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Chemistry of Extraction by Sulphoxides

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The present state of the chemistry of extraction equilibria involving sulphoxides of diverse structure—aliphatic, cyclic, and also mixtures of petroleum origin—is discussed, and results are given for the extraction of inorganic and organic acids and metal salts from aqueous solution. Comparison of the extraction properties of neutral organophosphorus compounds with those of sulphoxides shows a promising future in liquid extraction for cyclic sulphoxides, especially those of petroleum origin. The mechanism of extraction is discussed, and the dependence of extraction properties on the molecular structure of the sulphoxide is considered. A list of 153 references is included.

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I. INTRODUCTION

Methods for the extraction of metals that have been successfully employed in chemical nuclear technology are now beginning to be widely introduced into the industry of rare and non-ferrous metals. The chemistry of extraction has been very intensively studied in connection with the spread of extraction methods for concentrating and separating elements. The variety of approaches and methods of investigation and the great scope of work on the chemistry of extraction equilibria have ensured the solution of many extraction problems. Methods have been found for extracting almost every element.

Nevertheless, the range of extractants used in industry for the extraction of metals has hitherto been narrow (mainly tributyl phosphate, di(2-ethylhexyl) hydrogen phosphate, and amines) and inadequate for technical processes in the hydrometallurgy of rare and non-ferrous metals. The cost of an extractant is an extremely important factor in its application in the technology of such metals. In this connection there is a very pressing need to find and investigate new and powerful extractants possessing high selectivity and chemical stability while being comparatively cheap and suitable for large-scale manufacture. Another acute problem is the search for extractants to remove various organic compounds such as carboxylic and sulphonic acids and also phenols from industrial solutions and sewage.

Among promising extractants must be included sulphoxides, both individual and those of petroleum origin[1]. Resources for production of the latter are almost unlimited. Tens of thousands of tons of sulphoxides a year can be obtained at negligible cost (400–600 roubles per tonne[2]) from a single fraction of diesel fuel from Arlansk petroleum of the Bashkir ASSR (or West Surgut petroleum of Western Siberia). This is possibly why interest in sulphoxides as extractants for metal salts and acids has grown considerably during recent years among both Soviet and foreign scientists. The number of studies on the extraction properties of sulphoxides increases from one year to the next. Work on the chemistry of complexes of sulphoxides with inorganic and organic compounds has even grown considerably more.

The aim of the present Review is to systematise published data and the Reviewers' own results on the extraction equilibria of sulphoxides with metal salts and acids. Consideration is given to the properties both of individual sulphoxides of diverse structure (aliphatic, aromatic, cyclic with different ring sizes, etc.), as well as sulphoxides of petroleum origin.

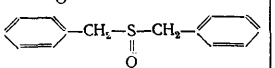
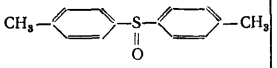
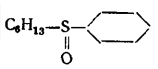
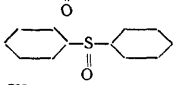
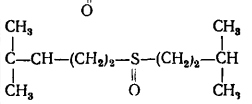
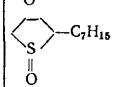
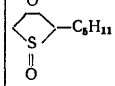
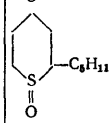
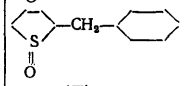
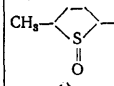
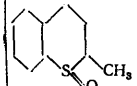
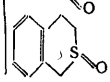
II. PLACE OF SULPHOXIDES AMONG EXTRACTANTS

Sulphoxides are organic oxides containing an S=O functional group. A quasi-tetrahedral configuration is probable for the molecule, in which one of the orbitals of the tetrahedron is represented by the lone pair of electrons of the sulphur atom. The molecular structure of sulphoxides agrees well with the chemical properties and with the assignment of the vibrational frequencies of the sulphinyl bond in the infrared and Raman spectra. Sulphur and oxygen atoms are joined not only by a σ bond but obviously also by interaction of a $3d$ orbital of sulphur with a $2p$ orbital of oxygen ($2p-3d$ hybridisation)[3,4]. Examination of the nature of the sulphur–oxygen bonds in a review[5] led to the conclusion that the electron cloud of an S=O double bond was displaced towards the oxygen atom. Recent studies also confirm a $\sigma + \pi$ bond[6,7].

Interaction of the sulphinyl group with the hydrocarbon substituents attached to the sulphur atom is inductive and electron-accepting in character, without involving conjugation, e.g. with aromatic and unsaturated radicals[8,9]. A carbon atom forming a bond with the sulphur atom is able to act as a donor of electrons (interaction of the lone pair of electrons of the sulphur with π orbitals of the hydrocarbon radical) and also as an acceptor of electrons (interaction of the d orbital of sulphur with π electrons of the hydrocarbon radical). The intramolecular interactions in the sulphoxide molecules and the character of the sulphur–oxygen bond govern the properties of these compounds towards complex formation and extraction. Sulphoxides for which data on these processes have been published are listed in Table 1.

Structure-group analysis of petroleum sulphides[10] indicates that petroleum sulphoxides are mixtures of

Table 1. Properties of most thoroughly studied sulphoxides in complex formation and extraction*.

