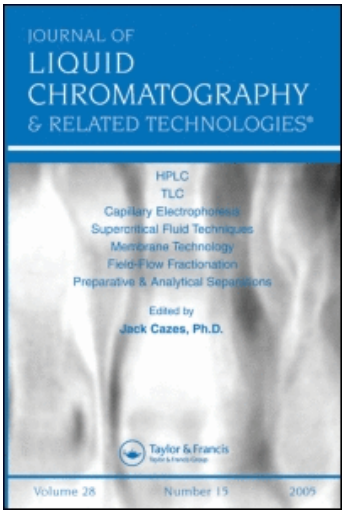

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Thin Layer Chromatography of Metal Ions Complexed with Anils (VII) Detection, Separation, and Determination

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THIN LAYER CHROMATOGRAPHY OF METAL IONS COMPLEXED WITH ANILS(VII) DETECTION, SEPARATION, AND DETERMINATION

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ABSTRACT

Dark colored chelates of p-dimethylaminoanil of 3-benzoyl-methylglyoxal bidentate ligand with Sb(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), ZrO(II), Y(III), La(III), Pr(III), Nd(III) Sm(III), Gd(III) and Dy(III) have been chromatographed on starch bound silica gel thin layers. New correlations of I.R. with R_f (resolving solvent) have been used to ascertain the colored spots.

Among various mixtures resolved qualitatively a few typical ones have been alanysed quantitatively. Errors in determinations and maximum separation limits have also been deduced.

INTRODUCTION

The mixtures, component compounds of which have high solubility in acidic and alkaline media, are generally resolved by liquid-liquid extraction and chromatographic methods, and are estimated volumetrically or colorimetrically. In such case gravimetric method of analysis fails even in the presence of masking agents and on controlling pH. The colored chelates of Sb(III), Mn(II), Fe(III),

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Co(II), Ni(II), Cu(II), ZrO(II), Y(III), La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) with p-dimethylaminoanil of 3-benzoylmethylglyoxal[1](D'MABG) having high solubility in common solvents under acidic and alkaline conditions have been, therefore, analysed qualitatively as well as quantitatively by thin layer chromatography in continuation to our work[2-7].

The use of R_F and infrared spectral correlations in identification of mixture components is the most interesting feature of these studies.

EXPERIMENTAL

Preparation of Solutions and TLC Plates :

Complexes isolated[8] as solids were dissolved in known quantities in their solvents to prepare the standard solutions.

Glass plates (16x3 cm and 16x10 cm) were coated with silica gel freed from iron and chloride ions and mixed with starch as binder (24:1, w/w) to prepare layers of 0.1 cm thickness by self designed apparatus[9]. Gel coated plates were dried at $\sim$ 100°C for 2-3 hrs in an oven. Dry loaded plates were developed in rectangular glass jars with ground-in-lids by ascending technique.

Loading and Development of TLC Plates :

For qualitative studies one or two drops of the test solutions were placed on 16x3 cm plates with thin glass capillaries. After drying the spots development was done in different solvents and the ascent was fixed as $\sim$ 10 cm in all cases. However, for quantitative analysis mixtures of varying concentrations of components were spotted on the plates of 16x10 cm with the help of micro pipette. After development plates were dried in oven and chromatogram fragments were scrapped and eluted with ethanol. Elutes were reduced to 5ml and optical densities were measured at their λmax. Elute concentrations were deduced from their respective

