The Separation of Cobalt(II), Copper(II), Zinc(II), Lead(II), and Cadmium(II) as Their 3-Methyl-1-phenyl-4-thiobenzoyl-5-pyrazolone (SBMPP) Chelates by Thin-layer Chromatography on Silica Gel

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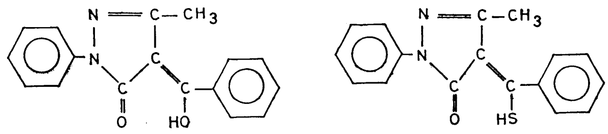
Thin-layer chromatographic separation technique has been employed for the separation of Co(II), Ni(II), Cu(II), Zn(II), Pb(II), and Cd(II) as their 3-methyl-1-phenyl-4-thiobenzoyl-5-pyrazolone (SBMPP) chelates. Metal chelates are intensely coloured and so no additional reagent was needed for the development of spots. Silica gel G was used as an adsorbent in the form of thin layer coating (0.25 mm) on glass plates (5 cm×20 cm). The R_f values of SBMPP and metal–SBMPP chelates have been determined by the ascending method with pure solvents and various binary solvent mixtures on thin layer of silica gel. In benzene the order of R_f values is Cd(II)<Pb(II)<Zn(II)<Co(II)<SBMPP<Ni(II)=Cu(II). By employing solvents like dichloromethane, benzene, and toluene, mutual separation of metal complexes was achieved successfully. The mixed solvents are more useful for the mutual separation of chelates than the pure solvents.

Thin-layer chromatography has been employed to separate metal ions using some chelating ligands.[1] In our laboratory extensive work has been conducted on the analytical applications of acylpyrazolones[2–6] in solvent extraction, spectrophotometric estimations and gravimetric determinations. Recently the authors have reported the solvent extraction of cobalt(II), zinc(II), and europium(III) with a new chelating ligand 3-methyl-1-phenyl-4-thiobenzoyl-5-pyrazolone (SBMPP),[5,7] Preliminary results on the utility of SBMPP[8] have been also published. It has been found that 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (BMPP) is comparable to thenoyl trifluoroacetone (TTA) in the solvent extraction of metals.[9] It is reasonable to expect SBMPP to be comparable to (thiothenoyl) trifluoroacetone (STTA) as analytical reagent since these are thioderivatives of BMPP and TTA respectively. In this paper the results of our original studies on thin-layer chromatographic separation of metals as their SBMPP chelates on silica gel are reported. Honjo and Kiba[10] have earlier described the separation of transition metals as their STTA chelates by thin-layer chromatography on silica gel.

Experimental

Apparatus and Reagents. Glass chromatographic plates (5 cm×20 cm), chromatographic chamber and universal applicator (Toshniwal) were used. Sample solutions were prepared by dissolving the metal chelates in acetone. Silica gel G (BDH), incorporating 13% calcium sulphate as binder was used as adsorbent for the thin-layer chromatography.

Developing Solvents. Analar reagent grade of methanol, ethanol, 2-propanol, 1-butanol, diethyl ether, dichloromethane, chloroform, carbon tetrachloride, benzene, toluene, cyclohexane, and hexane were used. They were purified by standard methods, if necessary. It has been found that SBMPP forms stable and extractable chelates with a specific color with many metal ions.[8] Spectrophotometric methods for the estimation of cobalt(II) and nickel(II) with SBMPP have been developed.[5] Solid complexes of cobalt(II), nickel(II), copper(II), zinc(II), lead(II), and cadmium(II) with SBMPP were prepared by dissolving their respective acetates in aqueous media followed by adding requisite amounts of ethanolic solution of SBMPP. The complexes were filtered, purified by recrystallization from suitable solvents and analysed. The ligand SBMPP was prepared by passing hydrogen sulphide gas and hydrogen chloride gas through a solution of BMPP in absolute ethanol, maintaining the temperature at 0 °C. This method is similar to the one employed by Honjo and Kiba[11] for the preparation of (thiothenoyl) trifluoroacetone. Structural formulas of SBMPP and BMPP are shown in Fig. 1. Cryoscopic determination of molecular weight in benzene gave a value of 296±4 (calculated molecular weight of SBMPP is 294). Analytical data and some important characteristics like λ_{max} and ε_{max} of the ligand SBMPP and complexes of SBMPP with metals are given in Table 1.