Sulphoxide	Abbrevn.	Formula	M.p., °C	n_D^{20}	Sulphinyl sulphur, mass %	Ref.
Dimethyl	DMSO	$CH_3-S(=O)-CH_3$	—	1.4780	—	20, 22
Dibutyl	DBSO	$C_4H_9-S(=O)-C_4H_9$	35	—	—	49, 153
Dipentyl	DPSO	$C_5H_{11}-S(=O)-C_5H_{11}$	51	—	16.1	36
Dihexyl	DHSO	$C_6H_{13}-S(=O)-C_6H_{13}$	60	—	14.7	43, 51
Dioctyl	DOSO	$C_8H_{17}-S(=O)-C_8H_{17}$	71	—	—	33, 34
Dodecyl ethyl	DoESO	$C_2H_5-S(=O)-C_{12}H_{25}$	—	—	—	34
Diphenyl	DPhSO	$C_6H_5-S(=O)-C_6H_5$	70	—	15.8	51, 114
Dibenzyl	DBzSO		133	—	—	114
Di-*p*-tolyl	DpTSO		93	—	—	113
Hexyl phenyl	HPhSO	$C_6H_5-S(=O)-C_6H_{13}$	30	—	15.0	51
Cyclohexyl hexyl	ChHSO		48	—	14.7	51
Dicyclohexyl	DChSO		83	—	14.8	51
Di-isopentyl	DIPSO		40	—	16.3	134
Thiolan 1-oxide	TlO		—	1.5195	—	52, 153
2-Heptylthiolan 1-oxide	HTlO		—	1.4820	15.1	36
2-Pentylthiolan 1-oxide	PtlO		—	—	—	42
2-Pentylthian 1-oxide	PThO		—	1.4962	16.0	51
2-Cyclohexyl-methylthiolan 1-oxide	ChMTlO		—	1.5204	15.3	36
2-Butyl-5-methyl-thiolan 1-oxide	BMTlO		—	1.4885	17.8	105
3-Methyl-2-thia-bicyclo[4,4,0] decane 2-oxide	MTBDO		44	—	16.4	36
1,2,3,4-Tetrahydro--2-thianaphthalene 2-oxide	THThNO		77	—	18.2	36

*Different authors have published different melting points, molecular refractions, and other physicochemical constants for sulphoxides. More complete characterisation of the purity of the product would evidently require an indication of the concentration of sulphinyl sulphur determined by potentiometric titration[152].

mono-, bi-, and tri-cyclic thiolans mainly of saturated structure. In order to obtain petroleum sulphoxides sparingly soluble in water (and therefore suitable for extraction) use is made of concentrates of petroleum sulphides or directly distilled fractions of high-sulphur petroleums boiling over the range 260–360°C.[2] The petroleum sulphides are oxidised with hydrogen peroxide[11,12]. A concentrate of petroleum sulphides can be obtained in various ways[13], but preferably by extraction with sulphuric acid[14]. The molecular structure remains almost unchanged when petroleum sulphides are oxidised to sulphoxides, so that the structure-group analysis of the sulphoxides is similar to that of the petroleum sulphides.

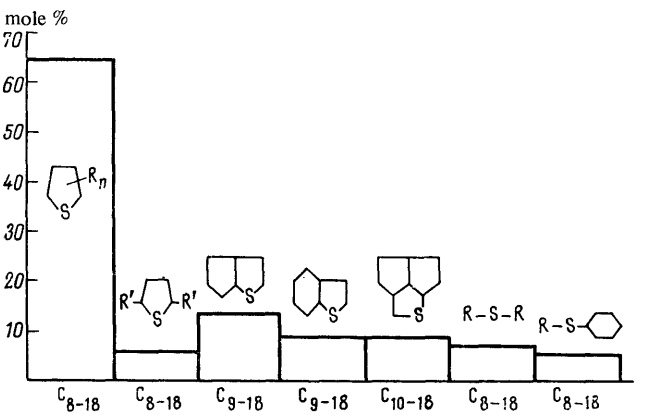


Figure 1. Relative contents of individual structural groups of sulphides and numbers of carbon atoms in molecules of concentrate of sulphides (190–360°C) from Arlansk petroleum.

Fig. 1 illustrates the composition of the most thoroughly studied sulphide concentrate of Arlansk petroleum (190–360°C).[10] Monocyclic and bicyclic thiolans evidently predominate. The composition of the petroleum sulphides is similar for the kerosene–gas-oil fractions of Western Surgutsk[15] and Romashkinsk[16] petroleums. The sulphides present in the kerosene–gas-oil fractions of petroleums confined to Devonian, Carboniferous, and Lower Cretaceous sandstones probably have similar structure-group analyses[17]. It follows from the structure-group composition of petroleum sulphides that the extraction properties of the sulphoxides can be compared with those of individual cyclic sulphides, which serve as model for the petroleum sulphoxides.

Metal salts and acids are usually dissociated and strongly hydrated in aqueous solution. In order to transfer them to an organic phase with a high partition coefficient on extraction it is therefore necessary to use a reagent having a strong tendency to complex formation, sufficient to overcome the bonds between the extractable compounds and water. Hence it is clear that the chemistry of extraction equilibria is closely related to that of complex formation.

The possible information by sulphoxides of complexes with metal salts and acids has been known for a long time. The study, carried out in 1907, of the interaction between iron(III)

chloride and a sulphoxide led to isolation of an equimolecular complex[18]. The interaction of sulphoxides with gaseous hydrogen chloride was discovered in 1916.[19] Later the protonation of dimethyl sulphoxide in sulphuric acid was investigated and the basicity estimated[20], which was followed[21] by the preparation of complexes of sulphoxides with perchloric acid. Complex formation by sulphoxides in aqueous and alcoholic media was studied intensively on dimethyl sulphoxide at the beginning of the 1960s.[22-27] The first communications on the possibility of using sulphoxides as extractants date from this time.

Nikolaev et al. formulated general requirements which should be satisfied by extractants, and noted the need to study the class of extractants R_nElO, among which sulphoxides were mentioned[28,29]. The possibility of using sulphoxides as extractants was suggested also by Cotton and Francis[30] in a study of the ligand properties of dimethyl sulphoxide.

