Gel Chromatography of β-Diketones and Their Metal Complexes. III. The Chromatographic Behavior of Metal(II, III) Chelates with Acetylacetone in Systems of a Poly(vinyl acetate) Gel and Various Eluting Solvents[1]

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Chelate compounds of acetylacetone (2,4-pentanedione) with metal ions (Al(III), Cr(III), Fe(III), Co(III), and Be(II)) were passed through a chromatograph in columns packed with a cross-linked poly(vinyl acetate) gel (Merckogel OR-2000). Various organic solvents (chloroform, benzene, toluene, 1,4-dioxane, ethyl acetate, butyl acetate, acetone, ethyl methyl ketone, and methanol) were used as the eluents. The distribution coefficient, K_{av}, for each chelate in a given column system was measured to within 0.7% of the relative standard deviation. The K_{av} values of a chelate were dependent on the solvent used. With most of the solvents, the K_{av} values of the metal(III)-chelates were close together and smaller than the K_{av} value of the Be(II)-chelate. The effective molar volume, V_{eff}, of the chelates thus determined, using calibration charts prepared on the basis of elution data for normal alkanes, depended strongly on the solvent used. With all the solvents except chloroform, the V_{eff} values of each chelate were smaller than the literature value of the molar volume for that chelate.

The uniqueness of gel chromatography can be found in its separation mechanism which is usually referred to as the molecular sieve effect resulting from the difference in the molecular dimensions of the solute species. This method is actively used in the fields of polymer and biological chemistry, not only as a method of separation, but also as a means of determining the molecular weight and size of solute molecules. Gel chromatography of neutral metal complexes has not yet been actively studied. Only a few papers have dealt with this subject.[2]

The program of the present study was initiated in an attempt to utilize the unique capabilities of gel chromatography in studying metal complexes in organic solvent media.[3] Acetylacetone (Hacac) and its metal chelates have been exclusively selected as model compounds and Merckogel OR-2000, a cross-linked poly(vinyl acetate) gel, has so far been used as the column-packing material. In the work dealing with metal(II, III) chelates with acac and normal alkanes in the column system, including tetrahydrofuran as an eluent, it was observed that these two sets of compounds are differ in their relationships between the distribution coefficient and the molar volume.[4] In an effort to elucidate this fact, the elution behavior of normal alkanes[5] and the degree of gel swelling[6] were investigated from a viewpoint of solvent effects.

In the present work, the distribution coefficients of some metal(II, III) chelates with acac were measured in various solvent systems, and determinations of the effective molar volume of these chelates were attempted.

Experimental

Metal Chelates. Tris(acetylacetonato)aluminum(III), -chromium(III), -iron(III), and -cobalt(III) (hereafter abbreviated to $[Al(acac)_3]$, $[Cr(acac)_3]$, $[Fe(acac)_3]$, and $[Co(acac)_3]$, respectively) were prepared and purified according to methods in the literature.[7-9] The results of elemental analysis are as follows. $[Al(acac)_3]$. Found: C, 55.19; H, 6.54%. Calcd: C, 55.56; H, 6.54%. $[Cr(acac)_3]$. Found: C, 51.87; H, 6.29%. Calcd: C, 51.56; H, 6.07%. $[Fe(acac)_3]$. Found: C, 51.02; H, 5.98%. Calcd: C, 51.00; H, 6.00%. $[Co(acac)_3]$. Found: C, 50.42; H, 5.99%. Calcd: C, 50.56; H, 5.95%. Bis(acetylacetonato)-beryllium(II) (hereafter abbreviated to $[Be(acac)_2]$) (Dojin Labs.) was further recrystallized from benzene and petroleum ether. Found: C, 57.99; H, 6.83%. Calcd: C, 57.77; H, 6.94%.

Solvents. Benzene, toluene, 1,4-dioxane, ethyl acetate, butyl acetate, acetone, ethyl methyl ketone and methanol were carefully distilled. Since the purified material was unstable, reagent-grade chloroform (Wako Chemicals) was used without further purification.

Columns and Apparatus. Most of the parts coming into contact with the liquids were made of PTFE or Pyrex, rather than metal, in order to avoid undesirable effects. The chromatographic column was a 100 cm long Pyrex tube with a 5-mm inside diameter packed with Merckogel OR-2000 (E. Merck) swollen by the solvent to be used. A Model FLC-350 syringe-type pump (JASCO) and a Model 1107L refractometric detector (L. D. C.) were used. The detection signal was fed into a JEC-5 computer (JEOL) for on-line data processing.

