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Dependence of the extraction ability of organic compounds on their structure

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Contents

I.	Introduction	973
II.	Monodentate neutral organophosphorus compounds	974
III.	Organic sulfoxides	976
IV.	Variation of extraction ability and the complex formation mechanism as the reaction centre is varied and the basicity of the extractants increases	977
V.	Characteristic features of extraction by amine and arsine oxides	979
VI.	Salts of amines and quaternary onium bases	979
VII.	The influence of the length and degree of branching of substituents on the extraction ability of organic compounds	980
VIII.	The use of quantum-chemical calculations for predicting extraction ability	982
IX.	Bidentate neutral organophosphorus compounds and the anomalous aryl stabilisation effect	984
X.	Polydentate neutral extractants — crown-ethers	989
XI.	Organic acids	991
XII.	Organic acid salts	994
XIII.	The influence of diluents on the extraction ability of organic compounds	995
XIV.	Examples of the development of new extractants	996

Abstract. Data on the dependence of the extraction ability of the principal classes of organic compounds on their structure are surveyed. Mono- and bi-dentate neutral organophosphorus compounds (NOPC), sulfoxides, amines, quaternary ammonium, arsonium, and phosphonium bases, amine and arsine oxides, organophosphorus acids and their salts, and crown-ethers are examined. It is shown that the extraction ability of the NOPC in relation to any metal increases with increase in the basicity of the extractant and diminishes when electronegative substituents are introduced into its molecule. With increase in the basicity of neutral extractants, qualitative changes in the complex formation mechanisms are observed. The influence of diluents on the extraction ability of organic compounds is analysed. Methods for predicting extraction ability are considered. Examples of the use of the above rules for the development of new extractants are presented. The bibliography includes 157 references.

I. Introduction

The search for highly effective extractants is an important scientific and practical problem. The understanding of the dependence of the extraction ability (EA) of organic compounds on their structure has played the role of a compass in this search.

Such a dependence is of interest also when the general problem of the reactivity of compounds is considered.

The extraction of metal salts and acids is based on the chemical interaction (complex formation) of these substances with the extractant and may be regarded as a heterogeneous chemical reaction. The effective extraction constant K_{ex} (the abbreviated term describing the equilibrium constant of the extraction reaction) is a quantitative characteristic of the extraction ability. For example, for the reaction

$$UO_2^{2+} + 2NO_3^- + 2TBP = UO_2(NO_3)_2(TBP)_2,$$

where TBP = tributyl phosphate, K_{ex} is determined from the Law of Mass Action taking into account the activity coefficients of the extracted compound in the aqueous phase ($\gamma_\pm$):

$$K_{ex} = \frac{\tilde{K}_{ex}}{\gamma_\pm^\nu},$$

$$\tilde{K}_{ex} = \frac{[UO_2(NO_3)_2(TBP)_2]}{[UO_2^{2+}][NO_3^-]^2[TBP]^2},$$

where $\tilde{K}_{ex}$ is the concentration extraction constant and ν the number of ions into which the metal salt dissociates in the aqueous phase ($\nu = 3$). The distribution coefficient (D) can be used as the characteristic of the EA, but only when the compounds present in the aqueous phase at macroconcentrations are not extracted. Otherwise, the changes in D when the structure is varied can reflect not only the changes in the EA of the extractant but also the changes in the concentration of the free extractant.† If the salt extracted from the aqueous phase is the same, the changes in the extraction constant when the structure of the extractant is varied reflect the changes in the constant for the complex formation

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† This happened, for example, in a pioneer study where an apparent linear correlation between the distribution coefficients of uranyl nitrate in extraction from nitric acid solutions by a series of NOPC and the P=O bond vibrational frequency was obtained solely due to experimental errors, which were discovered when the results of the above study [1] were compared with more accurate data.[2] In addition, the extraction constant is much more informative than the distribution coefficient: knowing $\tilde{K}_{ex}$, it is possible to reproduce the extraction isotherm and to find the dependence of D on the process conditions.

reaction between the salt and the extractant. Admittedly in the traditional approach to the description of extraction (see, for example, Sekine[3]) this is not quite correct. In this approach, the transfer of the extractant to the aqueous phase is considered as the first stage of the process, the formation of a complex with a metal or an exchange reaction with the latter in the aqueous phase is the second stage (or the third, if the extractant dissociated in the aqueous phase), while the transfer of the compound formed from the aqueous phase to the organic phase is considered to be the last stage. Under these conditions, the extraction constant is related in a complex manner to the complex formation constant in the aqueous phase β_{aq} and also depends on the distribution constants of the extractant and the complex, the last being usually unknown.

This approach arose in the initial period of the use of extraction when water-soluble extractants were employed (especially in analytical chemistry). However, extractants which are sparingly soluble in the aqueous phase are usually employed nowadays. The approach based on the consideration of complex formation in the organic phase[4] is therefore more useful.

For neutral sparingly soluble extractants, the Gibbs free energy of extraction ΔG_{ex} represents the difference between the Gibbs free enrgies of the solvation and hydration processes:[5,6]

$$\Delta G_{ex} = \Delta G_{solv} - \Delta G_{hydr}, \quad (1)$$

and since $\Delta G_{ex} = -RT\ln K_{ex}$ and $\Delta G_{solv} = -RT\ln\beta_{org}$, where β_{org} is the complex formation constant in the organic phase, we find

$$K_{ex} = \beta_{org} \exp \frac{\Delta G_{hydr}}{RT}, \quad (2)$$

i.e. K_{ex} is proportional to the complex formation constant in the organic phase β_{org} and characterises the stability of the complex.

The thermodynamic parameters of the hydration of many metals have been published[5-8] and most fully in the last of the studies quoted (examples are presented in Table 1). Evidently the hydration energies increase when the nitrate ion is replaced by the chloride ion, and with increase in the charge and with decrease in the radius of the cation. Extraction becomes correspondingly more difficult. For extraction to be effective (K_{ex} of the order of unity), it is necessary to compensate for the hydration energy, i.e. the complex formation energy in the organic phase must be of the same order as G_{hydr}. In principle, such complex formation energies may be attained if the process proceeds via an electron donor–acceptor (EDA) mechanism. However, for the extraction of alkaline eartth elements, a high electron-donating capacity of the extractants is necessary and for $AlCl_3$ it is altogether impossible to select effective extractants. To a certain extent, it is possible to obviate the difficulties associated with hydration by choosing salts with a reduced hydration of the anion; it is also possible to extract the ion with its hydration shell (the hydrate–solvate extraction mechanism[9]).

On the other hand, the most effective procedure involves the transition from the solvate to the cation-exchange mechanism of extraction:

$$M^{z+} + zA^- + z(HY)_2 = M(HY_2)_z + z(H^+ + A^-), \quad (3)$$

where HY is an organic acid. In the aqueous phase, the salt molecule MA_z is replaced by z molecules of the inorganic acid HA. Depending on the sign of the transhydration energy,

$$\Delta\Delta G_{hydr} = z\Delta G_{hydr}(HA) - \Delta G_{hydr}(MA_z)$$

it is actually possible to achieve a gain in extraction energy, which intensifies extraction.

The most correct method for predicting EA is the quantum-chemical calculation of the complex formation energy with subsequent determination of the partition functions and entropies of the components.‡ Unfortunately, this approach is possible only in a semiempirical approximation for inorganic acids or organic compounds.[10,11] In most cases, especially for *d* and *f* elements, the direct (especially nonempirical) quantum-chemical calculation for extraction complexes is impossible. Therefore, correlations between the extraction constant and various characteristics of the extractant associated with its reactivity are widely used for predicting EA. The following are usually employed: (1) the characteristics of the structural groups, for example the electronegativities of the groups in substituents,[12] the reaction constants of these groups [the Taft (σ^*)[18] and Kabachnik (σ^p)[13,14] constants] on the assumption that the influence of these groups is additive: (2) the characteristics of an isolated extractant molecule as a whole — the electron density (charge) on the functional atom, the ionisation potential[15], and the energy of the core 1*s* levels;[16] (3) the characteristics of the reactivity of the molecule as a whole — basicity, determined experimentally from the energies of test reactions with simplest electron acceptors[17-21] or by quantum-chemical calculations of the energies of complex formation with a proton [proton affinities (PA)], Li^+, LiH, etc.[16,22]

The dependences of EA on the structure of the extractants and the possibility of predicting it on the basis of various correlations are analysed in the present review. The dependences were established mainly in relation to the extraction of the actinides, but are nevertheless of a general character.§

II. Monodentate neutral organophosphorus compounds

At the time of the publication of the first studies on extraction using alcohols, ethers, and ketones, the chemical nature of the process was still obscure. Owing to the low EA of the reagent, the extraction isotherms obtained in these investigations did not in the main have a saturation section characteristic of the formation of compounds (Fig. 1, curves *1* and *2*). The relation between extraction ability and structure was not traced and it was only noted that EA diminishes with increase in the C/O ratio, i.e. as the hydrocarbon chain is lengthened.[23,24] The introduction of tributyl phosphate in the 1950s[25-30] led to revolutionary changes both in the technology (EA increased by 5–6 orders of magnitude and it became possible to extract uranyl and plutonium nitrates without employing salting-out agents) and in the theory of the processes [a saturation section, frequently indicating the formation of compounds (Fig. 1, curves *3* and *4*), appeared on the extraction isotherms].[30]

Table 1. The Gibbs free energies and enthalpies of hydration of salts of metals (kcal mol^{-1}).

Compound	$-\Delta G_{hydr}$	$-\Delta H_{hydr}$	Compound	$-\Delta G_{hydr}$	$-\Delta H_{hydr}$
HCl	10.7	14.8	$ThCl_4$	–	56.7
NaCl	2.1	−0.9	HNO_3	7.3	7.95
$MgCl_2$	30.3	37.2	$NaNO_3$	1.5	−4.9
$CaCl_2$	15.5	19.8	$Mg(NO_3)_2$	21.2	21.8
$LaCl_3$	21.0	33	$Ca(NO_3)_2$	12.8	4.5
$AlCl_3$	61.1	78.1	$LiNO_3$	5.6	0.6
UO_2Cl_2	16.4	28.1	$UO_2(NO_3)_2$	6.1	20.3

‡ Strictly speaking, a calculation taking into account the influence of the solvent is necessary. However, it has been established in a number of studies that a weakly polar solvent exerts a comparatively weak influence on the complex formation and extraction energies which is due to the compensation of diluent–extractant and diluent–extracted complex interactions (see below).

§ The review is based largely on the results of studies carried out under the supervision of A M Rozen during the last 30 years. Z I Nikolotova, N A Kartasheva, E I Moiseenko, Z I Nagnibeda, Yu I Murinov, B V Martynov, A S Skotnikov, L P Kharkhorina, V G Yurkin, and B V Krupnov participated actively in these investigations. Studies by other workers are naturally also discussed.

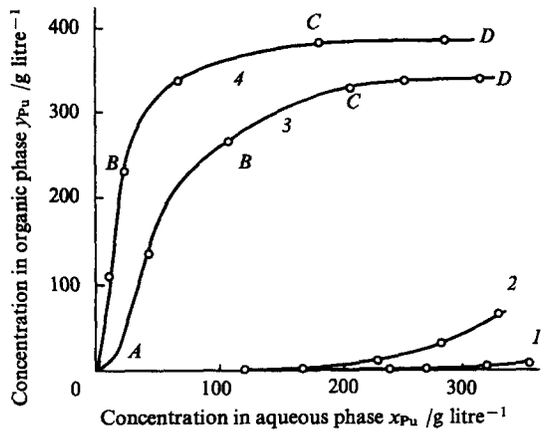


Figure 1. Isotherms for the extraction of Pu(IV) by neutral organic compounds (x_H = 0.1 M).
Extractant: (*1*) dibutyl ether (DBE); (*2*) diethyl ether (DEE); (3) TBP; (4) diisopentyl methylphosphonate (DPMP); *AB* — initial section of the isotherm determined by dissociation into ions; *BC* — section corresponding to moderate nonideality; *CD* — saturation section.

Neutral organophosphorus compounds are the first class of compounds for which the dependence of EA on the structure has been studied systematically. For phosphates, phosphonates, phosphinates, and phosphine oxides, the reaction centre (RC) is the PO group and the composition of the complexes remains unchanged (for example, the disolvates of tetravalent and hexavalent actinides, the trisolvates of trivalent actinides and lanthanides), while extraction ability increases appreciably. A correlation has been proposed[12] between $\ln K_{ex}$ for uranyl nitrate and nitric acid, on the one hand, and the sums of the electronegativities of the groups of the substituents (X) in the above series:

$$\ln K_{ex} = A - B\Sigma X - \rho\Sigma l, \qquad (4)$$

where A is a constant which depends on the reaction series (the class of the extractant and the individuality of the compound extracted), B is the coefficient of the sensitivity to electronegativity, ρ the coefficient of the sensitivity to the length of the hydrocarbon chain, l the effective length of the hydrocarbon chain of the substituent (in the case of normal groups, $l = n_C$), and the values of X are determined from the spectral scale (Table 2).

The following considerations also lead to Eqn (4).[31] On the one hand, since the complexes are formed via an EDA mechanism, one can suppose that EA is greater the greater the electron density on the donor atom. Rozen and Denisov[31] put forward more logical considerations,which may make it possible to estimate the coefficient B:

Table 2. The electronegativities and Taft constants for certain substituents.[6,12]

Substituent	X	σ^*
F	4.0	–
Cl	3.0	–
CCl_3	2.95	2.65
$ClCH_2$	2.60	1.05
$Cl(CH_2)_2$	2.32	–
C_6H_5	2.34	0.6
CH_3	2.07	0.0
Alk	2.0	−0.13
RO	2.9, 2.4[a]	1.50, 0.75[a]
H	2.3	0.49

[a] Effective values.

$$\ln K_{ex} = a + b|q|,$$

where a and b are constants and q is the charge. On the other hand, according to the results of approximate quantum-chemical calculations,[32,33]

$$|q| = a'' - b''\Sigma X,$$

where a'' and b'' are constants. When account is taken of these relations, Eqn (4) is obtained. When calculations are made relative to a standard compound, Eqn (4) leads to the Hammett–Taft equation.[14]

$$\ln\frac{K_{ex}}{K_0} = -B\sum_X(X - X_0) - \rho\sum_X(l - l_0) = r^*\Sigma\sigma^* + d\Sigma E_s. \qquad (5)$$

Here the subscript 0 refers to the characteristics of the standard state, r^* and d are coefficients, and E_s is the steric hindrance constant.

In fact it has been found[14] that $X = 2.07 + \sigma^*/2$, i.e. the Taft constants represent relative electronegativities.

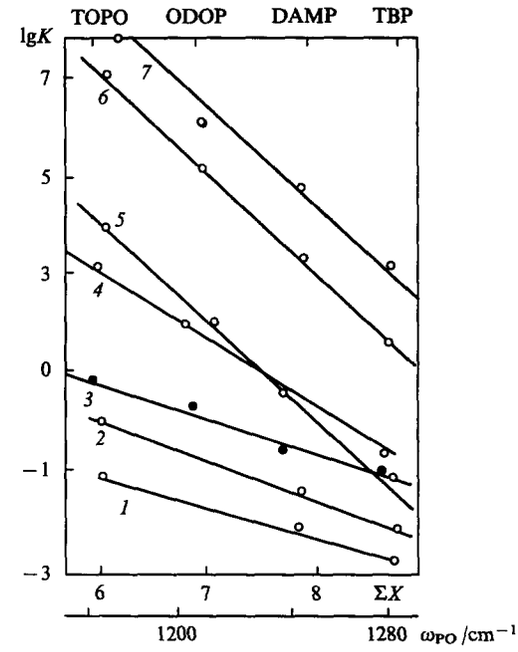


Figure 2. Dependence of EA on the sum of the electronegativities of the substituents (ΣX) and the stretching vibrational frequencies (ω_{PO}) in the extraction of certain compounds by monodentate NOPC.
Compound extracted: (*1*) manganese nitrate; (*2*) potassium permanganate; (*3*) nitric acid; (*4*) americium nitrate; (*5*) uranyl chloride; (*6*) uranyl nitrate; (*7*) plutonium nitrate. ODOP = octyl dioctylphosphinate; TOPO = trioctylphosphine oxide.

The following conclusion follows from Eqn (4): the EA of monodentate NOPC decrease after the introduction of electronegative substituents. This conclusion is fairly general, being valid for any metals (Fig. 2). However, in order to obtain a general correlation when a wider class of NOPC, including the C_6H_5, CCl_3, $ClCH_2$, and $Cl(CH_2)_2$ groups, is considered (Fig. 3), Eqn (4) had to be refined.[12,34] Effective (reduced) electronegativities were introduced for the alkoxy-groups (X_{ef} = 2.4 and σ^*_{ef} = 0.75). The possible reason for this is that X and σ^* describe only the inductive effect, whereas for RO the resonance effect is also observed.¶

¶ One cannot rule out also the explanation based on the jump in entropy on passing from one subclass to another (for example, from phosphates to phosphonates).[14]

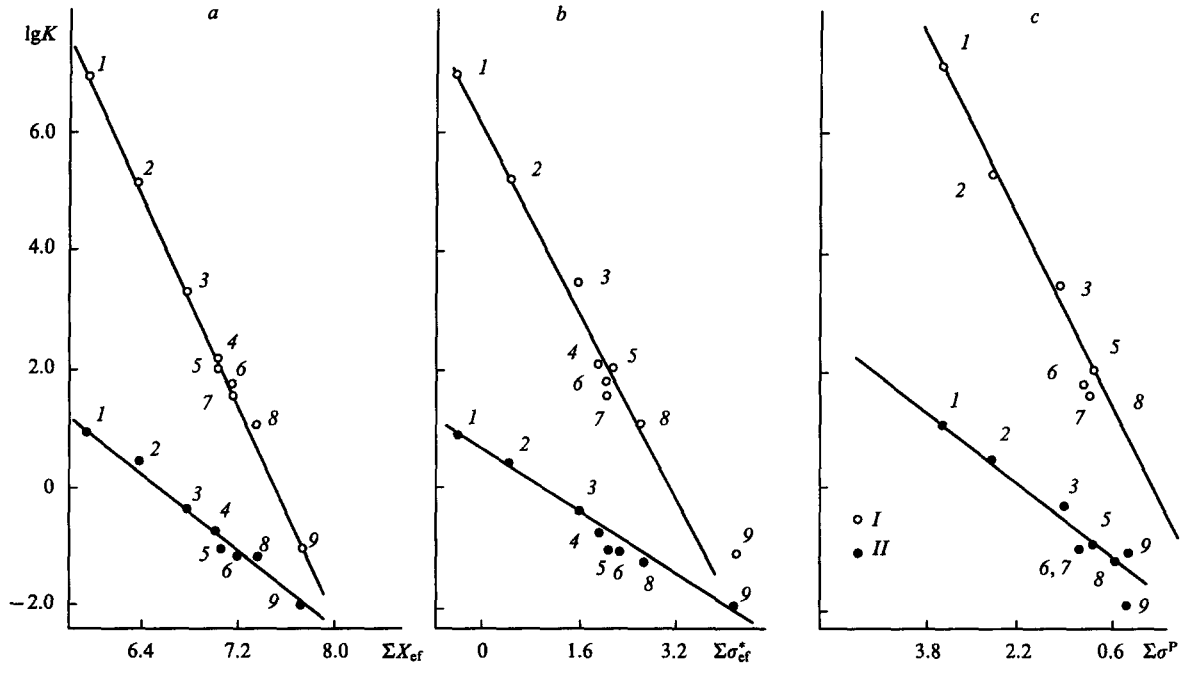


Figure 3. Dependence of the extraction ability of NOPC on the sum of the effective electronegativities (*a*), the effective Taft constants (*b*), and the Kabachnik constants (*c*) of the substituents.
Extractant: (*1*) TOPO; (*2*) ODOP; (*3*) DPMP; (*6*) TBP; (*7*) trioctyl phosphate; (*4*), (*5*), (*8*), and (*9*) (iso-$C_5H_{11}O)_2RPO$, R = C_6H_5 (*4*), $Cl(CH_2)_2$ (*5*), $ClCH_2$ (*8*), or CCl_3 (9); substance extracted: (*I*) $UO_2(NO_3)_2$; (*II*) HNO_3.

Instead of Eqn (4), one can write

$$\ln K_{ex} = A - B\Sigma X_{ef} - \rho\Sigma l = \quad (6)$$
$$= A - B\Sigma X + B'\Sigma\sigma_{res} - \rho\Sigma l,$$

where σ_{res} is the resonance interaction constant and $X_{ef} = X - \sigma_{res}B/B'$.

