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Descriptors for the Prediction of Partition Coefficients and Solubilities of Organophosphorus Compounds

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From literature data on partition coefficients and in some cases solubilities in nonaqueous solvents we have been able to determine Abraham descriptors for several series of organophosphorus compounds including the dialkyl- and diaryl-phosphates (dialkylphosphoric acids), trialkyl- and triphenyl-phosphates, dialkylphosphinic acids and diphenylphosphinic acid, trialkyl- and triaryl-phosphine oxides, and dialkylphosphites and triarylphosphines. Other organophosphorus compounds studied were dimethyl methylphosphonate and the flame retardant PBMP. For all these compounds, knowledge of the Abraham descriptors enables partition coefficients to be predicted for transfer from water to over 40 (wet) solvents. If the solubility of a given compound in just one dry solvent (out of a list of 47 dry solvents) is available, then the solubility in all the other listed dry solvents can be predicted through very simple equations.

INTRODUCTION

There are a very large number of applications of organophosphorus compounds, particularly as extraction agents for metals and as flame-retardants. A knowledge of water-solvent partition coefficients, P_s, is essential in studies of metal extraction, and a knowledge of solubilities in organic solvents, S_s, is very useful for the large-scale preparation and purification of flame-retardants. It would be extremely helpful if methods for the prediction of partition coefficients and solubilities of organophosphorus compounds were available, but there has been very little work reported in this area. Apostoluk and Robak (1) applied

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the Kamlet-Taft method (2) to the correlation and prediction of partition coefficients, as log Ps, from water to a variety of solvents for a number of organophosphorus compounds. Log P_s values for the dialkylphosphoric acids could be correlated with standard deviations, SD, between 0.58 and 0.65 log units, depending on the exact equation used. These correlations were re-examined by Kolarik (3) who concluded that although they could be regarded as satisfactory, they were not good enough for the prediction of further values of log P_s. For trialkylphosphine oxides and trialkylphosphates (1) the SD values were smaller (0.38 and 0.29 log units, respectively). No predictive methods for solubility that are specific to organophosphorus compounds appear to have been reported.

There are a number of general methods for the prediction of water-octanol partition coefficients, as log P_{oct} that can be applied to organophosphorus compounds. Even for rather simple compounds there is not much agreement between the most common methods. Log P_{oct} for triethylphosphine is given as 2.41, 2.30, 1.65, and 3.25 by the ACD software (4), the ClogP method of Leo (5), the PHA method (6), and SPARC (7), respectively; the AlogP software (8) lists calculated logP_{oct} values from −0.05 to 3.63 log units. For more complicated molecules there is also disagreement. For PhP(O)(OH)CH$_2$OH the corresponding values are −0.93 (4), −0.38 (5), −0.05 (6), and −0.32 (7) log units; the software package AlogP (8) lists values that range from −1.98 to 0.87 log units. Meyer and Maurer (9,10) have set out a method for the prediction of log P_s values for a large number of water-solvent systems, but their method requires solute properties that are not available for organophosphorus compounds. Toulmin et al. (11) use a method that starts with log P_{oct} and adjusts this with fragment contributions to obtain log P_{hex}, where P_{hex} is the water-hexadecane partition coefficient. The method failed, however, for the only organophosphorus compound examined, triphenylphosphine oxide. SPARC, however, can calculate log P_s values for almost any solvent, although the predicted values are not expected to be any more accurate than those for predictions of log P_{oct}.

There has been a great deal of work on solubilities in water, [see ref (12)], but the only organic solvent that has been examined in any detail is octanol (13–16). Yalkowsky et al. (13–15) studied a number of methods for the prediction of log S_{oct}. The two best methods were a group contribution method known as OCTASOL and a method based on a known solubility in water and a known log P_{oct} value (12). Neither are very useful for organophosphorus compounds. Raevsky et al. (16) employed an interesting method in which the solubility in octanol of a model solute as close in structure to the "unknown" solute as possible was used as a starting point. The method requires rather a large database of octanol solubilities in order that a suitable model solute can be found. For the only organophosphorus compound studied, fenchlorphos, it was not possible to find a suitable model solute.

Abraham and Acree et al. (12,17–19) have set out a general system for the prediction of log P_s and log S_s values that we describe in detail below. It is the purpose of this work to apply the Abraham-Acree method to a number of organophosphorus compounds and hence to be able to predict values of log P_s and log S_s for organophosphorus compounds in a range of solvents.

METHODS

We start with two linear free energy relationships, LFERS, Eq. (1) and Eq. (2).

$$\text{Log } P_s = c + eE + sS + aA + bB + vV \qquad (1)$$

$$\text{Log } K_s = c + eE + sS + aA + bB + lL \qquad (2)$$

The dependent variable in Eq. (1) is log P_s, and in Eq. (2) is log K_s where K_s is a given gas phase to solvent partition coefficient. The independent variables in Eq. (1) and Eq. (2) are the Abraham solute descriptors as follows (12,20,21). E is the solute excess molar refractivity in units of $(cm^3 \, mol^{-1})/10$, 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 in units of $(cm^3 \, mol^{-1})/100$, and L is the solute gas to hexadecane partition coefficient at 298 K. The coefficients in Eq. (1) and Eq. (2) are obtained by multiple linear regression analysis, and serve to characterize the system under consideration. Coefficients in Eq. (1) and Eq. (2) for several water to solvent and gas to solvent partitions are listed in Table 1 (12,22,23). Some of the solvents are water-saturated and some are neat (dry) solvents, as indicated in the first column of the table. As well as partitions from the gas phase to solvents, we also include coefficients for partitions from the gas phase to water.

There is one specific proviso to Eq. (1). For partitions from water to solvents with a high water content at saturation, the B-descriptor has to be replaced by an alternative B^o-descriptor for a few specific types of compound. These include sulfoxides (but not sulfones), alkylpyridines and alkylanilines.

Particular solvents for which B^o has to be used in Eq. (1) are water-saturated butanol, octanol, ethers, ethyl acetate, and butyl acetate, [see Table 1.] This means that if log P_s values are not available in at least one of these solvents, the B^o descriptor for a given compound cannot be determined.

The first step in the method is to determine the relevant solute descriptors for a given compound. Of the six descriptors in Eq. (1) and Eq. (2), V can always be calculated from the solute molecular formula and the number of bonds, N_B, in the molecule. The latter can be obtained from the total number of atoms, N_A, and the number of rings, N_R, in the molecule, using the algorithm of Abraham (20)

$$N_B = N_A - 1 + N_R \qquad (3)$$

If the solute is a liquid, E can be calculated (20) from the refractive index at 293 K. If the solute is a solid, the refractive index can be estimated using the (free) ACD software (4); alternatively, E can be estimated by Absolve software program (6). This leaves four descriptors to be determined. If four log P_s values are available, either directly or indirectly through solubilities, then the four descriptors can be evaluated through the four corresponding Eq. (1) equations. In practice, more than four log P_s values will normally be used, and the four descriptors found by a "best fit" method using the "Solver" add-on in Microsoft Excel. Solubilities can also be used, either alone or in combination with log Ps measurements.

