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COMMERCIAL CHELATING SOLVENT EXTRACTION REAGENTS

II. PURIFICATION AND PROPERTIES OF β -ALKENYL-8-HYDROXYQUINOLINE

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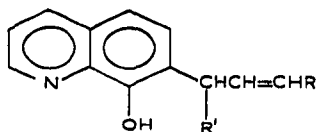
SUMMARY

The isolation of the pure active component of a proprietary β -alkenyl-8-hydroxyquinoline metal extractant, produced by the Ashland Chemical Co. under the name Kelex, is described, together with some of its properties and those of the commercially available materials.

INTRODUCTION

Both Kelex 100 and Kelex 120 were introduced by the Ashland Chemical (Columbus, Ohio, U.S.A.) to the field of solvent extraction in about 1968¹ as specific extractants for copper from acidic leach liquors. It has been known for some time that both these commercially available products contain the same active component, namely a β -alkenyl-8-hydroxyquinoline, produced by reaction of an alkyl or alkenyl chloride with a 8-hydroxyquinoline². The product of this type of reaction is Kelex 100, whereas Kelex 120 is a 20 vol. % solution of Kelex 100 in *p*-nonylphenol. This mixture was formulated presumably to improve the physical characteristics of a solvent made by dilution of Kelex 100 in an inert diluent.

As deduced from the patent covering the manufacture of Kelex 100, the molecule is an alkenyl derivation of 8-hydroxyquinol substituted in the 7-position².



While the Kelex extractants have not as yet been used in a commercial solvent extraction operation, sufficient data have been published to indicate that they have qualities which are attractive for use in the extraction of copper from acidic liquors^{3,4}.

Recently (1973), a purified form of Kelex 100 has become available and this will be the material available commercially in the future. This extractant is reported to have improved metal separation qualities over the originally produced material.

While data are available on these extractants as regards the extraction of copper and other metals from leach and similar liquors^{3,4}, together with a small amount of data on the extraction of copper in more fundamental studies⁵, nothing has been published regarding the pure reagent or its various properties, either chemical or physical.

Accordingly, studies were undertaken to obtain pure Kelex* from the commercially available material and to determine its physical and chemical properties, including proton-ligand and metal-ligand stability constants, and mechanisms of extraction metals. This paper describes the isolation of the pure reagent and some of its properties, together with some comments on the commercially available materials. Subsequent papers will deal with the other properties indicated above.

EXPERIMENTAL

Reagents and apparatus

All samples of Kelex 100 used in these studies are presumed to be regular production materials. No studies were done on Kelex 120, since this is a diluted form of Kelex 100.

Thin-layer chromatography (TLC) plates used were Eastman (Rochester, N.Y., U.S.A.) No. 6061 silica gel. The silica gel used for column chromatography was as described previously⁶. The mobile phase used for TLC was carbon tetrachloride and, for column chromatography, a carbon tetrachloride-acetone mixture (96:4).

TLC plates were developed using an ammoniacal copper solution, aluminum sulphate solution or an acidic vanadium(V) sulphate solution. All other reagents were of analytical reagent grade.

A Cary 118C recording spectrophotometer was used for spectrophotometric work in the UV-visible range. A Hewlett-Packard F and M Model 700 gas chromatograph was used for gas chromatographic (GC) work.

Analytical methods for the determination of 8-hydroxyquinoline and Kelex 100

Both Kelex 100 and 8-hydroxyquinoline (oxine) were determined in as-received material by GC. The column was 3.66 × 0.63 cm I.D. stainless steel, filled with 5 wt. % Dexsil 300 in Gas-Chrom Q. Retention times: oxine, 3.2 min at 200°; Kelex, 5.1 min at 250°. The helium flow-rate was 60 cm/min.

Silylation of both components was accomplished using N,O-bis(trimethylsilyl)acetamide (BSA) in dimethylformamide (DMF) solution. Calibration curves were obtained by plotting peak height *versus* weight of oxine or Kelex. Peaks in all cases were very sharp.

Oxine and Kelex in the as-received samples were determined by dissolving weighed amounts of extractant in DMF, silylating at room temperature for 5 min and injecting volumes of the resulting solution into the chromatograph at the

* The use of Kelex refers to the pure active component of Kelex 100.

appropriate temperature. Concentrations in the original extractants were calculated using the calibration graphs. Using this same procedure, but with a column temperature of 250°, the concentration of Kelex was determined in as-received material.

