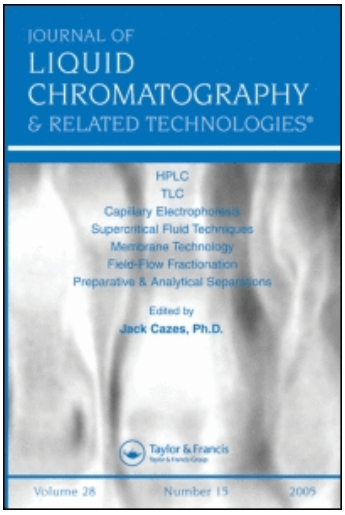

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Russell, David J.(1988) 'Calibration of High Performance size Exclusion Chromatography for Small Epoxy Molecules', Journal of Liquid Chromatography & Related Technologies, 11: 2, 383 — 394
To link to this Article: DOI: 10.1080/01483918809349947
URL: http://dx.doi.org/10.1080/01483918809349947

JOURNAL OF LIQUID CHROMATOGRAPHY, 11(2), 383-394 (1988)

CALIBRATION OF HIGH PERFORMANCE SIZE EXCLUSION CHROMATOGRAPHY FOR SMALL EPOXY MOLECULES

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ABSTRACT

Many epoxy resin formulations contain small oligomers (e.g., less than 1000 molecular weight units) as left over starting materials, reaction by products, or as active parts of the formulation. Modern high performance size exclusion columns are available which enable molecular weights of these oligomers to be determined if proper calibration techniques are employed. Data are presented which demonstrate the differences in calibration curves for epoxy molecules and polystyrene standards, n-alkanes, and phthalate esters for molecular weights under 1000 g/mole. Low MW epoxies are used to calibrate directly for epoxies rather than using molecular size conversion factors calculated from other standards such as polystyrenes.

INTRODUCTION

Modern column packings for high performance size exclusion chromatography (HPSEC) allow efficient separation of small molecules in the 100-1000 molecular weight range. In addition to

the separation and quantification of components of mixtures using size exclusion columns, valuable information can be gained if the molecular weights of impurities such as side-reaction products or degradation products can be accurately estimated. In addition, accurate estimations of molecular weights are essential if one component of a complex formulation is to be monitored.

Although HPSEC is commonly used to obtain molecular weight data, separation is based upon hydrodynamic volume in solution, e.g., molecular size. It has long been recognized that there are differences reported for the molecular sizes of molecules, depending upon the techniques used to calibrate the SEC system. The early work of Cazes and Gaskill demonstrated that separation was effected by the molecular volume rather than the chain length of oligomers (1). They also noted that this molecular volume could be changed by stereochemical interactions (1). They also reported that the adsorption of small molecules to the column packing (1) could increase the retention time and give a low molecular weight value. In another study of small molecules (2), they reported that solvent-solute interactions (when using THF as an eluent) could effectively increase the molecular size of a polar solute molecule (2). This would cause the analyte molecule to elute early, yielding an artificially high molecular weight. Lambert (3) recommended using n-alkanes as calibration standards. The molar volumes of some 380 molecules were calculated and compared to results based upon SEC using n-alkanes as calibration standards (4). Lambert also reported that THF could increase the

apparent size of molecules by forming hydrogen bonds with various polar groups (4).

In the past decade several new columns and packing materials have been introduced, and evaluated for their ability to separate small molecules (5-9). Typical evaluations include the calculations of specific resolution for a homologous series (5,6,10), calculations of the number of theoretical plates (5,8,9) and solvent effects (5,7,10).

Differences in column packings between manufacturers, and changes in the pore size of a given packing depending upon the mobile phase used (e.g., due to the degree of solvent swelling of the packing) can complicate the comparison of data. Further, one may expect the calibration for the determination of accurate molecular weights of various classes of compounds to be different.

