SOLVENT EXTRACTION OF SOME METALS FROM AQUEOUS SOLUTIONS

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The results for the extractions of divalent (manganese, cobalt, zinc and cadmium) and trivalent (gallium and indium) metals and hexavalent uranium from aqueous solutions by various extractants such as organophosphorus compounds (tributyl phosphate, trioctylphosphine oxide, di-(2-ethylhexyl)phosphoric acid and 2-ethylhexyl 2-ethylhexylphosphonic acid), sulfur-containing compound (dihexyl sulfoxide), high-molecular weight amines (trioctylamine and trioctylmethylammonium chloride) and 7-alkylated hydroxyquinoline (7-(5,5,7,7-tetramethyl-1-octen-3-yl)-8-hydroxyquinoline are discussed in the viewpoint of separation chemistry.

Introduction

As solvent extraction is very useful to separate metal ions in aqueous solutions, the distribution data between aqueous solutions containing metal ions and some extractants in organic solvents have been surveyed by a number of researchers, but the literatures on the mechanism of solvent extraction of metals are limited. In the present paper, therefore, the results for the liquid-liquid extraction of divalent and trivalent metals and hexavalent uranium are given in order to obtain further information on the mechanism of their solvent extractions in the viewpoint of separation chemistry.

Experimental

Reagents

Tributyl phosphate (TBP), di-(2-ethylhexyl)phosphoric acid (DEHPA, HX) and 2-ethylhexyl 2-ethylhexylphosphonic acid (EHEHPA, HA) (Daihachi Chemical Industry Co., Ltd.) were purified by usual methods.1,2 Trioctylphosphine oxide (TOPO) (Hokko Chemical Industry Co., Ltd.), trioctylamine (TOA) and TOMAC (trioctylmethylammonium chloride) (Koei Chemical Co., Ltd.) were of high purity and used without further purification. Dihexyl sulfoxide (DHSO) was synthesized...
by means of oxidation from dihexyl sulfide (Daihachi Chemical Industry Co., Ltd.) as described previously. Aqueous solutions of divalent manganese, cobalt, copper, zinc and cadmium and uranium(VI) were prepared by dissolving their chlorides (MnCl₂ · 4H₂O, CoCl₂ · 6H₂O, CuCl₂ · 2H₂O, ZnCl₂, CdCl₂ · 6H₂O and UO₂Cl₂ · 2H₂O) in hydrochloric acid and/or lithium chloride solutions. Aqueous trivalent gallium and indium solutions were prepared as follows. The solutions of chloride or nitrate of gallium were prepared by dissolving gallium metal (99.9999%, Swiss Aluminium, Ltd.) in hydrochloric or nitric acid; aqueous solutions of indium were prepared by dissolving its chloride or nitrate (InCl₃ or In(NO₃)₃ · 3H₂O) in hydrochloric or nitric acid of selected concentration, respectively.

**Extraction and analytical procedures**

Equal volumes (15 cm³ each) of the aqueous and organic phases, placed in 50 cm³ stoppered conical flasks, were shaken for 10 minutes (preliminary experiments showed that equilibration between the two phases for the extraction of each metal was achieved in 10 min) in a water bath maintained at the required temperature. After equilibration the mixture was centrifuged and separated, and then aliquots of both phases were pipetted to determine the distribution coefficient (E, the ratio of the equilibrium concentration of metal in the organic phase to that in the aqueous phase). Manganese, cobalt, copper and zinc in the organic phases were stripped with 0.1 mol · dm⁻³ HCl, cadmium and uranium with 0.1 mol · dm⁻³ HNO₃, and gallium with 0.1 mol · dm⁻³ HCl except 1 mol · dm⁻³ HCl for DEHPA and EHEHPA, and indium with 3 mol · dm⁻³ HNO₃. The metal concentrations were determined by EDTA titration using BT (Eriochrome Black T) for manganese, XO(Xylenol Orange) for cobalt, zinc, copper, uranium, gallium and indium and Cu-PAN (1-(2-pyridylazo)-2-naphthol) for cadmium as indicator.

**Spectrophotometry, IR, ESR, NMR and Raman spectral measurements**

The absorption spectra were obtained on a Hitachi Model 340 spectrophotometer, using matched 1.0 cm × 1.0 cm fused silica cells. The infrared (IR) spectra of the organic solutions were determined on a JASCO Models IRA-1 (4000–650 cm⁻¹) and IR-F (700–200 cm⁻¹) grating infrared spectrophotometers. The electron spin resonance (ESR) spectra were determined using a high-resolution X-band ESR spectrometer designed in the Research Institute of Electronics, Shizuoka University, and with a JEOL-PE-3X spectrometer, which operated at about 9.3 GHz, using 100 kHz field modulation. Nuclear magnetic resonance (NMR) spectra were obtained for samples dissolved in carbon tetrachloride, using a JEOL Model JNM-PMX60SI NMR spectro-