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Reversed phase liquid chromatography of PCBs as a basis for the calculation of water solubility and log K_{ow} for polychlorobiphenyls*

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Umkehrphasen-Flüssig-Chromatographie von PCBs als Grundlage zur Berechnung der Wasserlöslichkeit und des log K_{ow} für Polychlorbiphenyle

Summary. Water solubility (S_w) and log K_{ow} values have been determined for 154 possible polychlorobiphenyls using the retention indices obtained by RP-HPLC and structurally selected PCB congeners with known log K_{ow} values for the regression lines. The water solubility data are melting point corrected.

Introduction

The determination of log K_{ow} data including the water solubility of highly hydrophobic compounds using capacity factors k' obtained by reversed phase LC has become a standard method complementing the direct determinations of these important physical properties. The limitations and possibilities of this approach have been reviewed recently [1–4].

Log K_{ow} values are also often calculated from substituent constants [5]. For the polychlorobiphenyls this has been done quite extensively [6]. Values of the literature are summarized by Erickson [7].

Results

RP-HPLC of polychlorobiphenyls

Retention data can be expressed in a normalized way as retention indices (I) using the retention increments of the (CH_2)-group of a series of homologues as the unit for 100 I values. This approach has been widely used in gas chromatography and in liquid chromatography as well. The retention indices in this paper are based on the homologues 2-ketoalkanes for the stationary phases Nucleosil 5C 18 and Sepralyte Diphenyl, while for the stationary phase Nucleosil 5 CN they are based on the homologues phenylalkanes [8].

The measured values for the retention indices of 87 PCB congeners are summarized in Table 1. Retention index increments (Table 2) derived from symmetrical PCB congeners (Table 1) have been used to calculate the retention indices for those PCB congeners, which we had not been available as standards for a direct k' measurement [8].

Plotting the degree of chlorination against retention indices indicates that the PCBs have to be divided in two, but more strictly in three subgroups for all further calculations using regression lines. These subgroups are characterized by

1.1. PCBs with no chlorines in the ortho-position

1.2. PCBs with one chlorine in the ortho-position

2. PCBs with two or more chlorines in the ortho-position.

Most often the groups 1.1 and 1.2 can be considered together. They constitute the so called "planar" PCBs, which exhibit distinct biological activities as compared to group 2.

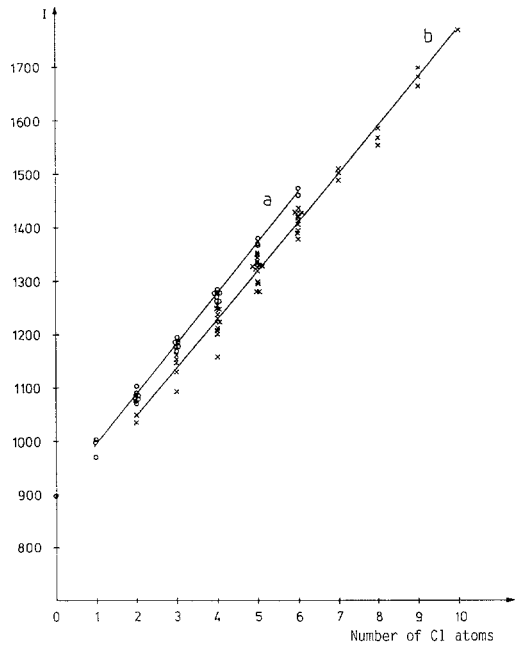

Fig. 1. Correlation of retention index and degree of chlorination of PCB's (RP-HPLC: Sepralyte Diphenyl/55% CH_3CN). ○ PCB with none chlorine in ortho-position (*a*): × PCB with two or more chlorines in ortho-position (*b*)

* Dedicated to Prof. Dr. W. Fresenius on the occasion of his 75th birthday

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Table 1. Retention indices of polychlorobiphenyls (PCBs) obtained for the phase systems Nucleosil 5C18 ($MeOH/H_2O$ and CH_3CN/H_2O), Sepralyte Diphenyl ($MeOH/H_2O$ and CH_3CN/H_2O) with 2-ketoalkanes as homologue standards and nucleosil 5 CN ($MeOH/H_2O$ and CH_3CN/H_2O) with phenylalkanes as homologue standards

