Analysis of the aqueous solubility of trialkyl phosphates, dialkyl alkylphosphonates, dialkylphosphites and alkyl dialkylphosphinates

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Abstract

Linear free energy relationship (*LFER*) analysis based on the molar intrinsic volume (V_x), McGowan hydrophile–lipophile balance (*HLB*) and cumulative Kabachnik constants ($\Sigma\sigma^{\phi}$) of considered solutes has been performed for the solubility of trialkyl phosphates, dialkyl alkylphosphonates, dialkyl phosphites and alkyl dialkylphosphonates in pure water (called also as their aqueous solubility). The descriptors mentioned above are known for all considered solutes and are strongly correlated with their aqueous solubility. From the correlation found for trialkyl phosphates, dialkyl alkylphosphonates and dialkyl phosphites it follows that the mean contribution of each methylene group in their structure ($\Delta\log S_w$) is a constant for these homologous series and equal to -0.41 . It means that within of homologous series the aqueous solubility of succeeding solutes decreases regularly. The established increment has been further used as a tool for the preliminary selection of solutes whose aqueous solubility at $25\text{ }^{\circ}\text{C}$ is in agreement with this condition. The adequate model (further denoted as AR model) based on the accessible data of temperature effects upon the aqueous solubility of tributyl phosphate, dibutyl butylphosphonate and butyl dibutylphosphinate has been formulated and then tested with positive results for the other solutes whose solubility is known at a selected constant temperature, e.g. at $25\text{ }^{\circ}\text{C}$. It should be noticed, however, that in this case there are some serious restrictions. First, the interpretation and formulation of conclusions for the solutes which aqueous solubility is known at one selected temperature (e.g. $25\text{ }^{\circ}\text{C}$) or if it has been determined at a few temperatures only, should be made with care. Second, the obtained results with AR model cannot be used for prediction of temperature effects upon the aqueous solubility of such solutes. Simultaneously, the results obtained with AR model have been compared with those following from the modified Abraham model. Such comparison has been possible due to a significant progress in the different application of Abraham model for several organophosphorus derivatives as monobasic dialkyl- and diarylphosphoric acids, dialkyl- and diphenylphosphinic acids, trialkyl- and triaryl phosphates, dimethyl methylphosphonate, dialkylphosphites and some of trialkyl- and triarylphosphine oxides, respectively.

Keywords Linear free energy relationship analysis · Aqueous solubility of esters of organophosphorus based acids · Trialkyl phosphates · Dialkyl alkylphosphonates · Dialkyl phosphites · Alkyl dialkylphosphinates

1 Introduction

Alkyl and aryl derivatives of organophosphorus based acids play a crucial role in the different areas of human activity. For instance, they are widely applied as extractants

or synergists in metal extraction systems, high temperature lubricants and flame retardants [1–4]. The physicochemical properties of these compounds affect their importance for practical purposes and determine their toxicity towards the natural environment and biosphere. From

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the last point of view, the extremely toxic are isopropyl methylphosphonofluoridate (sarin) and pinacolyl methylphosphonofluoridate (soman) which are considered as a chemical weapons of mass destruction [5]. The global application of organophosphorus compounds is very large and has an evident effect on the pollution of atmosphere, aquatic systems (mainly of the surface waters) and finally of soils. The aqueous solubility of organophosphorus compounds makes many difficulties in the purification of polluted water prior to its utilization for bath, washing, laundering, cooking, as well as drinking water for the human population, cattle and animals. For example, the problems existing in this field in Sweden have been adequately presented and discussed by Marklund and coworkers [6, 7].

Physicochemical properties of trialkyl phosphates, dialkyl phosphites (dialkyl hydrogen-phosphonates), dialkyl alkylphosphonates, alkyl dialkylphosphinates, and trialkyl- as well as of triarylphosphine oxides could be correlated with their molar intrinsic volumes (V_x) of McGowan, hydrophile-lipophile balances (HLB) in the McGowan scale and cumulative Kabachnik constants ($\Sigma\sigma^\phi$) of alkyl and alkoxy substituents [8–11]. Nevertheless, both two first descriptors are not sufficient to describe quantitatively the differences between the isomers [8, 9]. However, the cumulative Kabachnik constant $\Sigma\sigma^\phi$, which is equal to the sum of individual constants σ^ϕ of substituents on the atom of phosphorus, is specific for a given organophosphorus compound and differentiates it from its isomers [10, 11]. The descriptors mentioned above were used with some success in the previous papers of Apostoluk and coworkers [12, 13]. The present paper relates to the accessible data of aqueous solubility of trialkyl phosphates, dialkyl alkylphosphonates, dialkyl phosphites and alkyl dialkylphosphinates. This property of considered solutes has been analyzed in terms of the linear free energy relationships (LFER) method involving three descriptors, the same as used previously [13]. Their physical and chemical meaning has been indicated and discussed in Sect. 3. The same has been done for five solute descriptors involved in the model of Abraham [14, 15].

2 Collection of available data

2.1 Aqueous solubility of trialkyl phosphates, dialkylphosphites, dialkyl alkylphosphonates and alkyl dialkylphosphinates at 25 °C

The aqueous solubilities of considered compounds, treated as their concentrations in the saturated aqueous solutions, are presented in Table 1. From the most comprehensive experimental study performed at 1958 by Burger and Wagner it follows that at 25 °C the solubility of

considered compounds in water increases in the following order: trialkyl phosphates < dialkylphosphites and dialkyl alkylphosphonates < alkyl dialkylphosphinates < trialkyl phosphine oxides, which indicates the increasing polarity of P–O bonds in each mentioned homologous series [16]. It should be noted, however, that these authors studied only the solutes of low or a moderate aqueous solubility and concluded that the lowest members of each homologous series containing only methyl or ethyl groups attached to phosphorus atom through the C–P or C–O–P bonds are miscible with water [16]. However, this opinion is fallacious since the hydrophilicity of the corresponding lower members of trialkyl phosphates, dialkyl phosphites and dialkyl alkylphosphonates, expressed here in the scale of McGowan (HLB > 7), proves that they are mutually miscible with water and consequently, their aqueous solubility at 25 °C should be treated as a very high or as relatively high [1, 4]. On the other hand, the reported values of aqueous solubility of trimethyl phosphate (HLB = 9.73) may differ significantly. Indeed, in this case for instance the following values, i.e. 1000, 500 and 300 g/dm³, respectively, have been reported [1, 4, 17]. The highest aqueous solubility of trimethyl phosphate, equal to 1000 g/dm³, seems to be reasonable since the similar solubility of dimethylphosphite (HLB = 8.90) has been reported [4] and it could be also accepted. It is also surprising that Nikolotova and Kartashova [1] as well as Yalkowski et al. [17] reported in their monographs the same aqueous solubility of trimethyl and triethyl phosphates, both equal to 1000 or 500 g/dm³, respectively, even this quantity should decrease with the increasing molecular weight or with the decreasing hydrophilicity of solutes of the same homologous series. Therefore, one should find the appropriate tool necessary for the proper selection of available data and then for the formulation of the best correlation describing quantitatively the dependence of solubility of all considered compounds in water on their characteristic descriptors in AR [8, 11–13] and Abraham [14, 15] models, respectively.