It has indeed been shown that calibrations based upon different classes of compounds yield equations with different slopes for plots of Log Mw vs. retention time (or retention volume) even for a given column packing and solvent (6,7,10). Krishen and Tucker plotted the calibration curves from several classes of compounds and found unique slopes (6). A size factor was calculated for each compound to relate its molecular weight to that of an n-alkane eluting at the same retention volume (6). The different values obtained demonstrates that compounds having the same molecular weight may exhibit different hydrodynamic volumes during SEC separation. Mori and Yamakawa studied the retention behavior of several classes of compounds in THF and chloroform using various column sets. Several equations were published

enabling interconversions to relate molecular weights to oligostyrene or n-alkanes standards (7). For example, the molecular weight of an epoxy oligomer (M) could be calculated from the weight of a polystyrene oligomer (Ms) having the same elution volume (for a given column set and a given solvent) using the equation

$$M = 4.50\ Ms^{0.748} \qquad (1)$$

These data covered the molecular range of 340 to 1760 (7).

Chiantore and Guaita noted that calibrations should be performed using the same eluent and standards similar to the analyte molecules to avoid solvent effects (10). They pointed out, however, that sometimes a calibration for a given oligomer series may not be available or that the exact structure of the molecule may not be known, such as in decomposition studies (10).

Another situation where a calibration curve based upon a homologous series may not be applicable is in formulations containing several different resins. For example, low molecular weight epoxy resins may be added as a reactive diluent to higher molecular weight resins, or to serve as toughening agents or to modify the cure characteristics. In a case like this the accurate determination of molecular weights of a given component of the formulation may be necessary.

Experimental

Solvents - Tetrahydrofuran (THF), HPLC grade (Burdick and Jackson, Muskegon, MI).

Standards - Polystyrene Mw 35,000; 9000; 2000; and 800 (Supelco, Inc., Bellefonte, PA), Toya Soda Polystyrene Mw 402, Batch TS-54 (Varian Assoc., Sunnyvale, CA), dibutyl phthalate (Fisher Scientific, Fairlawn, NJ), diethyl phthalate and di-2-ethylhexyl phthalate (Eastman Organic Chemicals, Rochester, NY), dimethyl phthalate and di-isodecyl phthalate (Chemservices Inc., Westchester, PA), n-octane, dodecane, octadecane, tetracosane, octacosane, dotriacontane, and hexatriacontane (Fisher Scientific, Fairlawn, NJ), cyclopentene oxide, 1,2-epoxy-3-phenoxy propane (Aldrich Chemical Company, Milwaukee, WI), 4-vinylcyclohexene monoxide (Union Carbide, Danbury, CT), XD-7342 (Dow Chemical Corporation, Midland, MI), X-22 (Shell Chemical Corporation, Houston, TX).

Equipment

HPLC - A Perkin-Elmer Series 4 pump at 0.7 mL/min was used with a LC-85B variable wavelength detector operating at 279 nm and a Perkin-Elmer model LC-25 refractive index detector (thermostated at 30°C with a circulating water bath). A Perkin-Elmer ISS-100 autosampler was used for sample injection. A Perkin-Elmer model 3600 data station with Chromatographics 2 and GPC 5 software was used for data acquisition and processing.

Columns - Toya Soda TSK 3000 HXL, 2500 HXL, and a 1000 HXL column preceded by a TSK guard column (Varian Assoc., Sunnyvale, CA). These columns have a 5 micron particle size and pore sizes of 1500, 500, and 40 Å, respectively.

Mobile Phase - Tetrahydrofuran, HPLC grade, was used without further purification (Burdick and Jackson, Muskegon, MI).

Procedure - All compounds were prepared as solutions in the THF at approximately the following concentrations: epoxies, 5 mg/mL; phthalate esters, 3 mg/mL; n-alkanes, 2 mg/mL; and polystyrenes, 5 mg/mL. A 25 uL volume was used for each injection.