PCB-Congeneres		Nucleosil 5C18		Sepralyte Diphenyl		Nucleosil 5CN	
PCB-No.	Structure	MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN
0	Biphenyl	820	753	857	897	496	375
1	2-	859	810	947	974	553	450
2	3-	944	873	965	1,003	621	485
3	4-	928	870	967	999	617	498
4	2,2′	843	818	982	1,038	606	522
5	2,3	959	904	1,056	1,070	663	550
7	2,4	1,014	955	1,062	1,082	643	564
8	2,4′	982	926	1,067	1,086	671	573
9	2,5	997	935	1,059	1,078	647	563
10	2,6	890	851	1,009	1,052	597	521
11	3,3′	1,058	977	1,065	1,091	735	604
12	3,4	1,048	973	1,067	1,080	729	586
14	3,5	1,124	1,016	1,076	1,087	711	598
15	4,4′	1,003	986	1,064	1,107	722	612
18	2,2′,5	977	937	1,081	1,132	698	629
19	2,2′,6	868	865	1,022	1,092	661	594
21	2,3,4	1,100	1,025	1,174	1,177	764	644
24	2,3,6	1,014	949	1,116	1,150	703	624
26	2,3′,5	1,102	1,036	1,150	1,168	756	675
28	2,4,4′	1,101	1,053	1,164	1,178	762	692
29	2,4,5	1,156	1,062	1,176	1,181	743	656
30	2,4,6	1,094	1,014	1,131	1,155	680	632
31	2,4′,5	1,089	1,040	1,162	1,182	758	686
32	2,4′,6	885	919	1,064	1,164	705	662
33	2′,3,4	1,093	1,034	1,104	1,173	774	663
36	3,3′,5	1,151	1,068	1,163			
37	3,4,4′	1,114	1,068	1,170	1,195	826	706
40	2,2′,3,3′	1,022	1,005	1,192	1,215	816	707
41	2,2′,3,4	1,086	1,044	1,203	1,220	816	711
44	2,2′,3,5′	1,053	1,032	1,185	1,222	805	724
47	2,2′,4,4′	1,135	1,094	1,212	1,254	800	751
48	2,2′,4,5	1,080	1,035	1,144	1,205	741	704
49	2,2′,4,5′	1,118	1,079	1,191	1,238	791	744
50	2,2′,4,6	1,082	1,046	1,174	1,210	744	705
52	2,2′,5,5′	1,105	1,054	1,166	1,225	790	739
53	2,2′,5,6′	998	985	1,114	1,224	743	696
54	2,2′,6,6′	884	914	1,065	1,164	707	664
60	2,3,4,4′	1,177	1,119	1,293	1,277	875	769
61	2,3,4,5	1,278	1,148	1,315	1,275	857	742
65	2,3,5,6	1,173	1,072	1,238	1,235	798	722
67	2,3′,4,5	1,245	1,149	1,264	1,270	855	777
69	2,3′,4,6	1,176	1,099	1,208	1,243	789	739
70	2,3′,4′,5	1,202	1,136	1,258	1,264	863	774
75	2,4,4′,6	1,175	1,108	1,237	1,262	799	757
77	3,3′,4,4′	1,223	1,161	1,264	1,277	938	811
80	3,3′,5,5′	1,358	1,228	1,273	1,283	910	828
86	2,2′,3,4,5	1,266	1,172	1,342	1,331	906	808
87	2,2′,3,4,5′	1,191	1,147	1,298	1,326	908	825
93	2,2′,3,5,6	1,151	1,099	1,259	1,294	846	781
95	2,2′,3,5′,6	1,098	1,080	1,212	1,278	842	787
97	2,2′,3′,4,5	1,218	1,160	1,324	1,328	900	819
98	2,2′,3′,4,6	1,148	1,121	1,242			
100	2,2′,4,4′,6	1,212	1,169	1,261			
101	2,2′,4,5,5′	1,245	1,175	1,283	1,326	884	836
103	2,2′,4,5′,6	1,183	1,142	1,224	1,297	824	803
105	2,3,3′,4,4′	1,284	1,212	1,389	1,364	976	859
106	2,3,3′,4,5	1,362	1,231	1,403	1,358	972	864
112	2,3,3′,5,6	1,257	1,148	1,316	1,321	910	828
114	2,3,4,4′,5	1,332	1,230		1,377	969	877
115	2,3,4,4′,6	1,265	1,176	1,369	1,351	917	849
116	2,3,4,5,6	1,334	1,176	1,392	1,336	933	820
117	2,3,4′,5,6	1,249	1,161	1,354	1,348	921	853
119	2,3′,4,4′,6	1,268	1,198	1,319	1,344	894	837