TABLE-1

SPOT COLOUR, λmax, VISIBLE, I.R. FREQUENCIES AND R_F OF COMPLEXES

Complex	Spot colour	λmax (visible) nm	Infrared frequencies cm^{-1}		R_F							
			C=O	C=N	CH_2Cl_2	$CHCl_3$	CCl_4	C_6H_6	BuOH	C_6H_6-BuOH (1:2)	C_6H_6-BuOH (1:1)	C_6H_6-BuOH (2:1)
$Sb(DMABG)_2Cl_3.6H_2O$	Pink	350	1600	1560		0.03	0.25		0.00	0.97	0.98	0.99
$Mn(DMABG)_2Cl_2.H_2O$	Yellow	356	1610	1520		0.00	0.96		0.00	0.99	0.99	0.99
$Fe(DMABG)_2Cl_3.6H_2O$	Brown	356	1600	1520		0.00	0.00		0.00	0.96	0.98	0.99
$Co(DMABG)Cl_2$	Light brown	350	1610	1550		0.00	0.00		0.99	0.98	0.99	0.99
$Ni(DMABG)_2Cl_2.2H_2O$	Light brown	365	1610	1570		0.02	0.26		0.09	0.46	0.98	0.99
$Cu(DMABG)Cl_2.4H_2O$	Light brown	342	1600	1550	No migration	0.00	0.96	No migration	0.00	0.99	0.98	0.99
$(ZrOCl_2)_2(DMABG).9H_2O$	Pink	350	1590	1560		0.07	0.27		0.40	0.99	0.99	0.36
$(Y(DMABG)Cl_3)_2.2H_2O$	Canary yellow	348	1630	1580		0.04	0.96		0.99	0.93	0.99	0.99
$La(DMABG)_2Cl_3$	Canary yellow	345	1610	1570		0.00	0.98		0.00	0.99	0.99	0.99
$(Pr(DMABG)Cl_3)_2$	Yellow	355	1610	1580		0.00	0.10		0.08	0.98	0.99	0.99
$(Nd(DMABG)Cl_3)_2.5H_2O$	Light brown	365	1610	1580		0.04	0.98		0.00	0.96	0.99	0.99
$(Sm(DMABG)Cl_3)_2.2H_2O$	Light brown	345	1610	1580		0.00	0.14		0.57	0.97	0.98	0.99
$(Gd(DMABG)Cl_3)_2.2H_2O$	Canary yellow	345	1610	1580		0.00	0.98		0.00	0.95	0.99	0.98
$Dy(DMABG)_3Cl_3$	Yellow	360	1610	1570		0.00	0.99		0.00	0.99	0.99	0.99

Room temperature = 30 ± 2°C

TABLE - 2

METAL COMPLEX MIXTURES WITH RESOLVING SOLVENTS

Metal Ions in Complex Mixtures	Resolving Solvent
Co(II) or Fe(III) + Sb(III) or Ni(II) or Zr(IV) + Mn(II) or Cu(II) (0.00) (0.01) (0.24) (0.26) (0.26) (0.95) (0.96)	CCl_4
Sb(III) + Zr(IV) + Co(II) or Mn(II) or Fe(III) or Ni(II) or Cu(II) (0.76) (0.85) (0.98) (0.99) (0.99) (0.98) (0.99)	EtOH
Sb(III) or Mn(II) or Fe(III) or Cu(II) + Ni(II) + Zr(IV) + Co(II) (0.00) (0.00) (0.01) (0.02) (0.09) (0.40) (0.99)	BuOH
Ni(II) + Zr(IV) + Sb(III) or Mn(II) or Fe(III) or Co(II) or Cu(II) (0.38) (0.62) (0.99) (0.99) (0.99) (0.99) (0.99)	Aq.BuOH
Zr(IV) or Sb(III) + Ni(II) + Co(II) or Mn(II) or Fe(III) or Cu(II) (0.24) (0.25) (0.62) (0.97) (0.99) (0.98) (0.99)	AcOH-BuOH (1:1, v/v)
Zr(IV) + Co(II) or Ni(II) + Sb(III) + Mn(II) or Fe(III) or Cu(II) (0.33) (0.50) (0.54) (0.83) (0.99) (0.98) (0.99)	Aq.BuOH-AcOH (1:1, v/v)
Zr(IV) + Mn(II) + Sb(III) or Ni(II) or Fe(III) or Co(II) (0.68) (0.88) (0.95) (0.97) (0.98) (0.99)	Aq.BuOH-AcOH-$CHCl_3$ (5:5:3, v/v)
Ni(II) or Co(II) or Sb(III) + Zr(IV) + Mn(II) or Fe(III) or Cu(II) (0.36) (0.41) (0.41) (0.50) (0.96) (0.98) (0.99)	Aq.BuOH-$CHCl_3$ (5:2, v/v)
Mn(II) + Fe(III) + Sb(III) or Zr(IV) + Ni(II) (0.00) (0.08) (0.34) (0.38) (0.98)	$CHCl_3$-Hexane-BuOH (1:1:1, v/v)
Fe(III) or Co(II) or Cu(II) + Zr(IV) or Sb(III) + Mn(II) or Ni(II) (0.01) (0.00) (0.01) (0.18) (0.16) (0.99) (0.99)	$CHCl_3$-Hexane-BuOH (1:2:1, v/v)
Ni(II) or Mn(II) or Fe(III) or Cu(II) + Co(II) + Sb(III) or Zr(IV) (0.00) (0.02) (0.04) (0.06) (0.11) (0.20) (0.32)	$CHCl_3$-Hexane-BuOH (1:1:2, v/v)

