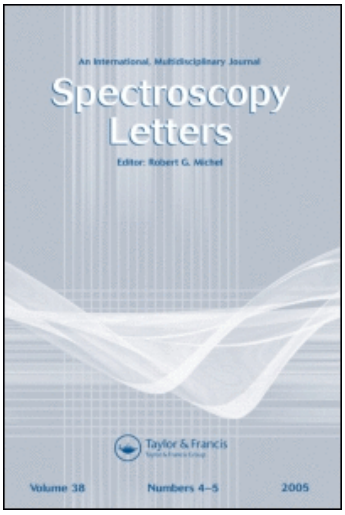

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DETERMINATION OF COMPOSITIONS OF SOME METAL-LIGAND COMPLEXES BY HPTLC-DENSITOMETRY

KEY WORDS

HPTLC-densitometry, complexes, Job's method, mole-ratio method.

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ABSTRACT

The well known methods of Job's continuous variations and mole-ratio were used for the determination of the compositions of some metal-N,N-diethyl-N'-benzoyl-thiourea complexes chromatographically using HPTLC-densitometry. A different and a simple application of these two methods makes the determination of the composition of metal-ligand complexes possible even when the maximum absorption wavelengths of ligand and complexes are close to each other.

INTRODUCTION

Complex formation leads to changes in many physical and chemical properties of solutions. The measurement of any parameter which varies in response to complex formation provides a possibility

for determination of the compositions and calculation of formation constants of the complexes[1].

Complex compositions are generally determined spectrophotometrically with the well known and widely used two analytical methods; Job's continuous variations and mole ratio methods[2] in which absorbance of complex was plotted with respect to solution composition. The position of the maximum in the curve is a function of the equilibrium constant of the complex as well as of stoichiometric ratio. In order to apply these methods, the selected wavelength at which the complex absorbs strongly must be different from that of the chelating agent and metal ions. Nevertheless, many complexes may not be fitted to this rule.

In the present study, a new chromatographical application of these two methods is presented as a solution for the problem arising from the closeness of the absorption wavelengths of metal complex and chelating agent. For this purpose, the determination of stoichiometry of Pd, Pt, Cu and Ru complexes with N,N-diethyl-N'-benzoylthiourea (DEBT) which have very close absorption maxima to that of DEBT were studied.

N,N-dialkyl-N'-benzoylthioureas have been successfully employed as selective complexing agents for metal ions, especially for the platinum group metals[3]. One of the best of these ligands, DEBT, forms highly stable complexes with various metal ions. DEBT enables the pH-selective complexation and enrichment of the platinum metals from complex matrices, such as alumina based catalysts, containing high quantities of interfering materials[4]. The chelates of the platinum metals, and those of Co(II), Cu(II) and Hg(II) show excellent thin layer chromatographic properties[5].

The crystal and molecular structure of Cu(II), Ni(II) and Pd(II)-DEBT complexes were studied previously by x-ray structure analysis[6-8]. The

stabilities of Ni(II), Zn(II), Cd(II), Co(II), Pb(II) and Tl(I)-DEBT complexes with DEBT were demonstrated with their high pK_s values which were determined potentiometrically[9].

In the potentiometric study reported[9] , it has been shown that metals with +1 valence state form 1:1 and +2 valence state form 1:2 M-DEBT complexes. In the literature, there is no study has been reported before for the complexes of + 3 ions with DEBT. In the present study, Pd(II), Pt(II), Cu(II) for M^{2+} ion and Ru(III) for M^{3+} ion were chosen as examples to determine the metal-DEBT ratios using densitometry.

EXPERIMENTAL

Apparatus. A Shimadzu CS-9000 Model TLC with dual-wavelength flying spot scanner in reflection and zig-zag mode was used.

A horizontal developing chamber, 10 x 10 cm, was used as the developing chamber.

Reagents and Standard Solutions.

Table (I) shows the chelating agent, DEBT and metal chelates prepared using the method reported in literature[5]. Standard stock solutions of metals in 1M HCl (1.00×10^{-3} M) from their salts of $PdCl_2$ (60 % Pd, Merck), K_2PtCl_4 (47 % Pt, Sigma), $CuCl_2.2H_2O$ (Merck) and $RuCl_3.H_2O$ (38 % Ru, Sigma), and standard stock solution of DEBT (1.00×10^{-3} M) in ethanol were prepared.

