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 Citores, M. J. , Alonso, R. M. and Fernández, L. A.(1994) 'A Study of the Purification and Acid-Base Behavior of the Commercial Extractants KELEX 100 and LIX 26', Separation Science and Technology, 29: 11, 1441 — 1459
To link to this Article: DOI: 10.1080/01496399408003030
URL: http://dx.doi.org/10.1080/01496399408003030

SEPARATION SCIENCE AND TECHNOLOGY, 29(11), pp. 1441–1459, 1994

A Study of the Purification and Acid–Base Behavior of the Commercial Extractants KELEX 100 and LIX 26

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ABSTRACT

Several methods for the purification of the active components of the 8-hydroxyquinoline derivative commercial extractants KELEX 100 and LIX 26 have been studied. Among the different methods tried (washing with different solutions, formation of insoluble metal complexes, and column chromatography), the best performance was observed for column chromatography. The active components of KELEX 100 from Ashland (producer up to 1976) and from Sherex (producer from 1976) were characterized using IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry as 7-(1′-vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline and 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline, respectively. In the case of LIX 26, a TLC "pure" fraction was isolated and characterized as a 7-alkyl substituted ($\approx$ 14 carbon) derivative of 8-hydroxyquinoline that could not be fully resolved. A study of the acid–base properties of the active components of the extractants has also been carried out, and their acidity constants have been calculated by means of both graphical and numerical methods. Finally, several methods for the spectrophotometric determination of these compounds have been proposed.

INTRODUCTION

Industrial solvent extraction of nonferric metals such as Cu, Ni, Co, etc. has been greatly developed using acidic (mainly carboxylic and phosphoric) and chelating extractants. In the last group, hydroxyoximes, β-

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diketones, and quinoline derivatives have perhaps been the most extensively reported.

The application of 8-hydroxyquinoline (oxine) in the separation and determination of many metal cations is well known and is therefore of great interest in analytical chemistry. Stary (1) performed a systematic study of the extraction of several metals using this reagent. However, the amphoteric nature of the reagent, its moderate solubility in aqueous phases [log $k_d = -2.66$ (2)], and its capacity to extract acids have prevented its use in industrial processes because the losses in their efficiency and of the reagent due to solubilization in the aqueous phases cannot be tolerated.

For this reason, the introduction of long alkylic chains as substituents in positions adjacent to the functional N and OH groups of oxine has been proposed as a way to render the reagent insoluble in aqueous phases. Three commercial products are available with these characteristics. In 1968 Ashland Chemical Corp. presented KELEX 100 (7-alkyl-8-hydroxyquinoline) and KELEX 120 (which contained 20% of the former product dissolved in nonylphenol) as alternatives to the series of α- and β-hydroxyoximes commercialized by General Mills Co. as LIX reagents for the extraction of copper. Later, Henkel Co. commercialized an alkylic oxine derivative under the name LIX 26. The KELEX reagents were claimed to have a higher selectivity for Cu over the ferric ion, based on kinetic effects arising from steric reasons and their low solubility in aqueous phases [≈ 4 ppm at pH 0.5 (3)]. However, the higher capacity of the oxine derivatives for extracting acids in the stripping stages as compared to the oxime extractants has limited their use on an industrial scale.

Despite this, several studies are available in the literature concerning the potential use of KELEX 100 in industrial processes (4–11), its kinetic behavior (12, 13), the possibility of using it for impregnating macroporous resins (14), and for the preconcentration of trace elements in seawater (15, 16). LIX 26 has been used in the refining of precious metals (17) and for the elimination of Al in the recovery of Mo and Co from spent dehydrodesulfuration catalysts (18).

Concerning the chemical structure of these oxine derivative extractants, up to 1976 the active component of KELEX 100 was identified as 7-(1′-vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline (19). After that year, Sherex Chemical Co. began producing this reagent and the active component changed to 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline (20). This was somewhat confusing since in some publications the composition of the active component was incorrect.

However, in any case the commercial products are complex mixtures of which about 78 wt% is the active component for KELEX 100 Ashland

(3) and 85 wt% for KELEX 100 Sherex (20). The remaining composition is usually a mixture of by-products from the synthesis (oxine, alkylated furoquinolines, etc.). LIX 26 has been described as a branched 7-alkylated oxine derivative composed of a mixture of isomers, of which $C_{11}H_{22}$ and $C_{12}H_{24}$ are the most important (17).

The complex composition of these reagents can influence their behavior in the processes in which they take part. Thus, if a unique interpretation of the results obtained is desired, it is necessary to isolate their active components in order to carry out basic studies with them in extraction systems. Following this, it is possible to take into account the influence of other components in the commercial products.

For this reason, several procedures have been described in the literature for isolating the active compounds: washing with different solutions, distillation, recrystallization, formation of insoluble metal compounds, and chromatography being the most widely used. In this sense, several procedures have been described for the purification of KELEX 100. These can be classified in the following categories:

Washing with HCl (10) or H_2SO_4 (13) solutions.
Formation of metal precipitates of the reagent with Al (14) or Pb (14, 20), followed by stripping of the metal with acids.
Distillation of the commercial product (16, 21), which can be followed by washing of the collected fractions (21) or formation of insoluble metal compounds (14, 20).

The absence of purification procedures such as column chromatography is worth noting. This procedure has proved to be very efficient in the case of oxime-type reagents such as LIX 63 (19), 8-sulfonamidoquinolines such as LIX 34 (22), and β-diketones such as LIX 54 (23).

In conclusion of the foregoing discussion, the absence of uniform criteria for obtaining "pure" components for performing basic studies with these reagents is pointed out.

