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Abstract

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CORRELATION OF THE EXTRACTION ABILITY OF ORGANOPHOSPHORUS EXTRACTANTS WITH THE σ CONSTANTS OF SUBSTITUENTS AT THE PHOSPHORUS ATOM

Already in the first reports on the study of organophosphorus extractants (see, for example, ([1–3])) it was noted that their extraction ability depends strongly on structure. It may be considered that, qualitatively, this dependence has been established and that the extraction mechanism is more or less clear ([1–18]).

A number of attempts are known to relate the extraction properties of organophosphorus compounds to parameters characterizing the electronegativity of substituents at the phosphorus atom, or the polarity of the phosphoryl group, or of the molecule as a whole ([2,4,6,8,11]). We note that in all cases no general quantitative regularities were found, and the comparisons were mainly qualitative in character.

In 1964 Rozen and Nikolotova ([19]) used, as a characteristic of the electronic influence of substituents, the electronegativity of radicals. To find these quantities, a linear dependence between the frequencies of P = O vibrations and the electronegativity of atoms bonded to phosphorus was used. On this basis an equation was proposed relating extraction ability to the electronegativities of groups and to steric factors. In 1964 Kucha applied the principle of the linear dependence of free energies to find a quantitative regularity between the extraction ability of organophosphorus compounds and their structure ([20]), using the extraction of plutonium nitrates as an example.

In connection with the appearance of Kucha's work ([20]), we publish some preliminary results on the correlation of the extraction ability of neutral organophosphorus extractants with their structure. In contrast to Kucha, to characterize the influence of substituents we used the constants σ, derived by one of us in 1956 from the ionization constants of phosphorus acids by means of the Ham-

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Fig. 1

Figure 1: Fig. 1

mett equation ([21]). These substituent constants have previously been used in the study of equilibria and kinetics of various reactions of organophosphorus compounds ([21–26]) and have comparatively broad limits of applicability in the field of organophosphorus chemistry. It could be assumed that the extraction ability of organophosphorus extractants would depend linearly on the sum of the constants σ of the substituents at the phosphorus atom. As a characteristic of the extraction ability of the extractants, the effective extraction constants (solvent–benzene) of uranyl nitrate were chosen; these were determined by us for a series of organophosphorus compounds.*

* The effective extraction constants were calculated by the formula:

$$\bar{K} = \frac{Y}{4X^3\gamma_{\pm}^3 \pm [T_0 - 2Y]^2},$$

where Y and X are the equilibrium concentrations of uranyl nitrate in the organic and aqueous (neutral) phases, $\gamma_{\pm}$ is the activity coefficient of uranyl nitrate ions in the aqueous solution, and T_0 is the initial concentration of the extractant in benzene.

comparison of the logarithms of the effective extraction constants found with the sums of the constants σ showed the existence between them of a linear dependence with a correlation coefficient of 0.994 (see Fig. 1, straight line I).

$$\lg \overline{K} = (-0.68 - 2.36\Sigma\sigma) \pm 0.26.$$

A linear dependence is also observed for the effective extraction constants of uranyl nitrate when carbon tetrachloride is used as the solvent for the extractants ([27]) (see Fig. 1, straight line II), as well as in the case of the stability constants of complex compounds of uranyl nitrate with certain organophosphorus compounds ([12,13]) (see Fig. 1, straight line III).

Fig. 1. Dependences of the logarithms of the effective extraction constants of uranyl nitrate by organophosphorus extractants (see notes to Table 1) in benzene and CCl_4 ([27]) (I, II) and the analogous dependence for the stability constants ([13,14]) of uranyl nitrate complexes with organophosphorus compounds* (III) on the sums of the constants σ of substituents at the phosphorus atom.