2.2 Temperature effect on the aqueous solubility trialkyl phosphates, dialkyl alkylphosphonates, and alkyl dialkylphosphinates

Burger and Wagner [16] indicated that the solubility of some trialkyl phosphates passes through the minimum at about of 70 °C. For instance, the solubility of diethyl *i*-butyl phosphate [16] at 75 °C is about 15% lower than that at 25 °C. However, the detailed studies were performed only in the case of tributyl phosphate whose solubility decreases with temperature, reaches the minimum at about 65 °C and then rises with temperature [16, 18]. Burger in the monograph [19] compared and critically evaluated the latter results obtained by different authors,

Table 1 Aqueous solubility (*S*) of neutral esters of organophosphorus based acids [1, 4, 7, 16–24]

Name of a compound	<i>t</i> (°C)	<i>S_w</i> (g/dm ⁻³)	<i>S_w</i> (mol/dm ⁻³)	log <i>S_w</i>	Ref.	Name of a compound	<i>t</i> (°C)	<i>S_w</i> (g/dm ⁻³)	<i>S_w</i> (mol/dm ⁻³)	log <i>S_w</i>	Ref.
<i>Phosphates</i>											
Trimethyl	25	1000	7.14	0.85	[1]	Dimethyl methyl	25	322	2.60	0.41	[4]
	25	500	3.57	0.55	[17]		25	34	0.0223	-0.65	[4]
	25	300	2.14	0.33	[4]		25	0.6	0.00270	-2.57	[16]
Triethyl	25	500	2.74	0.44	[17]	Diethyl hexyl	25	8.0	0.0384	-1.42	[16]
Tripropyl	25	6.45	0.0288	-1.54	[7]	Dibutyl methyl	25	6.0	0.0270	-1.57	[16]
	30	6.95	0.0310	-1.51	[17]	Dibutyl ethyl	25		0.00989*	-2.00	[20]
Tri- <i>i</i> -propyl	25	0.501	0.00223	-2.65	[4]	Dibutyl butyl	6		0.00672*	-2.17	[20]
Tributyl	3.4	1.075	0.00404	-2.39	[18]		13.4		0.00479*	-2.32	[20]
	4.0	1.012	0.00380	-2.42	[18]		21		0.00200	-2.70	[16]
	5.0	0.957	0.00359	-2.44	[18]		25	0.5	0.00276	-2.56	[19]
	5.4		0.000372*	-2.43	[20]		25	0.692	0.00394*	-2.40	[20]
	13	0.640	0.00240	-2.62	[18]		28.6		0.00341*	-2.47	[20]
	13.9		0.000234*	-2.63	[20]		35		0.00275*	-2.56	[20]
	19.3		0.000178*	-2.75	[20]		43.9		0.00236*	-2.63	[20]
	24.7		0.000151*	-2.82	[20]		48		0.00236*	-2.63	[20]
	25	0.39	0.00146	-2.84	[16]		100		0.00275*	-2.56	[20]
	25	0.422	0.00158	-2.80	[18]	Dibutyl hexyl	25	0.250	0.000898	-3.05	[19]
Tri- <i>i</i> -butyl	33.1		0.000123*	-2.91	[20]	Di- <i>i</i> -amyl methyl	25	1.9	0.00804	-2.09	[1]
	39.2		0.000110*	-2.96	[20]						
	50	0.285	0.00107	-2.97	[18]	<i>Phosphites</i>					
	65	0.25	0.00094	-3.03	[16]	Dimethyl	25	1000	9.09	0.96	[4]
	80.8		0.000110*	-2.96	[20]	Diethyl	25		1.55	0.19	[24]
	86		0.000123*	-2.91	[20]	Dibutyl	25	7.3	0.0376	-1.42	[16]
	94.5		0.000151*	-2.82	[20]	<i>Phosphinates</i>					
	25	0.264	0.000991	-3.00	[21]	Ethyl dibutyl	25	13	0.0630	-1.20	[16]
	25	0.00372	0.0000140	-4.85	[4]	Butyl dibutyl	3.7		0.0562*	-1.26	[20]
	26	0.617	0.00232	-2.64	[22]		7.7		0.0444*	-1.36	[20]
Tri- <i>s</i> -butyl	26	1.501	0.00564	-2.21	[22]		14.4		0.0308*	-1.52	[20]
Triamyl	26	0.019	0.0000616	-4.21	[22]		22.9		0.0209*	-1.68	[20]
Tri(2-methylbutyl)	26	0.024	0.0000778	-4.11	[22]		25	4.5	0.0192	-1.72	[16]
Tri- <i>s</i> -amyl	26	0.058	0.000188	-3.73	[22]		26.5		0.01745*	-1.76	[20]
Diethyl butyl	25	15	0.0714	-1.15	[16]		31.5		0.0146*	-1.84	[20]
Diethyl <i>i</i> -butyl	25	14	0.0666	-1.18	[16]		41		0.0111*	-1.96	[20]
Diethyl amyl	75	11.9	0.0566	-1.25	[16]		57.5		0.00855*	-2.08	[20]
	25	7.5	0.0334	-1.48	[16]		69.5		0.0077*	-2.11	[20]
	25	7.1	0.0317	-1.50	[16]		87		0.0077*	-2.11	[20]

Table 1 (continued)

Name of a compound	<i>t</i> (°C)	<i>S_w</i> (g/dm ⁻³)	<i>S_w</i> (mol/dm ⁻³)	log <i>S_w</i>	Ref.	Name of a compound	<i>t</i> (°C)	<i>S_w</i> (g/dm ⁻³)	<i>S_w</i> (mol/dm ⁻³)	log <i>S_w</i>	Ref.
Dibutyl ethyl	25	3.4	0.0143	-1.85	[16]						
Tri(2-chloroethyl)	25	7.0	0.0245	-1.61	[4]						

*Solubility of solutes in the molality scale (see the comments in Sect. 3)

however, the study carried out by Nikolayev et al. [20] had been omitted. These authors found that their results are in a good agreement with those reported for tributyl phosphate by Higgins et al. [18] and demonstrated that the aqueous solubility of dibutyl butylphosphonate and butyl dibutylphosphinate changes with temperature in a similar manner as that of tributyl phosphate. A main drawback of the work [20] lies in that the experimental results presented graphically were expressed in the scale of weight percent solubility of considered solutes in water while the densities of corresponding aqueous solutions were not indicated. In this case, however, there are two possible ways of calculation of the molar concentrations of solutes. First, the weight percent of a solute could be converted to its molar concentration assuming that the density of an aqueous solution is equal to the density of pure water at temperature expressed in °C. The effect of temperature within the range from 0 to 100 °C upon the density of water has been found from the experimental data reported in the tables of its physical properties [25]. Similarly as in the work of Jones and Harris [26] the polynomial quartic equation in temperature has been applied:

$$d_{\text{H}_2\text{O}} = 0.999881 + 5.961 \cdot 10^{-5}t - 7.782 \cdot 10^{-6}t^2 + 4.374 \cdot 10^{-8}t^3 - 1.374 \times 10^{-10}t^4$$
$$R^2 = 0.999998, \text{ } SD = 0.000018,$$
$$F = 12710275, \text{ } N = 101, \text{ } P = 0.0000.$$

(1)

Second, the weight percent of a solute can be easily recalculated to its molality, i.e. concentration in mole per one kilogram of pure water. In a sufficiently diluted solution the molality of a solute is practically equal to its molar concentration. The results obtained in both ways are identical for tributyl phosphate, and practically the same for dibutyl butylphosphonate. They are slightly different for butyl dibutylphosphinate, however, the differences are small and approximately equal to ±0.01 of logarithmic unit. The results obtained in both ways of calculation are indicated in Table 1 by an asterisk.

