Aqueous Solubility of Polychlorinated Biphenyls Related to Molecular Structure

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■ Aqueous solubilities of polychlorinated biphenyls show a linear relationship between logarithms of aqueous activity coefficients and total surface areas (TSA) or total molecular volumes (TMV). The aqueous activity coefficients were calculated from experimental solubility data and values taken from the literature. The correlations improved substantially if a differential heat capacity between supercooled liquid and solid chemical (ΔC_p) equal to the entropy of fusion (ΔS_f), instead of $\Delta C_p = 0$, was assumed. In addition, it was found that dissolution of 2,2′,4,4′-tetra- and 2,2′,4,4′,5,5′-hexachlorobiphenyl was accompanied by positive enthalpy and entropy changes, the entropy being dominant at room temperature. For the former compound, it was shown that the entropy of fusion is approximately 60 J K^{-1} mol^{-1}, which is in agreement with the Walden rule. For 2,2′,4,4′,5,5′-hexachlorobiphenyl, it was shown that a Hildebrand plot (the logarithm of the mole fraction solubility versus temperature) provides a constant slope. This supported the assumption that differential heat capacity (ΔC_p) equals the entropy of fusion.

Introduction

Hydrophobicity often plays an important role in describing and explaining the fate of many pollutants. Although the term hydrophobicity seems explanatory (i.e., "phobic" behavior in a "hydro" environment), a debate is going on about the exact nature of hydrophobic interactions (1, 2). The discussion is not limited to the nature of the hydrophobic interactions. It includes also the physicochemical parameter(s) that is (are) mainly controlled by the interactions and that might be used to represent them. In general, two types of parameters are used as representatives.

First, hydrophobic properties of a compound are usually measured by an equilibrium distribution ratio between two different physicochemical phases, such as octan-1-ol/water partitioning ($K_{d,oct}$) (3–6). However, since partitioning is not entirely regulated by interactions in the aqueous layer of the two phase systems (7), distribution or partition coefficients are debatable descriptors of the compound's hydrophobicity. Therefore, it seems to be more appropriate to use aqueous solubility as a hydrophobicity parameter (8, 9). However, solution of nonelectrolyte molecules is not only regulated by interactions between solute and solvent but also by interactions between the solute molecules (1, 9–11). In particular when the compound's melting point is above the experimental temperature, the solute–solute interactions make application of aqueous solubility as a hydrophobicity parameter rather complicated (7, 12–18). Although solute–solute interactions below the solute's fusion temperature are only one factor in the whole range of solute–solute, solute–solvent, and solvent–solvent interactions, they are important from both a theoretical and an experimental point of view.

Exclusion of the fusion term from the aqueous solubility expressions gives better information about the hydrophobic interactions in the aqueous phase, i.e., the solute's hydrophobicity (19–21). This is because all interactions, except those associated with fusion of solute molecules below the melting point, are considered in the hydrophobic interactions concept as defined by Kauzmann (22), and later by Ben-Naim (1, 11).

The hydrophobic interaction concept is likely to provide a better framework for the investigation and an understanding of the relationship between the hydrophobicity and solute structure.

In this study, the aqueous solubilities of 45 chlorinated biphenyls are investigated. Relationships between activity coefficients and chemical structure parameters [total surface area (TSA) and total molecular volume (TMV)] of extremely hydrophobic chemicals are studied, since such relationships may help to understand the nature of hydrophobicity. In addition, the relationships may enable one to make rapid estimates of the aqueous solubility of all 209 PCB's.

Materials and Methods

Chemicals. In the experiments, polychlorinated biphenyls were used that were available from previous experiments (23). The purity of all PCB's was >97% as confirmed by gas chromatography-electron capture detector (GC-ECD) and gas chromatography–mass spectrometry (GC–MS). Water samples were extracted with redistilled n-pentane, n-hexane, or toluene (Merck).

Water Saturation System. Two types of water circulation systems were used throughout the experiments.

(A) For most compounds, a water circulation system was used that has been described previously (23). The system contained 40 L of water at 22.0 ± 0.1 °C, which was circulated at a rate of approximately 40 L/h. The water was gradually saturated with the test compounds by pumping it through a column to which impregnated Chromosorb was added. The Chromosorb (W acid washed, 130–150 mesh) was previously washed with hexane and toluene.

(B) In a system comparable to that of system A, 2.5 L of water was circulated at a flow rate of 2 L/h. Two Millipore cellulose filters (0.22 μm) were placed directly after the circulation pump. In between these filters, impregnated Chromosorb was placed to saturate the water continuously. The filters were added to remove contaminated particles from water. For the thermodynamic investigations, the water was thermostated at temperatures between 22.2 ± 0.1 and 76.0 ± 0.1 °C.

Chemical Analysis. During the experiment, samples of 100, 250, or 500 mL of water were sampled and extracted twice with 25, 50, and 75 mL of organic solvent, respectively. After combining the two fractions, the extract was concentrated to 1 mL and analyzed on GC-ECD. A Tracor
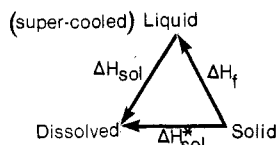
Figure 1. Relationships between solid, supercooled liquid, and dissolved states of solutes.

300 GC equipped with a [63]Ni ECD was used, with a 2 m × 2 mm i.d. Dexil 300 column (2% Chromosorb WAW 130–150 mesh).

TSA and TMV Calculations. The procedure for the shorthand calculations of TSA and TMV of the test compounds has been published elsewhere (13). The following interatomic distances and van der Waals radii were used:

van der Waals radii, Å	interatomic distances, Å
–C, 1.70	C–H aromatic, 1.08
–H, 1.20	C–C aromatic, 1.40
–Cl, 1.80	C–Cl aromatic, 1.70

For these compounds, planar rigid structures were considered with bond angles of 120°. The influence of vibrations and rotations on both TSA and TMV was neglected.

Aqueous Solubility Concept. Generally, the mole fraction aqueous solubility of a solute i ($X_{aq,i}$) can be considered to be an equilibrium partitioning between pure chemical and solution. Equilibrium is achieved if the solute's activities in pure solute (a_i) and in solution ($a_{aq,i}$) are equal (8, 10). Mole fraction solubilities are related to activities by

$$X_{aq,i} = a_i \gamma_{aq,i}^{-1} \qquad (1)$$

in which $\gamma_{aq,i}$ denotes the solute's activity coefficient. The mole fraction solubility can related to temperature changes by (10, 15)

$$\frac{d \ln x_{aq,i}}{dT} = \frac{\Delta H^*_{sol,i}}{RT^2} = \frac{\Delta H_{sol,i}}{RT^2} + \frac{\Delta H_{f,i}}{RT^2} \qquad (2)$$

in which $\Delta H^*_{sol,i}$, $\Delta H_{sol,i}$ and $\Delta H_{f,i}$ are the enthalpies of solution of a solid solute, solution of a (supercooled) liquid solute, and of fusion, respectively (Figure 1).

