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GEL PERMEATION CHROMATOGRAPHY ON CHEMICALLY MODIFIED SILICA USING DIFFERENT SOLVENTS

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SUMMARY

Gel permeation chromatographic separations of polystyrene, poly-2-vinylpyridine and polydextrans were carried out on porous silica gel chemically modified with an ether. Tetrahydrofuran, dimethylformamide and water were used as mobile phases. It was investigated to what extent a universal calibration plot could be applied to such systems. The non-universality of the "universal" calibration in applied systems was explained by the presence of some preferential interactions among polymer solvent and active sites on the gel. Chemically modified silica gel still exhibited adsorption properties.

Gel permeation chromatography (GPC), also known as steric exclusion chromatography (SEC), can be used to separate polymers in respect of their molecular size in solution using appropriate calibration curves based on their retention volumes.

For the most accurate method of calibration it is necessary to have monodisperse standards that have the same composition and conformation as the sample that is to be characterized. Such standards are often not available.

Another method of calibration, the so-called universal calibration method[1], is based on the assumption that molecules separate on the bases of their hydrodynamic volumes, $[\eta]M$. The hydrodynamic volume of any solute at a given elution volume can be then determined if a log $[\eta]M$ vs. elution volume plot (i.e. universal calibration plot) is established. This universal calibration, however, is not valid[2,3] when preferential interactions occur between polymer, solvent and gel. The elution volume of solutes is then governed not only by the steric exclusion mechanism of separation but also by a second mechanism resulting from the preferential affinity among the main components in the GPC system.

In the present study it was of interest to find out to what extent a universal calibration plot can be applied to a chemically modified silica as a column gel as well as to system used. Waters Assoc. (Milford, MA, U.S.A.) have been developed such a column packing, the so-called μBondagel, which consists of a monomolecular layer of a polyether chemically bonded onto the surface and pores of silica and which can be used with different organic as well as aqueous mobile phases[4]. The elution behaviour of polystyrene (PS from Waters Assoc., ArRo Labs., Joliet, IL, U.S.A. and Pressure Chem., Pittsburgh, PA, U.S.A.) and narrow molecular mass distribution poly-2-

vinylpyridine (P2VP) samples were examined in tetrahydrofuran (THF), dimethylformamide (DMF) and water as eluents.

The separations were performed with a Waters GPC set-up (Model 6000 A solvent delivery system, Model U6K universal injector and differential refractometer R 401), at constant temperature using a flow-rate of 1 cm³/min. Four µBondagel columns, E-1000, E-500, E-300 and E-125 (Waters designation), were employed. The injected volumes of polymer solutions amounted to 0.05 cm³ (conc. 0.02 %), and each measurement was repeated at least twice. The intrinsic viscosities of all the samples investigated were determined with an automatic viscometer[5].

The results are presented in Figs. 1–3. Fig. 1 shows the specific calibration plot (log M vs. V_R). Fig. 2 gives the dependence of log $[\eta]$ on the elution volume. Fig. 3 shows the universal calibration curves log $[\eta]$ M vs. V_R.
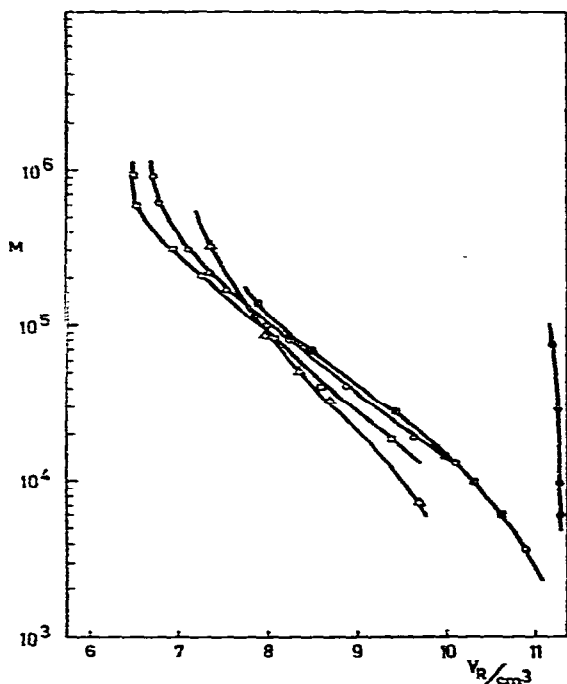

Fig. 1. Molecular mass vs. elution volume calibration plots in the µBondagel E-125, E-300, E-500 and E-1000 columns for the systems: PS–THF (O), P2VP–THF (●), PS–DMF (□), P2VP–DMF (■), and dextran–water–0.4 % sodium dodecyl sulphate (△).

