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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

An IR-Spectroscopic Examination of Copper–LIX984N Extractant Complexes

A. E. Buketova

Kazakh-British Technical University, Almaty, Kazakhstan

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Abstract—A comparative analysis was carried out for the IR spectra of dilute and neat LIX984N extractant and of the organic phase after copper extraction.

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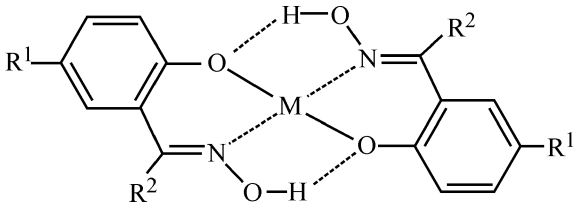
Organic composite LIX984N belongs to extractants most extensively and efficiently used for copper extraction from acid sulfate solutions [1]. Salicylaldoximes in its composition are responsible for its high selectivity and are identifiable by spectral methods [2–4].

The LIX984N composite is a mixture of molecules of 5-nonylsalicylaldoxime (aldoxime-1) and 2-hydroxy-5-nonylacetophenoxime (ketoxime-2). The high selectivity of extractant originates from the ability of hydroximes with the general formula R1–C_6H_3(OH)–C(R_2)=NOH to form stable chelate complexes with copper cations Cu^{2+}. The latter substitute two protons in the hydroxy groups of two extractant molecules, with the metal coordinated via nitrogen atoms:



It was found earlier [5] that ketoxime-2 in the extractant acts as modifier with respect to aldoxime-1 containing an alkyl group C_{12} or C_9, thereby generating synergistic extraction effect in the mixture. Earlier, LIX class extractants and their complexes were examined by molecular spectroscopy. However, complexing between the bidentate ligands in the LIX984N composition and copper cations was not investigated. The same is true of the mutual influence of the aldoxime and ketoxime molecules in complexing and the influence exerted by alkyl substituents on the extraction behavior of the composite.

Here, we measured and examined the IR spectra of neat (aldoxime-1–ketoxime-2 mixture without solvent) extractant LIX984N (Fig. 1), as well as of the extractant dissolved in aviation kerosene (Fig. 2), extractant samples with copper after single-batch extraction (Fig. 3), and maximally copper-saturated extractant (Fig. 4).

The IR absorption spectra were taken in the regions corresponding to the main frequencies of the stretching and bending vibrations of the functional groups in the extractant. The measurements were carried out on a Nicolet IR-200 IR Fourier spectrometer at 4000–400 cm^{-1}.

The IR spectra of the sample of neat LIX984N (Fig. 1) contain a broadened absorption peak at 3392 cm^{-1}, which suggests the lack of association of the molecules via the phenol hydroxy group, due evidently to steric hindrance. The spectrum of neat LIX984N also contains a band at 1267.31 cm^{-1}, which can be assigned to in-plane bending vibrations of the OH group. At 2960–2850 cm^{-1} there are intense bands νas and νs associated with stretching vibrations of the C–H bonds in CH_2 and CH_3 groups of the alkyl groups in the extractant components. The bands at 1465.10 and 1387.12 cm^{-1} are associated with the bending vibrations δ of these groups [6]. The bands at 1623.48, 1585.12, and 1496.44 cm^{-1} are to be assigned to the aromatic group.

The bands observed at 1300–1100 cm^{-1} are belong to the wagging, twisting, and rocking vibrations of the CH_2 groups in the aliphatic carbon chain.