On the other hand, the nature and position of substituents in the basic oxine molecule can affect the properties of these reagents due to the variation of their acid–base and kinetic characteristics and their steric effects. Because of this, it is well understood that basic information about these compounds, such as their acidity constants, is essential in order to interpret their behavior in metal extraction processes, which, in turn, can help in improving their properties.

However, the low solubility of these compounds in aqueous phases is a hindrance for the determination of their pK_a values using conventional potentiometric techniques. For this reason, mixed media have been sometimes used, although it is difficult to extrapolate the values obtained to

pure aqueous solutions. Due to these facts, the spectrophotometric determination of the acidity constants is normally preferred, taking advantage of the high molar absorptivities of their protolytic species. In this context, the use of hydroalcoholic media is advantageous because they can help the solubilization of the reagents without a drastic change in the properties of the media. Furthermore, the use of a constant ionic media keeps the activity coefficients of the species involved constant. If the media contains chloride, it helps to avoid interferences derived from the presence of other inorganic anions in the spectrophotometric determination of the compounds, which is normally carried out in the UV region.

Based on the preceding discussion, the work presented had two main objectives. First, to perform a comparative study of different procedures for obtaining the active components of the commercial extractants KELEX 100 (both Ashland and Sherex) and, second, to study their acid–base equilibria. A hydroalcoholic media of 0.125 $mol \cdot dm^{-3}$ ionic strength in KCl was selected for the acid–base equilibria study.

EXPERIMENTAL

Reagents and Solutions

Solutions of HCl, H_2SO_4, H_3PO_4, CH_3COOH, $AgNO_3$, $BaSO_4$, and Na_2CO_3 (Merck, p.a.), KOH and KCl (Fluka, p.a.), H_3BO_3 (Scharlau, p.a.), and $Al_2(SO_4)_3$ (Probus, p.a.) were prepared in double distilled water. Their concentrations were checked by standard procedures (24). Their dilutions were made by weight.

The organic solvents toluene, chloroform, hexane, xylene, heptane, dioxane, carbon tetrachloride, dimethylformamide, dimethylsulfoxide, ethanol, and methanol were all of analytical grade and were used without further purification.

The active components of the extractants KELEX 100 (both Ashland and Sherex) and LIX 26 were isolated by column chromatography, as described below.

For the thin-layer chromatography tests, Silica Gel 60 F_{254} aluminum sheets of 0.2 mm thickness from Merck were used. Development of the chromatographic plates was made with chloroform:hexane mixtures of different compositions (normally 50:50).

Apparatus

Spectrophotometric measurements were carried out in a Shimadzu 260 UV-V spectrophotometer in 1 cm pathlength quartz cells.

Potentiometric titrations were made in an automated system developed in our laboratory (25).

Standard pH measurements were carried out with a radiometer PHM64 pH-meter and a combined glass electrode fitted with an Ag(s)/AgCl(s) reference electrode.

Gas chromatographic measurements were carried out in an HP 5890 gas chromatograph fitted with an HP 5970A mass selective detector. Crosslinked methylsilicone capillary columns of 12 m length, 0.2 mm i.d., and 0.33 μm film thickness were used for KELEX 100 Ashland, and crosslinked methylsilicone with 5% phenyl radicals of 25 m length, 0.2 mm i.d., and 0.33 μm film thickness were used for KELEX 100 Sherex and LIX 26. For both cases the oven program was the same: 100°C, 20°C/min, 285°C for 5 minutes, T_i = 175°C, T_D = 290°C.

RESULTS

Purification of the Commercial Extractants KELEX 100 and LIX 26

Several methods proposed in the literature, together with some new ones, to determine the active components of the extractants have been tested in an attempt to compare their utility. Thin layer chromatography (TLC) and gas chromatography (GC) were used as purity criteria in the following way:

For TLC, a compound was considered pure when only one spot was found in the chromatographic plate independent of the composition of the eluent.

For GC, a product was considered pure if only one peak was present in the chromatogram.

Apart from these purity criteria, for each of the products obtained by different purification methods, potentiometric titrations in glacial acetic acid were carried out using perchloric acid as the titrant (26). According to Ritcey and Ashbrook (3), these titrations allow a gross estimation of the contents of the products, which may be of interest from an industrial practice point of view. However, taking into account the nature of the acid–base reaction involved (protonation of the basic quinolinic N), these reactions are not selective for a specific type of compound and, thus, the result must be viewed only as approximate because it is calculated by considering the molecular weight of the active component. Alternatively, it is possible to calculate an apparent molecular weight for the titrated product from the end point, which might be of interest in order to establish its composition. The details of the potentiometric system employed in these titrations are given elsewhere (25). The results obtained have been collected in Table 1.

TABLE 1
Results of the Potentiometric Titrations of the Products Obtained in the Purification of the Commercial Extractants KELEX 100 (Ashland and Sherex) and LIX 26 Using Different Procedures. The Results, Expressed as Percentages, Correspond to the Theoretical Purity Assuming a Molecular Weight Equal to That of the Active Component of the Product. The Values in Parentheses Indicate the Apparent Molecular Weight Calculated from the End Point of the Titrations

Purification method	KELEX 100 Ashland	KELEX 100 Sherex	LIX 26[a]
Wash with HCl and Na_2CO_3	87.8% (354)		
Wash with HCl		92.5% (323)	83.7% (372)
Wash with H_2SO_4		94.0% (318)	85.8% (363)
Column chromatography	92.4% (335)	91.5% (325)	79.0% (394)
Commercial product	92.8% (335)	92.8% (322)	82.1% (379)

[a] Purity has been calculated by assuming a 311 molecular weight.

The Commercial Products

The three commercial reagents are liquids. KELEX 100 from both Ashland and Sherex has a brown color. LIX 26 is blacker and syrupy, being considerably thicker than the others. All three have the characteristic quinoline smell.