Table 1. Continued

PCB-Congeneres		Nucleosil 5C18		Sepralyte Diphenyl		Nucleosil 5CN	
PCB-No.	Structure	MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN
121	2,3′,4,5′,6	1,316	1,223	1,287	1,328	870	844
128	2,2′,3,3′,4,4′	1,283	1,239	1,432	1,426	1,020	911
129	2,2′,3,3′,4,5	1,336	1,248	1,449	1,421	1,014	902
137	2,2′,3,4,4′,5	1,368	1,286	1,444	1,421	1,002	932
138	2,2′,3,4,4′,5′	1,326	1,263	1,410	1,428	1,006	920
140	2,2′,3,4,4′,6′	1,278	1,246	1,351	1,412	939	887
141	2,2′,3,4,5,5′	1,360	1,267	1,403	1,422	1,002	919
143	2,2′,3,4,5,6′	1,286	1,235	1,360	1,387	933	
151	2,2′,3,5,5′,6	1,251	1,198	1,315	1,378	935	882
153	2,2′,4,4′,5,5′	1,370	1,293	1,404	1,428	984	936
154	2,2′,4,4′,5,6′	1,326	1,272	1,350	1,407	923	893
155	2,2′,4,4′,6,6′	1,292	1,272	1,297	1,392	856	868
156	2,3,3′,4,4′,5	1,430	1,315	1,509	1,458	1,078	963
169	3,3′,4,4′,5,5′	1,489	1,363	1,471	1,470	1,143	1,017
171	2,2′,3,3′,4,4′,6	1,374	1,325		1,499	1,057	978
181	2,2′,3,4,4′,5,6	1,437	1,344	1,514	1,508	1,048	989
183	2,2′,3,4,4′,5′,6	1,415	1,346	1,462	1,501	1,044	992
185	2,2′,3,4,5,5′,6	1,412	1,311	1,462	1,484	1,066	980
200	2,2′,3,3′,4,5′,6,6′	1,450	1,422	1,508	1,563	1,070	1,008
202	2,2′,3,3′,5,5′,6,6′	1,414	1,397	1,466	1,553	1,167	1,001
204	2,2′,3,4,4′,5,6,6′	1,529	1,462	1,554	1,582	1,072	1,032
206	2,2′,3,3′,4,4′,5,5′,6	1,650	1,527	1,694	1,689	1,312	1,178
207	2,2′,3,3′,4,4′,5,6,6′	1,625	1,542	1,663	1,671	1,182	1,112
208	2,2′,3,3′,4,5,5′,6,6′	1,595	1,519	1,627	1,655	1,165	1,096
209	2,2′,3,3′,4,4′,5,5′,6,6′	1,765	1,636	1,790	1,763	1,310	1,195

Table 2. Retentionindex-increments I/2 obtained from symmetrically substituted polychlorobiphenyls (see Table 1)

Structure	Nucleosil 5C18		Sepr. Diphenyl		Nucleosil 5CN	
	MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN
0	410	376	428	448	248	188
2	422	409	491	519	303	261
3	529	488	533	545	368	302
4	502	493	532	553	361	306
23	511	503	596	608	408	354
24	568	547	606	627	400	376
25	553	527	583	610	395	370
26	442	457	532	582	354	332
34	612	581	632	638	469	406
35	679	614	636	642	455	414
234	642	619	716	713	510	456
245	685	646	702	714	492	468
246	646	636	648	696	428	434
345	745	682	735	735	572	508
2356	707	698	733	776	584	501
23456	883	818	895	882	655	598

