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## **Solvation parameters for mercury and mercury(II) compounds: calculation of properties of environmental interest**

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Descriptors have been determined for four inorganic mercury(II) species and for seventeen organic mercury(II) species, using experimental literature data. These descriptors can then be used in equations that we have already set out in order to estimate a large number of physicochemical properties. These include the water to octanol partition coefficient and the gas to water partition coefficient. For the organic mercury(II) species, including dimethylmercury and the methylmercury(II) halides, the latter has been estimated over the temperature range 273-373K.

### **Introduction**

Mercury and mercury(II) compounds are important species; dimethylmercury and methylmercury(II) compounds are known environmental pollutants. Although a number of thermodynamic properties are available especially for mercury<sup>1,2</sup> and mercury(II) halides,<sup>2</sup> many other properties that are relevant to environmental and health issues are not known. A number of computational methods can be used for the calculation of a range of properties of compounds, but many of these methods such as SPARC,<sup>3</sup> Advanced Chemistry Development<sup>4</sup> and PharmaAlgorithms,<sup>5</sup> cannot deal with any compounds that contain mercury atoms. COSMO-RS<sup>6</sup> can in principle calculate descriptors for mercury-containing compounds but the quality of predictions is expected to be lower than general because the element-specific adjustable parameter for mercury (the mercury COSMO-radius) has not been optimized. CODESSA<sup>7</sup> can be used in principle, but, as we shall show, the calculations are not at all reliable. There are several methods for the calculation of the environmentally important property  $\log P_{oct}$ , where  $P_{oct}$  is the water to octanol partition coefficient, of which the programs KOWWIN<sup>8</sup> and CLOGP<sup>9</sup> can deal with mercury atoms.

Over the last few years we have put forward equations, based on our solvation parameters,<sup>10,11</sup> that can be used for the prediction of a wide range of physicochemical and biochemical processes. Some of these processes are of environmental interest, such as the solubility of gases and vapours in water from 273 to 373K,<sup>12</sup> solubility in saline,<sup>13</sup> and permeation through human skin.<sup>14</sup> Other processes are of toxicological as well as environmental interest such the solubility of

gases and vapours in blood<sup>15</sup> and biological tissues,<sup>16-19</sup> the distribution of compounds between blood and brain<sup>20, 21</sup> and between blood and biological tissues,<sup>17-19</sup> and the toxicity of compounds towards a variety of organisms.<sup>22-26</sup>

It is the purpose of the work to obtain descriptors for mercury and mercury(II) species that can be used in the above equations to predict their effect on a very large number of environmental and toxicological processes.

### Methodology

We use two solvation equations, or linear free energy relationships, LFERs, eqn.(1) and eqn. (2).<sup>10, 11</sup>

$$SP = c + e \mathbf{E} + s \mathbf{S} + a \mathbf{A} + b \mathbf{B} + v \mathbf{V} \quad (1)$$

$$SP = c + e \mathbf{E} + s \mathbf{S} + a \mathbf{A} + b \mathbf{B} + l \mathbf{L} \quad (2)$$

In eqn. (1) and eqn. (2), the dependent variable, SP, is a set of solute properties in a given system. Eqn. (1) is used for processes in condensed systems, for example SP could be log Poct for a series of solutes, and also for gas to water partitions, as log Kw, where Kw is the unit less partition coefficient defined by eqn. (3).

$$Kw = (\text{conc of solute in water, mol/L})/(\text{conc of solute in gas phase, mol/L}) \quad (3)$$

Eqn. (2) is used for gas to solvent partitions, as log Ks, where Ks is defined similarly to Kw. Both eqn. (1) and eqn. (2) can be used for the gas to water partition. The independent variables in eqn.(1) and eqn.(2) are solute descriptors as follows.<sup>10, 11</sup> **E** is the solute excess molar refraction in units of (cm<sup>3</sup> mol<sup>-1</sup>)/10, **S** is the solute dipolarity/polarizability, **A** and **B** are the overall or summation hydrogen bond acidity and basicity, **V** is the McGowan characteristic volume<sup>27</sup> in units of (cm<sup>3</sup> mol<sup>-1</sup>)/100, and **L** is the logarithm of the gas to hexadecane partition coefficient at 298 K.

The use of eqn. (1) and eqn. (2) in the determination of descriptors has been described in detail,<sup>10, 11</sup> and numerous examples are available.<sup>28-32</sup> Equations on the lines of eqn. (1) and eqn. (2) are set up for a number of physicochemical processes, using solutes whose descriptors are known, and the corresponding SP values for a

given compound obtained from the literature. There are six descriptors in eqn. (1) and eqn.(2) that are required for any compound. However,  $V$  can usually be calculated from atomic and bond contributions,<sup>27</sup> and  $E$  can then be obtained by one of a variety of methods. If the refractive index of the liquid compound at 293K is available,  $E$  can be obtained directly. Otherwise  $E$  can be calculated by addition of fragments. This then leaves four descriptors to be evaluated,  $S$ ,  $A$ ,  $B$ , and  $L$ . In principle if four SP values were available for four calibrated systems, the four descriptors could be obtained. In practice, as many system equations as possible are used, and the descriptors that lead to the best fit of calculated and observed SP values are taken. The calculations are considerably aided by the ‘Solver’ program in Microsoft Excel,<sup>®</sup> that can be set up to find the best fit automatically.

It is possible to increase the number of available equations through eqn. (4), where  $P_s$  is a water to solvent partition coefficient and  $K_s$  is the corresponding gas to solvent partition coefficient.

$$\text{Log } P_s = \text{log } K_s - \text{log } K_w \quad (4)$$

If  $K_w$  is known, any set of  $\text{log } P_s$  values can be transformed into  $\text{log } K_w$  values, thus doubling the number of equations that can be used. If  $K_w$  is not known, it can be allowed to float as another descriptor to be obtained. Although this has the effect of increasing the number of unknown descriptors, it considerably increases the number of equations, especially as there are two different equations for  $\text{log } K_w$ , one in terms of eqn. (1) and one in terms of eqn. (2).

## Results

*Mercury.* For organic compounds,  $V$  can easily be calculated. However, for mercury this is not the case, and it is necessary to obtain a value for the McGowan volume,  $V_x$ , which is generally obtained from the corresponding parachor.<sup>28</sup> From the parachor of 130.25 listed by McGowan,<sup>28</sup>  $V_x$  is  $45.95 \text{ cm}^3 \text{ mol}^{-1}$ , considerably more than radon, at  $38.4 \text{ cm}^3 \text{ mol}^{-1}$ . McGowan seemed to prefer a value of  $35.36 \text{ cm}^3 \text{ mol}^{-1}$  but unfortunately no details are available.<sup>29</sup> Ben-Amotz and Herschbach<sup>30</sup> give values of molecular diameters,  $\sigma$ , obtained from the van der Waals equation, including a value for mercury. Comparison of the  $\sigma$  values, as  $\sigma^3$ , with  $V_x$  leads to a value of only 17.3