Preliminary tests using TLC revealed that the commercial products had a large amount of impurities. The GC-MS of these products yielded a chromatogram with a main peak of 311 MW for KELEX 100 Ashland, a well-resolved chromatogram with 16 peaks (the largest area corresponding to 299 MW and 7 peaks corresponding to several isomers of a compound with 429 MW) for KELEX 100 Sherex, and a poorly resolved broad peak for LIX 26 but with a much smaller range of retention times than for KELEX 100 Sherex. As both chromatograms were performed under identical conditions, there appears to be great structural similarity among the components.

The potentiometric titrations for these compounds indicated apparent molecular weights of 355, 322, and 379, respectively, for KELEX 100 Ashland, KELEX 100 Sherex, and LIX 26 (cf. Table 1).

The different purification procedures employed are detailed in the following.

Procedures Based on Washing the Commercial Products

Three different procedures were tried.

Washing with HCl and Na_2CO_3 Solutions. This procedure was tried only with KELEX 100 Ashland. 10 cm^3 of the commercial reagent were

shaken for 1 hour with an equal volume of 1 mol·dm^{-3} HCl. After washing the organic phase repeatedly with water, the product was shaken for another hour with 1 mol·dm^{-3} Na_2CO_3 and against washed with water. The entire sequence (HCl + Na_2CO_3) was repeated 3 times and, finally, the organic phase was thoroughly washed with water until no Cl^- was found (tested with $AgNO_3$, 0.1 mol·dm^{-3}). The final product obtained was impure according to TLC.

The following procedures were tried with both KELEX 100 Sherex and LIX 26.

Washing of the Commercial Product Dissolved in Toluene with HCl Solutions. 5 cm^3 of the commercial products were increased up to 10 cm^3 by the addition of toluene and shaken with equal volumes of HCl (1 mol·dm^{-3}) until the yellow color of the aqueous phases disappeared. This process was repeated 8 times. The organic phases were washed with water until no Cl^- was found, and the diluent was evaporated by heating under vacuum. In both cases the products obtained were not pure according to TLC.

Direct Washing of the Commercial Products with H_2SO_4. 5 cm^3 of the commercial products were shaken with equal volumes of H_2SO_4 (1 mol·dm^{-3}) until the yellow color of the aqueous phases disappeared. This process was repeated 8 times. The organic phases were washed with water until no traces of SO_4^{2-} were detected (by precipitation with 10% w/v $BaSO_4$). It was found by TLC that the products obtained were not pure.

Procedures Based on the Formation of Insoluble Compounds

Reference 14 describes a procedure for the purification of KELEX 100 based on the formation of an insoluble compound with lead. We have studied a similar procedure with LIX 26 based on a solid compound of this reagent with aluminum. This compound was observed in a previous investigation carried out in our laboratory (18).

A 0.2 mol·dm^{-3} xylene solution of LIX 26 was contacted with a 0.2 mol·dm^{-3} solution of $Al_2(SO_4)_3$ using mechanical stirring. The mixture was neutralized slowly by small additions of NaOH (0.5 mol·dm^{-3}) until the pH of the aqueous phase was between 8 and 9.5. In this pH zone a crystalline insoluble compound was formed in the organic phase. This compound was filtered and washed several times with 0.1 mol·dm^{-3} Na_2CO_3 and water, and a yellow powder was obtained. This solid was dissolved in xylene and contacted with a 1 mol·dm^{-3} HCl solution in order to strip the metal. Once the two phases were separated, the solvent

was eliminated. The resulting compound was found to be impure according to TLC.

Column Chromatography

Due to the similar characteristics of the reagents investigated, differing only in the alkylic chain in position 7 of the oxine group, the purification procedure by column chromatography was carried out under the same conditions as for TLC. 30 cm long columns of 5 cm i.d. were filled with silica gel 60 (70–230 mesh) and the commercial reagents (about 2 g each time) were eluted at atmospheric pressure with a 50:50 solution of chloroform:hexane. In this way, three TLC pure compounds were obtained for each of the commercial reagents after evaporation of the solvent.

The GC-MS chromatograms of these compounds yielded single peaks of MW 311 and 299 for KELEX 100 Ashland and Sherex, respectively. Characterization of these compounds was performed as described below.

For LIX 26 a substantially more resolved chromatogram than that of the commercial reagent was obtained. In it, one of the major peaks showed 311 MW with a fragmentation scheme identical to that of the active compound of KELEX 100 Ashland.

The corresponding potentiometric titrations of the products obtained by column chromatography revealed theoretical purities of 92.5, 91.5, and 79% or apparent molecular weights of 334, 325, and 394, respectively, for KELEX 100 Ashland, KELEX 100 Sherex, and LIX 26. These results point out the limitations of this method for the quantitative determination of the purity of the reagents.

Characterization of the Active Components

A characterization study of the active components of the extractants studied was carried out using ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy, and mass spectrometry. The complete details of this study, with band and transition assignments and the fragmentation schemes for the compounds of interest, are given elsewhere (27). The most relevant results of this study can be summarized by assigning the formulas of 7-(1′-vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline and 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline, respectively, to the active components of KELEX 100 Ashland and KELEX 100 Sherex, in agreement with previous findings (19, 20). In the case of the active component of LIX 26, analysis of the results pointed toward a 7-alkyl-substituted derivative of 8-hydroxyquinoline with 14 carbon atoms as the most abundant component in the purified product.

Acid–Base Behavior of the Active Components of KELEX 100 and LIX 26

In the following 7-(1′-vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline and 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline will be considered to be the active components of KELEX 100 Ashland and Sherex, respectively. For LIX 26, although the active component has not been obtained in a conclusive way, the product obtained by column chromatography will be considered as the active component in the acid–base study described below.

