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Partition and transfer of chlorophenoxy acids (herbicides) in water–non-aqueous media

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The distribution of various chlorinated compounds, 2,4-dichlorophenoxyethanoic acid, **2,4-D**, 2-(2,4-dichlorophenoxy)propionic acid, **2,4-DP**, 2,4,5-trichlorophenoxyethanoic acid, **2,4,5-T**, 2-(2,4,5-trichlorophenoxy)propionic acid, **2,4,5-TP** and 2,3,6-trichlorophenylethanoic acid, **2,3,6-T**, was investigated in mutually saturated water–non-aqueous solvent systems at 298.15 K. The data were used to calculate (i) the distribution constant, K_d, referred to the process involving ionic species in the aqueous phase and undissociated species in the organic phase and (ii) the dimerisation constant, K_{dim}, in aprotic media saturated with water. A new treatment used to derive these data is described. The K_d values in the mutually saturated solvents for the various pesticides are compared with corresponding data in the pure solvents derived from solubility measurements in water and in non-aqueous solvents. Data in water were corrected for ion-pair formation while those in the organic phase were corrected for dimerisation. Good agreement is found between the two sets of data.

Introduction

Chlorophenoxy acids[1–3] are known to be hazardous substances and although their use as herbicides has been banned in many countries, large quantities of these compounds are stockpiled in different sites. As a result, chlorophenoxy acids pose a serious threat to human health and the environment, mainly contaminating groundwater and drinking water.[4–7] The development of novel technological approaches for their removal from water and soil by the use of efficient extracting agents is a challenging task.[8] Indeed for the design of these agents, information regarding the solution properties of chlorophenoxy acids (target species) in water and in non-aqueous media is required.

The ratio of the equilibrium concentrations of a substance dissolved in a binary system consisting of two immiscible solvents has often been referred to as the partition coefficient. The main problem is that these data do not provide insight into the different speciations in solution. In addition, the model which appears to be reasonably simple for biochemical investigations serves no purpose for the derivation of thermodynamic data. Most partition studies involving chlorophenoxy acids have been carried out in the water–octanol solvent system, where octanol is considered a solvent representative of a biotic lipid.

As part of a research programme on the design of novel decontaminants based on calixarene derivatives for the removal of obsolete pesticides from ecosystems,[8] and as a follow up of previous work concerning partition in water–non-aqueous solvent systems,[9–12] distribution studies of chlorophenoxy acids [2,4-dichlorophenoxyethanoic acid; **2,4-D**, 2-(2,4-dichlorophenoxy)propionic acid; **2,4-DP**, 2,4,5-trichlorophenoxyethanoic acid; **2,4,5-T**, 2-(2,4,5-trichlorophenoxy)propionic acid; **2,4,5-TP** and 2,3,6-trichlorophenylethanoic acid; **2,3,6-T**] in water–aprotic (H_2O–s) media at 298.15 K were undertaken. In this paper a new treatment is formulated by which distribution data, D, are used to derive i) the dimerisation constant, K_{dim}, of chlorophenoxy acids (RCOOH) in the non-aqueous phase (s) [eqn. (1)]

$$\mathrm{RCOOH(s)} \xrightleftharpoons{K_{dim}} \frac{1}{2}\mathrm{(RCOOH)_2(s)} \qquad (1)$$

and (ii) the distribution constant, K_d, for the process shown in eqn. (2). In this process, both solvents are mutually saturated.

$$\mathrm{RCOO^-(H_2O)} + \mathrm{H^+(H_2O)} \xrightleftharpoons{K_d} \mathrm{RCOOH(s)} \qquad (2)$$

In an attempt to test the validity of the treatment used, K_d values were also obtained from solubility measurements of chlorophenoxy acids in water [where solubility data is corrected for ion association, eqn. (3)][13] and in the non-aqueous phase (solubility data is corrected for dimerisation) [eqn. (4)].

$$\mathrm{RCOOH(sol)} \xrightleftharpoons{K^o_{sp}} \mathrm{RCOO^-(H_2O)} + \mathrm{H^+(H_2O)} \qquad (3)$$

$$\mathrm{RCOOH(sol)} \xrightleftharpoons{K^\ominus} \mathrm{RCOOH(s)} \qquad (4)$$

In eqns. (3) and (4), sol, K^o_{sp} and $K^\ominus$ denote the solid, the thermodynamic solubility product in water and the thermodynamic solubility constant in the non-aqueous phase, respectively. Both K^o_{sp} and $K^\ominus$ refer to the standard state of 1 mol dm^{-3} for the ionic ($\mathrm{RCOO^-}$, $\mathrm{H^+}$) and neutral species (RCOOH).