$\text{cm}^3 \text{mol}^{-1}$  for mercury, which is less than that of argon,  $19.0 \text{ cm}^3 \text{mol}^{-1}$ . Hirschfelder et al.<sup>31</sup> list  $\sigma$  from viscosity measurements, including values for mercury(II) chloride and mercury(II) iodide. A similar comparison gives  $V_x$  for the mercury(II) compounds as 65.65 and 72.98, from which it follows that  $V_x$  for mercury is 17.0 or  $26.4 \text{ cm}^3 \text{mol}^{-1}$  respectively. Batsanov<sup>32</sup> has calculated van der Waals radii of atoms from bond distances, including values for mercury. He lists slightly different sets of values in his Table 5 and Table 6. If the radii are converted into volumes,  $V_{\text{van}}$ , there are reasonably good correlations between  $V_x$  and  $V_{\text{van}}$ :

$$V_x = -2.834 + 1.020 V_{\text{van}} \text{ (from Table 5 }^{32}) \quad (5)$$

$$N = 8, R^2 = 0.959, SD = 2.02, F = 593.4$$

$$V_x = -8.892 + 1.131 V_{\text{van}} \text{ (from Table 6 }^{32}) \quad (6)$$

$$N = 15, R^2 = 0.954, SD = 2.00, F = 1220.5$$

In these equations,  $N$  is the number of data points,  $R$  is the regression correlation coefficient,  $SD$  the standard deviation, and  $F$  the  $F$ -statistic. From the given<sup>32</sup> van der Waals radii for mercury,  $V_x$  may be calculated as 33.02 or  $36.30 \text{ cm}^3 \text{mol}^{-1}$  from eqn. (5) and eqn.(6) respectively, quite close to the suggested value of McGowan.<sup>29</sup> However, the disparity between  $V_x$  values obtained from different sources is so great that some additional method is needed.

Since one of the purposes of obtaining descriptors for mercury(II) species is to be able to predict solubilities and solubility related processes such as water-solvent partitions, it seemed logical to use known solubilities to obtain  $V_x$  (or  $V_x/100$  denoted as  $V$ ). The solubility of liquid mercury in water<sup>1,2</sup>,  $S_w$ , and in organic solvents<sup>2</sup>,  $S_s$ , is known and in Table 1 are listed the solubilities that have been used, as  $\log S_w$  and  $\log S_s$ . These can all be converted into water-solvent partition coefficients, using the known value<sup>1,2</sup> for  $\log S_w$  as -6.53, and in Table 1 are given the derived  $\log P_s$  values. Furthermore, the Henry's Law constant for mercury in water at 298K is known<sup>1,2</sup> as the gas to water partition coefficient,<sup>2</sup>  $\log K_w = 0.46$ . Then from  $\log K_w$  and  $\log S_s$ , the various  $\log K_s$  partition coefficients can be obtained through eqn.

(4); details are in Table 1. A preliminary analysis indicated that the log Ps values for methanol and wet octanol were considerably out of line, and these two solvents were considered no further. The remaining log Ps values together with the log Ss and log Ks values comprised no less than 33 data points to be fitted with the solvation descriptors. The **E**-descriptor could not be allowed to float, because it is derived from **V** and the refractive index of mercury at 293K, which is 1.68.<sup>33</sup> Initial values of **V** and **E** were obtained, and **V** and the refractive index were then used to obtain a better value of **E**. This was repeated until no further improvement in fits with the data was obtained. The other descriptors were allowed to float, the final set being **E** = 0.850, **S** = 0.43, **A** = 0.00, **B** = 0.04, **L** = 1.721 and **V** = 0.3400 (cm<sup>3</sup> mol<sup>-1</sup>/100). These descriptors gave calculated log Ps and log Ks values that fitted the observed 33 data points with a standard deviation of only 0.11 log units. This value of **V** from analysis of mercury solubilities, 0.3400, is very close to the values obtained from Batsanov's van der Waals radii, 0.3302 and 0.3630, and henceforth we take **E** = 0.85 and **V** = 0.3400 for mercury, to be used in the calculation of **E** and **V** for other mercury compounds. The coefficients of the equations we have used, together with others that are important, are in Table 2.

**Table 1** Solubilities of liquid mercury in water and solvents as log Ss and derived log Ps and log Ks values at 298K.

Solvent	Log Ss <sup>2</sup>	Log Ps	Log Ks
Water	-6.54 <sup>1</sup>		0.46 <sup>2</sup>
Water	-6.52		
Pentane	-5.24	1.29	1.75
Hexane	-5.20	1.33	1.79
Heptane	-5.19	1.34	1.80
Octane	-5.19	1.34	1.80
Decane	-5.17	1.36	1.82
Isooctane	-5.24	1.29	1.75
Cyclohexane	-4.93	1.60	2.06
Methylcyclohexane	-5.05	1.48	1.94
Tetrachloromethane	-5.12	1.41	1.87

Benzene	-4.93	1.60	2.06
Toluene	-4.92	1.61	2.07
Chlorobenzene	-4.93	1.60	2.06
Bromobenzene	-4.80	1.73	(2.19) <sup>a</sup>
Nitrobenzene	-5.04	1.49	1.95
Methanol	-5.55	(0.98) <sup>b</sup>	
Isopropanol	-5.57	0.96	1.42
Octanol/Wet	-5.93	(0.62) <sup>b,9</sup>	
Dibutyl ether	-5.15	1.38	1.84

<sup>a</sup> Not used, because of lack of the relevant equation. <sup>b</sup> Not used; out of line.

**Table 2** Coefficients in equations for water to solvent and gas to solvent partitions, at 298K<sup>a</sup>

Process	SP	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	<i>v</i>
Water to :								
Octanol	log Ps	0.088	0.562	-1.054	0.034	-3.460	0	3.814
Isobutanol	log Ps	0.249	0.480	-0.639	-0.050	-2.284	0	2.758
Pentanol	log Ps	0.175	0.575	-0.787	0.020	-2.837	0	3.249
Hexanol	log Ps	0.143	0.718	-0.980	0.145	-3.214	0	3.403
Decanol	log Ps	0.008	0.485	-0.974	0.015	-3.798	0	3.945
Dichloromethane	log Ps	0.314	0.001	0.022	-3.238	-4.137	0	4.259
Trichloromethane	log Ps	0.327	0.157	-0.391	-3.191	-3.437	0	4.191
Tetrachloromethane	log Ps	0.260	0.573	-1.254	-3.558	-4.588	0	4.589
1,2-Dichloroethane	log Ps	0.227	0.278	-0.167	-2.816	-4.324	0	4.205
Pentane	log Ps	0.369	0.386	-1.568	-3.535	-5.215	0	4.514
Hexane	log Ps	0.361	0.579	-1.723	-3.599	-4.764	0	4.344
Heptane	log Ps	0.325	0.670	-2.061	-3.317	-4.733	0	4.543
Octane	log Ps	0.223	0.642	-1.647	-3.480	-5.067	0	4.526
Nonane	log Ps	0.240	0.619	-1.713	-3.532	-4.921	0	4.482
Decane	log Ps	0.160	0.585	-1.734	-3.435	-5.078	0	4.582
Hexadecane	log Ps	0.087	0.667	-1.617	-3.587	-4.869	0	4.433
Cyclohexane	log Ps	0.159	0.784	-1.678	-3.740	-4.929	0	4.577
Methylcyclohexane	log Ps	0.246	0.782	-1.982	-3.517	-4.293	0	4.528
Isooctane	log Ps	0.288	0.382	-1.668	-3.639	-5.000	0	4.561
Benzene	log Ps	0.142	0.464	-0.588	-3.099	-4.625	0	4.491
Toluene	log Ps	0.143	0.527	-0.720	-3.010	-4.824	0	4.545
Chlorobenzene	log Ps	0.040	0.246	-0.462	-3.038	-4.769	0	4.640
Bromobenzene	log Ps	-0.130	0.394	-0.280	-3.331	-4.640	0	4.583



