Elution of Copper(II), Nickel(II), Cobalt(II) and Zinc(II) and the Separation of Nickel(II), Palladium(II) and Platinum(II) Complexes of Quinoxaline-2,3-dithiol, Using Reversed Phase Ion-pair HPLC

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Summary: The anionic complexes of Cu(II), Ni(II), Co(II), Zn(II), Pd(II) and Pt(II) with quinoxaline-2,3-dithiol ($\overline{qdt}$) were successfully eluted as ion-pairs with quaternary ammonium cations on the reversed phase Lichrosorb RP-18 (150 mm x 4.6 mm) column. The eluent used was ethanol:water (80:20) containing each in turn, tetrabutyl ammonium (TBA^+), tetraheptyl ammonium (THA^+) and cetyltrimethyl ammonium (CTA^+) as their bromide salts in concentrations ranging (0.05% to 0.2% w/v) at different pH.

The Ni(II) , Pd(II) or Pt(II)-qdt complexes were separated from Cu(II) or Zn(II) or Co(II)-qdt complexes using THA^+ ,or CTA^+ at pH 8.4 ± 0.1 . The separation of Ni(II), Pd(II) and Pt(II) -qdt complexes was achieved using (THA+) at pH 9.0 ± 0.1 with the cation salt concentration of 0.1% in ethanol: water (80:20) as eluent. The detection limits were at ng levels per injection.

Introduction

Quinoxaline-2,3-dithiol ($\overline{qdt}$) has been generated from S-2(3-dimercaptoquinoxalinyl) thiouronium chloride) ($\overline{mqt}$), for the gravimetric determination of Ni(II) [1], thermometric determination of Se(IV) and Ni(II) [2], the spectrophotometric determination of Ni(II) and Co(II) [3], Pd(II) [4] and heterogeneous complexes with Ni(II) and Cu(II) [5]. Some electrochemical studies of Cu(II), Ni(II) and Mo(II)-qdt complexes have also been reported [6-7]. The anionic complexes of qdt with Ni(II), Pd(II), Co(II), Pt(II) and Fe(II) have been solvent extracted as ion-pairs with ammonium, posphonium, arsonium and organic bases for their spectrophotometric determinations [8-11]. The Cu(II), Ni(II), Co(II), Zn(II) ,Pd(II) and Pt(II) complexes with qdt have also been solvent extracted as ion-pairs with quaternary ammonium cations into chloroform and eluted on the normal phase HPLC [12].

In the present work the anionic metal-qdt complexes were directly applied onto the reversed phase (ODS) HPLC column for the effective separation of Ni(II), Pd(II) and Pt(II) -qdt complexes,where, the cation generating salts were added into the eluent (80:20) ethanol :water.

Results and Discussion

Preliminary investigations for the separation of metal-qdt complexes on reversed phase HPLC column, were carried out using both single and binary solvent systems without ion pairing reagents. The retention volumes for metal complexes of Cu(II), Ni(II), Co(II) and Zn(II) tested were close together. Hence further tests were carried out using ion-pair chromatography where, 80:20 ethanol-water v/v with cation generating salts was found most useful as an eluent. In order to optimise the elution of various metal-qdt complexes, the effective cation concentrations of each in turn, with TBA^+, THA^+ and CTA^+ cations using 0.05% ,0.1% and 0.2% w/v were determined. These solutions were clear, except with

Table – 1: The chromatographic parameters for metal-qdt complexes using different quaternary ammonium salts, in the concentration range of 0.05 to 0.2% w/v in 80:20 ethanol: water.

Quaternary Salt	Concentration of the Salt	qdt V_R (ml)	Cu $(qdt)_2$ V_R (ml)	Ni $(qdt)_2$ V_R (ml)	Co $(qdt)_2$ V_R (ml)	Zn $(qdt)_2$ V_R (ml)	R_s Ni/ Cu
Tetrabutyl	0.05%	1.06	1.06	1.06	1.06	1.06	-
ammonium	0.1%	1.13	1.13	1.18	1.13	1.13	-
bromide	0.2%	1.15	1.13	1.15	1.13	1.13	-
Tetraheptyl	0.05%	1.06	1.08	1.08	1.06	1.06	-
ammonium	0.1%	2.4	2.46	2.92	2.45	2.4	0.96
bromide	0.2%	2.43	2.43	2.91	2.5	2.42	-
Cetyltri - methyl ammonium bromide	0.05%	1.08	1.08	1.11	1.08	1.08	-
	0.1%	2.33	2.33	4.63	2.33	2.33	5.7

0.2% CTA^+cation, probably due to the formation of micelles (18-20).