The first studies of the extraction properties of sulphoxides were made by Korpak[31-34], but he gave no quantitative interpretation of the extraction equilibria of sulphoxides with metal salts and acids. Nikolaev and his coworkers described the mechanism of extraction by sulphoxides[35-37]. Quantitative characteristics of extraction were obtained by the Reviewers[38-40], in the first investigation of the extractive properties of cyclic sulphoxides, which were found to model those of petroleum sulphoxides[41,42]. Papers giving quantitative characteristics of the mechanism of extraction by sulphoxides appeared also abroad[43-45].

Table 2. Basicity of extractants.

Extractant	pK	Ref.	Extractant	pK	Ref.
Diethyl ether	0.98	49	Di-isopentyl methylphosphonate	2.74	51
Oxolan	1.26	49	Trimethylphosphine oxide	3.49	49
Acetone	1.18	49	Dimethyl sulphoxide	2.53	49
Butan-2-one	1.18	49	Diphenyl sulphoxide	2.03	51
Cyclohexanone	1.30	49	Dihexyl sulphoxide	2.67	51
Triphenyl phosphate	1.73	49	Dicyclohexyl sulphoxide	2.77	51
Tributyl phosphate	2.56	51	2-Heptylthiolan 1-oxide	2.74	51

Before examining actual experimental results on the chemistry of extraction by sulphoxides, we shall discuss the position occupied by these compounds among oxygen-containing extractants (organic oxides) of type R_nXO. The latter form complexes with metal salts usually by an electronic mechanism of donor–acceptor interaction. The difference in extractive power (and in complex formation) among compounds R_nXO will be determined by the electron density on the oxygen atom†, as well as by the geometrical parameters of the molecules, which largely determine the entropy contribution.

Accurate determination (calculation) of electron density in polyatomic molecules R_nXO (where X = P, S, N, As, Se, etc.) is not yet possible at the present state of development of quantum chemistry, and the best comparative measure of the donor power of oxygen is the basicity of the extractant. This represents the free energy of protonation of the P=O, S=O, N=O, etc. groups[49]. Correlation of basicity with extractive power clearly establishes the position of sulphoxides in the sequence of organic oxides[50,51]. Table 2 indicates that they occur between ketones and phosphine oxides with respect to basicity; they occupy an intermediate position also with respect to extractive power. One reason for the enhanced reactivity of the sulphinyl in comparison with the carbonyl group is that the sulphur atom is larger than the carbon atom (r_S = 1.04 and r_C = 0.77 Å), and with a consequent diminished energy of bonding with oxygen ($E \propto e^{-m}$, where $m \geq 1$) and a smaller force constant k_e(SO).

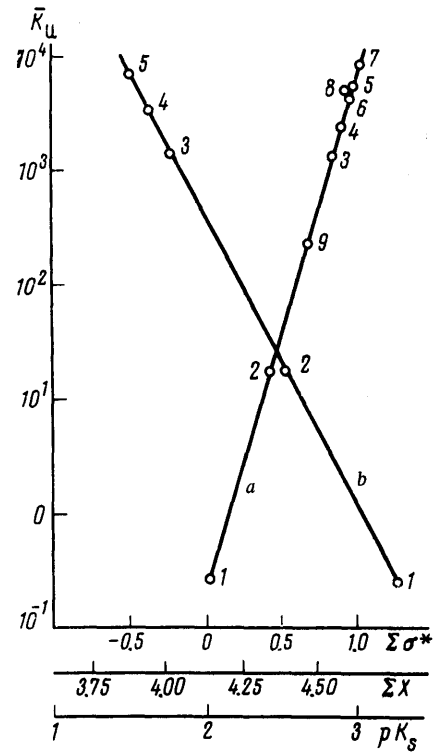


Figure 2. Dependence of extraction constants $\bar{K}_U$ for uranyl nitrate on: *A*) basicity pK_S; *B*) sum of electronegativities ΣX or Taft constants $\Sigma\sigma^*$ of: 1) DPhSO; 2) HPhSO; 3) DHSO; 4) [?]; 5) ChHSO; 6) HTlO; 7) PThO; 8) DPMP; 9) TBP.

The correlation between the basicity of sulphoxides and their extractive power for uranyl nitrate is well described by the equation[51]

$$\lg \bar{K}_U = -11.88 + 5.6\,pK_s \qquad (1)$$

which is clearly confirmed by Fig. 2. On passing from dialkyl to cyclic sulphoxides both the basicity of the oxygen atom and the extractive power increase. Values of $\bar{K}_U$ for tributyl phosphate (TBP) and di-isopentyl methylphosphonate (DPMP) fit satisfactorily into the general

† The coordination of metals to the sulphinyl oxygen atom has been established from the infrared spectra of the complexes isolated in numerous investigations. An exception is palladium, which is able to coordinate both with sulphur and with oxygen[46-48].

relationship. Dialkyl sulphoxides considerably surpass tributyl phosphate in extractive power, but are somewhat inferior to phosphonates, whereas cyclic sulphoxides are rather better than phosphonates. Cyclic sulphoxides are superior to aliphatic sulphoxides, of course, also in their complexing properties[52]. It must be concluded from the comparison of the extractive power of aliphatic sulphoxides that petroleum sulphoxides (PetrSO), being mixtures of cyclic sulphoxides, will surpass aliphatic sulphoxides and tributyl phosphate in extractive power. This view is supported by many experimental results[41,42,53,54].