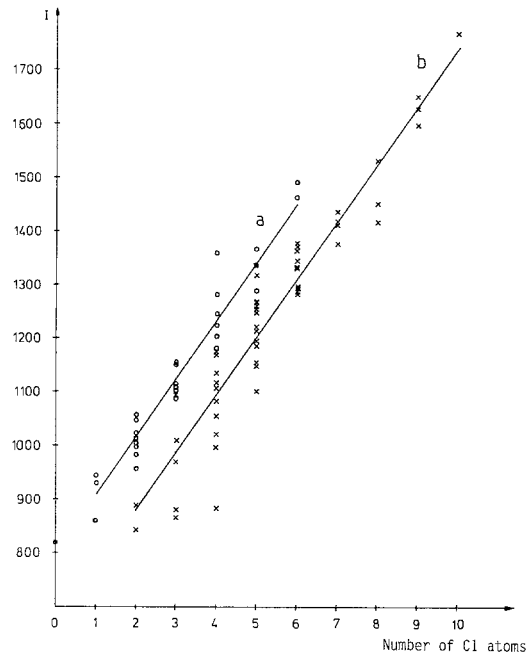

Fig. 2. Correlation of retention index and degree of chlorination of PCB's (RP-HPLC: Nucleosil 5C18/80% MeOH). ○ PCB with none or one chlorine in ortho-position (*a*). × PCB with two or more chlorines in ortho-position (*b*)

The least spreading of the retention indices of the same degree of chlorination is observed using the Sepralyte Diphenyl-phase and 55% acetonitril as eluent (Fig. 1). Structural pecularities are most pronounced using Nucleosil 5 C18 as the stationary phase and 80% MeOH as the eluent (Fig. 2). In terms of selectivity this system has the best performance. General aspects of the structural dependency of the chromatographic retention will be discussed separately.

The stationary phase Nucleosil 5 CN and 47.5% MeOH as eluent provide a separation system, which has a pronounced distinction between subgroups 1.1 (no chlorine in ortho-position) and subgroup 1.2 (one chlorine in ortho-position) (Fig. 3).

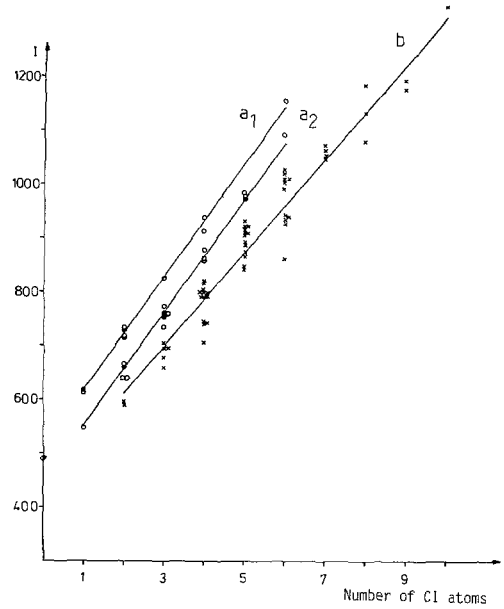

Fig. 3. Correlation of retention index and degree of chlorination of PCB's (RP-HPLC: Nucleosil 5CN/47.5% MeOH). ○ PCB with none chlorine in ortho-position (a_1); PCB with one chlorine in ortho-position (a_2) × PCB with two or more chlorines in ortho-position (b)

Calculations of log K_{ow}

The values for log K_{ow} are derived from the correlation

$$\log K_{ow} = \text{const}_1 + \text{const}_2 \, I \,. \quad (1)$$

where I stands for the retention index.

Table 3. Parameters of equation $\log K_{ow} = \text{const}_1 + \text{const}_2$ I for two PCB subgroups and the RP-HPLC systems. 5C18/MeOH, 5C18/CH_3CN, Diphenyl/MeOH and Diphenyl/CH_3CN

PCB group Structure	n	const_1	const_2 100	r	HPLC system
ortho ≦ 1	12	0.23	0.49	0.930	5C18/MeOH
ortho ≧ 2	13	1.50	0.39	0.969	5C18/MeOH
ortho ≦ 1	12	−0.23	0.57	0.979	5C18/CH_3CN
ortho ≧ 2	13	1.34	0.43	0.980	5C18/CH_3CN
ortho ≦ 1	12	−1.06	0.59	0.988	Diphenyl/MeOH
ortho ≧ 2	13	0.53	0.44	0.981	Diphenyl/MeOH
ortho ≦ 1	12	−1.80	0.64	0.987	Diphenyl/CH_3CN
ortho ≧ 2	13	0.17	0.46	0.979	Diphenyl/CH_3CN

Table 4. Log K_{ow} values and water solubility (log S_w) in mol/l. Literature values and values obtained from RP-HPLC data (Tables 1 and 2)