Of great interest is the correlation of the constants σ with distribution coefficients–the usual and well-studied characteristic of the effectiveness of extractants. We processed our own experimental results and literature data on the extraction of uranyl nitrate and plutonium nitrate (tetravalent and hexavalent) by organophosphorus compounds under various conditions. Approximately 30

extractants were included in the treatment, for which it was possible to compare distribution coefficients with the sums of substituent constants. In contrast to Kuchi ([20]), who used only data on the extraction of plutonium nitrate from dilute nitric acid solutions (fulfillment of the condition for applicability of the Hammett equation to distribution coefficients: [M] $\ll$ [S] and [NO_3]), we treated, by the least-squares method, data on extraction both from dilute and from more concentrated acid and neutral solutions. It turned out that between the logarithms of the distribution coefficients and the sums of the constants σ of substituents at the phosphorus atom there is a linear dependence (see Table 1), obeyed by phosphoric acid esters, mono- and dialkylphosphinic acids, trialkylphosphine oxides, and also dialkyl phosphites.

It should be noted that the distribution coefficients in extraction from neutral and moderately acid solutions (initial concentration HNO_3 1–2 mol/l) satisfy the linear dependence found better. A consistent decrease in the correlation coefficients is observed with increasing nitric acid concentration in the system (see Table 1, Nos. 12–18). Possibly this is associated with a change in the extraction mechanism as the acidity of the system increases ([28]) or with a leveling of the effectiveness of the extractants in strongly acid media, as is especially clearly indicated by the decrease in the tangent of the slope angle of the straight line (ρ).

The question of the applicability of the Hammett equation to distribution coefficients for extractants containing branched radicals requires further clarification. In general, compounds containing isopropyl and isobutyl radicals in the ester groups or at the phosphorus atom satisfactorily obey the linear dependence. For example, in the case of uranyl nitrate extraction, the only exception is triiso-

* In the case of tributyl phosphate and tributylphosphine oxide, the data given are accurate only within the order of magnitude ([13,14]).

Table 1

Correlation of the distribution coefficients (K_p) of a series of actinides for organophosphorus extractants with the values $\Sigma\sigma$ of substituents at the phosphorus atom

$$\lg K_p = (\lg K_p)_0 + \rho\Sigma\sigma$$

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No.	Extracted salt	Initial concentration: salt	Initial concentration: HNO_3, mol/l	Extractant concentration, mol/l	Solvent	$(\lg K_p)_0$	ρ	Correlation coefficient	Mean deviation from slope δ	Number of extractants n	Extractant Nos.*	Source
1	$UO_2(NO_3)_2$	0.01 mol/l	0.0	0.3	C_6H_6	−2.16	−1.06	0.973	0.23	12	2, 3, 4, 7, 8, 9, 10, 11, 13, 18, 23, 30	Present work
2	$UO_2(NO_3)_2$	0.01	2.0	0.3	»	−0.51	−0.96	0.968	0.22	15	2–11, 13, 18, 23, 27, 30	Same
3	$UO_2(NO_3)_2$	0.01	4.0	0.3	»	−0.04	−0.73	0.976	0.16	13	2–9, 11, 18, 23, 27, 30	»
4	$UO_2(NO_3)_2$	0.01	6.0	0.3	»	+0.10	−0.61	0.968	0.14	15	2–11, 13, 18, 23, 27, 30	»

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No.	Extracted salt	Initial concentration: salt	Initial concentration: HNO_3, mol/l	Extractant concentration, mol/l	Solvent	$(\lg K_p)_0$	ρ	Correlation coefficient	Mean deviation from slope δ	Number of extractants n	Extractant Nos.*	Source
5	$UO_2(NO_3)_2$	8.0	0.3	»	+0.10	−0.48	0.907	0.14	15	2–11, 13, 18, 23, 27, 30	»	
6	$UO_2(NO_3)_2$	maximum values K_p	0.3	»	−0.12	−0.81	0.975	0.18	13	2–9, 11, 18, 23, 27, 30	»	
7	$UO_2(NO_3)_2$	50 g/l	0.5	CCl_4	−1.62	−1.32	0.987	0.17	15	2, 9–15, 17, 18, 20, 21, 25, 29, 31	2, 9–15, 18, 20, 25, 31	(7, 9)
8	$UO_2(NO_3)_2$	50	1.0	0.5	»	−1.11	−1.21	0.981	0.19	12	2, 9–15, 18, 20, 25, 31	(7, 9)