Eqn (6) is equivalent to the use of Kabachnik constants:

$$\lg\frac{K_{ex}}{K_0} = r^P\Sigma\sigma^P,$$

where $\sigma^P = \sigma^P_{ind} + \sigma^P_{res}$ is the Kabachnik constant taking into account the resonance effect, and including also the term $\rho\Sigma l/r^P$. The correlation with σ^P does not therefore require the introduction of effective quantities.

The advantage of electronegativity over the constants σ^* and σ^P is a more clear-cut physical significance. Electronegativities may be determined independently of any reactions. Unfortunately, there are no independent methods for the determination of σ^P_{res}. The energy of the 1*s* orbitals is an independent quantum-chemical parameter characterising the molecule as a whole and equivalent to ΣX_{ef}. The decrease in EA with increase in the electronegativities of the substituents is characteristic of any class of neutral compounds (the only exception, in the case of bidentate NOPC, is discussed below).

III. Organic sulfoxides

Systematic studies on extraction by sulfoxides (in which the reaction centre is the SO group) began and developed vigorously at the beginning of the 1970s. The research groups led by Rozen, Mikhailov, and Torgov published more than 20 papers. They have been reviewed by Nikitin et al.[35]

It was established that, in terms of their extraction ability, aliphatic sulfoxides approach phosphonates. Cyclic sulfoxides are obtained by oxidising petroleum sulfides. Their EA is higher by a factor of 2–3 (owing to the contribution by the entropy factor) than that of aliphatic sulfoxides. The dependence of EA on the structure of the sulfoxide is described by Eqns (4) and (5). The difference from NOPC consists in a higher sensitivity of EA to the influence of substituents (higher values of *B* in the above equations). Thus the replacement of a single alkyl group by the phenyl group in NOPC lowers the degree of extraction of uranium by a factor of 17, while in the case of sulfoxides the decrease is by a

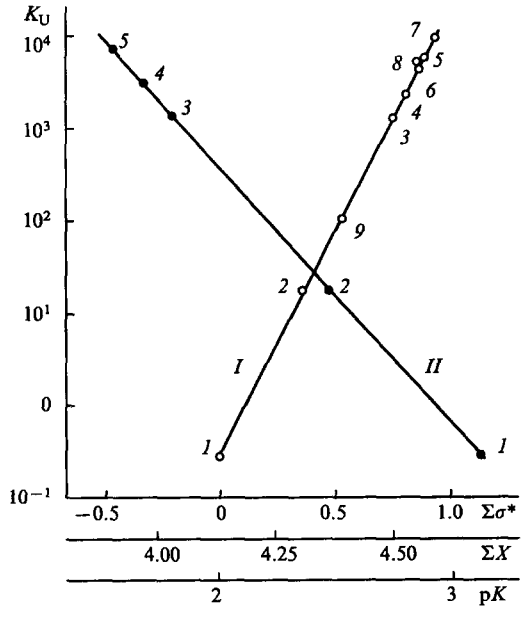


Figure 4. Dependence of the uranyl nitrate extraction constant on the basicity (*I*) and the sum of the electronegativities of the substituents or the Taft constants (*II*) of the extractants.
Extractant: (*1*) diphenyl sulfoxide; (*2*) hexyl phenyl sulfoxide; (*3*) dihexyl sulfoxide; (*4*) cyclohexyl hexyl sulfoxide; (*5*) hexyl tolyl sulfoxide; (*7*) 2-amyltetrahydrothiopyran sulfoxide; (*8*) DPMP; (*9*) TBP.

factor of 40. Fig. 4 presents the dependences of the extraction constant of uranyl nitrate (K_U) on the basicity and on the sum of the electronegativities or Taft constants of the sulfoxides.

IV. Variation of extraction ability and the complex formation mechanism as the reaction centre is varied and the basicity of the extractants increases

The dependence of extraction ability on the structure of organic compounds has also been investigated for carbonyl compounds and arsine and amine oxides (the reaction centres are the CO, AsO, and NO groups respectively). The extraction by compounds of this type is associated with the formation of electron donor–acceptor complexes, so that the more marked the electron-donating properties of the extractants (characterised by their basicity) the higher the EA. A linear correlation between $\ln K_{ex}$ and the basicity is frequently observed under these conditions [see, for example, Refs 34–37 (Fig. 5)]:

$$\ln K_{ex} = a + bpK. \quad (7)$$

We may note that the dependence of EA on the electronegativity of the substituents in the extracting molecule examined above is a special case of the dependence of EA on the basicity. It has been shown in relation to extraction by sulfoxides that the extraction of uranyl nitrate and the basicity of sulfoxides depend on the sum of the electronegativities of the substituents:

$$\ln K_{ex} = 3.04 - 5.23\Sigma(X - 2); \quad (8a)$$

$$pK = 2.67 - 0.94\,\Sigma(X - 2), \quad (8b)$$

which is equivalent to the dependence of the EA in relation to uranium on the basicity:

$$\ln K_{ex} = -11.38 + 5.6pK, \quad (8c)$$

i.e. Eqns (4) and (7) are equivalent for a class of extractants with a single reaction centre. Eqn (8b) implies that, when electronegative substituents are introduced into the extractant molecule, the electron-donating capacity of the latter (its basicity) diminishes and there is corresponding decrease also in the EA [Eqns (8a) and (8c)].

There exist several basicity scales which are determined experimentally [for example by titration with perchloric acid in nitromethane (pK),[17] by the reaction with pentachlorophenol,[8,19] and by the calorimetry of the interaction with antimony pentachloride (Gutmann donor numbers) and other Lewis acids].[20,21] In connection with the development of quantum chemistry and the ion cyclotron resonance spectroscopic methods, gas-phase basicity and proton affinity scales,[41,42] which are free from the influence of the solvent, are increasingly used at the present time.† Table 3 gives an idea about the above scales.

Table 3. Extractant basicity scales.

Compound	Proton affinity /kcal mol^{-1}	Donor number[43,44]	Energy of H bond with H_2O[45]	Taft–Rozen basicity[19] (C_6Cl_5OH)
ROH	189.0±1.5	18.0	–	–
R_2O	200.2	–		0.98
R_2CO	190.5	17.0	2.7	1.18
cyclo-C_6H_{11}	–	–		1.30
NR_2RCO	214.5	26.6; 27.8		–
$(NR_2)_2CO$	219.5	29.6		–
$(PhO)_3PO$	–	–		1.73
$(RO)_3PO$	217.0	23.7; 25.2	3.9; 4.0	2.56
$(RO)_2RPO$	–	31.2	4.0	2.74
$(RO)R_2PO$	–	32.0	4.8	–
R_3PO	224.5	33.8	5.0; 5.3	3.64
$(NR_2)_3PO$	229.5	38.6		–
R_2SO	–	29.8	4.4	2.58
R_3NO	238.0	–	6.9	–

† It has been shown[38,39] that considerable differences are observed between the proton basicities in the gas phase and in solution. At the same time, it has been found[40] that the differences between the energies of the complex formation reactions with metal salts in the gas phase and in weakly polar solvents are small.

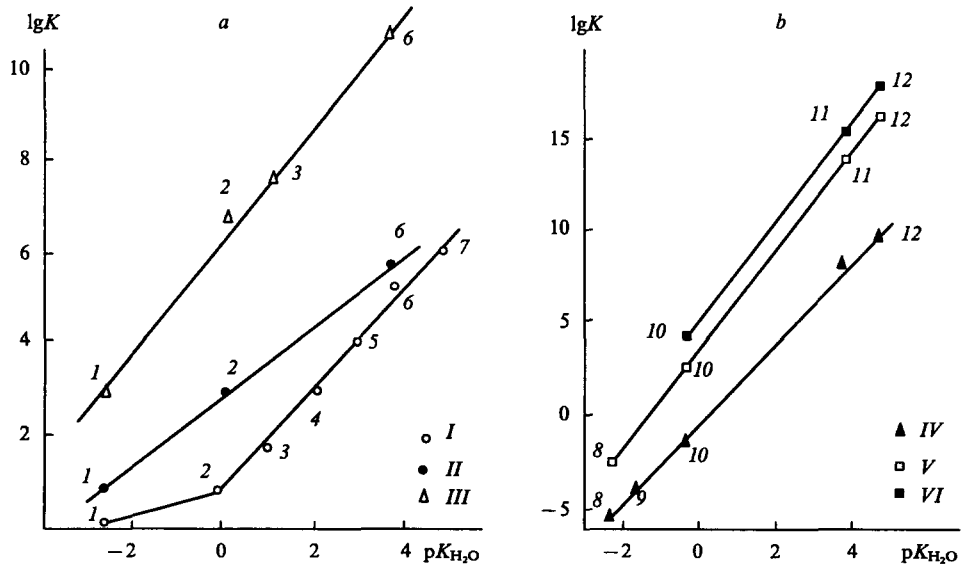


Figure 5. Dependence of the extraction constants of nitric acid (*I*), americium (*II*), and uranyl (*III*) nitrates (*a*) and of the monosolvates (*IV*) and disolvates (*V*) of perchloric and pertechnetic (*VI*) acids (*b*) on the basicity of neutral extractants.
Extractant: *a*: (*1*) Ph_3PO; (*2*) R_3PO; (*3*) Ph_3AsO; (*4*) Ph_2RAsO; (*5*) PhR_2AsO; (*6*) R_3AsO; (*7*) R_3NO; *b*; (*8*) TBP; (*9*) Ph_3PO; (*10*) TOPO; (*11*) R_3AsO; (*12*) R_3NO.

The above scales, based on allowance for the donor–acceptor interactions in solution, have a certain advantage in the prediction of complex formation constants in solutions. Here it is desirable that the nature of the interactions underlying the scale should not vary over the entire basicity range. This condition is not satisfied by the basicity scale based on the titration of the extractant with perchloric acid in nonaqueous media. Only the basicities of strong electron donors (ranging from R_3PO to R_3NO) have been determined by this procedure, while weak bases are not protonated under these conditions. Unfortunately the scales constructed using the interaction energy with weak proton donors (water or phenol) exhibit a low sensitivity to changes in the electron-donating capacities of the extractants. A more sensitive scale is based on the interaction energy with a stronger proton donor — pentachlorophenol. This scale has been used successfully in establishing correlations with EA for a wide range of extractants — from the weakest (alcohols, ethers, and ketones) to fairly strong (sulfoxides and NOPC).‡ The above condition is most readily fulfilled when the scale is constructed on the basis of the interaction with a metal salt. This is in fact the reason why the Gutmann donor number scale has come to be widely used.

With increase in the basicity of the extractant, not only is there an increase in the stability of the complex observed but the complex formation mechanism also changes. Thus in the extraction of nitric acid, the hydrate solvate mechanism [the coordination of an extractant molecule via a water molecule, for example $HNO_3 \cdot H_2O_2 \cdot (TBP)_2$] is readily replaced by the solvate mechanism (the formation of a molecular hydrogen-bonded complex with a direct bond between the donor atom of the extractant and the proton of the acid extracted, for example $TBP \cdot HNO_3$ and $TOPO \cdot HNO_3$). On further increase in basicity, complexes involving proton transfer are formed ($R_3XOH^+ \cdot NO^-$, where X = As or N).[34] A similar complex formation mechanism has been found also in the extraction of strong acids (HCl, H_3ClO_4, $HReO_4$, $HTcO_4$, etc.) with formation of both monocomplexes $[LH]^+A^-$ and dicomplexes $[LHL]^+A^-$.[46–48] The extraction constants for the latter are especially high (Table 4). The stronger the inorganic acid, the lower the basicity of the extractant for which the transition to the new mechanism takes place.

Table 4. The extraction constants of inorganic acids in the form of the proton-transfer complexes $[LH]^+A^-$ (K_1) and $[LHL]^+A^-$ (K_2).

Acid	Extractant			
	R_3AsO		R_3NO	
	K_1	K_2	K_1	K_2
HNO_3	–	–	8.0×10^7	4.0×10^{11}
HCl	–	–	5.0×10^5	3.0×10^7
$HReO_4$	1.0×10^{10}	4.8×10^{15}	3.6×10^{11}	7.2×10^{17}
$HTcO_4$	3.0×10^{10}	2.4×10^{16}	1.0×10^{12}	2.8×10^{18}

A change in the extraction mechanism leads to significant alterations of the extraction ability. The nature of the dependence of the degree of extraction of acids on the basicity of the extractant is then determined to a considerable degree by the strength of the acid being extracted. Torgov and Nikolaeva§ found that, in the extraction of weak acids (phenols, phosphoric or acetic acid), the extraction mechanism (the formation of a hydrogen bond) does not change over the entire range of basicities of the extractants and $\lg K_{ex}$ varies linearly with the donating capacity of the extractant. Amine oxides possess the highest extraction ability in relation to weak acids. It is of interest that amines are not included in these correlations: having a gas-phase proton affinity similar to that of amine oxides and a higher protonation energy in solution, amines form hydrogen-bonded complexes, the stability of which does not exceed that of complexes formed by phosphine oxides which are less basic in protonation reactions. Furthermore, amines extract weak acids with even lower distribution coefficients than phosphine oxides (for example 3.11 for the extraction of phenol with TOPO and only 1.23 for its extraction with trioctylamine); this may be associated with steric hindrance.

The dependences of $\ln K_{ex}$ on the basicity of the extractant for moderately strong acids (for example, nitric acid) have a break on passing from complexes with an intermolecular hydrogen bond to those involving proton transfer (Fig. 5).[36] Quantum-chemical calculations have shown[51] that this break is due to the increase in the sensitivity of the energy of the complex to the basicity of the extractant after the change in the complex formation mechanism. We put forward the hypothesis[11] that, by altering the 'threshhold' of the transition through the selection of the extractant and the diluent, it is possible to obtain a significant increase in the separation coefficients for acids in their mixtures.

The $\lg K_{ex}$ of strong acids (for example, perchloric and pertechnetic), which form proton-transfer complexes over the entire range of basicities of the extractant, increases almost linearly (by 15–18 units) with increase in basicity as the substituents and the reaction centre are varied (SO, PO, AsO, NO) (Fig. 5 *b*).[37,46,47]

The formation of proton-transfer complexes in the extraction of metal salts results in the manifestation, together with coordination to the oxide oxygen and the formation of a solvate [for example $UO_2(R_3XO)_2(NO_3)_3$], also of coordination to the cation LH^+, for example $R_3XOH^+UO_2(NO_3)_3^-$ (Rozen et al.[36] called this the amine mechanism). Attempts to separate the contributions of the oxygen and amine mechanisms have been undertaken.[36,47]

The discovery of the amine (anion-exchange) mechanism of the extraction of actinides by the oxides R_3AsO and R_3NO made it possible to explain the similarity of the distribution coefficients of uranium and plutonium in extraction by amines and amine and arsine oxides (Fig. 6).¶

For arsine oxides, a transition to the cation-exchange mechanism is observed in the region of low acidity.[49]

In the extraction of metal salts, the changes in the complex formation mechanism are similar to the changes in the mechanism of the formation of complexes by acids over a wide range of basicities of neutral extractants. In extraction by weakly basic extractants (for example, by ethers or ketones), the hydrate-solvate mechanism is favourable. In this case, the extractant is unable to displace a water molecule from the first hydration shell and the metal ion is extracted together with the latter, since the separation of the hydrated ion from the outer hydration shell requires less energy than its separation from the inner shell. Under these conditions, the extractant is in the outer sphere of the complex and is coordinated to the metal ion via a water molecule.†

Stronger extractants decompose the first hydration shell and extract the metal without water molecules.

The most basic extractants (arsine and amine oxides) extract the metal via the amine mechanism.

‡ One cannot be certain that the complex formation mechanism does not change for the strongest bases — for example, arsine and amine oxides. A change in this mechanism would lead to considerable errors in prediction.

§ I V Nikolaeva *Vzaimosvyaz' Ekstraktsionnoi Sposobnosti Oksidov 2-Nonilpiridina i Triizoamilfosfina i Sostoyaniya ikh Kompleksov s Kislotami v Nevodnykh Sredah* (Relation between the Extraction Ability of 2-Nonylpyridine and Triisopentylphosphine Oxides and the State of their Complexes with Acids in Nonaqueous Media). Author's abstract of Candidate Thesis in Chemical Sciences, Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 1996.

¶ For R_3NO, such similarity was observed as early as 1964 [50] but until the publication of the study of Rozen et al.[36] was not understood.

† For the characteristic features of the extraction via the hydrate-solvate mechanism, see Yu A Zolotov.[9]

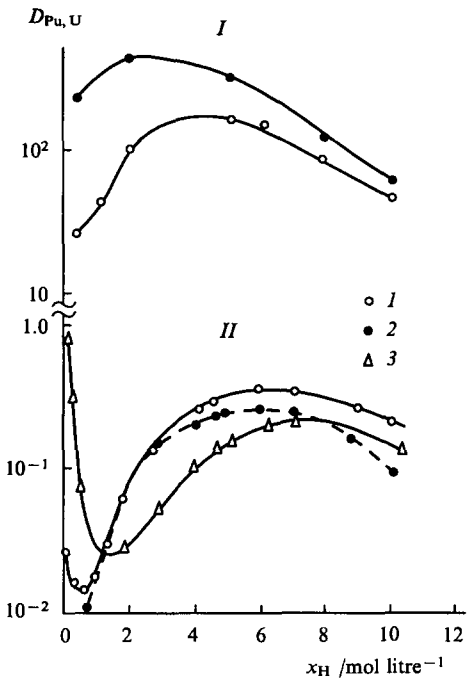


Figure 6. Dependence of the distribution coefficients of Pu^{4+} (*I*), and UO_2^{2+} (*II*) on acidity in extraction by trioctylamine oxide (*1*), trioctylamine (*2*), and trioctylarsine oxide (*3*) (extractant concentration in benzene 0.1 M).

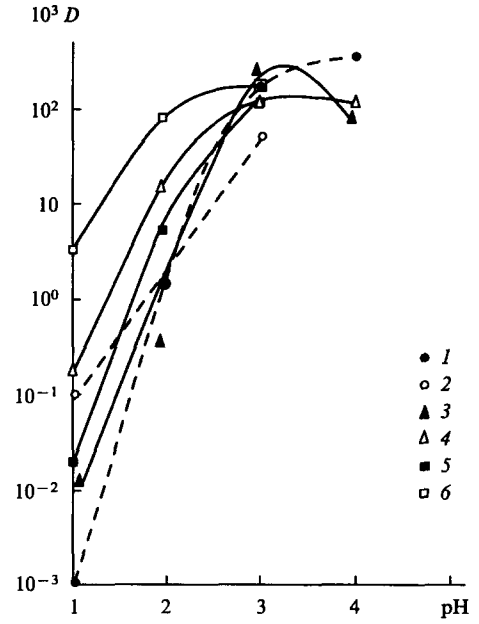


Figure 7. Dependence of the distribution coefficients of U(VI) (*1*, *2*), Pu(VI) (*3*, *4*), and Np(VI) (*5*, *6*) on the pH in extraction by arsine oxides Ph_3AsO (*1*, *3*, *5*) and R_3AsO (*2*, *4*, *6*).[52]

V. Characteristic features of extraction by amine and arsine oxides

In the extraction of metals by arsine and amine oxides, the formation of proton-transfer complexes $(LH^+)A$ between the extractant and the inorganic acid, similar to amine salts, is accompanied also by complex formation via the anion-exchange mechanism. For example, the complexes $LH^+[UO_2(NO_3)_3]^-$ and $(LH^+)_2[Pu(NO_3)_6]^{2-}$ where L = R_3AsO or R_3NO, are formed.[34] Thus at high basicities the boundary between neutral extractants and amines is obliterated.

At a low acidity of the aqueous phase, yet another change in the extraction mechanism is observed. It is particularly pronounced in the case of arsine oxides. Fig. 6 shows that, at HNO_3 concentrations less than 1.5 M, the distribution coefficient of uranium increases with decrease in x_H, i.e. R_3AsO begins to extract like an organic acid.[36] The dependence of the distribution coefficient on the pH (Fig. 7) characteristic of extraction by organic acids, i.e.

$$\lg D = a + z\text{pH} \qquad (9)$$

(z is the valence of the cation), is observed. One may conclude[36] that the arsine oxide molecule rearranges and tentatively is converted into the acid $R_3As(NO_3)OH$. The reaction proceeds via the cation-exchange mechanism, for example via the reaction

$$UO_2^{2+} + 2HY = UO_2Y_2 + 2H^+,$$

where Y is apparently $R_3As(NO_3)O$. Such rearrangement may account also for the surprising phenomenon observed in a number of studies:[52–55] in the weakly acid region, the degree of extraction of Pu(IV) and Pu(VI) increased after the replacement of the alkyl groups in the arsine oxide by the more electronegative phenyl groups, which, as we have seen above, leads to a weakening of extraction when NOPC and sulfoxides are employed. However, when account is taken of the 'acid rearrangement', everything becomes clear, since in extraction by organic acids an increase in the electronegativity of the substituents leads to an increase in the strength of the acid and in the degree of extraction by the cation-exchange mechanism.