Combination of eqns. (3) and (4) leads to the process described by eqn. (2). However the distribution constant derived from solubility data refers to the pure solvent rather than to the mutually saturated solvents. Therefore the notation $K'_d = K^\ominus/K^o_{sp}$ will be used to distinguish this parameter from K_d. Having stated this, it should be emphasised that previous work[14] has shown that for systems in which the mutual solubility of the solvents involved is low, $K'_d \cong K_d$. Within this context, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), toluene ($CH_3C_6H_5$) and hexane (C_6H_{14}) are aprotic solvents

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known to have low mutual solubility with water and therefore these solvents were selected for these studies.

Experimental

Chemicals

2,4-D (98%), **2,4-DP** (98%), **2,4,5-T** (97%) and **2,4,5-TP** (97%) were purchased from Aldrich Chemical Co., while **2,3,6-T** (98%) was obtained from Lancaster Synthesis Co. These were recrystallised from water and dried under vacuum at 80 °C for 24 hours and left in a desiccator over anhydrous $CaCl_2$ before use. The purity of these compounds was checked by ^1H NMR analysis in $CDCl_3$ using a Bruker AC-300 E NMR Spectrometer. As a representative example the ^1H-NMR data are given for **2,4-D** [^1H-NMR δ ($CDCl_3$) (300.135 MHz): 4.73 (s, 2H, CH_2), 7.18 (d 1H, $J = 2.7$ Hz, Ar–H), 7.21 (d, 1H, $J = 2.7$ Hz, Ar–H), 7.41 (d, 1H, $J = 2.7$ Hz, Ar–H)]. As far as the solvents are concerned, *n*-hexane (BDH, laboratory grade), dichloromethane, chloroform and toluene (Fisher Scientific, laboratory grade) were purified as described elsewhere.[15]

Distribution measurements

For these experiments, the solvents were mutually saturated to avoid changes when mixed.[9–11] Aqueous solutions of the various chlorophenoxy acids containing different concentrations of these acids were prepared (1.00×10^{-5}–9.00×10^{-4}, initial pH 4.5–5.5 and pH after equilibrium 5.0–5.5). Equal volumes (10 cm^3) of the aqueous solution and the appropriate organic solvent were used for the distribution experiments. The mixtures were vigorously shaken and left for several hours in a thermostat at 298.15 ± 0.05 K until equilibria were reached. The phases were then separated. Aliquots of the aqueous layer were taken and the amount of chlorinated compound was determined using a Cecil 8000 series UV spectrophotometer. Absorbances were registered within the 250–350 nm range. The sample concentrations in the solvent saturated water phases were derived from the absorbance values using appropriate calibration curves.

In all cases Beer's law was obeyed. For a few systems, the accuracy of the data was corroborated by gravimetric determinations of the amount of pesticide in the organic phase.

Conductometric measurements

A Wayne Kerr automatic bridge, type 7339 and meter were connected to a Russel platinum glass bodied electrode unit. The conductivity experiments were carried out at a fixed frequency of 1 kHz and resistance measurements were displayed automatically according to the chosen sensitivity.

Samples were introduced in a cylindrical glass vessel equipped with a three-necked lid and thermostated at 298.15 K. A magnetic stirrer was used to homogenise the solutions during experiments. Samples were injected into the vessel by means of an autoburette, which was previously calibrated by using the gravimetric technique.

The conductance cell constant was determined by sequentially adding aliquots of an aqueous solution of KCl (0.100 mol dm^{-3}) to the de-ionised water in the cell. Potassium chloride was previously purified as described elsewhere.[16]

Conductance readings were taken after each injection and these were recorded after allowing enough time for the solution to attain thermal equilibrium.

The molar conductance values of KCl (0.100 mol dm^{-3} in water at 298.15 K) were used to calculate the cell constant according to the procedure in the literature.[17] Molar conductances, Λ_m, of the solution containing the appropriate chlorophenoxy acid in the various solvents were measured at different concentrations and plotted against the square root of the ionic strength of the solution as described elsewhere.[17]

Solubility measurements

Saturated solutions of the appropriate chlorophenoxy acid were prepared in the solvent of interest. An excess of the solid was added to the solvent followed by vigorous stirring. Mixtures were left in a thermostat at 298.15 ± 0.05 K for several days to ensure that the equilibrium between the solid and the saturated solution was reached.