Polychlorobiphenyls				log P_{ow} (HPLC)				−log S_w in mol/l			
PCB-No.	log P_{ow}	−log S_w	T_m (°C)	Nucleosil 5C18		Sepralyte Diphenyl		Nucleosil 5C18		Sepralyte Diphenyl	
				MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN
0	3.94	4.28	71	4.14	4.06	4.00	3.94	4.19	4.19	4.19	4.16
1	4.50	4.66	34	4.33	4.39	4.53	4.43	4.66	4.60	4.13	4.66
2	4.65	5.16	17	4.65	4.75	4.63	4.62	5.53	5.36	5.33	5.34
3	4.55	5.32	78	4.55	4.73	4.64	4.59	5.36	5.33	5.35	5.30
4	4.90	5.45	61	4.25	4.86	4.85	4.94	5.64	5.84	5.79	5.64
5			28	4.82	4.92	5.17	5.05	5.23	5.26	5.47	5.43
6				4.84				5.26			
7		5.55	24	5.09	5.21	5.20	5.12	5.58	5.62	5.51	5.53
8	5.14		43	4.93	5.05	5.24	5.15	5.36	5.42	5.54	5.53
9	5.16	5.58	23	5.01	5.10	5.19	5.10	5.48	5.48	5.49	5.50
10	4.93		35	4.97	5.00	4.97	5.01	5.88	5.71	5.96	5.74
11	5.30		29	5.30	5.39	5.22	5.18	6.74	6.34	6.38	6.36
12	5.29		49	5.26	5.32	5.24	5.11	6.63	6.30	6.40	6.24
13				5.15				6.40			
14	5.37		31	5.63	5.56	5.29	5.16	7.45	6.72	6.49	6.31
15	5.35	6.60	149	5.03	5.39	5.22	5.28	6.17	6.46	6.37	6.50
16			28	5.12				6.10			
17				5.39				6.49			
18	5.60	5.60	44	5.31	5.37	5.29	5.37	6.40	6.28	6.41	6.30
19				4.88	5.06	5.03	5.19	5.76	5.80	6.04	6.02
21			101	5.51	5.61	5.87	5.73	6.06	6.12	6.26	6.29
22			73	5.29				5.80			
24				5.45	5.42	5.44	5.46	6.58	6.34	6.63	6.42
25				5.54				6.11			
26			40	5.52	5.68	5.72	5.68	6.07	6.19	6.10	6.22
28		5.99	57	5.51	5.77	5.81	5.74	6.10	6.32	6.19	6.30
29	5.68	6.44	78	5.78	5.82	5.88	5.76	6.42	6.38	6.27	6.33
30	5.47		61	5.77	5.70	5.51	5.48	7.03	6.75	6.72	6.46
31	5.79		67	5.46	5.70	5.80	5.76	5.99	6.22	6.18	6.33
32				4.95	5.29	5.21	5.52	5.86	6.15	6.30	6.52
33			60	5.48	5.66	5.98	5.71	6.02	6.18	6.40	6.26
34			58	5.71				6.30			