For a liquid solute a_i is unity, i.e., $\Delta H_{f,i}$ is zero, so that eq 2 can be simplified to

$$\frac{d \ln X_{aq,i}}{dT} = \frac{\Delta H_{sol,i}}{RT^2} \qquad (3)$$

Since for solid solutes $\ln a_i$ does not equal zero, eq 2, after integration, shows

$$\ln a_i = -\frac{\Delta H^m_{f,i}}{R} \frac{(T_{m,i} - T)}{TT_{m,i}} + \frac{\Delta C_{p,i}}{R} \frac{(T_{m,i} - T)}{T} - \frac{\Delta C_{p,i}}{R} \left(\ln \frac{T_{m,i}}{T} \right) \qquad (4)$$

in which $\Delta H^m_{f,i}$ indicates the solute's heat of fusion at the melting point (T_m) and $\Delta C_{p,i}$ denotes the differential heat capacity of solute i, between solid and supercooled liquid state, which can be expressed as

$$\Delta C_{p,i} = C_{p,i,solid} - C_{p,i,liquid} \qquad (5)$$

$\Delta H_{f,i}$ can be related to $\Delta H^m_{f,i}$ by

$$\Delta H_{f,i} = \Delta H^m_{f,i} - \Delta C_{p,i}(T_{m,i} - T) \qquad (6)$$

Since, to date, actual ΔC_p values are rather scarce for halogenated aromatic hydrocarbons, no simple calculation of $\ln a_i$ is possible for most nonelectrolyte solutes. Therefore, three assumptions about the differential heat capacity are made (7): (i) $\Delta C_{p,i} = 0$, (ii) $\Delta C_{p,i}$ = constant, (iii) $\Delta C_{p,i}$ = variable.

For chlorinated biphenyls and related compounds, it is often suggested that the first assumption holds, so that eq 4 can be expressed by (12, 15, 16, 19–21, 23)

$$\ln a_i = -\frac{\Delta H^m_{f,i}}{R} \frac{(T_{m,i} - T)}{TT_{m,i}} \qquad (7)$$

Since at the melting point

$$\Delta H^m_{f,i} = T_{m,i} \Delta S^m_{f,i} \qquad (8)$$

eq 7 can be expressed as

$$\ln a_i = -\frac{\Delta S^m_{f,i}}{R} \frac{(T_{m,i} - T)}{T} \qquad (9)$$

Recently it has been proposed that assumption ii, i.e., ΔC_p = constant, is more likely for nonelectrolytes (7), so that eq 4 is valid. In addition, Hildebrand et al. (10) reported that the assumption

$$\Delta C_{p,i} = \Delta S^m_{f,i} \qquad (10)$$

is at least as good as $\Delta C_{p,i} = 0$, so that eq 4 can be rewritten by (15)

$$\ln a_i = -\frac{\Delta S^m_{f,i}}{R} \left(\ln \frac{T_{m,i}}{T} \right) \qquad (11)$$

For the third assumption, i.e., $\Delta C_{p,i}$ is a variable, some evidence is reported for solutes that are unstable with temperature changes, such as proteins or micelles (24, 25). However, hitherto no indications of the validity of this assumption has been reported for nonelectrolyte solutes.

With the above assumptions, the aqueous mole fraction solubility for liquid and solid solutes can be expressed as follows:

(i) liquid solutes

$$-\ln X_{aq,i} = \ln \gamma_{aq,i} \qquad (12)$$

(ii) solid solutes (if $\Delta C_{p,i} = 0$)

$$-\ln X_{aq,i} = \ln \gamma_{aq,i} + \frac{\Delta S^m_{f,i}}{R} \frac{(T_{m,i} - T)}{T} \qquad (13)$$

(iii) solid solutes (if $\Delta C_{p,i} = \Delta S^m_{f,i}$)

$$-\ln X_{aq,i} = \ln \gamma_{aq,i} + \frac{\Delta S^m_{f,i}}{R} \left(\ln \frac{T_{m,i}}{T} \right) \qquad (14)$$

Results

TSA and TMV Calculations. The results of TSA and TMV calculations by the shorthand estimation method, for all PCB congeners for which solubility data are available, are shown in Tables I and II. In the shorthand TSA estimation method, only the surface area of the pure solute is calculated. This is in contrast with alternative methods in which a contribution is implemented for the solvent radius (26–28). The latter methods, however, have the disadvantage that the solute's TSA is dependent on the solvent's nature.

As shown, the TSA contribution from chlorine substitution is dependent on the place of substitution, which is due to the overlap of the substituent with adjacent atoms

Table I. Average TSA and TMV Changes of Hydrogen Replacement by Chlorine in Biphenyl

Cl place of substitution	ΔTSA, Å^2	ΔTMV, Å^3
isolated 3- or 4-position	12.9	17.0
isolated 2-position	8.2	10.9
2-substitution in 2,2′,6 or 2,2′,6,6′	3.9	4.1
Cl–Cl overlap in phenyl	−2.5	−3.7

(Table I). For 2,2′,6 and 2,2′,6,6′ substitutions, additional subtractions of TSA resulted from the overlap between the ortho substituents of the two phenyl rings.

As is shown in Table II, TSA data reported by Mackay et al. (21) differ significantly from the data of this study. In particular, for the higher chlorinated compounds large deviations are found. This is mainly due to the large difference in calculated TSA overlaps between adjacent chlorine atoms and the estimated contributions from chlorine substituents at isolated 3- or 4-positions.

To date no accurate literature data of the TMV's of chlorinated biphenyls are available to which the results of the present calculations could be compared.

Measuring Aqueous Solubility of PCB's. In both aqueous saturation systems, variation of the percentage Chromosorb impregnation [when >0.01% (w/w)] had no influence on the measured equilibrium concentrations.

For determination of the aqueous solubilities of PCB's reported in Table II, load percentages between 0.1 and 1.0% were used. All experimental solubility data are means of at least four replicate measurements. Standard deviations as percentage of the mean value ranged from 5.7 (2,2′,4,4′-tetrachlorobiphenyl) to 24.8% (decachlorobiphenyl). Additional solubility data obtained from the literature are also listed in Table II.

