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GEL CHROMATOGRAPHY OF β -DIKETONES AND THEIR METAL COMPLEXES

VI*. ELUTION BEHAVIOUR OF VARIOUS β -DIKETONES AND THEIR CHROMIUM(III) CHELATES ON DIFFERENT GELS

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SUMMARY

Seven β -diketones and their chromium(III) chelates were chromatographed on four gels with *p*-dioxan as eluent. Two poly(vinyl acetate) gels (Merckogel OR-PVA 500 and Merckogel OR-PVA 2000) and two polystyrene gels (Bio-Beads S-X8 and Poragel 60 A) were investigated. The distribution coefficients of each compound depend on the gel used. The increasing order of the distribution coefficients of both β -diketones and their chromium(III) chelates depend strongly on the gels, and cannot be simply correlated with the molecular weights of the compounds. The dependence of the distribution coefficients of β -diketones and their chromium(III) chelates on the gel is different from that of *n*-alkanes.

INTRODUCTION

Gel chromatography has a unique separation mechanism based on the molecular sieve effect, the chromatographic behaviour of a solute compound depending mainly on its molecular size. Gel chromatography, compared with adsorption and partition chromatography, is relatively new, but it has gained a key position in polymer and biological chemistry, not only as a method of separation but also as a means of determination of the molecular weight and size of solute species.

We decided to apply gel chromatography to metal complexes; only a few papers have appeared on this subject²⁻⁶, and little is known of the effects of the type of compounds, eluents and gel matrices. We have carried out a systematic investigation of the chromatographic behaviour of acetylacetone and its metal(II) and metal(III) chelates, selected as model compounds, on a poly(vinyl acetate) gel with various organic solvents as eluents^{1,7,8}, and the elution behaviour of *n*-alkanes⁹ and swelling of the gel¹⁰ in various solvent systems have also been examined.

This paper deals with the effects of gels on the chromatographic behaviour of

* For Part V, see ref. 1.

TABLE I
 β -DIKETONES AND THEIR CHROMIUM(III) CHELATES STUDIED
 The β -diketones have the following general formula (keto form): $R_1\text{-COCH}_2\text{CO-R}_2$.

Compound	Abbreviation	R ₁	R ₂	Mol. wt.	C (%)		H (%)	
					Calcd.	Found	Calcd.	Found
Acetylacetone	HAA	CH ₃	CH ₃	100.12	—	—	—	—
Trifluoroacetylacetone	HTFA	CH ₃	CF ₃	154.09	—	—	—	—
Benzoylacetone	HBA	C ₆ H ₅	CH ₃	162.19	—	—	—	—
Furoyltrifluoroacetone	HFTA	C ₄ H ₃ O	CF ₃	206.12	—	—	—	—
Benzoyltrifluoroacetone	HBFA	C ₆ H ₅	CF ₃	216.16	—	—	—	—
Thenoyltrifluoroacetone	HTTA	C ₈ H ₅ S	CF ₃	222.18	—	—	—	—
Dibenzoylmethane	HDBM	C ₆ H ₅	C ₆ H ₅	224.26	—	—	—	—
Tris(acetylacetonato)chromium(III)	Cr(AA) ₃	—	—	349.33	51.58	51.87	6.06	6.29
Tris(trifluoroacetonato)chromium(III)	Cr(TFA) ₃	—	—	511.24	35.24	35.87	2.37	2.30
Tris(benzoylacetona(o)chromium(III)	Cr(BA) ₃	—	—	535.54	67.28	68.09	5.08	5.44
Tris(furoyltrifluoroacetonato)chromium(III)	Cr(FTA) ₃	—	—	667.33	43.20	43.45	1.81	1.84
Tris(benzoyltrifluoroacetonato)chromium(III)	Cr(BFA) ₃	—	—	697.45	51.66	51.92	2.60	2.64
Tris(thenoyltrifluoroacetonato)chromium(III)	Cr(TTA) ₃	—	—	715.51	40.29	40.41	1.69	1.71
Tris(dibenzoylmethanato)chromium(III)	Cr(DBM) ₃	—	—	721.75	74.89	74.85	4.61	4.75

metal complexes and related compounds. The distribution coefficients of seven β -diketones and their chromium(III) chelates were measured on four gels with *p*-dioxan as the eluent. The gels were based on two types of matrix polymer: a poly(vinyl acetate) copolymer and a styrene-divinylbenzene (DVB) copolymer. The elution behaviour of *n*-alkanes were examined for comparison.