The study of the acid–base behavior of these compounds was performed in water–ethanol mixtures in order to avoid solubility problems and also because they do not pose difficulties for their spectrophotometric detection. Preliminary experiments showed that the minimum proportion of ethanol for a complete dissolution of the compounds in the whole pH range studied (1 to 13.5) was 40%. Below this proportion the solutions turned slightly opaque, causing erratic measurements. As an example, Fig. 1 shows the variation of the spectra of the active component of KELEX 100 Ashland with the composition of the water–ethanol mixture.

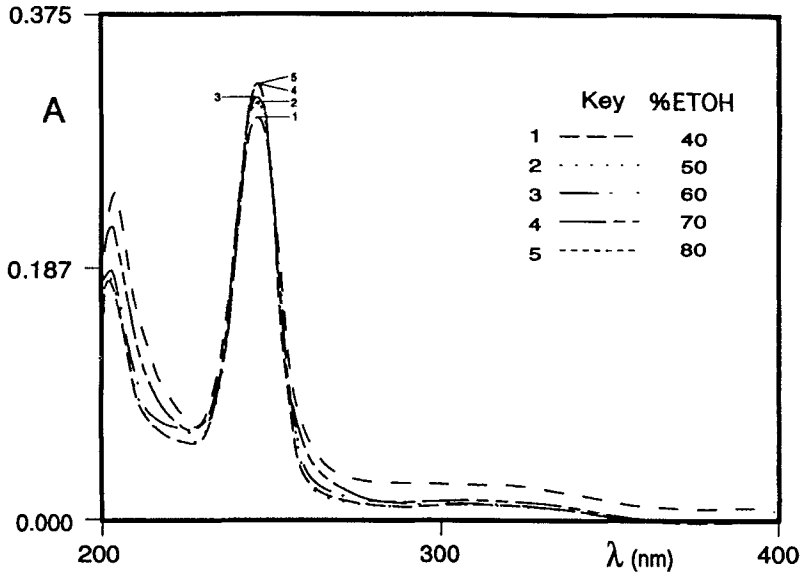

FIG. 1 Variation of the absorbance of 7-(1′-vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline solutions as a function of wavelength for different proportions of the ethanol:water solvent and $C_{HR} = 1.01 \times 10^{-5}$ mol·dm^{-3}.

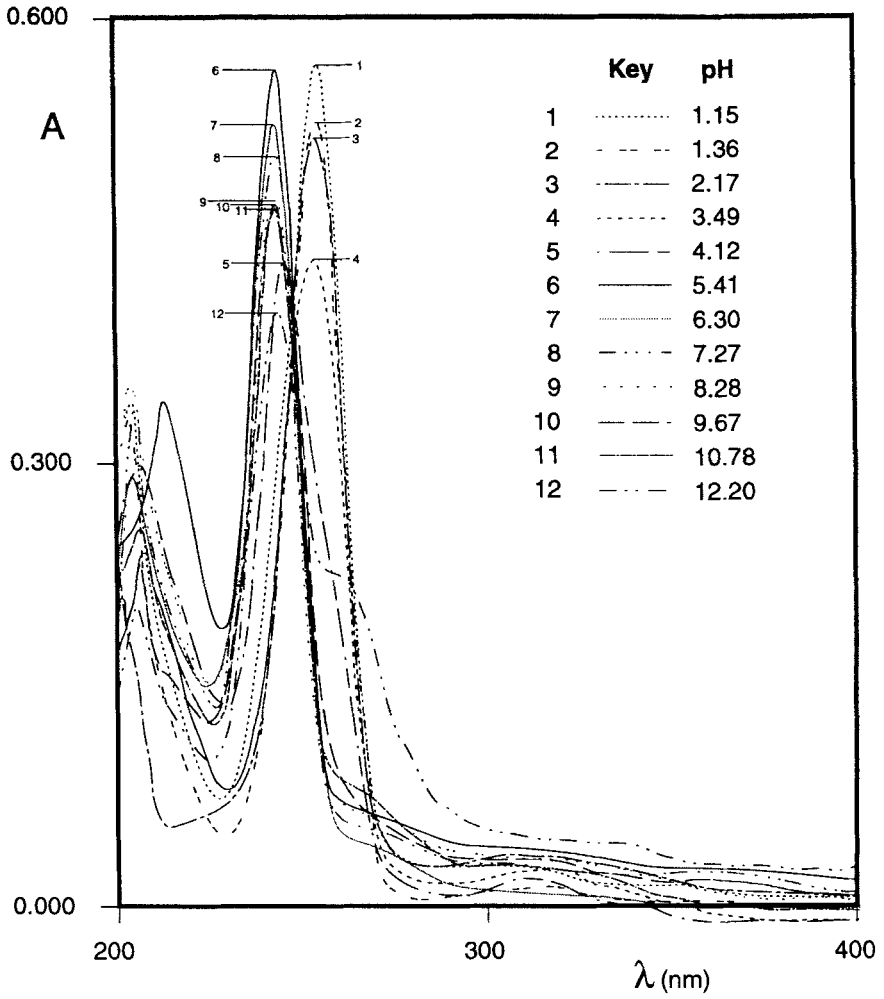

FIG. 2 Variation of the absorbance of 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline solutions as a function of wavelength at different pH values for $C_{HR} = 1.66 \times 10^{-5}$ mol·dm^{-3}.