During this period of time, samples were repeatedly shaken and additional amounts of the solid were added in cases where complete dissolution was observed. Samples for analysis were taken at the equilibrium temperature and analysed spectrophotometrically and gravimetrically. At least three analytical measurements were made on each of the equilibrium mixtures. Solvate formation was checked using the De Ligny method.[17] Blank experiments were carried out to ensure the absence of impurities in the system.

Results and discussion

Distribution of the chlorophenoxy acids between water and non-aqueous solvents at 298.15 K

For the distribution experiments, the concentration range of the chlorophenoxy acids in the aqueous solutions (saturated with the appropriated organic phase) was 1×10^{-5}–9×10^{-4} mol dm^{-3}. Taking into account the association constant of these acids in water (the reciprocal of the dissociation constant reported in the literature),[18,19] percentages of dissociation are in the order of 99.5 and 96%, respectively. Considering that the equilibrium concentrations of chlorophenoxy acids in the aqueous phase are lower than the initial concentrations used in these experiments, it is reasonable to consider that, under these experimental conditions, ionic species are predominantly in the aqueous phase. As far as the non-aqueous phase is concerned, in solvents of low permittivity, carboxylic acids are expected to be undissociated. This was corroborated by conductance measurements carried out at various concentrations of the acid in the appropriate solvent. A representative example for **2,4,5-T** in chloroform is given in Fig. 1, where molar conductances, Λ_m (S cm^2 mol^{-1}) are plotted against the square root of the concentration, $c^{\frac{1}{2}}$, of the acid. The relatively low values of Λ_m obtained clearly indicate that the acid is fully associated in this solvent. However it is well established that carboxylic acids undergo dimerisation [eqn. (1)] in aprotic media.[20] Based on the above statements the processes defined by eqns. (1) and (2) are considered to take place in the organic phase and in the water–organic phase, respectively. The equilibrium constants associated with these processes are defined by eqns. (5) and (6), respectively.

$$K_{\text{dim}} = \frac{[(\text{RCOOH})_2]^{1/2}(\text{s})}{[\text{RCOOH}](\text{s})} \qquad (5)$$

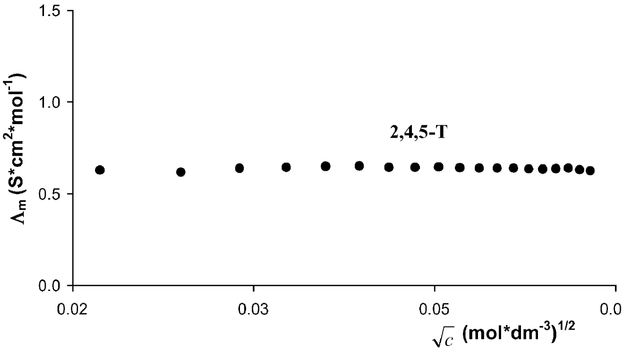

Fig. 1 Plot of Λ_m against the square root concentrations of **2,4,5-T** in chloroform at 298.15 K.

$$K_\mathrm{d} = \frac{[\mathrm{RCOOH}](\mathrm{s})}{[\mathrm{RCOO^-}]_{\mathrm{H_2O}}[\mathrm{H^+}]_{\mathrm{H_2O}}\gamma^2_{\pm\mathrm{H_2O}}} \qquad (6)$$

In eqn. (6), $\gamma_\pm$ denotes the mean molar activity coefficient of the ionic species in water. The activity coefficients of the neutral species in solution at low concentrations are considered to be approximately equal to 1. Having discussed the experimental conditions selected for the distribution experiments and on the basis that the main aim of this paper is to evaluate K_dim and K_d from distribution data, an equation to obtain these data is derived.

In practice distribution data, D_p [the ratio of the total equilibrium concentrations of all species, [Acid], in the organic (s) and water phase (H_2O)] [eqn. (7)] is used to derive K_dim and K_d values.

$$D_\mathrm{p} = \frac{[\mathrm{Acid}](\mathrm{s})}{[\mathrm{Acid}]_{\mathrm{H_2O}}} = \frac{[(\mathrm{RCOOH}) + 2(\mathrm{RCOOH})_2](\mathrm{s})}{[\mathrm{RCOO^-}]_{\mathrm{H_2O}}\gamma_{\pm\mathrm{H_2O}}} \qquad (7)$$

