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# Separation of Copper(II), Nickel(II), Palladium(II), and Cobalt(II) Chelates with 4-*S*-Benzyl-l-*p*-Cl-phenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) from Their Binary Mixture by Adsorption Thin-Layer Chromatography

Narayan S. Bhave[a]; Suchita R. Dhudey[a]; R. B. Kharat[a]
[a] CHEMISTRY DEPARTMENT, NAGPUR UNIVERSITY CAMPUS, NAGPUR, INDIA

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# NOTE

# Separation of Copper(II), Nickel(II), Palladium(II), and Cobalt(II) Chelates with 4-*S*-Benzyl-1-*p*-Cl-phenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) from Their Binary Mixture by Adsorption Thin-Layer Chromatography

NARAYAN S. BHAVE, SUCHITA R. DHUDEY,
and R. B. KHARAT

CHEMISTRY DEPARTMENT
NAGPUR UNIVERSITY CAMPUS
NAGPUR 440 010, INDIA



## Abstract

In the present work a suitable solvent system for the separation of Cu(II), Ni(II), Co(II), and Pd(II) as their chelates with 4-*S*-benzyl-1-*p*-Cl-phenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) from their binary mixtures has been suggested. The most applicable solvent system has been found to be benzene-cyclohexane (3: 1). The best separation is achieved within 15 min. $R_F$ values of Ni-$(BPPTB)_2$ and Co-$(BPPTB)_2$ decrease with time. The substitution of benzene in a benzene–cyclohexane (1: 1) solvent mixture by toluene decreases the $R_F$ value of metal chelates. Cu-$(BPPTB)_2$ and Pd-$(BPPTB)_2$ chelates do not migrate even with an increase in temperature. The $R_F$ value of Ni$(BPPTB)_2$ chelate increases with temperature, whereas the $R_F$ value of Co-$(BPPTB)_2$ remains practically constant.

Colored complexes of Co(II), Cu(II), Ni(II), and many other metals with STTA [1,1,1-trifluoro-4(2-thienyl)-4-mercapto-3-buten-2-one] were separated on thin layer of silica gel by developing with 19 pure solvents and 10 different binary 1: 1 mixtures by Honjo et al. (*1*). The separation was excellent by development with $CCl_4$, $CS_2$, EtOAc, cyclohexane–$CHCl_3$, $CHCl_3$–$CS_2$, and $CCl_4$–$CS_2$. Xanthates of Cu(II), Co(II), Ni(II), and many other metals were separated by using 10:1 $CCl_4$–$CHCl_3$ as solvent by Rao and Shekhar (*2*). Kostikov, Egorova, and Bulenkov (*3*) separated Cu(II), Co(II), and (Ni(II) quantitatively using 22:22:0.1 $Me_2CO$–$C_6H_6$–HOAc as solvent by adsorption thin-layer chromatography. Dithiozonates of certain metal ions including Cu(II), Pd(II), Ni(II), Co(II), and other metals were separated by silica gel thin-layer chromatography by using $C_6H_6$ or 1:7:4 $CHCl_3$–$CH_2Cl_2$–$C_6H_6$ mixture by Suzuki et al. (*4*). Johri and Mehra (*5*) separated Ni(II), Co(II), Cu(II), Pd(II), and other metal chelates of diphenylthiovioluric acid (I) on silica gel thin layer by using 5:2 $CHCl_3$–$Me_2CO$ and 4:2:1 $CHCl_3$–iso-BuEOMe–$C_6H_6$ for development. $R_F$ value decreased in the order Cu(II) > Co(II) > Fe(II) > Ni(II) and Pd(II) > Pt(IV) > Ru(II).

The solvent system chosen in this paper for the separation of Cu(II), Ni(II), Co(II), and Pd(II) as their chelates with 4-*S*-benzyl-1-*p*-Cl-phenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) is simple, rapid, and selective.

## EXPERIMENTAL

### Chemicals

The chelates of Cu(II), Ni(II), Co(II) and Pd(II) with BPPTB prepared in this laboratory (*6*) were used.

### Solutions

Solutions of all the above chelates were prepared in double-distilled chloroform. The spraying reagents were not needed for locating the chelates on the plate since each is of a different color.

### Solvent Mixtures

Double-distilled solvents were used for making the systems. The solvent mixtures used were benzene: cyclohexane, toluene: cyclohexane, and chloroform: cyclohexane.

### Instruments and Apparatus

Small chromatotanks (10 × 3.5 × 10.5 cm) were used to run small thin-layered chromatograms. Big chromatotanks (~15 × 12 × 30 cm) were used for running larger chromatograms. Glass plates were used for covering the chromatotanks. To prepare aqueous slurries, 14 g of purified silica gel G and 1 g of $CaSO_4$ as binder were mixed in 30 ml of distilled water, and this was spread uniformly on a glass plate with a spreader to prepare thin layer plate.

An oven (Tempo) was used to heat the plates at a controlled temperature (110°C) for 2 hr to activate the adsorbent.