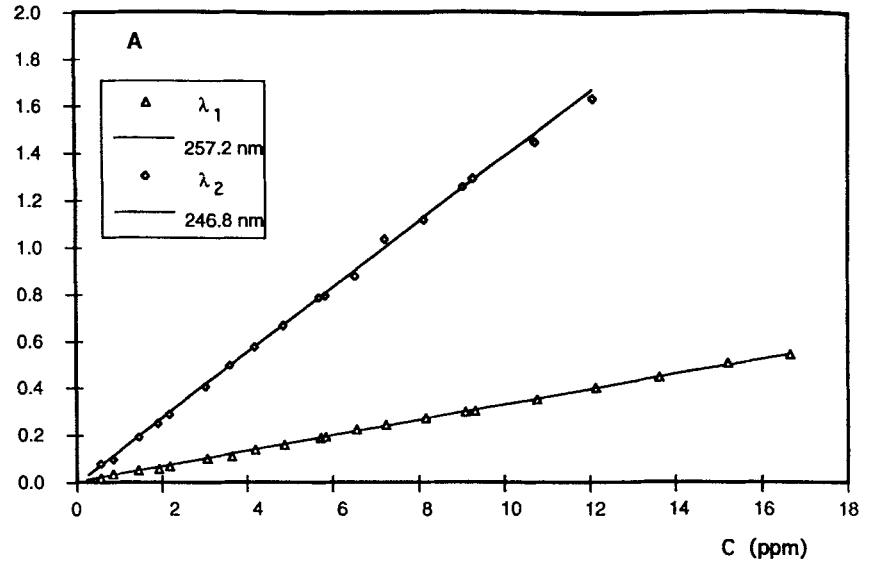

FIG. 3 Variation of the absorbance with the concentration of 7-(1'-vinyl-3',3',5',5'-tetramethylhexyl)-8-hydroxyquinoline solutions at different wavelengths and constant pH 7.85. The equations for the calibration lines are:

$$\lambda_1 = 257.2 \text{ nm}, \quad A = (3.99 \pm 1.38) \times 10^{-3} + (3.24 \pm 0.01) \times 10^{-2} C$$
$$\lambda_2 = 246.8 \text{ nm}, \quad A = (8.40 \pm 7.01) \times 10^{-3} + (1.37 \pm 0.01) \times 10^{-2} C$$

A constant 0.125 mol·dm^{-3} KCl ionic media was used in all the experiments. As can be observed, the absorbance of the spectrum peaks increases slightly between 40 and 60% ethanol. This can be due to the cooperative effects of the solvent: changes in the dielectric constant of the media, the specific interactions between the solvent and the functional groups in the molecules, and the change of the relative proportions of the protolytic species of the reagents. No further change in the spectra are observed above 70% ethanol. For this reason, 40:60 ethanol:water mixtures were used in the rest of the experiments described below.

The general composition of the solutions employed in these studies was $[HR]_{Tot} = C_{HR}$ mol·dm^{-3}, [KCl] = 0.125 mol·dm^{-3}, and $[H^+] = h$ mol·dm^{-3}.

Britton-Robinson buffers (0.02 mol·dm^{-3}) were used to keep the pH constant, and blank corrections were applied in all cases. The free proton concentration, h, was determined by using a combined glass electrode with Ag(s)/AgCl(s) reference electrode calibrated with two standard buffer solutions of pH 4.00 ± 0.02 and pH 7.00 ± 0.02 at 298 K.

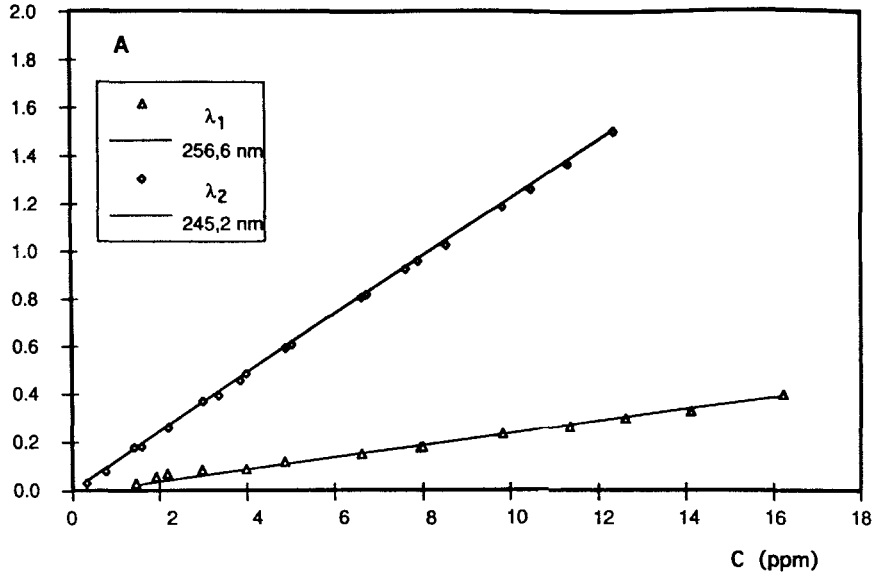

FIG. 4 Variation of the absorbance with the concentration of 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline solutions at different wavelengths and constant pH 8.20. The equations for the calibration lines are:

$\lambda_1 = 256.6$ nm, $A = (-4.75 \pm 3.93) \times 10^{-3} + (2.41 \pm 0.04) \times 10^{-2}C$
$\lambda_2 = 245.2$ nm, $A = (-4.76 \pm 3.25) \times 10^{-3} + (1.22 \pm 0.01) \times 10^{-2}C$

Variation of the Spectra with the pH

Figure 2 shows the variation of the spectra with pH for the active component of KELEX 100 Sherex. Similar results were obtained for KELEX 100 Ashland and LIX 26. The stability of the solutions was checked in all cases by the constancy of the spectra as a function of time in the entire pH range studied. Lowering the pH increases the absorbance of the maxima and produces a slight bathochromic shift, which can be attributed to the increase of the proportion of the acidic species resulting from protonation of the basic quinolinic N (H_2R^+). The increase of pH lowers the previously observed peak and shifts it to lower wavelengths, but for pHs higher than ~12 a shoulder is observed at ~265 nm, which can be attributed to the loss of the hydroxylic proton (R^-). Only one isobestic point is observed at ~250 nm in the pH range studied, corresponding to the transition between H_2R^+ and HR.