RESULTS AND DISCUSSION

The column set described above has an exclusion limit of 60,000 (as polystyrene). This makes it ideal for the study of many commercial epoxy resins and formulations which typically have Mw values less than 10,000. This column set also demonstrates sufficient resolution to enable low molecular weight oligomers and additives to be quantitated.

Initial work with low molecular weight epoxy resin was done by comparison to calibration curves prepared from polystyrene oligomers. Efforts to determine the identity of impurities (speculated to be dimers, trimers, etc.) in some samples were complicated by the difference between calculated values and measured values for epoxies in the low molecular weight range. Calibration curves based upon n-alkanes yielded a good correlation but with an entirely different slope for this column set. Further investigations into suitable standards demonstrated that common phthalate esters, often used as plasticizers, also resulted in a linear calibration but with an entirely different slope.

A calibration curve was constructed using five epoxy monomers under study in this laboratory. The resulting linear calibration curve is plotted in Figure 1, along with the curves for oligostyrenes, n-alkanes, and phthalate esters. The slopes of all of these are unique. The calibration curve for the epoxies yields the following equation:

$$\text{Log Mw} = -0.0674\ T + 5.21 \qquad r = 0.9957 \qquad (2)$$

where T is the retention time in minutes.

Mori and Yamakawa compared the calibration curves for a bisphenol A type epoxy resin and oligostyrenes in the molecular weight range of $340 \leq Mw \leq 1760$ for two Shodex A802 columns in THF (7). This relationship enabled the molecular weight of an epoxy to be calculated based on the molecular weight of an oligostyrene having the same elution volume in this molecular weight range.

Work in this laboratory included the study of some low molecular weight epoxy monomers not of the bisphenol A type. It was found that a linear relationship existed for the plot of molecular weight vs. retention time for these compounds of molecular weights less than 500 (see Figure 1). Further, these monomers are not part of a homologous series. Since polystyrene calibrations are often employed, and THF is a common SEC solvent, a procedure of this type is considered for the remainder of the discussion.

The retention times, molecular weights, and Log Mw for the oligostyrenes and epoxies are listed in Table 1. To explore the

TABLE 1
Retention Times and Molecular Weights for Test Samples and Calculated Molecular Weights for Hypothetical Oligostyrenes

Compound	Test Samples tR	Mw	Log Mw	Hypothetical Oligostyrenes Mw	Log Mw
oligostyrenes	42.5	162	2.21		
	39.89	266	2.42		
	38.15	370	2.57		
	36.95	474	2.68		
	36.02	578	2.76		
	35.27	682	2.83		
	34.67	786	2.90		
cyclopentene oxide	48.98	84	1.92	43	1.63
4-vinylcyclohexene monoxide	46.19	123	2.09	76	1.88
1,2-epoxy-3-phenoxy propane	44.60	150	2.18	105	2.02
X-22	39.41	340	2.53	295	2.47
XD-7342	38.00	464	2.67	389	2.59