From eqns. (5) and (6), the equilibrium concentrations of the dimer and monomer, respectively, can be derived. Thus

$$[(\mathrm{RCOOH})_2]\ (\mathrm{s}) = K_\mathrm{dim}{}^2[\mathrm{RCOOH}]^2\ (\mathrm{s}) \qquad (8)$$

and

$$[\mathrm{RCOOH}](\mathrm{s}) = K_\mathrm{d}[\mathrm{RCOO^-}]^2_{\mathrm{H_2O}}\gamma^2_{\pm\mathrm{H_2O}} \qquad (9)$$

Substituting eqn. (9) into eqn. (8) gives:

$$[(\mathrm{RCOOH})_2](\mathrm{s}) = K^2_\mathrm{dim}K^2_\mathrm{d}[\mathrm{RCOO^-}]^4_{\mathrm{H_2O}}\gamma^4_{\pm\mathrm{H_2O}} \qquad (10)$$

Subsequently introduction of eqn. (10) into the distribution data D_p eqn. (7) leads to:

$$D_\mathrm{p} = K_\mathrm{d}[\mathrm{RCOO^-}]_{\mathrm{H_2O}}\gamma_{\pm\mathrm{H_2O}} + 2K^2_\mathrm{dim}K^2_\mathrm{d}[\mathrm{RCOO^-}]^3_{\mathrm{H_2O}}\gamma^3_{\pm\mathrm{H_2O}} \qquad (11)$$

Simplifying eqn. (11), it follows that

$$\frac{D_\mathrm{p}}{[\mathrm{RCOO^-}]_{\mathrm{H_2O}}\gamma_{\pm\mathrm{H_2O}}} = K_\mathrm{d} + 2K^2_\mathrm{dim}K^2_\mathrm{d}[\mathrm{RCOO^-}]^2_{\mathrm{H_2O}}\gamma^2_{\pm\mathrm{H_2O}} \qquad (12)$$

Therefore a plot of $D_\mathrm{p}/[\mathrm{RCOO^-}]_{\mathrm{H_2O}}\gamma_{\pm\mathrm{H_2O}}$ against $[\mathrm{RCCO^-}]^2_{\mathrm{H_2O}}\gamma^2_{\pm\mathrm{H_2O}}$ should give a straight line of slope $2K_\mathrm{dim}{}^2K_\mathrm{d}{}^2$ and an intercept equal to K_d.

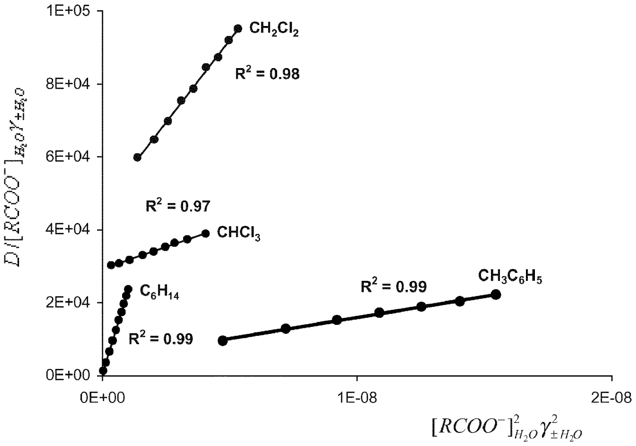

Fig. 2 Plot of $D_\mathrm{p}/[\mathrm{RCCO^-}]_{\mathrm{H_2O}}\gamma_{\pm\mathrm{H_2O}}$ against $[\mathrm{RCOO^-}]^2_{\mathrm{H_2O}}\gamma^2_{\pm\mathrm{H_2O}}$ of **2,4,5-T** in different water–organic solvent (dichloromethane, chloroform, toluene, *n*-hexane) systems at 298.15 K.

Table 1 Values of K_dim in water saturated organic solvents and K_d values (expressed as logarithms) for chlorophenoxy acids in mutually saturated water–organic solvent systems at 298.15 K[a]

	H_2O–CH_2Cl_2		H_2O–$CHCl_3$		H_2O–$CH_3C_6H_5$		H_2O–C_6H_{14}	
	logK_dim	logK_d	logK_dim	logK_d	logK_dim	logK_d	logK_dim	logK_d
2,4-D	1.2	4.3	1.3	3.5	1.6	3.2	2.3	1.9
2,4-DP	1.1	4.8	1.3	4.1	2.0	3.3	2.7	2.1
2,4,5-T	1.5	4.7	1.2	4.2	1.8	3.9	3.0	2.2
2,4,5-TP	1.9	4.7	2.4	4.8	2.8	4.1	3.1	3.6
2,3,6-T	1.4	4.3	1.2	4.8	1.7	4.2	2.0	4.1

[a] Estimated error for all the entries: ±0.2 log units.