In Table II it is shown that a large variation in the measured solubility data between the various studies is observed. The difference between the data cannot be explained by the small temperature differences applied in the various studies. Hence, the differences may be caused by the different methods applied for introduction of solutes into water (29). Sometimes organic cosolvents or cosolutes have been used for the introduction of hydrophobic chemicals into water, which can have significant influence on the measured solubility (30, 31). In several other studies, flow-through systems for saturation with loaded column techniques were applied (32–36). In this study, methods comparable to those reported by Weil et al. (32) and Bruggeman et al. (33) have been used.

The experimentally determined solubilities were in good agreement with data reported by Weil et al. (32), Bruggeman et al. (33), Miller et al. (34), and Dickhut et al. (48). Several other studies reported values that differed significantly (37, 38). Due to the variation of data originating from various studies, relationships between solubility data and chemical structure parameters will never have excellent correlation coefficients.

Thermodynamics of Solution. The aqueous solubility of 2,2′,4,4′-tetrachlorobiphenyl (mp 42 °C) was measured at various temperatures between 22.0 and 76.0 °C.

From a van't Hoff plot of ln $X_{aq,i}$ versus T^{-1} at temperatures >42 °C (eq 3), an enthalpy of solution (ΔH_{sol}) of 13 kJ mol^{-1} is calculated (Figure 2a). It can be calculated that at 42 °C the whole process of solution of 2,2′,4,4′-tetrachlorobiphenyl is dominated by the entropy, since

$$T\Delta S_{sol} = \Delta H_{sol} - \Delta G_{sol} = 13 \text{ kJ mol}^{-1} - 53 \text{ kJ mol}^{-1} =$$
$$-40 \text{ kJ mol}^{-1}$$

Both the negative entropy and the endothermic enthalpy
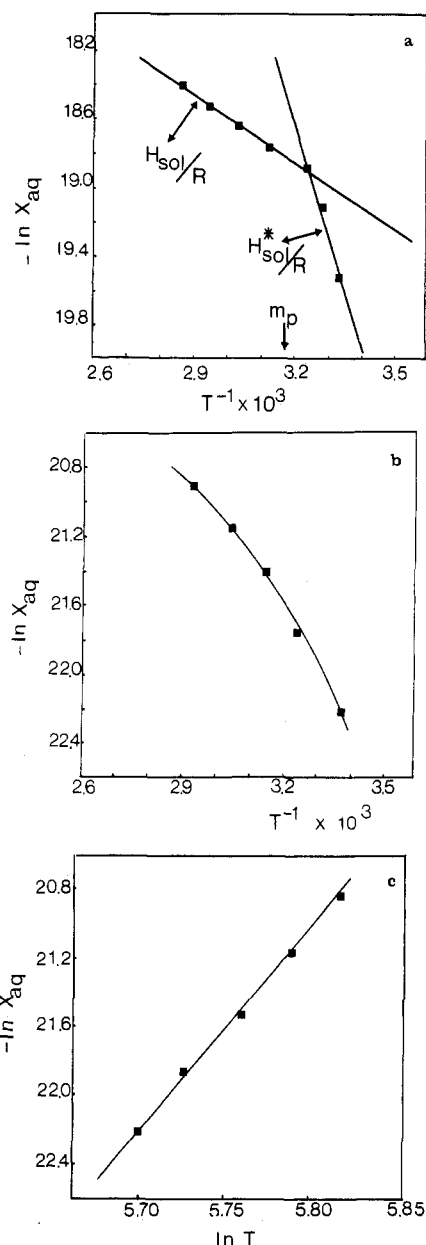
Figure 2. (a) van't Hoff plot (− ln X_{aq} versus T^{-1}) of 2,2′,4,4′-tetrachlorobiphenyl; mp indicates the melting point. (b) van't Hoff plot of 2,2′,4,4′,5,5′-hexachlorobiphenyl. (c) Hildebrand plot (−X_{aq} versus ln T) of 2,2′,4,4′,5,5′-hexachlorobiphenyl.

($\Delta H_{sol} > 0$) are unfavorable for the solution process.

As shown in Figure 2a, a further decrease in aqueous solubility is observed below 42 °C due to the contribution from the endothermic heat of fusion. A van't Hoff plot at lower temperatures gives a value for $\Delta H^{*}_{sol,i}$ of 32 kJ mol^{-1}. Thus, according to eq 2, assuming $\Delta C_p = 0$, the values of $\Delta H_{f,i} = 19$ kJ mol^{-1} and $\Delta S_{f,i} = 60$ J mol^{-1} K^{-1} for 2,2′,4,4′-tetrachlorobiphenyl are calculated. Application of eq 14, assuming $\Delta C_p = \Delta S_i$, results in a similar value for the enthalpy and entropy of fusion, because the minimum experimental temperature was only 17 °C below the melting point. The value of the entropy of fusion is in agreement with those reported previously for other PCB's (18, 21, 34). In addition, it is consistent with the Walden rule (18) about the constancy of the entropy of fusion for aromatic hydrocarbons at approximately 58 J mol^{-1} K^{-1}. The calculated value of the enthalpy of solution of 32 kJ mol^{-1} for 2,2′,4,4′-tetrachlorobiphenyl is close to the enthalpies of solution of biphenyl and seven solid PCB's reported recently (48).

In Figure 2b the van't Hoff plot of 2,2′,4,4′,5,5′-hexachlorobiphenyl is shown. From this plot it can be concluded that the enthalpy of solution is not constant over the experimental temperature range, which is not in agreement with eq 13, in which it is assumed that $\Delta C_p = 0$. In contrast, as shown in Figure 2c, a Hildebrand plot of $\ln X_{aq}$ versus $\ln T$ yields a straight line, which supports the assumption that $\Delta C_p = \Delta S_f$ (10).

From the slope of the line in Figure 2c, and by assuming the validity of the Walden rule for the entropy of fusion, an enthalpy of solution of supercooled liquid 2,2′,4,4′,5,5′-hexachlorobiphenyl (ΔH_{sol}) of +10 kJ mol^{-1} can be calculated. This value is very close to the enthalpy of solution of 2,2′,4,4′-tetrachlorobiphenyl calculated above. Hence, the lower aqueous solubility of the hexachlorobiphenyl relative to the tetrachloro congener is mainly a result of the much greater loss of entropy during solution. For instance, at $T = 42$ °C the value of $T\Delta S_{sol}$ is −40 kJ mol^{-1} for the tetrachloro congener, whereas a value of −52 kJ mol^{-1} can be calculated for the hexachloro congener.