Iodobenzene	log Ps	-0.181	0.410	-0.334	-3.300	-4.595	0	4.549
Nitrobenzene	log Ps	-0.181	0.576	0.003	-2.356	-4.420	0	4.263
Diethyl ether	log Ps	0.248	0.561	-1.016	-0.226	-4.553	0	4.075
Diisopropylether	log Ps	0.197	0.695	-1.220	-0.238	-4.921	0	4.388
Dibutylether	log Ps	0.252	0.677	-1.506	-0.807	-5.249	0	4.815
Ethyl acetate	log Ps	0.253	1.157	-1.397	-0.054	-3.755	0	3.726
Butyl acetate	log Ps	-0.468	0.712	-0.397	0.010	-3.743	0	3.865
Olive oil	log Ps	-0.011	0.577	-0.800	-1.470	-4.921	0	4.173
Tributylphosphate	log Ps	0.015	0.804	-0.862	1.389	-4.647	0	4.129
Carbon disulfide	log Ps	0.047	0.686	-0.943	-3.603	-5.818	0	4.921
Methanol/Dry	log Ps	0.329	0.299	-0.671	0.080	-3.389	0	3.512
Ethanol/Dry	log Ps	0.208	0.409	-0.959	0.186	-3.645	0	3.928
Propanol/Dry	log Ps	0.148	0.436	-1.098	0.389	-3.893	0	4.036
Butanol/Dry	log Ps	0.152	0.438	-1.177	0.096	-3.919	0	4.122
Pentanol/Dry	log Ps	0.080	0.521	-1.294	0.208	-3.908	0	4.208
Hexanol/Dry	log Ps	0.044	0.470	-1.153	0.083	-4.057	0	4.249
Heptanol/Dry	log Ps	-0.026	0.491	-1.258	0.035	-4.155	0	4.415
Octanol/Dry	log Ps	-0.034	0.490	-1.048	-0.028	-4.229	0	4.219
Decanol/Dry	log Ps	-0.062	0.754	-1.461	0.063	-4.053	0	4.293
Isopropanol/Dry	log Ps	0.063	0.320	-1.024	0.445	-3.824	0	4.067
Trifluoroethanol/Dry	log Ps	0.368	-0.505	-0.677	-1.756	-0.325	0	3.123
Ethyl acetate/Dry	log Ps	0.358	0.362	-0.449	-0.668	-5.016	0	4.155
Propanone/Dry	log Ps	0.335	0.349	-0.231	-0.411	-4.793	0	3.963
Butanone/Dry	log Ps	0.354	0.003	-0.164	-0.979	-4.706	0	4.160
Dimethylformamide/Dry	log Ps	0.105	0.317	0.462	1.154	-4.843	0	3.757
Acetonitrile/Dry	log Ps	0.413	0.077	0.326	-1.566	-4.391	0	3.364
Nitromethane/Dry	log Ps	0.023	-0.091	0.793	-1.463	-4.364	0	3.460
DMSO/ Dry	log Ps	-0.231	0.520	0.757	1.799	-4.652	0	3.428
Dibutyl ether/Dry	log Ps	0.203	0.369	-0.954	-1.488	-5.426	0	4.508
Gas to water	logKw	-0.994	0.577	2.549	3.813	4.841	0	-0.869
Gas to:								
Octanol	log Ks	-0.198	0.002	0.709	3.519	1.429	0.858	0
Dichloromethane	log Ks	0.121	-0.450	1.677	0.404	0.786	0.940	0
Trichloromethane	log Ks	0.116	-0.467	1.203	0.138	1.432	0.994	0
Tetrachloromethane	log Ks	0.282	-0.303	0.460	0.000	0.000	1.047	0
1,2-Dichloroethane	log Ks	0.011	-0.150	1.436	0.649	0.736	0.936	0
Pentane	log Ks	0.335	-0.276	0.000	0.000	0.000	0.968	0
Hexane	log Ks	0.292	-0.169	0.000	0.000	0.000	0.979	0
Heptane	log Ks	0.275	-0.162	0.000	0.000	0.000	0.983	0
Octane	log Ks	0.215	-0.049	0.000	0.000	0.000	0.967	0
Nonane	log Ks	0.200	-0.145	0.000	0.000	0.000	0.980	0
Decane	log Ks	0.156	-0.143	0.000	0.000	0.000	0.989	0

Hexadecane	log Ks	0.000	0.000	0.000	0.000	0.000	1.000	0
Cyclohexane	log Ks	0.163	-0.110	0.000	0.000	0.000	1.013	0
Methylcyclohexane	log Ks	0.318	-0.215	0.000	0.000	0.000	1.012	0
Isooctane	log Ks	0.275	-0.244	0.000	0.000	0.000	0.972	0
Benzene	log Ks	0.107	-0.313	1.053	0.457	0.169	1.020	0
Toluene	log Ks	0.121	-0.222	0.938	0.467	0.099	1.012	0
Chlorobenzene	log Ks	0.053	-0.553	1.254	0.364	0.000	1.041	0
Nitrobenzene	log Ks	-0.273	0.039	1.803	1.231	0.000	0.929	0
Diethyl ether	log Ks	0.245	-0.360	1.079	3.316	0.000	0.889	0
Isopropyl ether	log Ks	0.114	-0.032	0.685	3.108	0.000	0.941	0
Dibutylether	log Ks	0.145	0.074	0.250	2.621	0.000	1.019	0
Olive oil	log Ks	-0.230	0.009	0.795	1.353	0.000	0.888	0
Carbon disulfide	log Ks	0.101	0.251	0.177	0.027	0.095	1.068	0
Methanol/ Dry	log Ks	-0.004	-0.215	1.173	3.701	1.432	0.769	0
Ethanol/ Dry	log Ks	0.012	-0.206	0.789	3.635	1.311	0.853	0
Propanol/ Dry	log Ks	-0.028	-0.185	0.648	4.022	1.043	0.869	0
Butanol/Dry	log Ks	-0.039	-0.276	0.539	3.781	0.995	0.934	0
Pentanol/ Dry	log Ks	-0.042	-0.277	0.526	3.779	0.983	0.932	0
Hexanol/ Dry	log Ks	-0.035	-0.298	0.626	3.726	0.729	0.936	0
Heptanol/Dry	log Ks	-0.062	-0.168	0.429	3.541	1.181	0.927	0
Octanol/ Dry	log Ks	-0.120	-0.203	0.560	3.576	0.702	0.939	0
Decanol/ Dry	log Ks	-0.136	-0.038	0.325	3.674	0.767	0.947	0
Isopropanol/ Dry	log Ks	-0.060	-0.335	0.702	4.017	1.040	0.893	0
Trifluoroethanol/ Dry	log Ks	-0.133	-0.611	1.457	1.899	4.461	0.633	0
Ethyl acetate/ Dry	log Ks	0.203	-0.335	1.251	2.949	0.000	0.917	0
Propanone/ Dry	log Ks	0.154	-0.277	1.522	3.258	0.078	0.863	0
Dimethylformamide/Dry	log Ks	-0.161	-0.189	2.327	4.756	0.000	0.808	0
Acetonitrile/ Dry	log Ks	-0.007	-0.595	2.461	2.085	0.418	0.738	0
Nitromethane/ Dry	log Ks	-0.340	-0.297	2.689	2.193	0.514	0.728	0
DMSO/ Dry	log Ks	-0.619	0.131	2.811	5.474	0.000	0.734	0
Dibutylether/Dry	log Ks	0.165	-0.421	0.760	2.102	-0.664	1.002	0
Gas to water	log Kw	-1.271	0.822	2.743	3.904	4.814	-0.213	0

<sup>a</sup> Solvents are wet (ie saturated with water) unless shown as 'Dry'.