The influence of structure is illustrated by Fig. 2, which shows good correlation of extractive power with basicity within a class of sulphoxides, but for open-chain sulphoxides the extractive power may be predicted, as for other neutral extractants[55], from the electronegativities ΣX or the inductive constants σ^* of substituents adjacent to the sulphur atom[51]:

$$\lg \bar{K}_U = 2.34 - 2.54 \sum \sigma^* = 3.04 - 5.23 \sum (X - 2). \quad (2)$$

Equations (1) and (2) give rise to a relation between the basicity of sulphoxides and the electronegativities of substituents:

$$pK_s = 2.54 - 0.47 \sum \sigma^* = 2.67 - 0.94 \sum (X - 2). \quad (3)$$

A similar relation is obtained from a consideration of the extractive power of sulphoxides for nitric acid[56]:

$$\lg \bar{K}_H = -0.64 - 0.92 \Sigma \sigma^*. \quad (4)$$

The extraction properties of sulphoxides are more sensitive than those of neutral organophosphorus compounds to change in the electronegativity of a substituent. Thus replacing one aliphatic group ($X = 2.0$) by phenyl ($X = 2.54$) in the latter type of compound diminishes the extraction of uranium by a factor of 17, but in sulphoxides by a factor of 40.

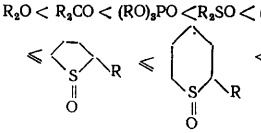
Table 3.

Compound	ν(SO), cm^{-1}	Compound	ν(PO), cm^{-1}
Dimethyl sulphoxide	1069	Tributyl phosphate	1274
Dibenzyl sulphoxide	1056	Triphenyl phosphate	1306
Benzyl phenyl sulphoxide	1054	Tributylphosphine oxide	1160
Diphenyl sulphoxide	1052	Triphenylphosphine oxide	1195

Another characteristic distinction is that extractive power cannot be predicted from the infrared spectra of sulphoxides, unlike those of neutral organophosphorus compounds. The introduction of aromatic substituents leaves the sulphur–oxygen stretching frequency almost unchanged[5,57–59], whereas the phosphorus–oxygen stretching frequency is raised[60] [Table 3]. Nor has the expected fall in absorption frequency ν(SO) been observed on passing to cyclic sulphoxides[59]. The improvement in extractive power on passing from aliphatic to cyclic sulphoxides is due not to an increase in energy of bonding of the resulting complexes but to the entropy factor[40].

From available data it may be concluded that on complex formation sulphoxides are more sensitive to molecular geometry than are neutral organophosphorus compounds. We note in conclusion that sulphoxides can be included in the sequence of neutral organic extractants of increasing extractive power:

$$R_2O < R_2CO < (RO)_3PO < R_2SO < (RO)_2R'PO \leqslant PetrSO \leqslant$$



$$< R_3PO < R_3NO.$$

III. EXTRACTION OF WATER AND INORGANIC ACIDS

Extraction of Water

Sulphoxides containing >10 carbon atoms are only sparingly soluble in water (0.1–4 g litre^{-1}),[44,61] but cyclic sulphoxides are rather more soluble. The use of salting-out agents during extraction lowers considerably the aqueous solubility of sulphoxides. Solubility is strongly influenced by the nature of the diluent. Thus it decreases by a factor of 200 in the sequence nonane–xylene–chloroform, and e.g. for petroleum sulphoxides in chloroform is 0.02 g litre^{-1}. The melting-point curves for aqueous dibutyl and di-isobutyl sulphoxides exhibit anomalies, but solid hydrates are not detected[62], which indicates weak interaction between the sulphoxides and water.

The extraction of water by sulphoxides can be represented by complex formation according to the equation

$$H_2O + q\,S \rightleftarrows H_2O \cdot q\,S, \quad (5)$$

where S is the sulphoxide and q the solvation number. When the activity of water is high ($a_{H_2O} > 0.6$) a monosolvate ($q = 1$) is formed[63]; with $a_{H_2O} > 0.4$ a disolvate appears[58,63]. The decrease in the solubility of water accompanying the decrease in its activity is slower than would be expected from the relation $[H_2O]_{org} \propto a_{H_2O}$. The influence of the diluent on the extraction of water by sulphoxides is analogous to that observed with tributyl phosphate[64]: the effective extraction constant of water K_{H_2O} diminishes in the sequence nonane–benzene–chloroform. The infrared spectra of sulphoxides with water exhibit no significant shift in the absorption frequency of the sulphinyl group, but a slight frequency shift in the symmetrical hydroxyl band (3640 cm^{-1}).[58] All this is evidence of comparatively weak interaction of the sulphoxide with water.

Extraction of Nitric Acid

The heightened interest in the extraction of nitric acid by sulphoxides[33,40] is due to the possible use of the latter as extractants of rare and radioactive elements from nitrate media. A sulphoxide will extract the acid by a solvation mechanism as an unhydrated monosolvate[65–72]:

$$H^+ + NO_3^- + S \rightleftarrows HNO_3 \cdot S. \quad (6)$$

The extractive power for nitric acid diminishes with increase in size of the hydrocarbon group in the dialkyl sulphoxide[45]. That of cyclic sulphoxides[65] is greater than

with dialkyl sulphoxides (K_H is ~1 and 0.78 respectively for 2-heptylthiolan 1-oxide and dipentyl sulphoxide, and the latter surpass tributyl phosphate and di-isopentyl methylphosphonate (0.2 and 0.33). The extraction of nitric acid is significantly influenced by the type of diluent of the sulphoxides. Thus K_H has the respective values 1.44 and 1.25 when alkanes[56] and aromatic hydrocarbons are used, whereas the values obtained with tetrachloromethane and chloroform are 0.70 and 0.26.[65] On extraction from concentrated nitric acid the acid concentration in the organic phase exceeds the stoichiometric value[69]. Direct calorimetric measurements of the interaction of nitric acid with various sulphoxides[73] show that the enthalpy of interaction of the second acid molecule with the monosolvate $HNO_3.S$ is considerably smaller than that of addition of the first acid molecule to the sulphoxide, and amounts to ~9 kcal mole^{-1}. The second molecule is probably attached to the anion of the acid in the monosolvate, as with tributyl phosphate. If the enthalpy of complex formation between nitric acid and sulphoxides depends on the groups attached to the sulphur atom, and for diheptyl, benzyl decyl, and diphenyl sulphoxides ΔH decreases from 30 to 28.7 and 24.8 kcal mole^{-1}.