EXPERIMENTAL*

Chemicals

The β -diketones and their chromium(III) chelates that were used are listed in Table I. The β -diketones were reagent-grade materials and were purified by recrystallization or distillation. The chromium(III) chelates, except for Cr(DBM)₃, were prepared by use of analogous methods to that for Cr(AA)₃¹¹, while Cr(DBM)₃ was prepared according to the method by Charles¹². The composition of each product, after purification by recrystallization, was checked by means of C and H elemental analysis.

n-Alkanes of carbon number 5, 6, 7, 8, 10, 12, 14 and 16 were standard-grade materials supplied by Tokyo Chemical Industry (Tokyo, Japan).

Reagent-grade *p*-dioxan was purified by distillation on sodium metal, after refluxing with hydrochloric acid and then removing the water by use of potassium hydroxide. The water content in the *p*-dioxan used as the eluent was determined to be 0.012% by the Karl Fischer method.

Gels

Merckogel OR-PVA 500 and Merckogel OR-PVA 2000 (E. Merck, Darmstadt, G.F.R.) are gels based on poly(vinyl acetate). Poragel 60 A (Waters Assoc., Milford, Mass., U.S.A.) and Bio-Beads S-X8 (Bio-Rad Labs., Richmond, Calif., U.S.A.) are gels based on styrene-DVB copolymers.

Apparatus

As β -diketones have a high reactivity with metals, special precautions were applied so as to ensure reproducible elution data. Most of the parts of the equipment coming into contact with liquid were made of PTFE or Pyrex rather than metal in order to avoid undesirable effects. The column (100 cm \times 5 mm I.D.) was a Pyrex tube fitted with a water jacket for temperature control. The inner wall of the column was deactivated by use of dimethyldichlorosilane. A syringe-type pump (Model FLC-350, Japan Spectroscopic Co., Tokyo, Japan) and an automatic sample injection valve (Type CSVA, Chromatronix, Berkeley, Calif., U.S.A.) were used. A UV absorptiometric detector operating at 254 nm (Model UV-254, Japan Spectroscopic Co.) and a refractometric (RI) detector (Model 1107L, Laboratory Data Control, Riviera Beach, Fla., U.S.A.) were used, and the detection signal was fed to a JEC-5 computer (JEOL, Tokyo, Japan) for on-line data processing.

Procedure

Each column was prepared as follows. The gel to be used, after being swollen in *p*-dioxan overnight, was packed into the column using a column packing apparatus

* For abbreviations, see Table I.

supplying the solvent at a flow-rate of 0.20 ml/min. After the gel bed had settled, the solvent was further pumped through the column for 24 h or more so as to ensure complete setting of the gel bed. Then, a column end-fitting was fitted in place of the packing apparatus.

Sample solutions of β -diketones and their chromium(III) chelates were prepared at a concentration of 0.06% in *p*-dioxan, and the sample solutions of *n*-alkanes were prepared with concentrations of *ca.* 0.7%. A 20- μ l portion of a sample solution was fed into the column with the aid of the injection valve and elution was carried out at a solvent flow-rate of 0.20 ml/min and a column temperature of $25.0 \pm 0.01^\circ$. The elution of β -diketones and their chromium(III) chelates was monitored with the UV detector and that of *n*-alkanes with the RI detector. With the former compounds, the UV absorption spectra of the eluates were also recorded with the aid of a spectrophotometer micro-flow cell in order to identify the species eluted from the column.