*Mercury(II) chloride*. For mercury(II) chloride, the value of  $V = 0.3400$  for mercury leads directly to  $V = 0.6278$ , but an estimate of  $E$  is desirable. We take  $E$  as the sum of  $E$  for mercury, 0.85, plus two chlorine atoms in chloroalkanes, 0.20 each, to give 1.25 as the total  $E$ . Solubilities are known for mercury(II) chloride in water<sup>1</sup> and in a variety of solvents<sup>34,35</sup> and can be combined to yield log Ps values. However, this

can only be done for rather nonpolar solvents, because for many polar (basic) solvents, solvates are formed. In Table 3 are given solubilities and derived log Ps values from water to dry solvents. The log Ps values in parenthesis were not used because of known or possible solvate formation. Also available<sup>9,36</sup> are partition coefficients from water to wet solvents, as shown in Table 3. The log Ps values can be transformed into log Ks values, giving a total of 30 data points. If log Kw is allowed to float we find that the 30 points can be fitted with an SD of only 0.110 log units with **E** = 1.25, **S** = 1.97, **A** = 0.50, **B** = 0.40, **L** = 4.765, **V** = 0.6278 and log Kw = 8.02. This is much larger than the value of 6.2 given by Persson et al.<sup>35</sup> and by Iverfeldt and Persson,<sup>37</sup> but the value from other measurements<sup>38</sup> is quite near to our value, as we discuss later.

Some years after the work of Eliezer,<sup>34</sup> Eliezer and Adida<sup>39</sup> re-measured the solubilities of mercury(II) chloride in organic solvents, including some solvents not studied before. Unfortunately, the later solubilities are not consistent with those determined earlier.<sup>34,35</sup> If the solubilities of Eliezer and Adida<sup>39</sup> are used to obtain partition coefficients, we find that for 36 data points, SD = 0.225 log units, considerably larger than SD = 0.110 using the earlier solubilities. We therefore used only the original solubilities of Eliezer,<sup>34</sup> and those of Persson et al.<sup>35</sup>

**Table 3** Solubilities of mercury(II) chloride at 298K, and derived log Ps and log Ks values

Solvent	Log Ss <sup>34</sup>	Log Ss <sup>35</sup>	Log Ps	Log Ks
Water	-0.57 <sup>2</sup>			8.02
Hexane	-3.80		-3.23	4.79
Heptane	-3.92		-3.35	4.67
Decane	-4.05		-3.48	4.54
Dodecane	-3.95		-3.38	4.64
Cyclohexane	-3.72		-3.15	4.87
Benzene	-1.66	-1.80	-1.16	6.86
Toluene	-1.62		-1.05	6.97
Ether		-0.77	-0.20	(7.82)

Propanone		0.51	(1.08)	
Acetonitrile		0.26	0.83	8.85
Methanol		0.30	(0.87)	
DMSO		0.30	(0.87)	
Wet octanol			-0.22 <sup>9</sup>	7.80
Wet ether			-0.58 <sup>9</sup>	7.44
Wet pentanol			0.25 <sup>36</sup>	8.27
Wet benzene			-1.08 <sup>36</sup>	6.94
Wet toluene			-1.12 <sup>36</sup>	6.90

*Mercury(II) bromide*. Solubilities in organic solvents<sup>34, 35</sup> and in water<sup>2</sup> are known; these are in Table 4 together with the corresponding log Ps values. As for mercury(II) chloride, solvates are formed with polar solvents and solubilities in these solvents cannot be used. **E** for mercury(II) bromide was estimated in the same way as for mercury(II) chloride, that is 0.85 for mercury and 0.35 for a bromine atom in bromoalkanes to give 1.55 for **E**. With **E** fixed at 1.55, and **V** fixed 0.7330, the total 20 values of log Ps and log Ks were fitted with an SD of 0.095 log units with **S** = 1.71, **A** = 0.43, **B** = 0.37, **L** = 5.332, and a floating value of 7.04 for log Kw. The solubilities of Eliezer and Adida<sup>39</sup> are again not compatible with the earlier work,<sup>34, 35</sup> and so were not used.

**Table 4** Solubilities of mercury(II) bromide at 298K and derived log Ps and log Ks values.

Solvent	Log Ss <sup>34</sup>	Log Ss <sup>35</sup>	Log Ps	Log Ks
Water	-1.77 <sup>2</sup>			7.04
Hexane	-3.52		1.75	5.29
Heptane	-3.62		1.85	5.19
Decane	-3.68		1.91	5.13
Dodecane	-3.68		1.91	5.13
Cyclohexane	-3.35		1.58	5.46
Benzene	-1.68	-1.80	-0.09, 0.03	7.13

Toluene	-1.64		-0.13	7.17
Ether		-1.17	-0.60	7.64
Propanone		(-0.02)		
Acetonitrile		-0.59	1.18	8.22
Methanol		(0.18)		
DMSO		(0.51)		
Dioxane	(-1.05)			

*Mercury(II) iodide*. Solubilities, as  $\log S_s$ ,<sup>34,35</sup> are in Table 5 together with derived  $\log P_s$  and  $\log K_s$  values. The values for ether, propanone and acetonitrile were well correlated, and so it appears that solvate formation in these solvents can be ignored. There are 20 data points to be correlated and with **E** fixed at 2.09 and **V** fixed at 0.8994, these 20 points were correlated by **S** = 1.35, **A** = 0.28, **B** = 0.37, and **L** = 6.316 with an SD of only 0.087 log units, when  $\log K_w$  ( 5.69) was allowed to float.

**Table 5** Solubilities of mercury(II) iodide at 298K and derived  $\log P_s$  and  $\log K_s$  values

Solvent	$\log S_s$ <sup>34</sup>	$\log S_s$ <sup>35</sup>	$\log P_s$	$\log K_s$
Water	-3.92 <sup>2</sup>			5.69
Hexane	-3.38		0.54	6.23
Heptane	-3.52		0.40	6.09
Decane	-3.62		0.30	5.99
Cyclohexane	-3.23		0.69	6.38
Benzene	-2.21	-2.12	1.71, 1.80	7.44
Toluene	-2.11		1.81	7.50
Ether		-2.08	1.84	7.53
Dioxane	(-0.98)			
Propanone		-1.51	2.41	8.10
Acetonitrile		-2.12	1.80	7.49
Methanol		(-1.17)		
DMSO		(0.63)		

*Alkylmercury(II) halides.*  $V$  for these compounds can now be calculated using  $V = 0.3400$  for mercury. For the chlorides,  $E$  was estimated from  $E = 0.850$  for mercury(II) chloride and experimental values of  $E$  for dialkylmercury(II) as listed in Table 6. The refractive indexes of the latter compounds were from ref. 33.

**Table 6** Some experimental and estimated values of  $E$ .

Species	$\eta$ at 293K	$V$	$E(\text{exp})$	$E(\text{est})$
Hg	1.680	0.3400	0.850	
Me <sub>2</sub> Hg	1.5327	0.6648	0.705	
Et <sub>2</sub> Hg	1.5399	0.9466	0.814	
Pr <sub>2</sub> Hg	1.5170	1.2284	0.763	
Bu <sub>2</sub> Hg	1.5057	1.5102	0.733	
HgCl <sub>2</sub>		0.6278		1.25
HgBr <sub>2</sub>		0.7330		1.55
HgI <sub>2</sub>		0.8994		2.09
MeHgCl		0.6463		0.98
EtHgCl		0.7872		1.03
PrHgCl		0.9281		1.01
BuHgCl		1.0690		1.00
MeHgBr		0.6989		1.13
MeHgI		0.7821		1.40
PhHgCl		1.1132		1.65

In the case of methylmercury(II) chloride, a large number of log Ps values are available from Stary and Kratzer,<sup>40</sup> and a few more are reported in the MedChem data base.<sup>9</sup> Iverfeldt and Persson<sup>37</sup> give a value of 4.72 for log Kw that enables all the log Ps values to be converted into log Ks values. This leads to a total of no less than 27 data points that can be fitted with an SD of 0.116 log units with  $E = 0.98$ ,  $S = 1.48$ ,  $A = 0.13$ ,  $B = 0.29$ ,  $L = 4.037$  and  $V = 0.6463$ . If log Kw is allowed to float, almost identical descriptors are obtained.