The variation in entropy in this sequence does not exceed 0.8 e.u. The effective extraction constant of nitric acid by sulphoxides correlates with the enthalpy of extraction and is described by the equation[73]

$$\lg \overline{K}_H = -0.079 - 0.866\,\Delta H_{extr}. \qquad (7)$$

Nevertheless, the extraction constant is almost independent of temperature[65], which indicates that entropy factors are decisive. The relatively large displacement of the sulphinyl absorption band in the infrared spectrum of the solvate of nitric acid to lower frequencies ($\Delta\nu$(SO) = 60 cm^{-1}) indicates a quite stable bond between the sulphinyl oxygen atom and the proton of the acid.

Hydrochloric Acid

In contrast to nitric acid, hydrochloric acid is extracted by a mechanism involving both hydration and solvation[74]:

$$H^+ + Cl^- + h\,H_2O + q\,S \rightleftarrows HCl \cdot h\,H_2O \cdot q\,S. \qquad (8)$$

Solvation numbers q determined by various authors[33,63,75,76] vary from 1 to 3, which indicates the presence of mono-, di-, and tri-solvates in the organic phase. The hydration number h also varies, from 3 to 1: i.e. $q + h = 4$, in good agreement with the coordination number 4 generally accepted for the oxonium cation.

Extraction by sulphoxides becomes appreciable only when the concentration of the acid in the aqueous phase exceeds 4 M; the extraction constants are small[45]. When the concentration of the aqueous acid is 6–7 M, the extraction isotherm passes through a maximum (with sulphoxides containing <11 carbon atoms), after which it drops sharply owing to rapid increase in the solubility of the complex in the aqueous phase[75]. The increase in solubility is due to formation of a trihydrate of the monosolvate $HCl.3H_2O.S$. With 10 M hydrochloric acid in the aqueous phase about 50% of sulphoxides enter from the organic phase[75]. On prolonged contact (5–6 h) with the concentrated acid, extensive reaction takes place with the sulphoxides[70,77], as indicated by disappearance of the sulphinyl band from the infrared spectra of the complexes and also by direct chemical analysis for the sulphoxide content.

Hydrofluoric, Hydriodic, and Hydrobromic Acids

Hardly any work has been done on the mechanism of the extraction of these acids by sulphoxides. Monosolvates are formed[70,78,79], which may be hydrated. Hydrobromic and hydriodic acids react chemically with sulphoxides as the acid concentration of the aqueous phase is increased[70]. The hydrohalic acids can be arranged in the sequence

$$HI > HBr > HCl > H_2F_2$$

of diminishing extractability by sulphoxides. The sequence may be connected with the type of hydration of the acid anion.

Extraction of Sulphuric Acid

The mechanism of the extraction of sulphuric acid by sulphoxides involves hydration and solvation[80]:

$$H^+ + HSO_4^- + h\,H_2O + q\,S = H_2SO_4 \cdot h\,H_2O \cdot q\,S. \qquad (9)$$

As in the extraction of hydrochloric acid, the solvation and hydration numbers depend on the concentration of acid in aqueous and organic phases. With an aqueous phase containing initially up to 3 M sulphuric acid the latter is present in the organic phase mainly as a dihydrated disolvate $H_2SO_4.2H_2O.2S$; but a trihydrated monosolvate $H_2SO_4.3H_2O.S$ predominates in the organic phase when the acid concentration of the aqueous phase is increased to 5 M, and this complex separates as a third phase; on further increase in the acid concentration it passes into the aqueous phase[80,81]. The displacement of the sulphinyl absorption frequency in the infrared spectra of complexes of sulphuric acid with sulphoxides is about −170 cm^{-1}, which may indicate strong protonation of the sulphinyl oxygen and perhaps transfer of a proton from the acid to this oxygen[45,81] (in concentrated sulphuric acid).

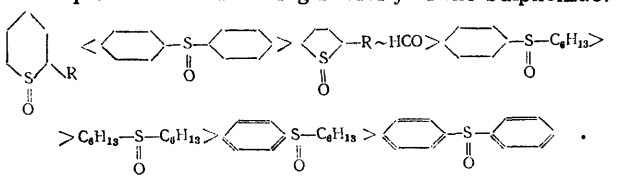
Extraction of Other Acids

Sulphoxides of diverse structure are good extractants for per-rhenic perchloric and boric acids as respectively a disolvate[65], a monosolvate[45,58], and a trisolvate[81]. Sulphoxides—especially those from petroleum—are of practical interest for the extraction of phosphoric acid from sulphuric and nitric acid media, the isolation of boron as boric acid from magnesium chloride solutions, and also the extraction of various heteropolyacids, e.g. molybdophosphoric acid[82].

