Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Saraiya, V. N. , Venkatesv-Arlu, K. S. and Shankar, J.(1974) 'Studies in Solvent Extraction of Ruthenium(III) From HCI Solutions by Sulfoxides', Separation Science and Technology, 9: 5, 423 — 429
To link to this Article: DOI: 10.1080/00372367408056077
URL: http://dx.doi.org/10.1080/00372367408056077

SEPARATION SCIENCE, 9(5), pp. 423–429, 1974

Studies in Solvent Extraction of Ruthenium(III) From HCl Solutions by Sulfoxides

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Abstract

Studies on the solvent extraction of Ru(III) by sulfoxides from hydrochloric acid solutions are reported. A kinetic effect has been observed in the extraction process. The extraction efficiency varies with the nature of the sulfoxide, the diluent employed, and the molarity of the acid.

INTRODUCTION

Very little work has been reported thus far on the extraction of ruthenium(III) by sulfoxides from acid solutions. Shanker (*1*) from this laboratory has mentioned that ruthenium(III) is not extractable by dibutyl sulfoxide (DBSO) from low molarity hydrochloric acid solution. If the extraction of ruthenium(III) follows a pattern similar to that of Fe(III) in halometal extractions, one should have in solution, at least partly, a complex of the type $HRuCl_4$. With this basic premise, a study of the extraction of Ru(III) by different sulfoxides from hydrochloric acid solutions was undertaken and the results are reported in this paper.

EXPERIMENTAL

Materials and Methods

All the extractants were obtained from the Aldrich Chemical Co. and were used without further purification. Diluents and acids were of B.D.H. AnalaR grade or E. Merck G.R. grade.

Ruthenium chloride of E. Merck extra pure used in this work was further purified according to the method described earlier (*2*). Ruthenium was labeled with ^{103}Ru as tracer before the chemical steps. Such a sample of $HRuCl_4$ was stored in concentrated hydrochloric acid at low temperature. The space above the solution was filled with nitrogen to avoid oxidation. The solvent extraction and measurement procedures were as described earlier (*2*).

Special care was taken to avoid oxidation of Ru(III) during equilibration in kinetics experiments.

RESULTS

Ruthenium(III) Extraction as a Function of Time

The extraction of Ru(III) was investigated at three different molarities of hydrochloric acid (1, 3, and 6 *M*) as a function of the time of contact of the two phases. The organic phase was 10 vol-% DBSO in benzene. The results are shown in Fig. 1. Extraction with 6 *M* HCl was identical to that of 1 *M* HCl. The extraction appears to follow the same pattern irrespective of the HCl molarity which influences only the extent of extraction. For data analysis the extraction was assumed to reach 100% over a very long period compared to the time of the experiment. The percentages of extracted ruthenium (E_t) at various times t, taken from Fig. 1, were subtracted from 100. This value ($100 - E_t$) was then plotted on a semilog paper as a function of time. The plot was resolvable into two linear components having different half-times of reaction. The fast rise in Fig. 1 corresponds to a $t_{1/2}$ of about 7 hr, while the subsequent slowly rising portion in this curve corresponds to a $t_{1/2}$ of about 90 hr. The values for 1 *M* HCl are 8 and 91 hr, while for 6 *M* HCl they are 8.5 and 93 hr.

From the above results it is evident that the kinetics of extraction was nearly independent of acidity while the extent of extraction depends on hydrochloric acid concentration. This is inherent in the assumption made in the beginning; i.e., the $HRuCl_4$ species has to be formed for extraction, and this depends upon the molarity of the hydrochloric acid. In this case the extraction shows a maximum in 3 *M* hydrochloric acid at a constant 3 hr of contact with 10% (v/v) DBSO in benzene, while in the case of tetramethylene sulfoxide it was in 2 *M* hydrochloric acid.

