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The Separation of Iron(III), Cobalt(II), Nickel(II), Copper(II), Zinc(II), Mercury(II), Lead(II), Cadmium(II), and Palladium(II) as Their SDBM (3-Mercapto-1,3-diphenyl-2-propen-1-one) Complexes by Thin Layer Chromatography on Silica Gel

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Synopsis. The separation of iron(III), cobalt(II), nickel(II), copper(II), zinc(II), mercury(II), lead(II), cadmium(II), and palladium(II) as their SDBM chelates has been achieved successfully on the thin layer of silica gel with such developing solvents as carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and carbon disulfide.

A new chelating reagent, 3-mercapto-1,3-diphenyl-2-propen-1-one(abbreviated as SDBM), has been found to form stable and extractable chelates of a specific color,[1,2] and it has been used for the determination of mercury(II) by means of the radioisotope dilution method[3] and for the spectrophotometric determination of iron(II, III), nickel(II), and copper(II).[4,5] In an attempt to widen the analytical application of this reagent, the metal ions have now been extracted in cyclohexane containg SDBM, and the metal chelates thus extracted have been chromatographed on the thin layer of silica gel with various organic solvents.

Experimental

The SDBM was synthesized by a modification of the method of Chaston *et al.*[6] A 5.0-g portion of dibenzoylmethane and 200 ml of absolute ethanol were put into a 500-ml flask, and then the vessel was cooled to 0—10 °C in an ice bath containing only ice or a freezing mixture with potassium chloride. The dried hydrogen chloride gas was passed through the solution for 10—30 min, after which the dried hydrogen sulfide gas was passed through for 1—2 h. There was no problem in the preparation of SDBM even if the hydrogen sulfide gas was passed into the solution first. The dehydration of ethanol, hydrogen sulfide, and hydrogen chloride might lead a worker to a successful synthesis of SDBM as in the synthesis of STTA.[7] The dark red solution was allowed to stand in an ice bath for 30—60 min and was then poured into ice water. The red crystalline product was filtered off, washed with water, and recrystallized from absolute ethanol or petroleum ether to give red crystals of the compound; yield, 60—70%; mp 76.5—78.0 °C. The developing solvents were all reagent-grade materials and were purified by the ordinary method, if necessary. The sample solutions for the thin layer chromatography were metal-SDBM chelates in cyclohexane, which were prepared as follows: a 10^{-2}—10^{-1} M salt solution was adjusted to pH 1—10, and then this solution was shaken with 10^{-3} M SDBM in cyclohexane for from 30 min to 2 h. The SDBM was found to remain mostly in the cyclohexane phase when the pH of the aqueous solution was below pH 10. Cadmium(II) and iron(III) gave large amounts of insoluble chelates in cyclohexane. Mercury(II), lead(II) and palladium(II) gave some insoluble chelates in cyclohexane. The experimental procedures and conditions for the thin layer chromatography of these metal chelates were almost the same as have previously been described.[8]

Results and Discussion

Each SDBM chelate extracted in cyclohexane showed its own specific color of the respective absorption maximum (Table 1), and was stable for at least several days. The results after the development of these SDBM metal chelates, including SDBM itself, with individual solvents on a thin layer of silica gel are given in Table 2. The compounds could be identified only by observing each specific color on the chromatoplate. The chelates may be classified into four groups in terms of their chromatographic behavior: 1) Chelates which do not migrate from the sample spot (with cyclohexane). 2) Chelates which can be developed to a moderate distance over a comparatively wide range (with carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, carbon disulfide, chloroform, benzene, chlorobenzene, and *o*-dichlorobenzene). By using these solvents, the mutual separation of various metal chelates was achieved successfully. 3) Chelates which move up to the solvent front (with acetone, ethyl acetate, and diethyl ether). 4) Chelates which cause a remarkable tailing during development (with methanol and ethanol). By using a binary mixture of solvents in a 1:1 volume ratio, SDBM and its metal chelates were developed to a moderate distance (Table 3). It was observed that the Co-SDBM chelate was trans-

Table 1. Color, absorption maxima, and extraction pH of SDBM and its metal chelates in cyclohexane

Compound	Color	Absorption maxima (nm)	Extraction pH
SDBM	Reddish orange	328, 410	—
$Fe(SDBM)_3$	Greenish brown	260, 324, 409	2—8
$Co(SDBM)_3$	Brown	305	6—8
$Ni(SDBM)_2$	Reddish brown	307, 400, 436	6—8
$Cu(SDBM)_2$	Olive brown	290, 345, 418	3—6
$Zn(SDBM)_2$	Yellow	310, 410	6—8
$Hg(SDBM)_2$	Pale yellow	276, 350	1—6
$Pb(SDBM)_2$	Orange yellow	318, 411	4—8
$Cd(SDBM)_2$	Yellow	275, 388	6—8
$Pd(SDBM)_2$	Orange	285, 460	1—8

TABLE 2. R_f VALUES OF SDBM AND ITS METAL CHELATES WITH VARIOUS PURE DEVELOPING SOLVENTS ON SILICA GEL AT ROOM TEMPERATURE (22—25 °C)