Capillaries of a few micrometers diameter were used to apply the spot of solution of metal chelates onto the thin layer.

A thermostatic bath with an automatic control was used to attain the desired temperature ($\pm 0.2$°C).

### General Procedure

The solvent mixture of the desired proportion was allowed to stand for 5 to 10 min in the chromatotank to saturate it with respect to solvent vapors which were in equilibrium with the solvent mixture. Spots of solution were applied by capillary on the base line which was drawn about 1.5 cm from the lower edge. The spot was allowed to dry. The thin-layer plate was kept in the solvent taken in a chromatotank so that the spot applied to the plate did not touch the solvent. Chromatograms were allowed to run for an appropriate time and dried. Chelates of particular metal ions could be located by their original colors. The $R_F$ value of each chelate denoted the extent of separation.

To study the temperature effect on $R_F$, the required temperature for each experiment was obtained by using a thermostatic bath. The chromatotank containing 100 ml of solvent mixture was kept in a thermostat to attain the desired temperature. After applying spots to thin-layer plates, they were dried and kept in a chromatotank. The chromatograms were run at known temperatures for a definite time. The plates were then dried and $R_F$ values measured.

## RESULTS AND DISCUSSION

### Choice of Solvent

Different solvents have been tried for the individual chromatograms of bis-(BPPTB)-Cu(II), bis-(BPPTB)-Ni(II), bis-(BPPTB)-Co(II), and bis-(BPPTB)-Pd(II). It was observed that the solvent systems $CCl_4$, acetone–$CHCl_3$ 5:2, isoBuCOMe–$CHCl_3$–benzene 2:4:1, and ethyl acetate–14 $M$ $HNO_3$ were not suitable for separation of the bis-chelates of BPPTB with Cu(II), Ni(II), Co(II), and Pd(II), since all of these chelates migrate with the solvent front. However, the solvent systems $CHCl_3$–$CCl_4$ 1:10, $CHCl_3$–cyclohexane 1:1, and benzene–cyclohexane 1:1 have been found suitable for the separation of these chelates from binary mixtures. The solvent system benzene–cyclohexane has been mainly used for the separation of metal chelates from their binary mixture, since Cu-$(BPPTB)_2$ remains at the origin, Co-$(BPPTB)_2$ migrates to little distance, Ni-$(BPPTB)_2$ migrates a distance a little less than the solvent front, and Pd-$(BPPTB)_2$ remains at the origin.

## Effect of Solvent System on $R_F$ Values

While keeping cyclohexane as one of the components constant, another component was changed and the effect of this change was observed on the $R_F$ values of the metal chelates. The results (Table 1) show that the $R_F$ value of all the chelates decreases by changing the solvent component



TABLE 1

Effect of Solvent System on $R_F$ Values[a]

| | | $R_F$ | | | |
|---|---|---|---|---|---|
| Solvent[b] | System | Cu-$(BPPTB)_2$ | Co-$(BPPTB)_2$ | Ni-$(BPPTB)_2$ | Pd-$(BPPTB)_2$ |
| Benz-cyclo (1:1) | Ni–Pd | — | — | 0.20 | 0.0 |
| Tolu-cyclo (1:1) | Ni–Pd | — | — | 0.10 | 0.0 |
| Benz-cyclo (1:1) | Co–Pd | — | 0.16 | — | 0.0 |
| Tolu-cyclo (1:1) | Co–Pd | — | 0.07 | — | 0.0 |
| Benz-cyclo (1:1) | Cu–Co | 0.0 | 0.09 | — | — |
| Tolu-cyclo (1:1) | Cu–Co | 0.0 | 0.07 | — | — |
| Benz-cyclo (1:1) | Cu–Ni | 0.0 | — | 0.38 | — |
| Tolu-cyclo (1:1) | Cu–Ni | 0.0 | — | 0.09 | — |
| Chloro-cyclo (1:1) | Cu–Ni | 0.0 | — | 1.00 | — |

[a]Time = 15 min.

[b]Benz = Benzene, cyclo = cyclohexane, tolu = toluene, and chloro = chloroform.

from benzene to toluene. However, in the case of the Cu–Ni system, the substitution of chloroform for benzene or toluene increases the $R_F$ value of the Ni-(BPPTB)$_2$ chelate.

## Effect of Varying Ratio of Benzene–Cyclohexane on $R_F$ Values

Since the benzene–cyclohexane system has been found the most suitable, the effect of varying the ratio of cyclohexane–benzene (1:1, 1:2, 1:3, 2:1, and 3:1) on $R_F$ values of the metal chelates of Cu(II), Ni(II), Co(II), and Pd(II) with BPPTB has been studied. It was observed that the best separation was achieved when the ratio of cyclohexane–benzene was 1:3. It was also observed that as the ratio of cyclohexane–benzene decreases, separation becomes difficult.

