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THE COMPLEX CHEMISTRY OF URANYLNITRATE - P - AMINOBENZOIC ACID SYSTEM

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Ö z e t : *Uranil iyonu ve p-aminobenzoik asit arasındaki kompleks oluşumu % 50 alkol-su ortamında spektrofotometrik olarak incelenmiştir. Neticeler, çok yüksek ligand konsantrasyonlarında bile bütün ligantın bağlandığını göstermektedir. Böylece, bir uranil iyonu ile kompleks yapan ligand moleküllerinin ortalama sayısı koordinasyon sayısını pek çok aşarak 170 ve daha da yüksek değerlere erişmektedir.*

A b s t r a c t : *The complex formation between uranyl ion and p-aminobenzoic acid has been investigated by spectrophotometry using 50% alcohol-water medium. The results indicate that even at very high relative concentrations, all the ligand is bound, so that the average number of ligand molecules complexed with one uranyl ion can exceed enormously the coordination number to reach values as high as 170 and even more.*

INTRODUCTION

In order to investigate the coordination compounds of uranyl ion, many experiments have been done. The Ahrland's spectrophotometric and potentiometric methods I are devoloped by Chie Miyake and H.W.Nürnberg 2. The Rossotti method 3 is the best way to investigate the coordination compounds that contain high ligand molecules. These methods are used to make an identification of the uranyl nitrate-p--aminobenzoic acid coordination compounds structure.

EXPERIMENTAL

Uranyl nitrate $UO_2.(NO_3)_2.6H_2O$ and p-aminobenzoic acid $NH_2.C_6H_4$ COOH solutions are prepared and mixed at differant portions for spectrophotometric experiments. The absorbancy of this mixtures are measured by using a Beckmann DU Ultraviole Spectrophotometer at room temperature.

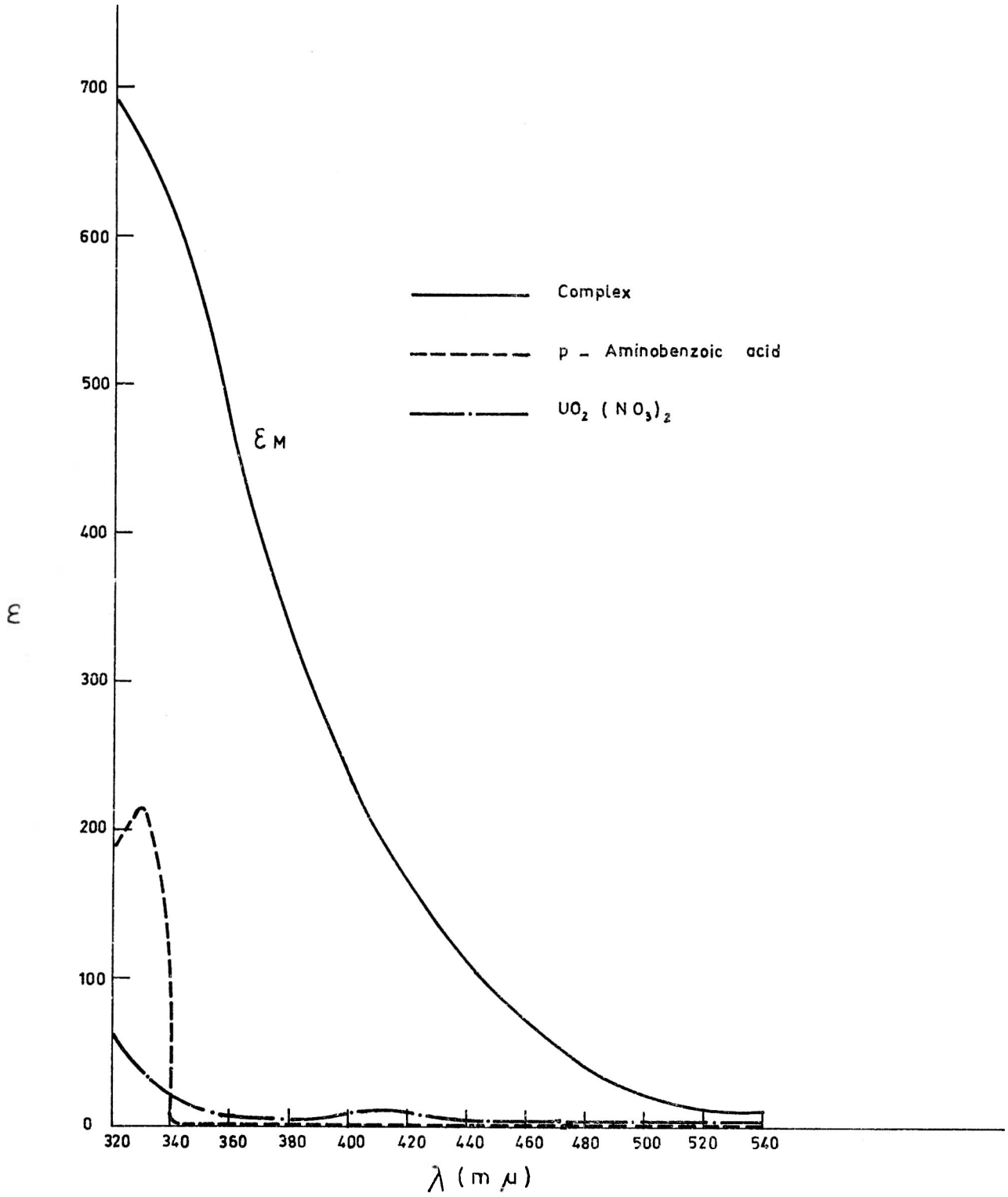
Water is poured to the differant mixtures of uranyl nitrate and p-aminobenzoic acid solutions in the gravimetric experiments. The precipitations obtained from the above mixtures filtered, dried, ignited and weighed.