BMPP SBMPP

Fig. 1. Structural formulas of SBMPP and BMPP.

Procedure. Chromatographic plates were prepared by applying 0.25 mm thick coating of silica gel slurry with the help of universal applicator. Coated plates of the silica gel were dried for 20—30 min at 25±2 °C and then they were activated in an oven for two hours at 110 °C. The plates were stored over calcium chloride in a desiccator. With the help of a capillary tube a 5-μl portion of sample solution is spotted on the thin layer at definite intervals within about 2 cm from one end of the plate. One millimolar solutions of the metal chelates in acetone were used to prepare the sample. The spots were then air dried at room temperature (25±2 °C). The plate was placed in a chromatographic chamber containing an organic solvent or solvent mixture (20 ml), so that the plate dips into the solvent upto 1 cm below the sample spot. The solvent migrates upwards through the thin layer separating the sample into spots by ascending development. When the solvent proceeded to ≈10 cm from the sample spot the development was stopped and the plate was taken out of the chromatographic chamber. It was then exposed to air. Since the metal chelates showed characteristic colours (colours are mentioned in Table 1) no spraying with additional developing reagent was needed.

The resulting chromatogram is generally characterized

Table 1. Analytical data and some characteristics of SBMPP and metal chelates of SBMPP

Compound	Colour	λ_{max} / nm	ε_{max}[a)] / $L\,M^{-1}\,cm^{-1} \times 10^{-3}$	Mp θ_m/°C	Carbon[b)] (%)	Hydrogen[b)] (%)
SBMPP	Greenish yellow	328	4.8	80— 82	69.4C 69.5F	4.75C 4.88F
$Co(L)_3$[c)]	Reddish brown	328	9.2	188—190	65.3C 65.6F	4.16C 4.21F
$Ni(L)_2$	Brick red	330	10.2	201—204	63.3C 63.0F	4.03C 4.23F
$Cu(L)_2$	Olive brown	328	7.4	256—258	62.8C 62.9F	4.00C 4.08F
$Zn(L)_2$	Bright yellow	330	12.3	178—180	62.6C 62.4F	3.99C 4.06F
$Pb(L)_2$	Orange	330	12.9	238—242	51.4C 51.2F	3.28C 3.35F

a) Absorption spectra measured in chloroform solution against the same solvent. ε_{max} values are approximate. b) C: Calculated, F: found. c) (L)−: Anion of SBMPP.

Table 2. R_f values of SBMPP and its metal chelates with various pure solvents on silica gel

Developing solvent	Dielectric constant	Developing length/cm	Developing time/min	Metal: Co	Ni	Cu	Zn	Pb	Cd	SBMPP
Methanol	32.6	12.0	20	1.0	1.0	1.0	0.98	0.97	0.98	0.98
Ethanol	24.3	9.8	30	0.97	1.0	1.0	0.98	0.98	1.0	0.98
2-Propanol	18.3	7.8	45	1.0	1.0	1.0	1.0	1.0	1.0	0.98
1-Butanol	17.1	9.0	45	0.96	0.97	0.98	0.98	0.97	0.95	0.94
Diethyl ether	4.3	9.5	25	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dichloromethane	9.08	10.2	40	0.29	0.49	0.40	0.30	0.27	0.13	0.54
Chloroform	4.8	10.3	30	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Carbon tetrachloride	2.2	10.2	55	0.0	0.0	0.0	0.0	0.0	0.0	0.14
Benzene	2.3	11.4	30	0.37	0.80	0.80	0.34	0.03	0.0	0.43
Hexane	1.9	11.2	35	0.0	0.0	0.0	0.0	0.0	0.0	0.03
Cyclohexane	2.0	11.7	38	0.0	0.0	a)	0.0	0.0	a)	0.01
Toluene	2.38	9.4	15	0.21	0.58	0.59	0.22	0.04	0.0	0.28

a) Spots disappear during development. Average deviation of R_f values=0.02.

by R_f values which are calculated from the following equation.

$$R_f = \frac{\text{Distance (cm) travelled by the substance}}{\text{Distance travelled by the solvent}}$$

Results and Discussion

The R_f value measures the velocity of movement of the spot relative to that of the solvent front. Moreover the R_f value is a measure of the interaction among solute, solvent and adsorbent and is reproducible and characteristic for each solute in a given solvent–adsorbent system under specified conditions.