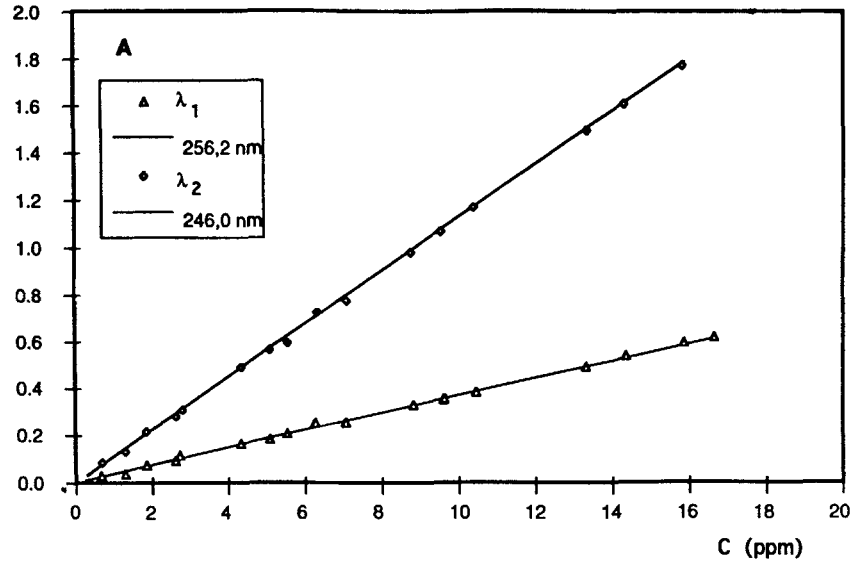

FIG. 5 Variation of the absorbance with the concentration of the active component of LIX 26 solutions at different wavelengths and constant pH 7.80. The equations for the calibration lines are:

$$\lambda_1 = 256.2 \text{ nm}, \quad A = (-0.60 \pm 3.68) \times 10^{-3} + (3.79 \pm 0.01) \times 10^{-2}C$$
$$\lambda_2 = 246.0 \text{ nm}, \quad A = (-4.11 \pm 5.43) \times 10^{-3} + (1.13 \pm 0.01) \times 10^{-2}C$$

From this study the predominance of the species H_2R^+ at pH $\leqslant$ 3.5, HR for 4 $\leqslant$ pH $\leqslant$ 12, and R^- for pH $\gtrsim$ 12 can be concluded.

Variation of the Absorbance with the Concentration of the Reagents

In order to verify Beer's law, which is the basis of treatments for the determination of the acidity constants of the reagents, a study of the variation of the absorbance with the concentration of the reagents at constant wavelength was performed. Two wavelengths were selected for each reagent, corresponding to the absorbance maxima in Fig. 2. The experiments were carried out at about neutral pH because this is the region in which the variation of the spectra with pH is less significant.

The results obtained are presented in Figs. 3–5. Beer's law is obeyed for each wavelength in the entire concentration range studied. The straight calibration lines were fitted by least squares using the Letagrop Model-Function Program (28). Global standard deviations of the fits lower than 2% were obtained in all cases.

Determination of the Acidity Constants of the Reagents

The determination of the acidity constants of the active components of the reagents was performed by measuring the absorbance of these compounds as a function of pH at constant wavelength and reagent concentration. The wavelengths were selected in each case to produce the highest variations in the absorbance. The results obtained are plotted in Figs. 6–8.

These results were treated by both graphical and numerical methods.

The graphical treatments were performed by means of a specially developed computer program called APH. This program uses the linear methods of Stenström–Goldsmith and Sommer and curve-fitting methods with one or two normalized variables [variable + parameter and Projection Strip (29)] methods. Other details of the program and the calculation methods employed are described in Reference 30.

The numerical treatment was carried out with the help of the SPEFO (31) version of the Letagrop Program (32). This program minimizes the error square sum defined by the following expression:

