

Liquid–liquid extraction of copper(II) with dialkyl sulphoxides

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Abstract. The extraction behaviour of Cu(II) from hydrochloric acid and lithium chloride solutions with di-*n*-pentyl sulphoxide (DPSO) and di-*n*-octyl sulphoxide (DOSO) has been investigated over a wide range of conditions. At a given strength of the extractant, the extraction increases with increase in HCl and LiCl concentrations. The extraction of the metal also increases with increase in extractant concentration at constant [HCl] or [LiCl]. The species extracted would appear to be $\text{CuCl}_2 \cdot 2\text{DPSO}/2\text{DOSO}$ and $\text{CuCl}_4^{2-} \cdot 2\text{DPSO}$. The extraction of the metal decreases with increase in initial aqueous metal concentration and also with increase in temperature. The extraction also depends on the nature of the diluent employed.

Keywords. Extraction; copper(II); dialkyl sulphoxides.

1. Introduction

An extensive literature study showed that a large number of extractants such as tri-*n*-butylphosphate (Trofimov and Belousov 1969; Sato 1972) trioctylphosphine oxide (Sato and Masuhiro 1972), bis(2-ethyl hexyl) hydrogen phosphate (Isao *et al* 1969), Aliquat 336 (Miller and Fuerstenau 1970) and trioctylamine (Ioffe and Ramazanov 1968) have been used for the extraction of Cu(II). Dialkyl sulphoxides have been successfully employed for the extraction of lanthanides (Subramanian and Pai 1973; Reddy and Reddy 1977) actinides (Mohanty and Reddy 1975) and transition elements (Shankar and Venkateswarlu 1970; Reddy *et al* 1982, 1984; Reddy and Reddy 1984) with efficiency and specificity. There is no published information on the extraction equilibria of Cu(II) with dialkyl sulphoxides. Hence, a detailed investigation on the extraction of Cu(II) with sulphoxides was thought worthwhile. The present paper reports on the extraction of Cu(II) from hydrochloric acid and lithium chloride solutions by di-*n*-pentyl sulphoxide (DPSO) and di-*n*-octyl sulphoxide (DOSO) in nitrobenzene with a view to elucidate the nature of the complexes extracted into the organic phase.

2. Experimental

Dialkyl sulphoxides were synthesized according to procedures described elsewhere (Mohanty and Reddy 1975). Analytical grade chemicals (BDH) were employed as necessary. Organic solvents were freshly distilled.

Distribution coefficients were determined by shaking equal volumes of aqueous (0.03 mol dm^{-3} Cu in HCl/LiCl) and organic phases (DPSO or DOSO in nitrobenzene) for 10 minutes in a separating funnel at $303 \pm 1 \text{ K}$. Trial experiments showed that extraction equilibrium is attained within 3 minutes. After equilibration the phases were separated and analysed for the metal. Cu(II) in the aqueous phase was estimated spectrophotometrically by reacting the metal ion with EDTA in pH: 2.4 acetate buffer solution and measuring the absorbance at 745 nm (Vogel 1969). The distribution coefficient, D , the ratio of the equilibrium metal concentration in the organic phase to that in the aqueous phase, was calculated.

3. Results and discussion

The extraction of Cu(II) by 0.3 mol dm^{-3} DPSO in nitrobenzene increases with increase in HCl concentration ($1-10 \text{ mol dm}^{-3}$), reaches a maximum at about 8 mol dm^{-3} HCl and decreases thereafter (figure 1). The initial increase in extraction may be attributed to the common ion effect. The slow increase or decrease in extraction at higher acidities is due to the formation of complex, HCl·DPSO (Korpak 1963) and its partial solubility in the aqueous phase. Furthermore, these complexes may not be able to solvate the metal to the same extent as does the free extractant. At low acidities, the small amount of the acid in the organic phase cannot seriously compete with the metal. Increase in H^+ concentration at a constant strength of Cl^- from a mixture of HCl + LiCl, has no influence on the extraction of the metal under the chosen