RESULTS AND DISCUSSION

Volumes of mobile and stationary phases

The total column volume, V_t , of each column was 19.63 ml. The column void volume, *i.e.*, the volume of mobile phase in the column, v_0 , was determined from measurements of the elution volume of standard polystyrene of mol. wt. 200,000 (Pressure Chemical Co., Pittsburgh, Pa., U.S.A.), which one can regard as a compound that is excluded completely from the network of the gels used in this work. The volume of the swollen gel phase, V_x , of each column could be calculated as $V_x = V_t - V_0$. The swollen gel is regarded as the stationary phase in the column system. The results are given in Table II, each value of V_0 being the result of 20 measurements or more.

TABLE II

VALUES OF V_0 , V_x AND V_t FOR THE COLUMNS USED

Solvent, *p*-dioxan; column temperature, 25.0° .

Column No.	Gel	V_0 (ml)	V_x (ml)	V_t (ml)
I	Merckogel OR-PVA 500	7.28	12.35	19.63
II	Merckogel OR-PVA 2000	6.55	13.08	19.63
III	Bio-Beads S-X8	8.85	10.78	19.63
IV	Poragel 60 A	7.25	12.38	19.63

Elution behaviour of β -diketones and their chromium(III) chelates

No compound gave an elution peak with excessive asymmetry. Typical chromatograms obtained are shown in Fig. 1.

A solute in gel chromatography is characterized by the distribution coefficient, K_{av} , derived from the following equation¹³:

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

where V_e is the elution volume of the solute. The values of K_{av} for β -diketones and their chromium(III) chelates could be obtained with high reproducibility, the relative

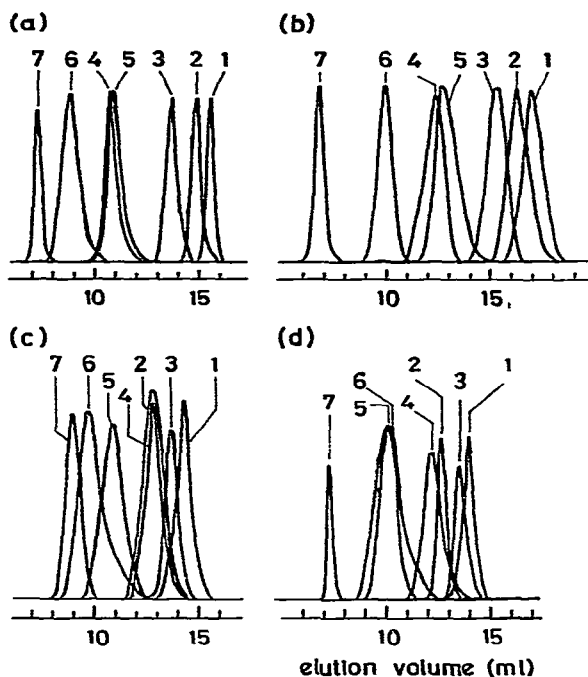


Fig. 1. Chromatograms of β -diketones and their chromium(III) chelates on columns packed with (a) Merckogel OR-PVA 500, (b) Merckogel OR-PVA 2000, (c) Bio-Beads S-X8 and (d) Poragel 60 A. Peaks: 1, HAA; 2, HTFA; 3, HDBM; 4, Cr(AA)₃; 5, Cr(TFA)₃; 6, Cr(DBM)₃; 7, polystyrene (mol.wt. 200,000). Column, 100 cm \times 5 mm I.D., 25.0°; Solvent, *p*-dioxan (0.20 ml/min). UV detector response in arbitrary units for each compound.

standard deviation in each instance being not more than 0.5%. The correction for the dead volume relating to the tubing and column end-fittings was, of course, made in advance of the calculation. The results are given in Table III, in which the values of the skew ratio, R , defined as the ratio of the slopes of the trailing and leading edges at their points of inflection¹⁴, are also shown. The skew ratio expresses the shape of elution peaks; thus, when the peak is symmetrical, $R = 1$, and when the leading slope is steeper than the trailing slope, $R < 1$.