In addition, since the values of the enthalpies of solution (ΔH^*_{sol}) of both PCB congeners are very close, i.e., 10 and 13 kJ mol^{-1}, respectively, the 61 K difference between the melting points of the two congeners has, due to the fusion energy, significant influence on the relative aqueous solubilities.

Discussion

Among the various types of chemical structure parameters, the total surface area (TSA) of nonelectrolyte solutes is often employed for correlations with aqueous solubility (20, 21, 27). For liquid solutes such relationships can be expressed by

$$-\ln X_{aq,i} = a(\text{TSA}) + b \qquad (15)$$

Since it is unlikely that the heat of fusion of solid solutes is influenced by the TSA, a more general expression of eq 15 for either solid or liquid solutes is (21, 50, 51)

$$\ln \gamma_{aq,i} = a(\text{TSA}) + b \qquad (16)$$

In Table III data from least-squares linear regression of this equation are shown, resulting from calculations with the following options: (1a) total surface areas reported by MacKay et al. (21) (TSA*); (1b) total surface areas calculated in this study (TSA); (2a) all available $X_{aq,i}$ data; (2b) selected solubility data, i.e., those measured in this study and those reported by Weil et al. (32); (3a) assuming the validity of $\Delta C_p = 0$, eq 13; (3b) assuming the validity of $\Delta C_p = \Delta S_f$, eq 14; (4) application of the Walden rule, i.e., $\Delta S^m_f = 58$ J mol^{-1} K^{-1}.

As is shown in Table III, application of all available solubility data to eq 16 gives correlation coefficients ranging from 0.929 to 0.952 due to the large scattering of measured solubilities. Since the aqueous saturation method used by Weil et al. (32) is comparable to the one used in this study, better results are obtained when only solubility data from selected studies are employed. It is remarkable that, although the absolute TSA and TSA* ranges are completely different the correlations of eq 16a and 16c in Table III are almost equal. The difference in total surface area range between these equations is expressed in the different slopes and intercepts. Better harmonization of the foundations of TSA calculation might reduce the scattering of the slopes and intercepts. The best relationship listed in Table III is eq 16h, which is based on the solubilities measured in this study and those reported by Weil et al. (32); the assumption $\Delta S_f \simeq \Delta C_p$ and TSA values calculated in this study.

Furthermore, it is shown that estimation of the solute's activity with $\Delta S_f \simeq \Delta C_p$ gives better correlation coefficients than $\Delta C_p \simeq 0$ for all combinations of $\ln X_{aq,i}$ and TSA data. If the TSA data from Mackay et al. (21) only were used, a better correlation is obtained if it is assumed that $\Delta C_p = 0$.

According to eq 16h in Table III, the aqueous solubilities at $T = 22$ °C for all PCB's can be estimated by

$$-\ln X_{aq} = 0.108(\text{TSA}) + 30.281 - 6.976 \ln T_m \qquad (17)$$

Correlation of estimated aqueous mole fraction solubilities employing eq 17 ($X_{aq,i,estd}$) to the measured mole fraction solubilities by means of least-squares statistics shows

$$1.005 \ln (X_{aq,i,estd}) - 0.251 = \ln X_{aq,i,measd} \qquad (18)$$

$$n = 45 \qquad r = 0.991 \qquad F = 651$$

Correlation of all measured solubility data to estimated solubilities shows (Figure 3)

$$1.000 \ln (X_{aq,i,estd}) - 0.458 = \ln X_{aq,i,measd} \qquad (19)$$

$$n = 117 \qquad r = 0.990 \qquad F = 629$$

The correlations obtained for these relationships are satisfactory. Hence, combining calculated TSA and melting points with eq 18 or 19 may give reliable estimates of the aqueous solubilities for all 209 PCB congeners.

The validity of eq 15 is based on the solution model initially proposed by Eley (52), which was later adopted by Hermann (27) and others (53–60). In this model, solution of a nonelectrolyte solute is a three-step process, including (i) loss of solute–solute interactions, (ii) creation of a cavity in the aqueous phase of the dimension of the solute, and (iii) placement of the solute into the cavity.

It has been advocated that a linear relationship between the TSA of solute and the Gibbs free energy of solution of the nonelectrolyte solute exists (27, 53, 54). For the enthalpy contribution of free energy, this has been supported by the studies of Krishnan and Friedman (62) and of Spencer et al. (57). Here it was assumed that step ii, where creation of cavities in water or other polar solvents occurs, results in a loss of polar interactions and hydrogen bonds. The corresponding enthalpic changes are shown to be proportional to the total surface area of the cavity. Placement of the hydrophobic chemical into the cavity (step iii) is accompanied by creation of London-dispersion interactions between solute and solvent, which are also proportional to the solute's surface area.

Furthermore, since it can be concluded from the data of Abraham (58) that the enthalpy of vaporization is also proportional to the solute's TSA, it follows that at least the enthalpy of solution is linearly related to the solute's total surface area.

However, as shown in this study, the thermodynamics of solution of 2,2′,4,4′-tetrachlorobiphenyl and 2,2′,4,4′,5,5′-hexachlorobiphenyl are not dominated by an endothermic enthalpy change but by the enormous loss of entropy during solution of these chemicals. For compounds of lower hydrophobicity, this contribution of the entropy to the standard free energy change is significantly less (10, 52, 53).

According to the data of Cabani et al. (61) and Abraham (58), it can be proposed that the negative solution entropy must be a result of contributions from the cavity formation and the actual placement of the solute into the cavities (steps ii and iii). This is because vaporization (step i) always gives a positive entropy change (57). On the basis of the observed dominating role of the large negative entropy of solution of PCB's in this study, it can thus be