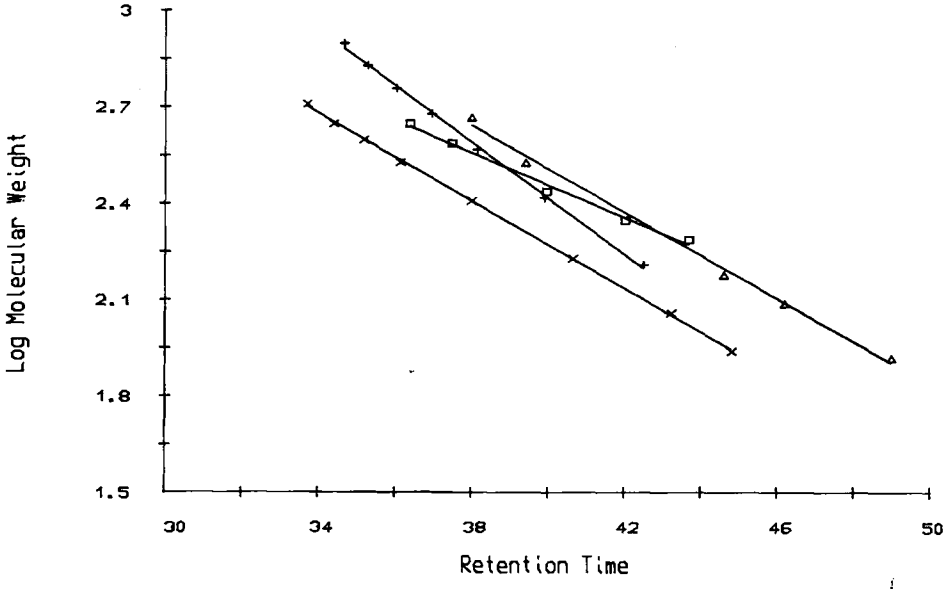

FIGURE 1. Calibration Curves for Different Classes of Compounds (+) Polystyrenes; (X) n-alkanes; (□) Phthalate Esters; (Δ) Epoxies

relationship between the calibration curves, the Log Mw and Mw of a hypothetical oligostyrene eluting at the same retention time as the epoxies in Table 1 were calculated using the relationship

$$\text{Log Mw} = -0.0875\ T + 5.92 \qquad r = 0.9984 \qquad (3)$$

for the polystyrene curve in Figure 1. The data are listed in Table 1 and plotted in Figure 2. From these data the interrelationship between the epoxy calibration curve and oligostyrenes can be calculated as

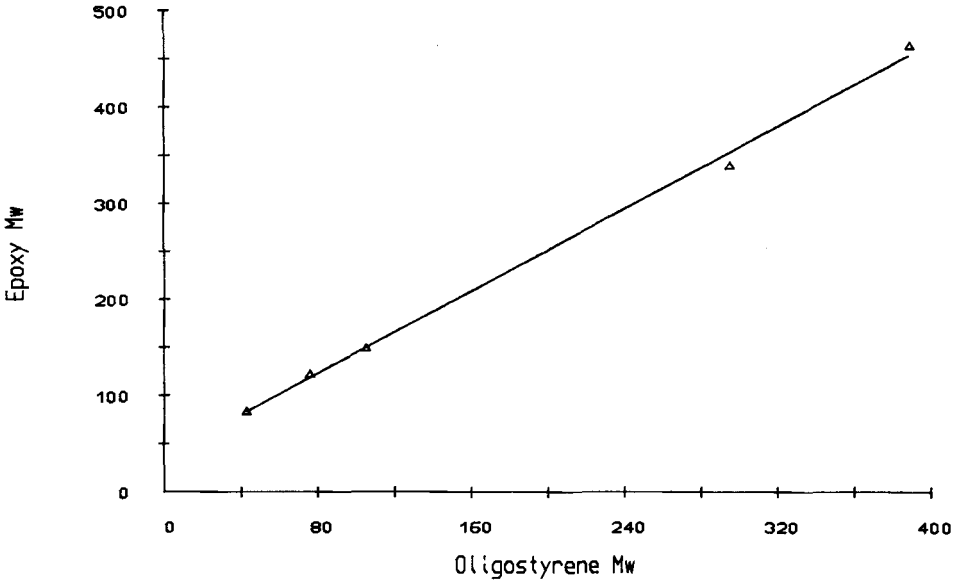

FIGURE 2. Relationship Between Molecular Weights of Epoxy Compounds and Oligostyrenes

