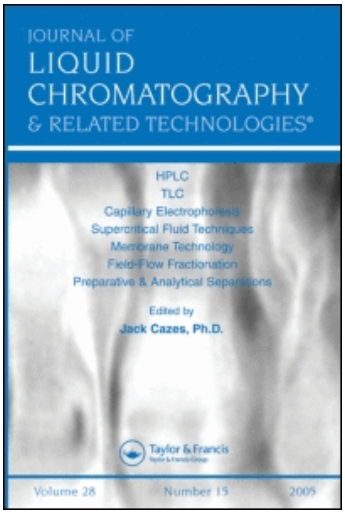

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Veggeland, K. , Nilsson, S. and Austad, T.(1995) 'Osmotic Effects in Gel Permeation Chromatography with Multicomponent Solvents', Journal of Liquid Chromatography & Related Technologies, 18: 16, 3163 — 3173
To link to this Article: DOI: 10.1080/10826079508010442
URL: http://dx.doi.org/10.1080/10826079508010442

JOURNAL OF LIQUID CHROMATOGRAPHY, 18(16), 3163-3173 (1995)

OSMOTIC EFFECTS IN GEL PERMEATION CHROMATOGRAPHY WITH MULTICOMPONENT SOLVENTS

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ABSTRACT

Secondary separation mechanisms are important in a GPC-column when multicomponent eluents are used. The solvent will be at a lower potential in the injected sample than in the eluent, leading to a separation or redistribution of components by the osmotic pressure differences. The smallest components will dominate the separation due to the highest diffusion rates. When charged macromolecules are present, the Donnan equilibrium also contributes to the redistribution of salt. For some surfactant systems, the micellar size is very sensitive to salt concentration, which can give quite complex GPC-chromatograms. In order to discuss GPC-results from polymer-surfactant systems with repulsive interactions, these secondary separation mechanisms must be included.

INTRODUCTION

It is known that components can be separated by gel permeation chromatography, GPC, according to their molecular sizes. In practice, however, various types of interactions occur among the components of the chromatographic system, and as a result, secondary separation mechanisms take place. These interactions and separation mechanisms are important in polymer-surfactant systems applicable for chemical flooding of oil reservoirs. When polymers and surfactants are coinjected in order to improve the oil recovery, phase separation and incompatibility are crucial for the process(1,2). Polymer-surfactant interactions have been studied by a GPC-approach(3-6) that is based on preferential solvation of macromolecules in mixed solvents(7-9). The surfactant solution is used as the eluent and the polymer is dissolved in the eluent and injected into the column. Both associative and repulsive interactions may be present in polymer-surfactant systems depending on charges, hydrophobic groups, etc.(10).

Associative interactions lead to formation of a polymer-surfactant complex, that is usually larger than the pure polymer. This is seen in GPC-chromatograms as a lower elution time for the complex peak than for the polymer peak. Also a negative peak related to the amount of surfactant associated with the polymer occurs. Studies of polymer-surfactant association are described in detail elsewhere(4-6). When it comes to repulsive interactions, the chromatograms for polymer-surfactant systems are more complex(5,6), due to different separation mechanisms and effects of the components in the solvent. Micellar size is affected by salt and very different results can be obtained for surfactant solution in the absence and presence of salt, as will be presented.

In order to distinguish between different secondary separation mechanisms, binary polymer systems have been studied. The eluent is a solution of one of the polymers at an appropriate concentration. Phase separation in the polymer1 - polymer2 solution must be avoided. With low concentrations of polymer, interactions are of little importance, but as will be shown osmotic effects are important. Due to the mobile counterions, charged macromolecules like polyelectrolytes are expected to give larger osmotic effects. For polyelectrolytes, the Donnan equilibrium(11) for salt distribution will also be a main separation mechanism.

The present GPC-method can be compared with dynamic dialysis, where the membrane is omitted. Of the secondary separation mechanisms that have to be considered in these experiments are osmosis and Donnan effect on salt equilibrium. Both these effects are also important in membrane equilibrium. The results from polymer-polymer separation studies illustrate some of the effects seen in the more complex polymer-surfactant systems(5,6). Also chromatograms for pure surfactant solutions in solvents of surfactant with and without salt show large redistribution effects that give insight into the polymer-surfactant systems.