$$U = \sum_{i=1}^{N_p} (A_{i,\text{exp}} - A_{i,\text{calc}})^2$$

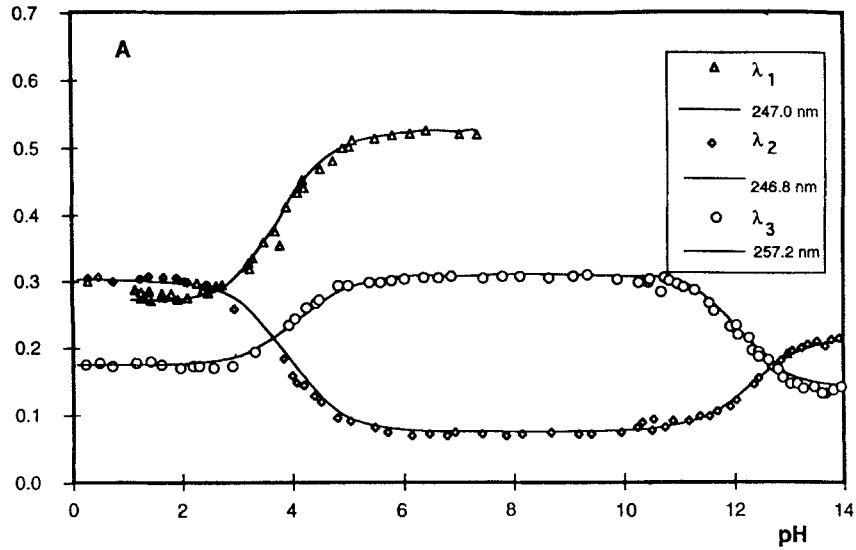

FIG. 6 Variation of the absorbance of 7-(1′-vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline solutions at constant wavelength as a function of pH for $C_{HR} = 1.14 \times 10^{-5}$ mol·dm^{-3} ($\lambda_1 = 247.0$ nm) and $C_{HR} = 6.85 \times 10^{-6}$ mol·dm^{-3} ($\lambda_2 = 246.8$ nm, $\lambda_3 = 257.2$ nm) in 40% ethanol:water mixtures and 0.125 mol·dm^{-3} KCl ionic media. The solid lines have been plotted using the constants and absorptivities given in Tables 2 and 3.

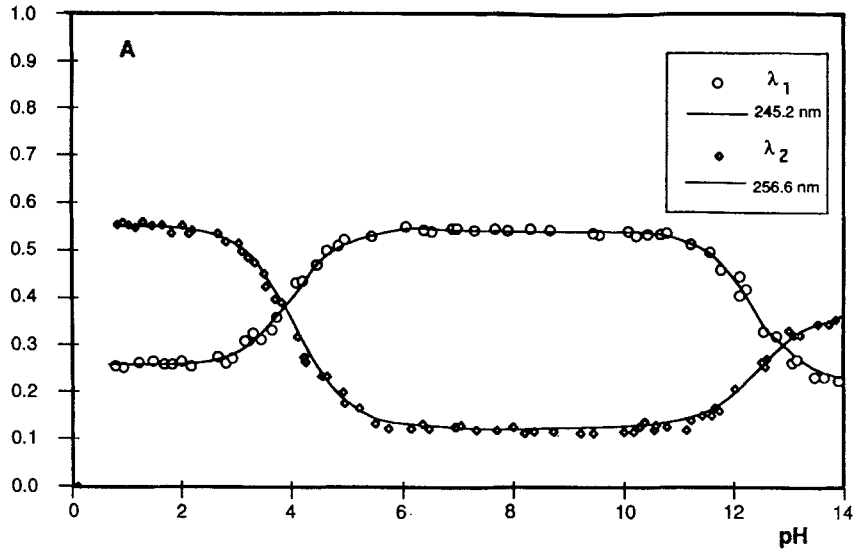

FIG. 7 Variation of the absorbance of 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline solutions at constant wavelength as a function of pH for $C_{HR} = 1.66 \times 10^{-5}$ mol·dm^{-3} (λ_1 = 245.2 nm, λ_2 = 256.6 nm) in 40% ethanol:water mixtures and 0.125 mol·dm^{-3} KCl ionic media. The solid lines have been plotted using the constants and absorptivities given in Tables 2 and 3.

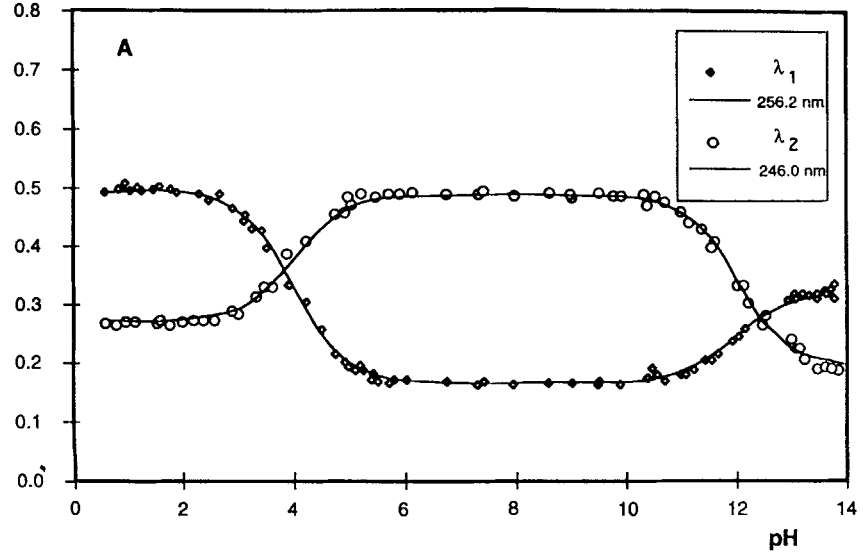

FIG. 8 Variation of the absorbance of the active component of LIX 26 solutions at constant wavelength as a function of pH for $C_{HR} = 1.41 \times 10^{-5}$ mol·dm^{-3} (λ_1 = 256.2 nm, λ_2 = 246.0 nm) in 40% ethanol:water mixtures and 0.125 mol·dm^{-3} KCl ionic media. The solid lines have been plotted using the constants and absorptivities given in Tables 2 and 3.

where N_p is the number of experimental points and $A_{i,\text{exp}}$ and $A_{i,\text{calc}}$ are, respectively, the absorbances experimentally measured and calculated by the program assuming a set of chemical species in the system together with their formation constants and absorptivities. With other statistical parameters of the fit, such as the errors in the fitted parameters (formation constants and absorptivities), the global standard deviation of the fit

$$\sigma(A) = [U/(N_p - N_{pm})]^{1/2}$$

where N_{pm} is the number of parameters fitted and the Hamilton R-factor

$$R = \left[U \Big/ \left(\sum_{i=1}^{N_p} A_{i,\text{exp}}^2 \right) \right]^{1/2}$$

are also calculated by the program.