IV. EXTRACTION OF ORGANIC ACIDS

During recent years several publications have appeared on the use of sulphoxides as extractants for organic acids[83–88]. Monocarboxylic acids are extracted by a solvation mechanism: i.e. unhydrated monosolvates RCOOH.S are formed[81]. The infrared spectra of the solvates show a ν(SO) absorption frequency shift of 20–40 cm^{-1} to longer wavelengths, which indicates formation of a hydrogen bond between the acid proton and the sulphinyl oxygen[89]. As the hydrocarbon group becomes larger, the extraction of the monocarboxylic acid increases, owing to its diminished hydrophilicity and transolvation energy. Extraction of the halogenated acids (such as chloroacetic) is described by Eqn. (6) and also involves formation of

unhydrated monosolvates[84,90]. The salting-out effect of cations in the extraction of halogenated carboxylic acids increases with decrease in the ionic radius of the cation and increase in its charge[81]. The heat of extraction of chloroacetic acid by a sulphoxide is ~4 kcal mole^{-1}. The extractive power of sulphoxides for organic acids decreases in the sequence of diminishing basicity of the sulphoxide:



Sulphoxides can be used also to separate organic acids. Thus the partition coefficient of chloroacetic and acetic acids after a single stage of extraction is 20. Most dicarboxylated acids are extracted as anhydrous disolvates—e.g. $(COOH)_2.2S$, $CH_2(COOH)_2.2S$, etc.—produced by hydrogen bonding. Exceptions are phthalic and maleic acids, which form monosolvates on extraction with sulphoxides. The mechanism of the extraction of keto-acids (pyruvic, oxoglutaric) is the same as in the extraction of mono- and di-carboxylic acids. However, the extraction of hydroxy-acids by sulphoxides involves formation of hydrated solvates[86], and the partition coefficient D is smaller than with monocarboxylic acids.

The extraction of organic sulphonic acids by sulphoxides has features in common with that of sulphuric acid: the mechanism of hydration and solvation gives complexes soluble in both aqueous and organic phases, and the sum of hydration and solvation numbers is 4. Sulphuric acid has a strong salting-out effect on the extraction of sulphonic acids. The shift of 80–100 cm^{-1} in the absorption band of the sulphinyl group in the infrared spectra of the complexes of sulphonic acids extracted by sulphoxides indicates stronger protonation of the sulphinyl oxygen by sulphonic acids than by mono- and di-carboxylic acids[81].

Sulphoxides are able to form complexes also with organophosphorus acids. Complex-formation constants $\widetilde{K}$ for di-(2-ethylhexyl) hydrogen phosphate with dihexyl sulphoxide and with 2-pentylthian 1-oxide are larger[91] than with tributyl phosphate (respectively 1.1, 1.8, and 0.65).

Thus the extraction of organic acids by sulphoxides exhibits several regularities. Extraction is greater for monocarboxylic than for dicarboxylic acids, and greater for the latter than for tricarboxylic acids containing the same number of carbon atoms. With increase in molecular mass (i.e. size of the hydrocarbon portion) in each series the introduction of halogens—chlorine, bromine, iodine—leads to an increase in the extraction constants, whereas carboxy-, hydroxy-, and sulpho-groups lower the extraction constant. Thus the extraction equilibrium constants for acids with sulphoxides are determined by the energy of transolvation of the acid on passing from aqueous to organic phases. Extraction entails formation of a hydrogen bond involving the sulphinyl oxygen atom. The extractive power of petroleum sulphoxides exceeds those of tributyl phosphate and phosphonates.

V. EXTRACTION OF METALS

1. Extraction of Metals from Nitrate Media

It is now recognised that sulphoxides are effective extractants for salts of rare metals[92-99]. In all such cases the mechanism remains almost unchanged on passing from tributyl phosphate and its analogues to sulphoxides, when the metal cation is directly coordinated to the sulphinyl oxygen[37].

EXTRACTION OF URANYL NITRATE

As with extraction by tributyl phosphate, sulphoxides extract uranyl nitrate into the organic phase as a disolvate[34,100-105] independently of the type of diluent used:

$$UO_2^{2+} + 2NO_3^- + 2S = UO_2(NO_3)_2 \cdot 2S. \qquad (10)$$

In conformity with this equation the extraction constant can be found from the formulae

$$K_U = \frac{y_U \cdot dil}{x_U (2x_H + x_U)^2 (s_0 - 2y_U - y_H)^2 \gamma_\pm^3} = \widetilde{K}_U \cdot \frac{dil}{\gamma_\pm^3} = \overline{K} \cdot dil, \qquad (11)$$

where K_U, $\widetilde{K}_U$, and $\overline{K}$ are thermodynamic, concentration, and effective extraction constants, x_U and y_U are the equilibrium concentrations of uranyl nitrate in aqueous and organic phases, x_H and y_H are the equilibrium concentrations of nitric acid (or x_H is the concentration of salting-out agent) in these phases, *dil* is a parameter representing the ratio of the activity coefficients of extracted complex and extractant in the organic phase, $\gamma_\pm$ the mean activity coefficient of uranyl nitrate, and s_0 the initial concentration of the extractant.

With increase in the concentration of nitric acid in the aqueous phase the extraction of uranyl nitrate first increases, passes through a maximum, and then falls[43,44], this decrease being due to competition for the free extractant. At a fixed ionic strength the extraction constant for uranyl nitrate and sulphoxides is almost unaffected by the hydrogen-ion concentration[44,104]. Nor is the extraction constant $\overline{K}$ appreciably affected by the length of the hydrocarbon chain in dialkyl sulphoxides from dipentyl to didecyl. Yet increase in the electronegativity of the groups attached to the sulphur atom lowers the extractive power (Fig. 2), which increases appreciably on passing from dialkyl to cyclic sulphoxides[39,105]. Among cyclic sulphoxides that have yet been studied 2-alkylthian 1-oxides possess the greatest extractive power. The properties of the extracted complexes of cyclic sulphoxides with uranyl nitrate change when the alkyl substituent is moved from the α to the β or γ position relative to the sulphur atom. This is apparent in stronger hydration of the complexes and a considerable diminution in their solubility in organic solvents[76]. When an α-alkyl group in thiolan 1-oxide is replaced by cyclohexylmethyl, the solvation number changes, and uranyl nitrate is extracted as a monosolvate $UO_2(NC_3)_2.S$, apparently owing to steric factors[39]. Complexes of uranyl nitrate with di-isopentyl sulphoxide also show a limited solubility in organic diluents[106], which may be due to polymerisation or to different lattice energies of complexes formed with sulphoxides of differing structure. The variation of the properties of the complexes and especially their solubility require separate investigation.