We assume that partition between water and a solvent is given by the ratio of solubilities of a solute in the solvent, S_s, and in water, S_w,

$$P_s = S_s/S_w \qquad (4)$$

As we have stressed before (12), Eq. (4) will only hold if

1. the same equilibrium solid form exists in both water and the organic solvent. Specifically, there is no hydrate or solvate formation, and that for compounds that exhibit polymorphism, the same polymorph exists in both phases,
2. the secondary medium activity coefficient of the solute in the two phases is near unity (in practice, this means that the solute should not be too soluble), and
3. the equation refers to the same chemical species in each phase; thus for ionizable species, it will be the undissociated form in each phase.

The log Ps values obtained through Eq. (4) can be used together with directly determined log Ps values.

It is possible to increase the number of equations by converting all the log P_s values into log K_s values through Eq. (5), where K_w is the gas to water partition coefficient (we use a unit-less coefficient, with concentrations in the gas phase and the aqueous phase in the same units, for example mol/L).

$$\text{Log } P_s = \log K_s + \log K_w \qquad (5)$$

TABLE 1
Coefficients in Eq. (1) and Eq. (2) at 298 K

	Solvent	c	e	s	a	b	l	v
Equations in log P_s, Eq. (1)								
w	Butan-1-ol	0.376	0.434	−0.718	−0.097	−2.350[a]	0.000	2.682
w	Pentan-1-ol	0.185	0.367	−0.732	0.105	−3.100[a]	0.000	3.395
w	Hexan-1-ol	−0.006	0.460	−0.940	0.142	−3.284[a]	0.000	3.792
w	Heptan-1-ol	0.041	0.497	−0.976	0.030	−3.438[a]	0.000	3.859
w	Octan-1-ol	0.088	0.562	−1.054	0.034	−3.460[a]	0.000	3.814
w	Nonan-1-ol	−0.041	0.562	−1.103	0.090	−3.540[a]	0.000	3.922
w	Decan-1-ol	−0.136	0.542	−0.989	0.046	−3.722[a]	0.000	3.996
w	Isobutanol	0.249	0.480	−0.639	−0.050	−2.284[a]	0.000	2.758
w/d	Oleyl alcohol	−0.096	0.148	−0.841	−0.438	−4.040	0.000	4.125
w/d	Dichloromethane	0.319	0.102	−0.187	−3.058	−4.090	0.000	4.324
w/d	Trichloromethane	0.191	0.105	−0.403	−3.112	−3.514	0.000	4.395
w/d	Tetrachloromethane	0.199	0.523	−1.159	−3.560	−4.594	0.000	4.618
w/d	1,2-Dichloroethane	0.183	0.294	−0.134	−2.801	−4.291	0.000	4.180
w/d	1-Chlorobutane	0.222	0.273	−0.569	−2.918	−4.883	0.000	4.456
w/d	Hexane	0.333	0.560	−1.710	−3.578	−4.939	0.000	4.463
w/d	Heptane	0.297	0.634	−1.755	−3.571	−4.946	0.000	4.488
w/d	Octane	0.241	0.690	−1.769	−3.545	−5.011	0.000	4.511
w/d	Decane	0.172	0.726	−1.750	−3.446	−4.496	0.000	4.489
w/d	Undecane	0.058	0.603	−1.661	−3.421	−5.120	0.000	4.619
w/d	Dodecane	0.114	0.668	−1.644	−3.545	−5.006	0.000	4.459
w/d	Hexadecane	0.087	0.667	−1.617	−3.587	−4.869	0.000	4.433
w/d	Cyclohexane	0.159	0.784	−1.678	−3.740	−4.929	0.000	4.577
w/d	Methylcyclohexane	0.246	0.782	−1.982	−3.517	−4.293	0.000	4.528
w/d	Isooctane	0.318	0.555	−1.737	−3.677	−4.864	0.000	4.417
w/d	Benzene	0.142	0.464	−0.588	−3.099	−4.625	0.000	4.491
w/d	Toluene	0.143	0.527	−0.720	−3.010	−4.824	0.000	4.545
w/d	Fluorobenzene	0.139	0.152	−0.374	−3.030	−4.601	0.000	4.540
w/d	Chlorobenzene	0.065	0.381	−0.521	−3.183	−4.700	0.000	4.614
w/d	Bromobenzene	−0.017	0.436	−0.424	−3.174	−4.558	0.000	4.445
w/d	Iodobenzene	−0.192	0.298	−0.308	−3.213	−4.653	0.000	4.588
w/d	Nitrobenzene	−0.152	0.525	0.081	−2.332	−4.494	0.000	4.187
w/d	Benzonitrile	0.097	0.285	0.059	−1.605	−4.562	0.000	4.028
w	Diethyl ether	0.248	0.561	−1.016	−0.226	−4.553[a]	0.000	4.075
w	Diisopropylether	0.472	0.413	−0.745	−0.632	−5.251[a]	0.000	4.059
w	Dibutylether	0.252	0.677	−1.506	−0.807	−5.249	0.000	4.815
w	Ethyl acetate	0.441	0.591	−0.699	−0.325	−4.261[a]	0.000	3.666
w	n-Butyl acetate	−0.475	0.428	−0.094	−0.241	−4.151[a]	0.000	4.046
w	Methyl isobutyl ketone	0.383	0.801	−0.831	−0.121	−4.441	0.000	3.876
w/d	Olive oil	−0.035	0.574	−0.798	−1.422	−4.984	0.000	4.210
w/d	Carbon disulfide	0.047	0.686	−0.943	−3.603	−5.818	0.000	4.921
w/d	Isopropyl myristate	−0.605	0.930	−1.153	−1.682	−4.093	0.000	4.249
w/d	Triolein	0.385	0.983	−2.083	−2.007	−3.452	0.000	4.072
d	Methanol	0.276	0.334	−0.714	0.243	−3.320	0.000	3.549
d	Ethanol	0.222	0.471	−1.035	0.326	−3.596	0.000	3.857
d	Propan-1-ol	0.139	0.405	−1.029	0.247	−3.767	0.000	3.986
d	Butan-1-ol	0.165	0.401	−1.011	0.056	−3.958	0.000	4.044
d	Pentan-1-ol	0.150	0.536	−1.229	0.141	−3.864	0.000	4.077

(*Continued*)