A second procedure for the determination of oxine employed separation by TLC followed by spectrophotometric determination and calculation from its molar absorptivity ($\log \epsilon_{242} = 4.55$).

Isolation of pure Kelex 100

TLC of Kelex 100, as produced prior to 1973 (referred to hereafter as Kelex I, to distinguish it from the newer purified material which will be designated Kelex II), indicated a substantial amount of a constituent which had a very low R_F value and fluoresced strongly under UV light. This material was markedly less in Kelex II, as indicated by TLC. It was also evident that the concentration of oxine in Kelex II was substantially higher than in Kelex I, and also that the number of components in the latter were greater than in the former. TLC plates are shown in Fig. 1.

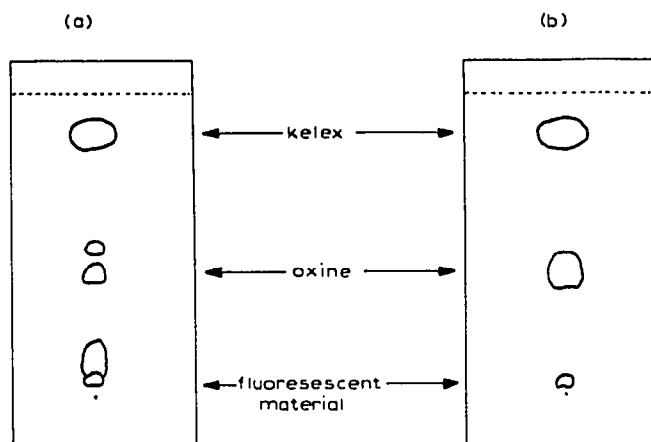


Fig. 1. TLC plates of (a) Kelex I and (b) Kelex II.

The presence of oxine in these extractants was confirmed by spectra, by TLC of pure oxine, and by analysis of samples of extractants spiked with oxine.

Column chromatography, using a 96:4 volume ratio of carbon tetrachloride-acetone (which gave better separation than carbon tetrachloride alone in column separations), gave excellent separation of Kelex and oxine from Kelex II, but with Kelex I good separation of Kelex from a green-black material was not readily accomplished. Thus the Kelex so produced was of a darker colour than that produced from Kelex II material. A second separation provided a purer looking material. Kelex products from both Kelex I and Kelex II showed only one spot after TLC.

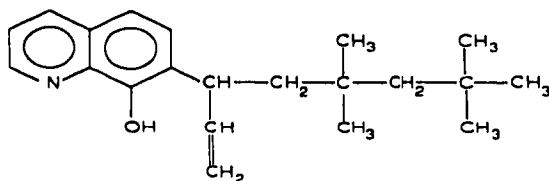
The dark fluorescent material in the Kelex I adhered strongly to the silica gel in column separations, but could be eluted with hot methanol. After removal of the methanol by evaporation, the product was a viscous, green-black material. Qualitative analysis of this material for metals showed iron to be a major metallic constituent.

The viscous material also extracted copper from acidic solution, could be titrated with acid in non-aqueous media, and thus resembled Kelex in these properties.

Pure Kelex obtained from column separations was a clear, pale brown, viscous liquid. No attempt was made to determine the per cent recovery or the concentrations of components in the as-received material other than oxine and iron.

RESULTS AND DISCUSSION

Concentrations of oxine, Kelex and iron in as-received samples of Kelex I and Kelex II are given in Table I. Elemental analysis of the pure Kelex obtained from column chromatographic separations of Kelex II gave: C 81.04%, H 9.41% and N 4.36%. These are in good agreement with calculated values for dodeceny-8-hydroxyquinoline: C 81.03%, H 9.32% and N 4.50%. It is concluded that the structure of the Kelex molecule is probably as shown below and that it has a molecular weight of 311.



The molecular weight of pure Kelex, determined by titration in non-aqueous solution⁷, was 318 ± 5 , while that for as-received Kelex II was 344 ± 5 . The density of the pure material is 0.977 ± 0.005 and of Kelex II it is 0.975 ± 0.005 , both at 24°. Allowing for the amount of oxine in Kelex II, the per cent Kelex in this material by titration is 83 wt. %. Analysis (GC) gave 77.7 wt. % Kelex; the discrepancy is probably due to other impurities in Kelex II, such as the fluorescent material.