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No.	Extracted salt	Initial concentration: salt	Initial concentration: HNO_3, mol/l	Extractant concentration, mol/l	Solvent	$(\lg K_p)_0$	ρ	Correlation coefficient	Mean deviation from slope δ	Number of extractants n	Extractant Nos.*	Source
9	$UO_2(NO_3)_2$	2.0	0.5	»	−0.96	−1.42	0.961	0.21	14	9-15, 17, 18, 20, 21, 25, 29, 31	[7, 9]	
10	$UO_2(NO_3)_2$	0.0 mol/l	0.5	»	−1.58	−0.80	0.976	0.17	13	2, 4, 6, 7, 9, 11, 13, 18, 21, 22, 24, 28, 29	[2]	
11	$UO_2(NO_3)_2$	$5.4 \cdot 10^{-4}$ mol/l	0.19	C_6H_6	−1.89	−1.30	0.986	0.29	6	2, 4, 9, 18, 25, 29	[3]	
12	$UO_2(NO_3)_2$	1.01 mol/l	0.732	CCl_4	−0.39	−0.89	0.970	0.26	8	2, 4, 16, 18, 23, 25, 26, 30	[11]	

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No.	Extractant salt	Initial concentration: salt	Initial concentration: HNO_3, mol/l	Extractant concentration, mol/l	Solvent	$(\lg K_p)_0$	ρ	Correlation coefficient	Mean deviation from slope δ	Number of extractants n	Extractant Nos.*	Source
13	$UO_2(NO_3)_2$	3.0	0.732	»	0.74	−0.56	0.924	0.27	8	2, 4, 16, 18, 23, 25, 26, 30		[11]
14	$UO_2(NO_3)_2$	5.0	0.732	»	1.06	−0.41	0.885	0.26	8	2, 4, 16, 18, 23, 25, 26, 30		[11]
15	$UO_2(NO_3)_2$	6.0	0.732	»	1.16	−0.31	0.836	0.24	8	2, 4, 16, 18, 23, 25, 26, 30		[11]
16	$UO_2(NO_3)_2$	8.0	0.732	»	1.00	−0.28	0.795	0.24	8	2, 4, 16, 18, 23, 25, 26, 30		[11]

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No.	Extracted salt	Initial concentration: salt	Initial concentration: HNO_3, mol/l	Extractant concentration, mol/l	Solvent	$(\lg K_p)_0$	ρ	Correlation coefficient	Mean deviation from slope δ	Number of extractants n	Extractant Nos.*	Source
17	$UO_2(NO_3)_2$	10.0	0.732	»		0.84	−0.18	0.643	0.26	8	2, 4, 16, 18, 23, 25, 26, 30	[11]
18	$UO_2(NO_3)_2$	12.0	0.732	»		0.70	−0.14	0.549	0.25	8	2, 4, 16, 18, 23, 25, 26, 30	[11]
19	$UO_2(NO_3)_2$	maximum values K_p	0.732	»		1.00	−0.49	0.932	0.22	8	2, 4, 16, 18, 23, 25, 26, 30	[11]
20	$Pu(NO_3)_4$	0.5 g/l	0.5		CCl_4	−1.61	−1.11	0.936	0.32	14	2, 9–15, 17, 18, 20, 21, 29, 31	[7, 9]

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No.	Extracted salt	Initial concentration: salt	Initial concentration: HNO_3, mol/l	Extractant concentration, mol/l	Solvent	$(\lg K_p)_0$	ρ	Correlation coefficient	Mean deviation from slope δ	Number of extractants n	Extractant Nos.*	Source
21	$Pu(NO_3)_4$	1.0	0.5	»	−0.89	−0.94	0.921	0.32	11	2, 9–15, 18, 20, 31		(7, 9)
22	$Pu(NO_3)_4$	2.0	0.5	»	0.64	−0.27	0.706	0.27	14	1, 2, 9–15, 18, 21, 25, 29, 31		(7, 9)
23	$Pu(NO_3)_4$	2.0	0.5	CCl_4	−1.24	−1.29	0.966	0.29	5	4, 10, 13, 18, 22		(2)
24	$Pu(NO_3)_3$	2.0	0.5	»	−1.26	−1.20	0.970	0.26	5	4, 10, 13, 18, 22		(2)