We may note yet another, albeit less striking, anomaly, which has been observed in the extraction of nitric acid by arsine oxides.[56] In the weakly acid region, the extraction constant K_{1H} for the first acid molecule depends on the electronegativity of the substituents and on the basicity of the arsine oxides in conformity with Eqns (4) and (7) (for Ph_3AsO, $Ph_2AlkAsO$, $PhAlk_2AsO$, and Alk_3AsO, the constant is 3×10^2, 3×10^3, 5×10^4 , and 5×10^5 respectively); in the strongly acid region, the isotherms for the extraction of HNO_3 by all four arsine oxides are virtually identical [see Rozen et al.[56] (Table 3)].

If inorganic acids are extracted by R_3AsO and R_3NO with extraction constants in the range 10^6–10^{10}, they immediately become actual competitors of the metals and are no longer salting-out agents (like HNO_3 in the extraction of metal salts by TBP).

In conclusion we may note that, by varying the substituents and the reaction centre (SO, PO, AsO, NO), it is possible to alter the EA of organic oxides in any required direction by 15–18 orders of magnitude (Fig. 5*b*).[37]

VI. Salts of amines and quaternary onium bases

Inorganic acids are extracted by amines via an addition reaction[55] with extraction constants of 10^5–10^7, characteristic of the formation of proton-transfer complexes, i.e. the amine salts, for example $(R_3NH)^+A^-$. Amine salts are in their turn effective extractants for acids and metal salts. In the latter case, extraction can be described either as anion exchange or as an addition reaction: the two types of reaction are thermodynamically indistinguishable. In the complexes formed [for example, $(R_3NH)^+(UO_2A_3)^-$ or $(R_3NH)_2^+(PuA_6)_2^{2-}$], the metal is present in the anion and the extractant is in the outer sphere of the complex.[57] However, in the extraction of platinum metals, very stable complexes with a direct metal–amine nitrogen atom coordinate bond, called insertion complexes, were detected together with the anion-exchange complexes.[58]

The electronegativity of hydrogen (2.3) is higher than that of an alkyl group (2.0), so that EA increases in the series primary amine salts < secondary amine salts < tertiary amine salts < quaternary ammonium (QA) salts (Fig. 8). The difference

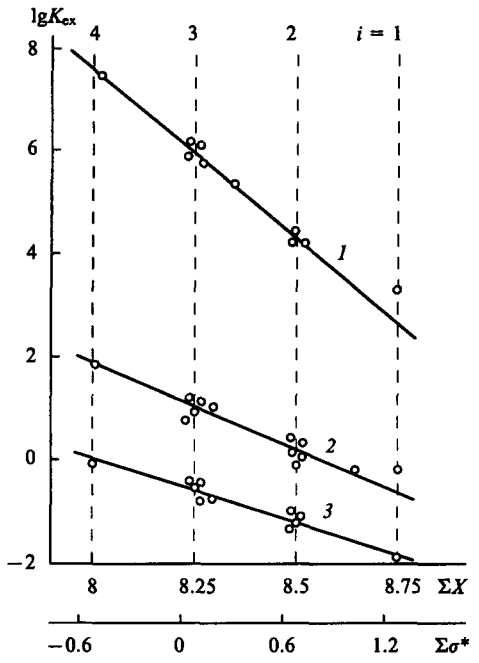


Figure 8. Dependence of EA on the electronegativities sum and the Taft constants of the extractants in the extraction of Pu(VI) (*1*), U(VI) (*2*), and HNO_3 (*3*) by salts of primary amines — quaternary ammonium bases series $[R_iNH_{4-i}]^+NO_3^-$, where i = 1, 2, 3, 4.[60]

between amines and NOPC consists in a higher sensitivity to changes in EA (B_{Pu} = 6.8 instead of 4.8 for NOPC) and the length of the substituents. The question of the influence of association requires separate discussion. One should only note that, owing to the differences between the degrees of polymerisation, the above series is sometimes found to break down: primary amines extract more effectively than tertiary amines.

The correlation for the EA of amine salts may be represented also in the form of the dependence on the basicity; a linear increase in $\lg K_{ex}$ with increase in pK is observed in the above series. When the nature of the substituents in the amine molecules is varied widely, linear correlations are observed for the EA within the limits of each subclass of amines — primary, secondary, etc. (the corresponding straight lines are parallel). The increase in EA with increasing pK is characteristic of the anion-exchange extraction mechanism while on formation of coordination insertion complexes the opposite relation holds: the stability of the complexes increases in the series tertiary amines < secondary amines < primary amines, i.e. as the steric hindrance to coordination is weakened.

The extraction ability of amine salts depends also on the nature of the anions. Shmidt[59] proposed a two parameter correlation of the extraction constant with the hydration parameter ΔG_{hydr} and the influence of the diluent (ID):

$$\lg K_{ex} = \lg K_{ex\,0} + a\Delta G_{hydr} + b\mathrm{BP}\,. \qquad (10)$$

The extraction ability of quaternary onium salts $R_4X^+NO_3^-$ (where R = octyl) in the series with X = N, As, or P has been investigated in relation to the extraction of nitric acid and uranyl and plutonium nitrates.[36] It was found that EA varies little in the above series. Thus the isotherms for the extraction of nitric acid by the nitrate salts of all three bases virtually coincide (Fig. 9 *a*), while for uranyl and plutonium nitrates (Figs 9 *b* and 9 *c*) a slight decrease in EA is observed [for example, the concentration constants for the extraction of the uranyl monocomplex $R_2X^+(UO_2(NO_3)_3^-$ are respectively 5.3, 5.0, and 4.7 for the above extractant salts] Fig. 9 shows that significant changes occur only when a second organic phase is formed: in the series N—As—P, the compatibllity of the complexes formed with the diluent (CCl_4) increases appreciably. Apparently the polarity and hence the degree of polymerisation of the extractants and complexes decrease somewhat in the above series. The first factor leads to a decrease in EA, whilst the second results in the improvement of the compatibility of the complexes with the solvent. The smallness of the changes in EA in the above series confirms the generally accepted idea that the interaction between the bulky cation in the outer sphere of the complex and the MA_{z+n}^{n-} n anion is predominantly electrostatic. The important role of the cation–anion hydrogen bond is indicated by the fact that the smallness of the changes in EA in the series N > As > P does not correspond to the change in the size of the central atom (N < P < As), but coincides with the EA series for the oxides R_3XO.

VII. The influence of the length and degree of branching of substituents on the extraction ability of organic compounds

The overall steric effect of the substituents in extraction by neutral and ion-exchange compounds is determined by at least five factors. An increase in the bulk and degree of branching of the substituents leads as a rule to a decrease in the electronegativity of the substituent, a decrease in the solubility of the extractant in the aqueous phase, an increase in the steric hindrance to complex formation, a decrease in the degree of polymerisation of the extractant, and a decrease in the rotational partition function.[61]

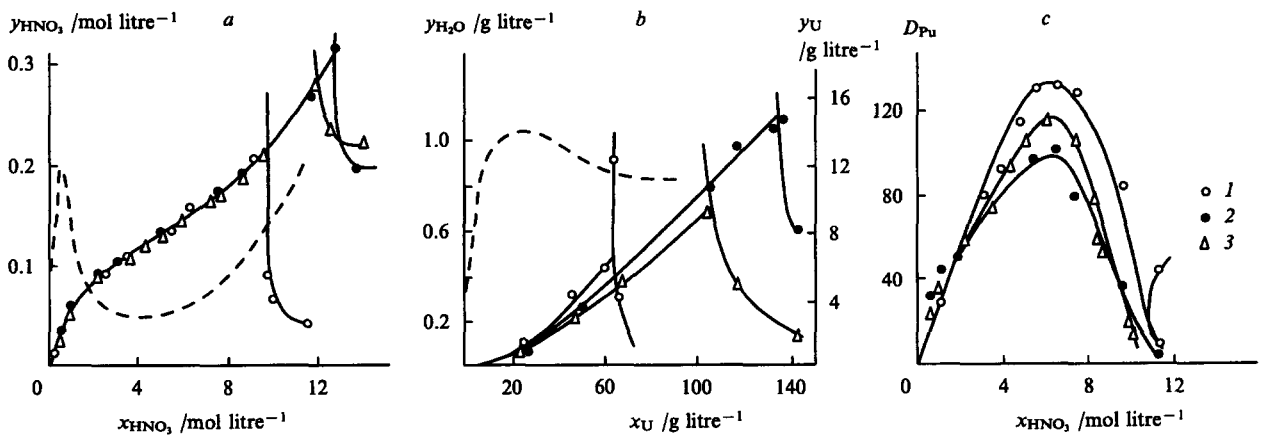


Figure 9. Extraction isotherms of nitric acid (*a*) and uranyl (*b*) and plutonium (*c*) nitrates by onium nitrates $R_4X^+NO_3^-$, where X = N (*1*), P (*2*), and As (*3*) (extractant concentration in CCl_4 0.1 M); dashed curves — extraction of water.

The first two factors promote an increase in EA, while the others tend to decrease it. Evidently, for a moderate length of the alkyl substituents, the first two factors exert the greatest influence, whilst the importance of the remaining factors increases as a rule for bulky and branched substituents.

The length of the hydrocarbon chain of the substituent n_C particularly for the normal structure, influences comparatively slightly the extraction ability of NOPC and amine salts. Weak maxima have been noted on the $K_{ex} = f(n_C)$ curves for $n_C = 5-8$ (Fig. 10). These can be readily accounted for by the operation of the factors listed above. For NOPC, the coefficient ρ in Eqn (4) is small: $\rho(UO_2) = \rho(Pu) = 0.01$; for amine salts, it is appreciably higher: $\rho(Pu) = 0.12$ (see also Fig. 10*b*).

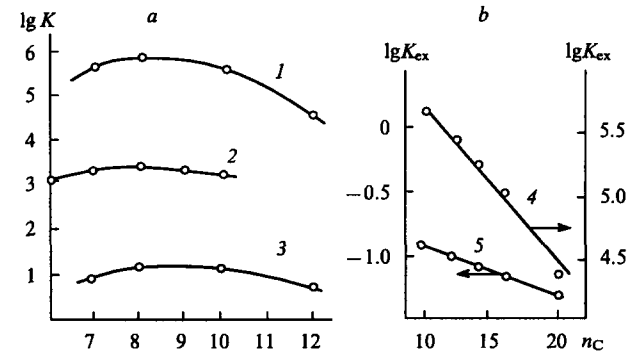


Figure 10. The influence of the length of the hydrocarbon chain in symmetrical trialkylamines on the extraction of uranyl and plutonium nitrates (*a*) and plutonium nitrate and nitric acid (*b*).
Substance extracted: (*1*) and (*4*) Pu(VI); (*2*) and (*3*) U(VI); (*5*) HNO_3. Extractant: (*1*), (*3*), and (*5*) amines; (*2*) and (*4*) phosphonates.

In the early studies on extraction (see, for example, Glueckauf and coworkers[23,24]) a marked decrease in the extraction constant with increase in the length of the hydrocarbon substituent was noted when extraction by undiluted alcohols and ethers was investigated. This relation could not be explained since the chemical nature of extraction was not yet understood. At the present time, the explanation is evident: when account is taken of the formation of complexes, the extraction constant (or more precisely the distribution constant) is proportional to L_0^q, where L_0 is the initial concentration of the extractant (on the molar scale) and q is the solvation number. The initial extractant concentration diminishes with increase in the length of the hydrocarbon chain and in the molecular mass ($L_0^q = 9.8$, 7.5, and 5.9 mol litre^{-1} for diethyl, dipropyl, and dibutyl ethers respectively). The third factor apparently also plays a role, because hydrocarbon chains are attached directly to the donor centre — the oxygen atom.

The branching of hydrocarbon chains influences not only EA but also the selectivity of the extraction [for example, di-2-ethylhexylphosphoric acid (D2EHPA) is more selective than di-n-octylphosphoric acid].

The influence of steric hindrance is clearly manifested in the extraction of uranyl and trivalent lanthanide and actinide nitrates by the amides of alkylphosphoric acids. Very high EA of such compounds have been reported, in particular of the hexabutyl phoshorous trisamide (HBTA), which greatly exceeds the EA of trialkylphosphine oxides.‡ A careful check of the extracting properties of HBTA[66] led to unexpected results. It was found that, in extraction by nitric acid, where monosolvates are formed both with HBTA and TOPO, the extraction isotherms virtually coincide (Fig. 11); a slight excess (in favour of HBTA) was observed only at a high HNO_3 concentration, i.e. in the region

‡ The greater complex-forming capacity of the amides is indicated also by the higher Gutmann donor number, although the gas-phase basicities of the amides and phosphine oxides are practically identical.[41]

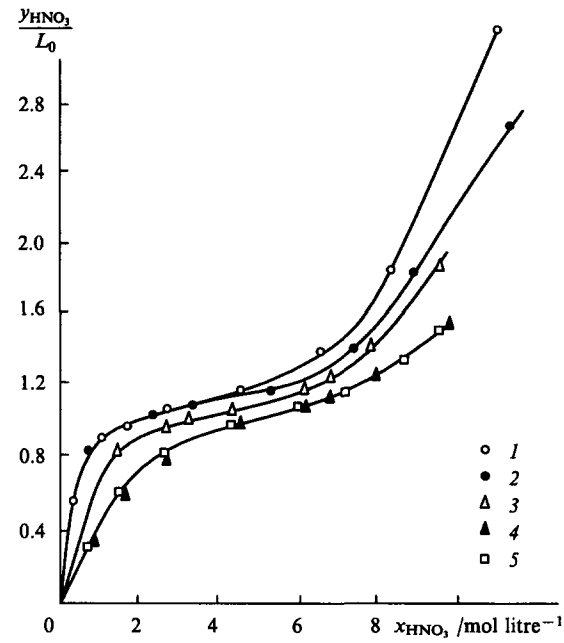


Figure 11. Extraction isotherms of HNO_3 by extractant solutions in benzene.
Extractant: (*1*) HBTA; (*2*) TOPO; (*3*) $(NBu_2)_2BuOPO$; (*4*) $NBu_2(BuO)_2PO$; (*5*) DPMP; extractant concentration (mol litre^{-1}): (*1*) and (*2*) 0.25; (*3*)–(*5*) 1.0.

where semisolvate and one-third solvates are formed. On the other hand, in extraction by hydrochloric, perchloric, and sulfuric acids, where disolvates are formed, HBTA extracts much less effectively than TOPO (Fig. 12, Table 5). A decrease in extraction occurs also in the extraction of uranyl nitrate, where disolvates are also

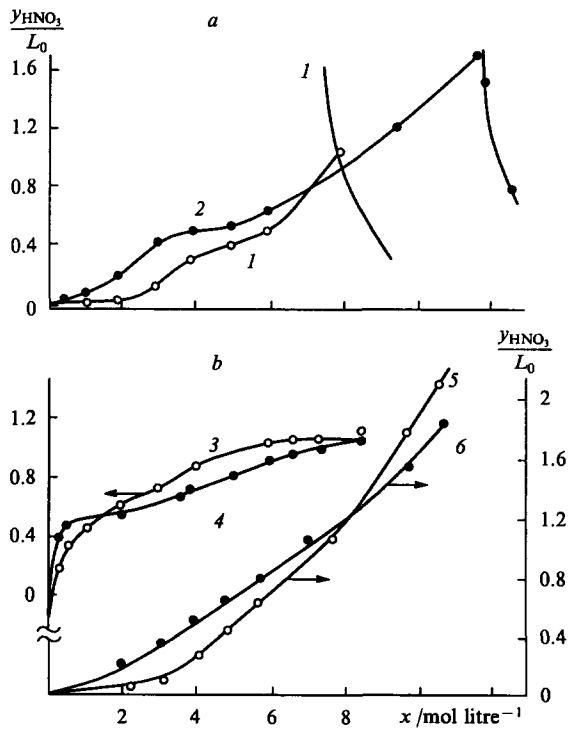


Figure 12. Extraction isotherms of acids by extractant solutions in benzene (0.25 M).
Acid: *a*: (*1*) and (*2*) H_2SO_4; *b*: (*3*) and (*4*) $HClO_4$; (*5*) and (*6*) HCl; extractant: (*1*), (*3*), and (*5*) HBTA; (*2*), (*4*), and (*6*) TOPO.

Table 5. Constants for the extraction of acids by solutions of TOPO and HBTA in benzene in the form of disolvates (K_2), monosolvates (K_1), hemisolvates ($K_{1/2}$), and one-third solvates ($K_{1/3}$).

Acid	Extractant	K_2	K_1	$10^3 K_{1/2}$ [a]	$K_{1/3}$ [a]
HNO_3	TOPO	0	18.5	1.7	1.4×10^{-5}
	HBTA	0	18.5	2.9	3.3×10^{-5}
$HClO_4$	TOPO	1620	0.98	0	0
	HBTA	112	0.91	0.0048	2
HCl	TOPO	0.146	0.02	2.2×10^{-4}	–
	HBTA	0.014	0.0049	–	2.34×10^{-2}
H_2SO_4	TOPO	29.7	0.27	2.8×10^{-4}	–
	HBTA	1.42	0.07	3.5×10^{-4}	–

[a] The increased constants $K_{1/2}$ and $K_{1/3}$ for HBTA may be associated with coordination to the nitrogen atom.

formed. The lowest degree of extraction (lower by 3–4 orders of magnitude) is that of the trivalent americium and cerium, which are extracted in the form of disolvates. These results can be explained solely by the influence of the steric hindrance generated by the amide groups, the steric effect increasing non-linearly. For example, for uranyl nitrate, we have

$$\lg K_{ex}[(NR_2)_nR_{3-n}PO] = \lg K_{ex}(R_3PO) - 0.15n^2.$$

The steric and electronic structures and the electron-donating capacities of a series of carbonyl compounds with amide groups, namely the ketone–carboxylic acid amide–urea series, have also been investigated. It was found that the nonadditivity of the influence of the amide groups in these systems (the strong influence of the first amide group and the weak influence of the second) is due to the geometrical hindrance to the conjugation in substituted amides and ureas. This hindrance increases with increase in the number of amide groups and in the length of the hydrocarbon groups (this system is examined in greater detail below). A characteristic feature of extraction with participation of amides is the strong influence of the length of the amide groups on the compatibility with HNO_3 solutions and even on the stoichiometry of the complex-formation reaction.[67] Thus, whereas, in the extraction of uranyl nitrate by the amide $OctC(O)NR_2$, where Oct = C_8H_{17}, the disolvate ($K_2 = 9.6$, $K_3 = 0.7$) is formed preferentially for R = Bu, in the case where R = $C_{12}H_{25}$ the main product is the trisolvate ($K_3 = 6.3$, $K_2 = 1.2$). Taking into account the increase in steric hindrance, one may postulate that the extractant molecule in the trisolvate is coordinated via a water molecule.

VIII. The use of quantum-chemical calculations for predicting extraction ability

It was shown above that equations similar to Eqns (4) and (5) have been obtained for neutral oxygen-containing compounds, amine salts, and quaternary ammonium salts. At the same time, the electronegativities and constants of the substituents may be used to predict EA only for short series of compounds with one reaction centre. The employment of these parameters is also limited by the assumption that the influence of the substituent is additive. This assumption is in many cases invalid.[67,68] Thus in the series of ketone–amide–urea carbonyl compounds, the effects of the first and second amide groups are not equivalent[54], i.e. there is no additivity. It is therefore useful to employ characteristics calculated by quantum-chemical methods, which are free from the assumption that the influence of the substituents is additive.

Examination of the correlation of EA with quantum-chemical parameters in different series of neutral compounds permits certain conclusions. It is possible to test the hypothesis put forward in early studies that EA is determined by the electron density (charge) on the functional atom. For this purpose, the effective charges on the oxygen atom of the phosphoryl group in a series of NOPC have been calculated. It was found that in the general case the accuracy of the estimates of the effective charges by different molecular orbital methods may be insufficient for a reliable prediction (which is aggravated also by the arbitrary features of the method of analysis of the Mulliken populations itself.)