According to the results, the elution series for increasing K_{av} of the β -diketones on the columns are as follows: on Merckogel OR-PVA 500, HDBM < HBFA < HBA < HTFA < HTTA < HFTA < HAA; on Merckogel OR-PVA 2000, HFBA < HDBM < HTTA < HBA < HFTA = HTFA < HAA; and on both Bio-Beads S-X8 and Poragel 60 A, HFTA < HTTA < HBFA < HTFA < HDBM < HBA < HAA. The elution series of the chromium(III) chelates are as follows: on both Merckogel OR-PVA 500 and OR-PVA 2000, Cr(DBM)₃ < Cr(BA)₃ < Cr(BFA)₃ < Cr(AA)₃ < Cr(TFA)₃ \leq Cr(TTA)₃ < Cr(FTA)₃; on Bio-Beads S-X8, Cr(FTA)₃ = Cr(TTA)₃ < Cr(BFA)₃ = Cr(DBM)₃ < Cr(TFA)₃ < Cr(BA)₃ < Cr(AA)₃; and on Poragel 60 A, Cr(FTA)₃ < Cr(TTA)₃ < Cr(BFA)₃ = Cr(DBM)₃ < Cr(TFA)₃ < Cr(BA)₃ < Cr(AA)₃.

It is well known that the gel chromatographic elution volumes of homologous compounds increase with a decrease in molecular weight. However, the elution order

TABLE III

VALUES OF K_{av} AND THE SKEW RATIO, R , FOR β -DIKETONES AND THEIR CHROMIUM(III) CHELATES ON FOUR DIFFERENT COLUMNS AT 25.0°

Column I, Merckogel OR-PVA 500; Column II, Merckogel OR-PVA 2000; Column III, Bio-Beads S-X8; Column IV, Poragel 60 A. Column size, 100 cm \times 5 mm I.D. Solvent, *p*-dioxan (0.20 ml/min).

Compound	Column I		Column II		Column III		Column IV	
	K_{av}	R	K_{av}	R	K_{av}	R	K_{av}	R
HAA	0.683	0.97	0.793	1.17	0.501	1.01	0.545	1.21
HTFA	0.608	0.67	0.738	1.23	0.369	0.92	0.429	0.85
HBA	0.590	0.95	0.731	1.22	0.474	0.99	0.525	1.00
HFTA	0.626	0.37	0.737	1.40	0.324	1.57	0.387	0.84
HBFA	0.530	0.52	0.659	1.18	0.348	1.41	0.410	0.85
HTTA	0.619	0.50	0.715	1.16	0.340	1.63	0.405	0.85
HDBM	0.527	0.94	0.672	1.22	0.445	0.96	0.501	0.89
Cr(AA) ₃	0.277	0.91	0.437	1.22	0.369	0.83	0.412	0.78
Cr(TFA) ₃	0.288	0.70	0.465	1.08	0.170	0.78	0.250	0.77
Cr(BA) ₃	0.188	0.57	0.332	1.08	0.199	0.57	0.295	0.72
Cr(FTA) ₃	0.305	0.68	0.469	0.93	0.089	0.59	0.182	0.69
Cr(BFA) ₃	0.193	0.77	0.346	1.06	0.099	0.59	0.202	0.68
Cr(TTA) ₃	0.288	0.77	0.470	0.94	0.090	0.64	0.189	0.69
Cr(DBM) ₃	0.123	0.68	0.250	1.01	0.099	0.58	0.220	0.62

of neither the β -diketones nor their chromium(III) chelates on any gel follows the decreasing order of their molecular weights. The fact that the elution series of both the β -diketones and their chromium chelates depend strongly on the gel used suggests that solute-gel interactions have a considerable effect on the gel chromatographic behaviour. For example, on the poly(vinyl acetate) gels (Merckogel OR-PVA 500 and 2000), most of the β -diketones that contain a $-\text{CF}_3$ group are eluted after HDBM. However, on the polystyrene gels (Bio-Beads S-X8 and Poragel 60 A), these β -diketones are eluted before HDBM. This result may be due to mutual interactions between polar functional groups in the β -diketone and the gel matrix, *i.e.*, trifluoromethyl and acetyl groups, and between the π -electrons of the phenyl groups in HDBM

TABLE IV

VALUES OF K_{av} FOR *n*-ALKANES ON DIFFERENT COLUMNS WITH *p*-DIOXAN AS AN ELUENT AT 25.0°

Columns I-IV as in Table III.