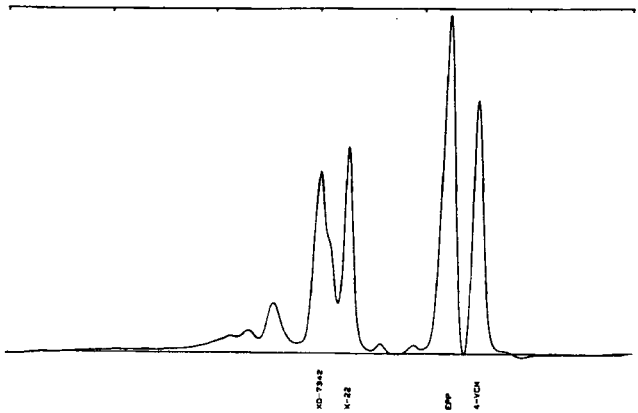

FIGURE 3a. Small Epoxy Standards

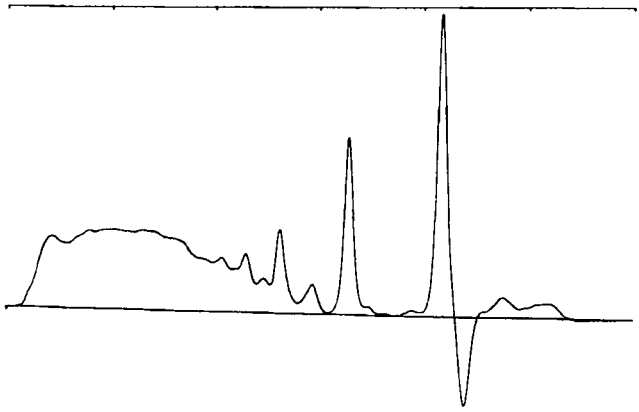

FIGURE 3b. Epirez SU-8

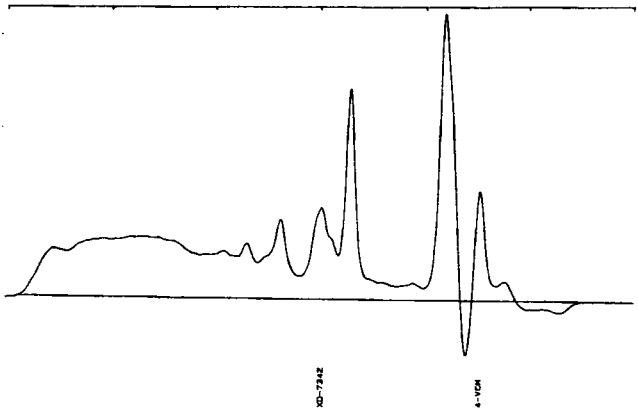

FIGURE 3c. Epirez SU-8 with XD-7342 and 4-VCM

$$Me = 1.071\ Ms + 37.8 \qquad r = 0.9972 \qquad (4)$$

and

$$\text{Log } Me = 0.772 \text{ Log } Ms + 0.642 \qquad r = 0.9948 \qquad (5)$$

where Me is the molecular weight of an epoxy molecule and Ms is the molecular weight of a polystyrene molecule.

An alternative approach to using these interconversion relationships when working with small molecular weight epoxies is to construct calibration plots using the epoxy monomers discussed here. It has been shown that this calibration curve is valid even for compounds not of a homologous series. Recent work has shown the utility of using high performance GPC for the estimation of plasticizers in PVC formulations (11). Similar quantification of low molecular weight epoxy monomers in epoxy resin formulations has been achieved using the method described here (12). For example, a chromatogram containing 4 small epoxy standards is shown in Figure 3a. Figure 3b shows a chromatogram of Epirez SU-8 (13) and a chromatogram of a mixture of SU-8, XD-7342, and 4-vinylcyclohexene monoxide is in 3c. It can be seen that with such a number of oligomers as found in the SU-8 that a reliable method is desired to identify the small epoxy additives in this blend. The accurate determination of molecular weights has increased the reliability of the data for mixtures such as this.

CONCLUSION

Different calibration curves for four classes of compounds are shown using a SEC column set suitable for low molecular weight

epoxy resins. Equations are given to allow the molecular weights of epoxies to be estimated from a polystyrene calibration curve. Alternatively, a series of low molecular weight epoxy compounds are given which can be used to calibrate directly to yield molecular weights for small epoxy molecules.

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