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NOTE

Enhancement of GPC Separations through Selective Solvent Interaction

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Gel permeation chromatography (GPC) has become the method of choice for the determination of molecular weight distributions of polymeric substances. It offers speed and excellent reproducibility, and provides details of the shape of the distribution at comparatively low cost.

It was reported earlier (*1*, *2*) that solvent–solute interactions involving small molecules are readily observed with GPC. Thus, in a hydrogen-bonding medium, the retention volume of a molecule is dependent upon the molar volume of the hydrogen-bonded species, and *not* upon the molar volume of the solute alone. Hydroxyl groups of alcohols and glycols, for example, can form hydrogen bonds with basic oxygen atoms with unshared electron pairs, such as those in ethers. The GPC column then sees an associated species with a much larger apparent molar volume than would be predicted on the basis of the solute molecular structure alone. Of course, the associative forces which hold the solvent and solute together must be great enough to survive entering and emerging from the pores of the column packing materials.

Generally, the GPC solvent is assumed to play a minor role, *if any*, in the separation process. One assumes that it merely serves as a low viscosity stationary phase and provides an *inert* moving carrier phase. With polymers, this is most often the case. However, with small molecules in a hydrogen-bonding medium, observed GPC retention volumes are often smaller than those predicted on the basis of their unassociated

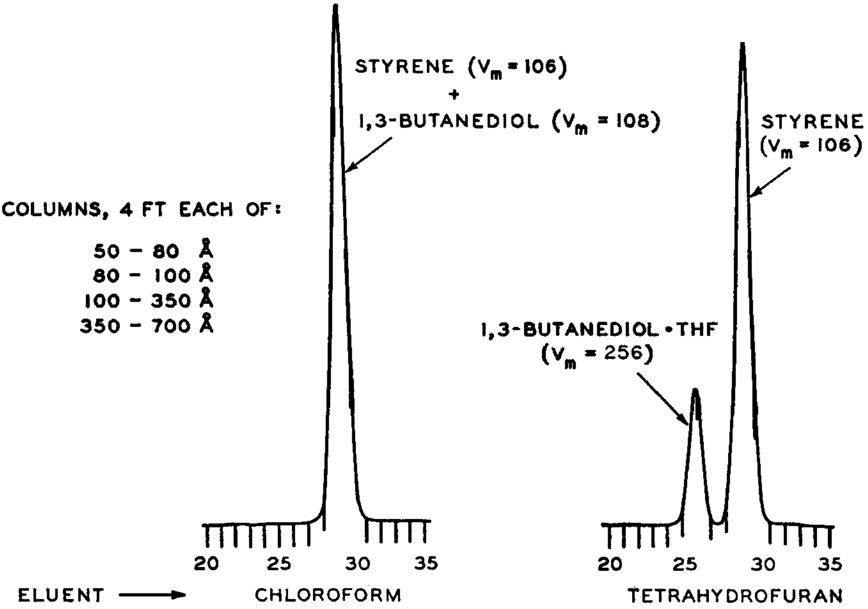

FIG. 1. Solvent–solute interactions may enhance GPC separations.

structures. This is, presumably, due to a relatively large increase in molar volume that results from association or complexation with one or more solvent molecules.

It should be possible to use this information to advantage. Judicious choice of solvent should provide a handle with which selective association of one or more components of a mixture would effect a separation between solutes of otherwise similar molar volumes. The two chromatograms in Fig. 1 will serve to illustrate this principle. They were recorded for a mixture of styrene and 1,3-butanediol (containing two hydroxyls) in two different solvents, but under otherwise identical conditions.* The two compounds exhibit identical retention volumes, as evidenced by the appearance of only a single chromatographic band. This is in agreement with

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* It is, of course, recognized that these two substances are quite different from each other chemically, and that there are other, more conventional, ways to effect a separation between them. However, they were chosen here because they are particularly well suited to illustrate the present concept.

their molar volumes (106 and 108 cm^3/g-mole, respectively) calculated by the method of Lydersen (*3*). When tetrahydrofuran (THF) is used as the eluent, hydrogen bonding occurs between the THF and 1,3-butanediol. The estimated molar volume for the associated species is 108 plus twice the molar volume of THF, since the glycol contains two hydroxyl groups that would be expected to associate with two molecules of THF. This is, no doubt, a crude approximation, but adequate for the present discussion. The styrene, on the other hand, does not undergo association with the solvent. The retention volume for styrene in THF is, therefore, identical to that observed in chloroform. The 1,3-butanediol–THF complex moiety has a larger effective volume in solution. This is reflected in its early emergence from the GPC column.

It has thus been shown that a GPC separation can be enhanced by proper choice of solvent. One has a *handle* for achieving separations between compounds having similar molar volumes but which differ in their ability to interact with the carrier solvent. This, together with the high resolving power of GPC in the low molecular weight region, should make it the fractionation tool of choice in many areas where it is not currently employed. The stigma connected with the application of GPC to small molecule separations because of the misconception that "GPC is a polymer characterization tool" will, no doubt, gradually disappear as more and more use is made of it in this area.

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