Some typical results of the development of SBMPP and its metal STTA chelates with individual pure solvents on a silica gel employing the ascending method are summarised in Table 2. Metal chelates can be divided into three groups on the basis of their chromatographic behaviour. (1) Chelates which do not migrate from the sample spot (with carbon tetrachloride, cyclohexane and hexane) (2) Chelates which can be developed to moderate distances over a comparatively wide range (with toluene, benzene and dichloromethane) (3) Chelates which move upto solvent front (methanol, ethanol, chloroform, diethyl ether, and 2-propanol). The average deviation of R_f values was 0.02. The R_f values of SBMPP chelates in benzene increased in the order of Cd(II)<Pb(II)<Zn(II)<Co(III)<SBMPP<Ni(II), Cu(II). By employing solvents like dichloromethane, benzene and toluene, separation of metal complexes was obtained successfully. Representative chromatograms of SBMPP and its metal chelates in benzene and dichloromethane are shown in Fig. 2. Results indicate that the distance of the development on the chromatographic plate depends on the polarity of the solvent. Honjo and Kiba[10)] reported that R_f values of STTA chelates generally increased in the order of: Cd(II)<Zn(II)<Pb(II), STTA<Hg(II)<Co(II), (III)<Cu(II)<Ni(II).

It was considered interesting to study the effect of binary mixtures of solvents in the thin layer chromatography of SBMPP and its metal chelates and some representative results are listed in Table 3. The average deviation of the R_f values is 0.02. It is seen that the mixed solvents could separate the SBMPP chelates of metals more successfully than the pure

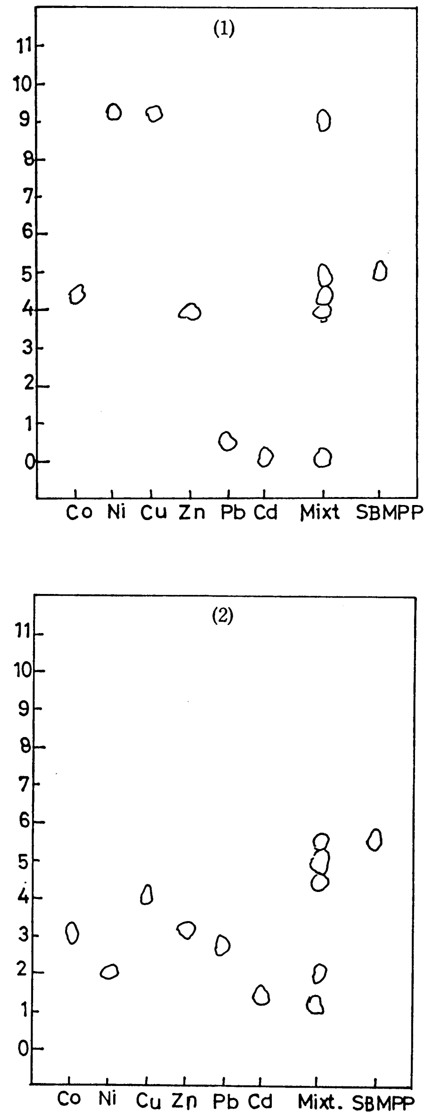


Fig. 2. Chromatogram of SBMPP and its metal chelates with single component solvent.
SBMPP, Chelate $\approx 5\times10^{-4}$ M; developing solvent (1) benzene (2) dichloromethane.
Y axis-migration distance (cm).