The extractive power of sulphoxides diminishes considerably with rise in temperature. Heats of extraction calculated from the dependence of $\overline{K}$ on $1/T$ remain almost unchanged on passing from dialkyl to cyclic sulphoxides. As mentioned above, the Reviewers attribute the enhanced extractive power of cyclic sulphoxides to entropy factors[40].

The effect of the solvents for the sulphoxides is well described by the parameter *dil* in Eqn. (11), as in the extraction of uranyl nitrate by neutral organophosphorus compounds. The extractive properties of sulphoxides

deteriorate in the sequence heptane–benzene–tetrachloromethane–chloroform. The reason for the impairment in the case of chloroform is its strong solvating action resulting from strong hydrogen bonding with sulphoxides[107].

EXTRACTION OF OTHER METALS

Zirconium and hafnium nitrates are extracted by sulphoxides as disolvates[108], and rare-earth metals (lanthanides) as trisolvates, perhaps partly hydrated in the organic phase[109]. Thorium nitrate is able to form with sulphoxides two solvates—a trisolvate in the presence of a large excess of free extractant[110], and a disolvate in other cases[108].

Gold(III), mercury, silver, and palladium(II) also are extracted by sulphoxides from nitric-acid solutions[36,37]. In contrast to other complexes, however, the last may involve coordination of the sulphinyl group at both sulphur and oxygen atoms, as is indicated by displacement of the sulphinyl absorption band to higher frequencies in the infrared spectrum[48].

Since sulphoxides surpass tributyl phosphate in extractive power, they extract several hydrolysed species of metal salts from nitrate and weakly acid media[111], according to the equation

$$M^+ + (z-m)\,A^- + (h+m)\,H_2O + q\,S \rightleftarrows M(OH)_mA_{z-m}\cdot H_2O\cdot q\,S + m\,H^+. \qquad (12)$$

Hydrolysed species of bismuth(III), iron(III), copper, cobalt, and nickel are well extracted from nitrate media by sulphoxides, and to a less extent those of zirconium and hafnium. The solvation numbers are 3 for copper and bismuth[112] and 4 for iron[111]. In the extracted complexes the metal is coordinated by the sulphinyl oxygen atom (except in the case of bismuth[112]) through a water molecule, as is indicated by the small shift (10–15 cm^{-1}) in the absorption frequency ν(SO).

The action of sulphoxides on many elements has been studied by reverse-phase paper chromatography with the sulphoxides as stationary phase and nitric acid as mobile phase[113–115]. The low R_f values for many elements indicate the possibility of effective extraction of several metals by sulphoxides, as well as their use in the analytical separation of metals in industry. Good separation of the metal pairs zirconium–hafnium, uranium–thorium, zinc–cadmium, iron–copper, etc. can be effected by means of sulphoxides.

2. Extraction of Metals from Chloride Media

By analogy with tributyl phosphate sulphoxides may be able to extract metal chlorides by two mechanisms[116]—as coordinatively solvated compounds (solvates)

$$M^{z+} + z\,A^- + q\,S \rightleftarrows MA_z\cdot q\,S \qquad (13)$$

and as complex anions present in ionic aggregates (as metal-complex acids)

$$M^{z+} + m\,H^+ + (z+m)\,A^- + q\,S \rightleftarrows H_mMA_{z+m}\cdot q\,S. \qquad (14)$$

Extraction by the second mechanism often involves the participation of water, i.e. hydration and solvation.

By the first mechanism (at hydrochloric acid concentrations below 5 M) sulphoxides extract as disolvates the chlorides of palladium[117–121], zinc[63], tellurium[108,122,123], thorium[124,125], uranium[34], zirconoium[126,127], hafnium[126], scandium[128], and perhaps lanthanides; and as monosolvates mercury[129] and silver[130] chlorides. All other metals, as well as most of the above with increase in the concentration of hydrochloric acid, are extracted as metal-complex acids by the second mechanism (14).

During extraction by the first mechanism the metals are coordinated directly to the sulphinyl oxygen (palladium is coordinated through the sulphur atom). In the second mechanism extraction is due to interaction of the proton of the metal-containing acid with the sulphinyl oxygen atom. As the concentration of hydrochloric acid in the aqueous phase is increased, the extraction of metals by sulphoxides passes in most cases through a maximum, independently of the mechanism of extraction. The decrease in partition coefficients with increase in the concentration of hydrochloric acid is due both to its coextraction and to formation of highly charged anions of the metal-containing acids, which are extracted less strongly than are anions having a lower charge or neutral[117] species.

Decrease in the extraction of metals is due to the enhanced solubility of the complexes they form with sulphoxides in concentrated hydrochloric acid. Ruthenium(II) chloride behaves rather unusually in comparison with other salts. With increase in the concentration of hydrochloric acid its extraction by sulphoxides diminishes, passes through a minimum (at 2–3 M HCl), and increases afresh. The descending part can be explained by poor extractability of the anionic complexes.