The pH conditions for the elution of metal-qdt complexes containing quaternary cation in different concentrations was at pH 8.4. However, the pH conditions were examined in the range of 7.4 to 9.0. The retention volumes (V_R), Table 1, show some degree of separation of Ni(II)-qdt complex from Cu(II), Co(II) and Zn(II)-qdt complexes, with the use of 0. 1 % w/v THA^+ and CTA^+ cations respectively in 80:20 ethanol water at pH 8.4 . The other metals of nickel group Pd(II) and Pt(II)-qdt complexes at this pH were tested and showed complete separation from Cu(II),Co(II) and Zn(II)-qdt complexes Fig. 1 and partial separation of Ni(II), Pd(II) and Pt(II)-qdt complexes (Table-2) Hence quantitative studies were made for the determination of Ni(II),Pd(II) and Pt(II)-qdt complexes separately. The linear calibration curves were obtained by plotting average peak heights against the amount in ng injected (1µl) each in turn with Ni(II), Pd(II) and Pt(II)-qdt complexes with coefficient of correlation (r^2) 0.9934, 0.9822 and 0.9571 respectivly. The regression equations for Ni(II), Pd(II) and Pt(II)-qdt complex were determined to be Y=7.4714x-1.75, Y=4.2448x-18.329 and Y=1.09x-8.2 respectively. The slope sensitivity for Ni(II)-qdt gave a peak height of 7.5 mm ng^{-1} compared with Pt(II)-qdt which was least sensitive with the peak height of 2.1 mm ng^{-1} and Pd(II)-qdt was intermediate with the peak height of 4.2 mm ng^{-1}

Table 2: Chromatographic parameters for nickel-group metal-qdt complexes using 0.1% THA^+ and CTA^+ in ethanol: water with the column eluent at pH 8.4

Quaternary ammonium Salt	Ni $(qdt)_2$ V_R (ml)	Pd $(qdt)_2$ V_R (ml)	Pt $(qdt)_2$ V_R (ml)	R_s Ni/Pd	Pd/Pt	Ni/Pt
THAB 0.1%	2.92	2.93	3.0	0.04	0.16	0.16
CTAB 0.1%	4.15	4.22	4.26	0.16	0.03	0.7

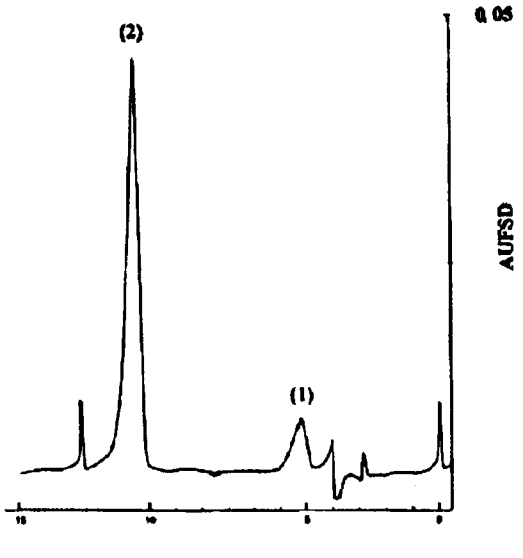

Fig. 1: HPLC separation of (1) Cu(II)-qdt (2) Ni(II)qdt complexes of CTAB ion pair at pH 8.4. Column Lichrosorb RP-18, 5µm (150x 4.6 mm,i.d) elution with ethanol: water (80:20 v/v) containing 0.1% CTAB. Flow rate 0.43 mL/min. Detection UV at 285 nm.