EXPERIMENTAL

Chemicals

Poly (ethylene oxide), PEO4, with average molecular weight of 4 000 g/mole was obtained from Merck. Dextrans, T500 and T10 were obtained from Pharmacia B, Uppsala Sweden, having an average molecular weight of 500 000 and 10 000. Poly(styrene sulfonic acid, sodium salt, 100% sulfonated), PSS500, with average molecular weight 500 000 from Polysciences, Inc.. These polymers were used as delivered. Xanthan, Xc 85-II F4, was produced by Bioferm Statoil, filtered and purified by precipitation with isopropanol and dried. Molecular weight range is $2\text{-}3\cdot10^6$. Sodium dodecylbenzene sulfonate, NaDDBS (Hard type),

D 0990, with Mw = 248.48 g/mole and 95 % active material from Tokyo Kasei Ltd., was used as delivered. NaCl p.a. delivered from Merck was used.

Chromatographic Instrumentation and Conditions.

The HPLC equipment consists of a 600E pump, a 715 Ultra Wisp Sample Processor, a 410 Differential Refractometer, all delivered from Waters. A NEC, APCIV^{TM}, Power Mate 486/33i integrator, a 991M photodiode array detector and a TI microLaser Plus complete the instrumental set-up. The samples were chromatographed on a Waters Ultrahydrogel^{TM} 250, 6μm GPC-column (7.8 x 300mm). Sample volumes have been 20-100μl. Flow rate was set at 0.5 ml/min. The column and the RI-detector was thermostated at 32°C.

Procedures.

The eluent was either a surfactant or a polymer solution depending on what system to be studied. Polymers were dissolved into the eluent at appropriate concentrations to avoid phase separation. All solutions were run through a 0.45μ Millipore filter prior to injection and degassed constantly with He-gas.

RESULTS AND DISCUSSION

The chromatograms in fig.1 show separation of two nonionic polymers, dextran T500 and poly(ethylene oxide) PEO4. Molecular weights are 500 000 and 4 000, respectively. The eluent is 0.60 wt% PEO4 (aq) and the concentration of T500 is 0.35 wt% in all chromatograms.

In a) T500 is dissolved in the eluent and injected. There is little interactions in the system, but a separation of the two polymers is clearly seen. The solvent in the sample is at a lower chemical potential than the solvent in the surrounding eluent. The separation is due to osmosis pressure difference and of course size exclusion. This will be more discussed later and is also illustrated by chromatograms b-d), where the same concentration, 0.35 wt% of T500 is dissolved in a solution with lower concentration of PEO4 than in the eluent, 0.56, 0.50 and 0.46 wt%, respectively. For c) and d) the concentrations were to low and negative peaks are observed. Estimations based on fig.1 indicate that 0.54 wt % of the eluent in the injected sample will provide osmotic equilibrium. Calculations, based on the Flory-Huggins model(12), gave that the chemical potential of water is unchanged if 0.6% PEO4 is replaced by 0.35% T500 + 0.48% PEO4. This is in reasonable agreement with the result in fig.1 where a

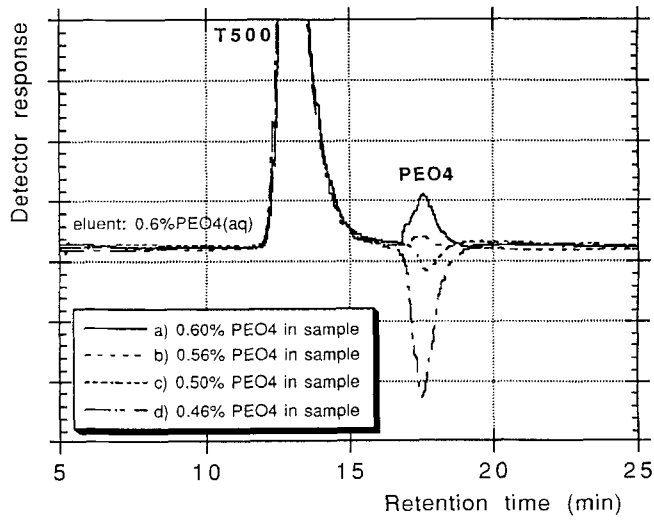

FIGURE 1. GPC-chromatograms where the eluent is 0.6wt% PEO4(aq), in a) 0.35% T500 dissolved in the eluent, in b) 0.35% T500 is dissolved in 0.56% PEO4, in c) 0.35% T500 is dissolved in 0.50% PEO4, and in d) 0.35% T500 is dissolved in 0.46% PEO4. The flow rate is 0.5 ml/min and an RI-detector is used.

