

GEL PERMEATION CHROMATOGRAPHY OF METALLOCENES

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Summary

The elution behaviour of ferrocene, ruthenocene and a series of substituted ferrocenes on a gel permeation chromatography support, cross-linked poly-(acryloyl morpholine) (Enzacryl[®] Gel), has been investigated. For most of the solutes an approximately linear relationship was obtained between logarithm molecular weight and the Wheaton Baumann absolute distribution coefficient (K_d), indicating that the separations were effected via a molecular sieving mechanism.

Introduction

To date gel permeation chromatography (GPC) has found little application as a separation technique in organometallic chemistry, although it is being used increasingly for the separation and purification of other small organic molecules [1]. Organometallic species are often labile and frequently undergo extensive decomposition on classical inorganic supports such as alumina and silica gel. In GPC there is minimal interaction between the solute and the gel matrix. Consequently it was thought that GPC would be an ideal technique for the isolation and purification of organometallic compounds. The GPC fractionation mechanism depends on mechanical and volumetric parameters and it rarely causes decomposition of labile molecules. Moreover the solute recovery is quantitative. Previous attempts to fractionate metallocenes by GPC were disappointing. Einarsson and Zeppezauer reported the chromatographic separation of some metallocenes and their derivatives on polystyrene gel beads crosslinked with 2% divinylbenzene using cyclohexane as the solvent [2]. However, separation was effected by sorptive interactions, that is weak interactions between the solute and the gel matrix, rather than by a molecular sieve mechanism. Thus in some of these separations the smaller molecules were eluted first and the values calcu-

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lated for the Laurent and Killander distribution coefficient, K_{av} , were all greater than unity [3].

Recently a new class of GPC support (Enzacryl[®] Gel) has been introduced which is suitable for use with organic solvents [4]. The support is based on crosslinked poly(acryloyl morpholine) and it is available in bead form. This matrix has been shown to be effective in fractionating monomers and low molecular weight polymers. The use of Enzacryl[®] gel in organic solvents as a GPC support for the separation of metallocenes is the subject of this report.

Results and discussion

In a preliminary experiment a mixture of ferrocene and 1,1'-dibenzoylferrocene was passed through a column of Enzacryl[®] Gel K2 in chloroform and a good separation was obtained. 1,1'-Dibenzoylferrocene, the larger, more polar molecule, was eluted before ferrocene (Fig. 1). This was the reverse order of elution to that obtained when alumina was the chromatographic support [5]. Similarly a mixture of ferrocene and phenylferrocene was passed through the same column and the phenylferrocene was eluted first (Fig. 2). These results were indicative of a separation by molecular sieving.

A series of substituted ferrocenes was chromatographed and the Wheaton and Baumann absolute distribution coefficients (K_d) were calculated (Table 1) [6]. For most of the solutes an approximately linear relationship was obtained be-