Table 4. Continued

Polychlorobiphenyls				log P_{ow} (HPLC)				$-\log S_w$ in mol/l			
PCB-No.	log P_{ow}	$-\log S_w$	T_m (°C)	Nucleosil 5C18		Sepralyte Diphenyl		Nucleosil 5C18		Sepralyte Diphenyl	
				MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN
36				5.76	5.86	5.80		7.74	7.22	7.41	
37		7.23	88	5.58	5.86	5.84	5.85	7.37	7.26	7.48	7.48
40			121	5.48	5.66	5.77	5.76	6.62	6.70	7.10	6.88
41				5.73	5.83	5.82	5.78	6.98	6.95	7.17	6.92
42			69	5.72				6.96			
44			47	5.61	5.78	5.74	5.79	6.80	6.87	7.06	6.93
45				4.84				6.30			
46				4.84				6.30			
47			42	5.93	6.04	5.86	5.94	7.26	7.27	7.23	7.16
48				5.71	5.79	5.56	5.71	6.95	6.89	6.80	6.81
49	5.73		66	5.86	5.98	5.77	5.86	7.16	7.18	7.10	7.04
50				5.72	5.84	5.70	5.74	6.96	6.96	6.99	6.85
51				5.51				6.65			
52			87	5.81	5.87	5.66	5.81	7.09	7.02	6.94	6.95
53				5.39	5.57	5.43	5.80	6.49	6.57	6.61	6.94
54			198	4.95	5.27	5.22	5.52	5.85	6.12	6.31	6.52
56				5.85				6.47			
60			142	5.89	6.15	6.57	6.37	6.51	6.78	7.06	7.08
61	5.72	7.18	92	6.38	6.31	6.70	6.36	7.15	6.99	7.21	7.08
63				6.10				6.77			
64				5.76				7.02			
65			79	6.07	5.95	5.98	5.85	7.47	7.13	7.39	7.02
66			128	5.98				6.63			
67				6.22	6.32	6.40	6.33	6.92	6.99	7.56	7.04
69				6.09	6.06	6.09	5.89	7.48	7.30	7.20	7.08
70			106	6.01	6.24	6.36	6.29	6.06	6.90	6.83	6.99
71				5.76				7.02			
74			125	6.10				6.77			
75				6.08	6.10	5.97	5.97	7.48	7.36	7.38	7.21
76				5.98				6.71			
77		8.59	180	6.11		6.40	6.37	8.55		8.46	8.40
80			164	6.77	6.77	6.45	6.41	8.98	8.77	8.57	8.51
84				5.60				6.78			
85				6.18				7.62			
86			100	6.44	6.38	6.43	6.29	7.99	7.77	8.04	7.70
87		7.86	112	6.14	6.27	6.24	6.27	7.60	7.62	7.77	7.67
89				5.60				6.78			
90				6.32				7.82			
91				5.87				7.17			
92				6.32				7.82			
93				5.99	6.06	6.07	6.12	7.34	7.30	7.52	7.44
95				5.78	5.98	5.86	6.05	7.05	7.18	7.23	7.32
97			82	6.25	6.33	6.36	6.28	7.72	7.70	7.93	7.68
98				5.98	6.16	5.99		7.33	7.45	7.42	
99				6.41				7.95			
100				6.23	6.37	6.08		7.69	7.75	7.54	
101	6.30	7.89	77	6.36	6.39	6.18	6.27	7.91	7.80	7.67	7.67
103				6.11	6.25	5.92	6.14	7.52	7.58	7.30	7.46
105			103	6.41	6.68	7.14	6.93	7.14	7.44	7.71	7.80
106				6.79	6.79	7.22	6.89	7.60	7.57	7.80	7.75
110				6.20				7.65			
112				6.40	6.28	6.70	6.25	7.93	7.62	7.88	7.63
113				6.45				7.95			
114			99	6.65	6.78			7.43	7.57		7.90
115				6.43	6.40	6.55	6.38	7.98	7.80	8.21	7.84
116	6.30	7.68	124	6.70	6.40	6.65	6.32	8.37	7.80	8.36	7.73
117				6.37	6.33	6.49	6.37	7.89	7.70	8.12	7.82
118			106	6.57				7.33			
119				6.44	6.49	6.33	6.35	8.00	7.94	7.90	7.79
121				6.63	6.60	6.19	6.28	8.21	8.10	7.70	7.68
123				6.64				7.42			
128	6.98	8.91	150	6.50	6.67	6.83	6.73	8.12	8.22	8.61	8.37
129			85	6.71	6.71	6.90	6.71	8.38	8.26	8.72	8.33
131				6.78				8.48			