For ethylmercury(II) chloride, Ealy et al.<sup>41</sup> give log Ps values for benzene (1.57), toluene (1.44) and cyclohexane (0.08) and there is also a value for ether (1.22)<sup>9</sup> available. These give a total of 10 equations that can be fitted with SD = 0.037 log unit using **E** = 1.03, **S** = 1.50, **A** = 0.13, **B** = 0.28, **L** = 4.569 and **V** = 0.7872; log Kw was allowed to float as 4.58. From the solubility of ethylmercury(II) chloride in water given by Tajima and Kai,<sup>42</sup> log Sw = -2.376, and the gas phase concentration,<sup>43</sup> log Cg = -7.142 a value of 4.77 is found for log Kw, in good agreement with the value we estimate. For propylmercury(II) chloride, log Ps values are known only for ether and benzene,<sup>9</sup> and for butylmercury(II) chloride and pentylmercury(II) chloride only for ether.<sup>9</sup> We obtained the descriptors listed in Table 7 by fixing **A** = 0.13 and **B** = 0.27 by comparison to those for ethylmercury(II) chloride.

There are but few experimental data for other alkylmercury(II) halides. Stary and Kratzer<sup>40</sup> give log Ps as 0.04 and 1.74 for water to isooctane and water to benzene partitions of methylmercury(II) bromide, Ealy et al.<sup>41</sup> give 1.64 for partition to benzene, and Iverfeldt and Persson<sup>37</sup> give log Kw as 3.94. With **E** fixed at 1.13 and **V** at 0.6989, we find the other descriptors **S** = 1.40, **A** = 0.10, **B** = 0.21 and **L** = 4.182 can fit the eight equations with SD = 0.076 log units. There was no better fit if log Kw was allowed to float.

For methylmercury(II) iodide, Stary and Kratzer<sup>40</sup> give log Ps as 0.95 and 2.45 for water to isooctane and water to benzene partitions, and Early et al.<sup>41</sup> give 2.26 for the latter. Iverson and Persson<sup>37</sup> give log Kw as 3.15, but with this as fixed quantity, the six available equations could be fitted to only 0.170 log units. If log Kw was allowed to float and to take the value 3.69, the six equations were fitted with SD = 0.013 log units. The descriptors were **E** = 1.40, **S** = 1.31, **A** = 0.07, **B** = 0.20, **L** = 4.839 and **V** = 0.7821.

*Phenylmercury(II) halides.* Stary and Kratzer<sup>40</sup> give a number of log Ps values for phenylmercury(II) chloride, and a water to octanol partition coefficient is also available.<sup>9</sup> **E** was estimated as 1.65 by comparison to aromatic solutes and with **V** = 1.1132, the total of 26 equations were fitted with **S** = 1.82, **A** = 0.17, **B** = 0.43 and **L** = 6.841 with SD = 0.094 log units. Log Kw was allowed to vary, the obtained value for it being log Kw = 6.36. From the aqueous solubility,<sup>44</sup> log Sw = -4.22 and the

saturated vapor concentration at 298 K (obtained from the given equation for the temperature variation of vapour pressure)<sup>45</sup>  $\log C_g = -10.19$  a value for  $\log K_w$  of 5.97 is found. Our 'floating' value of 6.36 is in reasonable agreement. In a later paper, Sary and Kratzer<sup>46</sup> give  $\log P_s$  values for phenylmercury(II) bromide and iodide in benzene, chloroform and tetrachloromethane. Values of **E** and **V** can be calculated as before, and there is just enough data to obtain the descriptors given in Table 7.

Sary and Kratzer<sup>46</sup> also give  $\log P_s$  for phenylmercury(II) thiocyanate but only for benzene and chloroform, and there is not quite enough data to obtain reliable descriptors.

**Table 7** Descriptors for mercury and mercury(II) species

Species	<b>E</b>	<b>S</b>	<b>A</b>	<b>B</b>	<b>V</b>	<b>L</b>	Log $K_w$
Hg	0.85	0.43	0.00	0.04	0.3400	1.721	0.46 <sup>2</sup>
HgCl <sub>2</sub>	1.25	1.97	0.50	0.40	0.6278	4.765	8.02
HgBr <sub>2</sub>	1.55	1.71	0.43	0.37	0.7330	5.332	7.04
HgI <sub>2</sub>	2.09	1.35	0.28	0.37	0.8994	6.316	5.69
MeHgCl	0.98	1.48	0.13	0.29	0.6463	4.037	4.72 <sup>37</sup>
EtHgCl	1.03	1.50	0.13	0.28	0.7872	4.569	4.58 <sup>a</sup>
PrHgCl	1.01	1.52	0.13	0.27	0.9281	5.065	4.46
iso-PrHgCl	0.98	1.49	0.10	0.30	0.9281	5.02	4.39
BuHgCl	1.00	1.52	0.13	0.27	1.0690	5.549	4.34
PeHgCl	1.00	1.52	0.13	0.27	1.2099	5.959	4.24
MeHgBr	1.13	1.40	0.10	0.21	0.6989	4.182	3.94 <sup>37</sup>
EtHgBr	1.18	1.39	0.12	0.20	0.8398	4.709	3.87
MeHgI	1.40	1.31	0.07	0.20	0.7821	4.839	3.69 <sup>b</sup>
EtHgI <sup>c</sup>	1.45	1.38	0.07	0.20	0.9230	5.40	3.79
Me <sub>2</sub> Hg	0.705	0.62	0.00	0.00	0.6648	2.983	0.41
Et <sub>2</sub> Hg <sup>c</sup>	0.814	0.70	0.00	0.00	0.9466	4.13	0.41
Pr <sub>2</sub> Hg <sup>c</sup>	0.764	0.69	0.00	0.00	1.2284	5.18	0.14



iso- Pr <sub>2</sub> Hg <sup>c</sup>	0.760	0.60	0.00	0.00	1.2284	5.10	-0.01
Bu <sub>2</sub> Hg <sup>c</sup>	0.733	0.68	0.00	0.00	1.5102	6.25	-0.14
PhHgCl	1.65	1.82	0.17	0.43	1.1132	6.841	6.36 <sup>d</sup>
PhHgBr	1.80	1.75	0.15	0.33	1.1658	7.142	5.66
PhHgI	2.07	1.75	0.06	0.32	1.2490	7.770	5.35
Ph <sub>2</sub> Hg	2.05	1.63	0.00	0.60	1.5986	8.845	5.84
MeOCH <sub>2</sub> CH <sub>2</sub> HgCl	1.07	1.68	0.13	0.75	0.9868	5.364	6.98

<sup>a</sup> Experimental value 4.77 see text <sup>b</sup> 3.15 from Ref. 38. <sup>c</sup> Estimated values. <sup>d</sup> Also 5.97, see text.