Table II. Some Physicochemical Properties and Structure Characteristics of Some PCB's

compd	M_r	mp, °C	TSA,[a] Å²	TSA*,[b] Å²	TMV, Å³	S,[c] µg/L	ref	$-\ln X$[d]	$\ln \gamma_1$	$\ln \gamma_2$[e]
biphenyl	154.2	71.0	224.1	192.5	207.0	6960	12	14.02	12.83	12.91
						6700	34	14.06	12.87	12.96
						7080	40	14.04	12.85	12.93
						7480	41	13.95	12.76	12.85
monochlorobiphenyls										
2	188.7	34.0	232.3	208.4	215.2	4130	32	14.75	14.49	14.50
						5057	34	14.54	14.29	14.30
						5900	42, 43	14.39	14.14	14.15
3	188.7	25.0	237.0	210.0	224.0	1300	32	15.90	15.90	15.90
						3500	42, 43	14.91	14.91	14.91
4	188.7	77.7	237.0	210.0	224.0	900	32	16.30	14.91	15.02
						15.1	37	20.36	18.99	19.10
						1170	42, 43	16.01	14.64	14.75
						1300	44	15.93	14.54	14.66
						400	45	17.08	15.72	15.83
dichlorobiphenyls										
2,2'	223.1	61.0	240.5	224.4	228.8	790	32	16.57	15.63	15.69
						21.2	37	20.19	19.25	19.31
						1500	42, 43	15.93	14.99	15.05
						900	45	16.27	15.34	15.39
2,4	223.1	24.4	245.2	226.0	234.9	1400	43	16.00	16.00	16.00
2,4'	223.1	42.0	245.2	226.0	234.9	620	32	16.81	16.33	16.35
						139	37	18.31	17.83	17.84
						637	38	16.78	16.30	16.32
						1880	42, 43	15.93	14.99	15.04
2,5	223.1	23.0	245.2	227.6	234.9	580	32	16.92	16.92	16.92
						200	33	17.99	17.99	17.99
						1940	34	15.79	15.79	15.79
						2028	46	15.67	15.67	15.67
2,6	223.1	36.0	240.5		228.8	540 ± 24	f (5)	16.99	16.62	16.62
						1390	34	16.07	15.77	15.77
						1452	46	16.00	15.70	15.70
4,4'	223.1	149.0	249.9	227.6	241.0	56	32	19.26	16.10	16.62
						80	42, 43	18.90	15.75	16.27
						62	46	19.16	16.00	16.52
trichlorobiphenyls										
2,2',5	257.5	44.0	253.4	242.0	245.8	640	32	16.92	16.42	16.43
						61.4	37	19.27	18.67	18.69
						248	38	18.51	18.01	18.03
2,3',4'	257.5	60.0	255.6	242.0	248.8	78	42, 43	19.03	18.12	18.19
2,4,4'	257.5	57.0	258.1	234.6	248.2	67 ± 8	f (8)	19.18	18.35	18.39
						260	32	17.82	16.99	17.03
						85	42, 43	19.30	18.19	18.24
2,4,5	257.5	78.0	255.6	242.0	248.2	92	32	18.86	17.50	17.61
						162	34	18.30	16.93	17.04
2,4',5	257.5	64.0	258.1		251.9	90	f (3)	18.88	17.87	17.94
2,4,6	257.5	61.3	252.7		245.8	226	34	17.96	17.06	17.11
3,3',4	257.5	88.0	260.3	243.3	254.3	15.2	32	20.66	19.05	19.20
tetrachlorobiphenyls										
2,2',3,3'	297.0	121.0	261.3	255.6	255.4	34	42, 43	19.98	17.53	17.86
2,2',3,5'	292.0	47.0	263.8	257.6	259.1	170	32	18.37	17.79	17.81
2,2',4,4'	292.0	42.0	266.3	259.6	262.8	54.1 ± 20.1	f (16)	19.52	19.09	19.10
						68	42, 43	19.29	18.86	18.87
2,2',4,5'	292.0	87.0	266.3	259.6	262.8	16.4	34	20.72	19.69	19.77
2,2',5,5'	292.0	87.0	266.3	259.6	262.8	15.3 ± 1.9	f (16)	20.78	19.19	19.34
						74	33	19.21	17.62	17.77
						27	34	20.21	18.62	18.77
						22.25	37	20.41	20.12	20.27
						26.5	38	20.23	18.64	18.79
						46	43	19.68	18.09	18.24
						6.01	47	21.72	20.12	20.27
2,2',6,6'	292.0	198.0	246.7		237.0	2.7 ± 0.4	f (4)	22.52	18.12	19.06
2,3',4,4'	292.0	128.0	268.5	259.2	265.2	58	42, 43	19.93	17.31	17.68
2,3,4,5	292.0	92.0	263.5	255.2	257.8	19.2	32	20.55	18.84	19.01
						20.9	34	20.47	18.75	18.92
2,3',4',5	292.0	104.0	268.5	259.2	265.2	16	33	20.71	18.69	18.92
						41	43	19.80	17.78	18.06
3,3',4,4'	292.0	180.0	270.7	267.6	267.6	1.8 ± 0.3	f (7)	22.92	18.98	19.76
						0.75	32	23.79	19.86	20.63
						175	43	18.34	14.40	15.17
						0.57	48	24.07	20.13	20.91
pentachlorobiphenyls										
2,2',3,4,5	326.4	100.0	274.2	271.2	268.7	9.8	32	21.34	19.42	19.63
2,2',3,4,5'	326.4	112.0	276.7	273.2	272.4	4.5	32	22.12	19.90	20.17
						23	43	20.48	18.27	18.54
2,2',3,4,6	326.4	100.0	264.4	271.6	259.5	12	32	21.14	19.22	19.43

Table II (Continued)