Note that the aqueous solubility of the other considered solutes were usually determined in the molar scale at 25 °C and sporadically at a slightly higher temperatures [17, 22]. The set of analyzed data is presented in Table 1 where the data written in italics have been omitted in further calculations.

Table 2 Property parameters of neutral esters of organophosphorus based acids [7–10]

Name of a compound	V_x	HLB	$\Sigma\sigma^\phi$	n_{HBA}	n_{HBD}	Name of a compound	V_x	HLB	$\Sigma\sigma^\phi$	n_{HBA}	n_{HBD}
<i>Phosphates</i>						<i>Phosphonates</i>					
Trimethyl	97.07	9.73	−0.36	4	0	Dibutyl ethyl	189.83	5.10	−1.84	3	0
Triethyl	139.34	8.30	−0.63	4	0	Dibutyl butyl	217.01	4.19	−1.95	3	0
Tripropyl	181.61	6.88	−0.96	4	0	Dibutyl hexyl	246.19	3.20	−2.02	3	0
Tri- <i>i</i> -propyl	181.61	6.88	−1.23	4	0	Di- <i>i</i> -amyl methyl	203.92	4.63	−1.96	3	0
Tributyl	223.88	5.46	−1.11	4	0	<i>Phosphites</i>					
Tri- <i>i</i> -butyl	223.88	5.46	−1.38	4	0	Dimethyl	77.11	8.90	−0.24	3	1
Tri- <i>s</i> -butyl	223.88	5.46	−1.32	4	0	Diethyl	105.29	7.95	−0.42	3	1
Triamyl	266.15	4.03	−1.17	4	0	Dipropyl	133.47	7.00	−0.64	3	1
Tri(2-methylbutyl)	266.15	4.03	−1.50	4	0	Di- <i>i</i> -propyl	133.47	7.00	−0.92	3	1
Tri- <i>s</i> -amyl	266.15	4.03	−1.44	4	0	Ethyl hexyl	161.65	6.05	−0.64	3	1
Diethyl butyl	167.52	7.35	−0.79	4	0	Dibutyl	161.65	6.05	−0.74	3	1
Diethyl <i>i</i> -butyl	167.52	7.35	−0.88	4	0	Di- <i>i</i> -butyl	161.65	6.05	−0.92	3	1
Diethyl amyl	181.61	6.88	−0.81	4	0	Diethyl	218.01	4.15	−0.86	3	1
Dibutyl methyl	181.61	6.88	−0.86	4	0	Diethyl	274.37	2.25	−1.00	3	1
Dibutyl ethyl	195.70	6.40	−0.95	4	0	<i>Phosphinates</i>					
Tri(2-chloroethyl)	176.06	7.07	0.09	4	0	Ethyl dibutyl	183.86	3.80	−2.63	2	0
<i>Phosphonates</i>						Butyl dibutyl	212.14	2.85	−2.79	2	0
Dimethyl methyl	91.20	8.43	−1.20	3	0	<i>Trialkyl phosphine oxides</i>					
Dimethyl propyl	119.38	7.48	−1.34	3	0	Tributyl	206.07	1.55	−3.64	1	0
Diethyl ethyl	133.47	7.01	−1.52	3	0	Triethyl	375.35	−4.15	−3.93	1	0
Diethyl hexyl	189.83	5.10	−1.70	3	0	Tri(2-ethylhexyl)	375.35	−4.15	−4.23	1	0
Dibutyl methyl	175.74	5.58	−1.70	3	0						

V_x [cm³mole^{−1}], HLB [dimensionless in Mc Gowan scale]

3 Models and descriptors

3.1 AR model

At a constant temperature the set of solubility in water (S_w) of organophosphorus compounds collected in Table 1 has been analyzed according to Eq. (2):

$$\log S_w = f(V_x, HLB, \Sigma\sigma^\phi) \quad (2)$$

where S_w stand for the molar concentration of solutes in the saturated aqueous solutions and V_x , HLB and $\Sigma\sigma^\phi$ are their characteristic descriptors collected in Table 2. The values of V_x and HLB have been calculated from the composition and structure of solutes, i.e. according to the formulae:

$$V_x = \Sigma n_i V_{x,i} - 6.56 n_B \quad (3)$$

$$HLB = 7 - 0.0337 V_x + 1.5 n_O \quad (4)$$

where n_i and $V_{x,i}$ stand for number of i th atoms and their molar volume, n_B denotes the total number of bonds, irrespective of their nature (single, double or triple) [8]. Since the studied esters belong to the different homologous series, therefore, their hydrophile–lipophile balances in the scale of McGowan have been calculated from the

known values of V_x and the number of oxygen atoms (n_O) attached to the phosphorus atom in their structure and acting as the hydrogen bond acceptors from water molecules [9]. The cumulative Kabachnik constants, $\Sigma\sigma^\phi$, have been calculated from the individual σ^ϕ constants of alkyl and alkyloxy substituents attached to the phosphorus atom. The individual σ^ϕ constants of several alkyl and alkyloxy substituents can be found elsewhere [10, 11]. They can be also calculated from their structure according to our approach [13]:

$$\sigma^\phi = f(N_C, \log N_C, Z, n, m) \quad (5)$$

where N_C stands for a number of carbon atoms in the chain of substituent; Z is equal to 0 and 1 for alkyl and alkyl ester groups, respectively; n is equal to 1, 2 or 3 for primary, secondary and tertiary carbon atom in C–P and/or C–O–P bonds, respectively; m is a total number of branches of the carbon chain. The found correlation of excellent quality ($R^2 = 0.9983$, $SD = 0.018$, $F = 3326$, $P = 0.0000$) reproduces nicely the values of individual σ^ϕ constants of 30 substituents and indicates that σ^ϕ values of ester groups are always by (0.84 ± 0.01) unit higher than those of corresponding alkyl substituents with the same length and structure of carbon chain [13].