Procedure. A sample solution was prepared by dissolving 15 mg of a metal chelate and 5 mg of a mono-dispersed polystyrene standard (M_w=200 000, Pressure Chemical Co.) in 5 cm^3 of the solvent used as the eluent. With methanol, methylated blue dextran which had been prepared by methylation of Blue Dextran 2000 (Pharmacia)[5] was used in place of polystyrene. A 0.05-cm^3 portion of the sample solution was fed into the column with the aid of a loop injector, and elution was carried out at a solvent flow-rate of 0.20 cm^3 min^{-1} and at a column temperature of 25.0±0.02 °C. The UV and visible absorption spectra of the eluates were recorded in order to confirm the species eluted. Each experiment on a sample in a given column system was carried out at least three times.

Results and Discussion

Shape of Elution Curves. The chelates except for $[Fe(acac)_3]$ gave elution curves without excessive skewness in all solvent systems studied, with the values of the skew ratio[10] ranging from 0.9 to 1.0. $[Al(acac)_3]$ gave an exceptionally skewed elution curve with methanol. On the other hand, $[Fe(acac)_3]$ gave somewhat tailing elution curves in all solvent systems used.

Table 1. K_{av} values of metal chelates with acac in systems of Merckogel OR-2000 and various eluting solvents at 25.0 °C

No.	Eluting solvent	K_{av}[a]				
		$Al(acac)_3$	$Cr(acac)_3$	$Fe(acac)_3$	$Co(acac)_3$	$Be(acac)_2$
1	Chloroform	0.220	0.218	0.295	0.217	0.271
2	Benzene	0.326	0.342	0.439	0.335	0.542
3	Toluene	0.384	0.400	0.439	0.397	0.653
4	1,4-Dioxane	0.430	0.436	0.455	0.432	0.570
5	Tetrahydrofuran[b]	0.497	0.517	0.536	0.523	0.620
6	Ethyl acetate	0.565	0.609	0.618	0.623	0.702
7	Acetone	0.588	0.622	0.638	0.648	0.660
8	Ethyl methyl ketone	0.597	0.628	0.630	0.654	0.653
9	Butyl acetate	0.725	0.790	0.802	0.728	0.828
10	Methanol	—	0.677	—	0.608	1.02

a) The relative standard deviation in each instance is less than 0.7%.
b) Data from Ref. 4.

Table 2. K_d values of metal chelates with acac on Merckogel OR-2000 columns

No.	Eluting solvent	K_d[a]				
		$Al(acac)_3$	$Cr(acac)_3$	$Fe(acac)_3$	$Co(acac)_3$	$Be(acac)_2$
1	Chloroform	0.290	0.288	0.389	0.286	0.358
2	Benzene	0.479	0.503	0.645	0.492	1.20
3	Toluene	0.687	0.716	0.786	0.711	1.17
4	1,4-Dioxane	0.615	0.623	0.651	0.618	0.815
5	Tetrahydrofuran	0.726	0.755	0.783	0.764	0.905
6	Ethyl acetate	0.848	0.914	0.927	0.935	1.05
7	Acetone	0.858	0.908	0.931	0.946	0.964
8	Ethyl methyl kotone	0.895	0.942	0.945	0.981	0.980
9	Butyl acetate	1.23	1.34	1.36	1.24	1.41

a) Values converted from the K_{av} values.

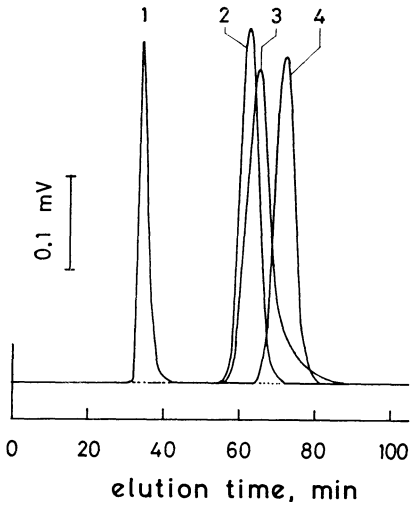

Fig. 1. Elution curves of (1) polystyrene (M_w= 200 000), (2) $[Cr(acac)_3]$, (3) $[Fe(acac)_3]$, and (4) $[Be(acac)_2]$.
Merckogel OR-2000 column, 100 cm×5 mm I. D., 25.0±0.02 °C; eluting solvent, 1,4-dioxane, 0.2 $cm^3 \cdot min^{-1}$; R. I. Detector, sens. 16 for (1), (2), and (4), sens, 8 for (3).

With methanol, both $[Al(acac)_3]$ and $[Fe(acac)_3]$ gave such skewed elution curves that no elution data with high reproducibility could be obtained for these two chelates. Typical elution curves obtained are shown in Fig. 1.