Unfortunately, the vibrations of the carbon-nitrogen bond in the oxime –C=NOH group that should be

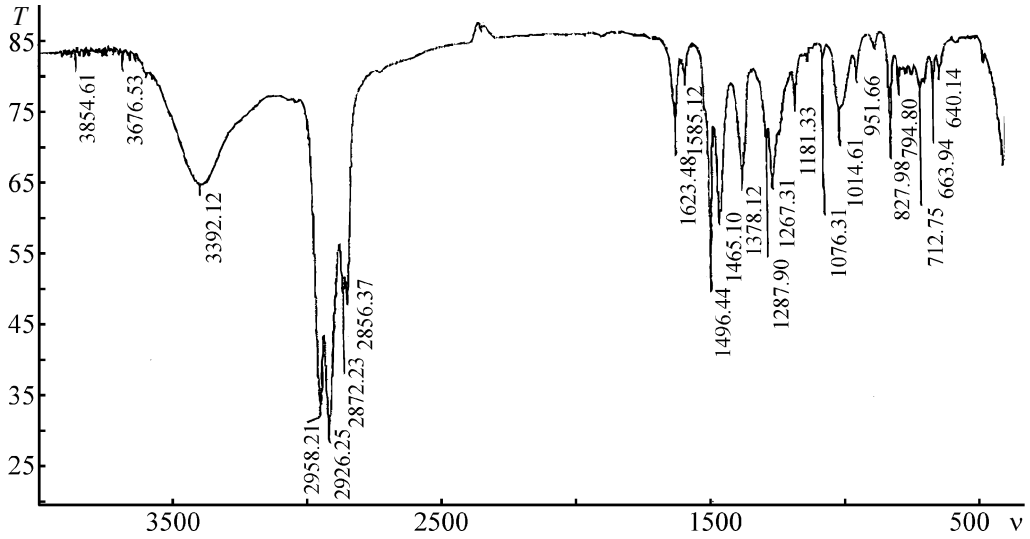


Fig. 1. IR spectrum of neat LIX984N extractant: (*T*) Transmission and (ν) wavenumber, cm^{-1}; the same for Figs. 2–4.

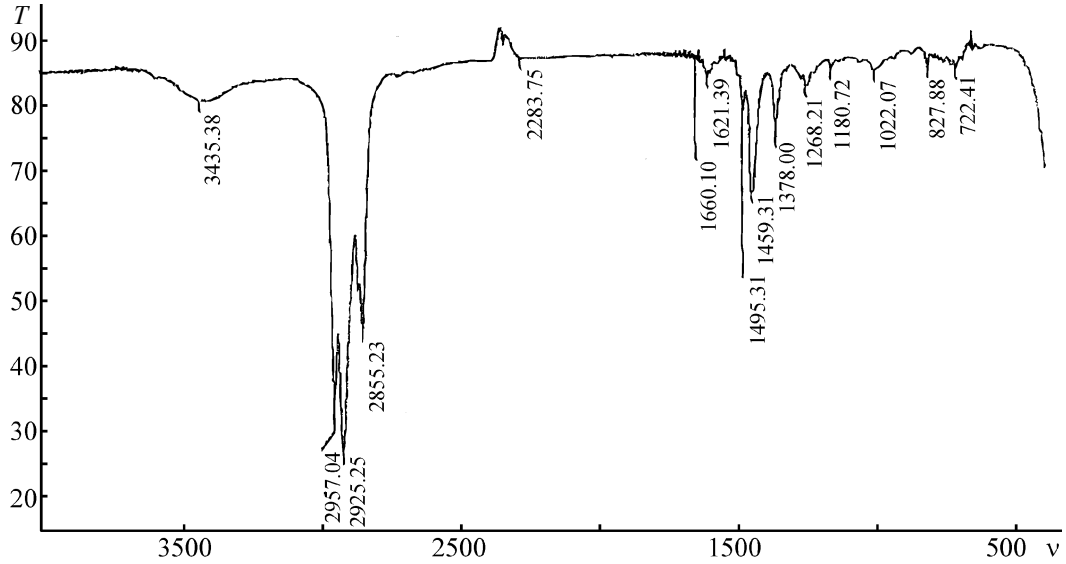


Fig. 2. IR spectrum of LIX984N extractant (17%) in kerosene.

observed at 1690–1650 cm^{-1}, are not clearly manifested in the spectrum, because they coincide with the absorption bands associated with vibrations of the aromatic ring.

