

SOLVENT EXTRACTION OF Cd(II) COMPLEXES WITH 1-ALKYL-1,2,4-TRIAZOLE

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1-alkyl-1,2,4-triazole are very weak bases, however they form in the aqueous solution and in the solid state complexes with some transition metals.

The purpose of this study was to investigate the influence of the alkyl chain length in position 1 of the triazole ring on extraction of the Cd(II) complexes with 1-alkyl-1,2,4-triazoles (where alkyl = butyl, pentyl, hexyl, heptyl, nonyl and undecyl). Stability and distribution constants of the Cd(II) complexes were determined from extraction data using the liquid – liquid partition method, at 25 °C and a fixed ionic strength of the aqueous phase ($I = 0.5$; $(\text{HL})\text{NO}_3$, KNO_3 , 2-Ethylhexanol and p-xylene were used as organic solvent. The Cd(II) concentration was determined by titration with a standardized EDTA solution and by atomic absorption spectrophotometry.

Partition of Cd(II) between the organic and aqueous phases was characterized by a ratio of metal partition as a function of the pH of the aqueous phase. The so-called distribution ratio, D_M , of the metal ion was derived from the measured concentrations and calculated from eq.1:

$$D_M = \frac{C_M^0 - C_M}{C_M} = \frac{C_{Cd(II)(org)}}{C_{Cd(II)(aq)}} \quad (1)$$

where: C_M^0 and C_M denote analytical concentrations of the Cd(II) in the aqueous phase before and after reaching partition equilibrium, respectively.

The results of the extraction experiments for all the systems studied are presented as plot of logarithms of the distribution ratio between the aqueous and organic phase vs. pH ($\log D_M = f(\text{pH})$) separately for 2-ethylhexanol and p-xylene. The curves are shifted towards lower pH values of the aqueous phase upon elongation of the 1-alkyl substituent. This finding is of practical importance, since the extraction of Cd(II) with a more hydrophobic alkyltriazole can be performed at a lower concentration of the heterocyclic base in the solvent.

Extraction of particular complex (ML_n) depends on partition constants (P_n) and stability constants (β_n) of the complexes formed in the aqueous phase [1-3]:

$$D_M = \frac{P_n \beta_n [L]^n + P_{n+1} \beta_{n+1} [L]^{n+1} + \dots + P_N \beta_N [L]^N}{\sum_{n=0}^{n=N} \beta_n [L]^n} \quad (2)$$

where: P_n , β_n and $[L]$ denote the partition constant, stability constant and the free ligand concentration (mol/L) in the aqueous phase, respectively, and n is the number of ligands particles in the first Cd(II) complex which is so hydrophilic that it freely passes into the organic phase.

The values of the stability constants β_1 and the partition constants P_1 of the investigated complexes were determined by the method of curve-fitting using Rydberg's formula [1-3] (Eq.3):

$$\frac{[L]^n}{D_M} = \frac{\sum_{n=0}^{n=N} \beta_n [L]^n}{P_n \beta_n} \quad (3)$$

It was found that the stability constants (β_1) of Cd (II) complexes with 1-alkyl-1,2,4-triazole in the aqueous phase increased slightly with an increasing in 1-alkyl chain length of the 1,2,4-triazole.

The partition constants (P_n) values are low for all the compounds, and dependent of the 1-alkyl substituent. Partition constants (P_n) are dependent on the solvent used, too. Those in 2-ethylhexanol are larger then the constants recorded in p-xylene.

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