Distribution Coefficient. The elution volume, V_e, of a substance passed through a chromatograph in a given column system is expressed by

$$V_e = V_o + K_{av}V_x, \quad (1)$$

where V_o, V_x, and K_{av} are the column void volume, the volume of the gel phase, and the distribution coefficient, respectively.[11] In the present work, the K_{av} value of each chelate was calculated according to the relation,

$$K_{av} = (V_e - V_o)/(V_t - V_o), \quad (2)$$

where V_t is the total volume of the column ($V_t = V_o + V_x$). The V_t values of all columns used in this work were exactly 19.63 cm^3. The V_o value of the column was determined from a measurement of the V_e value of either a polystyrene standard or methylated blue dextran which are regarded as substances to be completely excluded from the Merckogel OR-2000 gel network. The dead volume related to that part of the tubing was corrected for in the calculation of the K_{av}

Table 3. Separation factor, α, for the $[Be(acac)_2]$-$[Cr(acac)_3]$ pair on Merckogel OR-2000 columns at 25.0 °C

No.	Eluting solvent	α
1	Chloroform	1.24
2	Benzene	1.58
3	Toluene	1.63
4	1,4-Dioxane	1.31
5	Tetrahydrofuran	1.20
6	Ethyl acetate	1.15
7	Acetone	1.06
8	Ethyl methyl ketone	1.04
9	Butyl acetate	1.05
10	Methanol	1.51

value.

The K_{av} values of the metal chelates were obtained with high reproducibility, the relative standard deviation in each instance being not more than 0.7%. However, precise data for $[Al(acac)_3]$ and $[Fe(acac)_3]$ could not be obtained in the systems with methanol. The results are given in Table 1 together with previous data on the system with tetrahydrofuran.

The gel chromatographic behavior of a solute substance is characterized also by the elution parameter K_d, derived from the relation,

$$V_e = V_o + K_d V_i, \quad (3)$$

where V_i is the volume of the internal solvent in the swollen gel beads. When V_x is assumed to be equal to the sum of V_i and the volume of the gel matrix, V_g, K_d can be obtained from K_{av} according to the following relation,

$$K_d = (V_x/V_i)K_{av} = [Q/(Q-1)]K_{av}, \quad (4)$$

where Q is the degree of gel swelling defined as the reciprocal of the volume fraction of the gel matrix in the swollen gel. The K_d values of metal chelates thus calculated from the available K_{av} and Q values[6] are given in Table 2.

It is obvious that both the K_{av} and K_d values of the chelates are strongly dependent on the solvent used. The solvents are arranged in Tables 1 and 2 in order of increasing K_{av} and K_d values for $[Al(acac)_3]$.

The K_{av} values of metal(III) chelates in a solvent are close together. This fact implies that separation of these chelates is not easy if a solvent is used as the eluent. The K_{av} value of $[Be(acac)_2]$ is larger than that of a metal(III) chelate in any solvent. The separation factor, α, defined as the ratio of the K_{av} values, for the $[Be(acac)_2]$-$[Cr(acac)_3]$ pair is given in Table 3. The α value for this solute pair depends on the solvent used, which reveals the importance of the choice of the solvent as the eluent for gel chromatographic separation.

Effective Molar Volume. For large molecules such as polymers, the molecular weight is frequently used as a size parameter for a compound in gel chromatography, whereas for small molecules having molecular weights less than 1000, the molar volume, V_m, is an effective size parameter.[12] The molar volume experimentally determined by means of gel chromatography

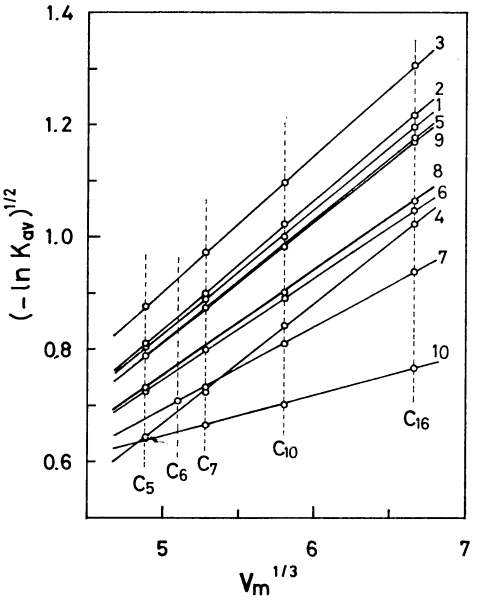

Fig. 2. Relationship between K_{av} and V_m for normal alkanes in the systems of Merckogel OR-2000 and various eluting solvents.
C_5, C_6, C_7, C_{10}, and C_{16} denote pentane, hexane, heptane, decane, and hexadecane, respectively. Numerals 1—10 denote solvents as in Table 1.

is termed the effective molar volume, V_{eff}, as distinct from V_m.[13,14] The V_{eff} values of the metal chelates were obtained in this work using the calibration charts based on the elution data for normal alkanes.