Figure 2 shows that the positions of the absorption bands remained virtually unchanged, but their intensities slightly decreased. The band corresponding to the stretching vibrations of the hydroxy group exhibited a shift and got more flattened (3435.38 cm^{-1}). The shift and decline in intensity are evidently due to a decrease in the concentration of the main substance. The bands corresponding to vibrations of the ring also decreased in intensity, and this was accompanied by decreases in absorption band frequencies (1621.10 and 1459.31 cm^{-1}).

Figure 3 shows the IR spectrum of the organic phase obtained after single-batch extraction of copper from a solution containing 5 g l^{-1} copper in 17% LIX984N (solvent kerosene). Figure 4 shows the IR spectrum of the organic phase with copper, obtained after multiple-batch extraction aimed to achieve a maximal copper concentration in the organic phase.

Figures 3 and 4 show that, in the spectra of the copper extract, the band at 3100–3400 cm^{-1} corresponding to the stretching vibrations of the hydroxy group has a negligible intensity. A decrease in intensity of the characteristic band of the hydroxy group, a shift of the band belonging to the bending O–H vibrations, and disappearance of the band corresponding to the out-of-plane O–H vibrations at 1267.31 cm^{-1} suggest chemical

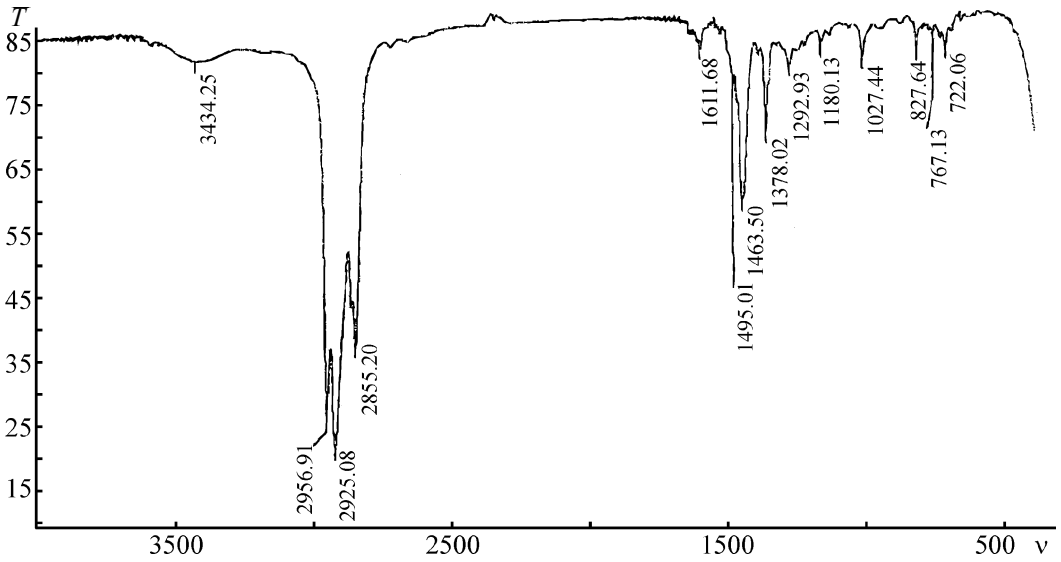


Fig. 3. IR spectrum of the organic phase after single-batch copper extraction.