*Dialkylmercurys.* The only compound for which there are relevant physicochemical data is dimethylmercury, and even in here, the data is rather sparse. The MedChem data <sup>9</sup> base lists experimental values for log Ps for octanol as 2.59 and 2.26 and a value for log Kw of 0.72. Talmi and Mesmer <sup>47</sup> give a value of 0.51 for log Kw, and Wilhelm et al. <sup>48</sup> give log Ks values into toluene at 276, 296, and 308K from which a value 3.55 for log Ks at 298K can be obtained. We can also obtain a value for log Kw from log Sw = -2.23, <sup>44</sup> and log Cg = -2.48 <sup>49</sup> giving 0.25 for log Kw. If we take log Ps for octanol as 2.42, the average of the two values, we can fit the available data with an SD of 0.039 with the descriptors shown in Table 7. The calculated value of log Kw is 0.41 in good agreement with the two experimental values. We have also estimated descriptors for a few other dialkylmercurys, by comparison to dimethylmercury, as given also in Table 7.

*Diphenylmercury.* V can be calculated as usual, and E estimated as for phenylmercuric(II) chloride. Ramsey et al. <sup>50</sup> have measured a large number of retention indexes on non-polar gas chromatographic stationary phases. They combined results on OV-1 and SE-30 phases to give a single retention index, RI, for non-drug compounds, including diphenylmercury with RI = 1873. There are enough compounds in the list with known descriptors to characterize the combined phase:

$$RI = 125.8 + 48.2 E + 12.7 S + 144.4 A + 29.7 B + 194.5 L \quad (7)$$

$N = 89$ ,  $SD = 54.0$ ,  $R^2 = 0.990$ ,  $F = 1665.3$

Solubilities of diphenylmercury in heptane, ether, dioxane, chloroform and benzene at 293K have been recorded.<sup>50</sup> The solubility in water at various temperatures is known,<sup>51</sup> and another value at 298K is available;<sup>36</sup> these yield  $\log S_w = -4.63$  at 293K and combination with the solubilities in the non-aqueous solvents gives  $\log P_s$  values. Only those in heptane and ether were used, because of possible solvate formation. The descriptors shown in Table 7 account for the GLC data and partition coefficients. *2-Methoxyethylmercury(II) chloride*. Although this has been used as an \*\*\* under the name 'Aretan', the only physicochemical data we have been able to find are the vapour pressure<sup>45</sup> that corresponds to  $\log C_g = -7.75$  at 298K, and the aqueous solubility<sup>52</sup> that yields  $\log S_w = -0.77$ ; from these,  $\log K_w = 6.98$ . The descriptors given in Table 7 are approximate only, in that they simply reproduce the  $\log K_w$  value.

## Discussion

The value of  $V$  that we have selected for mercury, and the subsequent descriptors yield calculated  $\log K_w$ ,  $\log K_s$ ,  $\log P_s$  and a number of GLC retention data that are in good agreement with experimental values. There are only a few cases where this is not so. For mercury itself, the  $\log P_{oct}$  value<sup>1,2,53</sup> and  $\log K_s$  in methanol<sup>1,2</sup> are not fitted at all well. However, the  $\log K_s$  value in propan-2-ol is fitted reasonably well (observed value 1.42, fitted value 1.53). In addition, Okouchi and Sasaki<sup>53</sup> give the solubility of mercury in dry octanol as  $\geq 4.0 \times 10^{-6} \text{ mol dm}^{-3}$ . When combined with the vapor concentration of mercury at 298K,<sup>1,2</sup>  $\log C_g = -6.98$ , this yields an observed value of  $\log K_s$  in dry octanol as  $\geq 1.58$ , by comparison with a predicted value of 1.59, from the descriptors in Table 7 and the equation in Table 2. Hence of the one observed  $\log P_s$  and three observed  $\log K_s$  values that pertain to alcohols, two are out of line and two are fitted reasonably well.

Our calculated  $\log K_w$  values for mercury(II) chloride, bromide and iodide are in disagreement with the values recorded by Iverfeldt and Persson;<sup>37</sup> these values were obtained, as usual, from the saturated vapor pressure and solubility in water at 298K. However, we have been unable to reproduce the calculations. From recorded vapor

pressure equations,<sup>38</sup> we can calculate the saturated vapor pressure at 298K, and then the corresponding vapor concentration,  $C_g$ , in  $\text{mol dm}^{-3}$ . The solubilities of the mercury(II) halides in water,  $C_w$ , are well known<sup>1</sup> and then  $K_w$  can be obtained through eqn. (3); details are in Table 8. Although the calculated log  $K_w$  values from our descriptors are larger than the experimental values, the differences are not very great, bearing in mind the difficulty of the vapor pressure measurements. We can also use the vapour pressure for mercury(II) chloride at 298K of Phillips et al.<sup>45</sup> that leads to  $\log C_g = -8.59$  and a value for log  $K_w$  that is the same as our calculated value. The values of Iverfeldt and Persson seem much too small.

**Table 8** Calculation of the gas to water partition coefficient, as log  $K_w$ .

Species	Log $C_g$	Log $C_w$	Log $K_w$		
			Log ( $C_w/C_g$ )	From descriptors	Ref 37
Mercury(II) chloride	-8.17 <sup>38</sup>	-0.57 <sup>1</sup>	7.60	8.02	6.20
Mercury(II) chloride	-8.59 <sup>45</sup>	-0.57 <sup>1</sup>	8.02	8.02	
Mercury(II) bromide	-8.23 <sup>38</sup>	-1.77 <sup>1</sup>	6.46	7.04	5.12
Mercury(II) iodide	-9.07 <sup>38</sup>	-3.92 <sup>1</sup>	5.15	5.69	3.68

One of the most important parameters in calculations of environmentally important processes is the water to octanol partition coefficient, as log  $P_{oct}$ . As we mentioned in the introduction, most of the general methods for calculating compound properties cannot be used for species that contain mercury, and those that can be used are not very reliable. We have checked on the CODESSA method and this is also unreliable. Of the specific methods for log  $P_{oct}$ , both ClogP and KOWWIN can deal with mercury containing compounds, and we give in Table 9, calculated, and where available, experimental values of log  $P_{oct}$ . Neither method is very reliable. This is no reflection on the methods, but is simply a result of lack of compounds in the training sets. With the lone exception of mercury itself, the calculated values from our descriptors and our equation for log  $P_{oct}$  agree with the limited experimental data, and appear to be reasonable. We suggest that, at the moment, the calculated values are the most reliable estimates of log  $P_{oct}$ .

**Table 9** Experimental and calculated values of log Poct

Species	Exp	Calc	ClogP	KOWWIN
Hg	0.62	1.27	0.62	0.62
HgCl <sub>2</sub>	-0.22	-0.26	-1.32	0.15
HgBr <sub>2</sub>		0.69	-1.32	0.33
HgI <sub>2</sub>		2.00	-1.32	1.16
MeHgCl	0.41	0.54	0.41	0.39
EtHgCl		1.12	0.93	0.88
PrHgCl		1.66	1.46	1.37
BuHgCl		2.19	1.99	1.86
PeHgCl		2.73	2.52	2.35
MeHgBr		1.19	1.17	0.48
EtHgBr		1.80	1.69	0.97
MeHgI		1.79	-0.44	0.89
EtHgI		2.28	0.09	1.38
Me <sub>2</sub> Hg	2.26, 2.59	2.37	2.56	0.62
Et <sub>2</sub> Hg		3.42	3.62	1.61
Pr <sub>2</sub> Hg		4.48	4.68	2.59
Bu <sub>2</sub> Hg		5.52	5.74	3.57
PhHgCl	1.78	1.86	1.77	1.60
PhHgBr		2.56	3.07	1.69
PhHgI		3.06	1.00	2.11
Ph <sub>2</sub> Hg		3.54	3.77	3.06

The other very important environmental parameter is the gas to water partition coefficient,  $K_w$ , especially for the more volatile organomercury compounds. In Table 10 are listed our calculated values together with what experimental data there is. We include a few representative calculations through CODESSA, but it is clear that the method can lead to very considerable errors. As for log Poct, we suggest that the calculated values in Table 10 are the most reasonable estimates at present.