concentration of 0.54% PEO4 was needed together with 0.35% T500 to remove osmotic pressure effects. The calculations gave the same result regardless of whether interaction parameters were included or not (interaction parameters were taken from ref.13). With the small concentrations used in the GPC-experiments the effect is dominated by the entropy of mixing and interactions are usually of marginal importance.

The osmotic separation mechanism is illustrated in fig.2. The column is equilibrated by the eluent, which is a nonionic polymer A dissolved in a solvent, s, (e.g.water). Region I represents pure eluent. Region II shows the injected volume of the sample. The sample is a solution of B (another nonionic polymer, $Mw_A < Mw_B$) dissolved in the eluent. It is assumed no net flow in the column.

The chemical potentials of the solvent, s, in the different regions I and II are:

in the eluent, I: $$\mu_S(I) = \mu_S^0 + RT \ln x_S(I) \approx \mu_A^0 - RTx_A \quad (1)$$

in the sample, II: $$\mu_S(II) = \mu_S^0 + RT \ln x_S(II) \approx \mu_A^0 - RTx_A - RTx_B \quad (2)$$

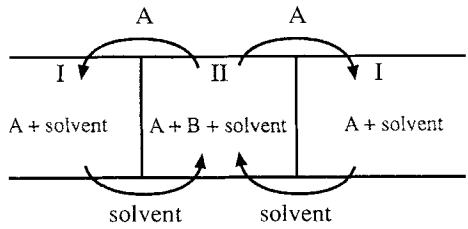

FIGURE 2. A schematic illustration of a GPC-column divided into two regions I and II. The injected sample B is dissolved in the eluent (A+solvent). No net flow in the column.

where x_A and x_B are the mole fractions of A and B, respectively. The chemical potential of the solvent in the sample (region II) is lower than in the eluent. Assuming no net flow the osmotic pressure difference, due to the lower chemical potential of the solvent in the sample, will provide a mainly entropic, thermodynamic driving force for the water molecules to diffuse into the sample to gain osmotic equilibrium. To maintain a constant volume of the injected solution, other components have to diffuse out of the sample. Here A is the smallest component, thereby having higher diffusion rate than B, and is transported away from the sample region. From fig.1 it is seen that by reducing the concentration of A in the sample region (here PEO4) the redistribution of the two nonionic polymers is reduced. It is possible to find an equilibrium concentration of A in the sample that removes the osmotic separation.

If the solvent in fig.2 contains salt, the salt ions will dominate the diffusion from region II to region I, due to the higher diffusion rate. This is experimentally shown in fig.3, where two dextrans, T500 and T10 with molecular weights of 500 000 and 10 000, respectively, are studied in the absence and presence of NaCl. With 0.5 wt% T10 (aq) as eluent 0.25 wt% T500 is dissolved in the eluent and injected. The polymers are separated by the mechanism described above and can also be compared to fig.1a. The osmotic pressure difference between the eluent and the injected sample will provide a driving force for the water molecules to diffuse into the sample to gain osmotic equilibrium. To maintain a constant volume of the injected solution, other components have to diffuse out of the sample. The smallest components will have the highest rate of diffusion and leads to a peak of T10 which has been separated from T500 molecules due to osmosis and size exclusion. The retention time of T10 is the observed retention time for T10 also with water as eluent in the same column and under the same conditions, so a "complete" separation has taken place. With 50mM NaCl added to the eluent, the chromatogram is different as seen in fig.3. The components diffusing from the injected sample are mainly the salt ions. In a sample with several constituents the components with the fastest diffusion will take over the response to give osmotic equilibrium as water diffuses into the sample. As can be seen the T10 peak has almost disappeared.