TABLE 1
Continued

	Solvent	c	e	s	a	b	l	v
d	Hexan-1-ol	0.115	0.492	−1.164	0.054	−3.978	0.000	4.131
d	Heptan-1-ol	0.035	0.398	−1.063	0.002	−4.342	0.000	4.317
d	Octan-1-ol	−0.034	0.489	−1.044	−0.024	−4.235	0.000	4.218
d	Decan-1-ol	−0.058	0.616	−1.319	0.026	−4.153	0.000	4.279
d	Propan-2-ol	0.102	0.315	−1.020	0.532	−3.865	0.000	4.023
d	Isobutanol	0.161	0.310	−1.069	0.183	−3.774	0.000	4.040
d	s-Butanol	0.194	0.383	−0.956	0.134	−3.606	0.000	3.829
d	t-Butanol	0.197	0.136	−0.916	0.318	−4.031	0.000	4.112
d	3-Methylbutan-1-ol	0.123	0.370	−1.243	0.074	−3.781	0.000	4.208
d	2-Pentanol	0.115	0.455	−1.331	0.206	−3.745	0.000	4.201
d	Ethylene glycol	−0.270	0.578	−0.511	0.715	−2.619	0.000	2.729
d	Trifluoroethanol	0.395	−0.094	−0.594	−1.280	−1.274	0.000	3.088
d	Diethyl ether	0.330	0.401	−0.814	−0.457	−4.959	0.000	4.320
d	Tetrahydrofuran	0.207	0.372	−0.392	−0.236	−4.934	0.000	4.447
d	Dioxane	0.098	0.350	−0.083	−0.556	−4.826	0.000	4.172
d	Dibutylether	0.203	0.369	−0.954	−1.488	−5.426	0.000	4.508
d	Methyl t-butyl ether	0.376	0.264	−0.788	−1.078	−5.030	0.000	4.410
d	Methyl acetate	0.351	0.223	−0.150	−1.035	−4.527	0.000	3.972
d	Ethyl acetate	0.328	0.369	−0.446	−0.700	−4.904	0.000	4.150
d	Butyl acetate	0.248	0.356	−0.501	−0.867	−4.973	0.000	4.281
d	Propanone	0.313	0.312	−0.121	−0.608	−4.753	0.000	3.942
d	Butanone	0.246	0.256	−0.080	−0.767	−4.855	0.000	4.148
d	Cyclohexanone	0.038	0.225	0.058	−0.976	−4.842	0.000	4.315
d	Propylene carbonate	0.004	0.168	0.504	−1.283	−4.407	0.000	3.421
d	Dimethylformamide	−0.305	−0.058	0.343	0.358	−4.865	0.000	4.486
d	Dimethylacetamide	−0.271	0.084	0.209	0.915	−5.003	0.000	4.557
d	Diethylacetamide	0.213	0.034	0.089	1.342	−5.084	0.000	4.088
d	Dibutylformamide	0.332	0.302	−0.436	0.358	−4.902	0.000	3.952
d	N-Methylpyrolidinone	0.147	0.532	0.225	0.840	−4.794	0.000	3.674
d	N-Methyl-2-piperidone	0.056	0.332	0.257	1.556	−5.035	0.000	3.983
d	N-Formylmorpholine	−0.032	0.696	−0.062	0.014	−4.092	0.000	3.405
d	N-Methylformamide	0.114	0.407	−0.287	0.542	−4.085	0.000	3.471
d	N-Ethylformamide	0.220	0.034	−0.166	0.935	−4.589	0.000	3.730
d	N-Methylacetamide	0.090	0.205	−0.172	1.305	−4.589	0.000	3.833
d	N-Ethylacetamide	0.284	0.128	−0.442	1.180	−4.728	0.000	3.856
d	Formamide	−0.171	0.070	0.308	0.589	−3.152	0.000	2.432
d	Acetonitrile	0.413	0.077	0.326	−1.566	−4.391	0.000	3.364
d	Nitromethane	0.023	−0.091	0.793	−1.463	−4.364	0.000	3.460
d	Dimethylsulfoxide	−0.194	0.327	0.791	1.260	−4.540	0.000	3.361
d	Sulfolane (303 K)	0.000	0.147	0.601	−0.318	−4.541	0.000	3.290
d	Tributylphosphate	0.327	0.570	−0.837	−1.069	−4.333	0.000	3.919
n/a	Gas-water	−0.994	0.577	2.549	3.813	4.841	0.000	−0.869
Equations in log K_s, Eq. (2)								
w	Butan-1-ol	−0.095	0.262	1.396	3.405	2.565	0.523	0.000
w	Pentan-1-ol	−0.107	−0.001	1.188	3.614	1.671	0.721	0.000
w	Hexan-1-ol	−0.302	−0.046	0.880	3.609	1.785	0.824	0.000
w	Heptan-1-ol	−0.159	0.018	0.825	3.539	1.425	0.830	0.000

(*Continued*)

TABLE 1
Continued

	Solvent	c	e	s	a	b	l	v
w	Octan-1-ol	−0.222	0.088	0.701	3.478	1.477	0.851	0.000
w	Nonan-1-ol	−0.197	0.141	0.694	3.616	1.299	0.827	0.000
w	Decan-1-ol	−0.302	0.233	0.741	3.531	1.177	0.835	0.000
w	Isobutanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000
w/d	Oleyl alcohol	−0.268	−0.392	0.800	3.117	0.978	0.918	0.000
w/d	Dichloromethane	0.192	−0.572	1.492	0.460	0.847	0.965	0.000
w/d	Trichloromethane	0.157	−0.560	1.259	0.374	1.333	0.976	0.000
w/d	Tetrachloromethane	0.217	−0.435	0.554	0.000	0.000	1.069	0.000
w/d	1,2-Dichloroethane	0.017	−0.337	1.600	0.774	0.637	0.921	0.000
w/d	1-Chlorobutane	0.130	−0.581	1.114	0.724	0.000	1.016	0.000
w/d	Hexane	0.320	0.000	0.000	0.000	0.000	0.945	0.000
w/d	Heptane	0.284	0.000	0.000	0.000	0.000	0.950	0.000
w/d	Octane	0.219	0.000	0.000	0.000	0.000	0.960	0.000
w/d	Decane	0.159	0.000	0.000	0.000	0.000	0.972	0.000
w/d	Undecane	0.113	0.000	0.000	0.000	0.000	0.971	0.000
w/d	Dodecane	0.053	0.000	0.000	0.000	0.000	0.986	0.000
w/d	Hexadecane	0.000	0.000	0.000	0.000	0.000	1.000	0.000
w/d	Cyclohexane	0.163	−0.110	0.000	0.000	0.000	1.013	0.000
w/d	Methylcyclohexane	0.318	−0.215	0.000	0.000	0.000	1.012	0.000
w/d	Isooctane	0.264	−0.230	0.000	0.000	0.000	0.975	0.000
w/d	Benzene	0.107	−0.313	1.053	0.457	0.169	1.020	0.000
w/d	Toluene	0.121	−0.222	0.938	0.467	0.099	1.012	0.000
w/d	Fluorobenzene	0.181	−0.621	1.432	0.647	0.000	0.986	0.000
w/d	Chlorobenzene	0.064	−0.399	1.151	0.313	0.171	1.032	0.000
w/d	Bromobenzene	−0.064	−0.326	1.261	0.323	0.292	1.002	0.000
w/d	Iodobenzene	−0.171	−0.192	1.197	0.245	0.245	1.002	0.000
w/d	Nitrobenzene	−0.295	0.121	1.682	1.247	0.370	0.915	0.000
w/d	Benzonitrile	−0.075	−0.341	1.798	2.030	0.291	0.880	0.000
w	Diethylether	0.206	−0.169	0.873	3.402	0.000	0.882	0.000
w	Dipropylether	0.065	−0.202	0.776	3.074	0.000	0.948	0.000
w	Diisopropylether	0.114	−0.032	0.685	3.108	0.000	0.940	0.000
w	Dibutylether	0.369	−0.216	0.026	2.626	−0.499	1.124	0.000
w	Ethyl acetate	0.130	0.031	1.202	3.199	0.463	0.828	0.000
w	n-Butyl acetate	−0.664	0.061	1.671	3.373	0.824	0.832	0.000
w	Methyl isobutyl ketone	0.244	0.183	0.987	3.418	0.323	0.854	0.000
w/d	Olive oil	−0.159	−0.277	0.904	1.695	−0.090	0.876	0.000
w/d	Carbon disulfide	0.101	0.251	0.177	0.027	0.095	1.068	0.000
w/d	Triolein	0.147	0.254	−0.246	1.520	1.473	0.918	0.000
d	Methanol	−0.039	−0.338	1.317	3.826	1.396	0.773	0.000
d	Ethanol	0.017	−0.232	0.867	3.894	1.192	0.846	0.000
d	Propan-1-ol	−0.042	−0.246	0.749	3.888	1.076	0.874	0.000
d	Butan-1-ol	−0.004	−0.285	0.768	3.705	0.879	0.890	0.000
d	Pentan-1-ol	−0.002	−0.161	0.535	3.778	0.960	0.900	0.000
d	Hexan-1-ol	−0.014	−0.205	0.583	3.621	0.891	0.913	0.000
d	Heptan-1-ol	−0.056	−0.216	0.554	3.596	0.803	0.933	0.000
d	Octan-1-ol	−0.147	−0.214	0.561	3.507	0.749	0.943	0.000
d	Decan-1-ol	−0.139	−0.090	0.356	3.547	0.727	0.958	0.000