Compound	No. of carbon atoms	Mol.wt.	K_{av}			
			Column I	Column II	Column III	Column IV
<i>n</i> -Pentane	5	72.15	0.553	0.659	0.683	0.696
<i>n</i> -Hexane	6	86.17	0.515	—	0.658	0.674
<i>n</i> -Heptane	7	100.20	0.474	0.593	0.623	—
<i>n</i> -Octane	8	114.22	—	—	0.600	—
<i>n</i> -Decane	10	142.29	0.371	0.493	0.542	0.598
<i>n</i> -Dodecane	12	170.34	0.318	—	0.520	0.562
<i>n</i> -Tetradecane	14	198.40	0.276	—	—	0.531
<i>n</i> -Hexadecane	16	226.45	—	0.350	—	—

and polystyrene. However, so far the details of such solute-gel interactions have not been elucidated.

In all instances, a β -diketone has a larger K_{av} value than its chromium(III) chelate, which indicates that the dominant factor in the gel chromatography of these compounds is the molecular sieve effect.

Elution behaviour of *n*-alkanes

The K_{av} values for *n*-alkanes are given in Table IV. The K_{av} values on each gel decrease with increasing molecular weight of the *n*-alkanes, as shown graphically in Fig. 2. Such a clear correlation between K_{av} and molecular weight is not observed with the β -diketones or their chromium(III) chelates.

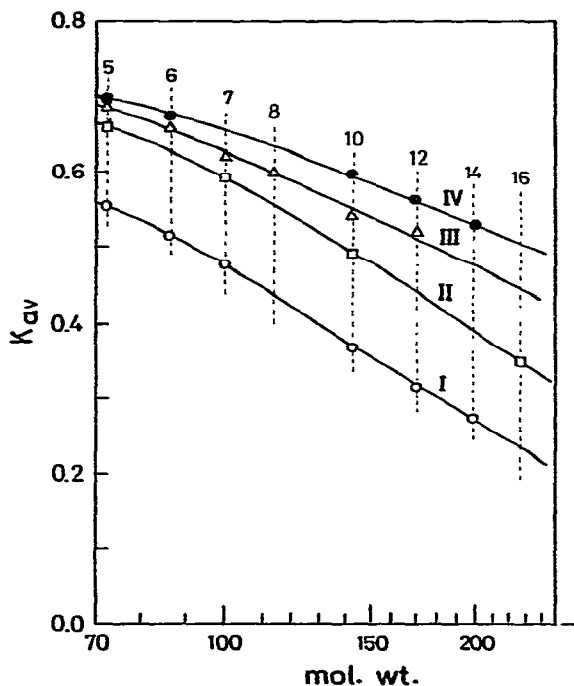


Fig. 2. K_{av} versus molecular weight for *n*-alkanes in different column systems. I-IV denote columns as in Table III. Numerals 5-16 denote carbon numbers of *n*-alkanes.

According to Fig. 2, the K_{av} values for each *n*-alkane on the different gels increase in the following order: Merckogel OR-PVA 500 < Merckogel OR-PVA 2000 < Bio-Beads S-X8 < Poragel 60 A. It is clearly shown in Fig. 3 that the effect of the gels on the K_{av} values of the *n*-alkanes is different from that for the β -diketones and their chromium(III) chelates. However, it can be seen that for any compound Merckogel OR-PVA 2000 gives a larger K_{av} value than Merckogel OR-PVA 500, and Poragel 60 A gives a larger K_{av} value than Bio-Beads S-X8.