The numerical treatment was performed by considering the whole set of data at all the wavelengths studied for each reagent.

As a summary of these calculations, Tables 2 and 3 show, respectively, the values of the acidity constants and absorptivities obtained by numerical treatment of the data. The results obtained by graphical methods are all similar to those presented in these tables.

DISCUSSION

Several of the methods proposed in the literature for the purification of commercial oxine derivative extractants have been evaluated with respect to their ability to yield a unique "active component" in these mix-

TABLE 2
Values of the Acidity Constants and Statistical Parameters of the Fit Obtained in the Numerical Treatment with the SPEFO Version of the Letagrop Program for the Active Components of the Extractants KELEX 100 Ashland and Sherex and LIX 26 in 40:60 Ethanol:Water Mixtures and 0.125 mol·dm^{-3} Ionic Media

Compound	pK_{a1}	pK_{a2}	$U_{\min}$	$\sigma(A)$	R
7-(1′-Vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline	3.77 ± 0.05	12.17 ± 0.06	6.58×10^{-3}	0.006	3.45×10^{-2}
7-(1′-Methyl-4′-ethyloctyl)-8-hydroxyquinoline	3.98 ± 0.04	12.40 ± 0.07	6.66×10^{-3}	0.008	2.20×10^{-2}
Active component of LIX 26	3.92 ± 0.05	12.04 ± 0.07	7.36×10^{-3}	0.008	2.03×10^{-2}

TABLE 3
Values of the Absorptivities of the Protolytic Species of the Active Components of the Extractants KELEX 100 Ashland and Sherex and LIX 26 Obtained in the Numerical Treatment with the SPEFO Version of the Letagrop Program in 40:60 Ethanol:Water Mixtures and 0.125 mol·dm^{-3} Ionic Media

Compound	Species	$\epsilon_{\lambda 1}$	$\epsilon_{\lambda 2}$	$\epsilon_{\lambda 3}$
7-(1′-Vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline. λ_1 = 247.0 nm, λ_2 = 246.8 nm, λ_3 = 257.2 nm	H_2R^+	(2.39 ± 0.01) × 10^4	(2.14 ± 0.01) × 10^4	(3.85 ± 0.02) × 10^4
	HR	(4.47 ± 0.01) × 10^4	(3.82 ± 0.01) × 10^4	(9.36 ± 0.01) × 10^3
	R^-		(1.52 ± 0.02) × 10^4	(2.62 ± 0.02) × 10^4
7-(1′-Methyl-4′-ethyloctyl)-8-hydroxyquinoline. λ_1 - 245.2 nm, λ_2 = 256.6 nm	H_2R^+	(1.82 ± 0.01) × 10^4	(3.90 ± 0.03) × 10^4	
	HR	(3.86 ± 0.01) × 10^4	(9.29 ± 0.01) × 10^3	
	R^-	(1.56 ± 0.03) × 10^4	(2.63 ± 0.03) × 10^4	
Active component of LIX 26. λ_1 = 246.0 nm, λ_2 = 256.2 nm	H_2R^+	(1.86 ± 0.01) × 10^4	(3.50 ± 0.01) × 10^4	
	HR	(3.47 ± 0.01) × 10^4	(1.19 ± 0.01) × 10^4	
	R^-	(1.35 ± 0.02) × 10^4	(2.29 ± 0.02) × 10^4	

tures. The conclusion is that most of them fail in obtaining a unique product which can be used in model extraction studies or in the assessment of the basic properties of these extractants. The reasons for these failures, when considering washing procedures or the formation of insoluble metal precipitates, are probably their intrinsic lack of resolution, the great structural similarities of the active components (probably differing only in the length and branching of the alkylic chains in position 7 of the oxine group), and the great number of by-products from their synthesis. Only higher resolution procedures, such as column chromatography, have shown enough potential for the separation of the mixtures' components. This conclusion has been encountered in similar studies with other families of commercial extractants (19, 22, 23). However, we are not claiming that the other purification procedures are not valid if what is sought is a gross elimination of the major impurities that would produce less reproducible results in conventional studies for the separation of metals.

Apart from this fact, the limited value of analytical techniques such as potentiometry for the determination of the gross contents of the active components has also been pointed out.

Using spectrometric techniques, the active components of the extractants KELEX 100 Ashland and KELEX 100 Sherex have been characterized as 7-(1′-vinyl-3′,3′,5′,5′-tetramethylhexyl)-8-hydroxyquinoline and 7-(1′-methyl-4′-ethyloctyl)-8-hydroxyquinoline, respectively. In the same way, the active components of LIX 26 have been described as a mixture of 7-alkyl derivatives of oxine, one of whose major components shows

the same molecular weight and mass spectra as the active component of KELEX 100 Ashland.

Regarding the spectrophotometric study of the acid–base behavior of the active components of the extractants, the potential utility of this technique for the determination of the concentration of these compounds in, for instance, distribution studies between aqueous and organic phases such as those commonly used in solvent extraction processes must be emphasized.

On the other hand, the acidity constants of these compounds have been determined in hydroalcoholic media because their high insolubility in pure aqueous media would make this determination extremely difficult by conventional analytical techniques. We consider that the information obtained in this way is of enough value to model the behavior of these compounds, as has been demonstrated in other solvent extraction processes developed in this laboratory (18).

ACKNOWLEDGMENTS

The help of Dr. C. Iriondo and Dr. M. J. Villagrá, Departments of Organic Chemistry and Chemical Engineering of the UPV/EHU, in the interpretation of the IR, ^{1}H-NMR, ^{13}C-NMR, and GC-MS spectra obtained for the characterization of the different compounds encountered in this work is gratefully acknowledged.

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Received by editor August 12, 1993