A more reliable characteristic of the distribution of electron density in the molecule is the energy of the molecular core levels, the values of which not only depend on the effective charge on the atom but also take into account the influence of the field of other atoms.

The correlation between the energy of the 1*s* core levels of the donor oxygen atom (E_{1sO}) and EA is characteristic for a large series of extractants with different reaction centres (Fig.13). The nonlinearity of the dependence of $\ln K_{ex}$ on E_{1sO} is apparently due to the changes in the complex formation mechanism (noted above) with increase of the extractant basicity. On the other hand, the deviation of the points corresponding to amides and ureas indicates the restricted nature of the correlations deduced from the characteristics of isolated extractant molecules. The point is that in compounds of this kind an appreciable stabilisation of the system occurs directly on complex formation as a result of the conjugation of the bonds. The use of the energies of test reactions for prediction of EA therefore appears more justified. In addition, such energies make it possible to take into account simultaneously components of the energy of the EDA interactions such as the electrostatic, charge-transfer, geometrical ligand rearrangement, and polarisability components. Indeed, the points corresponding to amides and ureas, which deviate in Fig. 13, in Fig. 14 are found to be close to the overall correlation describing the dependence of EA on the energy of the simplest test reaction, namely protonation.

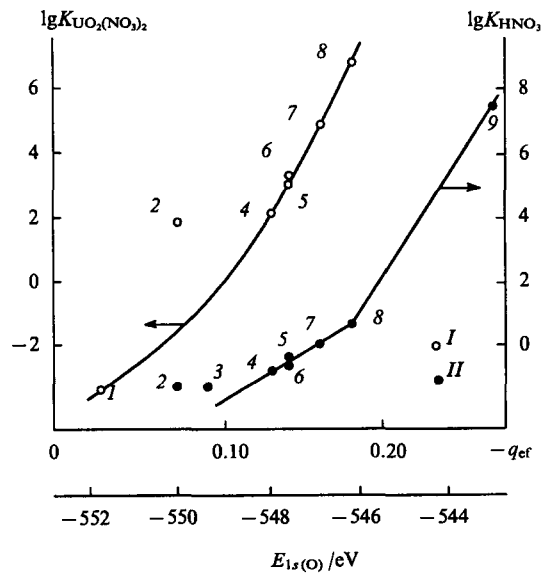


Figure 13. Dependence of the uranyl nitrate (*I*) and nitric acid (*II*) extraction constants on the energy of the 1*s* core levels of the oxygen atom and the effective charge on the oxygen atom.
Extractant: (*1*) R_2CO; (*2*) $(NR_2C)RCO$; (*3*) $(NR_2)_2CO$; (*4*) $(RO)_3PO$; (*5*) R_2SO; (*6*) $(RO)_2RPO$; (*7*) $(RO)R_2PO$; (*8*) R_3PO; (*9*) R_3NO.

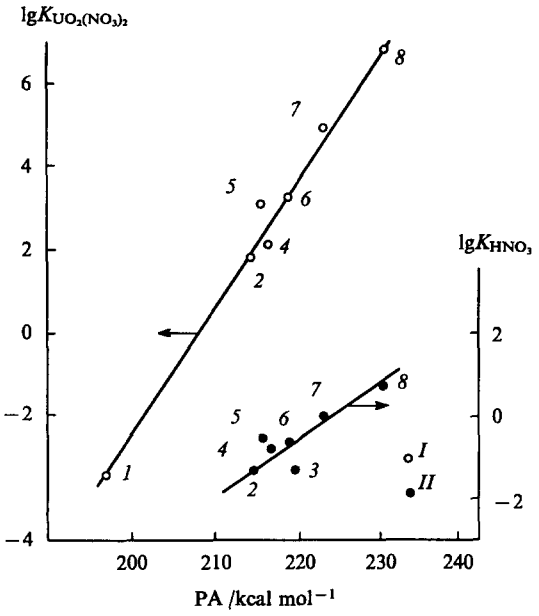


Figure 14. Dependence of the uranyl nitrates (*I*) and nitric acid (*II*) extraction constants on the proton affinity calculated by the AM1 method. Extractant: (*1*) R_2CO; (*2*) $(NR_2C)RCO$; (*3*) $(NR_2)_2CO$; (*4*) $(RO)_3PO$; (*5*) R_2SO; (*6*) $(RO)_2RPO$; (*7*) $(RO)R_2PO$; (*8*) R_3PO.

The ketone–carboxylic acid amide–urea series (three points in Fig. 15) merits a more detailed consideration because this is one of the examples of the nonadditivity of the influence of the substituents. The effects arising from the introduction into the ketone molecule of the first and second amide groups are non-equivalent. The introduction of the first group increases the degree

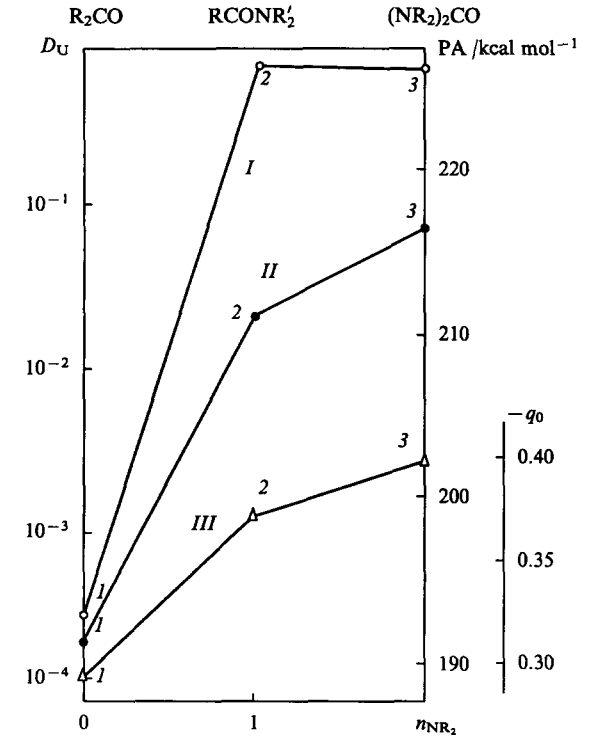


Figure 15. Dependence of the distribution coefficient of uranyl nitrate (*I*), the proton affinity (*II*), and the effective charge on the oxygen atom (*III*) on the structure of the extractants.
Extractant: (*1*) ketone; (*2*) carboxylic acid amide; (*3*) urea.

of extraction of uranyl nitrate by three orders of magnitude, whilst the second contributes little.§ The frequencies of the carbonyl group vibration (ν_{CO}), the solvate shift of the frequency of the hydroxy-groups of phenol on complex formation ($\Delta\nu_{OH}$), the Gutmann donor number (D_N), and the entropy of formation of a complex with BF_3 (ΔH) also change in steps (Table 6). It is clear that, since the standard correlation approaches presuppose the additivity of the influence of the substituents, they are ineffective in this case. On the other hand, the characteristics calculated by the quantum-chemical method — the charges on the oxygen atom, the energies of the core levels, and the proton affinity (PA) — also vary stepwise in the above series, like the physicochemical properties (Fig. 15), and may be used for correlation with extraction data (PA is employed for correlation within a large series of compounds with different reaction centres). The advantages of the quantum-chemical approach to the interpretation and prediction of EA have been strikingly manifested for the series of compounds considered.[68,69]

Table 6. Properties of carbonyl compounds.

Compound	$10^2 D$		ν_{CO} /cm^{-1}	$\Delta\nu_{OH}$ /cm^{-1}	D_N	ΔH /kcal mol^{-1}
	U(VI)	Pu(VI)				
R_2CO	0.037	0.068	1730	74	17.0	18.2
$NR_2C(O)R$	88.5	26.0	1640	200	27.8	26.8
$(NR_2)_2CO$	89.0	56.4	1642	208	29.6	26.0

Together with protonation, reactions with the simplest Lewis acids — H_2O, HNO_3,[16] Li^+, LiH, LiCl, $AlBr_3$, AlH_3, etc. — may also be used as the test reactions.[22] The thermodynamic parameters of the complex formation reactions between NOPC and the above acceptors have been calculated quantum-chemically by the modern semiempirical MNDO and AM1 methods.[69] It was found that the above reaction series is isentropic, which demonstrates the validity of the correlation between EA and the enthalpies of complex formation.

An advantage of the prediction of EA from the values of PA is the relative simplicity of the calculation of EA. At the same time, limitations have also been discovered. Calculations have shown that, in the case of complexes with a weak EDA interaction, alkylphosphine oxides form more stable complexes than their phenyl-substituted analogues, i.e. the phenyl group behaves as an electronegative substituent.[22] This is manifested also in all the known cases of the extraction of metals by monodentate NOPC.[6,12,34] For example, in the NOPC series, the introduction of one phenyl group instead of an alkyl group diminishes the extraction constant by a factor of 17 for uranyl nitrate and a factor of 8 for americium nitrate. On the other hand, in the formation of more stable complexes with a proton an inversion is observed: phenyl substituents become electron donors. Therefore in the presence of amphoteric substituents in the reaction series, reactions not with a proton but with a weaker acceptor must be used as the test processes. The test reaction with water, which is ideal from this standpoint, suffers from a significant disadvantage — a small variation of the enthalpy of complex formation within the limits of the reaction series.

§ The main cause of the weak influence of the second amide group is the steric hindrance to the conjugation of the lone pair on the nitrogen atom of the amide group with the π-electron system of the carbonyl bond.

IX. Bidentate neutral organophosphorus compounds and the anomalous aryl stabilisation effect

Bidentate neutral organophosphorus compounds (BDNOPC) are powerful extractants. Analysis of the dependences of the distribution coefficients of americium presented in Figs 16 and 17 shows that in extraction by BDNOPC these coefficients are higher by 3–6 orders of magnitude than in extraction by monodentate NOPC. In particular, they are promising for the extensive extraction of the actinides from waste in radiochemical industries. At the same time, they are of considerable interest because of the unusual dependence of EA on the structure of the extractants. Deviations of relations (4) and (7) have been observed in the study of the extraction ability of alkylenediphosphine dioxides $R'_2P(O)(CH_2)_nP(O)R''_2$,¶ and carbamoylmethylphosphine oxides $R'R''P(O)CH_2C(O)NR'''_2$ (abbreviated to $R'R''/R'''$). Admittedly, on formation of complexes with monodentate coordination, characteristic of the extraction of inorganic acids (HNO_3, $HClO_4$),[70,71] relations (4) and (7) hold qualitatively. The introduction of electronegative substituents at the phosphorus atom in place of alkyl groups lowers the degree of extraction [in particular, in the 4Oct–2Oct2Ph–4Ph series (Fig. 18)].

Eqn (4) then holds quantitatively for HNO_3: the dependence of the logarithm of the extraction constant on the sum of the electronegativities or the Taft constants of the substituents is linear.[70] Deviations from linearity have been observed for $HClO_4$ (Fig. 19): the introduction of the first two phenyl groups greatly reduces EA, while the introduction of the next two groups has a smaller effect. In the extraction of trivalent actinides and lanthanides, complexes with bidentate coordination are formed. In this case, the replacement of alkyl groups by more electronegative groups such as AlkO or $Cl(CH_2)_2$ also lowers EA (Table 7). However, when phenyl (or other aryl) group which have the electronegativity like $Cl(CH_2)_2$ are introduced into molecules of extractants Nos 1 and 4, instead of alkyl groups, relations (4) and (7) are infringed. Despite the increase in the electronegativity of the substituents and the decrease in the basicity of the methylenediphosphine dioxides, the distribution coefficients and extraction constants of trivalent americium and the lanthanides increase almost by two orders of magnitude (Figs 16 and 20). This effect, first observed by Rozen et al.[74] and discussed in a number of communications,[22,72–79,81–87] has been called the anomalous aryl stabilisation (AAS). The data presented in Table 7 indicate

¶ The following abbreviations have been adopted below: if $n = 1$ and $R' = R''$ the extractant is designated by 4R, if $R' \neq R''$ the designation is 2R'2R'', and if $n > 1$ and $R' = R'' =$ Ph the designation of the extractant is $4Ph(CH_2)_n$.

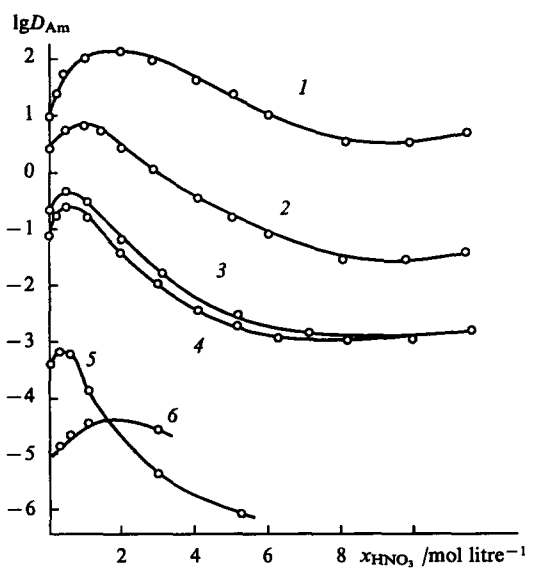


Figure 16. Dependence of the distribution coefficient of americium in extraction by solutions of methylenediphosphine dioxides in dichloroethane (0.01 M) and of triphenylphosphine oxide and TOPO in dichloroethane (0.02 M) on the acidity.
Extractant: (*1*) 4Ph; (*2*) 2Ph2Oct; (*3*) 4Oct; (*4*) 4Bu; (*5*) TOPO; (*6*) triphenylphosphine oxide (TPPO).

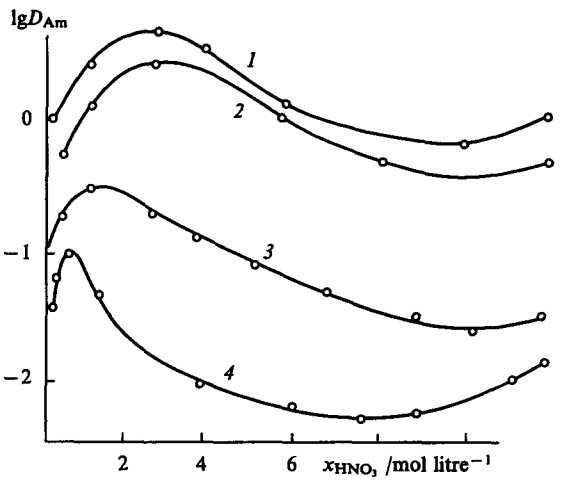


Figure 17. Dependence of the distribution coefficient of americium nitrate in extraction by solutions of carbamoylmethylphosphine oxides in dichloroethane (0.05 M).
Extractant: (*1*) Tol_2/Bu_2; (*2*) Ph_2/Bu_2; (*3*) $OctPh/Bu_2$; (*4*) Oct_2/Bu_2.

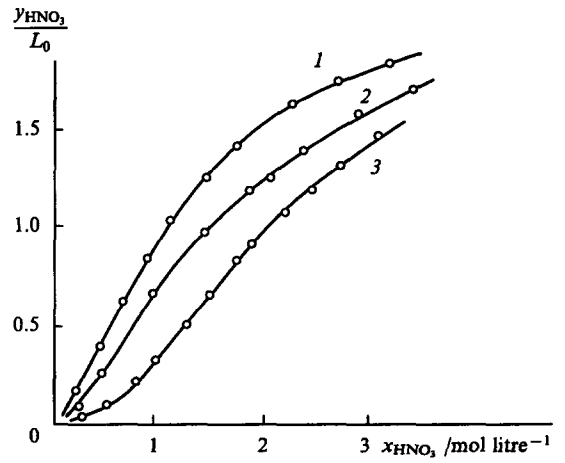


Figure 18. Isotherms for the extraction of nitric acid by solutions of methylenediphosphine dioxides in dichloroethane (0.025 M).
Extractant: (*1*) 4Oct; (*2*) 2Oct2Ph; (*3*) 4Ph.

Table 7. The effective constants for the extraction of americium(III) from nitric acid solutions of $R'_2P(O)CH_2P(O)R''_2$ in the form of disolvates (determined by a method involving dilution in dichloroethane).[72–74]

No	Extractant		ΣX	K_{ex}
	R'	R''		
1	Oct	Oct	8.0	1.6×10^7
2	BuO	Bu	9.6	5.0×10^3
3	$Cl(CH_2)_2$	$Cl(CH_2)_2$	9.32	3.5×10^3
4	Oct	Ph	8.66	1.0×10^8
5	Ph	Ph	9.32	6.5×10^8
6	Bz	Bz	–	8.0×10^3
7	EtO	Ph	9.46	2.2×10^3

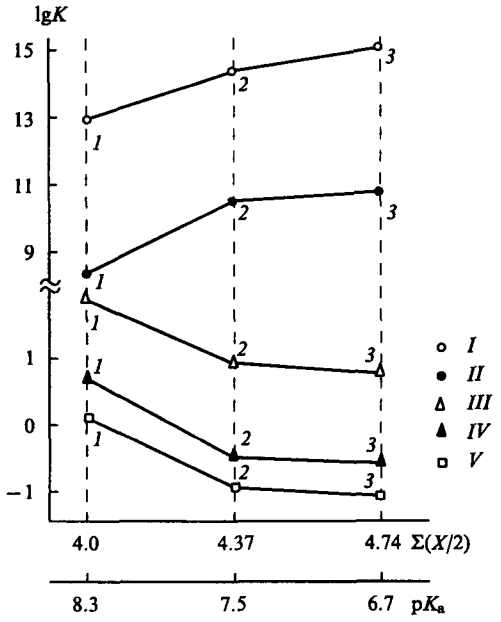


Figure 19. Dependence of the effective perchloric acid and americium extraction constants on the basicity and the sum of the electronegativities of methylenediphosphine dioxides.[71]
Substance extracted: (*I*) americium trisolvate; (*II*) americium disolvate; (*III*) molecular form of perchloric acid disolvate; (*IV*) perchloric acid monosolvate; (*V*) ionic form of perchloric acid disolvate; extractant: (*1*) 4Oct; (*2*) 2Oct2Ph; (*3*) 4Ph.

that the effect is associated not with the electronegativity but with the chemical nature of the aryl groups.

Yatsimirskii, Kabachnik, and coworkers[80] found in their conductimetric study of the formation of complexes by methylenediphosphine dioxide with certain metals in acetonitrile that the constant for the formation of a complex between NaI and 4Ph is somewhat higher than for the alkyl-substituted dioxide. However, they did not pay attention to this result, did not point it out in their conclusions, and did not note the anomaly. This may have been because the dependence of the complex formation constant on the basicity of the ligand was not investigated (and possibly also because the effect differs little from the experimental error, which in view of the abundance of assumptions made in the method, the authors estimated very optimistically as within the limits of 20%). The authors confined themselves to the hypothesis that an exotic compound is formed: a six-membered ring is not closed via two oxygen atoms through a metal cation but via an anion — through phosphorus. After more than a decade since the anomaly had been discovered by Rozen et al.[74], Yatsimirskii et al.[80] carried out a systematic study in which they replaced acetonitrile by tetrahydrofuran and found[81] that the AAS effect is observed on formation of complexes of alkali metal and copper ions with methylenediphosphine dioxides and carbamoylmethylphosphine oxides in ionising solvents (Table 8).

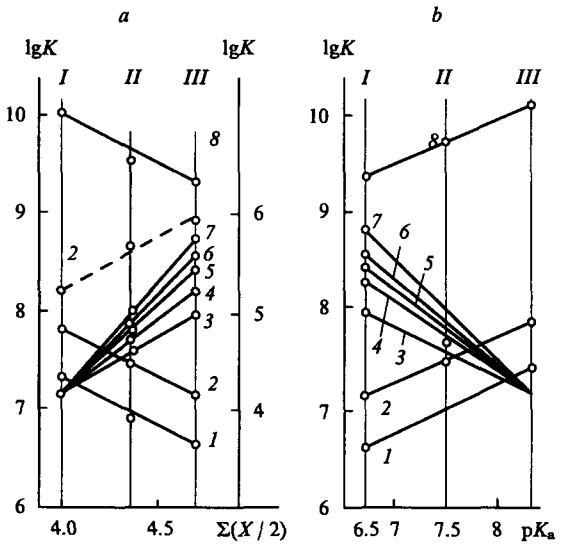


Figure 20. Dependence of the extraction constants for the actinides and lanthanides by extraction with solutions of methylenediphosphine dioxides on the sum of the electronegativities of the substituents (*a*) and the basicity (*b*).
Diluent: dichloroethane (continuous lines, left-hand scale), chloroform (dashed line, right-hand scale); extractant: (*I*) 4Ph; (*II*) 2Oct2Ph; (*III*) 4Oct; substance extracted: (*1*) Pu(VI); (*2*) U(VI); (*3*) Pr(III); (*4*) Pm(III); (*5*) Eu(III); (*6*) Cm, Pu(III); (*7*) Am(III); (*8*) Pu(IV).