**Table 10** Experimental and calculated values of log Kw at 298K

Species	Exp	Calc	CODESSA
MeHgCl	4.72 <sup>37</sup>	4.72	0.96
EtHgCl	4.77 <sup>a</sup>	4.58	
PrHgCl		4.46	
BuHgCl		4.34	
PeHgCl		4.24	
MeHgBr	3.94 <sup>37</sup>	3.94	
EtHgBr		3.87	
MeHgI	3.15 <sup>37</sup>	3.69	1.06
EtHgI		3.79	
Me <sub>2</sub> Hg	0.26, <sup>a</sup> 0.51 <sup>37</sup>	0.41	0.41
Et <sub>2</sub> Hg		0.41	
Pr <sub>2</sub> Hg		0.14	
Bu <sub>2</sub> Hg		-0.13	
PhHgCl	5.97 <sup>a</sup>	6.36	
PhHgBr		5.66	
PhHgI		5.35	
Ph <sub>2</sub> Hg		5.84	
MeOCH <sub>2</sub> CH <sub>2</sub> HgCl	6.98 <sup>a</sup>	6.98	

<sup>a</sup> See text.

From an environmental point of view, it is desirable to be able to estimate Kw not only at 298K but at other temperatures as well. We have used<sup>12</sup> a general equation to calculate log Kw at any temperature from 273 to 373K,

$$\Delta G_w^{\circ}(T) = (T/298) \times \Delta G_w^{\circ}(298) - [(T - 298)/298] \times \Delta H_w^{\circ}(298) + \Delta C_{p_w}[T - 298 - T \ln(T/298)] \quad (8)$$

In eqn. (8),  $\Delta G_w^\circ(298) = -RT \ln K_w$  at 298K, and  $\Delta G_w^\circ(T) = -RT \ln K_w$  at any temperature T.  $\Delta H_w^\circ(298)$  is the enthalpy of hydration on transfer from the gas phase to water, and  $\Delta C_{p_w}$  is the corresponding heat capacity of hydration. To obtain  $\Delta G_w^\circ(T)$  or the equivalent  $\log K_w(T)$ , three input values are needed:  $\log K_w(298)$ ,  $\Delta H_w^\circ(298)$  and  $\Delta C_{p_w}$ . We have devised equations for the prediction of  $\Delta H_w^\circ(298)$  and  $\Delta C_{p_w}$ , as follows with values in  $\text{kJ mol}^{-1}$  and  $\text{J mol}^{-1}$  respectively:<sup>12, 53</sup>

$$\Delta H_w^\circ(298) = -6.952 + 1.412 \mathbf{E} - 2.859 \mathbf{S} - 34.086 \mathbf{A} - 42.686 \mathbf{B} - 22.720 \mathbf{V} \quad (9)$$

$$\Delta C_{p_w} = 103.6 - 65.3 \mathbf{E} - 91.6 \mathbf{S} - 3.1 \mathbf{A} - 119.3 \mathbf{B} + 404.0 \mathbf{V} \quad (10)$$

Thus from the descriptors in Table 7, we can calculate all three input quantities. More realistically, if we have  $\log K_w$  at 298K available, as in Table 10, then a calculation of  $\Delta H_w^\circ(298)$  and  $\Delta C_{p_w}$  will enable  $\log K_w$  at any other temperature to be estimated.

There are only a few values of  $\Delta H_w^\circ(298)$  for organomercury(II) species that are available, or can be calculated, as a test of eqn. (9). Details are in Table 11; the enthalpies of solution in water for the alkylmercury (II) halides were obtained from the temperature variation of the solubilities given by Tajima et al.<sup>55</sup> The predicted values are from eqn. (9). There is excellent agreement between experimental and predicted values; any of the differences would lead to only trivial differences in calculated values of  $\log K_w(T)$ . We therefore use predicted values of  $\Delta H_w^\circ(298)$  and  $\Delta C_{p_w}$  obtained through eqn. (9) and eqn. (10), together with the  $\log K_w$  values at 298K in Table 10 to predict  $\log K_w$  for organomercury(II) compounds through eqn. (8). Results are in Table 12. As pointed out before,<sup>12</sup> the key parameter in the calculation of  $\log K_w(T)$  is the value taken for  $\log K_w(298)$  and hence all the  $\log K_w(T)$  values in Table 12 rely on the correctness of the input  $\log K_w(298)$ . We give  $\log K_w(T)$  for various temperatures, but there is no need to interpolate values at intermediate temperatures; the spreadsheet that is available from ref. 12 can be used to calculate  $\log K_w(T)$  at any desired temperature.

**Table 11** Experimental and predicted values of  $\Delta H_w^{\circ}(298)$  in  $\text{kJ mol}^{-1}$ 

Species	$\Delta H_V^{\circ}(298)$	$\Delta H_{\text{Soln}}^{\circ}(298)$	Exp	Pred
MeHgCl			-48 <sup>37</sup>	-41
MeHgCl	65 <sup>43</sup>	20 <sup>a</sup>	-45	-41
EtHgCl	76 <sup>43</sup>	20 <sup>a</sup>	-56	-57
MeHgBr	68 <sup>43</sup>	21 <sup>a</sup>	-47	-52
Me <sub>2</sub> Hg			-19 <sup>37</sup>	-23

<sup>a</sup> From data in ref. 55.**Table 12** Predicted values of log Kw for organomercury(II) compounds from 273 to 373K

Species/ T:	298	273	293	303	323	343	353	363	373
MeHgCl	4.72	5.41	4.84	4.60	4.18	3.84	3.69	3.55	3.43
EtHgCl	4.58	5.32	4.71	4.45	4.01	3.66	3.51	3.37	3.26
PrHgCl	4.46	5.26	4.60	4.33	3.86	3.50	3.35	3.22	3.10
BuHgCl	4.34	5.21	4.49	4.20	3.71	3.33	3.18	3.05	2.94
PeHgCl	4.24	5.17	4.40	4.09	3.58	3.19	3.04	2.91	2.80
MeHgBr	3.94	4.58	4.05	3.83	3.46	3.15	3.03	2.91	2.81
EtHgBr	3.87	4.57	3.99	3.75	3.35	3.03	2.90	2.79	2.69
MeHgI	3.65	4.29	3.76	3.54	3.17	2.88	2.76	2.64	2.56
EtHgI	3.79	4.49	3.91	3.67	3.28	2.97	2.84	2.73	2.64
Me <sub>2</sub> Hg	0.41	0.83	0.48	0.35	0.15	0.02	-0.02	-0.05	-0.07
Et <sub>2</sub> Hg	0.41	0.96	0.50	0.33	0.07	-0.08	-0.13	-0.16	-0.17
Pr <sub>2</sub> Hg	0.14	0.82	0.25	0.04	-0.26	-0.44	-0.49	-0.52	-0.52
Bu <sub>2</sub> Hg	-0.13	0.67	0.00	-0.25	-0.60	-0.80	-0.85	-0.87	-0.88
PhHgCl	6.36	7.36	6.54	6.19	5.59	5.11	4.90	4.72	4.55
PhHgBr	5.66	6.60	5.83	5.50	4.96	4.52	4.39	4.18	4.03
PhHgI	5.35	6.26	5.51	5.20	4.68	4.27	4.10	3.95	3.82
Ph <sub>2</sub> Hg	5.81	7.02	6.02	5.61	4.98	4.38	4.16	3.97	3.81

