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EXTRACTION OF COBALT(II), NICKEL(II), AND COPPER(II) FROM STRONGLY ALKALINE MEDIA BY 4-n-DODECYL-6-(2-THIAZOLYLAZO)RESORCINOL

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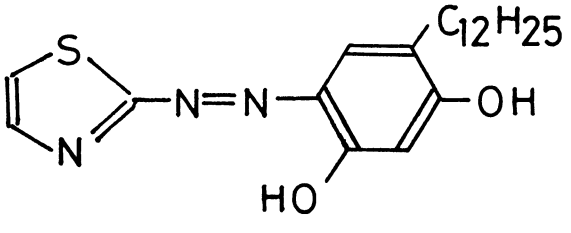
A new extracting reagent, 4-n-dodecyl-6-(2-thiazolylazo)-resorcinol, has been synthesized. The extraction characteristics of this reagent have been examined for several heavy metal ions. Cobalt(II), nickel(II), and copper(II) can be extracted into 4-methyl-2-pentanon from strongly alkaline solutions without additional organic reagents such as quarternary ammonium salts.

Since many kinds of metal ions tend to precipitate as metal hydroxides in a concentrated sodium hydroxide solution, little attention has been denoted to the solvent extraction of them from such media. Alkaline solutions, however, are often used for the complete degradation of mineral ores and analytical samples containing metal elements. Therefore, the direct process for the extraction and the concentration of metal ions from such strongly basic media must be of a great advantage to hydrometallurgy and analytical chemistry.

Very few reagents have been proposed for the extraction of heavy metal ions from strongly alkaline solutions.[1,2] It is noteworthy that the reagents so far reported mostly contain the substituents of long alkyl chains. Therefore, the addition of a hydrophobic character to common analytical reagents may afford the extractants suitable for the present purpose. In confirmation of this assumption, n-dodecyl derivative (DTAR) of 4-(2-thiazolylazo)resorcinol (TAR) has been synthesized and its extraction characteristics have been studied. Since TAR is well-known as a good colorimetric reagent, the present derivative is expected to act as a highly sensitive reagent in the



DTAR

quantitative analysis as well as an excellent extractant for metal ions.

The reagent, 4-n-dodecyl-6-(2-thiazolylazo)resorcinol, was prepared by a coupling reaction between 4-dodecylresorcinol and diazotized 2-aminothiazol in a similar procedure to that described in the literature.$^{3)}$ The chemical structure of the reagent was confirmed by elemental analysis, ^{1}H-NMR and ^{13}C-NMR spectroscopies. The concentration of metal ions was determined by atomic absorption spectrophotometry.

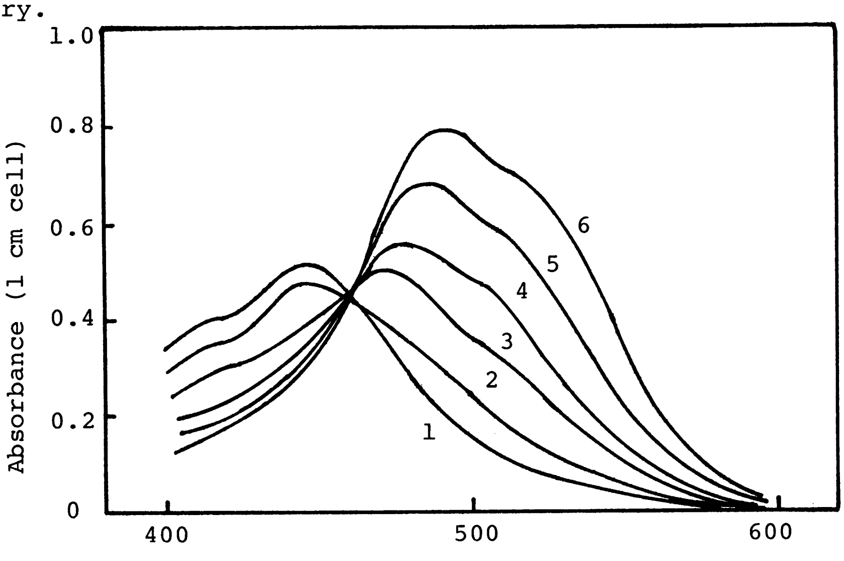


Fig.1. The visible absorption spectra of DTAR extracted into MIBK from aqueous solutions at various pH. [DTAR]=2.5 x 10^{-5} mol dm^{-3}, 1: pH=9.4, 2: 9.9, 3: 10.3, 4: 10.8, 5: 11.7, 6: 13.9.

Figure 1 shows the visible absorption spectra of the reagent extracted into 4-methyl-2-pentanon (MIBK) from aqueous solutions at various pH. An isosbestic point was observed at 460 nm. On the basis of the spectral characteristics of TAR,$^{4)}$ it was deduced that the spectra at pH lower than 9.4 is due to the neutral species (H_2L) and that having a maximum at 495 nm corresponds to the mono-anionic species (HL^-) extracted as an ion-pair with sodium ion. The determination of sodium ion co-extracted with DTAR well supported this assignment. The molar extinction coefficient of H_2L at 455 nm is 1.99 x 10^4 $mol^{-1}dm^3cm^{-1}$, which resembles to that of TAR (2.0 x 10^4 $mol^{-1}dm^3cm^{-1}$, at 439 nm in 20% dioxane$^{4)}$).

The distribution ratio (D) of DTAR in water-MIBK system is given in Fig. 2 as a function of NaOH concentration. The value of log D is relatively small at pH 13, but increases with an increase in the concentration of sodium hydroxide. As stated above, DTAR seems to be extracted into MIBK as a mono- or a di-sodium salt from a concentrated sodium hydroxide solution owing to its strongly hydrophobic property.