The contribution of a molar volume V_x of solutes is always negative since it reflects an endoergic effect of cavity formation in the structure of solvent, in this case of water. Within each homologous series V_x regularly increases while HLB decreases, which means that the aqueous solubility of solutes regularly decreases due to the increase of their hydrophobicity. However, the values of V_x and HLB , being strongly correlated from definition (4), are the same for the isomers of a corresponding solutes, e.g. for tributyl, tri-*i*-butyl and tri-*s*-butyl phosphates with $\Sigma\sigma^\phi$ values equal to -1.11 , -1.38 and -1.32 , respectively. Thus, the different values of $\Sigma\sigma^\phi$ distinguish them as independent solutes and indicate also the effect of branching of carbon chain on the formation of hydrogen bonds with water molecules. The deeper insight into a nature of this descriptor gives its splitting on the appropriate parts in accordance with the correlation (6) found for twenty five neutral esters with the straight and branched carbon chains of alkyl- or alkyl ester substituents, respectively, and four dialkylphosphites which are the potential hydrogen bond donors:

$$\begin{aligned} \Sigma\sigma^\phi = & -(3.131 \pm 0.145) - (0.599 \pm 0.46) \frac{V_x}{100} + (0.823 \pm 0.034)n_{HBA} \\ & + (0.866 \pm 0.069)n_{HBD}, \quad (6) \\ R^2 = & 0.9730, SD = 0.110, F = 299.9, N = 29, P = 0.0000, \end{aligned}$$

where n_{HBA} stands for the number of oxygen atoms in the structure of all esters and n_{HBD} denotes the number of H–P bonds and is equal to 0 for all neutral alkyl esters and to 1 for dialkylphosphites, respectively. Both positive effects of the hydrogen bond acceptors and donors, respectively, compensate the negative effect of V_x on hydrophilicity of homologous series of esters, but do not distinguish the differences between their isomers. The isomers of neutral esters may deviate from correlation (6) more than ± 3 SD, for instance tri-*i*-propyl phosphate with the straight carbon chain of substituents and involving secondary C–O–P bonds is only one outlier with the deviation equal to -3.44 SD. The observed deviations of isomers from Eq. (6) seem to be clear in terms of the approach (5) and our calculation performed previously [13]. Both positive effects of the hydrogen bond accepting and donating abilities of all esters are reasonable and justified in terms of their physicochemical properties and from the statistical criteria.

The effect of temperature on the aqueous solubility of an organophosphorus based ester can be studied in accordance with the model:

$$\log S_w = f(t, t^2) \quad (7)$$

where t stands for temperature expressed in the scale of Celsius. The temperature at which the particular solute attains minimum of its solubility in pure water has been

calculated from the derivative $d \log S_w/dt$ of an equation based on the model (7). If the different solutes are compared it is obvious that their descriptors, V_x , HLB and $\Sigma\sigma^\phi$, affect the temperature of their minimal solubility in water. Consequently, the derivative ($d \log S_w/dt$) should also depend upon the descriptors of solutes:

$$(d \log S_w/dt) = \varphi(V_x, HLB, \Sigma\sigma^\phi) \quad (8)$$

Combination of the simple models (2), (7) and relation (8) leads to the following form of AR model:

$$\log S_w = f(t, t^2, V_x, HLB, \Sigma\sigma^\phi, t \cdot V_x, t \cdot HLB, t \cdot \Sigma\sigma^\phi), \quad (9)$$

which previously has never been used.

3.2 Abraham model

The model of Abraham [14, 15] for such phenomenon as the aqueous solubility (S_w) of different solutes at a constant temperature is as follows:

$$\log S_w = c + eE + sS + aA + bB + v \frac{V_x}{100} \quad (10)$$

where S_w is the molar aqueous solubility of a solute. The symbols c , e , s , a , b and v stand for the regression coefficients, whereas E , S , A , B and V_x are the solute descriptors. E is the solute excess molar refractivity, S is the solute dipolarity/polarizability, A and B denote its hydrogen bond acidity and basicity, respectively, and V_x is identical with the McGowan molar intrinsic volume of solute used in AR model.

If the solute is liquid, E can be easily calculated [27] in units $(\text{cm}^3 \text{ mol}^{-1})/10$ from its refractive index (n_D^{20}) determined at 20 °C. V_x in Eq. (10) is calculated from the composition and structure of a solute with the known McGowan and Abraham [8, 14] algorithms and then is expressed in units $(\text{cm}^3 \text{ mol}^{-1})/100$. The unknown values of S , A and B of solute descriptors could be estimated from their properties and behavior in several processes and phenomena, e.g. partition in the two phase liquid systems, partition between gas phase and liquids and solubility in organic solvents [15]. Except of dialkyl phosphites, which are a relatively weak hydrogen bond donors with A equal to 0.10, the neutral alkyl esters of phosphoric, alkylphosphonic and dialkylphosphinic acids, respectively, and trialkyl phosphines are only the hydrogen bond acceptors [15] with A equal to 0. The reported values of Abraham solutes descriptors [15] for five trialkyl phosphates, five dialkyl phosphites, dimethyl methylphosphonate and three trialkylphosphine oxides, respectively are collected in Table 3. Note that for the other considered solutes the list of descriptors is incomplete. As has been stated above, the calculation of V_x is very simple, but the determination of the excess molar refractivity (E) of solutes is not so trivial

Table 3 Abraham descriptors of trialkyl phosphates, dialkyl alkylphosphonates, dialkyl phosphites and alkyl dialkylphosphinates [13, 14]

Name of a compound	<i>E</i>	<i>S</i>	<i>A</i>	<i>B</i>	Name of a compound	<i>E</i>	<i>S</i>	<i>A</i>	<i>B</i>
<i>Phosphates</i>					<i>Phosphonates</i>				
Trimethyl	0.113	1.27	0	0.96	Dibutyl ethyl			0	1.52*
Triethyl	−0.003	1.12	0	1.05	Dibutyl butyl	−0.003*		0	1.71*
Tripropyl	−0.055	0.88	0	1.19	Dibutyl hexyl			0	1.74*
Tri- <i>i</i> -propyl	−0.018*		0	1.38*	Di- <i>i</i> -amyl methyl	0.008*		0	1.71*
Tributyl	−0.091	0.62	0	1.29	<i>Phosphites</i>				
Tri- <i>i</i> -butyl	−0.157		0	1.42*	Dimethyl	0.219	0.89	0.10	0.87
Tri- <i>s</i> -butyl			0	1.38*	Diethyl	0.142	0.98	0.10	0.90
Triamyl	−0.110	0.52	0	1.33	Dipropyl	0.111*		0.10	0.96*
Tri(2-methylbutyl)			0	1.45*	Di- <i>i</i> -propyl	0.045*		0.10	1.06*
Tri- <i>s</i> -amyl			0	1.42*	Ethyl hexyl	0.096*		0.10	0.94*
Diethyl butyl	−0.040*		0	1.15*	Dibutyl	0.064	1.06	0.10	0.92
Diethyl <i>i</i> -butyl			0	1.20*	Di- <i>i</i> -butyl	0.047*		0.10	1.09*
Diethyl amyl			0	1.15*	Dihexyl	0.030	1.19	0.10	0.96
Dibutyl methyl			0	1.17*	Diocetyl	0.015	1.33	0.10	1.06
Dibutyl ethyl	−0.083*		0	1.21*	<i>Phosphinates</i>				
Tri(2-chloroethyl)			0		Ethyl dibutyl			0	2.14*
<i>Phosphonates</i>					Butyl dibutyl	0.167*		0	2.21*
Dimethyl methyl	0.205	1.62	0	1.01	<i>Trialkyl phosphine oxides</i>				
Dimethyl propyl			0		Tributyl	0.10	1.09	0	1.66
Diethyl ethyl			0	1.49*	Triocetyl	0.10	−0.11	0	2.68
Diethyl hexyl			0		Tri(2-ethylhexyl)	0.10	0.32	0	2.87
Dibutyl methyl			0						