Laurent and Killander[11] have proposed the following equation,

$$K_{av} = \exp[-\pi L(r_r + r_s)^2], \quad (5)$$

where r_s is the radius of the solute molecule, and L and r_r are constant for a given combination of gel matrix and solvent. Assuming r_s to be proportional to the cube root of V_m, we can write

$$(-\ln K_{av})^{1/2} = k_1 + k_2 V_m^{1/3}, \quad (6)$$

where k_1 and k_2 are constants in a column system. The $(-\ln K_{av})^{1/2}$ *versus* $V_m^{1/3}$ plots in Fig. 2 are based on the K_{av} values for normal alkanes on Merckogel OR-2000[5] and the V_m values calculated from the molecular weight and density data for the respective compounds.[15] When these plots are used for calibration, the V_{eff} values of the chelates were obtained by comparing their K_{av} values with the plots. The results are given in Table 4. It is obvious that the V_{eff} values for each chelate is strongly dependent on the solvent used. The V_{eff} values of $[Cr(acac)_3]$, for example, range from 27 to 317 $cm^3\ mol^{-1}$.

Irving and Smith have shown that the partial molar volume of $[Cr(acac)_3]$ is nearly constant in different organic solvents[16] and Irving have reported V_m values of the chelates as follows: $[Al(acac)_3]$, 271; $[Cr(acac)_3]$, 267; $[Fe(acac)_3]$, 269; $[Co(acac)_3]$, 261 $cm^3 \cdot mol^{-1}$.[17] When the semi-empirical relation expressed by

$$V_{m,M(acac)_n} = 0.9\,nV_{m,Hacac}, \quad (7)$$

is used, the V_m value of $[Be(acac)_2]$ is estimated to be

Table 4. The V_{eff} values of metal chelates with acac determined using the calibration charts based on the gel chromatographic data for normal alkanes

No.	Eluting solvent	V_{eff}/cm^3 mol^{-1}				
		$Al(acac)_3$	$Cr(acac)_3$	$Fe(acac)_3$	$Co(acac)_3$	$Be(acac)_2$
1	Chloroform	315	317	245	317	266
2	Benzene	211	202	150	210	108
3	Toluene	150	143	126	144	56
4	1,4-Dioxane	234	230	217	232	155
5	Tetrahydrofuran	133	125	117	122	86
6	Ethyl acetate	128	106	102	99	65
7	Acetone	143	120	110	104	94
8	Ethyl methyl ketone	111	97	96	86	88
9	Butyl acetate	48	27	23	47	13
10	Methanol	—	95	—	216	—

184 cm^3 mol^{-1}, where $V_{m,Hacac}$ and $V_{m,M(acac)_n}$ are the molar volumes of Hacac (=102 cm^3 mol^{-1}) and of its metal chelate containing an integral number n of $(acac)^-$ anions, respectively.[18] Comparing the V_m value of a chelate with the V_{eff} values shown in Table 4, it is obvious that the latter values are different from the former value. The V_{eff} values of the chelates, except for $[Fe(acac)_3]$ in chloroform, are marked larger than the V_m values of the respective chelates. Considering that many metal chelates with acac form solvated species in chloroform,[19,20] the larger V_{eff} values observed in this solvent may refer to solvations. Despite the fact that the V_m values of the 4 metal(III) chelates studied are close together, the V_{eff} values of $[Fe(acac)_3]$ are smaller than those of other metal(III) chelates in many solvents. Recalling that $[Fe(acac)_3]$ gave elution curves with a tailing and larger K_{av} values relative to other metal(III) chelates, and considering that Fe(III)-chelate is known to be a labile complex, it is deduced that some partial dissociation of the chelate occured in the chromatographic process. It is reasonable to consider that the relatively smaller V_{eff} values for $[Fe(acac)_3]$ result from such anomalous chromatographic behavior.

The fact that the K_{av} value for $[Be(acac)_2]$ in a given solvent is larger than the K_{av} values of the metal(III) chelates indicates that one of the factors governing the chromatographic behavior of those compounds is the molecular sieve effect. Considering that V_{eff} values of the chelates are different from the expected values (V_m values) and also that the K_d values, in some instances, are larger than unity, it is reasonable to assume that gel chromatography of the chelates is based not only on the molecular sieve effect but also on some other effects caused by interactions among the solute, solvent and gel matrix.

The selection of an appropriate eluting solvent is quite important for the purpose of estimating the molar volume of a solute species. According to the available data, the V_{eff} value of a metal chelate with acac obtained using 1,4-dioxane as an eluent appears to be close to the V_m value.

The solvent dependence of the gel chromatographic behavior is an attractive problem to be further elucidated. The details of the solvent effects and the so-called secondary effect in gel chromatography will be treated in a subsequent paper.

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