Figure 3 shows the effect of NaOH concentration on the extraction of cobalt(II), nickel(II), and copper(II) along with the effect of pH. Cobalt(II) and copper(II) can be extracted within a few minutes of shaking under the present experimental conditions, while more than 30 min is required for nickel(II) to attain the equilibrium. A depression in the extractability of these metal ions was observed in a high pH region, but it is again restored with an increase in the concentration of sodium hydroxide. Similar trends have been observed in the extraction systems with the related reagents, such as Kelex-100 (a long alkenyl derivative of 8-quinolinol)$^{1)}$ and alkylpyrocatechols.$^{2)}$ In the case of TAR, the interaction between the reagent and these metal ions must be very small in the strongly alkaline solutions, since the visible spectra of the solutions containing both TAR and the metal ions were similar to those observed in the

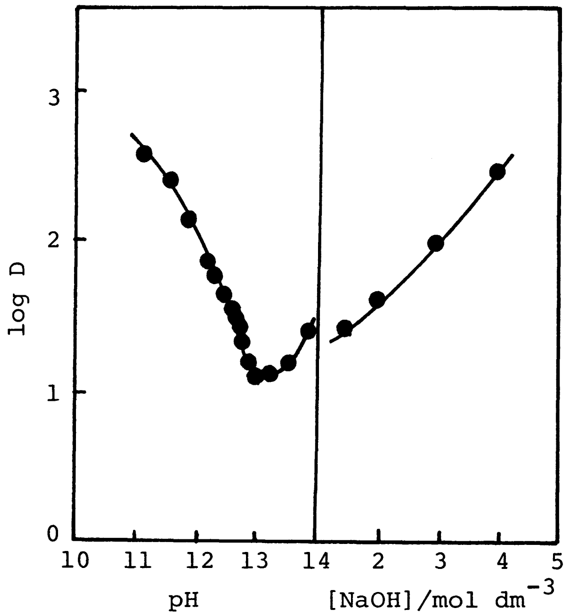


Fig.2. Variation of log D of DTAR with pH or NaOH concentration. Solvent: 4-methyl-2-pentanon.

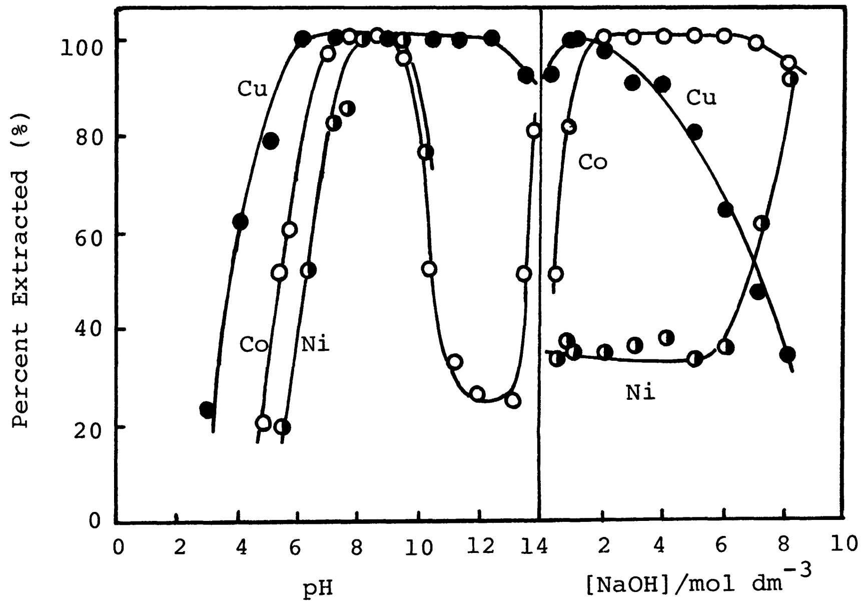


Fig.3. Effect of pH and the concentration of NaOH on the extraction of cobalt(II), nickel(II), and copper(II). [metal]=2 x 10^{-5}mol dm^{-3}, [DTAR]=2 x 10^{-4}mol dm^{-3}.

absence of the metal ions. These results indicate that the hydrophobic alkyl groups play an important role to bring about the unusual characteristics.

According to the molar ratio and the continuous variation method, the compositions of the complexes extracted were determined to be 1 : 2 (metal : reagent) for both cobalt(II) and copper(II) under the strongly alkaline condition ([NaOH]= 2 mol dm^{-3}). At pH 9.2, cobalt(II) was also extracted as 1 : 2 complex, whereas copper(II) was extracted as 1 : 1 complex which clearly differs from the species extracted from the strongly alkaline solution. The lower extractability of cobalt(II) at pH around 13 was not restored by the addition of sodium chloride or tetrabutylammonium bromide. On the basis of these results, we tentatively interpreted the extraction behaviour of cobalt(II) as follows; (i) at pH 9.2, cobalt(II) is normally extracted by a proton exchange reaction with DTAR which is present as the neutral form (H_2L) in the MIBK phase. (ii) at pH 13, the extraction is significantly inhibited by the competed hydrolysis. (iii) in the concentrated alkaline solution, the extractability is restored by the increase in the concentration of sodium ion acting as a counter cation, as well as by the enhanced formation of a di-anionic species (L^{2-}) which has much stronger complexation ability than the other species of DTAR.

Gallium(III), iron(III), and zinc(II) can not be extracted from concentrated sodium hydroxide solutions by DTAR, whereas gallium(III) is extracted by Kelex-100.1) Although sufficiently hydrophobic ligands must be effective for the extraction of metal ions from strongly basic media, their selectivity seems to depend on the ligating moiety of the reagents.

References

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