Note

Gel chromatography of β-diketones and their metal chelates

VII. Gel chromatographic data for β-diketones and their metal chelates on a polystyrene gel

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In our laboratory a systematic investigation of the gel chromatographic behaviour of metal complexes is in progress using metal chelates with β-diketones as model compounds. Most of the work reported so far in this series was carried out with the use of poly(vinyl acetate) gel as a column packing material[1–5]. It was previously established that the retention order of the chromium(III) chelates with various β-diketones was strongly dependent on the gel material used[6].

In this paper, we report the chromatographic data for seven β-diketones and their beryllium(II) and chromium(III) chelates in column systems of polystyrene gel and various organic solvents.

EXPERIMENTAL

Reagents

Table I lists the compounds investigated. Reagent-grade β-diketones (Dojin Labs., Kumamoto, Japan) were purified by either recrystallization or distillation. Both HTFA and HFTA were, however, used without further purification. The beryllium chelates were prepared by methods described in the literature[7,8]. The chromium chelates had been prepared in previous work[6].

Benzene, toluene, *p*-dioxane, tetrahydrofuran, ethyl acetate and *n*-butyl acetate were distilled after appropriate chemical treatment and drying.

Shodex 801 gel (Showa Denko, Tokyo, Japan) is a styrene–divinylbenzene copolymer. According to the manufacturer's data, this gel has an exclusion limit of molecular weight 1000 (for polystyrene in tetrahydrofuran). The 10–15-μm fraction was used.

Apparatus

The chromatograph was equipped with a syringe-type pymp (Model FLC-350, Japan Spectroscopic Co., Tokyo, Japan), a sample injection valve with a capacity of 50 μl, a Pyrex column (50 cm × 8 mm I.D.) with a water-jacket, and a PTFE tube (0.5 mm I.D.) connecting these devices. A Japan Spectroscopic Model UVIDEC-1

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TABLE I

β-DIKETONES AND THEIR METAL CHELATES STUDIED

The β-diketones have the formula R_1–$COCH_2CO$–R_2 in the keto form.

Solute	Abbreviation	R_1	R_2	V_m (ml/mole) [*]
Acetylacetone	HAA	CH_3	CH_3	108
Benzoylacetone	HBA	CH_3	C_6H_5	174
Dibenzoylmethane	HDBM	C_6H_5	C_6H_5	241
Trifluoroacetylacetone	HTFA	CF_3	CH_3	123
Furoyltrifluoroacetone	HFTA	CF_3	C_4H_3O	167
Thenoyltrifluotoacetone	HTTA	CF_3	C_4H_3S	182
Benzoyltrifluoroacetone	HBFA	CF_3	C_6H_5	189
Bis(acetylacetonato)beryllium(II)	Be(AA)$_2$	—	—	194
Bis(benzoylacetonato)beryllium(II)	Be(BA)$_2$	—	—	314
Bis(dibenzoylmethanato)beryllium(II)	Be(DBM)$_2$	—	—	433
Bis(trifluoroacetylacetonato)beryllium(II)	Be(TFA)$_2$	—	—	221
Bis(furoyltrifluoroacetonato)beryllium(II)	Be(FTA)$_2$	—	—	300
Bis(thenoyltrifluoroacetonato)beryllium(II)	Be(TTA)$_2$	—	—	327
Bis(benzoyltrifluoroacetonato)beryllium(II)	Be(BFA)$_2$	—	—	341
Tris(acetylacetonato)chromium(III)	Cr(AA)$_3$	—	—	292
Tris(benzoylacetonato)chromium(III)	Cr(BA)$_3$	—	—	471
Tris(dibenzoylmethanato)chromium(III)	Cr(DBM)$_3$	—	—	650 [*]
Tris(trifluoroacetylacetonato)chromium(III)	Cr(TFA)$_3$	—	—	332
Tris(furoyltrifluoroacetonato)chromium(III)	Cr(FTA)$_5$	—	—	451
Tris(thenoyltrifluoroacetonato)chromium(III)	Cr(TTA)$_3$	—	—	490
Tris(benzoyltrifluoroacetonato)chromium(III)	Cr(BFA)$_3$	—	—	511

[*] Calculated value of molar volume.

spectrophotometer with a pair of micro-flow cells (path length 10 mm and volume 24 µl) was used as a detector.