(*Continued*)

TABLE 1
Continued

	Solvent	c	e	s	a	b	l	v
d	Propan-2-ol	−0.062	−0.327	0.707	4.024	1.072	0.886	0.000
d	Isobutanol	0.012	−0.407	0.670	3.645	1.283	0.895	0.000
d	s-Butanol	−0.017	−0.376	0.852	3.740	1.161	0.867	0.000
d	t-Butanol	0.071	−0.538	0.818	3.951	0.823	0.905	0.000
d	3-Methylbutan-1-ol	−0.014	−0.341	0.525	3.666	1.096	0.925	0.000
d	2-Pentanol	−0.031	−0.325	0.496	3.792	1.024	0.934	0.000
d	Ethylene glycol	−0.887	0.132	1.657	4.457	2.325	0.565	0.000
d	Trifluoroethanol	−0.092	−0.547	1.339	2.213	3.807	0.645	0.000
d	Diethylether	0.288	−0.347	0.775	2.985	0.000	0.973	0.000
d	Tetrahydrofuran	0.189	−0.347	1.238	3.289	0.000	0.982	0.000
d	Dioxane	−0.034	−0.354	1.674	3.021	0.000	0.919	0.000
d	Dibutylether	0.165	−0.421	0.760	2.102	−0.664	1.002	0.000
d	Methyl t-butyl ether	0.278	−0.489	0.801	2.495	0.000	0.993	0.000
d	Methyl acetate	0.129	−0.447	1.675	2.625	0.213	0.874	0.000
d	Ethyl acetate	0.182	−0.352	1.316	2.891	0.000	0.916	0.000
d	n-Butyl acetate	0.147	−0.414	1.212	2.623	0.000	0.954	0.000
d	Propanone	0.127	−0.387	1.733	3.060	0.000	0.866	0.000
d	Butanone	0.112	−0.474	1.671	2.878	0.000	0.916	0.000
d	Cyclohexanone	−0.086	−0.441	1.725	2.786	0.000	0.957	0.000
d	Propylene carbonate	−0.356	−0.413	2.587	2.207	0.455	0.719	0.000
d	Dimethylformamide	−0.391	−0.869	2.107	3.774	0.000	1.011	0.000
d	Dimethylacetamide	−0.308	−0.736	1.802	4.361	0.000	1.028	0.000
d	Diethylacetamide	−0.075	−0.434	1.911	4.801	0.000	0.899	0.000
d	Dibutylformamide	−0.002	−0.239	1.402	4.029	0.000	0.900	0.000
d	N-Methylpyrrolidinone	−0.128	−0.029	2.217	4.429	0.000	0.777	0.000
d	N-Methyl-2-piperidone	−0.264	−0.171	2.086	5.056	0.000	0.883	0.000
d	N-Formylmorpholine	−0.437	0.024	2.631	4.318	0.000	0.712	0.000
d	N-Methylformamide	−0.249	−0.142	1.661	4.147	0.817	0.739	0.000
d	N-Ethylformamide	−0.220	−0.302	1.743	4.498	0.480	0.824	0.000
d	N-Methylacetamide	−0.197	−0.175	1.608	4.867	0.375	0.837	0.000
d	N-Ethylacetamide	−0.018	−0.157	1.352	4.588	0.357	0.824	0.000
d	Formamide	−0.800	0.310	2.292	4.130	1.933	0.442	0.000
d	Acetonitrile	−0.007	−0.595	2.461	2.085	0.418	0.738	0.000
d	Nitromethane	−0.340	−0.297	2.689	2.193	0.514	0.728	0.000
d	Dimethylsulfoxide	−0.556	−0.223	2.903	5.036	0.000	0.719	0.000
d	Sulfolane (303 K)	−0.414	0.084	2.396	3.144	0.420	0.684	0.000
d	Tributylphosphate	0.097	−0.098	1.103	2.411	0.588	0.844	0.000
n/a	Gas-water	−1.271	0.822	2.743	3.904	4.814	−0.213	0.000

[a]This is the coefficient for B^o.

Then if, say, four log P_s are available (either direct or via solubilities), four more equations in log K_s can be used, and two more equations in log K_w are also available. Log K_w will normally have to be found by trial-and-error, so that it is an extra descriptor to be determined. However, starting with four log P_s values, no less than ten equations will be available, with ten dependent variables, to calculate the five missing descriptors (S, A, B, L, and log K_w). This method has been applied extensively to the solubility of solids by Acree et al. (17–19,24–28). Analysis of the series of equations was carried out using the "Solver" add-on program in Microsoft Excel; this uses a trial-and-error method to find the best fit descriptors that lead to the smallest standard deviation in the calculated log P_s and log K_s values.