compd	M_r	mp, °C	TSA,[a] Å²	TSA*,[b] Å²	TMV, Å³	S,[c] µg/L	ref	$-\ln X$[d]	$\ln \gamma_1$	$\ln \gamma_2$[e]
2,2',4,5,5'	326.0	77.0	276.7	275.2	276.1	4.2	32	22.19	20.85	20.95
						18.9	34	20.68	19.34	19.45
						10	38	21.34	19.98	20.09
						31	42, 43	20.19	18.85	18.95
						10	46	21.34	19.98	20.09
						4.24	47	22.18	20.84	20.94
						12.1	48	21.13	19.79	19.09
2,3,4,5,6	326.4	124.0	271.7	269.2	265.4	13.6 ± 3.1	f (5)	21.01	18.48	18.83
						6.8	32	21.73	19.18	19.53
						6.5	34	21.92	19.3.	19.74
hexachlorobiphenyls										
2,2',3,3',4,4'	360.9	150.0	282.1	286.8	282.4	0.44	32	24.54	21.36	21.89
						0.28	34	24.99	21.81	22.34
						9.9	49	21.43	18.25	18.78
2,2',3,3',4,5	360.9	85.0	282.1	286.8	286.1	0.85	32	23.88	22.34	22.48
2,2',3,3',5,6	360.9	100.0	287.3	287.2	276.9	0.91	32	23.81	21.90	21.11
2,2',3,3',6,6'	360.9	112.2	269.5		263.6	6.03	34	21.93	19.85	20.11
						9.9	47	21.43	19.35	19.61
						3.25	48	22.54	20.46	20.77
2,2',4,4',5,5'	360.9	103.0	287.1	290.8	289.4	1.15 ± 0.11	f (15)	23.54	21.54	21.77
						1.20	32	23.54	21.54	21.77
						5.0	33	22.11	20.11	20.34
						0.95	38	23.75	21.75	21.89
						8.8	43	21.55	19.55	19.78
						1.05	47	23.67	21.67	21.90
2,2',4,4',6,6'	360.9	114.0	272.5	291.5	271.0	1.09 ± 0.10	f (8)	23.63	21.36	21.65
						0.90	32	23.83	21.55	21.84
						0.41	34	24.61	22.34	22.63
heptachlorobiphenyls										
2,2',3,3',4,4',6	395.3	122.4	289.9		286.5	2.17	34	23.04	19.99	20.53
						6.2	49	21.99	18.94	19.47
2,2',3,4,5,5',6	395.3	149.0	298.8	302.8	298.8	0.47	32	24.57	21.41	21.93
octachlorobiphenyls										
2,2',3,3',4,4',5,5'	429.8	159.0	302.9	317.9	308.6	0.124 ± 0.009	f (6)	25.98	22.75	23.17
						0.72	32	25.20	21.79	22.39
						3.01	43	22.79	19.38	19.98
2,2',3,3',5,5',6,6'	429.8	162.0	293.3	318.7	292.0	0.18	32	25.61	22.13	22.75
						0.39	34	24.83	22.35	22.97
						0.15	48	25.81	22.33	22.95
nonachlorobiphenyls										
2,2',3,3',4,4',5,5',6	464.2	206.0	306.9	331.9	309.1	0.078 ± 0.010	f (4)	26.52	21.93	22.94
						0.112	32	26.16	21.57	22.58
						0.025	48	27.64	23.05	24.59
2,2',3,3',4,5,5',6,6'	464.2	182.8	301.2		299.8	0.18	34	25.69	21.14	22.20
decachlorobiphenyl										
2,2',3,3',4,4',5,5',6,6'	498.7	305.0	309.1	345.9	309.4	0.021 ± 0.005	f (9)	27.91	20.81	22.91
						0.016	32	28.28	21.20	23.20
						0.0075	34	28.95	21.86	23.95
						0.0006	48	31.37	24.28	26.37

[a] TSA calculated by the method reported in ref 13. [b] TSA* obtained from ref 21. [c] Not included are theoretical values such those reported in ref 8 and 39. [d] X is the mole fraction solubility (mol/mol) at $T = 22.0$ °C. [e] In γ^1 and $\ln \gamma^2$ are calculated from $\ln X$ and eq 13 and 14, respectively ($T = 22.0$°C). [f] Experimental data from this study ($T = 22.0$ °C); number of measurements in parenthesis.

Table III. Correlations of the Relationship $\ln \gamma_{aq} = a\,(TSA) + b$ (Equation 16)

eq	options	n	a	b	r	F
16a	1a, 2a, 3a, 4	109	0.066	1.964	0.931	251
16b	1a, 2a, 3b, 4	109	0.069	1.211	0.949	418
16c	1b, 2a, 3a, 4	117	0.098	−6.948	0.925	276
16d	1b, 2a, 3b, 4	117	0.115	−11.678	0.947	412
16e	1a, 2b, 3a, 4	38	0.053	5.093	0.948	196
16f	1a, 2b, 3b, 4	38	0.056	4.631	0.936	143
16g	1b, 2b, 3a, 4	45	0.093	−5.822	0.953	191
16h	1b, 2b, 3b, 4	45	0.106	−9.095	0.967	335

proposed that according to the "cavity free volume" concept as proposed by Frank (55) there may be a linear relationship between $\ln \gamma_{aq}$ and solute's total molecular volume (TMV).

Although it can be assumed that there is some proportionality between a solute's molecular volume (volume/molecule) and its molar volume (volume/mol), which are not identical (51), application of the latter parameter is less desirable. However, it was shown previously that for a variety of hydrophobic solutes a relationship between molar volume and aqueous solubility gives satisfactory results (50, 51, 60, 63–65).

In Figure 4 the relationship between total molecular volumes of PCB's and aqueous activity coefficients is shown, which is based on all aqueous solubility data. The relationship can be expressed by

$$\ln X_{aq,i} = 0.089\,TMV - 4.405 \qquad (20)$$

$$n = 117 \qquad r = 0.994 \qquad F = 758$$

The high correlation coefficient is in agreement with the theory about the TMV–entropy relationship and with the observed influence of entropy changes on the solution of hydrophobic chemicals in aqueous environments.

Multiple linear regression applied to $\ln \gamma_{aq}$, TSA, and TMV will obviously improve the correlation coefficient (r^2). Although such a multiple linear relationship may be ex-
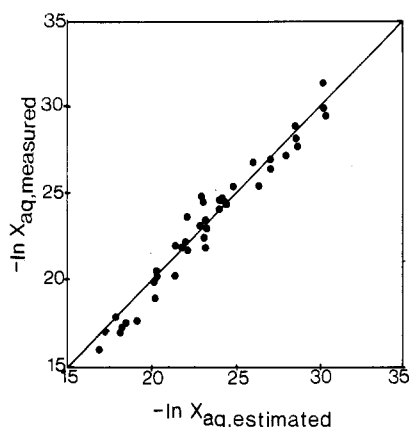
Figure 3. Relationship between estimated (eq 17) and measured mole fraction solubilities in water (X_{aq}) of all PCB's listed in Table II.
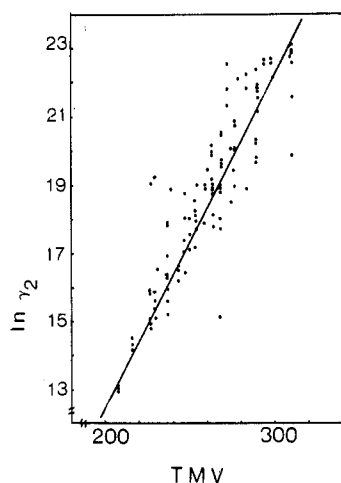

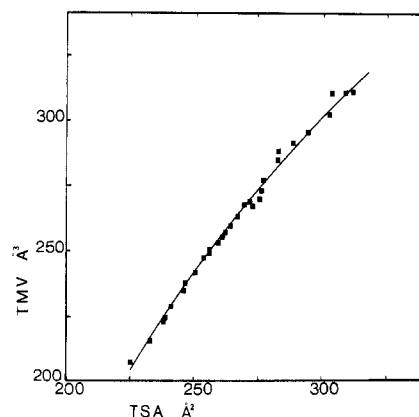**Figure 4.** Relationship between TMV and ln γ_2 of all PCB's listed in Table II.