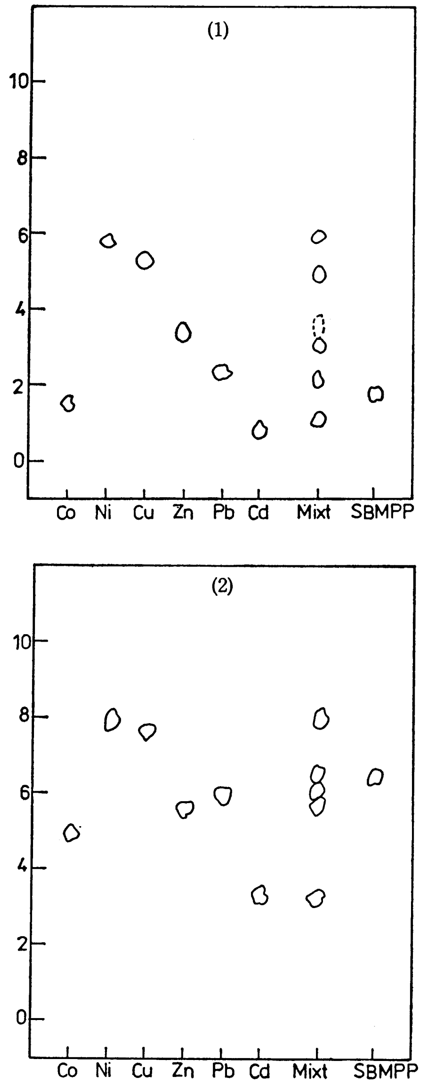


Fig. 3. Chromatogram of SBMPP and its metal chelates with binary solvent mixture.
SBMPP, Chelate $\approx 5\times10^{-4}$ M; developing solvent (1) benzene–carbon tetrachloride (2) toluene– chloroform.
Y axis-migration distance (cm).

Table 3. R_f values of SBMPP and its metal chelates with various mixed developing solvents on silica gel

Developing solvent (1:1, v/v)	Developing length/cm	Developing time/min	Metal						
			Co	Ni	Cu	Zn	Pb	Cd	SBMPP
Benzene-carbon tetrachloride	9.5	32	0.15	0.60	0.55	0.34	0.24	0.07	0.17
Benzene-chloroform	8.6	20	0.73	1.0	1.0	1.0	0.21	0.11	0.24
Benzene-cyclohexane	11.0	35	0.03	0.32	0.31	0.91	0.14	0.0	0.13
Benzene-ethanol	11.7	45	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Toluene-carbon tetrachloride	11.5	35	0.07	0.38	0.38	0.07	0.07	0.0	0.10
Toluene-chloroform	10.5	15	0.46	0.75	0.73	0.53	0.55	0.31	0.6
Toluene-ethanol	11.0	40	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Chloroform-carbon tetrachloride	8.5	35	0.31	0.92	0.95	0.63	0.30	0.0	0.30

Average deviation of R_f values = 0.02.

solvents. Some typical results are shown in Fig. 3. Among these binary solvent mixtures the pairs of benzene–carbon tetrachloride, toluene–chloroform, and chloroform–carbon tetrachloride were suitable for the separation of metal chelates. The R_f values of SBMPP chelates in benzene–carbon tetrachloride increased in the order Cd(II) < Co(III) < SBMPP < Pb(II) < Zn(II) < Cu(II) < Ni(II).

The effectiveness of binary solvent mixtures in the separation of SBMPP chelates is probably due to some demixing of mixed solvents leading to some changes in the solvent ratio. Since the adsorbability of each solvent on the silica gel is different, this may lead to better separation of the developed spots. According to Honjo and Kiba[10] binary mixtures of solvents show a similar beneficial effect in the thin layer chromatographic separation of STTA chelates of metals on silica gel.

The sequence of R_f values obtained with the SBMPP chelates differs from the acetylacetonate series,[12,13] the dithiazonate series[14,15] or the diethyldithiocarbamate.[16,17] Chelates of SBMPP are similar to those of STTA and do not form hydrates like acetylacetonate chelates of metals. Further nickel chelate of SBMPP is red and diamagnetic while that of BMPP is green dihydrate which is paramagnetic.[4,5] Cobalt(II) forms stable paramagnetic chelate with BMPP which is a dihydrate while it forms diamagnetic chelate containing three moles of ligand with SBMPP in which cobalt is present in the oxidation state three.[4] Though there are some differences, the behaviour of SBMPP chelates is closer to that of STTA chelates than others such as dithiazonates and acetylacetonates.

In conclusion it can be stated that thin layer chromatographic separation technique is useful for the separation of transition metal ions as their SBMPP chelates using certain solvents and mixtures of solvents.

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