RESULTS AND DISCUSSION

Apostoluk and Robak (1) have collected values of log P_s for a large number of organophosphorus compounds in a variety of water-solvent systems. One of the most comprehensive sets of log P_s values is for the acids $(RO)_2P(O)OH$; Kosolapoff (29) refers to these as dialkylphosphates but Apostoluk and Robak (1) and Kolarik (3) name them as dialkylphosphoric acids. Apostoluk and Robak (1) give equations for the correlation of their log P_s values against various solvent parameters that include a term for the variation of log P_s against the ionic strength, I, as $1.68(\sqrt{I}/(1 + \sqrt{I})$ or $1.02(\sqrt{I}/(1 + \sqrt{I})$, but Kolarik uses different correlations for log P_s values at different ionic strengths. We decided to use only log P_s values at zero or very low (I = 0.01) ionic strength. The descriptor E was obtained from known values of the refractive index for the liquids at 20°C, and V was calculated as usual (20,30). Then using our method of obtaining extra equations through Eq. (5), we could analyze a very large number of equations for several of the dialkylphosphates using log P_s values recorded by Apostoluk and Robak (1) and by Kolarik (3) and determined by Wolfenden and Williams (31). Results for a typical dialkylphosphate are in Table 2, using the recorded log P_s values (1,3). N is the number of data points, that is the number of equations, and SD is the standard deviation between calculated and observed values of the dependent variable. The SD for the 14 calculated and observed log P_s values is 0.050 log units with the descriptors given in Table 3. We give in Table 3 the obtained descriptors for all the dialkylphosphates we have studied, including log K_w. In Table 2 are also listed the predicted log Ps values for diethylphosphate for a number of water-(wet) organic solvents; these are obtained automatically from the equations in Table 1 and the descriptors in Table 3. The descriptors alter so regularly along the homologous series of alkyl groups that we were able to estimate descriptors for a number of other dialkylphosphates. For all of the dialkylphosphates in Table 3 values of log P_s and log K_s can be predicted in exactly the same way as for diethylphosphate. Note that the predicted values refer to zero ionic strength. For dibutylphosphate the observed and calculated values for partition into wet diisopropyl ether agree well, and for diethylphosphate they do also bearing in mind the different ionic strength (log P_s obs = −1.75 at I = 1.0, log P_s calc = −1.92 at I = 0). Since partition into wet diisopropyl ether requires the alternative B^o descriptor, we can deduce that for the dialkylphosphates $B^o = B$. Wolfenden and Williams (31) determined log P_s for partition of dipropylphosphate into seven solvents, but on our method they did not seem to be self-consistent. All we can say is that our estimated descriptors reasonably predict the Wolfenden and Williams log P_s values for some of the solvent partitions.

We also attempted to obtain descriptors for bis-2-ethylhexylphosphate. The descriptors given in Table 3 yield

TABLE 2

Calculation of descriptors for diethylphosphate; predicted[a] values of water-solvent partition coefficients, as log P_s, and gas-solvent partition coefficients, as log K_s

	Log P_s or log K_s	
	Log P_s(pred)	Log P_s(obs)
Trichloromethane	−2.09	−2.13
Tetrachloromethane	−4.11	
1,2-Dichloroethane	−2.56	
1-Chlorobutane	−3.40	
Hexane	−5.07	−5.08
Heptane	−5.12	−5.08
Octane	−5.19	−5.12
Decane	−4.62	
Dodecane	−5.25	
Hexadecane	−5.18	
Cyclohexane	−5.20	
Isooctane	−5.18	−5.20
Gas-water	9.57	9.59
Benzene	−3.33	
Toluene	−3.52	
Chlorobenzene	−3.38	
Bromobenzene	−3.38	
Nitrobenzene	−2.40	
MIBK	−0.87	−0.89
	Log K_s(fit/pred)	Log K_s(obs)
Trichloromethane	7.41	7.46
Tetrachloromethane	5.41	
1,2-Dichloroethane	7.05	
1-Chlorobutane	6.33	
Hexane	4.49	4.51
Heptane	4.48	4.51
Octane	4.45	4.47
Decane	4.45	
Dodecane	4.38	
Hexadecane	4.41	
Cyclohexane	4.61	
Isooctane	4.52	4.39
Gas-water	9.61	9.59
Benzene	6.23	
Toluene	6.04	
Chlorobenzene	6.18	
Bromobenzene	6.19	
Nitrobenzene	7.04	
MIKB	8.69	8.70

[a]Where observed values are available, those listed as predicted are actually fitted values.

the calculated log P_s shown in Table 4, along with the observed log P_s at I = 0 or I = 0.1. There is very poor agreement between our calculated and the observed values. However, we note that for several partitions there is little

TABLE 3
Descriptors for dialkylphosphates, $(RO)_2P(O)OH$, and diarylphosphates, $(ArO)_2P(O)OH$

R / Ar	E	S	A	B^a	V	L	Log K_w	N	SD
Ethyl	0.173	1.00	0.97	1.07	1.1116	4.411	9.59	14	0.050
Propyl^b	0.129	0.89	0.96	1.07	1.3934	5.270	9.05		
Butyl	0.091	0.80	0.96	1.09	1.6752	6.133	8.63	18	0.111
Pentyl^b	0.058	0.66	0.96	1.09	1.9570	7.071	8.01		
Hexyl	0.033	0.52	0.95	1.06	2.2388	7.921	7.24	10	0.186
Heptyl^b	0.020	0.42	0.96	1.10	2.5206	8.871	6.96		
Octyl	0.015	0.30	0.97	1.12	2.8024	9.817	6.56	12	0.126
Nonyl^b	0.010	0.18	0.96	1.11	3.0842	10.672	5.91		
EtHex^c	0.010	0.27	0.96	1.12	2.8024	9.950	6.43	10	0.138
Phenyl	1.22	1.58	0.95	1.40	1.7673	8.658	12.64	4	0.029
4-Methyl	1.19	1.57	0.95	1.32	2.0454	9.635	11.99	6	0.208
4-Chloro	1.44	1.76	0.95	1.20	2.0084	9.926	12.09	12	0.292
Benzyl	1.20	1.52	0.95	1.34	2.0454	9.724	11.98	16	0.206

^{a}For the dialkylphosphates $B = B^o$.
^{b}Estimated.
^{c}2-Ethylhexyl.

agreement between the various recorded values. Thus we have log P_s as 3.01 or 4.79 for partition into toluene. The variation in experimental values helps to explain why neither Apostoluk and Robak (1) nor Kolarik (3) could obtain very good correlations of log P_s values for dialkylphosphates in different solvents.

More satisfactory calculations were carried out for the diarylphosphates, using the log P_s values listed by Kolarik at $I = 0.01$; the obtained descriptors are in Table 3. Values of E, S, and B are all larger than those for the dialkylphosphates due to the presence of the two aromatic groups.

We cannot compare the predicted values of log P_s against experimental values at zero ionic strength for compounds with estimated descriptors, because there are

almost no such log P_s values. However, we can make comparisons with log P_s values at an ionic strength $I = 1.0$ as shown in Table 5 for dipentylphosphate (1,3). As expected, the predicted values at $I = 0$ are all more negative than the observed values at $I = 1.0$; the only exception is for log P_s in the water-dibutyl ether system.

Partition coefficients for the trialkylphosphates at zero ionic strength are given by Apostoluk and Robak (1) and a large number are listed in the BioLoom data base (4). For trimethylphosphate and triethylphosphate, gas chromatographic, GLC, retention data were available (32) on a capillary polydisiloxane column at 80°C in terms of log tr where tr is the relative retention time with respect to dodecane (log tr = 3.00). The system has to be characterized by determination of log tr values for compounds with known descriptors. We also characterized a silicon oil

TABLE 4
Calculated and observed values of log P_s for bis-2-ethylhexylphosphate

	Log P_s	
Solvent	Calc	Obs (1,3)
Octanol	6.65	4.40
Trichloromethane	5.48	4.80, 4.90
Tetrachloromethane	4.27	1.26
Hexane	3.42	3.48
Heptane	3.44	3.04, 3.20
Octane	3.40	2.66, 3.34, 3.44, 3.48
Isooctane	3.26	3.37
Dodecane	3.16	2.33
Benzene	4.42	3.25
Toluene	4.40	3.01, 4.79

TABLE 5
Comparison of predicted values of log P_s for dipentylphosphate at $I = 0$ with observed values (1,3) at $I = 1.0$

	Log P_s	
Solvent	Pred, $I = 0$	Obs, $I = 1.0$
Trichloromethane	1.71	1.78
Tetrachloromethane	0.08	0.38
Heptane	−0.86	−0.41
Cyclohexane	−0.91	0.11
Toluene	0.45	0.69
MIBK	2.51	2.64
Dibutyl ether	2.22	1.39

TABLE 6
System coefficients for GLC stationary phases

System	c	e	s	a	b	l	N	SD	R^2
Polydisiloxane	−0.404	0	0.149	0.434	0.00	0.600	90	0.052	0.996
Silicone oil	0.024	0.061	0.056	0.000	0.00	0.210	55	0.026	0.996

column at 213°C for which retention indices, I, were available for a number of other phosphorus compounds (33). Details are in Table 6.