As these complexes are completely insoluble in water but fairly soluble in ethanol and soluble in chloroform, toluene and benzene, the solutions of complexes in chloroform were used in all studies.

All the other chemicals were of analytical reagent grade.

HPTLC-silica gel 60_{F254}, plates (Merck), 20 x 20 cm as stationary phase and benzene as mobile phase were used in the determinations.

Table (1)

Experimental parameters for the preparation of chelates

Metal	pH	Color	Complexation temperature
Pd(II)	0-7	orange	room temp.
Pt(II)	0-7	yellow	at 40° C
Cu(II)	0-7	green	room temp.
Ru(III)	0-2	brown	at 60° C

Procedure

For Job's method, ten different mixtures of the equimolar solutions of the metal ions and the reagent (DEBT) were employed in varying volumes keeping total volume 5.0 mL at suitable temperature and pH conditions.

In mole ratio method, again the equimolar solutions of metal ions and the reagent were used. Keeping the volume of metal ion solution constant as 1.0 mL varying volumes of chelating agent from 0.5 to 4.0 mL were added. The total volume of 5.0 mL was obtained by adding distilled water when it was needed. In this way, ten different mixtures were prepared. In both of the methods, the mixtures were extracted with 5 mL of chloroform at the end.

A 1 μL of extract from the samples for each method was injected to a HPTLC silica gel plate as a spotwise manner using Hamilton microsyringe. After sample application, plates were preconditioned for 2 h before starting the chromatographical run in the horizontal developing chamber which was maintained at 50% relative humidity obtained by the use of 43% (w/v) H_2SO_4. Plates were developed at

room temperature for a distance of 4 cm beyond the starting line that was located 1 cm above the bottom of the plate. Then, the measurements were taken at 280 nm with dual-wavelength HPTLC-densitometer in zig-zag mode.

Results and Discussion

The spectra of DEBT and metal chelates are similar regarding the absorption wavelengths although their molar absorptivities at these wavelengths are different. Table (2) shows the maximum wavelength and maximum molar absorptivity values obtained in this study. These are quite comparable with the previously reported values[3]. The absorption maxima of the chelating agent remain either unchanged or suffer from slight shifts in the complexes. As a result, a resolved spectrum could not be obtained for the chelates in the presence of excess ligand in the solvent. The excess ligand can be separated from chloroform extracts of metal chelates either by chromatographic separation or by reacting with 0.1 M NaOH[5]. Because of its acidity, only DEBT but not the neutral metal chelates was decomposed in this highly basic medium. Otherwise, due to the closeness of maximum absorption bands of metal complexes and DEBT, Job's continuous variations and mole ratio methods could not be applied for the determination of their complex compositions.

The chromatographic properties of DEBT and the metal complexes on HPTLC silica gel plate using several organic solvents of medium polarity as mobile phases were studied. The medium polarity solvents were tested as the metal complexes were insoluble in both highly polar and non-polar solvents. The hR_F values (100 x R_F) of metal chelates obtained in toluene, xylene and benzene were compared. The best separation of DEBT and metal chelates was resulted when the

Table (2)

UV-absorption bands of DEBT and metal complexes

	λ_{max}	ε_{max}(L/mol.cm)
DEBT	241, 282	10971, 18524, 1092
$Pd(DEBT)_2$	244, 273, 378	39642, 52872, 4868
$Pt(DEBT)_2$	249, 265, 278, 326	28017, 25515, 25206, 9726
$Cu(DEBT)_2$	257, 283, 363	32782, 44019, 9072
$Ru(DEBT)_3$	275	22111

benzene was used as the solvent. The minumum volume of benzene (approximately 2 mL) was used for each plate and chromatographic separation was carried out in a fume-hood because of its harmful effects. Two different hR_F values obtained for Ru(III) (0 and 32) belong to two isomers of the metal chelate in Table (3). A similar behaviour is observed in thin layer chromatographic separations of octahedral complexes on silica gel, the trans-isomers of these complexes show higher hR_F values than the corresponding cis-isomers provided that single-component solvent systems are used[10].

In order to get reproducible hR_F values, the plates after the application of spots were preconditioned in a constant humidity medium which was supplied by saturating the tank atmosphere with 43% H_2SO_4 solution for 2 h. As a result, a better precision in hR_F values was accomplished, than.

