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V. M. Shinde[a]
[a] DEPARTMENT OF CHEMISTRY, SHIVAJI UNIVERSITY, KOLHAPUR, INDIA

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REVIEW

Solvent Extraction Separation of Selected Transition Metals with Mesityl Oxide

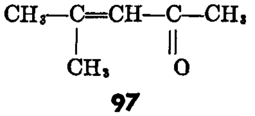
V. M. SHINDE

DEPARTMENT OF CHEMISTRY
SHIVAJI UNIVERSITY
KOLHAPUR-4, INDIA

Summary

Mesityl oxide (4-methyl-3-pentene-2-one) has been used for the solvent extraction studies of some transition metals such as Th, Zr, U, Pd, Pt, V, Cr, Mo, W, Re, Fe, Au, and Ga. In the present article optimum conditions for the extraction of the above metals have been given based on a critical survey of the relevant factors such as the effect of acid concentration, reagent concentration, salting-out agent, period of extraction, and diverse ions. The mechanism underlying these extractions is also discussed. The mesityl oxide has proved to be an excellent extractant as it provides clean-cut separation of a large number of ions in minimum time.

Oxygen-containing solvents have been extensively employed in recent years for the extraction of ion-association compounds. The ability of the oxonium solvents to compete with water for the acidic metal ion depends on the basicity of the oxygen in the molecule. The incorporation of the solvent molecule in the coordination sphere of the metal ion is responsible for the solubility of the ion-pair complex in organic solvent. Mesityl oxide, also known as 4-methyl-3-pentene-2-one



$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3$$

TABLE 1

Optimum Conditions for the Extraction of Different Metals with Mesityl Oxide

		Organic phase					
Metal	Aqueous phase	Mesityl oxide (%)	Diluent	Separation from	Interfering ions	Remarks	Refs.
Th	1.2 *M* HNO_3 + 2.5 *M* $Al(NO_3)_3$	100	—	Yttrium and several anions	—	Extraction period is 20 sec to a few minutes with equal volume of mesityl oxide	*2–4*
Zr	4 *M* HNO_3 + 4 *M* $NaNO_3$	100	—	—	—	Extractable species is $Zr(NO_3)_4 \cdot 2MeO$	*9*
U	1 *M* HNO_3 + 0.5 *M* NH_4NO_3	100	—	—	Hg, Cu, Fe, Ce	10 min shaking	*10*
Pd	6 *M* HCl + 3 *M* $AlCl_3$	100	—	Ce, Co, Ni	Selenite and arsenite	30 sec shaking	*11*
Pt	5 *M* HCl + 2 *M* $AlCl_3$	100	—	—	Ir, Rh	—	*11*
V	6 *M* HCl	100	—	Cu, Ni, etc.	Hg, Sb, Pd	10 sec shaking species is $VOCl_3 \cdot 3MeO$	*12*
Cr	1 *M* HCl + 2.5 *M* KCl	100	—	Co, Ni, Mn	Fe	1 min shaking	*13*
Mo	1 *M* HCl + 8 *M* LiCl	100	—	—	Ru, Hg, citrate	Species is $MoO_2Cl_2 \cdot 2MeO$	*14*
W	1 *M* HCl + 12 *M* LiCl	75	MIBK	Cr, Th, Ce, Co, Ni,	Mo, Sb, Ir	2 min shaking	*15*

Re	1 *M* HCl + 1 *M* KCl	75	MIBK	Large number of cations and anions	—	30 sec shaking	*16*
Fe	3.25 to 5 *M* HCl	100	—	—	Os, vanadate, phosphate, thiocynate	Species is $HFeCl_4 \cdot 2MeO$	*17*
Au	4.5 to 5.5 *M* HCl	100	—	Large number of cations and anions	—	10 min shaking	*18, 19*
Ga	3 to 6 *M* HCl	100	—	Large number of cations and anions	—	2 min shaking	*20*

possesses one carbonyl oxygen, the donor characteristics and angular variations of which were studied by Cook (*1*). The solvent has a low dielectric constant, i.e., 15, which facilitates the formation of an ion-pair complex. Levine and Grimaldi (*2*) and later Travesi et al. (*3*) introduced this solvent for the extraction of thorium. Studies in our laboratory have revealed that mesityl oxide can also be used as an extractant for such metal ions as Zr, U, Pd, Pt, V, Cr, Mo, W, Re, Fe, and Au (*5*, *6*). Table 1 summarizes the extraction conditions for these metals.

In the present article we discuss the various experimental parameters such as the effect of acidity, the effect of reagent concentration, the effect of salting-out agent, the effect of period of extraction, and the probable composition of the extractable species.