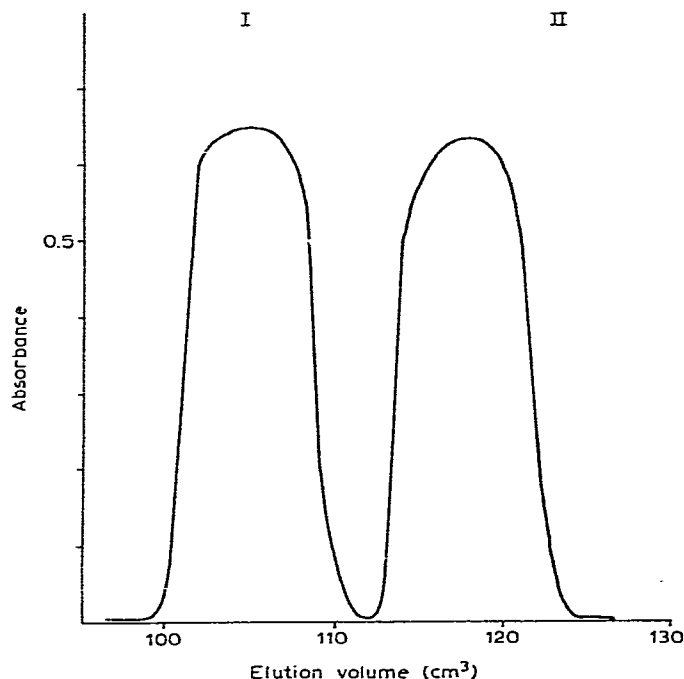


Fig. 1. Separation of 1,1'-dibenzoylferrocene (peak I) and ferrocene (peak II) on Enzacryl[®] Gel K2 in chloroform.

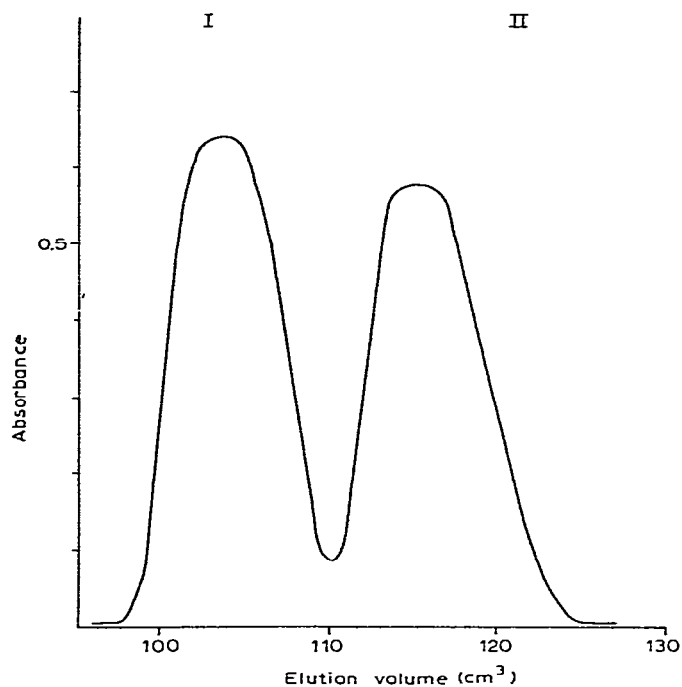


Fig. 2. Separation of phenylferrocene (peak I) and ferrocene (peak II) on Enzacryl[®] Gel K2 in chloroform.

TABLE I

WHEATON AND BAUMANN ABSOLUTE DISTRIBUTION COEFFICIENTS (K_d) OF FERROCENE DERIVATIVES AND RUTHENOCENE ON ENZACRYL[®] GELS K0 AND K2

Solute	Mol. weight	K_d (Gel K0 in DMF)	K_d (Gel K0 in CHCl_3)	K_d (Gel K2 in CHCl_3)
1-Diphenylphosphino-2-dimethylaminomethylferrocene	427.3	—	—	0.040
1,1'-Bis(diphenylphosphino)ferrocene	554.4	0.672	0.161	0.711
Diphenylphosphinoferrocene	370.2	0.883	0.269	0.802
1,1'-Bis(benzoyl)ferrocene	394.3	0.792	0.315	0.774
Benzoylferrocene	290.1	0.935	0.358	0.857
Acetylferrocene	228.1	1.013	0.435	0.920
Cyanoferrocene	211.1	1.022	0.543	—
<i>o</i> -Carboxyphenylferrocene methyl ester	320.2	0.897	0.320	—
1,1'-Bis(hydroxymethyl)ferrocene	246.1	0.800	2.836	—
Hydroxymethylferrocene	216.1	0.990	1.375	1.430
Ruthenocene	231.2	1.352	0.511	0.961
Ferrocene	186	1.178	0.543	0.961