Procedure

The inner wall of the column was treated with dimethyldichlorosilane. Snodex 801 gel, after being swollen overnight in the solvent to be used as the eluent, was packed into the column by use of a packing reservoir into which the solvent was pumped at a flow-rate of 1 ml/min. When the column had been packed with the gel, an adjustable column end fitting was placed at the end of the column. Table II gives the properties of the columns this prepared. The column void volume was determined by mea-

TABLE II

COLUMN PARAMETERS

Gel, Shodex 801; column, 8 mm I.D.; temperature, $25.0 \pm 0.1°$.

Solvent	Height of gel bed (cm)	V_0 (ml)	V_x (ml)	V_t (ml)
Benzene	46.2	7.31	15.91	23.22
Toluene	46.9	7.78	15.79	23.57
p-Dioxane	45.3	6.61	16.16	22.77
Tetrahydrofuran	46.7	6.62	16.85	23.47
Ethyl acetate	46.7	8.36	15.11	23.47

surement of the elution volume of a mono-dispersed polystyrene standard of molecular weight 200,000 (Pressure Chemicals, Pittsburgh, Pa., U.S.A.) using a refractive index detector.

A 50-μl portion of a sample solution with a concentration between 0.25 and 1.0 mM was introduced into the column. Elution was carried out at a solvent flow-rate of 0.5 ml/min and a column temperature of 25.0 $\pm$ 0.1°. The spectrophotometer used as a detector operated at a wavelength of 300 nm. The output of this detector was delivered to an on-line computer (JEC-5, JEOL, Tokyo, Japan) for data processing. Each experiment on a sample was carried out at least in triplicate.

RESULTS AND DISCUSSION

No compound gave an elution curve with excessive skewness. Typical elution curves obtained with ethyl acetate are shown in Fig. 1.
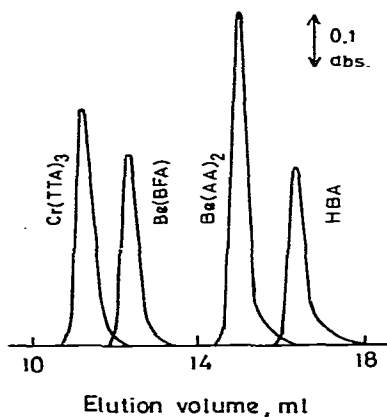

Fig. 1. Elution curves for various compounds. Shodex 801 column (46.7 cm $\times$ 8 mm I.D.); solvent, ethyl acetate, 0.5 ml/min; samples, 50-μl portion of 0.25 M solutions; detection, at 300 nm.

A compound in gel chromatography can be characterized by the distribution coefficient, K_{av}, derived from the equation

$$K_{av} = (V_e - V_0)/V_x \tag{1}$$

where V_e, V_0 and V_x are the elution volume, void volume and volume of the swollen gel, respectively[9]. The K_{av} values of β-diketones and their beryllium and chromium chelates obtained in various solvent systems are summarized in Table III. It is obvious that the K_{av} value of each compound depends on the solvent used. The solvent series with increasing order of K_{av} values for a particular compound is not always the same with other compounds. For example, the solvent series tetrahydrofuran $<$ ethyl acetate $<$ benzene $<$ p-dioxane $<$ n-butyl acetate $<$ toluene applies with HAA, but not with either its beryllium or its chromium chelates.

In order to examine the correlation between K_{av} and molar volume, V_m, the V_m value of each compound was determined as described below.

TABLE III

K_{av} VALUES FOR β-DIKETONES AND THEIR BERYLLIUM(II) AND CHROMIUM(III) CHELATES ON SHODEX 801 GEL WITH ORGANIC SOLVENT SYSTEMS