TABLE I
CONSTITUENTS OF KELEX 100

Constituent	Kelex I (wt. %)	Kelex II (wt. %)
Kelex (free)	$71.0 \pm 0.1^*$	$77.7 \pm 0.1^*$
Oxine (free)	$0.64 \pm 0.03^*$ 0.65^{**}	$3.70 \pm 0.2^*$ —
Iron	0.10	<0.01

* By GC.

** By TLC and spectrophotometry.

Kelex decomposes before it boils, at atmospheric pressure, the liquid becoming darker as its temperature is increased. TLC on this dark material showed the presence of a fluorescent material which did not move on the plate, and hence resembled the fluorescent material found in Kelex I. This suggests that the fluorescent material in Kelex I is the result of decomposition during its manufacture. The as-received mate-

rial can be distilled under vacuum, but separation of components is not achieved by this method. This material distills at 135–137° at 0.5 mmHg.

Some comments on the differences between Kelex I and Kelex II, as reported here, appear to be in order with regard to data already published on metal extractions using these extractants. It is also interesting to speculate on the possibilities for metal separations which are indicated by the similarities between Kelex and oxine.

It would appear that the preparation of Kelex II is being carried out in equipment from which iron pick-up is considerably less than was the case for Kelex I, or that the distillation of the product has been substantially improved. Semi-quantitative spectrographic analysis of residue obtained from ignition of Kelex I showed the major constituent to be iron, with lower concentrations of nickel and chromium and trace amounts of manganese, copper and molybdenum. This suggests the use of stainless-steel reaction vessels.

Whether the iron complex in the Kelex was ferric oxinate or a ferric-Kelex complex, was not investigated since this is now only of academic interest. It would seem, however, that ferric oxinate would be the more likely.

Assuming that the same process of manufacture was used, then the concentrations of oxine in each product should be about the same. Analysis shows this not to be so. What was undoubtedly determined by analysis was free oxine rather than total oxine. Thus, silylation is not expected to affect the complexed oxine, and GC analysis would then give only free oxine. Further, TLC has been shown to separate free oxine from Kelex and other constituents of Kelex I and Kelex II, and the agreement between GC and TLC analysis is strong evidence for the oxine concentrations given in Table I to be free rather than total oxine.

However, the total oxine concentration in Kelex I, calculated from free oxine plus that which would be complexed with the iron and other metals, does not equal the free oxine present in Kelex II. In fact, only about 0.1 wt. % complexed oxine can be accounted for, giving a total oxine concentration of approximately 0.8 wt. % in Kelex I.

The presence of free and complexed oxine in the Kelex extractants also raises the problem of the determination of Kelex concentrations in solvent. In determinations using titration in non-aqueous media, both oxine and Kelex will titrate; thus the calculated Kelex concentration will be high. The same situation obtains if the procedure of loading the solvent with copper, determining the copper concentration and relating this to the concentration of Kelex (assuming a 2:1 Kelex-copper complex) is used.

The presence of free oxine in the as-received Kelex extractants can account for some of the apparently anomalous data published on the extraction of metals using these reagents. For example, it has been shown that the extraction of ferric iron by Kelex II is independent of pH over the pH range 0.5 to 2.2 (ref. 4), that is, the extraction coefficient is constant. This is interpreted as being the result of extraction of iron by oxine rather than by Kelex, and calculation of the iron extracted as ferric oxinate, using the amount of oxine present in the Kelex II solvent, agrees remarkably well with the experimental data. The extraction data⁴ also indicate that the kinetics of formation of ferric oxinate are much faster than for the ferric-Kelex complex, since little or none of the latter appears to have been extracted.

Other evidence⁸ also suggests that oxine is not readily lost from a Kelex-

kerosene solvent in several months of intermittent extraction and stripping cycles, which might have been expected from the solubility of oxine in aqueous solution⁹.

The presence of oxine, iron and other metals in the commercial Kelex products could affect the data obtained on metal extractions, and the conclusions drawn from such data, especially in fundamental studies using very low metal concentrations. Thus, the validity of the interpretation of data reported on the extraction of copper by Kelex I using the as-received material⁵ may be doubtful, especially with tracer concentrations of copper and relatively high concentrations of Kelex I in the solvent. The free oxine may have had a considerable influence on the extraction of copper, especially if the formation constants of copper oxinate and the copper-Kelex complex differ significantly.

This problem is always present when commercially produced materials are used in fundamental studies, and unfortunately is not always considered. Even in process studies, where high metal concentrations are used, the effects of other components in extractants can have significant effects. This will undoubtedly be the case with Kelex II, because of the high oxine concentration.

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