Table 8. The logarithms of the stability constants of the alkali metal complexes ML^+ of $R'R''P(O)CH_2C(O)NEt_2$ and $R_2P(O)CH_2P(O)R_2$ in tetrahydrofuran.[81]

M	Ph_2/Et_2	$PhBu/Et_2$	Bu_2/Et_2	4Ph	4Bu
Li	3.69	3.38	3.11	4.72	3.92
Na	3.59	3.24	3.08	–	–
K	2.73	2.48	2.35	–	–

The AAS effect is observed in various media [HNO_3 (Fig. 16), HCl, and H_2SO_4 (Fig. 21)] and is particularly large in perchloric acid solution (Fig. 22), which we believe can be accounted for by the increase in the solvation number as a consequence of the decrease in the denticity of the metal–anion bond (the extraction constant for the trisolvate is $\sim 10^{13}$). The increase in $\lg K_{ex}$ as phenyl groups are introduced is nonlinear (the first two groups make the main contribution).[77] The AAS effect depends also on the nature of the trivalent element (Fig. 20).[74,78] In the case of tetravalent and hexavalent actinides, the distribution coefficients increase following the replacement of alkyl groups by phenyl groups, while the extraction constants diminish slightly [there is 'apparent' stabilisation (Fig. 23)]. This can be explained by the

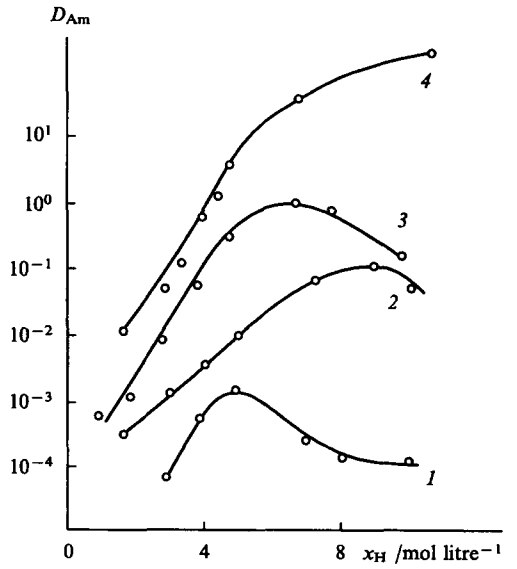


Figure 21. Dependence of the distribution coefficient of americium in extraction by solutions of diphosphine dioxides in dichloroethane (0.01 M) from sulfuric acid (*1*, *3*) and hydrochloric acid (*2*, *4*) solutions on the acidity: (*1*) and (*3*) 4Oct; (*2*) and (*4*) 4Ph.

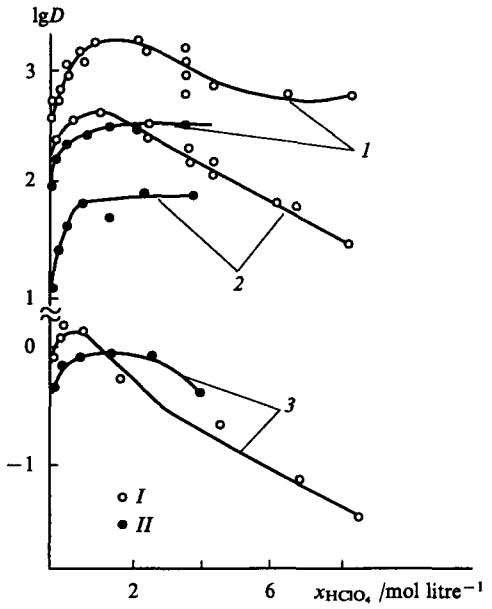


Figure 22. Dependence of the distribution coefficients of americium (*I*) and europium (*II*) in extraction by solutions of methylenediphosphine dioxides in dichloroethane (0.001 M) from perchloric acid solutions.[75]
Extractant: (*1*) 4Ph; (2) 2Oct2Ph; (*3*) 4Oct.

fact that the increment in ΔG due to the AAS ($\sim$3 kcal mol^{-1} for two phenyl groups according to the estimate by Rozen et al.[78]) is insufficient for the given elements to overcome the negative inductive effect of the phenyl groups (we may recall that the coefficients of the sensitivity to electronegativity B in extraction by NOPC are 3.1 for americium and 4.6 for tetravalent and hexavalent actinides, i.e. are much greater). On the other hand, the increase in the distribution coefficient is attained as a result of the suppression of the extraction of HNO_3 by electronegative aryl groups and the corresponding increase in the concentration of the free extractant.[82]

When chloroform is used as the diluent, true AAS is observed for tetravalent and hexavalent actinides (Fig. 20*a*). This can be explained by the enhancement of the oxygen–chloroform interaction in the 4Ph–2Ph2Oct–4Oct series with a corresponding decrease in the EA for oxygen. When chloroform is employed, the solvation number probably increases from two to three[5,76] as a consequence of the depolymerisation of the extractant.[76] Nor can

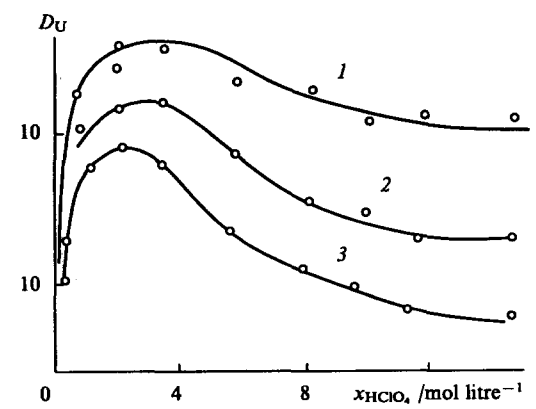


Figure 23. Dependence of the distribution coefficients of uranium in the extraction of uranyl nitrate by methylenediphosphine dioxides (apparent AAS).
Extractant: (*1*) 4Ph; (*2*) 2Oct2Ph; (*3*) 4Oct.

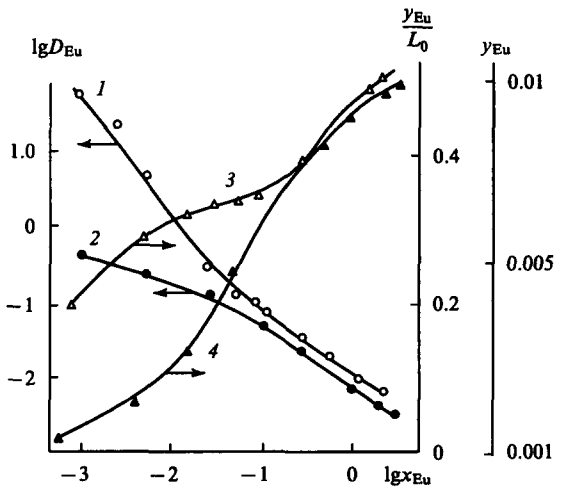


Figure 24. Distribution coefficients (*1*, *2*) and isotherms (*3*, *4*) for the extraction of macroamounts of europium by solutions of methylenediphosphine dioxides in dichloroethane (0.02 M).
Extractant: (*1*) and (*3*) 4Ph; (*2*) and (*4*) 4Oct.

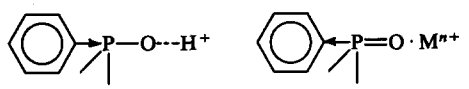
one rule out the interaction of chloroform with the methylene bridge of the dioxide.[78]

An unexpected result was observed in the extraction of macroamounts of europium nitrate by solutions of tetraalkyl- and tetraphenyl-methylenediphosphine dioxides in dichloroethane. Whereas in the extraction of microamounts of americium or europium by the above extractants in dichloroethane the formation of disolvates was observed (according to data concerning the influence of dilution in dichloroethane), in the extraction of europium nitrate the distribution coefficient diminishes rapidly as the extractant is saturated with europium, owing to the formation of a trisolvate [a small plateau is observed on the extraction isotherm (Fig. 24)], after which the distribution coefficients for the extractants are the same.[76]

The anomalous aryl stabilisation in the extraction of americium has been noted also for carbamoylmethylphosphine oxides (Fig. 17);[84–87] as for methylenediphosphine dioxides, the effect is enhanced in perchloric acid solution.[88–90] However, owing to the lower extraction ability of carbamoylmethylphosphine oxides compared with methylenediphosphine dioxides, extraction from sulfuric acid solutions was not observed. Finally, the AAS has been observed[81] in the formation of complexes of alkali metal ions and CuCl with carbamoylmethylphosphine oxides and methylenediphosphine dioxides (Table 8).

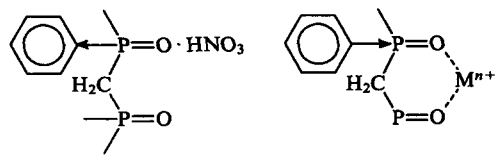
The occurrence of the AAS and the breakdown of relations (4) and (7) in extraction with BDNOPC indicate a significant rearrangement of the extractant molecule on complex formation. Therefore, as in extraction by amides, the prediction of EA on the basis of the characteristics of an isolated extractant molecule becomes incorrect.

The question arises of the nature of the AAS. Calorimetric measurements (unfortunately there has only been one such study[76]) indicate the bonding nature of the effect. A possible explanation, first put forward by ourselves,[22] is the amphoteric nature of the aryl groups. Depending on the electron-accepting capacity of the group to which the phenyl group is attached, the latter may function both as an electron donor and acceptor.[22] Quantum-chemical calculation has shown[22] that in a complex of a monodentate NOPC with a proton (structure **1**), the phenyl group is an electron donor. When the proton is replaced by a metal cation (structure **2**) or an acid molecule, the phenyl group behaves as an electronegative substituent.



1 2

This means that the electron accepting capacity of the group attached to the phenyl substituent in structure **2** is lower than in structure **1** and is insufficient for the conversion of Ph from an electron-accepting into an electron-donating substituent. The same has been observed in the formation of a complex by a BDNOPC with monodentate coordination for example, in the extraction of nitric acid (structure **3**).



3 4

On the other hand, for the bidentate coordination of the extractant to the metal (structure **4**), the six-membered ring formed has a reduced electron-accepting capacity and the phenyl group is converted from an electron acceptor into an electron donor.

The disappearance of the AAS when the phenyl group is separated from the phosphorus atom by a CH_2 group (in the extraction of the tetrabenzyl derivative of methylenediphosphine dioxide) indicates the $\pi-\pi$ conjugation of the Ph group with the PO group, arising on formation of the complex (a six-membered ring) and also on delocalisation of the electron density from the Ph group to the ring. The decrease in the AAS almost by three orders of magnitude when the methylene bridge between the phosphorus atom is replaced by an ethylene group, its complete disappearance after the introduction of a propylene bridge (Fig. 25), and its restoration when a vinylene bridge is introduced (despite the expansion to a seven-membered ring), as well as the high mobility of the protons of the methylene bridge† in the complex also indicate the chemical nature of the effect. One may postulate that the ring is 'aromatised' — the formation of a single system of conjugated bonds.

Thus there are arguments in support of the chemical (electronic) nature of the AAS effect. On the other hand, some evidence indicates its entropic character. Firstly, this conclusion has been reached[74] on the basis of the determination of the enthalpy of extraction from the temperature variation of the concentration extraction constant for trivalent americium in the series 4Oct – 2Oct2Ph – 4Ph (Table 9). Secondly, the changes in the extraction of HNO_3, in the IR spectra of the PO group, and in X-ray photoelectron spectra indicate a decrease in the electron-donating capacity of the oxygen atom in the phosphoryl group in the above series (which, admittedly, does not rule out stabilisation on complex formation and cyclisation via the metal cation).

† Shcherbakova has shown[76] that these protons aquire the capacity for deuterium exchange, which is absent in the isolated extractant molecule.

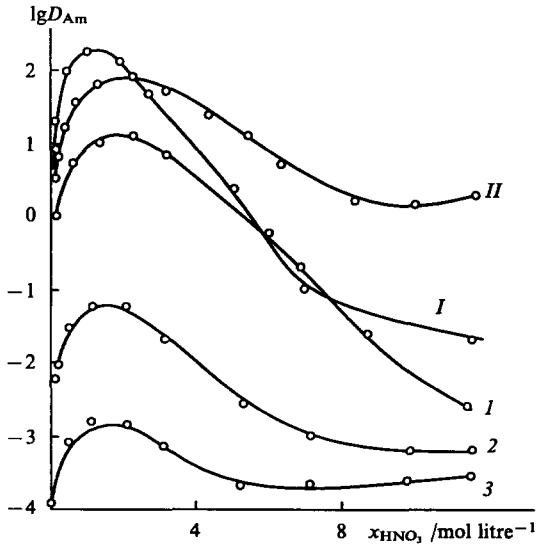


Figure 25. The influence of the length and structure of the bridge on the extraction of americium by *cis*-$R_2P(O)CH=CHP(O)R_2$ and $Ph_2P(O)(CH_2)_nP(O)Ph_2$.
Extractant: (*I*) *cis*-4Tol with a vinylene bridge; (*II*) *cis*-4Ph with a vinylene bridge; (*1*)–(*3*) 4Ph$(CH_2)_n$, where n = 1 (*1*), 2 (*2*), 3 (*3*).

Table 9. The americium extraction constants and the enthalpies of extraction calculated from their temperature dependence (0.01 M solutions of the extractants in dichloroethane).[74]

Parameter	4Oct	2Oct2Ph	4Ph	4Ph$(CH_2)_2$
K_{Am}	1.5×10^7	1×10^8	6.3×10^8	5×10^5
$-\Delta H$ (calc) /kcal mol^{-1}	15.0	14.2	13.0	11.6

In their study of the extraction of Am(III) by carbamoylmethylphosphine oxides, Chiarizia and Horwitz[91] noted that the AAS is observed only for a high polarity of the diluent (when the diluent parameter ID > 3, for example, nitrobenzene, nitromethane, and chloroform). In weakly polar media (tetrachloroethene, carbon tetrachloride, and *o*-xylene) the effect is absent; the solvation number then increases from 2 to 3. Taking into account these data, the authors concluded that the AAS is an effect of the diluent. However, by analysing our results,[83] we found that in extraction by methylenediphosphine dioxides the AAS effect is observed also when a weakly polar solvent (benzene) is employed (Fig. 26). It may be that the results of the above study[91] can be accounted for by the loss of bidentate coordination with increase in the solvation number. At the same time Japanese investigators,[92,93] who studied the NMR spectra, showed that carbamoylmethylphosphine oxides in trisolvates are coordinated as bidentate species to cerium and europium atoms. Admittedly, the highly polar deuterochloroform was used as the diluent, which may be the reason for the retention of the bidentate coordination.

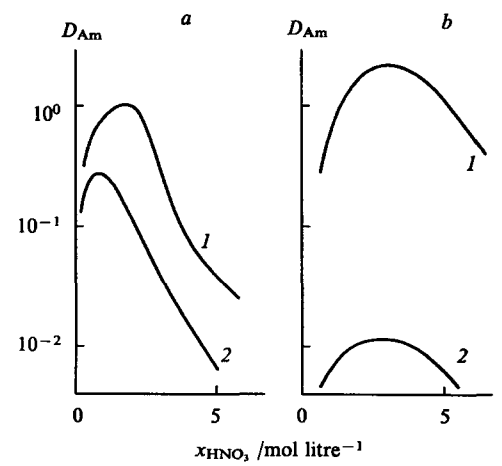


Figure 26. Isotherms for the extraction of americium(III) by 0.01 M solutions of methylenediphosphine dioxides in benzene (*a*) and chloroform (*b*).
Extractant: (*1*) 4Ph; (*2*) 2Ph2Oct.

Thus the causes of the AAS have not been fully established and the contributions of the electronic and entropic effects have not been separated. Despite this, the AAS effect is useful in practice. In contrast to monodentate NOPC, including phosphine oxides which extract effectively tetravalent and hexavalent actinides but are ineffective in the extraction of trivalent actinides and lanthanides, the bidentate NOPC, especially those containing aryl groups, extract trivalent actinides with very high distribution coefficients.

The extraction ability of BDNOPC is influenced by the length and structure of the alkylene bridge. It was found that this influence depends both on the nature of the substituents in the BDNOPC molecule and on the properties of the compound extracted. For example, in the extraction of uranyl nitrate by alkylenediphosphine dioxides with alkyl substituents, the influence of the length of the bridge is small and the highest EA is observed in the case of the ethylene bridge (Fig. 27 *a*).[94] The chelation effect is then small (<10), but, if uranyl nitrate is replaced by the perchlorate, the chelation effect is 10^5 and is suppressed on lengthening the bridge, i.e. the AAS effect, which is suppressed following an increase in the length of the bridge, is observed. In the case of aryl substituents, the effect of the bridge length is very strong (Figs 25 and 27) probably because the AAS effect is suppressed; in the case of the propylene bridge, the EA is lowest and corresponds to the electronegativity of the aryl

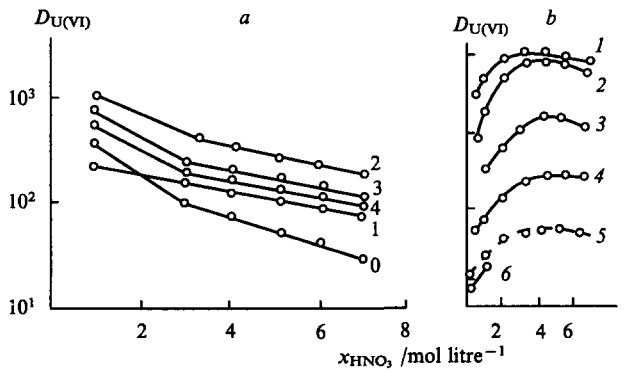


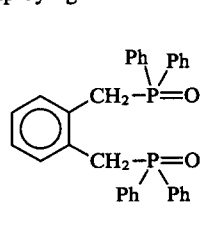
Figure 27. The influence of the length and structure of the bridge on the extraction of U(VI) by diphosphine dioxides.
(*a*) Extraction by tetrahexylalkylenediphosphine dioxides; the numerals opposite the curves indicate the length of the alkylene bridge; (0) extraction by TOPO; (*b*) extraction by dioxides with vinylene and alkylene bridges.
Extractant: (*1*) *cis*-4Tol; (*2*) *cis*-4Ph; (*3*) 4Ph; (*4*) 4Ph$(CH_2)_2$; (*5*) $EtPh_2PO$; (*6*) *trans*-4Ph.

substituents. As we have already mentioned, when a vinylene bridge is introduced in the *cis*-position, the conjugation and the AAS are restored but in the case of uranyl nitrate an appreciably higher EA is attained than for the dioxide 4Ph,[95] while in the extraction of americium the EA is lower[88] (Figs 27*b* and 25) by an order of magnitude in nitric acid and by as much as three orders of magnitude in perchloric acid. The dioxide with a vinylene bridge 'catches up' with the dioxide 4Ph only when the phenyl substituents are replaced by tolyl substituents (Fig. 25). Apparently the electronic and steric effects also play a role in this case. We may note that the difference between the shapes of the $D = f([HNO_3])$ curves for UO_2^{2+} and Am^{3+} can be explained by the difference between the stoichiometries: in the reaction with UO_2NO_3, the monosolvate is formed together with the disolvate,[95] which lowered the displacing effect of HNO_3 and shifts the maximum in the distribution coefficient towards higher nitric acid concentrations.

The study of the influence of the replacement of hydrogen in the methylene bridge of methylenediphosphine dioxides and carbamoylmethylphosphine oxides by various substituents, for example, in the compounds $Ph_2P(O)CHY(O)PPh_2$ (Y = C_3H_7, CH_3, or Cl) in the extraction of the actinides, showed that in all cases such replacement lowers appreciably the distribution coefficients.[87,97,98] We found[97] that the AAS vanishes for Y = C_6H_5, i.e. both protons of the methylene bridge are needed for the appearance of the effect. Despite the decrease in EA, which is particularly marked (by four orders of magnitude) in perchloric acid solution, the selectivity diminishes. However, in the case of the methylenediphosphine oxide 4Ph, the introduction of a pyridine group into the methylene bridge increases significantly the distribution coefficient for the transplutonic element/lanthanide element pair.[100] For alkali metals, the introduction of methyl groups into the bridge increases the stability of the complexes.[81] Steric effects apparently play an important role.