**E* and *B* descriptors calculated or estimated in this work

[27]. The refractive indices, n_D^{20} , necessary for its calculation are not always known [1, 15, 29, 30]. The calculated values of *E* descriptor are also indicated in Table 3. The estimation of dipolarity/polarizability (*S*) and hydrogen bond basicity (*B*) of solutes is laborious, time consuming and requires the advanced techniques of calculations [15]. In such case for instance, the approximate hydrogen bond basicity of solutes (except of dimethyl methylphosphonate and tributylphosphine oxide which have been excluded) can be evaluated from the simple correlation:

$$B = (0.8576 \pm 0.0506) - (0.0866 \pm 0.0345) \frac{V_x}{100} - (0.1287 \pm 0.0345) n_{HBD} - (0.5492 \pm 0.0271) \Sigma \sigma^{\phi} \quad (11)$$

$$R^2 = 0.9957, SD = 0.053, F = 615.5, N = 12, P = 0.0000,$$

valid for trimethyl-, triethyl-, tripropyl-, tributyl- and triamyl phosphates, dimethyl-, diethyl-, dibutyl-, dihexyl- and dioctylphosphites, as well for trioctyl- and tri(2-ethylhexyl)phosphine oxides, respectively. Hence, it is clear that hydrogen atom attached directly to phosphorus in dialkylphosphites decreases their hydrogen bond basicity. Equation (11) is also in a good accordance with the

conclusions presented in Sect. 4.2. In Table 3 the values of *B* estimated from Eq. (11) are written in italics. Unfortunately, there is no of any reasonable rule for the rough estimation of dipolarity/polarizability of solutes, i.e. their *S* descriptors.

3.3 Direct comparison of both models

Having in mind that both models differ in the number of solute descriptors we have been selected the set of four

trialkyl phosphates and three dialkyl phosphites for which the aqueous solubility at room temperature and appropriate solute descriptors are known. The direct comparison of models should indicate these descriptors of Abraham model which affect the aqueous solubility of solutes in question. The results of preliminary calculations show that both classes of solutes in Abraham model are correlated

with V_x , E and A descriptors. Further calculations have been performed for the aqueous solubility at 25 °C of the six from the initial set of solutes and that of five mixed trialkyl phosphates, three dialkyl alkylphosphonates and butyl dibutylphosphinate. The final set of aqueous solubilities has been completed with those of tri(*i*-butyl), triamyl and tri(2-methylbutyl) phosphates, respectively, determined at 26 °C.

AR model

$$\log S_w = (0.464 \pm 0.793) - (2.484 \pm 0.153) \frac{V_x}{100} + (0.255 \pm 0.070) HLB - (0.811 \pm 0.133) \Sigma \sigma^p$$

$$R^2 = 0.9918, SD = 0.142, F = 567.2, N = 18, P = 0.0000,$$
(12)

with two Studentized deviations > 2, but none > 3.

Abraham model

$$\log S_w = (3.166 \pm 0.176) - (3.754 \pm 1.077)A + (0.705 \pm 0.124)B - (3.063 \pm 0.086) \frac{V_x}{100}$$

$$R^2 = 0.9932, SD = 0.130, F = 677.4, N = 18, P = 0.0000,$$
(13)

with one deviation of the absolute value equal to 2.92 SD . The established correlations (12) and (13) prove that both models are suitable for the modeling of aqueous solubility of all considered solutes. Formally, correlation (13) does not confirm the conclusion that aqueous solubility of considered classes of esters in the Abraham model depends on V_x , E and A descriptors. The more important in this case is fact that the original values of B and those estimated by us from Eq. (11) are known for all eighteen solutes whereas the values of E are accessible for thirteen solutes only (see Table 3). Instead of Eq. (13) one can consider the correlation (14):

$$\log S_w = (3.426 \pm 0.277) - (2.709 \pm 0.136) \frac{V_x}{100} + (1.615 \pm 0.605)E - (6.377 \pm 1.641)A$$

$$R^2 = 0.9884, SD = 0.183, F = 256.5, N = 13, P = 0.0000,$$
(14)

with one deviation equal to 3.76 SD for dibutyl butylphosphinate.

Consequently, the aqueous solubility of trialkyl phosphates, alkyl dialkylphosphonates and alkyl dialkylphosphinates, which are not the hydrogen bond donors, depends in the Abraham model on the molar intrinsic volume, excess molar refractivity or basicity of solutes. Therefore, the effect of temperature on the aqueous solubility of tributyl phosphate, butyl dibutylphosphonate and butyl dibutylphosphinate should be considered according to the modified form of Abraham model:

$$\log S_w = f(t, t^2, V_x, E, t \cdot V_x, t \cdot E),$$
(15)

which is evidently simpler than that presented by Eq. (9).

The statistical assessment of all derived correlations has been characterized by means of their determination coefficient (R^2), standard deviation (SD) of explained variable ($\log S_w$), standard deviations of the regression coefficients of explanatory variables in the model used, the number of experimental points (N) and the level (P) of their statistical significance.

The predictive power of Eqs. (23) and (24) resulting from both models have been characterized with their internal cross validation coefficient (Q^2) calculated by means of the leave-one-out (LOO) procedure [31, 32] and corresponding sets of data [18, 20]. It should be also added that the number of diverse solutes and limited sets of experimental data [18, 20] are rather not enough for validation of derived correlations through the many-leave-out (MLO) method or through the comparison of training and test sets of data, respectively (Fig. 1).

4 Results and discussion

4.1 Effect of methylene groups on the aqueous solubility of trialkyl phosphates at 25 °C

The set of aqueous solubility of diethyl butyl, diethyl *i*-butyl, diethyl amyl, dibutyl methyl, dibutyl ethyl, tributyl

and tri(2-chloroethyl) phosphates, determined at 25 °C by Burger and Wagner [16], has been completed with those of trimethyl phosphate [1] and tripropyl phosphate [7] and then used for the calculation of logarithmic increment of methylene groups involved in the structure of mentioned phosphates. Application of the model (2) leads to the correlation of excellent quality presented in Fig. 2, where the absolute values of deviations are not higher than 2SD:

$$\log S_w = (3.652 \pm 0.117) - (2.969 \pm 0.076) \frac{V_x}{100} - (0.236 \pm 0.069) \Sigma \sigma^p$$

$$R^2 = 0.9969, SD = 0.062, F = 956, N = 9, P = 0.0000$$
(16)

Fig. 1 Plot of experimental and predicted aqueous solubility of all considered solutes analyzed with: **a** with AR (•) and Abraham (□) models, respectively, according to Eq. (12) and Eq. (13); **b** predicted aqueous solubility of analyzed solutes according to AR and Abraham models