The elution behaviour of PS and P2VP in two eluents differing in their polarities is compared in Fig. 1. It is seen that µBondagel columns separate PS samples in THF quite well, but all the P2VP samples are on the right-hand side of the plot and elute together. Different locations of the specific curves for PS and P2VP can be expected because THF is a better solvent for PS than for P2VP. This is explained by the different values of the Mark–Houwink constant, a, for the two polymers in THF at 293°K:

$$[\eta] = 1.18 \cdot 10^{-2} \, M_w^{0.709} \text{ for PS (molecular mass range: } 1.0 \cdot 10^4 - 9.55 \cdot 10^5)$$
$$[\eta] = 1.49 \cdot 10^{-2} \, M_w^{0.663} \text{ for P2VP (molecular mass range: } 6 \cdot 10^3 - 1.34 \cdot 10^5)$$
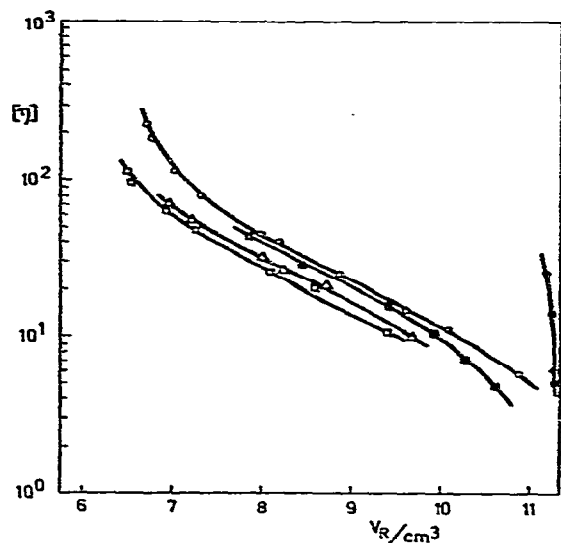
Fig. 2. Limiting viscosity number *vs.* elution volume calibration plots in μBondagel E-125, E-300, E-500 and E-1000 columns for the systems: PS–THF (O), P2VP–THF (●), PS–DMF (□), P2VP–DMF (■), dextran–water–0.4% sodium dodecyl sulphate (△).
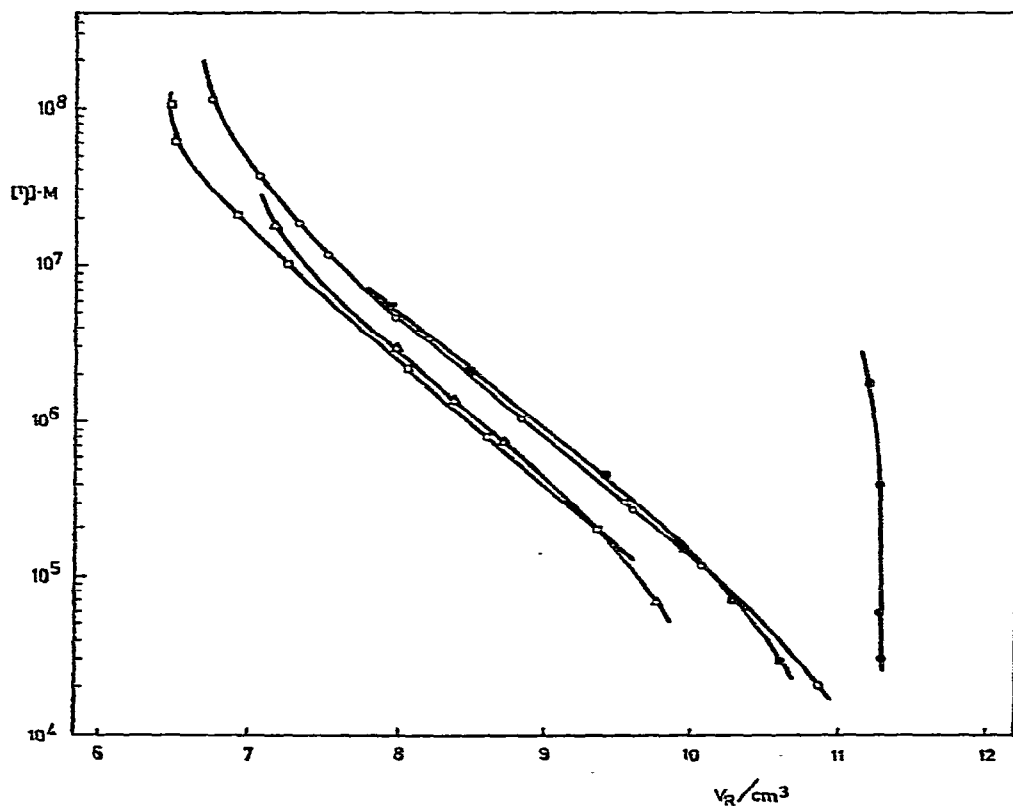