tween logarithm molecular weight and the K_d values (Fig. 3). These results confirmed that the separation of the metallocenes was being effected via a molecular sieving mechanism [7]. This is in contrast to the results reported by Einarsson and Zeppezauer using a polystyrene—cyclohexane system [2]. Metallocene separations of similar efficiency were obtained with Enzacryl[®] Gel K0 in chloroform and Enzacryl[®] Gel K0 in dimethylformamide. Chromatography with these systems led also to approximately linear relationships between logarithm solute molecular weight and the K_d values (Fig. 3). The compounds with K_d values which deviated from the linear relationships were hydroxymethylferrocene and 1,1'-bis(hydroxymethyl)ferrocene. These ferrocenyl alcohols were retarded in chloroform but they were eluted sooner than expected in dimethylformamide. It has been noted previously that nitrogen-containing molecules often exhibit unexpected retardation [4]. 1-diphenylphosphino-2-dimethylaminomethylferrocene falls within this group.

A possible explanation for these observations may be given in terms of the structure of the gel. This consists of a chloroform solution of poly(acryloyl morpholine) chains whose movement, relative to one another, is constrained by cross-linking. The solvated chains form regions of solution in which the poly(acryloyl morpholine) concentration is very high. Solutes with a high affinity

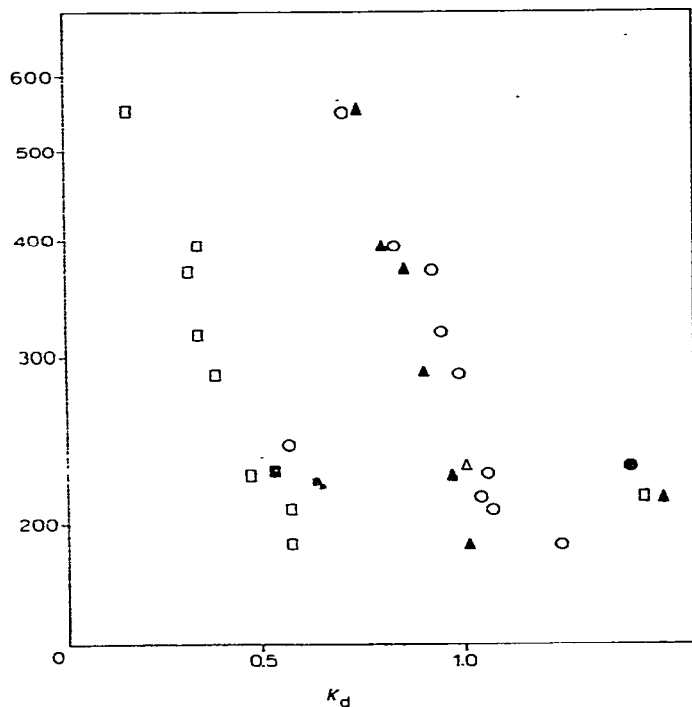


Fig. 3. Relationship between logarithm molecular weight and distribution coefficient for ferrocene, ruthenocene and substituted ferrocenes chromatographed in chloroform on Enzacryl[®] Gel K0 (□) and Enzacryl[®] Gel K2 (▲) and in dimethylformamide on Enzacryl[®] Gel K0 (○). Ruthenocene ■, ▲ and ● respectively.

for poly(acryloyl morpholine) will partition in favour of the regions of high poly(acryloyl morpholine) concentration. Such solutes will be retarded. On the other hand partition of a solute in favour of regions of the gel consisting of essentially pure solvent leads to apparent accelerations of the solute and the phenomenon of "additional exclusion". Thus small deviations from ideality can be rationalized in terms of micro-partition effects within the gel. The gradient of the linear relationships in the three gel-solvent combinations investigated was approximately the same in each case but the plots intersected the axis at different points.