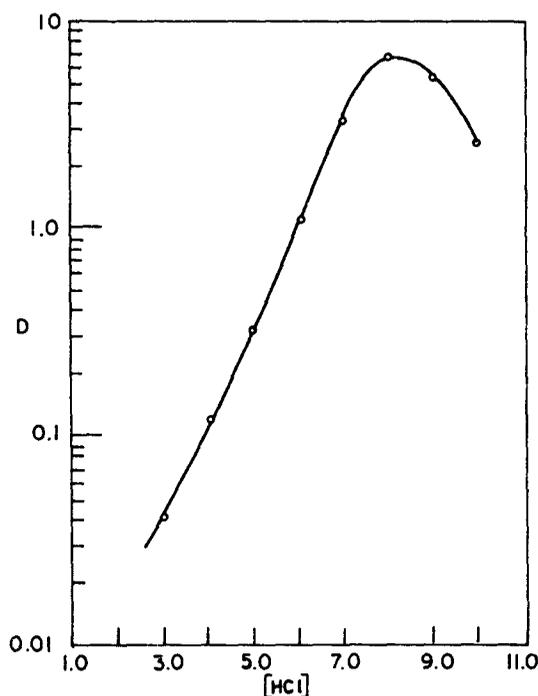


Figure 1. Effect of hydrochloric acid concentration on the extraction of Cu(II) by di-*n*-pentyl sulphoxide (DPSO) in nitrobenzene.

experimental conditions. On the other hand, the distribution of the metal into the organic phase increases with increase in Cl^- concentration ($4\text{--}7.0 \text{ mol dm}^{-3}$) at a given acidity (0.1 mol dm^{-3}). The mean ionic activity coefficients of the mixed electrolyte ($\text{HCl} + \text{LiCl}$) system were calculated (Robinson and Stokes 1959; Harned 1968). The $\log D - \log a_{\text{Cl}^-}$ (logarithm of the mean ionic activity of HCl at constant H^+ concentration) plot is linear with slope equal to 2, confirming the extraction of the species CuCl_2 .

The extraction of Cu(II) from lithium chloride solutions by DPSO in nitrobenzene (0.3 mol dm^{-3}) also increases with increase in molarity of LiCl ($5\text{--}8 \text{ mol dm}^{-3}$). The increase may be attributed to the formation of metal chloro-complexes which are stabilized in lithium chloride solution owing to strong bonding of water by the lithium ion. The slope of the plot $\log [\text{LiCl}]$ against $\log D$ is four, indicating the extraction of the species $\text{CuCl}_4^{2-} \cdot n\text{SO}$. This is in good agreement with the earlier reports for the extraction of Cu(II) from lithium chloride solutions by tri-*n*-butyl phosphate (Balukova *et al* 1971). It is generally observed that the extraction of Cu(II) from lithium chloride solutions is greater than from hydrochloric acid solutions.

The dependence of the extraction of Cu(II) from 5 mol dm^{-3} HCl was investigated with respect to DPSO and DOSO concentration in nitrobenzene ($0.2\text{--}0.6 \text{ mol dm}^{-3}$ each). The extraction increases with increase in the extractant concentration (percent extraction from 11 to 54). The $\log D - \log [\text{extractant}]$ plots are linear with slopes nearly equal to 2 for dialkyl sulphoxides, suggesting that the extracted species are disolvates, $\text{CuCl}_2 \cdot 2\text{DPSO}/2\text{DOSO}$. Furthermore, the extraction of Cu(II) from 5 mol dm^{-3} lithium chloride solutions also increases with increase in DPSO concentration ($0.2\text{--}1.0 \text{ mol dm}^{-3}$) and the slope of the plot, $\log D - \log [\text{DPSO}]$ is 2, indicating the extraction of the species, $\text{CuCl}_4^{2-} \cdot 2\text{DPSO}$. The extraction efficiencies decrease with the extractant in the order: $\text{DPSO} > \text{DOSO}$.

Increase in the initial aqueous phase metal ion concentration (0.02 to 0.05 mol dm^{-3}) slightly decreases the extraction efficiency of Cu(II) . The $\log\text{--}\log$ plot of equilibrium organic phase metal concentration against the equilibrium aqueous phase metal concentration is linear with slope nearly equal to unity indicating the extraction of mononuclear species.

The extraction of Cu(II) from 5 mol dm^{-3} HCl by 0.3 mol dm^{-3} I PSO in various diluents decreases in the order: nitrobenzene ($D = 0.33$) > chlorobenzene > benzene toluene > carbon tetrachloride > chloroform ($D = 0.04$). The extraction of the metal from 5 mol dm^{-3} HCl by 0.3 mol dm^{-3} DPSO and 0.3 mol dm^{-3} DOSO in nitrobenzene decreases (D values 0.5 to 0.2) with increase in temperature (283 to 313 K). From the slopes of the linear Arrhenius plots the values of the enthalpy change (ΔH) are calculated. The negative values of ΔH indicate that the extraction process is slightly exothermic. The other thermodynamic functions such as free energy change (ΔG) and entropy change (ΔS) are also given in table 1.

Table 1. Values of thermodynamic functions for the extraction of Cu(II) by DPSO and DOSO .

Extractant	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS ($\text{JK}^{-1} \text{ mol}^{-1}$)
DPSO	-21	5.3	-307
DOSO	-22	5.3	-320

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