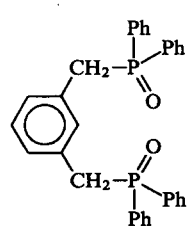
The influence of substituents in the benzene ring on the EA of the tetraarylmethylenediphosphine dioxides 4Ar in chloroform has been investigated[101] in relation to the extraction of uranium (trisolvates are extracted; $K_U = 0.7 \times 10^8$ may be found from the data[101] for 4Ph). On passing from the unsubstituted phenyl group to *p*-tolyl (i.e. after the introduction of the CH_3 group into the benzene ring), the extraction constant increased by a factor of 1.5; after the introduction of a *p*-CH_3O group, the increase was by two orders of magnitude; the CH_3O group in the *meta*-position does not increase the degree of extraction. The replacement of CH_3O by C_4H_9O causes an additional increase in the constant by a factor of ~ 2. The introduction of halogen-containing groups diminishes the solvation number from 3 to 2 and leads to a very marked decrease in the degree of extraction: for Ar = ClC_6H_4, BrC_6H_4, *p*-$CF_3C_6H_4$, and *m*-$CF_3C_6H_4$, the extraction constants are respectively 130, 110, 70, and 14, i.e. diminish with increase in the electronegativity of the groups introduced. When alkyl groups attached to phosphorus atoms were introduced into the benzene rings of carbamoylmethylenephosphine oxides,[102] an increase in the degree of extraction was observed, as for methylene diphosphine dioxides. The influence of the substituent at the nitrogen atom on the EA of carbamoylmethylphosphine oxides has also been investigated;[103] it proved to be weak and, when a phenyl group was introduced, there was no AAS effect.

Chmutova, Myasoedov, and coworkers[104,105] investigated the extraction of nitric acid, americium, uranium, and plutonium by bidentate organophosphorus compounds with a rigid bridge (a benzene ring fragment) — the *ortho*- and *meta*-isomers of xylylenediphosphine dioxides (see also Rozen's review[79]). It was found that the introduction of two $CH_2P(O)Ph_2$ groups in the *ortho*-position increases the selectivity of the separation of the U/Pu and Pu/Am pairs: the separation factor reaches $10^3 - 10^4$. This result has no practical significance (such separation factors are obtained also in extraction by TBP), but it is important because it indicates a possible way of increasing the selectivity by employing steric hindrance or rigid units ‡.[99]



ortho-isomer

5



meta-isomer

6

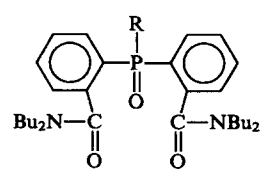
‡ The idea that rigid units should be used to improve selectivity is due to Kabachnik.[100]

It is of interest that the *meta*-isomer of tetraphenylxylylenediphosphine **6** exhibits a much lower selectivity and basicity than the *ortho*-isomer **5**,[194,105] but it extracts actinides with appreciably greater distribution coefficients. The degree of extraction of americium by the *meta*-isomer is higher by three orders of magnitude — for example, $K_{ex\,o} = 3.26 \times 10^2$ and $K_{ex\,m} = 4.9 \times 10^5$ for tetra(*p*-tolyl)xylylenediphosphine dioxide. On the other hand, the degree of extraction of uranium and plutonium increases only severalfold on passing from the *ortho*- to the *meta*-isomers. The uranium/americium separation factor therefore diminishes by two orders of magnitude. These surprising results were explained[106] by the fact that, owing to steric hindrance, in the extraction by the *ortho*-isomer only complexes involving monodentate coordination are formed with the actinides. Under these conditions, the trivalent elements are poorly extracted (as in extraction by TBP), so that the An(IV)/An(III) or An(VI)/An(III) separation improves. On the other hand, in extraction by the *meta*-isomer complexes involving bidentate coordination are formed as a consequence of the decrease in steric hindrance, the degree of extraction of americium increases, and the Am/U and Am/Pu separation is less effective.

Judging from data on the extraction of nitric acid by tetraphenylxylylenediphosphine dioxide, the *meta*-isomer should be more basic: $K_{1o} = 0.0336$, $K_{1m} = 0.51$. This has also been confirmed by the AM1 quantum-chemical calculation: the *meta*-isomer forms more stable complexes with nitric acid than the *ortho*-isomer ($\Delta H = -8.6$ and -7.1 kcal mol^{-1} respectively), which agrees with the observed difference between the extraction constants. It has been suggested[106] that, in the determination of *ortho*-isomer basicity by titrating the reagent with perchloric acid in nitromethane, a complex involving the bidentate coordination of the proton is formed. This in fact leads to an increased formal basicity. Indeed, our calculations by the AM1 method have shown that the *ortho*-isomer effects the bidentate coordination of the proton (the distance between the oxygen atoms of the phosphoryl groups is $R = 2.3$ Å) and with a much higher interaction energy (PA = 256.2 kcal mol^{-1}) than the *meta*-isomer, for which the coordination of the proton is monodentate ($R_{O\ldots O} = 6.1$ Å, PA = 224.1 kcal mol^{-1}). On the other hand, the *meta*-isomer forms a more stable complex with the lithium cation than the *ortho*-isomer ($R_{O\ldots O} = 2.8$ and 3.9 Å, $\Delta H = -41.8$ and -6.8 kcal mol^{-1}).

A phenomenon resembling the true AAS has been observed in such systems for a ten-membered ring.[105] The americium extraction constants have been determined for tetra(*p*-tolyl)-*m*-xylylenediphosphine and tetrabutyl-*m*-xylylene dioxides as 4.89×10^5 and 2.5×10^5 respectively. However, an americium extraction constant of 1.45×10^4 has been found for tetraphenyl-*m*-xylylenediphosphine dioxide, i.e. there is no true aryl stabilisation. Apparently for this ring size the energy increment corresponding to the AAS (~1 kJ per mole of Ph) is small and is insufficient to overcome the negative inductive effects of the phenyl group; the operation of steric factors may also prove to be important.

Carboxylic acid diamides are also effective bidentate extractants, for example, $CH_2[C(O)NOctMe]_2$, which has been proposed as an extractant for the actinides.[107] The tridentate dicarbamoylphosphine oxides **7** are interesting because the AAS effect is observed when the methyl group is replaced by the phenyl group.[108]



7

The study of extraction by polyphosphine oxides containing three and four phosphoryl groups showed that the increase in EA compared with that of the dioxides was insignificant.[109]

X. Polydentate neutral extractants — crown-ethers

Polydentate extractants (crown-ethers) are known to be stereospecific. The stereospecificity is manifested predominantly (not always owing to the flexibility of the rings) in the electrostatic interaction occurring in processes involving the extraction of alkali and alkaline earth metals. In the extraction of acids and metal salts (strong electron acceptors), electronic effects, especially EDA interaction play an important role.[110-113]

In order to obtain quantitative data necessary for the determination of the dependence of the EA of crown-ethers on the structure, a study was made[98] of the extraction of nitric acid and plutonium, neptunium, uranyl, and thorium nitrates by crown-ethers of the type 18-crown-6 with different substituents. 18-Crown-6, dibenzo-18-crown-6, dicyclohexyl-18-crown-6, as well as dibenzo-ethers with alkyl or alkoxy-groups introduced into the benzene ring were used.§

The data obtained permit the conclusion that the rules characteristic of extraction by monodentate compounds hold. Thus, with increase in acidity, curves with a maximum (Pu) are observed. These are due to the combination of the salting-out and displacing effects of the acid.[27] The concave initial section of the uranium and thorium extraction isotherms is due to the dissociation of the salts in the aqueous phase. Plutonium and thorium form disolvates with crown-ethers, whilst uranium and HNO_3 form monosolvates. The extraction of actinides by crown-ethers depends greatly on their oxidation state as, in the case where monodentate extractants, for example, TBP, are used. The extraction ability increases in the sequence Th(IV) < Np(IV) < Pu(IV), etc.

At the same time, the equilibria involving crown-ethers are more complex than those involving monodentate extractants. The intense extraction of HNO_3 by crown-ethers is noteworthy: for an acidity > 6 M, it is much more pronounced than the extraction employing the most 'powerful' extractant among the NOPC — the phosphine oxide TOPO (Fig. 28 *a*). The complexes $(HNO_3)_i(H_2O)_h \cdot L$, containing from one to twenty or more acid molecules per ligand molecule, are formed. The equilibrium has been described[110] as the formation of a polymer chain with attenuation (a decrease in the constant for the addition of the last acid molecule with increase in its number). The usual description with the aid of a single constant[111] is inappropriate here. The first extraction constants observed for crown-ethers are higher than for ordinary ethers by two-three orders of magnitude, which indicates polydentate coordination. The thorium extraction isotherm was found to be complex. For thorium, dilution yields an apparent solvation number of 1, whereas according to saturation data it is 2. This contradiction has been explained[110] by the dissociation of the complex in the organic phase. The constants for extraction by crown-ethers are presented in Table 10.

§ The extraction of HNO_3 and actinide nitrates has been investigated by Yakshin and coworkers.[111,112] Unfortunately the complexity of the equilibria in systems with crown-ethers (especially in the extraction of HNO_3, see below) was not taken into account in the above studies, the extraction constant was determined from one point, and a check was not made to make sure that the isotherm as a whole is described for this value of the constant (distribution data are not presented by Yakshin et al.[111]). As a result,the quantitative extraction characteristics found by Yakshin and coworkers[111,112] and quoted in a review[114] are only qualitative and may differ from the true values severalfold.

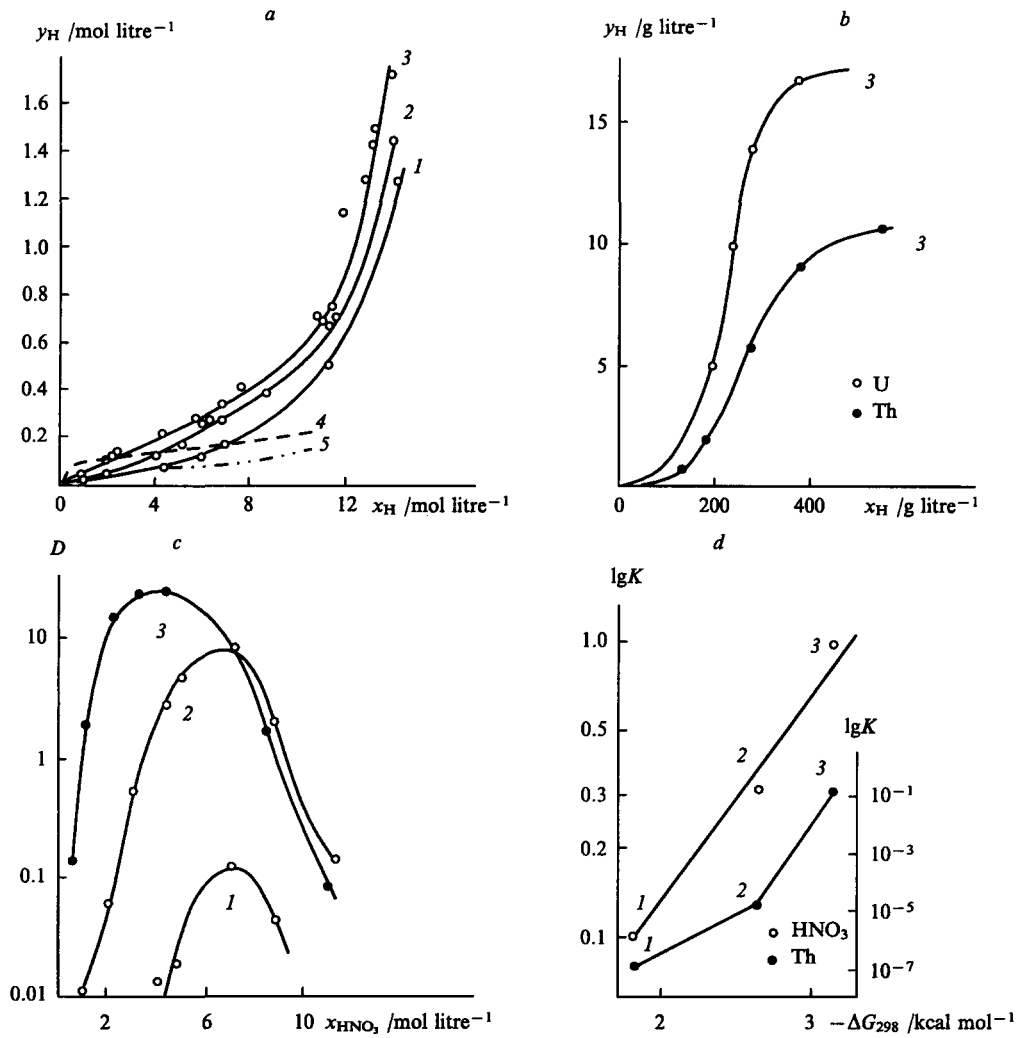


Figure 28. Isotherms for the extraction of HNO_3 (*a*), uranium and thorium (*b*), and plutonium (*c*) by solutions of crown-ethers in dichloroethane (0.1 M) and dependence of the extraction constant on the basicity (the energy of the interaction with phenol) (*d*).
Extractant: (*1*) dibenzo-18-crown-6; (*2*) 18-crown-6; (*3*) cyclohexyl-18-crown-6; (*4*) TOPO; (*5*) TBP.

The dependence of the extraction ability of crown-ethers on structure is similar to that for neutral monodentate compounds. In particular, it is possible to control the EA of crown-ethers by varying the substituents. According to Eqns (4) and (7), EA increases with decrease in the electronegativity of the substituents (phenyl < alkyl < cyclohexyl) and the corresponding increase in the basicity of the crown-ether (for example, the energy of the reactions of the ethers with phenol[113]) in the series dibenzo-18-crown-6 < 18-crown-6 < dicyclohexyl-18-crown-6 (Fig. 28 *d*).

The nonlinearity of the correlation may be associated with an insufficiently correct allowance for the solubility of 18-crown-6 in the aqueous phase. The introduction of alkyl groups into the benzene ring of dibenzo-18-crown-6 has little effect on its EA, while an alkoxy-group increases the EA to the level of the EA of 18-crown-6 (i.e. the same rules are observed as in extracton by BDNOPC, but they are less stringent).

The results constitute fairly convincing proof of the important role of electronic factors. A detailed survey of data on the extraction properties and the complex-forming capacities of crown-ethers may be found in a monograph.[114] Different contributions to the complex-formation energy have been analysed.[115,116]

Unfortunately crown-ethers extract trivalent actinides and lanthanides very weakly (the basicity of the oxygen in the ether group is low). It would be useful to develop macrocyclic extractants for the extraction and fine separation of trivalent actinides and lanthanides.

Table 10. The concentration ($\tilde{K}$) and effective (K) constants for extraction by crown-ethers (0.1 M in dichloroethane).[110]

	HNO_3	$UO_2(NO_3)_2$	$Th(NO_3)_4$	$Pu(NO_3)_4$	$Np(NO_3)_4$
Dibenzo-18-crown-6					
$\tilde{K}$	0.1 (0.026)	0.004 (0.062)	6.5×10^{-10}	~5	–
K	–	0.01	1.6×10^{-7}	–	~1.5
18-Crown-6					
$\tilde{K}$	0.3 (0.036)	– (0.036)	3.0×10^{-8}	~40	–
K	0.01	–	1.0×10^{-5}	–	~5
Dicyclohexyl-18-crown-6					
$\tilde{K}$	1.0 (0.50)	0.20 (0.72)	5.0×10^{-4}	~1000	–
K	0.15	0.5	0.1	–	~100

Note. The numbers in brackets represent the data from Refs 111–113.

XI. Organic acids

Organophosphorus acids (R^1R^2POOH) and carboxylic acids (RCOOH) are frequently used as extractants. The presence of the functional groups PO and OH in the organophosphorus acids and of CO and OH in carboxylic acids permits the extraction of a metal via both the cation-exchange and solvate or mixed mechanisms. We shall consider these mechanisms in relation to organophosphorus acids (OPA).

1. Extraction via the cation-exchange mechanism

The cation-exchange extraction mechanism predominates in the weakly acid region. When account is taken of the dimerisation of the acid, the process is described by Eqn (3) and the extraction ability is characterised by the equilibrium constant of this reaction. The metal cation extracted replaces the proton of the organic acid and is at the same time coordinated to the oxygen atom of the phosphoryl group.

Thus both functional groups (PO and OH) participate in the coordination. This is the reason for the characteristic feature of the influence of the structure of the OPA on their extraction ability in extraction via the cation-exchange mechanism. The change in the electronegativity of the substituents X has the opposite effect on the reactivity of the groups PO and OH: with increase in the electronegativity, the strength of the acid and the EA of the OH group increase, but the electron-donating capacity and the extraction ability of the oxygen atom of the phosphoryl group diminish.[34] As a result, in contrast to NOPC for which the dependence of EA on the structure is universal, in extraction by OPA the nature of the influence of the structure depends on the nature of the element extracted and on the way in which this element reacts with each centre. Thus the acid strength and the degree of extraction of trivalent actinides and lanthanides, which form predominantly an ionic bond and are weakly coordinated to the oxygen atoms of the PO group, increase in the series R_2POOH–R(RO)POOH–$(RO)_2PCOH$ (i.e. with increase in the electronegativity of the substituents). Conversely, the degree of extraction of tetravalent and hexavalent actinides, which are strongly coordinated to the PO group (they form predominantly a covalent bond) weakens in this series (Fig. 29). One may assume that[6,34,49]

$$\lg \tilde{K}_{ex} = A' + (B_{OH} - B_{PO})\Sigma X. \qquad (11)$$

In the extraction of trivalent actinides and lanthanides, $B_{OH} > B_{PO}$ and the extraction ability of OPA increases with increase in the electronegativity of the substituents. $B_{OH} < B_{PO}$ in the extraction of uranyl, so that the opposite dependence of EA on the electronegativity holds.

The above explanation was confirmed also by semi-empirical AM1 and PM3 quantum-chemical calculations.[117] We used the enthalpy (ΔH_{exch}) of the gas-phase exchange reaction as a characteristic of the EA

$$(HY)_2 + Kat^+ = (HY \cdot KatY) + H^+ .$$

In the determination of ΔH_{exch} (in contrast to the determination of the enthalpy of the extraction reaction), no account was taken of the hydration energies of protons and cations (transhydration energies), which remain unchanged if only the extractant is varied. The assumption that the nonspecific solvation has only a slight effect on the process energy relations is therefore fully justified. The overall process may be represented as consisting of two stages: (1) deprotonation of the acid dimer molecule; (2) formation of cyclic complexes. ΔH_{exch} is the sum of the enthalpies of these reactions. The acids R^1R^2POOH, where R^1, R^2 = R, RO (R = Alk), and Cl, were examined and model ions were chosen as the acceptor (Kat^+) — 'hard' $AlBr_2^+$ and 'soft' (HgH^+). According to Pearson's theory, the former ion should form predominantly ionic bonds and the latter predominantly covalent bonds.

As can be seen from Fig. 30, the calculated ΔH_{exch} increases for $AlBr_2^+$ and decreases (slightly) for HgH^+ with increase in acid strength in the series R_2POOH–RORPOOH–$(RO)_2POOH$–Cl_2POOH, which agrees with the experimental extraction data presented above.

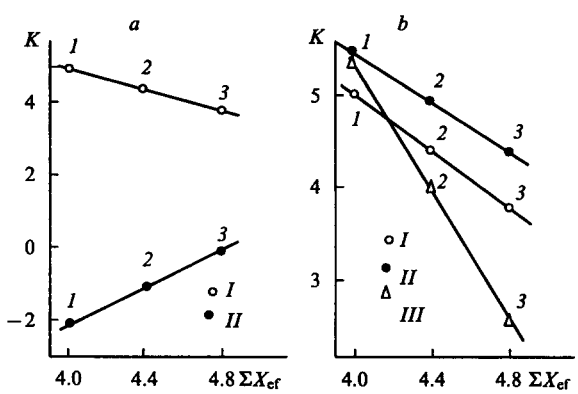


Figure 29. Dependence of the extraction ability of organophosphorus acids [the $(RO)_2POOH$ (*1*) – RORPOOH (*2*) – R_2POOH (*3*) series] on the sum of the effective electronegativities.
(*a*) Constants for the extraction of UO_2^{2+} (*I*) and Am^{3+} (*II*) via the ion-exchange mechanism; (*b*) constants for the extraction of UO_2 via the ion-exchange (K_1) (*I*), exchange-solvate (K_{12}) (*II*), and solvate (K_2) (*III*) mechanisms.

