM 63C, ASTM 64C, ASTM 65C, and/or ASTM 66C thermometers. These thermometers have been tested for accuracy by comparison with standards certified by the National Bureau of Standards and have a stated accuracy of ±0.1 °C.

Procedure. The system was conditioned for ca. 7 days at 20 °C higher than the highest sampling temperature with a gas flow of ca. 15 mL/min. During this step, a large exit trap consisting of XAD-2 resin was employed for removing the analyte from the exit air. This step ensures that all parts of the apparatus downstream from the generator column were coated with the compound. Henceforth, the bath temperature and flow rate of the gas were adjusted to the desired setting and the apparatus was allowed to run for ca. 12 h before sampling. Samples were taken by putting a clean, freshly packed Florisil trap in line and collecting the desired volume of gas, 1 or 2 L. The Florisil trap was removed from the system and the analyte was eluted with hexane. The analyte was quantified by using gas chromatography with flame ionization or electron capture detection. The vapor density was calculated from the experimental data, and the vapor pressure was calculated from the vapor density by using the ideal gas law.

Results and Discussion

Vapor pressures, Clapeyron equation coefficients, and average enthalpies of sublimation are listed for each compound in Table I. These enthalpies were calculated from the slope of the Clapeyron equation, assuming constant enthalpies of sublimation. In Table II, experimental and literature values are listed for vapor pressures at 25.0 °C.

The validity of the generator column technique for producing air saturated with the analyte has been shown by Sonnefeld et

Table II. Vapor Pressures (Pascals) for Biphenyl, 4-Chlorobiphenyl, 2,2',3,3',5,5',6,6'-Octachlorobiphenyl, and Decachlorobiphenyl at 25.0 °C[a]

compd	this work	lit. values
biphenyl	1.19 ± 0.03	1.03,[b] 1.29,[c] 0.579,[d] 0.969[e]
4-chlorobiphenyl	0.175 ± 0.006	0.61[f]
2,2',3,3',5,5',6,6'-octachlorobiphenyl	(2.90 ± 0.20) × 10^{-5}	
decachlorobiphenyl	(5.30 ± 0.31) × 10^{-8}	

[a] All values are extrapolated or interpolated from log vapor pressure vs. $1/T$ relationship. The uncertainty is the standard deviation determined from the average of the ratio of the standard deviation to the mean for each compound. [b] Reference *5*. [c] Reference *6*. [d] Reference *7*. [e] Reference *8*. [f] Reference *9*. This value was calculated by extrapolating from liquid vapor pressures and then making the melting point correction.

al. (*1*) using polyaromatic hydrocarbons. We have checked the validity of this method and of our experimental apparatus by using biphenyl as a test analyte. Vapor pressures and enthalpies of sublimation determined in this investigation for biphenyl are in good agreement with the published experimental values (Table II). Also, there is fair agreement between the experimental value from this investigation and the calculated vapor pressure for 4-chlorobiphenyl.

The total uncertainty in the measured vapor pressures (Table I) was estimated by performing a propagation of error analysis on the method of Thomson (*4*) with estimated maximum errors. The uncertainty was estimated to be less than 6.1%. The largest portions of the uncertainty were attributed to the actual quantification of the analyte (ca. 75%), to the estimation of the partial pressure of the water vapor in the inverted volumetric flask (ca. 22%), and to the temperature of the inverted volumetric flask (ca. 3%). The uncertainties attributed to the other temperatures and pressures were small.

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Registry No. Biphenyl, 92-52-4; 4-chlorobiphenyl, 2051-62-9; 2,2',3,3',5,5',6,6'-octachlorobiphenyl, 2136-99-4; decachlorobiphenyl, 2051-24-3.

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Solubility of Hydrogen in the Molten $Li_{17}Pb_{83}$ Alloy

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The equilibrium $H_2 \rightleftarrows 2H$ (dissolved) in a liquid $Li_{17}Pb_{83}$ alloy was studied at various temperatures in order to obtain the thermodynamic data required for the use of the alloy as a blanket material of fusion reactors. It is found that the system $Li_{17}Pb_{83}/H$ is characterized by a very small value of $X_H/P_{H_2}^{1/2}$ ratio at infinite dilution and by strong deviations from the ideal behavior as the concentration of hydrogen rises in the alloy. An empirical equation, which correlates the activity coefficients and the concentration of hydrogen in the alloy, is proposed.

Introduction

During the last few years many studies have been carried out on the properties of the Li/Pb alloy, due to their increasing scientific interest.

It has been pointed out that these alloys belong to a particular class that exhibits unusual properties due to the partial electron transfer from one component to another producing an ionic species.

Many studies have confirmed the hypothesis that saltlike characteristics, which derive from the partial localizing of electrons on the Pb atoms to form lead anions, are particularly pronounced in the stoichiometric composition Li_4Pb. However, strong deviations from ideal behavior, short-range order in the liquid and solid states, and a preferred heterocoordination for nearest neighbors show themselves in alloys of all compositions (*1-4*).

Besides being of basic scientific interest, the study of these systems' behavior is of particular interest because they have been proposed as a potential alternative candidate for thermonuclear blanket material (*5, 6*). This happened because some of their properties have advantages over other materials proposed: low tritium solubility, a good tritium breeding ratio, high blanket energy multiplication, and relatively good chemical stability at elevated temperatures.

In order to use these alloys as blanket material it is necessary therefore to study the behavior of the ternary system Li/Pb/hydrogen and its isotopes. This study can be particularly interesting because of the complex interactions which can develop in this system. Hydrogen, in fact, shows entirely different behavior with the two components of the alloy. lithium is a metal in which hydrogen presents the highest solubility value (*7-10*) and it forms one stable stoichiometric hybrid. On the