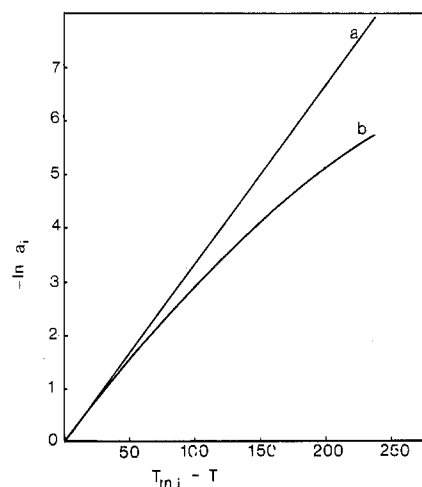**Figure 5.** Relationships between TSA and TMV of PCB's listed in Table II.

Figure 6. Relationships between solute melting point (T_m) and ln a_i as estimated by eq 9 (line a) and 11 (line b) for an experimental temperature of 295 K.

pected on the basis of the scaled particle theory of hydrophobic solutes in water (53), no simple interpretation of increasing r^2 values can be formulated, since TSA and TMV are mutual dependent parameters.

The observation that both TSA – ln γ_{aq} and TMV – ln γ_{aq} relationships will generally give satisfactory correlations can probably be explained by the fact that calculated TMV and TSA are almost proportional for most classes of solutes, over limited ranges of TMV and TSA. This, for instance, can be shown for the TSA and TMV values of 80 polynuclear aromatic and hetero aromatic compounds reported by Pearlman et al. (51).

In Figure 5 the TSA/TMV relationship is shown for PCB data reported in Table II. From this figure it can be seen that for PCB's the TMV/TSA ratio is not constant. In particular for the higher chlorinated compounds this ratio deviates significantly from that of biphenyl, due to the higher TMV/TSA ratio of chlorine compared to carbon and hydrogen. For the lower chlorinated biphenyls the deviation is very limited, so that both parameters will give almost similar correlations when they are related to experimental aqueous activity coefficients. In addition, since the solubility data show large scattering, no choice can be made for statistical preference of either a ln γ_{aq} – TMV or a ln γ_{aq} – TSA relationship.

It must be noted that describing the molal aqueous solubility of solid solutes with low to moderate melting points (<250 °C), both with the assumption $\Delta C_p = 0$ and with $\Delta C_p = \Delta S_f$, will usually give satisfactory results. This since the difference between the estimated ln a_i values with the methods at T = 25 °C is limited. In Figure 6 the

different ln a values of PCB's at 25 °C calculated with either eq 9 and 11 are shown. It is obvious that for solutes with melting points below 150 °C the resulting deviation between the two ln a_i calculation foundations is very small. For chemicals with high melting points such as highly chlorinated biphenyls, however, the differences are significant, i.e., Δ ln a_i being $\simeq 2$ for decachlorobiphenyl. Furthermore, it should be noted that $\Delta C_p = 0$ probably underestimates the actual ΔC_p value, which may result in an underestimate of the mole fraction solubility. This in contrast to the assumption $\Delta C_p = \Delta S_f$, which may overestimate ΔC_p, and thus leads to an overestimate of the solubility (15).

For many investigations of the aqueous solubility of extremely hydrophobic chemicals deviations between the estimation methods will not be sufficient to indicate the validity of either eq 13 or 14, due to the large deviations in the experimentally determined aqueous solubilities. For chemicals with high melting points such as highly chlorinated biphenyls, however, the use of $\Delta C_p = \Delta S_f$, rather than $\Delta C_p = 0$, may improve the relationship between chemical structure and aqueous activity coefficient significantly.

Conclusions

Saturation of water with extremely hydrophobic chemicals is difficult, and application of different saturation methods usually gives variable results. This experimental problem implies that statistical validation of relationships between molal aqueous solubility and structure parameters

can be rather debatable. Application of solubility data obtained with comparable saturation techniques reduces the scattering of data.

Calculated aqueous solute activity coefficients of biphenyls with 0–10 chlorine atoms correlate well with both total molecular volume and total surface area of both liquid and solid solutes. For solid PCB's, the best results are obtained if it is assumed that the differential heat capacity (ΔC_p) between supercooled liquid and solid state is equal to the entropy of fusion at the melting point. The validity of the latter assumption is supported by the Hildebrand plot of 2,2',4,4',5,5'-hexachlorobiphenyl, which shows a linear relationship between $\ln X_{aq}$ and $\ln T$.

Finally after investigation of the full thermodynamics of solution of two congeners, it has become evident that the solution process of PCB's is dominated by losses of entropy during dissolution and not by enthalpy changes.