For the trialkylphosphates, $A = 0$ and so there is one descriptor less to obtain. Values of E and V were determined as for the dialkylphosphates. For trimethyl-, triethyl-, tripropyl-, and tributyl-phosphate there were enough partition coefficients to construct 19-26 equations, so that the derived descriptors are soundly based. We also estimated descriptors for tripentylphosphate by comparison to those for the other four phosphates. Details are in Table 7. A combination of the given descriptors with the coefficients listed in Table 1 enables log P_s and log K_s for these five trialkylphosphates to be predicted for the very large number of solvent systems in Table 1. For some of these phosphates log P_s is known for the water-wet octanol system. These log P_s values are in-line with the other values and so we can be sure that for the trialkylphosphates $B^o = B$. For triphenylphosphate, log P_s is known for the water-octanol partition as 4.59 (5), and we can estimate descriptors as shown in Table 7 so that they yield the correct value for the water-octanol partition coefficient.

Apostoluk and Robak (1) include dialkylphosphinic acids, $R_2P(=O)OH$, but only for dibutylphosphinic acid are there enough logP_s values to obtain descriptors. We estimated $E = 0.23$ using values of E obtained from refractive indices for related compounds, and V is calculated as before. Apostoluk and Robak (1) list also pKa values; for dibutylphosphinic acid pKa = 3.40 so that it is a weaker proton acid than the dialkylphosphates. Calculations for dibutylphosphinic acid are shown in Table 8 with the descriptors given in Table 9. The SD for the 12 fitted and observed dependent variables, at 0.345, is larger than usual. For the higher dialkylphosphinic acids, the only data available are pKa values and a water-benzene partition coefficient at $I = 0$. We have estimated the descriptors for these dialkylphosphinic acids, noting the variation of descriptors with the size of the alkyl group for the dialkyl-phosphates, and ensuring that the estimated descriptors reproduced the observed log P_s values for the water-benzene system. These estimated descriptors are in Table 9, together with those for dibutylphosphinic acid itself. For dibutylphosphinic acid, the observed and calculated log P_s values for partition into diisoproylether are in good agreement, so that again $B = B^o$. Zhang et al. (34) have determined solubilities of diphenylphosphinic acid in water and in a number of dry solvents, so that we can then deduce log P_s for transfer from water to these solvents through Eq. (4). The deduced log P_s values, and hence the original solubilities, are very self-consistent and yield the descriptors given in Table 9.

The final set of compounds for which Apostoluk and Robak (1) were able to collect several log P_s values are the higher trialkylphosphine oxides, from tributylphosphine oxide onward. In addition, Akiba et al. (35) have determined log P_s for trioctyl-, tris-2-ethylhexyl- and triphenyl-phosphine oxide into a number of solvents. All these log P_s values are at $I = 0.10$, so that our descriptors will then yield predictions for further log P_s values at this ionic strength. There are enough recorded values for log P_s for tributyl-, trioctyl-, and tri(2-ethylhexyl)-phosphine oxide to obtain descriptors as given in Table 10. We have no experimental log P_s values in solvents such as wet octanol or wet ethyl acetate, and so we are unable to deduce

TABLE 7
Descriptors for trialkylphosphates, $(RO)_3PO$

R	E	S	A	B^a	V	L	log K_w	N	SD
Me	0.113	1.27	0.00	0.96	0.9707	3.793	6.12	23	0.103
Et	−0.003	1.12	0.00	1.05	1.3934	5.001	5.72	26	0.200
Pr	−0.055	0.88	0.00	1.19	1.8161	6.278	5.40	19	0.123
Bu	−0.091	0.62	0.00	1.29	2.2388	7.522	4.82	25	0.127
Pe[b]	−0.110	0.52	0.00	1.33	2.6615	8.755	4.51		
Ph[b]	1.83	1.66	0.00	1.10	2.3714	11.259	7.62		

[a]$B^o = B$.
[b]Estimated values, see text.

TABLE 8

Calculated and observed values of water-solvent partition coefficients, as log P_s, and gas-solvent partition coefficients, as log K_s, for dibutylphosphinic acid

Dry solvent

	Log P_s(calc)	Log P_s(obs)
Trichloromethane	0.20	−0.20
Tetrachloromethane	−1.51	−1.28
Gas-water	8.19	8.27
Benzene	−1.13	−0.70
Diisopropyl ether	−0.65	−0.76
Methyl isobutyl ketone	0.39	0.20
	Log K_s(calc)	Log K_s(obs)
Trichloromethane	8.35	8.07
Tetrachloromethane	6.58	6.99
Gas-water	8.25	8.27
Benzene	7.07	7.57
Diisopropylether	8.10	7.51
Methyl isobutyl ketone	8.60	8.47

any possible values of B^o. However, results of triarylphosphine oxides indicate that B^o will be less than B for the trialkylphosphine oxides. Although the various log P_s values for each of the phosphine oxides are reasonably self-consistent, as judged from the SD values in Table 10, there is no consistency between the phosphine oxides. We suggest that the descriptors for trioctylphosphine oxide and tri(2-ethylhexyl)phosphine oxide should not be used to predict further values of log P_s until such time as they can be verified. The log P_s values of Akiba et al. (35) for triphenylphosphine oxide are quite self-consistent, and consistent also with those recorded in BioLoom (5) and those determined by Leahy et al. (36); the latter gives an experimental value for partition into wet octanol (log $P_s = 2.83$). Hu et al. (37) record solubilities of triphenylphosphine oxide in a few solvents, and we could incorporate these into our calculations using a trial-and-error calculation of the solubility in water (log $S_w = -2.81$). Results are in Table 10. By inspection, they are reasonably

consistent with results for tributylphosphine oxide but not with those for the other two phosphine oxides. From the value of log P_s for partition into wet octanol we calculate that $B^o = 1.29$ for triphenylphosphine oxide, and so we expect that for the aliphatic phosphine oxides, B^o will also be less than the corresponding values of B. Solubilities of tri(4-methoxyphenyl)phosphine oxide have been determined by Guo and Wang (38) but we were not able to determine the corresponding descriptors. Guo et al. (39) determined solubilities of the flame retardant (2,5-dihydroxyphenyl)diphenylphosphine oxide, HPO, in water, and a number of solvents that yield log P_s values through Eq. (4). These are all very self-consistent and lead to the descriptors given in Table 10. An estimated value of log P_s for transfer to wet octanol, 1.56 (5), gives an estimated value of 1.82 for B^o. The value for $A = 0.35$ seems at first sight very small for a compound with two phenolic groups, but in addition to electronic effects one of the phenolic groups is likely to be strongly internally hydrogen bonded to the P=O oxygen atom.