The chemicals used in these used in these experiments uranyl nitrate $UO_2.(NO_3)_2$ $6H_2O$ (Fluka) and p-aminobenzoic acid $NH_2.C_6H_4.COOH$ (Fluka),solved in 50% alcohol-water medium. Aliminiumoxide (Al_2O_3,Fluka) column is used to get clean solutions of p-aminobenzoic acid.

RESULTS AND DISCUSSIONS

According to the uranyl nitrate and p-aminobenzoic acid solutions the complex system shows very high absorbancy between 320-540 mu (Figure I). This figure indicates that even at very high relative concentrations, all the ligand is bound, so that the average number of ligand molecules complexed with one uranyl ion can exceed enormously the coordination number, to reach values as high as 170 and even more. Such enormously high values are incompatible with simple coordination and should be explained by an association process which links several ligand molecules successively.

These complexes, however, decompose upon addition of water to the mixtures of p-aminobenzoic acid and uranyl nitrate solutions and the product that precipitates contains 2-3 ligand molecules per uranyl ion. From these observations, it should be concluded that the extra molecules whose number exceeds 2 should be bound differantly. The observations that the precipitated material contains on the average of a little more than 2 ligand molecules per one uranyl ion is probably due to the low solubility of p-aminobenzoic acid in water.


700
600
500
400
300
200
100
0
ε
εM
Complex
p – Aminobenzoic acid
UO2 (NO3)2
320
340
360
380
400
420
440
460
480
500
520
540
λ (mμ)

Another interesting fact that the unassociated part of the ligand is negligible even when the ligand concentration is as high as about 100 times that of the uranyl nitrate.

Essentially the same picture is observed when p-aminobenzoic acid is replaced with o-aminobenzoic acid, N.N-dimethyl p-aminobenzoic acid and methyl p-aminobenzoite.

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2- Chie Miyake and H.W.Nurnberg, J.Inorg.Nucl.Chem.29,24II(1967)

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