Developing solvent	Dielectric constant	Developing time (min)*	Metal									
			Fe	Co	Ni	Cu	Zn	Hg	Pb	Cd	Pd	SDBM
Methanol	32.6	70	0.94	0.40—0.95	0—0.88	0—0.92	0.85—0.99	a)	0.94	0—0.92	0—0.92	0.71—0.92
Ethanol	24.3	80	0.86—1.00	0.73—0.99	0.38—0.99	0.76—0.96	0.86—0.99	0.92	0.86—0.99	0.86—0.99	0.62—0.98	0.97
Acetone	20.7	17	0.99	0.98	0.99	0.98	0.99	0.99	0.99	0.99	0.98	0.99
Ethyl acetate	6.0	30	1.00	0.99	0.91	0.99	0.99	0.94	0.99	0.99	0.99	0.99
Diethyl ether	4.3	18	a)	0.94	0.95	0.93	0.97	a)	a)	a)	a)	0.96
Carbon tetrachloride	2.2	70	0.14	0.05	0.23	0.15	0	0	0.39	0	0.19	0.43
Chloroform	4.8	50	0.43	0.83	0.91	0.90	0	0.48	0.77	0	0.92	0.86
1,1,1-Trichloroethane	7.5	43	0.41	0.53	0.66	0.62	0	0.49	0.69	0	0.64	0.69
Trichloroethylene	3.4	36	0.16	0.29	0.57	0.54	0.06	0.09	0.66	0.01	0.63	0.64
Tetrachloroethylene	2.3	38	0.18	0.04	0.17	0.12	0.03	0	0.41	0	0.16	0.43
Carbon disulfide	2.6	15	0.11	0.05	0.15	0.12	0.03	0.02	0.42	0	0.16	0.43
Cyclohexane	2.0	60	0	0	0	0	0	0	0.08	0	0	0.09
Benzene	2.3	36	0.93	0.91	0.93	0.88	0	a)	0.90	0	0.94	0.90
Chlorobenzene	5.6	28	a)	0.68	0.90	0.84	0.01	0.09	0.80	0	0.96	0.84
o-Dichlorobenzene	9.9	70	a)	0.96	0.97	0.95	0	0.10	0.87	0	0.87	0.92

* The developing time for a distance of 10 cm. The average deviation of the R_f values was 0.01. a) The spots disappeared during the development.

TABLE 3. R_f VALUES OF SDBM AND ITS METAL CHELATES WITH VARIOUS MIXED DEVELOPING SOLVENTS ON SILICA GEL AT ROOM TEMPERATURE (22—25 °C)

Developing solvent (1 : 1, v/v)	Developing time (min)*	Metal					
		Co	Ni	Cu	Zn	Cd	SDBM
Cyclohexane-Chloroform	40	0.26	0.49	0.46	0.08	0	0.63
Cyclohexane-o-Dichlorobenzene	50	0.05	0.15	0.13	0.03	0	0.29
Carbon tetrachloride-Chloroform	45	0.50	0.76	0.74	0	0	0.75
Carbon tetrachloride-Carbon disulfide	20	0.06	0.20	0.17	0.07	0	0.49
Chloroform-Carbon disulfide	22	0.43	0.70	0.64	0.01	0.06	0.72

* The developing time for a distance of 10 cm. The average deviation of the R_f values was 0.01.

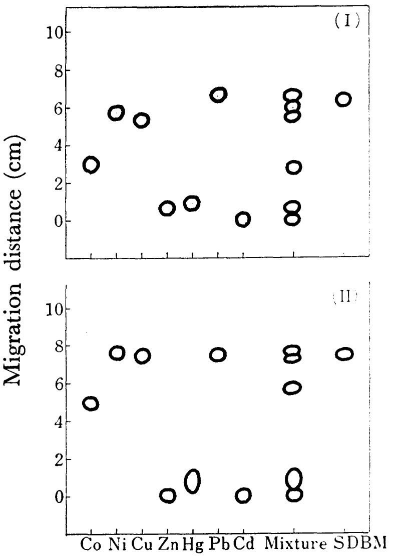

Fig. 1. Chromatogram of SDBM, its metal chelates, and the chelate mixtures with single component solvent and binary solvent mixture. SDBM, Chelate: *ca.* 5×10^{-4} M (3—6 μl).
Developing solvent: (I) Trichloroethylene, (II) carbon tetrachloride-chloroform.

formed into $Co(SDBM)_3$ chelates.[8] Some representative chromatograms of SDBM and its metal chelates with pure solvents and their mixture are shown in Fig. 1. In general, the greater the polarity of the solvent, the greater the distance of the development of metal chelates on the chromatographic plate. The R_f values of the SDBM chelates with various solvents generally increased in the following order: Cd(II), Zn(II)<Hg(II)<Fe(III), Co(III)<Cu(II)<Ni(II), Pd(II)<Pb(II), (SDBM). The R_f values of the SDBM chelates of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with the binary solvent mixture have the same tendency in their change as those of the single solvents. The R_f values of the SDBM chelates are smaller than those of the STTA chelates, while the R_f sequence of the SDBM chelates is almost the same as that of the STTA chelate series except for the Pb(II) complex, the R_f of which behaves much like the ligand; the latter sequence is: Cd(II)< Zn(II) < Pb(II), (STTA) < Hg(II) < Co(II, III) < Cu(II)<Ni(II).[9] In general, the discrepancy in the R_f values of the ligands and their metal chelates may be caused by the differences in hydrogen bonding or dipole-dipole interaction among the ligands, each chelate, and silanol or siloxane on the surface of silica gel involving the competition adsorption of the developing solvents and metal chelates with or without the ligands. In conclusion, carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and carbon disulfide were found to be suitable developing solvents for the mutual separation of metals as their SDBM chelates by means of thin layer chromatography on silica gel.

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