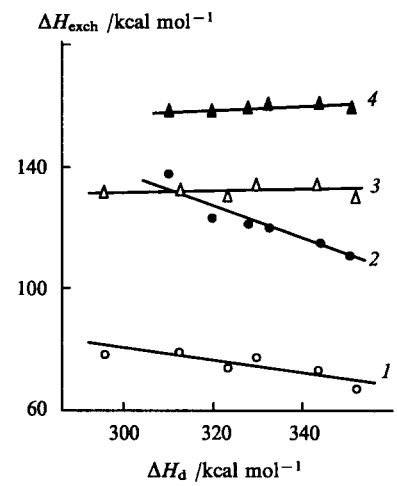


Figure 30. Dependence of the enthalpy (ΔH_{exch}) of the exchange reaction between organophosphorus acids and $AlBr_2^+$ (*1*, *2*) and HgH^+ (*3*, *4*) on the enthalpy of the organophosphorus acid deprotonation reaction (ΔH_d). Calculation by the AM1 (*1*, *3*) and PM3 (*2*, *4*) methods.

Figure 31 presents the variation of constants for the extraction of trivalent americium and promethium by organophosphorus acids over a wide range of variation of ΣX and the acid strength (p*K*).[118] Evidently, by increasing the electronegativity of the substituents and hence the acid strength, it is possible to increase the extraction of trivalent lanthanides and actinides by several orders of magnitude. Alkylphenylphosphoric acid has the highest EA (pK = 1.4);¶ a further increase in EA could probably be achieved by the replacement of the alkoxy-group by PhO (pK = 0.8) and ClC_6H_4O (pK = 0.2).

¶ The quality of the correlation is unsatisfactory possibly because we employed old data; as in the case of NOPC, an effective electronegativity (X_{ef} = 2.2) had to be introduced for the RO group.

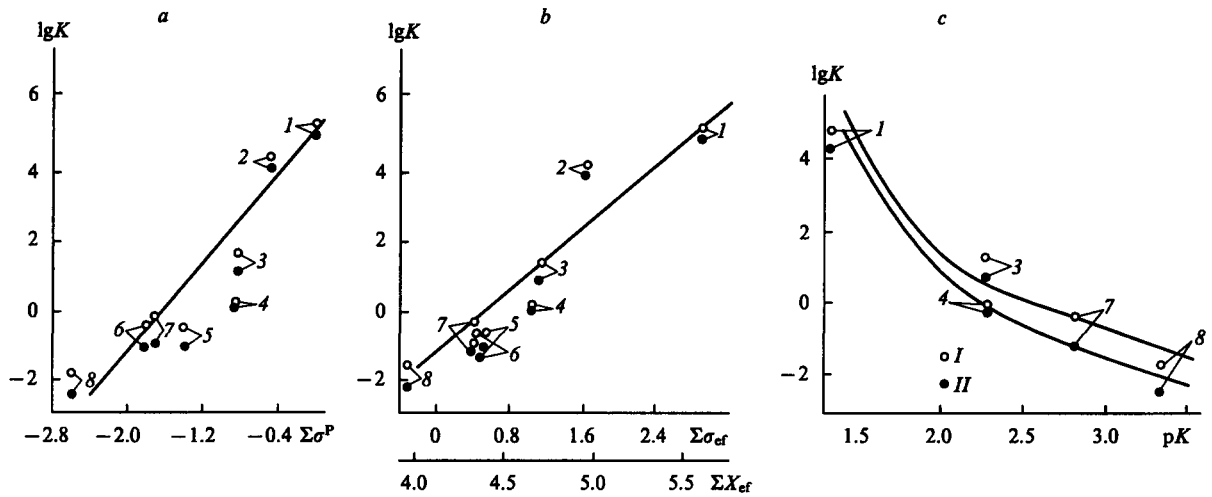
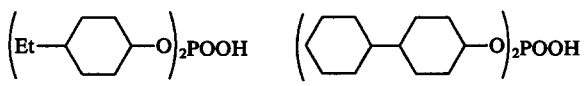


Figure 31. Dependence of the constants for the extraction of promethium (*I*) and americium (*II*) by the organophosphorus acids R^1R^2POOH on the Kabachnik (*a*) and Taft (*b*) substituent constants and p*K* (*c*) over a wide range of basicities.
Extractant: (*1*) ROC_6H_5L; (*2*) $ROClCH_2L$; (*3*) ROC_6H_5L; (*4*) $(RO)_2L$; (*5*) $ROCH_3L$; (*6*) RC_6H_5L; (*7*) RORL; (*8*) R_2L, where R = di-2-ethylhexyl and L = POOH.

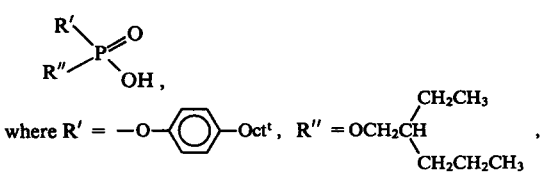
Together with the increase in EA, an important aspect of the improvement of OPA as extractants is, firstly, an increase in the phase stability of their complexes as a result of the suppression of polymerisation which leads to the formation of gels insoluble in the diluent and reducing the capacity of the extractant; secondly an increase in selectivity, especially in the separation of lanthanides and actinides. Both problems can be solved by optimising the hydrocarbon chain. About 30 years ago, diethylhexylphosphoric acid (D2EHPA) began to be used. It exhibits a higher selectivity and phase stability than di-n-octylphosphoric acid as a result of the branching in the β-position. However, it has been recently observed that free D2EHPA and some of its complexes are polymerised to an extent exceeding dimerisation.[119,120] A further improvement of the properties of OPA by lengthening the hydrocarbon chain is possible, but a better solution has been proposed[121] — the replacement of alkyl substituents by the bulky ethylcyclohexyl [diethylcyclohexylphosphoric acid (DiECHPA)] or cyclohexylcyclohexyl [dicyclohexylcyclohexylphosphoric acid (DiCHCHPA)] substituents:



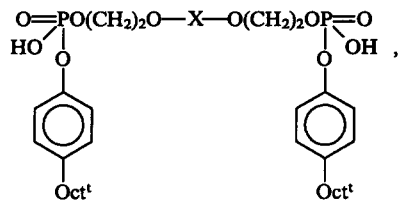
DiECHPA DiCHCHPA

The bulky substituents suppress polymerisation in the extraction of the lanthanides; the formation of gels was not observed and the capacity c_M/c_{HR} increased (for example to 40% and 35% respectively in the case of neodymium instead of 25% for D2EHPA) and the total energy of the complexes $Nd(HR_2)_3$, calculated by the molecular modelling method, increased by a factor of 2 and 3 — from 550 for D2EHPA to 1120 for DiECHPA and 1700 kcal mol^{-1} for DiCHCHPA. There was also a significant increase, compared with D2EHPA in the extraction ability for DiCHCHPA (by 1–2 orders of magnitude) (Fig. 32) and in the selectivity (especially for the La/Ce and Gd/Ho pairs).

It has been shown[122] that the monobasic acid (a D2EHPA analogue)



is a more effective extractant than D2EHPA. It was shown in the above study that dibasic acids having the general formula



are effective for the extraction and separation of the lanthanides. Here X may be $-(CH_2)_2-$, *o*-C_6H_4, or *p*-C_6H_4. The dibasic acid containing a phenyl group in the *para*-position (*p*-DA) in the middle of the bridge proved to be the most effective and selective (predominantly in relation to the heavy lanthanides). The authors explain their results by the steric hindrance generated by the bridge and the advantage of *p*-DA by the rigidity of the bridge with a phenyl group in the *para*-position. It is noted that *p*-DA is

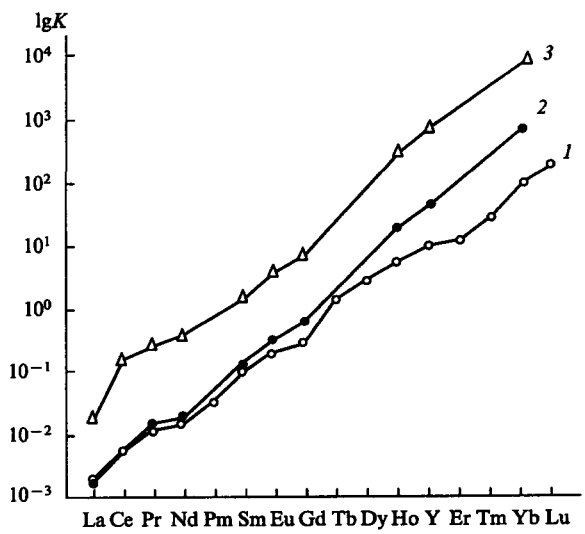


Figure 32. Dependence of the extraction equilibrium constant on the atomic number of the lanthanide.
Extractant: (*1*) D2EHPA; (*2*) DiECHPA; (*3*) DiCHCHPA.

Table 11. Extraction of the lanthanides by the organophosphorus acids R^1R^2POOH.

R^1	R^2	pK_a	lgK_{ex}				$\beta_{Sm/Nd}$	$\beta_{Yb/Y}$
			Nd	Sm	Y	Yb		
$PenCHMeCH_2CH_2O$	$PenCHMeCH_2CH_2O$	3.25	1.56	2.23	4.36	5.23	4.68	7.41
$PenCHMeCH_2CH_2$	Me_3CCH_2O	4.15	−0.55	0.61	2.86	3.75	14.45	7.76
$PenCHMeCH_2CH_2$	$BuCHEtCH_2O$	4.21	−0.99	0.12	2.55	3.61	12.88	11.48
$PenCHMeCH_2CH_2$	HexCHMeO	4.37	−1.46	−0.51	1.89	2.94	8.91	11.22
$PenCHMeCH_2CH_2$	$PenCHMeCH_2CH_2O$	4.08	−0.81	0.34	2.75	3.99	14.13	17.38
Pr^i	Me_3CCH_2O	4.37	−0.80	0.86	2.76	3.24	45.71	3.02
Pr^i	$PenCHMeCH_2CH_2O$	4.36	−0.56	0.61	2.59	3.72	4.79	13.49
$BuCHEtCH_2O$	Me_3CCH_2O	4.39	−1.19	−0.14	2.21	3.14	11.22	8.51
$BuCHEtCH_2O$	$PenCHMeCH_2CH_2O$	4.42	−1.45	−0.40	1.88	2.91	11.48	10.72
HexCHMe	Me_3CCH_2O	4.51	−1.24	0.11	2.22	2.71	22.39	3.09
HexCHMe	$PenCHMeCH_2CH_2O$	4.37	−0.92	−0.06	2.30	3.31	7.20	10.23
$PenCHMeCH_2CH_2$	$PenCHMeCH_2CH_2$	5.12	−2.20	−1.27	0.93	2.06	8.51	13.49

Note. The following designations have been adopted: Pen = C_5H_{11}; Hex = C_6H_{13}.

present in solution as the trimer (the remaining dibasic acids are dimerised).[122]

Interesting results have been obtained in the study of Yuan et al.[123] The influence of steric factors was investigated in relation to the extraction of the lanthanides by alkylphosphonic acids R(RO)POOH with different structures of the alkyl and alkoxy-chains. It was noted that, for a virtually identical basicity ($pK = 4.1-4.5$), the acids differ by an order of magnitude as regards both their EA and selectivity (Table 11). The branching of the alkyl chain increases the degree of separation predominantly of the heavy lanthanides, while the branching of the alkoxy-chain increases the separation of the light lanthanides. The influence of branching is greater the closer it is to the central phosphorus atom.

In the same study,[123] an attempt was made to discover by the molecular mechanics and quantum-chemical methods the optimum conformation of the acids and to investigate the influence of their structure on electronic characteristics.

2. Extraction by the exchange-solvate and solvate mechanisms

We have already mentioned that the extraction by OPA is not confined to the cation-exchange complex-formation mechanism. With increase in the acidity of the aqueous phase, this mechanism is suppressed and new mechanisms arise. We shall examine this problem in relation to the extraction of uranyl as example.

In the weakly acid region, the cation-exchange extraction mechanism predominates; for example, for uranyl we have

$$UO_2^{2+} + 2NO_3^- + 2(HY)_2 \xrightarrow{K_{11}} UO_2(HY_2)_2 + 2(H^+ + NO_3^-).$$

Under these conditions, the distribution coefficient of uranium (like those of other metals) rapidly diminishes with increasing acidity ($D_U \sim x_{HNO_3}^{-2}$). However, as can be seen from Fig. 33, this decrease is replaced by an increase — a minimum and then a maximum in the distribution coefficient is observed (at acidities of 3 and 6 M respectively for D2EHPA).[49,127] This indicates a change in the complex formation mechanism. It has been

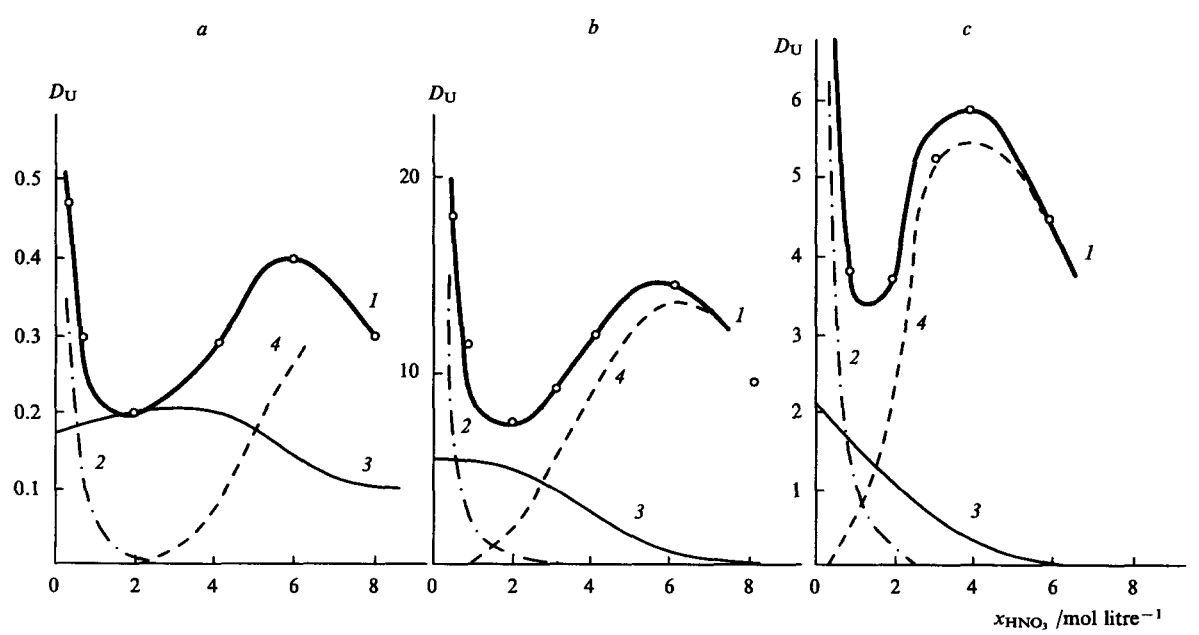


Figure 33. The contributions of different mechanisms to the extraction of U(VI) by diheptylphosphoric (*a*), phosphonic (*b*), and phosphinic (*c*) acids (0.0005 M in *o*-xylene).
(*1*) Experimental data; (*2*) ion-exchange mechanism; (*3*) exchange-solvate mechanism; (*4*) solvate mechanism.

suggested [125, 126] that the cation-exchange extraction mechanism is replaced by the solvate mechanism:

$$UO_2^{2+} + 2NO_3^- + 2(HY)_2 \xrightarrow{K_{22}} UO_2(NO_3)_2 \cdot 2(HY)_2 . \quad (12)$$

However, it has been shown [124, 127] that the ideas of the above workers [125, 126] are too simplified and that the description of the result is erroneous. Agreement with experiment was achieved on the assumption that the activity coefficients of uranyl nitrate in the aqueous phase $\gamma_\pm$ are constant,whereas they increase from 0.5 to 2.5, i.e. by a factor of 5, as the ionic strength is raised from 0.5 to 10, while the value of $\gamma_\pm^3$ in the equation of the Law of Mass Action increases by a factor of 100.

In reality it was found that, as the acidity increases, the second extraction reaction is not reaction (12) but the formation of an exchange-solvate complex containing one inorganic and one organic anion:

$$UO_2^{2+} + NO_3^- + 2(HY)_2 \xrightarrow{K_{12}} UO_2NO_3HY_2(HY_2)_2 + H^+ . \quad (13)$$

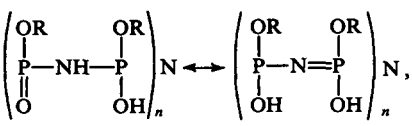
On the other hand, reaction (12) hardly occurs for D2EHPA: $K_{11} = 10^4$, $K_{12} = 3 \times 10^4$, and $K_{22} < 10$, possibly owing to steric hindrance (for di-n-octyl phosphoric and di-n-heptylphosphoric acids, $K_{22} = 5 \times 10^2$, i.e. an appreciable albeit relatively small value).

The role of solvate formation by reactions (12) and (13) increases in the series alkylphosphoric–phosphonic–phosphinic acids, i.e. with increase in the electron-donating capacity of the oxygen atom of the phosphoryl group.[34, 49] The 'sensitivity' of the extraction constant to changes in the structure of the substituents (their electronegativity) in the course of the transition from the ion-exchange to the exchange-solvate and solvate mechanisms intensifies (Fig. 29).

In the extraction of ions of higher valence, the picture becomes more complicated, since there is a possibility of the appearance of several exchange-solvate complexes, for example, the formation of MY_3NO_3, $MY_2(NO_3)_2$, and $MY(NO_3)_3$ for Pu(IV). The hypothesis has been put forward[49] that the symmetrical exchange-solvate complex $MY_2(NO_3)_2$ exists, but no evidence was quoted. We may note that the extraction of Pu(IV), which is effectively coordinated by the oxygen atom in the phosphoryl group,[30] weakens, like that of uranyl, in the series phosphinic–phosphonic–phosphoric acids, i.e. with increase in the electronegativity of the substituents and with decrease in the EA of the PO group.[49]

3. Extraction by bidentate phosphonitrilic acids

The extraction ability of OPA is greatly reduced by dimerisation, which results in the bindmng of both reaction centres — PO and OH. Accordingly there is a possibility of a new way of controlling their EA: the creation of obstacles to dimerisation, for example, the employment of multiunit polyphosphonitrilic acids. These acids have been proposed as extractants by Laskorin et al.[128] Indeed, it has been found[129, 130] that the constants for the extraction of americium and europium by polyphosphonitrilic acids are 8 orders of magnitude higher than the constants for the extraction of these elements by D2EHPA. For the tetravalent and hexavalent actinides, the increase in EA was comparatively small. This can be accounted for by the fact that the intensification of the extraction of Am(III) and Eu(III) was assisted by the imide rearrangement



since the number of OH groups, successfully coordinating trivalent elements, increased, but at the same time the PO groups, which coordinate tetravalent and hexavalent actinides most effectively, disappeared.

An advantage of the polydentate phosphonitrilic acids as extractants is a very high EA, whilst their disadvantage is a low selectivity.

XII. Organic acid salts

The acid salts of certain metals (Zr, Hf, Ti, etc.) are known to exhibit higher EA than the corresponding phosphoric acids.[131–133] This phenomenon is usually explained by the enhancement of the acid properties; the salt [for example, $ZrY_4(HY)_2$] may be regarded as a strong metalloacid (for example, H_2ZrY_6), assuming implicitly that the dependences of EA on the structures of the acids and their salts obey common rules. In this case, one may postulate that the possibilities for increasing the EA of the salts (and hence of increasing the concentration of the inorganic acid at which these extractants are capable of extracting radionuclides effectively) are far from exhausted. Stronger organic acids, for example, sulfonic acids, may be used.