Zo et al. (40) have determined solubilities of dialkylphosphites in hydrocarbon solvents for the lower members of the series and solubilities in water for some of the high members. They also give vapor pressures, VP, but it is not clear if these have been determined by Zo et al. (40) or are taken from the literature; no references are given. Kosolapoff (29) records the boiling points and vapor pressures of dimethylphosphite and diethylphosphite from which we have constructed Eq. (6) and Eq. (7);

$$\text{Log VP/mm(dimethylphosphite)} = 8.346 - 2420.4/T \quad (6)$$

$$N = 5, \ SD = 0.086, \ R^2 = 0.992, \ F = 367$$

$$\text{Log VP/mm(diethylphosphite)} = 8.407 - 2552.1/T \quad (7)$$

$$N = 13, \ SD = 0.059, \ R^2 = 0.993, \ F = 1560$$

Values of VP/mm from Eq. (6) are 1.23 at 293 K and 1.69 at 298 K; Zo et al. (39) give 0.95 at 293 K. From

TABLE 9

Descriptors for dialkylphosphinic acids, $R_2P(=O)OH$, and diphenylphosphinic acid

R	E	S	A	B^a	V	L	log K_w	N	SD
Bu	0.23	0.64	0.70	1.26	1.5578	5.714	8.27	12	0.345
Pe	0.23	0.44	0.68	1.20	1.8396	6.579	7.11		
Hex	0.23	0.45	0.67	1.21	2.1214	7.608	6.92		
Hept	0.23	0.45	0.67	1.26	2.4032	8.614	6.88		
Oct	0.23	0.43	0.67	1.22	2.6850	9.630	6.46		
Ph	1.51	0.66	0.33	1.37	1.6462	7.657	8.02	14	0.070

$^a B = B^o$.

TABLE 10
Descriptors for trialkyl- or triaryl-phosphine oxides, R_3PO

R	E	S	A	B^a	V	L	log K_w	N	SD
Bu	0.10	1.09	0.00	1.66	2.0607	7.610	8.13	22	0.121
Oct	0.10	−0.11	0.00	2.68	3.7535	13.60	9.47	18	0.197
2-Ethylhexyl	0.10	0.32	0.00	2.87	3.7535	10.23	7.75	18	0.274
Ph	1.94	2.16	0.00	1.48	2.1953	10.49	9.99	25	0.165
HPO	2.33	2.22	0.35	1.90	2.3127	11.47	13.51	8	0.028

[a]B^o for triphenylphosphine oxide is 1.29 and B^o is estimated as 1.70 for HPO: (2,5-dihydroxyphenyl)diphenylphosphine oxide.

Eq. (7) values are 0.50 at 293 K and 0.70 at 298 K; Zo et al. (39) give 0.50 at 293 K. We took VP at 298 K from Eq. (6) and Eq. (7) to obtain log K_s for solution into the hydrocarbon solvents. For the higher dialkylphosphites we used the ratio VP(298)/VP(293) of 1.40 to convert the values of Zo et al. (40) at 293 K into values at 298 K and then to obtain log K_w. The BioLoom data base (5) lists log P_s for partition into tetrachloromethane as −1.55 for dimethylphosphite and -0.51 for diethylphosphite. The dialkylphosphites are known to be only weak acids; Guthrie (41) estimated pKa for diethylphosphite as 6.1, and the ACD software program calculates pKa as 9.2 (4). It is, therefore, not surprising that our calculations for the dialkylphosphites always yielded very small values for the A-descriptor. For consistency we took $A = 0.10$ for all the dialkylphosphites. Refractive indices are known for the phosphites, so that E and V could easily be obtained; results for dimethylphosphite and diethylphosphite are very self-consistent and are in Table 11. For the other dialkylphosphines we only had a value of log K_w and so we estimated descriptors that yielded the log K_w values. By analogy with other compounds, we suggest that $B^o = B$ for the dialkylphosphites.

One series that is of particular interest is that of the trialkylphosphines, because knowledge of the descriptors would lead to some estimate of the ''intrinsic basicity'' of the central phosphorus atom. Refractive indices and a few vapor pressures (29) are available, but we could find neither partition coefficients nor solubilities for any of the trialkylphosphines. For triphenylphosphine, solubilities in seven solvents have been determined by Burgess and Peacock (42), in five solvents by Gao et al. (43) and in methanol and ethanol by Wang et al. (44). The solubilities are mostly consistent except for those in benzene where there is marked disagreement. In addition, the solubilities in benzene and toluene did not fit at all to the calculated values; possibly there is solvate formation in these cases. None of the three papers (42–44) mentioned any attempt to test for solvate formation. The BioLoom data base lists log P_s values for (wet) octanol, 5.69, and for heptane, 4.91 (5). The observed and calculated values of log P_s are in Table 12; they are based on a trial-and-error fit of -6.38 for log S_w. The obtained descriptors are in Table 13. Less extensive data are available for tri(4-methoxyphenyl)phosphine, Guo and Wang (38) having determined solubilities in a number of solvents. As before, values in benzene and toluene were out of line and we obtained a not-very-good fit for the remaining data, (see Table 12). The calculated and observed values for the water to wet octanol partition coefficient are in good agreement, Table 12, and so we can deduce that for the phosphines $B^o = B$.

A very extensive series of phosphorus compounds is that of the dialkyl alkylphosphonates, $RP(=O)(OR)_2$, the variation in alkyl groups leading to a large number of synthesized compounds (29). Only in the case of dimethyl methylphosphonate, DMMP, is there sufficient data available to determine descriptors. Leggatt (45,46) determined log P_s values into several (wet) solvents, both at zero ionic strength and from water saturated with sodium chloride. We use only values at zero ionic strength. A value of

TABLE 11
Descriptors for dialkylphosphites, $(RO)_2POH$

R	E	S	A	B	V	L	log K_w	N	SD
Me	0.219	0.89	0.10	0.87	0.7711	2.882	5.30	10	0.095
Et	0.142	0.98	0.10	0.90	1.0529	3.912	5.42	10	0.069
Bu	0.064	1.06	0.10	0.92	1.6165	6.190	5.19		
Hex	0.030	1.19	0.10	0.96	2.1801	8.640	5.19		
Oct	0.015	1.33	0.10	1.06	2.7437	11.60	5.54		

TABLE 12
Calculation of descriptors for triphenylphosphine;
calculated and observed values of water-solvent partition
coefficients, as log P_s, and gas-solvent partition coefficients,
as log K_s