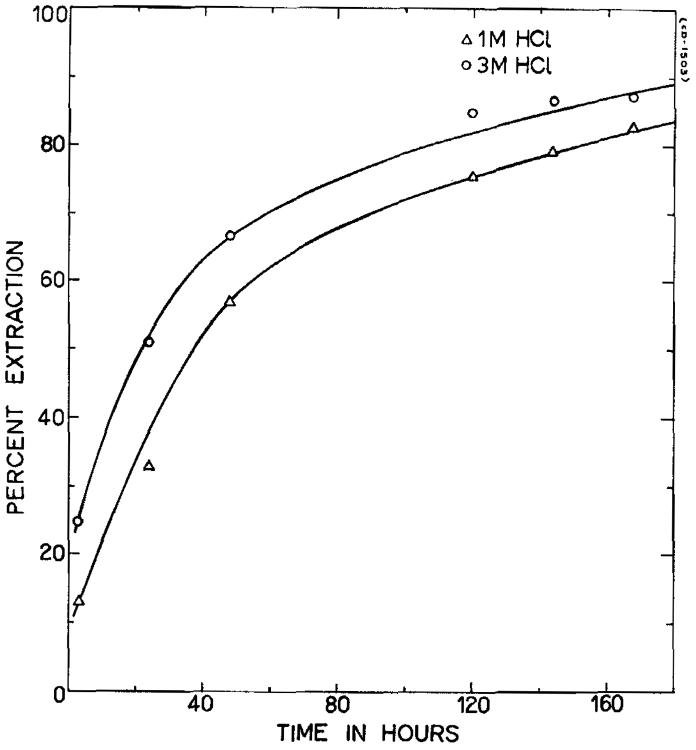

Fig. 1. Extraction of Ru(III) by DBSO in benzene as a function of time.

Extraction Dependence on the Nature of Sulfoxide

In the next series of experiments the type of sulfoxide was varied. The electron density on the sulfuryl oxygen can be influenced by the nature of the organic groups attached to the sulfur. For this purpose dibenzyl sulfoxide (DBeSO), diphenyl sulfoxide (DPSO), and tetramethylene sulfoxide (TMSO) were chosen. In the case of DPSO, electron sinks, viz., phenyl groups, are attached directly to the sulfur, whereas in dibenzyl sulphoxide a —CH_2— group intervenes between the phenyl groups and the sulfur. From electromeric effects it is to be expected that, compared to DBSO, DBeSO will show less extraction capability and DBSO should show much less. It would also be interesting to study the extraction properties when sulfur itself becomes a part of the ring as in TMSO.

Experiments similar to those described above were carried out at 3 *M* acidity with the extractants dissolved in benzene. It was noticed that DPSO shows negligible extraction even for long periods of contact time. The order of extraction observed was DBSO > TMSO > DBeSO. Thus in TMSO the donor properties of sulfuryl oxygen are reduced only to a slight degree as a result of sulfur becoming a part of the ring system. This is probably due more to steric reasons than to electromeric effects. As expected, the extraction power of DBeSO is considerably lower than that of DBSO. The data for TMSO and DBeSO were analyzed in the same way as was that for DBSO. The half reactions times obtained, given below, are longer than the values obtained for DBSO:

DBSO in C_6H_6: $t_{1/2}$, 7 hr; $t'_{1/2}$, 90 hr
TMSO in C_6H_6: $t_{1/2}$, 12 hr; $t'_{1/2}$, 280 hr
DBeSO in C_6H_6: $t_{1/2}$, 46 hr; $t'_{1/2}$, Very long

Thus the rate of uptake of the Ru(III) species depends upon the structure of the groups attached to the sulfur.

Dependence on Extractant Concentration

DBSO and TMSO in benzene were chosen as extractants. The aqueous phase was kept at 3 *M* hydrochloric acid for DBSO and at 2 *M* HCl for TMSO because the percentage extractions were better at these acid molarities. Contact times of 3 and 24 hr were selected. The percentage extraction was measured as a function of extractant concentration.

A plot of log extraction coefficients vs log sulfoxide concentration (Fig. 2) gave straight line with a slope value of 2 in both the cases.

Extraction Dependence on the Nature of Diluent

To investigate the effect of diluent on extraction, a series of experiments were carried out with different diluents. Contact times of 3 and 24 hr were chosen, and HCl in the aqueous phase was kept at 3 *M*. The organic phase was 10% (v/v) DBSO in each of the diluents.

The data in Table 1 clearly indicate the diluent effect. With benzene, where π-electrons of the aromatic ring give a weakly basic character to the diluent, the possibility exists for significant stabilization of cations in the organic phase. However, such an interaction is absent when carbon tetrachloride is used as the diluent. Cyclohexane, where no electrostatic interac-

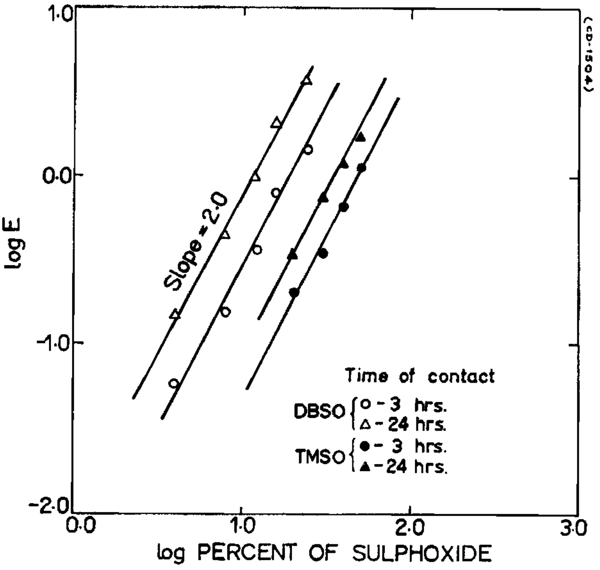

FIG. 2. Data analyses of extractant (DBSO and TMSO) dependency.

