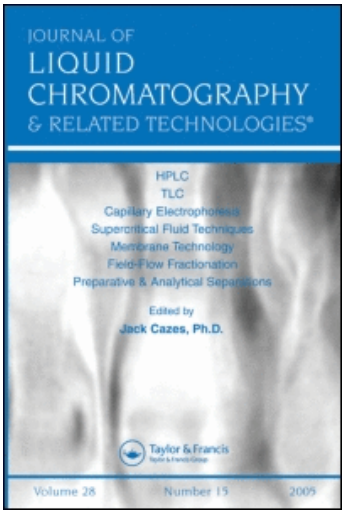

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Note on Complexity of Concentration Effects in SEC

Josef Janča[a]
[a] Institute of Analytical Chemistry Czechoslovak Academy of Sciences 611 42 Brno, Czechoslovakia

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NOTE ON COMPLEXITY OF CONCENTRATION EFFECTS IN SEC

Josef Janča

Institute of Analytical Chemistry
Czechoslovak Academy of Sciences
611 42 Brno, Czechoslovakia

The paper by Chiantore and Guaita (1) published in this special issue deals with concentration dependence of the elution volumes in Steric Exclusion Liquid Chromatography (SEC) of polymers. The observed dependence is surprisingly high. Their main conclusion is that macromolecular coil contraction seems to account for 50-80 % of the total elution volume changes. This result is in quantitative variance with our findings cited in their paper, that viscosity phenomena account for about 80 % of the total concentration effects in the central part of the calibration curve.

The total increments of the elution volumes $\Delta V_t = (V_{e,c}-V_{e,o})$, where $V_{e,c}$ and $V_{e,o}$ are the elution volume at the concentration c and the elution volume extrapolated to c = 0, respectively, were taken from Fig. 3 of the ref. (1) for some polystyrene standards and for the concentrations of 10 and 20 mg/cm^3. The values of ΔV_t were multiplied by the corresponding $\left[d(\Delta V_s)/dc\right] / \left[d(\Delta V_t)/dc\right]$ values (a factor of the

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fractional amount of the contribution due to the coil size contraction over the total change of the elution volume), taken from Table 1, ref. (1). The resulting values of ΔV_s were added to the corresponding $V_{e,o}$ thus obtaining the corrected elution volumes $V_{e,c}^{corr}$ at given concentrations minus the contribution of the viscosity phenomena. By using these corrected elution volumes, the apparent molecular weights M_{app} were taken from the calibration graph on Fig. 1, ref. (1). Further the change of the swelling factor ε (see ref. (2)) with the change of concentration from zero to the given concentration and the ratio $\varepsilon/\varepsilon_o$ (ε_o is the swelling factor at c = 0 and ε is the swelling factor at given concentration) were calculated. The ratio $\varepsilon/\varepsilon_o$ is proportional to the contraction of the macromolecular coil when changing the concentration from zero to the given value. If the ratio $\varepsilon/\varepsilon_o$ is equal to the ratio of the true molecular weight of the polystyrene standard in question to the apparent molecular weight M_{app} found from the calibration graph by a procedure described for $V_{e,c}^{corr}$, the whole change of the elution volume corrected for the viscosity phenomena would correspond to the contraction of the macromolecular coils in solution. All the results are summarized in Table 1.

As can be seen from Table 1, the ratios M/M_{app} are systematically higher than the $\varepsilon/\varepsilon_o$ values by about 60 % or more. It means that the contribution of the macromolecular coil contraction calculated by using Rudin's theory (3) is lower than considered (1). On the other hand it means at the same time that also other phenomena (e.g. adsorption) are probably operative at the given experimental conditions and should be considered to explain the whole change of the elution volumes as a consequence of the concentration effects.

TABLE 1

Polystyrene molecular weight M	$V_{e,c}^{corr}$ c_1	$V_{e,c}^{corr}$ c_2	M_{app} c_1	M_{app} c_2	M/M_{app} c_1	M/M_{app} c_2	$\varepsilon/\varepsilon_o$ [x] c_1	$\varepsilon/\varepsilon_o$ [x] c_2
17500	6.63	6.75	10000	6400	1.75	2.73	1.05	1.09
200000	5.40	5.60	112900	85000	1.77	2.35	1.31	1.61
670000	4.85	5.02	243000	183300	2.76	3.66	1.92	2.84

x) Taken and calculated from ref. (2);
c_1 = 10 mg/cm^3, c_2 = 20 mg/cm^3

The support for the relative importance of the viscosity phenomena was given by applying Rudin's theory (3) to experimental data (4). However, the results by Chiantore and Guaita (1,5) as well as numerous previously published papers by other authors indicate the enormous complexity of the processes underlying the concentration effects in SEC of polymers and the need for further investigation.

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