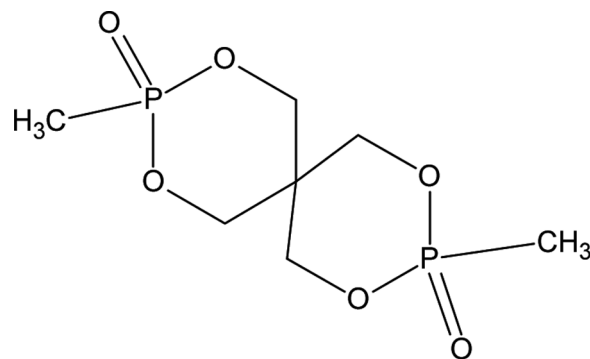| Solvent	Calc	Obs	
Log P_s			
Octanol, wet	5.47	5.69(5)	
Heptane	4.89	4.91(5)	
Water	6.00	6.01	
Cyclohexane[a]	5.63	6.49(42)	
Benzene[a]	6.92	7.50(42)	6.11(43)
Toluene[a]	6.81	5.92(43)	
Methanol, dry	5.23	5.30(44)	5.29(42)
Ethanol, dry	5.56	5.51(44)	5.65(42) 5.44(43)
Propan-2-ol, dry	5.29	5.26(43)	
Tetrahydrofuran, dry	6.86	6.79(42)	
Dioxane, dry	6.75	6.69(42)	
Acetone, dry	6.37	6.25(43)	
Acetonitrile, dry	5.75	5.88(42)	
Log K_s			
Octanol, wet	11.69	11.70(5)	
Heptane	11.06	10.92(5)	
Water	6.05	6.01	
Cyclohexane[a]	11.40	12.50(42)	
Benzene[a]	13.02	13.51(42)	12.12(43)
Toluene[a]	12.89	11.93(43)	
Methanol, dry	11.25	11.31(44)	
Ethanol, dry	11.46	11.52(44)	
Propan-2-ol, dry	11.24	11.27(43)	
Tetrahydrofuran, dry	12.84	12.80(42)	
Dioxane, dry	12.69	12.70(42)	
Acetone, dry	12.28	12.26(43)	
Acetonitrile, dry	11.83	11.89(42)	

[a]Not used in the calculations.

FIG. 1.   Structure of PBMP.

−0.66 for log P_s into (wet) octanol is also available (5). Abraham and Grellier (47) have determined $L = 3.98$ by a direct measurement on hexadecane, and retention times on the capillary polydisiloxane column at 80°C were known (32) A value of E can be obtained from the known refractive index (29), V is calculated as usual, and A can be taken as zero. We found that log P_s into wet octanol (obs −0.66, calc −1.52) and ether (obs −1.49, calc −2.17) were out of line and were left out, but for 22 equations, the SD between observed and calculated values was 0.20 log units with the descriptors given in Table 14. The L-value obtained by analysis of all 22 equations was 3.90 in excellent agreement with the directly determined value (3.98). Log P_s values into the solvents ethyl acetate and isobutanol were satisfactorily fitted, and we conclude that for DMMP, and probably for the other dialkyl alkylphosphonates, $B^o = B$. Krikorian et al. (48) determined log P_s into wet octanol for a number of dialkyl alkylphosphonates by a chromatographic method but the values do not seem to be internally very consistent and we did not use this data.

A number of organophosphorus compounds have been studied as flame retardants, including 3,9-dimethyl-3,9-dioxide-2,4,8,10-tetraoxo-3,9-diphosphaspiro-[5.5]-undecane,

TABLE 13
Descriptors for triarylphosphines, Ar_3P

Ar	E	S	A	B	V	L	log K_w	N	SD
Ph	2.22	1.84	0.00	0.60	0.7711	11.33	6.02	20	0.083
4-MeOC6H4	2.39	2.06	0.00	1.24	2.7354	13.98	9.33	10	0.155

TABLE 14
Descriptors for the phosphorus compounds DMMP and PBMP

Compound	E	S	A	B	V	L	log K_w	N	SD
DMMP	0.205	1.62	0.00	1.01	0.9120	3.903	7.24	22	0.200
PBMP	0.500	1.73	0.00	1.96	1.6391	7.033	11.76	11	0.235

PBMP, see Fig. 1. PBMP can be regarded as a dimer of a cyclic ester of methylphosphonic acid, and so is quite related to dimethyl methylphosphonate. Guo et al. (49) have reported solubilities of PBMP in several solvents. The solubility in water is known as $\log S_w = 0.275$ (49), and we can deduce $\log P_s$ values from water to the dry solvents through Eq. (4). By analogy with DMMP we take $E = 0.50$, we know V, and can take $A = 0$. The data then lead to the descriptors in Table 14.

Another important series of organophosphorus compounds is the trialkylphosphites, several of which are industrial chemicals. The trialkylphosphites, however, are easily hydrolyzed in water and determination of partition coefficients is then very difficult. We could find only one value, 2.26 for partition of tripropylphosphite into octanol (5), and we were thus unable to determine descriptors for the trialkylphosphites.

ESTIMATION OF LOG P_S AND LOG K_S VALUES

The estimation of $\log P_s$ values from water to wet solvents or from water to dry solvents is very straightforward. The descriptors listed in Tables 3, 7, 9, 11, 13, and 14 can be combined with the system coefficients in Table 1 to yield estimated values of $\log Ps$ directly. This is probably the simplest method available for the prediction of water-solvent or gas-solvent partition coefficients. The gas-solvent partition coefficients are important in that they are the inverse of Henry's Law constants, with due regard to units. The only complication arises for the phosphine oxides in Table 10 for which the B^o descriptor has to be used for partition from water into solvents that contain substantial quantities of water at equilibrium; these solvents are shown in Table 1 with the superscript 'a' under the column headed 'b'. If B^o is not available, then values of $\log Ps$ for these specific solvents cannot be estimated. An exactly similar method can be used to estimate K_s values, now starting with the descriptors in Eq. (2), but the complication over the B^o descriptor no longer obtains. Although the difficulty of variable basicity of certain compounds in certain solvent systems has long been known (50,51), there has been no explanation of the phenomenon. One possibility is that it applies to compounds that are heavily hydrated by water in a water-saturated solvent. Triphenylphosphine oxide is known to be so strongly hydrated that it forms a stable solid hydrate $Ph_3PO.H_2O$ (52), and this may distinguish the phosphine oxides from the other organophosphorus compounds we have studied.

It is possible to use the descriptors for all the compounds studied to estimate solubilities through Eq. (4). Once values of $\log Ps$ have been estimated, it requires only the solubility in one solvent to estimate solubilities in all the other solvents. For example, the observed solubility of PBMP in ethanol, as $\log S_{etoh}$, is -1.73 (47), and the observed value of $\log P_{etoh} = -2.01$, so that from Eq. (4),

$$P_s = S_s/S_w \text{ and } P_{etoh} = S_{etoh}/S_w \qquad (8)$$

then for any other solvent

$$S_s = P_s * S_{etoh}/P_{etoh} \qquad (9)$$

$$\log S_s = \log (P_s * S_{etoh}/P_{etoh}) = \log P_s + 0.28 \qquad (10)$$

In the above case, an observed value for $\log P_s$ for the "reference solvent" was available, because $\log S_w$ was known. More generally, $\log S_w$ is not known but to take the present example Eq. (9) could be recast as Eq. (11) so that only one solubility is needed—the other unknowns in Eq. (11), $P_s(calc)$ and $P_{etoh}(calc)$, are obtained from the compound descriptors as usual.

$$S_s = P_s(calc) * S_{etoh}/P_{etoh}(calc) \qquad (11)$$

Equation (11) represents a simple and very general method for the estimation of solubilities for any compound for which the descriptors in Eq. (1) are available.

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