Ni(II) (0.64) or Sb(III) (0.81) or Zr(IV) (0.84) + Co(II) (0.94) or Cu(II) (0.95) or Fe(III) (0.97) or Mn(II) (0.98)	MeOH
Zr(IV) (0.82) + Ni(II) (0.88) + Cu(II) (0.96) or Sb(III) (0.98)	Me_2CO
Sb(III) (0.10) or Zr(IV) (0.15) + Ni(II) (0.33) + Mn(II) (0.96) or Fe(III) (0.98) or Co(II) (0.99) or Cu(II) (0.98)	AcOH-BuOH (1:2, v/v)
Sb(III) (0.28) + Ni(II) (0.54) + Mn(II) (0.97) or Fe(III) (0.99) or Co(II) (0.99) or Cu(II) (0.99) or Zr(IV) (0.99)	AcOH-BuOH (2:1, v/v)
Dy(III) (0.40) or Sm(III) (0.44) + La(III) (0.57) or Pr(III) (0.56) + Nd(III) (0.93) or Gd(III) (0.99) or Y(III) (0.99)	AcOH-BuOH (1:1, v/v)
Gd(III) (0.05) or Nd(III) (0.06) or Pr(III) (0.07) + La(III) (0.13) or Sm(III) (0.13) or Dy(III) (0.15) + Y(III) (0.99)	$CHCl_3$-Hexane-BuOH (1:1:1, v/v)
La(III) (0.00) or Nd(III) (0.00) or Gd(III) (0.02) or Dy(III) (0.00) + Pr(III) (0.08) + Sm(III) (0.57) + Y(III) (0.99)	BuOH
Pr(III) (0.16) + Sm(III) (0.36) + Y(III) (0.98) or La(III) (0.98) or Nd(III) (0.99) or Dy(III) (0.99) or Gd(III) (0.99)	AcOH-BuOH (1:2, v/v)
Sm(III) (0.28) + Dy(III) (0.34) + Y(III) (0.98) or La(III) (0.98) or Pr(III) (0.99) or Nd(III) (0.99) or Gd(III) (0.99)	Aq.BuOH-$CHCl_3$ (5:2,v/v)

R_F Values of complexes are given in parenthesis.

calibration curves prepared under similar conditions of temperature and solvent.

Physical Measurements

Infrared spectra of complexes were recorded on Perkin Elmer-621 infrared spectrophotometer in Nujol mull in full range. Optical density measurements on the complex solutions were done by Bausch & Lomb Spectronic-20 spectrophotometer.

RESULTS AND DISCUSSION

TLC data (table-1) of individually migrated complexes in CH_2Cl_2, $CHCl_3$ and CCl_4 evidently show an adverse effect of solvent polarity on R_F. Almost all complexes have shown high migration in C_6H_6-BuOH mixtures than their component solvents. In the absence of any chemical reaction of migrating compounds with the solvents, this abnormality could only be attributed to azeotropic properties of mixture solvents. Migration of each complex has been found to be independent on the presence of others and on plate size but layer thickness has adverse effect on it.

Among various solvents used those giving differential migrations of individual complexes and could resolve their diverse ternary and quaternary mixtures have been noted in table-2 alongwith R_F values. All the mixtures were qualitatively resolved but only a few typical ones could be tried for quantitative analysis. Maximum limit of separations of different mixtures is exhibited by the quantities of each mixture components resolved (Table-3). Errors determined in each estimation (Table-3) show the precision of this method. In BuOH-AcOH mixture solvents trailing effect was observed but it did not obstruct separations.

Stretching frequencies of metal sensitive azomethine and carbonyl groups of DMABG in complexes have been correlated with their R_F values in almost all the resolving solvents. These

Table-3

QUANTITATIVE ANALYSIS DATA ON TYPICAL MIXTURES

Mixture	Complex applied on plate (μg)	Comolex recovered (μg)	Error (%)
$Sb(DMABG)_2Cl_3.6H_2O$	90.50	90.00	-0.55
$(ZrOCl_2)_2(DMABG).9H_2O$	60.40	60.00	-0.66
$Co(DMABG)Cl_2$	69.75	70.00	+0.36
$Cu(DMABG)Cl_2.4H_2O$	35.25	35.00	-0.71
$(Pr(DMABG)Cl_3)_2$	49.75	50.00	+0.50
$(Nd(DMABG)Cl_3)_2.5H_2O$	39.75	40.00	+0.63
$Dy(DMABG)_3Cl_3$	35.00	35.00	0.00
$(Y(DMABG)Cl_3)_2.2H_2O$	35.25	35.00	-0.71
$La(DMABG)_2Cl_3$	30.00	30.00	0.00
$(Gd(DMABG)Cl_3)_2.2H_2O$	50.25	50.00	-0.50

relationships of ν(C=N) and ν(C=O) with R_F of components of diverse mixtures in their resolving solvents have been used in the identification of chromatogram fragments.

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