The internal volume available to metallocenes within the Enzacryl[®] Gel K0 beads proved to be much less in chloroform than in dimethylformamide. Enzacryl[®] Gel K0 has been characterized previously in both these solvents using poly(ethylene glycols) and styrene oligomers [8]. The gel was shown to have very similar elution characteristics with respect to poly(ethylene glycols) in both solvents, but the aromatic solutes appeared to be retarded in dimethylformamide and were eluted sooner than expected in chloroform. Enzacryl[®] Gel K2 has been characterized previously with these solutes in chloroform [4] and in this case too the early elution of polystyrenes with respect to poly(ethylene glycols) was observed. It was not surprising therefore that pronounced "additional exclusion" of metallocenes occurred on the denser chromatographic packing, Enzacryl[®] Gel K0 in chloroform, resulting in a marked difference in elution behaviour to that in dimethylformamide (Fig. 3). Ferrocenylmethanol was the only metallocene to be retarded in chloroform and this was ascribed to hydrogen bonding between the hydroxyl group of this molecule and the gel matrix. In dimethylformamide the metallocenes were all retarded slightly (Fig. 3). Retardation could occur if all the metallocenes were adsorbed to a similar extent. However these results are best explained in terms of favourable micropartition of the solutes with the regions of the gel matrix corresponding to the poly(acryloyl morpholine) chains in dimethylformamide.

For the majority of solutes considered, the mechanism of separation was principally molecular sieving. In addition to the mildness of this technique which makes it eminently suitable for organometallic molecules there is the further advantage of there being a certain amount of predictability. Providing that groups, such as hydroxymethyl and nitrogen-containing species are absent then the elution volume of a metallocene should be predictable, within small limits, by comparison with similar solutes.

Experimental

Apparatus and Materials

Enzacryl Gel K0 fine and medium grades and Enzacryl Gel K2 medium grade were obtained from Koch—Light Labs., (Colnbrook, Great Britain). General-purpose reagent grade solvents were used. Chloroform was dried (magnesium sulphate) and redistilled and dimethylformamide was dried (calcium chloride) and redistilled. The solutes were prepared via literature methods. The chromatographic columns were made out of precision bore tubing (Jobling, Stone, Great Britain) closed at both ends with identical pistons fitted with polytetrafluoroethylene sieves. The solutes in dimethylformamide were estimated with a

Waters Type R401 differential refractometer (Waters Associates Inc., Framingham, U.S.A.). The solutes in chloroform were assayed manually using a Unicam SP500 spectrophotometer (Pye—Unicam, Cambridge, Great Britain).

Packing of columns

Enzacryl[®] Gel K0, swollen in dimethylformamide, was poured as a slurry directly into the column (91.5 × 1.5 cm) and it was allowed to settle under gravity. Since Enzacryl Gel floats in chloroform it was necessary in this solvent to use a slurry of the gel. The slurry was poured into the column which was fitted with an extension tube. Packing was effected by applying a high flow-rate.

Determination of column and gel parameters

For the columns of Enzacryl[®] Gel K2 and K0 the void volumes, V_0 , were estimated from the elution volumes of the totally excluded solutes polystyrene (relative molecular mass 390 000) and polyethylene glycol (relative molecular mass, 20 000) respectively. The precise internal volume of the gel, V_i , available to a totally included molecule of solute or the solvent, was calculated by subtracting V_0 from the elution volume, V_s , of the deuterated solvent. For partially included solutes, permeation behaviour was characterized by relating elution volume, V_e , to the absolute distribution coefficient, K_d , using the Wheaton and Baumann equation [6]:

$$K_d = \frac{V_e - V_0}{V_i} = \frac{V_e - V_0}{V_s - V_0}$$

Analysis of column effluents

Column effluents were collected in 1-ml or 2-ml fractions. The concentrations of polystyrene and the organometallic molecules were measured spectrophotometrically. Polyethylene glycol was determined, by differential refractometry. Deuteriochloroform was estimated by mass spectrometry, the peak height for $CD^{37}Cl_2^+$ ion was related to deuteriochloroform concentration with the aid of a linear calibration obtained on assay of standard chloroform—deuteriochloroform mixtures. Perdeutero-dimethylformamide was estimated via differential refractometry.

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