

Separation of copper(II) from manganese(II), cobalt(II), nickel(II) and zinc(II) using acetylacetone

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The separation of copper(II) from binary mixtures of divalent metal ions, Cu-Mn, Cu-Co, Cu-Ni and Cu-Zn has been studied using acetylacetone(Hacac) in chloroform as the extractant. The pH of the aqueous phase has been kept at 4.34 using Britton-Robinson buffer (CH₃COOH-NaOH). From the plot of log K_d versus log[Hacac], the nature of the extracted species is found to be Cu(CH₃COO)(acac).

Acetylacetone(Hacac), one of the simplest β -diketones, has been extensively used as an extractant for a number of metal ions such as vanadium¹, chromium², molybdenum³, copper^{4,5} and other metals⁶⁻¹⁰. But there has been no serious attempt to use this simple and readily available extractant for separation purposes. For instance, copper(II) has been extracted using Hacac in benzene with nearly 86% recovery, but no effort has been made to separate copper(II) from its 3d-congeners^{4,5} or other metal ions. Keeping this in view and because of increasing interest in the industrial applications of the solvent extraction technique¹¹, we decided to carry out separation of copper(II) from binary mixtures of 3d-metal ions using acetylacetone.

Experimental

Reagents and solution preparations—The materials used like copper(II) acetate and metal sulphates (Mn,Co,Ni,Zn) were recrystallised from distilled water and dried before use. Acetylacetone, EDTA, CHCl₃, CH₃COOH, CH₃COONa and NaOH were of AR quality and used as such. A 0.1M copper(II) acetate solution was prepared in a Britton-Robinson¹² buffer (CH₃COOH-NaOH) of pH 4.34. Another buffer of pH 5-6 was prepared from 0.2M CH₃COONa and 0.2M CH₃COOH (Walpole acetate buffer). Hacac solutions of molarities 0.05 to 0.50 were prepared in CHCl₃. A 0.05N EDTA solution was prepared in distilled water. For studying the effect of other metal ions, the solutions of the metal salts of different molarities (MnSO₄.4H₂O, 0.1 to 1.0M; CoSO₄.7H₂O, 0.1 to 0.6M; ZnSO₄.7H₂O, 0.1

to 1.0M; NiSO₄.7H₂O, 0.1 to 1.0M) were prepared in distilled water.

Procedure for extraction—For extraction in the absence of the other metal ions, a solution of copper(II) acetate(2ml, 0.1M) was stirred with the buffer (3ml) of pH 4.34 and Hacac(5ml) in CHCl₃ in a stoppered round-bottomed flask on a magnetic stirrer. The equilibrium period was kept at 20 min. The contents were transferred to a separatory funnel and allowed to stand for some time and then the chloroform layer was separated. The procedure for the study of interference of metal ions was similar. Here 1 ml of the metal ion solution of a particular molarity was added to 2 ml of 0.1M copper(II) acetate plus 3 ml of a buffer of pH 4.34 and 5 ml of Hacac in CHCl₃. Organic layer in each case was treated with 5 ml of dilute H₂SO₄ when copper(II) transferred to the aqueous phase. Copper(II) was estimated by titrating the buffered (pH 5-6) copper(II) solution against 0.05M EDTA using 1-(2-pyridylazo)-2-naphthol as the indicator. The end point was marked by the change in color from pink to straw yellow¹³.

The distribution coefficient K_d was calculated from the relation:

$$K_d = \frac{\text{Amount of copper in the organic layer/ml}}{\text{Amount of copper in the aqueous layer/ml}}$$

and the percent extraction was calculated using the relation:

$$\%E = \frac{(100 \times K_d)}{K_d + \frac{V_{aq}}{V_{org}}}$$

where V_{aq} and V_{org} denote the volumes of the aqueous and organic phases respectively.

Results and discussion

For the plot of log K_d versus log[Hacac], the slope was found to be nearly 1. Thus, the nature of the extracted species appears to be Cu(CH₃COO)(acac). From Table 1, it can be seen that increasing the concentration of Hacac increases the extraction of copper(II) and the extraction becomes nearly quantitative for 0.50M Hacac, i.e., [Hacac]/[Cu] ~ 2.5. This is in contrast to a very high ratio, 30 to 150, of [Hacac]/[Cu] used for the extraction of copper(II) by Irving and Al-Niimi⁵ employing benzene in place of

Table 1—Extraction data of copper(II) using different Hacac concentrations

[Hacac] M	Amount of Cu(II) extracted (mg)	K_d	% E
0.05	8.9	2.8	73.7
0.075	9.1	3.6	78.3
0.10	10.2	7.7	88.5
0.15	10.7	10.0	90.9
0.20	10.8	10.8	91.5
0.25	11.1	19.5	95.1
0.30	11.7	26.5	96.4
0.40	12.1	41.2	97.6
0.50	12.6	50.4	98.0

Amount of Cu(II) taken for each extraction, 12.7mg

CHCl_3 . Thus, chloroform is a far superior solvent for the extraction as compared to benzene. Moreover, in benzene, it was observed that the resulting complex had low solubility as shown by the formation of the suspended particles in the organic layer. This may be the reason that despite the use of very high concentration of Hacac by Irving and Al-Niaimi⁵, the percent extraction was about 85% and not quantitative as in the present case.

In the separation studies, copper(II) was separated from binary mixtures of divalent metal ions, Cu-Mn, Cu-Co, Cu-Ni and Cu-Zn. The percent extraction of copper(II) was about 97% in the presence of different molarities of the metal ions added. This percentage is the same as expected in the absence of the metal ions added, viz., 96% while using 0.3M Hacac (Table 1). Addition of 6 to 10-fold excess of interferent metal ion caused no interference. Under

the experimental conditions, there was no transfer of any of these metal ions to the organic layer. This was checked by performing extraction in the absence of the copper(II).

In conclusion, it may be stated that acetylacetone affords a simple method of separating copper(II) from a binary mixture of divalent Mn, Co, Ni and Zn.

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