The reliable quantitative evaluation of chromatograms largely depends on the stability of the densitometric intensity of spots. For this reason, the intensity measurements of spot were controlled with 15 min

Table (3)

hR_f values of DEBT and metal complexes in benzene

	hR_f (lit)	hR_f (study)
DEBT	10	10
$Pd(DEBT)_2$	69	66
$Pt(DEBT)_2$	64	64
$Cu(DEBT)_2$	76	76
$Ru(DEBT)_3$	0, 32	0/29

intervals within 3 h. No significant decrease was observed in intensity within this period.

The optimized experimental parameters are given in Table (4). Using these parameters, Job's continuous variations and mole-ratio methods for Pd(II), Pt(II), Cu(II) and Ru(III) were carried out chromatographically.

The densitograms and the graphs of Pd(II)-DEBT and Ru(III)-DEBT complexes for the applications of Job's continuous variations and mole ratio methods are given in Figure (1) and Figure (2) as the typical examples. Each point on the graphs is the average of ten replicate scanning of the densitograms with a precision of 0.64 to 1.91 as % relative standard deviation (RSD). When the chromatographic separation of the complexes are repeated ten times, the overall precision ranged from 1.64 to 2.53 as %RSD was obtained for the method employed.

The data of densitograms obtained for Pd(II)-DEBT and Ru(III)-DEBT complexes with two methods were evaluated in the same way as it is

Table (4)

Optimum experimental conditions for metal-DEBT complexes

Stationary Phase	: HPTLC-silica gel 60_{F254}, Merck
Mobile Phase	: Benzene
Relative Humidity	: 50 %
Solvent Front	: 4 cm
Scanning λ	: 280 nm
Scanning Mode	: Zig-zag, dual-wavelength
Time of Run	: 8 min

done in ordinary spectroscopic methods. The tangents from the inflection points of the resultant parabolic curves were plotted. The best fitted tangent lines were obtained with the correlation coefficients of 0.985 to 0.999 and the intersection points of the tangents were found to be as 0.328 for Pd(II)-DEBT and 0.297 for Ru(III)-DEBT with Job's method; and 1.891 for Pt(II) and 2.988 for Ru(III) with mole ratio method. A similar data treatment was carried out for the Pt(II) and Cu(II)-DEBT complexes. The densitograms obtained for both of the methods confirmed a ratio of 1:2 metal to ligand for the metals having oxidation state of (II), like Pd, Pt, Cu and a ratio of 1:3 for the metals having oxidation state of (III), like Ru. The results, found for metal ions with the oxidation state of (II) are in agreement with those found potentiometrically[9].

In this way, it was shown that the compositions of metal chelates can be directly found from the obtained densitograms without drawing the Job's and mole-ratio plots. The difference in hR_F values of chelating

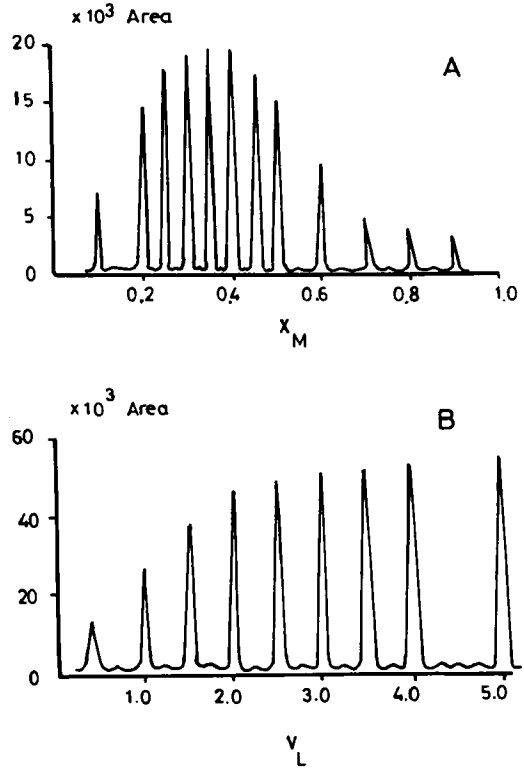

Figure 1. The densitograms (a) and the graphs (b) of Pd(II)-DEBT complex

A)Job's continuous variations method; area vs mole fraction of metal, $[Pd^{2+}] = [reagent] = 1.00x10^{-3}$ B) mole ratio method; area vs mole ratio of [L] / [M]