No.	Solute	K_{av}					
		Benzene	Toluene	p-Dioxane	Tetra-hydrofuran	Ethyl acetate	n-Butyl acetate
1	HAA	0.476	0.516	0.476	0.408	0.474	0.504
2	HBA	0.458	0.507	0.457	0.358	0.544	0.543
3	HDBM	0.439	0.482	0.436	0.315	0.598	0.556
4	HTFA	0.403	0.415	0.371	0.308	0.324	0.349
5	HFTA	0.397	0.405	0.337	0.272	0.322	0.344
6	HTTA	0.404	0.424	0.352	0.275	0.364	0.371
7	HBFA	0.383	0.401	0.362	0.281	0.374	0.379
8	Be(AA)$_2$	0.335	0.397	0.361	0.333	0.450	0.498
9	Be(BA)$_2$	0.296	0.364	0.326	0.258	0.525	0.456
10	Be(DBM)$_2$	0.263	0.316	0.285	0.196	0.585	0.542
11	Be(TFA)$_2$	0.267	0.291	0.265	0.206	0.231	0.259
12	Be(FTA)$_2$	0.247	0.262	0.219	0.162	0.212	0.232
13	Be(TTA)$_2$	0.255	0.272	0.236	0.165	0.247	0.259
14	Be(BFA)$_2$	0.234	0.253	0.239	0.169	0.268	0.272
15	Cr(AA)$_3$	0.295	0.378	0.370	0.351	0.581	0.740
16	Cr(BA)$_3$	0.231	0.289	0.276	0.214	0.521	0.572
17	Cr(DBM)$_3$	0.188	0.242	0.220	0.146	0.456	0.436
18	Cr(TFA)$_3$	0.225	0.245	0.233	0.168	0.205	0.247
19	Cr(FTA)$_3$	0.195	0.205	0.182	0.120	0.164	0.185
20	Cr(TTA)$_3$	0.200	0.224	0.192	0.125	0.192	0.206
21	Cr(BFA)$_3$	0.182	0.192	0.194	0.128	0.205	0.213

According to the method for determining molar volume at the normal boiling point[10,11], the V_m value is assumed to be the sum of the atomic volumes of the individual atoms constituting a compound. When each β-diketone is assumed to be in the enol form with a six-membered ring due to intramolecular hydrogen bonding, the V_m value is calculated from the following values of the atomic volume[10]: C, 14.8; H, 3.7; O (carbonyl), 7.4; O (alcohol), 12.0; F, 8.7; S, 25.6; O (ether), 11.0; five-membered ring, -11.5; and six-membered ring, -15.0 ml. The V_m value of a metal chelate, ML_n of a β-diketone, HL, can be calculated by using the semi-empirical equation[12] $V_{ML_n} = 0.9nV_{HL}$, where V_{ML_n} and V_{HL} are the V_m values of ML_n and HL, respectively, and n is the number of ligands in the ML_n molecule. The V_m values thus calculated are given in Table I.

Fig. 2 shows the relationships of the K_{av} values with the V_m values. It is interesting that the present compounds can be classified into two groups with respect to the correlation between K_{av} and V_m: one group includes fluorinated β-diketones and their metal chelates, and the other non-fluorinated compounds and their derivatives. The compounds belonging to the former and the latter groups are distinguished in Fig. 2 by closed and open circles, respectively. With a less polar solvent, such as benzene, both fluorinated and non-fluorinated compounds have approximately normal K_{av} versus V_m relationships in which the K_{av} value decreases with increase in the V_m value. However, with more polar solvents such as ethyl acetate, fluorinated compounds exhibit such scattered K_{av} versus V_m plots that the chromatographic behaviour of
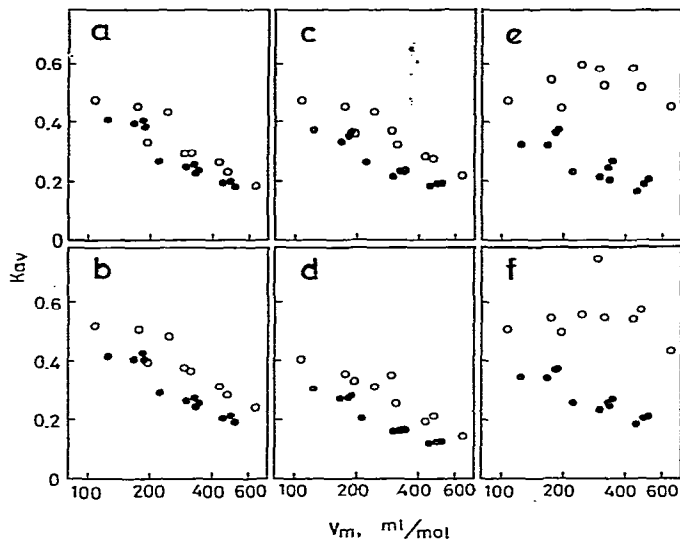
Fig. 2. K_{av} versus V_m plots in various solvent systems. Solvent: (a) benzene; (b) toluene; (c) p-dioxane; (d) tetrahydrofuran; (e) ethyl acetate; (f) n-butyl acetate. Open and closed circles represent non-fluorinated and fluorinated compounds, respectively.

these compounds cannot be explained only from the viewpoint of the molecular sieving effect.

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