Similar equations to eqn. (9) have been constructed for the enthalpy of solvation from the gas phase to various pure solvents.<sup>56, 57</sup> These could be used for this purpose, but also as a further test of the predictive ability of the equations. A number of values of enthalpies of solvation from the gas phase to solvents can be obtained from corresponding enthalpies of vaporization (either for the liquid or solid)  $\Delta H_V^\circ(298)$ ,<sup>37, 43, 58-62</sup> and enthalpies of solution<sup>38, 59-62</sup> (either for the liquid or solid)  $\Delta H_{Soln}^\circ(298)$ , as shown in Table 13. Equations for enthalpies of solvation into methanol, ethanol and cyclohexane are,<sup>56, 57</sup>

$$\Delta H_S^\circ(\text{MeOH}, 298) = 1.636 - 11.797 \text{ E} - 9.336 \text{ S} - 41.378 \text{ A} - 15.984 \text{ B} - 27.891 \text{ V} \quad (11)$$

$$\Delta H_S^\circ(\text{EtOH}, 298) = 4.411 - 11.175 \text{ E} - 9.123 \text{ S} - 52.352 \text{ A} - 12.074 \text{ B} - 32.384 \text{ V} \quad (12)$$

$$\Delta H_S^\circ(\text{Cyclo}, 298) = 3.046 - 8.735 \text{ E} - 6.353 \text{ S} - 1.264 \text{ A} - 2.449 \text{ B} - 33.550 \text{ V} \quad (13)$$

Results shown in Table 13 indicate that there is reasonable agreement between observed and predicted enthalpies of solvation, especially bearing in mind that the enthalpies of vaporization are obtained by the van't Hoff method and not by the more accurate calorimetric method. The differences between observed and predicted values would have little effect on any calculation of log Ks values at different temperatures.

**Table 13.** Observed and predicted values of enthalpies of solvation from the gas phase to solvents,  $\Delta H_S^\circ(298)$ , in  $\text{kJ mol}^{-1}$

Species	Solvent	$\Delta H_V^\circ(298)$	$\Delta H_{Soln}^\circ(298)$	$\Delta H_S^\circ(298)$	
				Obs	Pred
MeHgCl	Water	64.9 <sup>43</sup>	15.9 <sup>38</sup>	-49.0	-41.3
MeHgCl	Ethanol	64.9 <sup>43</sup>	17.4 <sup>59</sup>	-47.5	-51.3
MeHgBr	Ethanol	67.8 <sup>43</sup>	16.7 <sup>59</sup>	-51.1	-51.4
MeHgI	Methanol	65.3 <sup>43</sup>	16.5 <sup>59</sup>	-48.8	-55.0
EtHgCl	Methanol	76.1 <sup>43</sup>	21.8 <sup>60</sup>	-54.3	-56.3



EtHgBr	Methanol	76.6 <sup>43</sup>	19.2 <sup>60</sup>	-57.4	-56.8
EtHgI	Methanol	79.5 <sup>43</sup>	20.1 <sup>60</sup>	-59.4	-60.2
Me <sub>2</sub> Hg	Water			-18.8 <sup>37</sup>	-22.8
Me <sub>2</sub> Hg	Ethanol	34.6 <sup>58</sup>	2.5 <sup>59</sup>	-32.1	-30.6
		33.9 <sup>59</sup>	2.5 <sup>59</sup>	-31.4	
Et <sub>2</sub> Hg	Methanol	42.2 <sup>60</sup>	5.7 <sup>60</sup>	-36.5	-40.9
Pr <sub>2</sub> Hg	Methanol	53.6 <sup>61</sup>	6.0 <sup>61</sup>	-47.6	-48.1
iso-Pr <sub>2</sub> Hg	Methanol	52.3 <sup>61</sup>	6.4 <sup>61</sup>	-45.9	-47.2
Ph <sub>2</sub> Hg	C <sub>6</sub> H <sub>12</sub>	112.8 <sup>58, 62</sup>	33.3 <sup>62</sup>	-79.5	-80.3

In addition to the equations, above and in Table 2, for partition of compounds between the gas phase and solvents, we have also obtained equations for partition between the gas phase and biological phases.<sup>15-19</sup> Hursh<sup>63</sup> has obtained the partition coefficients for mercury between air and blood and between air and plasma at 310K (the temperature at which our equations refer to). The relevant equations are eqn. (14) and eqn. (15) from which we can predict partition coefficients for mercury. We find for the air to blood partition,  $\log K(\text{obs}) = 0.62$  and  $\log K(\text{pred}) = 0.53$ , and for the air to plasma partition,  $\log K(\text{obs}) = 0.38$  and  $\log K(\text{pred}) = 0.24$ . It is therefore possible that for mercury itself we can use our equations for partitions between the gas phase and biological tissues such as brain,<sup>16</sup> muscle,<sup>17</sup> fat,<sup>18</sup> and liver<sup>19</sup> to predict partition coefficients.

$$\text{Log } K(\text{air-blood}) = -1.069 + 0.456 \mathbf{E} + 1.083 \mathbf{S} + 3.738 \mathbf{A} + 2.580 \mathbf{B} + 0.376 \mathbf{L} \quad (14)$$

$$\text{Log } K(\text{air-plasma}) = -1.435 + 0.543 \mathbf{E} + 1.677 \mathbf{S} + 3.518 \mathbf{A} + 3.982 \mathbf{B} + 0.192 \mathbf{L} \quad (15)$$

The situation for organic mercury is not straightforward. Our equations refer to partition between air and tissue and between blood and tissue of specific chemical species. For methylmercury(II) chloride, our calculated partition coefficients would refer to the concentration of methylmercury(II) chloride in tissue and the concentration of methylmercury(II) chloride in blood. For methylmercury(II)

bromide, our calculated partition coefficients would refer to the concentration of methylmercury(II) bromide in tissue and the concentration of methylmercury(II) bromide in blood. Thus we would calculate different partition coefficients for methylmercury(II) chloride and methylmercury(II) bromide. But analyses of biological samples for 'organic mercury' or 'methylmercury' do not refer to any particular species. A usual method for the analysis of methylmercury(II) is to digest a tissue homogenate with hydrochloric acid and to extract the formed methylmercury(II) chloride into benzene.<sup>64</sup> The actual species present in the tissue is unknown. In addition, methylmercury(II) is actively transported across the blood-brain barrier,<sup>65</sup> whereas our equations refer to passive transport. Our equations are therefore of little help in predicting 'practical' air-tissue or blood-tissue distributions of methylmercury(II) or of alkylmercury(II).

### **Conclusion**

We have obtained descriptors for mercury(II) species that can be used in already available equations to predict properties of environmental importance. These include the water to octanol partition coefficient, the partition of gases and vapors between the gas phase and water at 298K, and the temperature variation of the partition coefficient. Although we have concentrated on the prediction of values for environmentally important processes, the descriptors given in Table 7 can be used to predict values for any physicochemical process that has been characterized through eqn. (1) or eqn. (2). The characteristic coefficients for various processes are in Table 2, and it is trivial to obtain the required SP values from the descriptors in Table 7.

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