## Effect of Time on $R_F$ Values

To study the effect of time on the $R_F$ values of Cu-(BPPTB)$_2$, Ni-



TABLE 2

Effect of Time on $R_F$ Values[a]

| Binary mixture[b] | Time (min) | $R_F$ | | | |
|---|---|---|---|---|---|
| | | Cu-(BPPTB)$_2$ | Co-(BPPTB)$_2$ | Ni(BPPTB)$_2$ | Pd-(BPPTB)$_2$ |
| Cu–Ni | 15 | 0.0 | — | 0.91 | — |
| | 30 | 0.0 | — | 0.54 | — |
| | 45 | 0.0 | — | 0.46 | — |
| | 60 | 0.0 | — | 0.36 | — |
| Cu–Co | 15 | 0.0 | 0.77 | — | — |
| | 30 | 0.0 | 0.55 | — | — |
| | 45 | 0.0 | 0.45 | — | — |
| | 60 | 0.0 | 0.29 | — | — |
| Pd–Co | 15 | — | 0.70 | — | — |
| | 30 | — | 0.51 | — | — |
| | 45 | — | 0.39 | — | — |
| | 60 | — | 0.25 | — | — |
| Pd–Ni | 15 | — | — | 0.79 | 0.0 |
| | 30 | — | — | 0.48 | 0.0 |
| | 45 | — | — | 0.40 | 0.0 |
| | 60 | — | — | 0.31 | 0.0 |

[a]Solvent system = cyclohexane-benzene (1:3).

[b]Cu = Cu-(BPPTB)$_2$, Ni = Ni(BPPTB)$_2$, Co = Co-(BPPTB)$_2$, and Pd = Pd-(BPPTB)$_2$.

(BPPTB)$_2$, Co-(BPPTB)$_2$, and Pd-(BPPTB)$_2$ chelates in the cyclohexane–benzene 1:3 solvent system, chromatograms of a particular binary chelate mixture were run for different times. The results (Table 2) show that the $R_F$ values of Cu-(BPPTB)$_2$ and Pd-(BPPTB)$_2$ remain zero with time, whereas the $R_F$ values of Ni-(BPPTB)$_2$ and Co-(BPPTB)$_2$ decrease with time. This may be due to greater migration of the solvent front with time.

## Effect of Temperature on $R_F$ Values

Various experiments have been performed to study the effect of temperature on the $R_F$ values of Cu-(BPPTB)$_2$, Co-(BPPTB)$_2$, Ni-(BPPTB)$_2$, and Pd-(BPPTB)$_2$. The results (Table 3) clearly indicate that Cu(II) and Pd(II) chelates do not migrate with increasing temperature. The $R_F$ value of Ni(II) chelate increases with temperature. However, the $R_F$ value of Co(II) chelate increases only slightly with temperature.

TABLE 3

Effect of Temperature on $R_F$ Values[a]

| Binary mixture[b] | Temperature (°C) | $R_F$ | | | |
|---|---|---|---|---|---|
| | | Cu-(BPPTB)$_2$ | Co-(BPPTB)$_2$ | Ni(BPPTB)$_2$ | Pd-(BPPTB)$_2$ |
| Cu–Ni | 15 | 0.0 | — | 0.45 | — |
| | 25 | 0.0 | — | 0.59 | — |
| | 35 | 0.0 | — | 0.74 | — |
| | 45 | 0.0 | — | 0.95 | — |
| Cu–Co | 15 | 0.0 | 0.51 | — | — |
| | 25 | 0.0 | 0.62 | — | — |
| | 35 | 0.0 | 0.65 | — | — |
| | 45 | 0.0 | 0.69 | — | — |
| Pd–Ni | 15 | — | — | 0.34 | 0.0 |
| | 25 | — | — | 0.66 | 0.0 |
| | 35 | — | — | 0.68 | 0.0 |
| | 45 | — | — | 0.83 | 0.0 |
| Pd–Co | 15 | — | 0.48 | — | 0.0 |
| | 25 | — | 0.49 | — | 0.0 |
| | 35 | — | 0.50 | — | 0.0 |
| | 45 | — | 0.59 | — | 0.0 |

[a]Time = 30 min, solvent system = cyclohexane–benzene (1:3).
[b]Cu = Cu-(BPPTB)$_2$, Ni = Ni-(BPPTB)$_2$, Co = Co-(BPPTB)$_2$, and Pd = Pd-(BPPTB)$_2$.

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### REFERENCES

1. T. Honjo and T. Kiba, *Bull. Chem. Soc. Jpn.*, *46*, 3786 (1973).
2. A. L. J. Rao and C. Shekar, *Z. Anal. Chem.*, *277*, 126 (1975).
3. A. P. Kostikov, S. N. Egorova, and T. I. Bulenkov, *Chem. Abstr.*, *82*, 38218h (1975).
4. M. Suzuki, F. Kaiho, and S. Takitani, *Eisei Kagaku*, *21*, 47 (1975).
5. K. N. Johri and H. C. Mehra, *Chromatographia*, *8*, 244 (1975).
6. N. S. Bhave and R. B. Kharat, Unpublished Work.

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