Fig. 2 Plot of experimental versus predicted aqueous solubility of selected trialkyl phosphates according to Eq. (16)

Correlation (16) can be used for prediction of some unknown or verification of uncertain and/or misleading aqueous solubility of trialkyl phosphates. As an example the tri(*i*-butyl) phosphate can be used. Its aqueous solubility at 25 °C reported in the review [4] is equal to 0.264 g/dm³. However, the aqueous solubility of tri(*i*-butyl) phosphate at 25 °C calculated from Eq. (15) is equal to 0.583 g/dm³ and does not differ significantly from the value of 0.617 g/dm³ determined experimentally [22] at (26 ± 1) °C. Logarithmic increment of the aqueous solubility of trialkyl

phosphates is calculated per one methylene group in their structure. The molar intrinsic volume V_x of methylene group [7] is equal to 14.09 cm³ and according to Eq. (16) its contribution to the aqueous solubility of trialkyl phosphates is a constant:

$$\Delta \log S_w = -0.02969 \cdot 14.09 = -0.42 \quad (17)$$

In Eq. (16) the negative contribution of McGowan molar volume of a particular trialkyl phosphate predominates over the positive contribution of its cumulative Kabachnik constant. Therefore, the calculated increment (17) could be used for the rough estimation of unknown values of the aqueous solubility of trialkyl phosphates. For instance, the estimated solubility of triamyl phosphate is equal to 0.0205 g/dm³ and comparable with the value of 0.019 g/dm³ determined experimentally [22] at (26 ± 1) °C. From the reasons indicated in Sect. 2.1, all reported values of the aqueous solubility of triethyl phosphate [1, 7] are erroneous. The next correlation (18) has been obtained involving the aqueous solubility of tri(*i*-butyl) and triamyl and tri(2-methylbutyl) phosphates determined experimentally [22] at (26 ± 1) °C:

$$\log S_w = (3.885 \pm 0.118) - (3.120 \pm 0.082) - (0.265 \pm 0.089) \Sigma \sigma^{\phi} \\ R^2 = 0.9967, SD = 0.087, F = 1369, N = 12, P = 0.0000. \quad (18)$$

As has been expected the absolute deviations from Eq. (18) are lower than 2 SD . In this case, however, the value of methylene group increment, $\Delta \log S_w$, is a slightly lower and equal to -0.44. As a result, Eq. (18) relates to the aqueous solubility of trialkyl phosphates at room temperature.

4.2 Aqueous solubility of trialkyl phosphates, dialkyl alkylphosphonates, dialkylphosphites and alkyl dialkylphosphinates at 25 °C

The set of aqueous solubility of trialkyl phosphates used for the formulation of correlation (16), has been completed with the solubility of dibutyl ethyl-, dibutyl butyl-, dibutyl hexyl- and di-*i*-amyl methylphosphonates, dimethyl, diethyl, and dibutyl phosphites and butyl dibutylphosphinate, respectively. Further calculations have been performed in order to explain the behavior of three dialkyl phosphites, which can act simultaneously as a hydrogen bond acceptors and donors, respectively, in comparison with the neutral trialkyl phosphates, dialkyl alkylphosphonates and alkyl dialkylphosphinates. From this reason, apart from V_x and $\Sigma\sigma^\phi$ descriptors, two additional explanatory variables have been introduced, namely n_{HBA} and n_{HBD} , the same as those in Eq. (6). Application of the step wise selection of explanatory variables leads to the very interesting result:

$$\begin{aligned} \log S_w = & (3.61 \pm 0.141) - (2.97 \pm 0.09) \frac{V_x}{100} \\ & - (0.427 \pm 0.080)n_{HBD} - (0.294 \pm 0.044)\Sigma\sigma^\phi \\ R^2 = & 0.9942, SD = 0.095, F = 690, N = 16, P = 0.0000, \end{aligned} \quad (19)$$

with two absolute deviations of 3.33 SD for di-*i*-amyl methylphosphonate and equal exactly to 3 SD for butyl dibutyl phosphinate. Correlation (19) neglects entirely the hydrogen bond acceptance of all considered esters and indicates the negative contribution of hydrogen bond donating ability of dialkyl phosphites. These facts are clear from the following reasons: (1) in the homologous series the molar volume of analogous solutes decreases regularly by a constant value ($6.87 \text{ cm}^3 \text{ mol}^{-1}$) per one $-\text{CH}_2\text{O}-\text{P}$ bond in their structure; (2) the value of σ^ϕ of hydrogen atom bonded directly to phosphorus is equal from definition to 0, thereby the aqueous solubility of dialkyl phosphites are always greater than those of corresponding trialkyl phosphates and dialkyl alkylphosphonates. As a result, the mean increment ($\Delta \log S_w$) calculated from Eq. (19) per one methylene group is equal to -0.41 , irrespective of the homologous series of considered esters. It is important and useful conclusion. For instance the aqueous solubility at 25 °C of dimethyl methylphosphonate should be higher than the reported value [4] of 322 g/dm^3 ($\log S_w = 0.41$). The solubility in water of diamyl hexylphosphonate, equal to 0.090 g/dm^3 at non specified temperature ($\log S_w = -3.53$), is probably overestimated [28] assuming that it has been determined at 25 °C, similarly as that for dibutyl hexylphosphonate [23].

Fig. 3 Effect of temperature on the aqueous solubility of tributyl phosphate according to Eq. (20). The experimental data have been taken from the appropriate references: O—[17]; ●—[19]; Δ—[18]; x—[15, 17]

4.3 Effect of temperature on the aqueous solubility of tributyl phosphate, dibutyl butylphosphonate and butyl dibutylphosphinate and its analysis in terms of AR and Abraham models

The effect of temperature on the solubility of tributyl phosphate in water was studied in a sufficiently large range of temperature [18, 20]. Both sets of data are in very good agreement which is demonstrated in Fig. 3. Except of the points of lowered [18] solubility at 25 °C and elevated [18] at 50 °C, the parabolic shape of this dependence is confirmed by the following correlation,

$$\begin{aligned} \log S_w = & -(2.324 \pm 0.008) - (0.0245 \pm 0.0005)t \\ & + (0.000205 \pm 0.000006)t^2 \\ R^2 = & 0.9961, SD = 0.015, \\ F = & 1539, N = 15, P = 0.0000, \end{aligned} \quad (20)$$

with only one absolute deviation exceeding 2 SD . From the derivative of Eq. (20) versus temperature it follows that the minimum aqueous solubility of tributyl phosphate lies at about of 60 °C.

Aqueous solubility of dibutyl butylphosphonate reported [16, 23], at 25 °C are lower than that predicted from Eq. (19). This conclusion is also confirmed by the analysis of Russian workers data [20]:

$$\begin{aligned} \log S_w = & -(1.887 \pm 0.019) - (0.0224 \pm 0.00089)t \\ & + (0.000150 \pm 0.000073)t^2 \\ R^2 = & 0.9940, SD = 0.019, \\ F = & 497, N = 9, P = 0.0000, \end{aligned} \quad (21)$$

with only one absolute deviation equal to 2.01 *SD*. According to Eq. (21), the minimum of dibutyl butylphosphonate solubility in pure water is achieved at about of 75 °C.