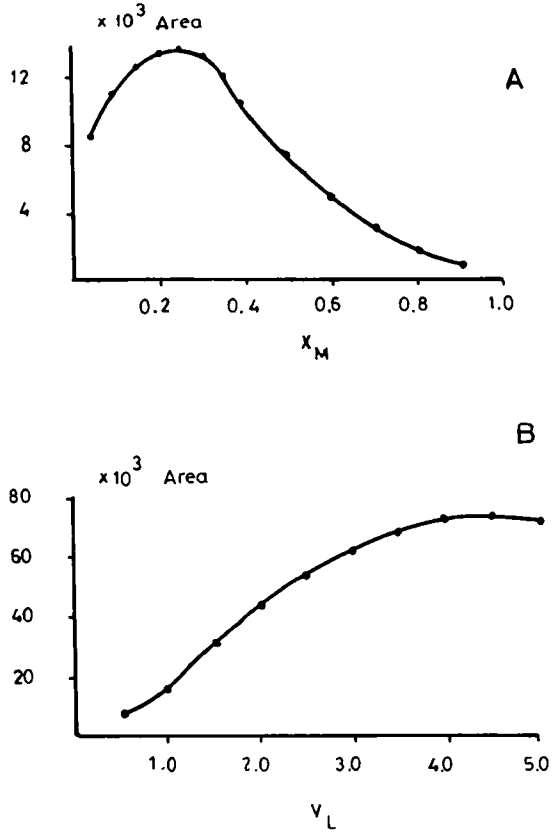

Figure 2. The densitograms (a) and the graphs (b) of Ru(III)-DEBT complex

A)Job's continuous variations method; area vs mole fraction of metal, $[Ru^{3+}]$ = [reagent] = 1.00×10^{-3} B) mole ratio method; area vs mole ratio of [L] / [M]

agent and metal complexes makes it possible to obtain completely interference free absorbance values from the densitograms.

This new approach provides an easy application of these methods using HPTLC densitometry for the determination of metal complexes regardless of whether the metal complexes and chelating agent have similar maximum absorption wavelengths or not. The only requirement is the different migration rates of chelating agent and metal complexes in the mobile phase. It can also be stated that the simultaneous application of the samples of different mole compositions shortens the analysis time, which requires only ten minutes to take a densitogram.

For the new chromatographic application described in this paper, the highly stable metal complexes of DEBT was used. However, these two spectrophotometric methods can readily be applied to the metal chelates of well known chelating agents such as dithizone and dithiocarbamates which are known to have good chromatographic properties on silica plates [11,12].

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REFERENCES

1. M. T. Beck, I. Nagypal, Chemistry of Complex Equilibria, John Wiley and Sons, New York: 1990.

2. D. T. Sawyer, W. R. Heineman and J. M. Beebe, Chemistry Experiments for Instrumental Methods, John Wiley and Sons, New York: 1984.

3. K. H. König, H. J. Pletsch and M. Schuster, Z. Anal. Chem. 1984: 319: 66.

4. R. S. Aygün, M. Merdivan, N. Külcü, Mikrochimica Acta, in press.

5. M. Schuster, B. Kugler and K. H. König, Fresenius J. Anal. Chem. 1990: 338: 717.

6. V. R. Richter, L. Beyer, J. Kaiser, Z. Anorg. Allg. Chem. 1980: 461: 67.

7. P. Knuuttila, H. Knuuttila, H. Hennig, L. Beyer, Acta Chemica Scandinavica 1982: A 36: No 6.

8. V. G. Fitzl, L. Beyer, J. Siele, R. Richter, J. Kaiser, E. Hoyer, Z. Anorg. Allg. Chem. 1977: 433: 241.

9. K. H. König, H. J. Pletsch and M. Schuster, Fresenius Z. Anal. Chem. 1986: 325: 621.

10. M. B. Celap, G. Vuckovic, M. J. Malinar, J. Chromatogr. 1980: 196: 59.

11. W. Schunk, G. schwedt, Chromatogr. 1983: 17: 37.

12. P. Bruno, M. Caselli, F. Faracassi, A. Traini, Anal. Lett. 1984: 17B: 397.

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