Representative examples for various chlorophenoxy acids are shown in Fig. 2, where the linear relationships observed unambiguously demonstrate that eqn. (12) holds for the various systems considered. Thus K_d and K_dim values for chlorophenoxy acids in the various solvents systems in terms of logarithms are shown in Table 1. Mean molar activity coefficients in aqueous media were calculated through the limiting Debye–Hückel equation. The results show that as far as dimerisation constants are concerned, slight increases in the logK_dim values are observed as the permittivity of the medium decreases. However the opposite trend is found for the distribution constants. The above statements are based on the dielectric constants of the dry solvents. Having stated this, it is worth mentioning that the water solubility in these non-aqueous media is relatively small (5.44×10^{-3}, 3.05×10^{-2}, 4.00×10^{-3} and 1.33×10^{-1} mol dm^{-3}, respectively for *n*-hexane, toluene, chloroform and dichloromethane)[21] compared with that for protic solvents such as 1-octanol (2.55×10^0 mol dm^{-3})[22] which has been extensively used in distribution experiments involving chlorophenoxy acids. After obtaining experimental values of K_dim and K_d and taking into account the relatively low mutual solubility of the various solvents used, we then proceeded with the calculation of the distribution constants from the solubility of these chlorophenoxy acids in the individual solvents (pure water and dry organic solvents).

Solubility of chlorophenoxy acids in water and non-aqueous solvents at 298.15 K

Solubility data for chlorophenoxy acids in dichloromethane, chloroform, toluene and *n*-hexane at 298.15 K are reported in Table 2. The data are the result of triplicate analyses carried out on saturated solutions from at least three equilibrium mixtures. The standard deviations of the data are also included in the Table. Solvate formation was checked in all cases and, as shown in Table 2, some of these compounds undergo solvation. Given that the calculation of the thermodynamic solubility constant requires the same composition of the solid in equilibrium with the saturated solution, solubility data were corrected for dimerisation and therefore these are referred to the process described in eqn. (4).

Solubility data for chlorophenoxy acids in water at 298.15 K are those from the literature.[22,23] In cases where these data were not available at the standard temperature, these were determined experimentally. Taking into account the association constant (reciprocal of the dissociation constant) of these compounds in water at the required temperature,[18,19] solubility data were corrected for association using K_a values given in Table 2. The extended Debye–Hückel[24] equation was used to calculate the mean molar activity coefficients, $\gamma_\pm$ for the dissociated species in water. The ion size parameters given are estimated values. It should be emphasised that changes in the $a°$ values do not alter significantly the numerical value of $\gamma_\pm$.[14] Therefore the thermodynamic solubility product K°_sp is referred to the process described in eqn. (3).

In both cases, equilibrium data for the process defined by eqns. (3) and (4) are referred to the standard state of 1 mol dm^{-3}. Combination of solubility data in the non-aqueous solvent and the solubility product in water leads to the calculation of distribution constant K'_d [eqn. (13)] of these

Table 2 Solubility of chlorophenoxy acids in water and non-aqueous solvents at 298.15 K

Chlorophenoxy acids	Solubility in water (mol dm^{-3})	K_a [a]	$a°/A°$ [a]	K^o_{sp} [a]
2,4-D	3.06×10^{-3}	5.37×10^{2}	5	3.89×10^{-5}
2,4-DP	1.49×10^{-3}	1.26×10^{3}	5.2	5.62×10^{-7}
2,4,5-T	1.09×10^{-3}	6.72×10^{2}	5.1	5.13×10^{-7}
2,4,5-TP	2.63×10^{-4}	6.92×10^{2}	5.3	2.82×10^{-8}
2,3,6-T	8.35×10^{-4}	5.01×10^{3}	5.1	1.02×10^{-7}