TABLE 1

Extraction of Ru(III) by DBSO as a Function of the Diluent

	% Extraction		Dielectric constant
	In 3 hr	In 24 hr	
Cyclohexane	14.65	40.3	2.02
Tetrachloroethylene	32.6	67.0	2.30
Carbon tetrachloride	37.0	75.9	2.24
Benzene	43.7	89.2	2.28
Xylene	42.7	87.2	2.37
Nitrobenzene	96.7	100.0	34.74

tion between the diluent and the extracted species is expected, shows the least extraction among the different diluents employed. Nitrobenzene, with a high dielectric constant, shows the maximum extraction. The experiments indicate that not only the dielectric constant but also the chemical nature of the diluent influences the pattern of liquid–liquid extraction (*3*).

DISCUSSION

Different equilibria may be written for the extraction of Ru(III) by an extractant of the DBSO type. For simple systems such as the extraction of $HClO_4$, Shanker and Venkateswarlu (*4*) showed that it was extracted by DBSO–benzene as an ion pair. The extraction of strong acids such as $HClO_4$ by basic extractants would involve competition between the basic extractants, the anion, and the water for proton.

It has been recently shown by Ohyoshi et al. (*5*) by paper electrophoresis that at 0.46 M chloride, the percentages of different ruthenium species are as follows: Ru^{3+} 5%, $RuCl^{2+}$ 10%, $RuCl_2^+$ 25%, $RuCl_3$ 45%, and $RuCl_4^-$ 15%.

The cationic species almost disappear with increasing molarity of HCl. Obviously, in 1 to 3 M HCl the predominent species will be neutral $RuCl_3$ and anionic $RuCl_4^-$. A solvent dependency of 2, postulated by White and Ross (*6*) as due to a species $FeCl_3 \cdot 2TOPO$, may be true in the present case also, the extracted species being $RuCl_3 \cdot 2DBSO$.

On the other hand, the decrease in extraction with increased acidity from 3 M could only mean that chloride is competing with the species extracted. Obviously this can only be with $RuCl_4^-$. Thus there appear to be two species being extracted into the organic phase. These may be $RuCl_3 \cdot 2DBSO$ and $[RuCl_4 \cdot 2DBSO]^-$. Kinetic evidence supports the above postulate.

It is pertinent at this point to examine whether the faster process having a $t_{1/2}$ in the neighborhood of 8 hr relates to the extraction of the neutral species. As mentioned earlier, the diluent influences the course of liquid–liquid extraction. While the $t_{1/2}$ of the fast component did not alter very much in carbon tetrachloride, the $t_{1/2}$ of the slower process increased by over 10 hr. Since ion pair extraction into carbon tetrachloride will be relatively slower than into benzene, one might tentatively assign the slower process as being due to the extraction of the anionic species. The faster process, being unaffected by the chemical nature of the diluent, could then be assigned to the extraction of the neutral species.

Another way of looking at the data is provided by the coordination model developed for non aqueous solvents by Drago et al. (*7*). The coordination model for the Fe(III) system has been discussed by Meek (*8*) and applied by Shanker and Venkateswarlu (*9*) to solvent extraction. On the basis of this model, the solvent enters the coordination sphere of the Fe^{3+} cation, and the subsequent disproportionation of an adduct, such as $FeCl_3S_x$ (where S is the solvent molecule and x is their number), will give $[FeCl_{3-x}(S)_n]^{x+} + x[FeCl_4]^-$. When $x = 2$ (an extractant dependency of 2), such a species in the case of Ru(III) may be written as $[RuCl \cdot 2DBSO]^{2+} \cdot 2[RuCl_4]^-$. This disproportionation reaction will provide two species for extraction and will also provide a basis for the kinetic effect. It may exhibit a certain amount of acid dependency, and it will also account for the competition of chloride ions in the extraction process. The cationic species is better solvated in such diluents as benzene and nitrobenzene.

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Received by editor March 8, 1974