Fig. 3. Universal calibration plots in the μBondagel E-125, E-300, E-500 and E-1000 columns for the systems: PS–THF (O), P2VP–THF (●), PS–DMF (□), P2VP–DMF (■), dextran–water–0.4% sodium dodecyl sulphate (△).

However, such a high volume for P2VP cannot be explained only by the molecular size in solution. It is evident that P2VP interacts strongly with the μBondagel, probably owing to the non-bonding electron pair on the nitrogen atom which makes it very polar.

The elution behaviour of PS in DMF is also unexpected. PS molecules in DMF are eluted earlier than expected from the constant a in the Mark-Houwink equation in DMF at 293°K:

$$[\eta] = 4.65 \cdot 10^{-2} \, M_w^{0.609} \text{ for PS (molecular mass range: } 1.85 \cdot 10^4 - 9.34 \cdot 10^5)$$
$$[\eta] = 9.1 \cdot 10^{-3} \, M_w^{0.728} \text{ for P2VP (molecular mass range: } 6 \cdot 10^3 - 1.34 \cdot 10^5)$$

It seems that DMF, as a very polar aprotic solvent, preferentially interacts with the gel and PS is "repulsed" from the gel.

Comparing the elution of P2VP in the two eluents, we must take into consideration a component due to the polar forces of solubility of DMF, $\delta_p = 13.7 \cdot 10^3$ $(J/m^3)^{1/2}$, which is significantly different from the corresponding value of THF, $\delta_p = 5.7 \cdot 10^3 \, (J/m^3)^{1/2}$. One can conclude that DMF is an eluent strong enough to prevent the adsorption of P2VP on to μBondagel.

The curves in Fig. 2 show the influence of solvent–polymer interactions in GPC columns. The effects are the same as discussed above for Fig. 1.

The combination of the curves plotted in Figs. 1 and 2 represent the universal calibration curves (Fig. 3). If the concept of Grubisic et al.[1] of universal calibration holds for the pure steric exclusion mechanism of separation only, and if limiting viscosity numbers are precise enough to describe the size of polymer coils, then the wide spacing of the "universal calibration" curves shows the presence of the secondary separation effects in μBondagel columns.

The elution of polydextrans in water as eluent was also examined. Dextrans remain completely adsorbed on the μBondagel if no moderator is added. No separation according to molecular mass occurred until 0.4% sodium dodecyl sulphate was added. Further addition of moderator had no effect on the elution volume of dextrans.

Consequently, taking the above results into account, it can be concluded that chemically modified silica still exhibits adsorption properties due to unreacted silanol groups and due to hydrophobic interactions. The extent of polymer adsorption on to μBondagel is influenced by changing the thermodynamic interactions between the components of the GPC system. In addition, the GPC separation mechanism on chemically modified silica is complex, consisting of at least two effects. Therefore, the "universal calibration" cannot be applied for the μBondagel columns and for the systems used in this work.

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