Chlorophenoxy acids	Solubility (mol dm^{-3})	K_{dim} [a]	C_m (mol dm^{-3}) [b]	$\log K'_d$ [a]	$\log K_d$ [b]
CH_2Cl_2					
2,4-D	$(9.8 \pm 0.2) \times 10^{-2}$	Solvate formation	—	—	—
2,4-DP	$(4.8 \pm 0.2) \times 10^{-1}$	Solvate formation	—	—	—
2,4,5-T	$(2.00 \pm 0.01) \times 10^{-2}$	32	1.69×10^{-2}	4.5	4.7
2,4,5-TP	$(8.69 \pm 0.04) \times 10^{-3}$	85	7.25×10^{-3}	5.4	5.2
2,3,6-T	$(1.75 \pm 0.01) \times 10^{-1}$	Solvate formation	—	—	—
$CHCl_3$					
2,4-D	$(6.98 \pm 0.09) \times 10^{-2}$	19	5.44×10^{-2}	3.1	3.5
2,4-DP	$(3.65 \pm 0.09) \times 10^{-2}$	Solvate formation	—	—	—
2,4,5-T	$(1.06 \pm 0.01) \times 10^{-2}$	16	9.92×10^{-3}	4.3	4.2
2,4,5-TP	$(8.20 \pm 0.01) \times 10^{-3}$	269	6.08×10^{-3}	5.3	5.1
2,3,6-T	$(2.32 \pm 0.01) \times 10^{-1}$	Solvate formation	—	—	—
$CH_3C_6H_5$					
2,4-D	$(3.1 \pm 0.2) \times 10^{-2}$	42	2.44×10^{-2}	2.8	3.2
2,4-DP	$(2.7 \pm 0.2) \times 10^{-2}$	Solvate formation	—	—	—
2,4,5-T	$(1.23 \pm 0.01) \times 10^{-2}$	68	1.01×10^{-2}	4.3	3.9
2,4,5-TP	—	—	—	—	—
2,3,6-T	$(1.22 \pm 0.01) \times 10^{-1}$	Solvate formation	—	—	—
C_6H_{14}					
2,4-D	$(1.8 \pm 0.2) \times 10^{-3}$	218	1.59×10^{-3}	1.6	1.8
2,4-DP	$(1.1 \pm 0.2) \times 10^{-4}$	467	1.07×10^{-4}	2.3	2.1
2,4,5-T	$(8.9 \pm 0.4) \times 10^{-5}$	998	8.56×10^{-5}	2.2	2.2
2,4,5-TP	$(2.5 \pm 0.2) \times 10^{-3}$	1146	1.80×10^{-3}	4.8	4.5
2,3,6-T	$(3.39 \pm 0.01) \times 10^{-3}$	93	3.05×10^{-3}	4.5	4.1

[a] See text for notations. [b] Concentration of monomer.

compounds in water–non aqueous solvent systems.

$$K'_d = \frac{[\mathrm{RCOOH}](\mathrm{s})}{[\mathrm{RCOO^-}]_{\mathrm{H_2O}}[\mathrm{H^+}]_{\mathrm{H_2O}}\gamma^2_{\pm\mathrm{H_2O}}} = \frac{K_s(\mathrm{s})}{K^o_{\mathrm{sp\,H_2O}}} \qquad (13)$$

These data (expressed as $\log K'_d$) are included in Table 2. The difference between K_d [eqn. (6)] and K'_d [eqn. (13)] is that, in the former process, both solvents are mutually saturated while the latter refers to the pure solvents. Comparison between the two sets of data show that, within the experimental error, a reasonable agreement is found between these data. Thus the use of eqn. (12) to calculate distribution, K_d and dimerisation constants, K_{dim} is corroborated.

It should be added that very small changes in solubility were observed for these chlorinated compounds in the pure relative to the water saturated solvents and *vice versa* (water and solvent saturated water). A few representative examples are given in Table 3.

Table 3 Solubility of chlorophenoxy acids in water saturated organic solvents at 298.15 K

	Chlorophenoxy acid		
Solvent	**2,4,5-T**	**2,4,5-TP**	**2,3,6-T**
CH_2Cl_2	$(2.0 \pm 0.2) \times 10^{-2}$	$(8.5 \pm 0.9) \times 10^{-3}$	—
$CHCl_3$	$(1.3 \pm 0.1) \times 10^{-2}$	$(8.2 \pm 0.1) \times 10^{-3}$	$(2.51 \pm 0.02) \times 10^{-1}$
$CH_3C_6H_5$	$(1.51 \pm 0.04) \times 10^{-2}$	—	$(1.56 \pm 0.07) \times 10^{-1}$

Conclusions

From the above discussion it follows that distribution data for chlorinated compounds can be used to determine the extent of dimerisation of these compounds in aprotic media as well as the distribution constants in phase transfer systems. As far as the latter data are concerned, this information is required in solvent extraction technology involving extracting agents. Indeed a quantitative analysis on the effect of the presence of these agents in the organic phase for the removal of chlorinated compounds from aqueous media must be accompanied by distribution studies in the absence of the extracting agent.

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