Correlation between K_{av} and solvent regain of gel beads

The solvent regain for the gels used in this work in *p*-dioxan have not been

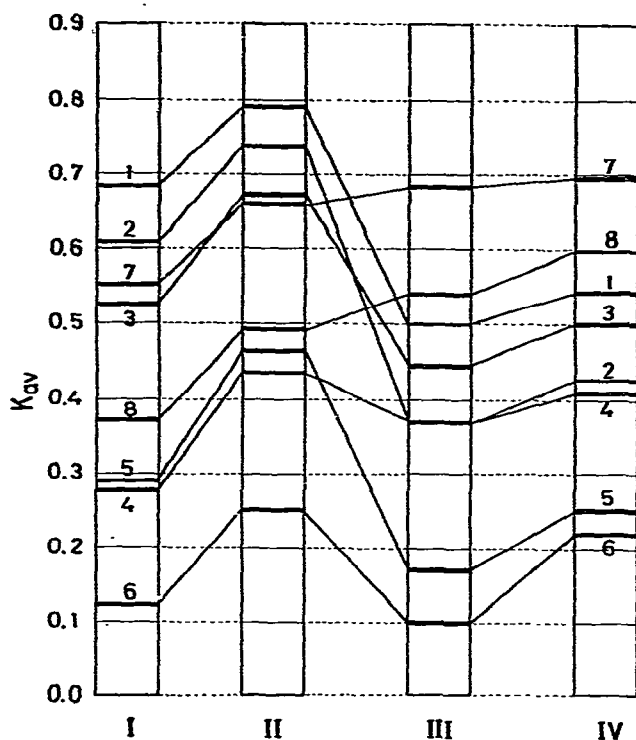


Fig. 3. Graphical demonstration of dependence of K_{av} values on gels. 1, HAA; 2, HTFA; 3, HDBM; 4, Cr(AA)₃; 5, Cr(TFA)₃; 6, Cr(DBM)₃; 7, *n*-pentane; 8, *n*-decane. I-IV denote columns as in Table III.

reported elsewhere. According to the equilibration method¹⁰, the solvent regain, S_r , in millilitres of *p*-dioxan used per gram of dry gel can be measured with high precision. The results are shown in Table V. The fact that Merckogel OR-PVA 2000 has a larger S_r value than Merckogel OR-PVA 500 implies that the former gel has a less cross-linked structure than the latter. It is reasonable to postulate that the larger K_{av} value for each compound on Merckogel OR-PVA 2000 than on Merckogel OR-PVA 500 results from the difference in the densities of the gel networks of these two gels. Similar considerations apply to Bio-Beads S-X8 and Poragel 60 A.

TABLE V
SOLVENT REGAIN OF GELS IN *p*-DIOXAN AT 25.0°

Gel	Solvent regain*
Merckogel OR-PVA 500	1.24 ± 0.06
Merckogel OR-PVA 2000	1.95 ± 0.12**
Bio-Beads S-X8	0.93 ± 0.04
Poragel 60 A	0.96 ± 0.07

* In millilitres of *p*-dioxan per gram of dry gel. Each value includes the 95% confidence limit.

** Value from ref. 10.

CONCLUSION

The gel chromatographic behaviour of β -diketones and their chromium(III) chelates depends strongly on the gels used. These compounds are different from *n*-alkanes with respect to the dependence of the K_{av} values on the gel. The results obtained reveal that the selection of the gel is important for the separation of some compounds by gel chromatography. For example, the difference in the K_{av} values for $\text{Cr}(\text{AA})_3$ and $\text{Cr}(\text{TFA})_3$ on Merckogel OR-PVA 500 is less than that on Poragel 60 A. On the other hand, the difference in the K_{av} values for $\text{Cr}(\text{TFA})_3$ and $\text{Cr}(\text{DBM})_3$ on the former gel is greater than that on the latter.

The details of the separation of metal chelates with various β -diketones will be published elsewhere.

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