Registry No. biphenyl, 92-52-4; 2-chlorobiphenyl, 2051-60-7; 3-chlorobiphenyl, 2051-61-8; 4-chlorobiphenyl, 2051-62-9; 2,2'-dichlorobiphenyl, 13029-08-8; 2,4-dichlorobiphenyl, 33284-50-3; 2,4'-dichlorobiphenyl, 34883-43-7; 2,5-dichlorobiphenyl, 34883-39-1; 2,6-dichlorobiphenyl, 33146-45-1; 4,4'-dichlorobiphenyl, 2050-68-2; 2,2',5-trichlorobiphenyl, 37680-65-2; 2,3,4'-trichlorobiphenyl, 38444-85-8; 2,4,4'-trichlorobiphenyl, 7012-37-5; 2,4,5-trichlorobiphenyl, 15862-07-4; 2,4',5-trichlorobiphenyl, 16606-02-3; 2,4,6-trichlorobiphenyl, 35693-92-6; 3,3',4-trichlorobiphenyl, 37680-69-6; 2,2',3,3'-tetrachlorobiphenyl, 38444-93-8; 2,2',3,5-tetrachlorobiphenyl, 70362-46-8; 2,2',4,4'-tetrachlorobiphenyl, 2437-79-8; 2,2',4,5'-tetrachlorobiphenyl, 41464-40-8; 2,2',5,5'-tetrachlorobiphenyl, 35693-99-3; 2,2',6,6'-tetrachlorobiphenyl, 15968-05-5; 2,3',4,4'-tetrachlorobiphenyl, 32598-10-0; 2,3,4,5-tetrachlorobiphenyl, 33284-53-6; 2,3',4',5-tetrachlorobiphenyl, 32598-11-1; 3,3',4,4'-tetrachlorobiphenyl, 32598-13-3; 2,2',3,4,5-pentachlorobiphenyl, 55312-69-1; 2,2',3,4,6-pentachlorobiphenyl, 55215-17-3; 2,2',4,5,5'-pentachlorobiphenyl, 37680-73-2; 2,3,4,5,6-pentachlorobiphenyl, 18259-05-7; 2,2',3,3',4,4'-hexachlorobiphenyl, 38380-07-3; 2,2',3,3',4,5'-hexachlorobiphenyl, 55215-18-4; 2,2',3,3',5,6-hexachlorobiphenyl, 52704-70-8; 2,2',3,3',6,6'-hexachlorobiphenyl, 38411-22-2; 2,2',4,4',5,5'-hexachlorobiphenyl, 35065-27-1; 2,2',4,4',6,6'-hexachlorobiphenyl, 33979-03-2; 2,2',3,3',4,4',6-heptachlorobiphenyl, 52663-71-5; 2,2',3,4',5,5',6-heptachlorobiphenyl, 52663-68-0; 2,2',3,4,5'-pentachlorobiphenyl, 38380-02-8; 2,2',3,3',4,4',5,5'-octachlorobiphenyl, 35694-08-7; 2,2',3,3',5,5',6,6'-octachlorobiphenyl, 2136-99-4; 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl, 40186-72-9; 2,2,3,3',4,5,5',6,6'-nonachlorobiphenyl, 52663-77-1; 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl, 2051-24-3.

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Formation of Chlorinated Aromatic Hydrocarbons by Thermal Decomposition of Vinylidene Chloride Polymer

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■ Two kinds of wrapping film made of poly(vinylidene chloride) were pyrolyzed under an airstream, and the pyrolysis products were identified by capillary gas chromatography–mass spectrometry. Many chlorinated aromatic compounds and polynuclear aromatic hydrocarbons were detected. Important products were chlorinated benzenes, styrenes, phenols, phenylacetylenes, naphthalenes, biphenyls, and benzofurans. Most of these compounds were newly detected. It was also found that many chlorinated aromatic compounds were produced by pyrolysis even at 200 °C. Small amounts of chlorodibenzofuran and dichlorodibenzofuran were detected in the pyrolysate at 600 °C.

Introduction

It has been confirmed that toxic chlorinated organic compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are formed during combustion of compounds containing chlorine substituents (*1–8*). Particularly, pyrolysis of polychlorinated biphenyls (PCBs) has been investigated in detail regarding PCDFs (*9–16*). Also, polymers containing chlorine substituents are one of many potential sources for emission of some chlorinated compounds into the atmosphere. Thermal decomposition of poly(vinyl chloride) has already reported by several researchers. Iida et al. detected polychlorinated benzenes with aromatic hydrocarbons by pyrolysis of poly(vinyl chloride) (*17, 18*). Yamazaki et al. reported that aliphatic and aromatic hydrocarbons, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and 1,1,1,2-tetrachloroethane were formed together with a large amount of hydrogen chloride by pyrolysis of poly(vinyl chloride) (*19, 20*). Ahling et al. have confirmed the formation of polychlorinated benzenes, ranging from dichlorobenzene to hexachlorobenzene, during combustion of poly(vinyl chloride) (*21*). However, it was observed by Hawley-Fedder et al. (*22*) that the major components produced during combustion of a mixture of polyethylene, polystyrene, and poly(vinyl chloride) over 800 °C were alkylbenzenes and aliphatic and polynuclear aromatic hydrocarbons and that the contents of chlorinated compounds were very low.

Poly(vinylidene chloride) is widely used as wrapping material in the world as well as poly(vinyl chloride). Reports on pyrolysis of poly(vinylidene chloride) are very few, compared with poly(vinyl chloride). Hiramatsu determined the formation of chloroethylene by pyrolysis of poly(vinylidene chloride) (*23*). Ballistreri et al. observed

the formation of dichloroethylene, trichlorobenzene, and tetrachloronaphthalene by pyrolysis of poly(vinylidene chloride) in an ion source of mass spectrometer (*24*). Dougherty and Collazo-Lopez (*25*) showed that compounds tentatively identified on pyrolysis products of poly(vinylidene chloride) at 1000 °C were hexachlorobenzene, pentachlorophenol, chlorinated styrenes, chlorinated naphthalanes, PCBs, chlorinated polynuclear aromatic compounds, etc. Recently, Yamaguchi et al. (*26*) presented the emission of a fairly large amount of polychlorinated benzenes and PCBs from the reclaimed land in Japan and also suggested that the compounds might come from thermal decomposition of polymers containing chlorine substituents. It is extremely important and interesting to investigate what kinds of compounds are formed from poly(vinylidene chloride) during combustion in incinerators or thermal decomposition in reclaimed land. Moreover, it is a serious and emergent problem from a viewpoint of environmental pollution and toxicology that polymers containing chlorine substituents might be another source for toxic chlorinated compounds such as PCBs and polychlorinated naphthalenes (PCNs) even in reclaimed lands. From these viewpoints, we investigated the pyrolysis of poly(vinylidene chloride), which is consumed in large quantities. It was confirmed that many kinds of chlorinated aromatic compounds were formed in fairly large quantities. Many compounds were newly detected. This paper describes these results.

Experimental Section

Materials. Two kinds of vinylidene chloride polymers were used. Both polymers (A and B) are food wrapping films made by Asahi Kasei Co. and Kureha Kagaku Co. (both in Japan), respectively, and contain derivatives of fatty acids and epoxides of vegetable oils as plasticizer and stabilizer.

Thermal Decomposition. Samples were put in a small boat-type container made of quartz and inserted into a quartz tube that was heated at 500 °C under the airflow of 300 mL/min and then kept standing for 20 min. Air used here was prepared by mixing pure oxygen and pure nitrogen at the ratio of 1:4. Thermal decomposition occurred immediately after insertion, and evolved gas was passed through hexane (each 20 mL) in ice-cooled traps joined in series. This apparatus is shown in Figure 1. Details of samples are shown in Table I. After decomposition, combined hexane solution was dried on anhydrous sodium sulfate and concentrated carefully by rotary