Table 4. Continued

Polychlorobiphenyls				log P_{ow} (HPLC)				$-\log S_w$ in mol/l			
PCB-No.	log P_{ow}	$-\log S_w$	T_m (°C)	Nucleosil 5C18		Sepralyte Diphenyl		Nucleosil 5C18		Sepralyte Diphenyl	
				MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN	MeOH	CH_3CN
132				6.20				7.65			
134				6.20				7.65			
135				6.32				7.82			
137			77	6.84	6.87	6.88	6.71	8.56	8.51	8.68	8.33
138			79	6.67	6.77	6.73	6.74	8.32	8.36	8.47	8.38
140				6.48	6.70	6.47	6.66	8.06	8.25	8.38	8.27
141				6.80	6.79	6.70	6.71	8.52	8.38	8.43	8.34
143				6.52	6.65	6.51	6.55	8.10	8.18	8.16	8.09
144				6.45				8.01			
146				6.85				8.58			
148				5.74				6.99			
149				6.41				7.94			
151			100	6.38	6.49	6.32	6.51	7.90	7.94	7.87	8.03
153	6.90	8.47	103	6.84	6.90	6.71	6.74	8.61	8.56	8.43	8.38
154				6.67	6.81	6.47	6.64	8.32	8.42	8.09	8.23
155	7.55	8.60	114	6.54	6.81	6.24	6.57	8.16	8.43	7.76	8.13
156				7.13	7.26	7.84	7.53	8.00	8.17	8.51	8.55
158				6.78				8.48			
163				6.78				8.48			
164				6.63				8.27			
167				7.29				8.21			
169			201	7.42	7.54	7.62	7.61	8.90	9.08	8.84	8.60
170			135	7.08				8.90			
171	6.68		122	6.86	7.04		7.06	8.59	8.76		8.88
172				7.21				9.10			
174			131	6.85				8.59			
175				6.92				8.68			
176				6.55				8.15			
177				6.73				8.42			
178				6.85				8.59			
179				6.41				7.94			
180			109	7.21				9.10			
181				7.10	7.12	7.19	7.11	8.95	8.88	9.12	8.94
182			152	6.92				8.68			
183				7.02	7.13	6.96	7.07	8.82	8.90	8.80	8.89
185		8.92	149	7.01	6.98	6.96	7.00	8.84	8.68	8.80	8.78
187				6.92				6.68			
188				6.78				8.49			
189			162	7.72				8.72			
190			116	7.08				8.90			
191				7.21				9.10			
192				7.21				9.10			
193				7.21				9.10			
194		9.19	159	7.62				9.70			
195				7.35				9.29			
196				7.43				9.42			
197			132	7.21				9.10			
198				7.43				9.42			
199				7.21				9.10			
200				7.16	7.54	7.16	7.36	9.02	9.38	9.08	9.33
201				7.35				9.29			
202	7.12	9.37	162	7.01	7.35	6.98	7.31	8.86	9.23	8.82	9.26
203				7.49				9.50			
204				7.46	7.63	7.37	7.45	9.46	9.64	9.37	9.46
205				7.62				9.70			
206		9.61	206	7.94	7.91	7.98	7.94	10.18	10.07	10.25	10.22
207				7.84	7.97	7.85	7.86	10.00	10.15	10.06	10.09
208	8.16			7.72	7.87	7.69	7.78	9.83	10.00	9.83	9.97
209	8.23	10.49	305	8.38	8.37	8.41	8.28	10.83	10.76	10.85	10.74

The thermodynamic basis of the Eq. (1) is the general relationship of partition coefficients of different water-solvent systems:

$$\log K_{ow} = a \log K_{solv} + b . \quad (2)$$

This explains why variations in the stationary and the mobile phase in RP-HPLC must lead to varying values for $const_1$ and $const_2$ in Eq. (1).

The values of $const_1$ and $const_2$ of Eq. (1) are derived from PCB standards with known log K_{ow} values either based on direct measurements or molecular increment calculations. The standards are differentiated by their assignment to either group 1 (no or one ortho-substituent) or group 2 (two are more orthosubstituents). The parameters of Table 3 have been used.

Calculations of water solubility (S_w)

The solubility of PCBs in water (S_w in mol/liter) is derived from Eq. (3)

$$-\log S_w = const_3 + const_4 I \quad (3)$$

based on PCB standards with known water solubility and measured or calculated values for I. As most PCBs have a melting point T_m above room temperature a correction has to be applied [1, 8]:

$$-\log S_w - 0.01\ T_m = const_5 + const_6 I . \quad (4)$$

This correlation has often been used in the past [1].

A correlation of the calculated values for S_w based on either Eq. (3) or Eq. (4), respectively, indicates no stringent necessity of the melting point correction as expressed in Eq. (4) [8].

Table 4 summarizes the values for log K_{ow} and log S_w (mol/liter) of 154 PCB congeners calculated by Eqs. (1) and (4), respectively, using the log K_{ow} and S_w values derived from literature for the regression lines. The literature values are also included in Table 4.

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Note added in proof

An updating of the OECD Test Guideline 107 "Partition coefficient N-octanol/water" and the inclusion of the HPLC method is reported by Klein W, Kördel W, Weiß M, Doranski HJ (1988) Chemosphere 17:361–386. A compilation of experimental water solubility values of PCBs measured at 25°C is given by Doucette WJ, Andren AW (1988) Chemosphere 17:243–252. The same authors report about an evaluation of six methods for the estimation of octanol/water partition coefficients for highly hydrophobic hydrocarbons including 25 polychlorobiphenyls (1988) Chemosphere 17:345–359. Experimentally determined aqueous solubility data of 26 PCB congeners are reported by Dunnivant FM, Elzerman AW (1988) Chemosphere 17:525–541.