* **Extractants used:**
1) (iso-$C_4H_9)_3PO$,
2) (n-$C_4H_9)_3PO$,
3) (iso-$C_4H_9)_2P(O)OC_4H_9$-n,
4) (n-$C_4H_9)_2P(O)OC_4H_9$-n,
5) (n-$C_4H_9)_2P(O)OC_3H_7$-n,
6) (n-$C_4H_9)_2P(O)OC_2H_5$,
7) (n-$C_4H_9)_2P(O)OCH_3$,
8) iso-$C_4H_9P(O)(OC_4H_9$-$n)_2$,
9) n-$C_4H_9P(O)(OC_4H_9$-$n)_2$,
10) n-$C_3H_7P(O)(OC_4H_9$-$n)_2$,

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11) $C_2H_5P(O)(OC_4H_9\text{-}n)_2$,
12) $n\text{-}C_4H_9P(O)(OC_4H_9\text{-iso})_2$,
13) $CH_3P(O)(OC_4H_9\text{-}n)_2$,
14) $n\text{-}C_3H_7P(O)(OC_4H_9\text{-iso})_2$,
15) $C_2H_5P(O)(OC_4H_9\text{-iso})_2$,
16) $n\text{-}C_4H_9P(O)(OC_2H_5)_2$,
17) $CH_3P(O)(OC_4H_9\text{-iso})_2$,
18) $(n\text{-}C_4H_9O)_3PO$,
19) $(n\text{-}C_4H_9O)_2P(O)OC_3H_7\text{-}n$,
20) $(n\text{-}C_4H_9O)_2P(O)OC_4H_9\text{-iso}$,
21) $(n\text{-}C_4H_9O)_2P(O)OCH_3$,
22) $(n\text{-}C_4H_9O)_2P(O)OCH_3$,
23) $(n\text{-}C_3H_7O)_3PO$,
24) $C_8H_5P(O)(OC_2H_5)_2$,
25) $(\text{iso-}C_4H_9O)_3PO$,
26) $(\text{iso-}C_3H_7O)_3PO$,
27) $ClCH_2P(O)(OC_4H_9\text{-}n)_2$,
28) $n\text{-}C_4H_9OP(O)(OC_2H_5)_2$,
29) $(n\text{-}C_4H_9O)_2PHO$,
30) $(C_2H_5O)_3PO$,
31) $(\text{iso-}C_4H_9O)_2PHO$.

tributylphosphine ([7], [9]), for which a sharp deviation is observed, probably associated with shielding of the phosphoryl group by isobutyl radicals, which leads to a decrease in the distribution coefficients. In the case of extraction of plutonium nitrate, along with triisobutylphosphine oxide, triisobutyl phosphate also drops out; moreover, this deviation cannot be explained by steric shielding of the phosphoryl group, since it would lead to a decrease, and not to an increase, in the distribution coefficient. The linear dependences without taking these two points into account have satisfactory correlation coefficients (equations Nos. 20, 21).

It should be noted that the maximum values of the distribution coefficients for each extractant also obey a linear dependence (the maximum on the curve K_p –initial HNO_3 concentration) (see equations Nos. 6, 19).

The question of a theoretical justification for the applicability of the Hammett equation to distribution coefficients in extraction from undiluted solutions remains open for the time being. The condition for the applicability of correlation equations to distribution coefficients given by Kuča (20) is probably not always necessary. It does not take into account all factors of the extraction process, in particular extraction of nitric acid by the extractant and other factors.

The overall distribution coefficients determined in extraction experiments are a function of several variables. These include the constants of complex formation, salt formation (in acidic media), hydration constants, and the partial distribution coefficients of the substances participating in the equilibrium. If the constants of complex and salt formation and the hydration constants must

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obey the Hammett equation, the applicability of the latter to partial distribution coefficients is not obvious. From the fact that the logarithms of the overall distribution coefficients depend linearly on the sum of the substituent constants σ, it follows that the partial distribution coefficients in the cases considered also obey the Hammett equation.

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