All reported values of butyl dibutylphosphinate solubility in pure water [16, 20] fulfill the following dependence upon temperature:

$$\begin{aligned}\log S_w &= -(1.172 \pm 0.011) - (0.0266 \pm 0.0006)t \\ &\quad + (0.000184 \pm 0.0000067)t^2 \\ R^2 &= 0.9984, SD = 0.013, \\ F &= 2459, N = 11, P = 0.0000.\end{aligned}\quad (22)$$

The quality of correlation (22) could be considered as excellent even the solubility [2] at 87 °C with the absolute deviation equal to 5.38 *SD* should be excluded. According to Eq. (22), the solubility of butyl dibutylphosphinate passes through the minimum at about of 72 °C.

Tributyl phosphate, dibutyl butylphosphonate and butyl dibutylphosphinate (see Sect. 3.3) are not the hydrogen bond donors and properties of these three solutes depend only on $\frac{V_x}{100}$ and *E* descriptors. Since the number of solutes is greater than the number of descriptors, the model of Abraham leads to the excellent result:

$$\begin{aligned}\log S_w &= (7.443 \pm 1.287) - (0.1962 \pm 0.0260)t + (0.1769 \pm 0.0057)\frac{t^2}{1000} - (4.270 \pm 0.586)\frac{V_x}{100} \\ &\quad + (2.606 \pm 0.272)E + (7.871 \pm 1.177)\frac{t \cdot V_x}{10000} + (1.962 \pm 0.561)\frac{t \cdot E}{100} \\ R^2 &= 0.99781, Q^2 = 0.9668, SD = 0.0250, F = 2201, N = 36, P = 0.0000,\end{aligned}\quad (23)$$

with one absolute deviation of 2.32 *SD* for dibutyl butylphosphonate at 43.9 °C. The minima of aqueous solubility of compared solutes, computed from Eq. 23, are equal to 61.5, 72 and 73 °C for tributyl phosphate, dibutyl butylphosphonate and butyl dibutylphosphinate, respectively.

The analysis of temperature upon the aqueous solubility of tributyl phosphate, dibutyl butylphosphonate and butyl dibutylphosphinate is possible with AR model if the next solute is involved. According to Burger and Wagner [16], the aqueous solubility of diethyl-*i*-butyl phosphate at 25 and 75 °C, respectively, has been used as a reference assuming a priori that its dependence on temperature passes through the minimum at about of 70 °C. Consequently, the correlation of high statistical importance has been obtained:

$$\begin{aligned}\log S &= (145.4 \pm 25.9) + (2.577 \pm 0.528)t + (0.1789 \pm 0.0058)\frac{t^2}{1000} - (0.3110 \pm 0.0515)V_x \\ &\quad - (10.65 \pm 1.95)HLB + (18.02 \pm 3.39)\Sigma\sigma^\phi - (0.518 \pm 0.105)\frac{t \cdot V_x}{100} - (0.194 \pm 0.040)t \cdot HLB \\ &\quad + (0.341 \pm 0.069)t \cdot \Sigma\sigma^\phi, \\ R^2 &= 0.9984, Q^2 = 0.9973, SD = 0.025, F = 2124, N = 37, P = 0.0000,\end{aligned}\quad (24)$$

Fig. 4 Plot of experimental versus predicted aqueous solubility of tributyl and diethyl-*i*-butyl phosphates, dibutyl butylphosphonate and butyl dibutylphosphinate according to Eq. (24)

with only one absolute deviation greater than 2 *SD*, namely 2.51 *SD* for butyl dibutylphosphonate at 43.9 °C.

The obtained result is presented in Fig. 4. The minima of solubility of tributyl phosphate, dibutyl butylphosphonate and butyl dibutylphosphinate calculated from the appropriate derivatives $d\log S_w/dt$ of Eq. (24) are attained at 61.5, 72 and 73 °C, respectively, and are identical with those determined from Eq. (23). Note that these results are in fairly good accordance with those estimated above from Eqs. (20), (21) and (22), respectively.

The statistical quality of correlation (24) is excellent since it predicts nicely the aqueous solubility of diethyl *i*-butyl phosphate [16] at 25 and 75 °C, respectively. However, we find that our AR model predicting the temperature effects upon the aqueous solubility of four solutes mentioned above, it is also able to predict at room temperature

Fig. 5 Plot of experimental versus predicted aqueous solubility of all solutes analyzed according to Eq. (25)

the solubility in water of a solute with the known values of its characteristic descriptors. Hence, it is interesting to check the predictive power of further correlation based on AR model against the aqueous solubility of all solutes taken from Table 1, except of those indicated in italics. Tri(2-chloroethyl) phosphate and di(*i*-amyl) methylphosphonate have been excluded as the outliers from the following correlation:

$$\begin{aligned} \log S_w = & -(11.68 \pm 0.33) + (0.488 \pm 0.018)t + (0.1590 \pm 0.0167)\frac{t^2}{1000} + (1.186 \pm 0.042)HLB \\ & -(2.53 \pm 0.08)\Sigma\sigma^\phi - (0.101 \pm 0.003)\frac{t \cdot V_x}{100} - (0.038 \pm 0.002)t \cdot HLB \\ & + (0.068 \pm 0.003)t \cdot \Sigma\sigma^\phi \\ R^2 = & 0.9932, Q^2 = 0.9865, SD = 0.086, F = 932, N = 53, P = 0.0000, \end{aligned} \quad (25)$$

with only one absolute deviation greater than 2 SD, namely 2.51 SD for tri(2-methylbutyl)phosphate at 26 °C. It should be pointed out that correlation (25) is fulfilled by eighteen solutes, involving ten trialkyl phosphates, three dialkyl alkylphosphonates, butyl dibutylphosphinate and three dialkyl phosphites, respectively. The obtained results are illustrated in Fig. 5.

4.4 Final remarks

The determined increment of the aqueous solubility per one methylene group added in the structure of trialkyl phosphates, dialkyl alkylphosphonates, dialkyl phosphites and alkyl dialkylphosphinates is a constant for all considered solutes and it can be used for the estimation

of their approximate solubility in water. Such increments are also constant for Kovats retention indices (*I*) of analogous trialkyl phosphates and dialkyl alkylphosphonates [33] which, according to our knowledge, are strongly correlated with the aqueous solubility of mentioned solutes. The recent work of Maksimov and Kovalenko [34] and references therein do not affect on the results of our calculations of tributyl phosphate concentration in the aqueous solutions. Stenzel et al. [35] used the model of Abraham for determination of polyparameter linear free energy relationship for established and alternative flame retardants, but considered only three solutes, namely triethyl phosphate, tri(2-chloroethyl) phosphate and diethyl ethylphosphonate, which are interesting for us, but we have been unable to check the utility of their reported descriptors.