EFFECT OF ACIDITY

Both nitric acid and hydrochloric acid systems were employed for extraction studies. The quantitative extraction of metal ions such as V, Fe, and Au is feasible from 3 to 6 *M* hydrochloric acid solution, even in the absence of salting-out agent. The extraction of metal ions in mesityl oxide at different acid concentrations in the aqueous phase showed that the extraction coefficient increases with increasing acid concentration, attains a maximum value, and then decreases (in a few cases). The initial increase of the extraction coefficient with an increase in acid concentration is due to the salting-out effect of the anions. The subsequent decrease of the extraction coefficient is attributed to the fact that the acid itself is extracted into mesityl oxide and much less of the solvent is available for extraction purposes. The formation of ion-pair complexes in combination with anions and mesityl oxide must involve the following mechanism:

$$M^{+n} + X^- + y\text{MeO} \rightleftharpoons M(X)_n \cdot (\text{MeO})y$$

where X^- is the anion reacting with 'n'-valent metal ion, M, and y is the number of mesityl oxide molecules incorporated in the complex.

EFFECT OF SALTING-OUT AGENTS

The extraction of metal ions such Th, Zr, U, Pd, Cr, Mo, W, and Re was enhanced by the use of neutral salts such as nitrates or chlorides of Na, K, Li, ammonium, and Al. The addition of these neutral salts, better called salting-out agents, generally increases the extraction through three important roles: (a) they provide a higher concentration of complexing anion which, by mass-action, increases the concentration of the complex and thus improves extraction. (b) The added salt has a strong ability to bind water molecules and thus reduce the water activity. (c) They lower the dielectric constant of the aqueous phase to favor ion-pair formation. The extent of enhancement of extraction by the added salt depends on the charge as well as on the ionic size of the added cation for a given anion. However, in a few cases there is a reduction in extraction with an increase in the concentration of the salting-out agent. This is due to the competition of the anion for the solvent.

EFFECT OF REAGENT CONCENTRATION

The concentration of mesityl oxide was varied from 19 to 100% with methyl isobutyl ketone as the diluent. It was found that except for W and Re, undiluted and pure mesityloxide is needed for complete recovery of metal ions. The use of diluent solvent reduces the extractability in proportion to the decrease in the concentration of the oxygenated solvent because the solubility of metal salts in oxygenated solvents depends primarily on specific interaction of the solvent oxygen and the solute. The extent to which dilution of the oxygenated solvent may be carried out depends on the strength of the bonding of the metal ions and the solvent oxygen and also on the resemblance of the ion-pair complex to the diluent solvent. The highest extraction efficiency is expected with the diluent with the lowest tendency to form hydrogen bonding, i.e., to participate in extraction equilibrium. Solvents such as methyl isobutyl ketone, nitrobenzene, and *n*-butyl ether are donor-type diluents and are characterized by the lowest suppressing activity. Various other solvents such as chloroform, carbon tetrachloride benzene, toluene, xylene, *n*-butanol, and isobutyl acetate were also tried as diluents but they had no specific effect on the extraction behavior of the metal ions.

NATURE OF THE EXTRACTABLE SPECIES

To ascertain the nature of the extractable species, log D was plotted against the log of mesityl oxide concentration, keeping the acidity of the aqueous phase constant. The slope of the straight line predicts the number of solvent molecules coordinated to the metal ion. Mesityl oxide forms either mono- or disolvated species. Vanadium, however, gives trisolvated species analogous to other trisolvate species, e.g., $VOCl_3 \cdot 3TBP$ (*7*).

PERIOD OF EXTRACTION

Mesityl oxide has an advantage over other oxygenated solvents in that the extraction is quick and selective. The extraction period varies from 10 sec to 1 min in most cases. Prolonged shaking, however, has an adverse effect on the extraction of the metal ion (*3*, *8*).

EFFECT OF FOREIGN IONS

A number of representative ions were carried through the procedure and tested for interference. The tolerence limit was set at the amount required to cause a $\pm 2\%$ error in metal recovery. A large number of cations and anions are tolerated, thus making separation possible. A few other ions vitiate the process of extraction. However, the interference due to anions can be eliminated by making use of an anion-exchange resin whereas interference with cations can be eliminated by making use of sequestering agents which are capable of forming water-soluble negatively charged complexes unextractable by mesityl oxide.

ADVANTAGES OF MESITYL OXIDE

Various solvent extraction methods are available for the separation of above metal ions, but the existing methods suffer from many drawbacks, e.g.,

(a) They need multiple extraction.
(b) The extraction period is unusually long.
(c) The aqueous phase should be either heated or cooled before extraction.
(d) The aqueous phase should be preequilibrated.
(e) Critical temperature control of the aqueous phase is needed.
(f) A high concentration of reagents should be employed.

The proposed separation methods are free from these drawbacks. Thus, mesityl oxide shows its superiority over other oxygen-containing solvents.

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