For the separation of Ni(II), Pd(II) and Pt(II) - qdt complexes, , when eluted at pH 9 using THA^+ and CTA^+cations a well resolved profile of these metal-qdt complexes was obtained Fig-2, the retention data at different pH is given in Tables 3 and 4. However, a substantial increase in the retention volumes V_R of these metal complexes was observed maintaning the complete separation of metal complexes . It may be suggested that some deterioration of the column at higher pH of the eluent was occuring and was affecting day to day reproducibility in the retention volumes. Hence some

quantitative studies were made for the determination of Ni(II), Pd(II) and Pt(II) -qdt complexes separately, Peak heights were measured and plotted against the amount in nanograms for each of the metal-qdt complex when, 1 µl of each standard was injected. The linear correlation curves were obtained with coefficient of correlation (r^2) 0.9856, 0.9982 and 0.9708 for Ni(II), Pd(II) and Pt(II)-qdt complexs respectively. The regression equation were calculated Y= 11.48x +11, Y=6.84x+1.5 and Y= 5x -10 for Ni(II), Pd(II) and Pt(II)-qdt complexes respectively. The slope sensitivity for Ni(II)-qdt, gave a peak height of 7.0 mm ng^{-1} compared with Pt(II)-qdt which is the least sensitive with the peak height of 2.0 mm ng^{-1} and Pd(II)-qdt was the most sensitive with the peak height of 18 mm ng^{-1}. The chromatograms for Ni(II)-qdt was recorded at 310 nm and those of Pd(II) and Pt(II)-qdt complexes at 285 nm with the maximum detector sensitivity of 0.05 AUFS and 10mV full scale on the recorder. The separation of Ni/Pt with the resolution R_s of 2.48 and partial separation of Ni/Pd, with resolution R_s of 1.3 and Pd/Pt with resolution, R_s of 1.15 was achieved. A profile of the three metals eluted together is represented in Fig.2 and the retention data is given in Table-4. The calibration curve for the Ni(II)qdt and Pd(II)-qdt complexes are linear upto 10 ng and that of for Pt(II)qdt upto 12.5 ng.

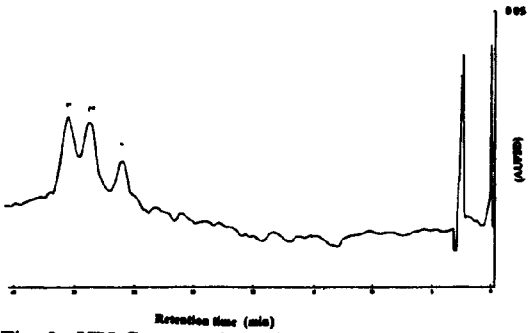

Fig. 2: HPLC separation of Ni(II), Pd(II) and Pt(II) qdt complexes as THAB ion pairs at pH 9. Column Lichrosorb RP-18, 5µm (150x 4.6 mm,i.d) elution with ethanol: water (80:20 v/v) containing 0.1% CTAB. Flow rate 0.5 ml/min. Detection UV at 285 nm.

Experimental

The instrument used was the same as described [13,14] using, a Haskel differential pump, a Cecil variable wavelength UV detector and an x-t recorder. The sample injection was based on "Stopped flow" principle. The stainless steel columns were packed in the laboratory [15-16]. These columns were of medium efficiency (N ≅2500-5000). The efficiencies of the columns, in use, were tested on daily basis, using phenetol, nitrobenzene and acetophenone organic standards. The reagent qdt was generated from S-2(3- dimercaptoquinoxalinyl) thiouronium chloride (mqt) at pH 8.5 .The solution was deaerated by bubbling nitrogen through it to avoid aerial oxidation of the reagent [17]. Tetrabutyl ammonium bromide (TBAB), tetraheptyl ammonium bromide (THAB) and cetyltrimethyl ammonium bromide (CTAB) were obtained form (BDH Chemicals Ltd) . The solvents used were of analytical grade (BDH Chemicals Ltd).

Table-3: The chromatographic parameters recorded for nickel-group metal-qdt complexes eluted with 0.1% cetyl trimethyl ammonium bromide in 80: 20 ethanol: water at different pH.

pH of the Column Eluent	$Ni(qdt)_2$ V_R (ml)	$Pd(qdt)_2$ V_R (ml)	$Pt(qdt)_2$ V_R (ml)
8.4	4.52	5.04	5.48
9.0	3.05	3.24	3.41

Table-4: The chromatographic parameters recorded for nickel-group metal-qdt complexes eluted with 0.1% tetraheptyl ammonium bromide in 80:20 ethanol: water at different pH

pH of the column Eluent	$Ni(qdt)_2$ V_R (ml)	$Pd(qdt)_2$ V_R (ml)	$Pt(qdt)_2$ V_R (ml)	R_s Ni/Pd	Pd/Pt	Ni/Pt
8.4	2.28	2.32	2.45	0.07	0.44	0.44
9.0	17.0	19.0	20.75	1.3	1.15	2.48

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