5 Conclusions

The accessible literature data on the solubility data of neutral esters of phosphoric, phosphonic and phosphinic acids are rather limited, mainly for dialkyl alkylphosphonates, dialkyl phosphites and particularly for alkyl dialkylphosphinates. The same relates to the solutes of high and low hydrophobicity in terms of their HLB in the McGowan scale. In general, the values of the aqueous solubility of trialkyl phosphates, dialkyl alkylphosphonates, dialkyl phosphites and alkyl dialkylphosphinates could be estimated applying the calculated mean contribution

of each methylene group in their molecular structure or can be verified by means of the appropriate correlations established in the present work.

The AR model (9) has been proposed for interpretations of temperature effect upon the aqueous solubility of tributyl phosphate, butyl dibutylphosphonate and butyl dibutylphosphinate and it has been found that after addition of existing data for the solubility of diethyl *i*-butyl phosphate at 25 and 75 °C, respectively, the correlation (24) of excellent quality reproduces all considered experimental data. Based on the model (9) and correlation (24), the derived relationship (25) of a good statistical quality is fulfilled by eighteen solutes: (1) eleven trialkyl phosphates; (2) three dialkyl alkylphosphonates and three dialkylphosphites; (3) butyl dibutylphosphinate; (4) tri(2-chloroethyl)

phosphate and di(*i*-amyl) methylphosphonate are the outliers. The appropriate modification of Abraham model (15) have been also proposed and it has found as a more convenient for the interpretations of temperature effect upon the aqueous solubility of tributyl phosphate, butyl dibutylphosphonate and butyl dibutylphosphinate as the analogous solutes. Both models predict the same temperatures of minimal solubility of solute in question. On the other hand, they can be also used for the prediction of aqueous solubility of a solute at temperature at which the experimental value is not known. However, there are some serious restrictions in the interpretation and formulation of conclusions for the solute whose aqueous solubility is known at one selected temperature (e.g. 25 °C) or if it has been determined at a few temperatures only. In such situation it is obvious that there are some serious restriction in application of the correlation (25) for the estimation of dependence $\log S_w = f(t)$ for solutes for which the aqueous solubility is known at only one temperature. When the aqueous solubility of a solute is known at two different temperatures one can consider the following cases: (1) diethyl *i*-butyl phosphate for which the difference of

temperature of experimental solubility is equal to 50 °C; (2) tripropyl phosphate for which this difference is equal to 5 °C, respectively. As been mentioned in Sect. 4.3, the aqueous solubility diethyl *i*-butyl phosphate has been an exception, whereas the other solutes cannot be treated in such a way, i.e. the estimation of $\log S_w = f(t)$ dependences are not permissible.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

Human and animal rights The performed LFER studies of aqueous solubility of titled compound have not involved any experiments with of Human Participants and/or Animals.

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Appendix

Phosphates		Phosphites
Trimethyl, $R_1 = R_2 = R_3 = \text{CH}_3$		Dimethyl, $R_1 = R_2 = \text{CH}_3$	
Triethyl, $R_1 = R_2 = R_3 = \text{C}_2\text{H}_5$		Diethyl, $R_1 = R_2 = \text{C}_2\text{H}_5$	
Tripropyl, $R_1 = R_2 = R_3 = \text{C}_3\text{H}_7$		Dipropyl, $R_1 = R_2 = \text{C}_3\text{H}_7$	
Tri- <i>i</i> -propyl, $R_1 = R_2 = R_3 = i\text{-C}_3\text{H}_7$		Di- <i>i</i> -propyl, $R_1 = R_2 = i\text{-C}_3\text{H}_7$	
Tributyl, $R_1 = R_2 = R_3 = \text{C}_4\text{H}_9$		Ethyl hexyl, $R_1 = \text{C}_2\text{H}_5, R_2 = \text{C}_6\text{H}_{13}$	
Tri- <i>i</i> -butyl, $R_1 = R_2 = R_3 = i\text{-C}_4\text{H}_9$		Dibutyl, $R_1 = R_2 = \text{C}_4\text{H}_9$	
Tri- <i>s</i> -butyl, $R_1 = R_2 = R_3 = s\text{-C}_4\text{H}_9$		Di- <i>i</i> -butyl, $R_1 = R_2 = i\text{-C}_4\text{H}_9$	
Triamyl, $R_1 = R_2 = R_3 = \text{C}_5\text{H}_{11}$		Diethyl, $R_1 = R_2 = \text{C}_6\text{H}_{13}$	
Tri(2-methylbutyl), $R_1 = R_2 = R_3 = \text{CH}_2(\text{CHCH}_3)\text{CH}_2\text{CH}_3$		Dioctyl, $R_1 = R_2 = \text{C}_8\text{H}_{17}$	
Tri- <i>s</i> -amyl, $R_1 = R_2 = R_3 = s\text{-C}_5\text{H}_{11}$		Phosphinates
Diethyl butyl, $R_1 = R_2 = \text{C}_2\text{H}_5, R_3 = \text{C}_4\text{H}_9$			
Diethyl <i>i</i> -butyl, $R_1 = R_2 = \text{C}_2\text{H}_5, R_3 = i\text{-C}_4\text{H}_9$			
Diethyl amyl, $R_1 = R_2 = \text{C}_2\text{H}_5, R_3 = \text{C}_5\text{H}_{11}$			
Dibutyl methyl, $R_1 = R_2 = \text{C}_4\text{H}_9, R_3 = \text{CH}_3$			
Dibutyl ethyl, $R_1 = R_2 = \text{C}_4\text{H}_9, R_3 = \text{C}_2\text{H}_5$			
Tri(2-chloroethyl), $R_1 = R_2 = R_3 = \text{ClCH}_2\text{CH}_2$		Ethyl dibutyl, $R_1 = R_2 = \text{C}_4\text{H}_9, R_3 = \text{C}_2\text{H}_5$	
Phosphonates		Butyl dibutyl, $R_1 = R_2 = R_3 = \text{C}_4\text{H}_9$	
		Trialkyl phosphine oxides
Dimethyl methyl, $R_1 = R_2 = R_3 = \text{CH}_3$			
Dimethyl propyl, $R_1 = \text{C}_3\text{H}_7, R_2 = R_3 = \text{CH}_3$		Tributyl, $R_1 = R_2 = R_3 = \text{C}_4\text{H}_9$	
Diethyl hexyl, $R_1 = \text{C}_6\text{H}_{13}, R_2 = R_3 = \text{C}_2\text{H}_5$		Trioctyl, $R_1 = R_2 = R_3 = \text{C}_8\text{H}_{17}$	
Dibutyl methyl, $R_1 = \text{CH}_3, R_2 = R_3 = \text{C}_4\text{H}_9$		Tri(2-ethylhexyl), $R_1 = R_2 = R_3 = \text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$	
Dibutyl ethyl, $R_1 = \text{C}_2\text{H}_5, R_2 = R_3 = \text{C}_4\text{H}_9$			
Dibutyl butyl, $R_1 = \text{C}_4\text{H}_9, R_2 = R_3 = \text{C}_4\text{H}_9$			
Dibutyl hexyl, $R_1 = \text{C}_6\text{H}_{13}, R_2 = R_3 = \text{C}_4\text{H}_9$			
Di- <i>i</i> -amyl methyl, $R_1 = \text{CH}_3, R_2 = R_3 = i\text{-C}_5\text{H}_{11}$			

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