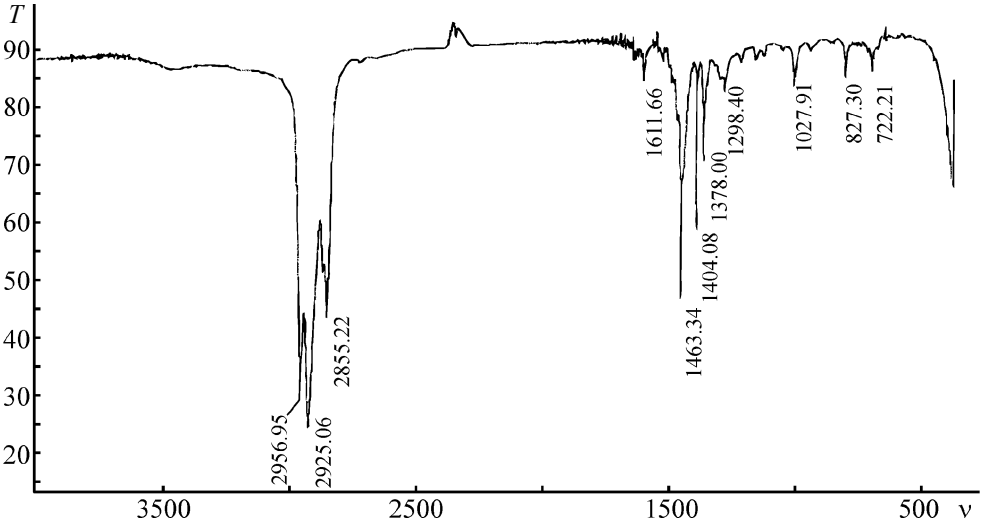


Fig. 4. IR spectrum of the maximally copper-saturated organic phase at the corresponding extractant concentration.

substitution of hydrogen in the hydroxy group of the extractant by copper cation. The observed weakening and broadening of the band is typical for formation of chelates. Notably, in the IR spectra of the extract saturat-ed with copper (Figs. 3, 4) the band near 2872 cm^{-1}, from the asymmetric vibrations of the methyl group in the ketoxime molecule disappears. This is due to formation of a rigid cyclic moiety hampering asymmetric vibrations.

As known, strong hydrogen bonding is fairly clearly manifested in IR spectra. Presumably the complexing is responsible for formation of weak intermolecular bonds whose vibrations are not identified in the IR spectrum. In view of the formation of a rigid framework of the complex, it can be presumed that the stability of the complex is provided by chemical bonding of metals with oxygen in hydroxy groups of the both ligands and the donor–acceptor interaction with the nitrogen in the oxime functional groups, rather than by strong hydrogen bonding. This should be responsible for nonplanar configuration of the complex, as suggested by preliminary quantum-chemical calculations.

The region of bending vibrations for the initial mixture of the extractant and extract with copper contains a number of identical absorption bands. For example, characteristic absorption bands corresponing to the C=C stretching vibrations of the aromatic ring are observed at 1585, 1496, and 1465 cm^{-1} (Fig. 1). The stretching vibrations of the N–O (nitrogen and oxygen in the oxime group) and C–O bonds (benzene carbon and

oxygen from the phenol hydroxy functional group) are observed near 1267 and 1240 cm^{-1}, respectively.

CONCLUSION

Comparative analysis of the IR spectra of dilute and neat LIX984N extractant and organic phase after copper extraction confirms the assumption made earlier for copper complexes with some different hydroximes: Copper extraction with LIX984N extractant from acid sulfate solutions yields stable chelate complexes of the copper cations Cu^{2+} with the molecules of hydroximes-1, 2, having nonplanar structures.

REFERENCES

1. Kodorsky, G., *The Chemistry of Metals Recovery Using LIX Reagents*, Henkel, 1997.
2. Borowiak-Resterna, A. and Szymanowsky, J., *J. Radional. Nucl. Chem*., 1990, vol. 150, no. 2, pp. 235–246.
3. Lazarova, Z. and Lazarova, M., *Solvent Extraction Ion Exchange*, 2005, vol. 23, no. 5, pp. 695–711.
4. Menoyo, B., Ocio, A., and Elizalde, M.-P., *Chromatographia*, 2007, vol. 65, nos. 1/2, pp. 35–44.
5. *Solvent Extraction Using Henkel Liquid Ion Exchange Reagents: Mid Redbook*, MID Henkel Corporation Staff, Eds., 1997.
6. Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, London: Methuen, 1958.