The composition of the complexes formed during extraction by the first mechanism has been established most reliably—$TeCl_4.2S$,[122] $PdCl_2.2S$,[117–121] $UO_2Cl_2.2S$,[34] $ZrCl_4.2S$,[127] $HfCl_4.2S$,[126] $MoO_2Cl_2.2S$,[131] $WO_2Cl_2.2S$,[131] and $SeCl_3.2S$.[128]

In the analysis of extraction equilibria from aqueous hydrochloric acid the most difficult task is to establish the composition of the complexes formed by mechanism (14). The difficulty is to determine the concentration of the free extractant, since hydrochloric acid may be extracted by sulphoxides as three solvates differing in degree of hydration. It is difficult also to allow for the possible extraction of metal-containing acids differing in the composition of the anionic portion (e.g. $CuCl_3^-$, $CuCl_4^{2-}$, etc.). Direct elementary analysis of the complexes obtained by saturation does not always give an unambiguous answer, since higher solvates may also be present in solution.

Knowing the composition of the complexes extracted, confirmed by infrared, Raman, and proton magnetic resonance spectral data, we can confidently accept that the metal-containing acids—$HGaCl_4.H_2O.3S$, $H_2CuCl_4.3H_2O.2S$, $HFeCl_4.2H_2O.2S$, $HInCl_4.2H_2O.2S$, and $HInCl_4.H_2O.S$ (on saturation)—are extracted by a hydration–solvation mechanism[63]. Thallium is extracted as the acid $HTlCl_4.2S$ by a solvation mechanism.

From the results of reverse-phase chromatography (with hydrochloric acid as eluant) and the low R_f values for most elements[113,114] it may be concluded that sulphoxides will find application for the extraction of noble metals and certain non-ferrous and rare metals. Large separation factors have been obtained by the use of sulphoxides for the elements selenium–tellurium, molybdenum–tungsten[131], iron–cobalt–nickel[132], tantalum–niobium[133], palladium–rhodium, platinum, etc.

Summarising the results for the extraction of metals from aqueous hydrochloric acid by sulphoxides, we must emphasise that extraction equilibria for this system are still difficult to describe quantitatively—in the sense of interpreting the mechanism of extraction and the formation of extractable complexes—because the aqueous phase may contain several complexes of the same metal, differing in composition and extracted by different mechanisms.

3. Extraction of Metals from Mixed Media and by a Mixture of Extractants

Zirconium, hafnium, uranium[76,134], and thorium are well extracted by sulphoxides from mixed aqueous hydrochloric and nitric acids. As when tributyl phosphate is used, the partition coefficient for zirconium and hafnium is greater from the mixed solutions than from either acid separately[38]. This effect can be explained by enhanced extraction of a mixed complex of the type $ZrCl_n(NO_3)_{4-n}.2S$.[135]

From aqueous sulphuric acid containing a fluoride tantalum and niobium are effectively extracted by sulphoxides[53,136-147] as fluorotantalic and fluoroniobic acids. In most cases these metals form on extraction monohydrated trisolvates of the types $HTaF_6.H_2O.3S$ and $H_2NbOF_5.H_2O.3S$. Concentration extraction constants of petroleum sulphoxides for tantalum and niobium are respectively 10 and 2.5. These sulphoxides can be used to separate the metals by extraction[53].

Tellurium is extracted as a chloride complex from aqueous sulphuric acid containing a chloride, but the mechanism of extraction has not yet been studied in detail.

Sulphoxides in synergistic mixtures. Comparison of the general laws of the extraction of metals by sulphoxides and by neutral organophosphorus compounds suggests that sulphoxides should have an enhancing effect as donor additions to synergistic mixtures of extractants. Indeed, constants for addition of the first and second molecules of dibutyl sulphoxide to europium tris(2-thenoyltrifluoroacetone) $[Eu(TTA)_3]$ [148] are closely similar to or slightly higher than those for tributyl phosphate. In the extraction of uranium by an equimolecular mixture of a sulphoxide and bis-2-ethylhexyl hydrogen phosphate[149] three types of complex—$UO_2A_2.2HA$, $UC_2A_2.2S$, and $UO_2A_2.HA.S$, where A is the anion of the acid HA, and S is the sulphoxide—are present in the organic phase. The main reaction responsible for synergism in the extraction[150,151] can be regarded as

$$UO_2^{2+} + H_2A_2 + 2S \rightleftarrows UO_2A_2 \cdot 2S + 2H^+. \quad (15)$$

The synergistic effect increases with the basicity of the sulphoxide. Partition coefficients of the metal are considerably higher with sulphoxides than when tributyl phosphate is used as the synergistic additive.

It follows from the above discussion that sulphoxides resemble organophosphorus compounds in the mechanism of complex formation during extraction, but differ in a greater tendency to polymerisation (association) in the organic phase. For example, the extraction constants for uranyl nitrate increase with the metal concentration, which indicates at least dimerisation. This difference is apparently due to the highly polar character of sulphoxide molecules (dipole moment ~4, and for tributyl phosphate ~3) and diminished steric hindrance to association (two groups present instead of the three in neutral organophosphorus compounds). The extracted sulphoxide complexes usually dissolve preferentially in organic solvents of high dielectric constant, are less soluble in aromatic solvents, and exhibit limited solubility in alkanes. It is advisable to use aromatic and chlorinated solvents with sulphoxides as extractants for acids and metal salts.

Study of the chemistry of extraction has shown that sulphoxides—especially those from petroleum—are promising extractants for many radioactive, rare, trace, and non-ferrous metals, as well as inorganic and organic acids. Cyclic sulphoxides (thiolan and thian homologues) possess the strongest complexing power. Since research on the extraction and coordination chemistry of these compounds has only just begun, valuable new data may be expected on the properties of cyclic sulphoxides.

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