At the same time we do not believe that this is the only explanation, since an increase in acidity may be accompanied by the simultaneous decrease in the energy of the complex formation reaction with the metal cations. Quantum-chemical calculation has shown that OPA salts are indeed stronger extractants than the acids themselves,[117] but the main reason for the differences between the extraction abilities of the OPA and their acid salts with metals are the differences between the energies of the steric strain in the ligands.[134]

The salts of organic acids with inorganic bases, for example R_4NY (binary extraction proposed by Khol'kin[135, 136]) are of great interest as extractants. The binary extractant belongs to the neutral group. For example, the extraction reaction of the acid H_mB takes place in accordance with the equation:

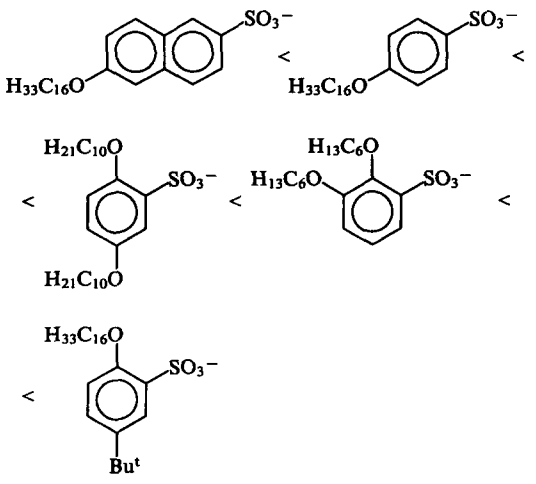
$$mH^+ + B^{m-} + mR_4NY = (R_4N)_mB + mHY .$$

However, the initial section of the extraction isotherm is linear and the distribution coefficient is approximately constant,[135–137] whereas in the extraction by the usual neutral extractants at $x \to 0$, $D \to 0$.[27] It can be shown that the binary process is analogous to extraction by neutral extractants with dissociation of the compounds in the organic phase:

$$mH^+ + B^{m-} + qL_o = mH^+L_{q+} + B^{m+}L_{q-}; mq_+ + q_- = q.$$

In both cases the number of species (ions) does not change in the extraction process, so that we have $D(0) = \text{const}$, when $x \to 0$.[137, 140] However, there are incomparably greater possibilities for controlling the binary process. In particular, the EA of the binary extractant may be increased by employing a weaker acid HY; the extraction constant $K(H_mB) \approx K_a^{-m}$, where K_a is the dissociation constant of the acid HY. This fact has been confirmed in the extraction of inorganic acids and platinum metals.[138] In the latter case, the binary extractants have a great advantage over inorganic salts of amines and quaternary ammonium bases because they do not form insertion complexes and make it possible to achieve back-extraction readily.

We may note that the EA of binary extractants may be determined not only by the strength of the acids but also by the operation of steric factors. For example, the degree of extraction of H_2PdCl_4 by tetraoctylammonium alkyl(alkoxy)sulfonates increases in the series of the following anions derived from sulfonic acids of similar strength:



i.e. it increases with increase in the number of substituents and in the length of the chains of the alkyl groups.[138]

Cobalt dicarbolides, which effectively extract caesium (at HNO_3 concentrations up to 4–6 M), strontium, and trivalent actinides and lanthanides, are unusual acid extractants.[139]

XIII. The influence of diluents on the extraction ability of organic compounds

The nature of the diluent has a comparatively weak influence on extraction by monodentate neutral compounds, for example, NOPC, but has a strong influence on extraction by BDNOPC. What is the explanation? We may recall that the effective extraction constant is[5, 34, 140]

$$K = \frac{K_T \gamma_L^q}{\gamma_c}, \tag{14a}$$

where K_T is the thermodynamic extraction constant, γ_L and γ_c are the activity coefficients of the extractant and the complex respectively, and q is the solvation number. The thermodynamic constant is independent of the nature of the diluent and its influence is determined by the parameter

$$\text{dil} = \frac{\gamma_L^q}{\gamma_c}. \tag{14b}$$

The activity coefficients of the extractant and the complex in basic diluents (saturated and aromatic hydrocarbons, aprotic chloroderivatives) have been determined experimentally in relation to the extraction of uranyl nitrate by TBP [the complex $UO_2(NO_3)_2L_2$][141, 142] and the uranyl salt of D2EHPA [the complex $UO_2(HY_2)_2$],[143] Table 12 presents the values of γ_L and γ_c at zero concentrations of the extractants complexes and also the values of dil(0) and $\text{dil}/\text{dil}_{CCl_4} = D/D_{CCl_4}$. Comparison of the measured values of dil with experimental extraction data indicates satisfactory agreement. The coefficients γ_L for various diluents differ markedly (for example, by an order of magnitude for benzene and hexane). Since in the above systems $q = 2$, one might have expected differences between the parameters dil and D by two orders of magnitude. However, as can be seen from Table 11, the activity coefficients of the complex change 'in the same direction' as γ_L and a compensation takes place — the values of dil and D for various diluents differ little from one another (dilution with chloroform, where dil and D are significantly reduced, is an exception).

In order to understand the results, one has to take into account the fact that the activity coefficients and dil are determined by the operation of three factors:[34] (1) the athermal effect (the increase in entropy on mixing molecules differing in size and shape); (2) van der Vaals forces; (3) chemical interaction (the last factor diminishes both γ_L and γ_c). It can be shown that the effects of the first two factors on γ_L and γ_c cancel out even for the opposite sign of nonideality (for example, for hexane and benzene). The compensation is most complete on formation of monosolvates (in particular, this is why HNO_3 is most sensitive to the nature of the diluent) and is satisfactory on formation of disolvates, but when trisolvates are formed the athermal effects for benzene and CCl_4 cancel out incompletely; since $\gamma^3_{L,atherm} \ll 1$, dil and D decrease compared with saturated hydrocarbon diluents. On the other hand chemical reactions do not cancel out at all. They are in fact decisive, the interaction with the extractant diminishing dil and D while that with the complex increasing them. The chemical interactions with the diluents CCl_4 and C_6H_6 are comparatively weak and do not play any role; in the case of C_6H_{14}, they are altogether absent. On the other hand, the interaction with $CHCl_3$ is significant (a hydrogen bond having an energy of ~5 kcal mol^{-1} is formed with TBP) and is stronger with the extractant than with the complex because in the latter the oxygen of the PO group is blocked by the metal extracted. There is a corresponding significant decrease in γ_L^2 and in the degree of extraction [by a factor of 30 for TBP (Table 11)].

Table 12. Characteristics of diluents based on measurements of the activity coefficients and extraction data.[5]

Parameter	CCl_4	C_6H_6	C_6H_{14}	$CHCl_3$
Extraction of uranyl nitrate by TBP [complex extracted $UO_2(NO_3)_2(TBP)_2$]				
$\gamma_L(0)$	0.38	0.38	4.36	0.01
$\gamma_c(0)$	0.15	0.06	13.3	0.08
$\text{dil}(0) = \gamma_L^2(0)/\gamma_c(0)$	1.0	2.42	1.55	0.013
$\text{dil}/\text{dil}_{CCl_4} = (D/D_{CCl_4})$ (experiment)	1.0	2.35	1.5	0.03
Extraction of uranyl by D2EHTA [complex extracted $UO_2(HR_2)_2$]				
$\gamma_L(0)$	0.052	0.040	0.61	0.0039
$\gamma_c(0)$	0.0047	0.0028	0.15	0.00016
$\text{dil}(0) = \gamma_L^2(0)/\gamma_c(0)$	0.58	0.55	2.44	0.097
$\text{dil}/\text{dil}_{CCl_4}$	1.0	0.95	4.2	0.16
D/D_{CCl_4} (experiment)	1.0	0.97	4.7	0.14

In the absence of appreciable chemical interactions, the activity coefficients of the extractants and the complex are correlated,[34] which makes it possible to describe the influence of the diluent by means of one parameter.[144]

Thus in the extraction of metals and acids by monodentate extractants, the inert diluent does not usually affect the dependence of EA on the structure of the extractants. Hence in the vast majority of the systems investigated, the degree of extraction by the organic oxides R_nXO increases in the sequence TBP < dioctyl sulfoxide (DOSO) < 2-nonylpyridine-*N*-oxide (2-NPO) < triisopentylphosphine oxide (TPPO) regardless of the nature of the diluent and the compound extracted. The extraction of acids by solutions of 2-NPO and TPPO in diluents with different solvating capacities constitutes the few existing exceptions.[145, 146] The relative extraction abilities of these extractants are determined by the form in which the complexes extracted exist, the latter depending on the nature of the acid and the diluent.[145, 146] For example, in the extraction of moderately strong acids (HNO_3) in weakly solvating diluents (heptane, CCl_4, benzene), hydrogen-bonded complexes are formed for both extractants, their extraction constants being higher for TPPO than for 2-NPO. In more strongly solvating diluents (chloroform, 1,2-dichloroethane), the state of the complex with TPPO does not change whereas the complex with 2-NPO exists as an ion pair. Owing to

the increased solvation of the ion pair by the diluent, the extraction constants for 2-NPO are higher than those for TPPO.

For bidentate extractants (diphosphine dioxides and carbamoylphosphine oxides), the influence of the diluent proved very strong (see, for example, Fig. 26). When chloroform, which interacts with the reaction centres of BDNOPC is used, the degree of extraction is reduced, as in the case of monodentate extractants. However, when a polar diluent (dichloroethane), which reacts weakly with oxygen, is employed, a marked increase (almost by two orders of magnitude) in the degree of extraction is observed. Apparently dichloroethane reacts with the complex (possibly with the protons of the methylene group [83]), which, as stated above, leads to an increase in the degree of extraction. When different substituents are introduced into the methylene bridge of methylenediphosphine dioxides and carbamoylmethylphosphine oxides in place of one of the hydrogen atoms, not only does the degree of extraction diminish and the AAS disappear, but the influence of diluents is also significantly weakened.[147] Apparently diluents do indeed interact with the bridge protons[83] and their acidity falls sharply on substitution.

We may note that diluents capable, like chloroform, of reacting with the reaction centres and of blocking them may alter qualitatively the dependence of EA on the extractant structure. If this dependence is described by Eqn (4) and the extractant–diluent interaction constant (K_{Ld}) is described by a similar equation but with other values of the coefficients A′ and B′, the following equation is valid:

$$\lg K = \lg \frac{K_0}{K_{Ld}} = A - A' + (B - B')\Sigma X, \qquad (15)$$

where K_0 is the extraction constant in the absence of interaction of the extractant with the diluent. If $B' > B$, the dependence of $\lg K$ on ΣX may change sign, which is in fact observed in the extraction of tetravalent and hexavalent actinides by methylenediphosphine dioxides when dichloroethane is replaced by chloroform (Fig. 20*a*).

XIV. Examples of the development of new extractants

The regularities described above were used to solve two problems of practical importance in the radiochemical technology.

1. Improvement of the first principal extraction cycle in the regeneration of spent fuel from atomic power plants. Development of an extractant as a substitute for tributyl phosphate

Tributyl phosphate, which is widely used in the radiochemical technology, has optimal extraction properties. It extracts uranium and plutonium very effectively and there is no need for salting-out agents. The second essential operation — back-extraction (stripping) of the above elements — is also carried out comparatively readily if TBP is used; here there is no need for the introduction of additional reagents and it is sufficient to alter the acidity and the temperature of the medium. However, TBP suffers from a series of disadvantages. The main one is the comparatively low solubility of plutonium disolvated by TBP in saturated hydrocarbons. For 30% solutions of TBP in alkanes (with a hydrocarbon chain length $n_C = 12-14$) at room temperature, the solubility exceeds only slightly 30 g litre^{-1} in terms of plutonium. Therefore, in the processing of mixed uranium–plutonium fuel with a high plutonium concentration and also in the refining of plutonium, there is a risk of the formation of a second organic phase and danger of inadmissible process perturbations (in particular, the loss of nuclear safety). Furthermore, TBP is comparatively readily soluble in the aqueous phase, which leads to loss of the extractant, and in refining it can lead to contamination of the product with phosphorus.

In the search for new extractants (taking into account the results described above), it was endeavoured to retain the extraction ability at the level of that of TBP but at the same time to alter the physical properties of the extractant.

It has been shown that EA changes markedly following a change in the chemical nature of the substituents in the extractant molecule and only slightly when the hydrocarbon chain is altered. Consequently, it is necessary to retain the chemical nature of the substituents, i.e. to employ trialkyl phosphates (if phosphonates, even those containing only the electronegative phenyl substituent, are used, difficulties arise with back-extraction). On the other hand, the physical properties may be 'regulated' by optimising the hydrocarbon chain — by increasing its length and by employing branching (this lowers the tendency towards polymerisation, improves compatibility with diluents, and at the same time lowers the solubility in the aqueous phase).

In accordance with these recommendations, the extraction properties of certain trialkyl phosphates, in which the overall length of the hydrocarbon chain varied from 12 (TBP) to 21 (triheptyl phosphate), were investigated. Triisopentyl phosphate (TIPP, $n_C = 15$) and diisobutyl isooctyl phosphate (DIBIOP, $n_C = 16$) proved to be best.[148–150]

The use of TIPP solves the problem of the extraction of plutonium from concentrated solutions, because a second organic phase is not formed even after the complete saturation of the extractant by plutonium. On the other hand, if one goes over to DIBIOP, i.e. the hydrocarbon chain is increased by one more atom, then the second organic phase is ruled out also in the presence of thorium nitrate (Fig. 34). The distribution coefficients differ little from one another when TIAP, TIBIOP, and TBP are used (Fig. 35) and the rates of phase separation are comparable. An advantage of both extractants is reduced (by a factor greater than 10) solubility in the aqueous phase, which diminishes the contamination of the products with phosphorus subject to the condition that mechanical losses have also been eliminated.

Triisopentyl phosphate and diisobutyl isooctyl phlosphate have undergone successful tests on the highly irradiated fuel (100 GW d t^{-1}) in fast reactors (the activity of the solutions was up to 10^3 Ci litre^{-1} and the concentration of plutonium was up to 30 g litre^{-1}). The risk of radiation damage to the extractant was prevented by employing centrifugal extractors with a short phase contact time.

The parameters of the extraction and purification of valuable components were better than in the case where TBP was employed (including its use on a cascade of mixing-settlers).[151] Under the

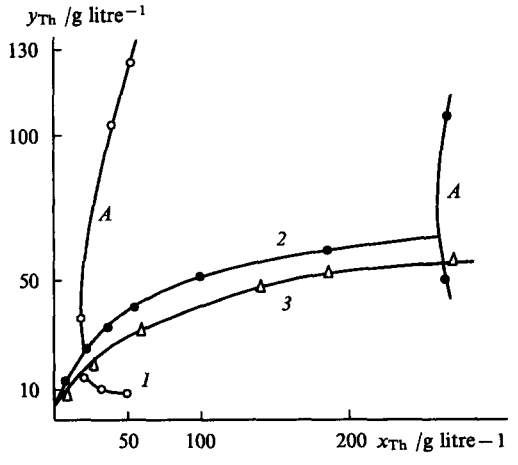


Figure 34. Isotherms for the extraction of thorium by 30% TBP (*1*), 33% TPAP (*2*), and 35% diisobutyl isooctyl phosphate (DIBIOP) (*3*) in *n*-tetradecane.
Concentration of extractant in n-tetradecane (%): (*1*) 30, (*2*) 33, (*3*) 35; *A* – region corresponding to separation into two phases.

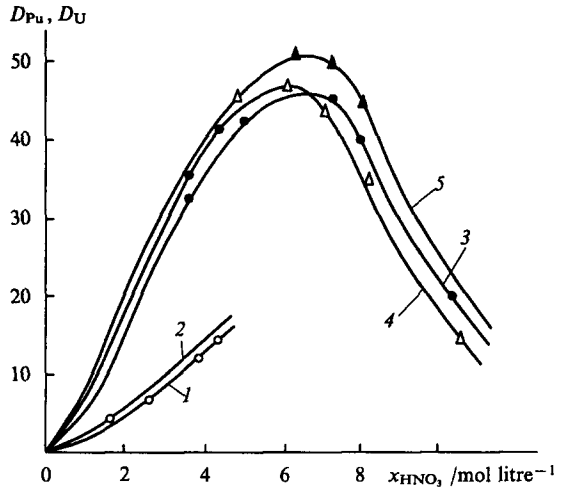


Figure 35. Dependence of the distribution coefficients of Pu(IV) (*1*, *2*) and U(VI) (*3*–*5*) on acidity in extraction by solutions of TBP (*1*, *4*), TPAP (*2*, *5*), and DIBIOP (*2*, *3*) in n-tetradecane.

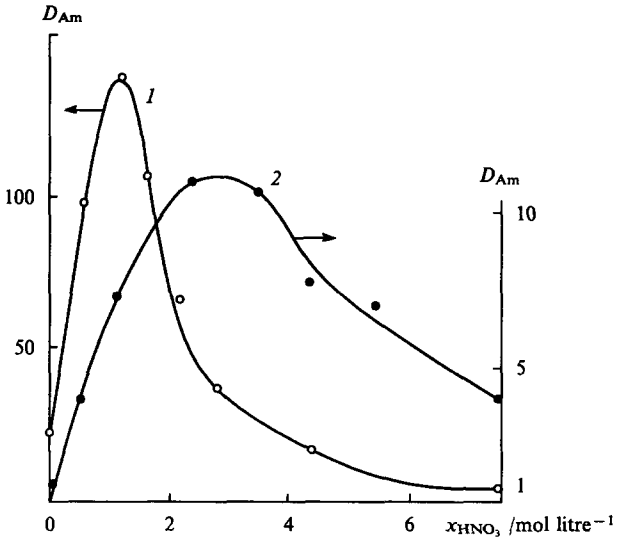


Figure 36. Dependence of the distribution coefficient of Am(III) on acidity in extraction by solutions of 2Tol2Ph (*1*) and Tol_2/Bu_2 (*2*) in trichlorobenzene. Concentration of lanthanides in the aqueous phase 10 g litre^{-1}; concentration of the extractant in the organic phase 0.3 M.

supervision of Nikiforov, Zakharkin, Smelov, and others, triisoamyl phosphate has been used successfully, instead of TBP, on an industrial scale under factory conditions for the regeneration of the spent fuel from water–water power reactors (more than 100 m^3 of the 33% extractant in a hydrocarbon diluent was employed).[152–154] As expected, the new extractant did not introduce negative aspects into the technology: the uranium, plutonium, and neptunium separation factors as well as the decontamination coefficients from radionuclides characteristic of systems with TBP were consistently reproduced. At the same time, it made it possible to reduce appreciably (by a factor of 1.5) the losses of the extractant. This effect is more pronounced if the mechanical loss of the organic phase, which is the same for TIPP and TBP, is eliminated. The employment of TIPP in the refining extraction of plutonium fundamentally expanded the technological possibilities in this stage of the process: the degree of concentration of plutonium was increased and the monitoring of its accumulation in different stages within extractors was simplified.

2. Extractants for the deep extraction of transplutonic elements from radiotechnological waste

Monodentate organophosphorus extractants (even the strongest phosphine oxides, for example, TOPO) are relatively unsuitable for the extraction of transplutonic elements from waste. When TBP is used, it is necessary to introduce a salting-out agent,while phosphine oxides extract americium effectively, but only at a low acidity (up to 0.3 M)[155] and their use requires the neutralisation of the solution. The decrease in the degree of extraction with increase in acidity is associated with the competition by nitric acid for the free extractant: the nitric acid extraction constant is high and the concentration of the free extractant is inversely proportional to it.

Thus an extractant with an increased EA in relation to trivalent actinides and at the same time with a reduced EA in relation to HNO_3 is needed. Surprisingly, these seemingly incompatible requirements can be met by employing the unusual properties of the bidentate organophosphorus compounds — methylenediphosphine dioxides and carbamoylmethylphosphine oxides. Indeed, when electronegative aryl substituents are introduced into the molecules of these compounds, an AAS effect is observed and the extraction of americium and other actinides, involved in bidentate coordination, is enhanced; at the same time, these substituents supprees the extraction of HNO_3, which is involved in monodentate coordination. As a result, a double gain is achieved (Figs 16 and 17): the distribution coefficients of americium increase (compared with the distribution coefficients when phosphine oxides are used) by 3–5 orders of magnitude and a possibility is created for extensive extraction of the actinides from solutions of any acidity without any kind of preparation of the latter.

The extractants recommended in Refs 156 and 177 — carbamoylphosphine oxide and diphosphine dioxides — have undergone a successful test in the processing of the highly irradiated fuel mentioned above (the activity of the initial aqueous solution was ~ 10^3 Ci litre^{-1}).[151] The distribution coefficients are presented in Fig. 36. (In order to simulate the conditions in the extraction from the vaporised refined product in the first cycle, 10 g litre^{-1} of lanthanides was introduced into the aqueous phase.)

The above developments are protected by patents.[148,156]

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