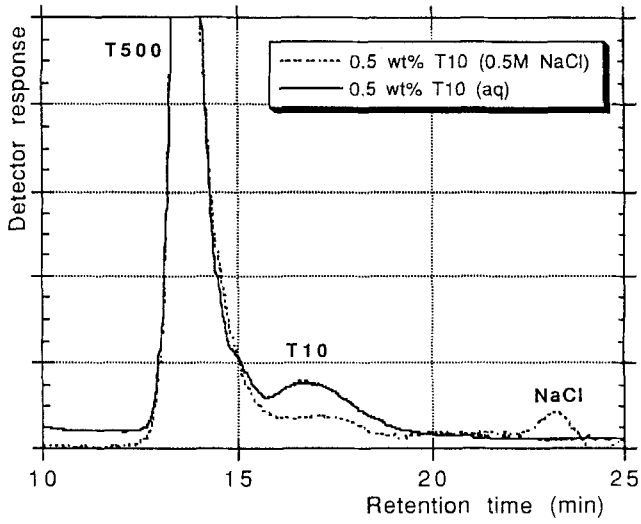

FIGURE 3. GPC-chromatograms, where the eluent is 0.5% T10(aq) (——) and 0.5% T10 in 50mM NaCl (·····). In both cases are 0.25% T500 dissolved in the eluents and injected into the column. The flow rate is 0.5 ml/min and an RI-detector is used.

Fig.4 compares the separation between two nonionic polymers and between a negatively charged polyelectrolyte and a nonionic polymer, both in the presence of salt. In chromatogram a) 0.6 wt% PEO4 in 10mM NaCl is the eluent and 0.25 wt% T500 is dissolved in the eluent and injected into the column. Separation of both PEO4 and NaCl from the larger dextran T500 is seen. The separation mechanism is the osmotic effect described above. NaCl does not dominate the diffusion as much as in fig.3, since the NaCl concentration is lower, 10mM compared to 50mM NaCl. This means that at a high enough salinity, the two polymers will not separate due to diffusion, only the salt will redistribute.

In chromatogram b) in fig.4 the sample is changed from the nonionic dextran, T500, to a charged polymer with the same molecular weight and at the same concentration, namely poly(styrene) sulfonate(Na-salt), PSS500. The eluent is the same, 0.6 wt% PEO4 in 10mM NaCl. Polyelectrolytes will give a larger osmotic effect due to the mobile counterions as is seen in the figure. The charged macromolecules will also influence the distribution of salt between injected sample and surrounding eluent, the Donnan effect. To obtain ion equilibrium across the "invisible membrane" between the injected sample and the eluent, an increased diffusion of NaCl from the sample must take place as is also seen in the figure. The reason for the higher retention time for the PEO4-peak in the polyelectrolyte sample is not understood.

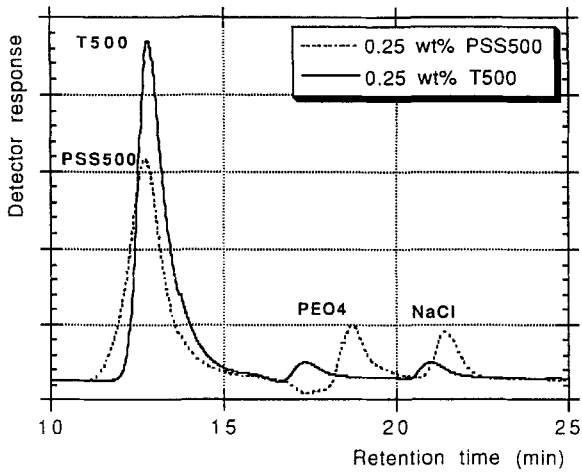

FIGURE 4. GPC-chromatograms where the eluent is 0.6% PEO4 in 10mM NaCl. Samples dissolved in the eluent and injected are 0.25% T500 (——) and 0.25% PSS500 (·····). The flow rate is 0.5 ml/min and an RI-detector is used.

In surfactant systems the consequences of the osmotic redistribution effects discussed above can be much larger. The eluent in fig.5 is 10mM of NaDDBS and the injected samples are a) 7mM NaDDBS and b) 20mM of NaDDBS which, as can be expected, gives one negative and one positive peak. The peaks at about 25 minutes are related to monomers and impurities like salt. If, however, the experiment is repeated after adding 10mM NaCl to the eluent and the injected samples, the result becomes quite different, see fig.6. In fig.6a the result is still a normal negative peak when 7mM NaDDBS is injected, but the injection of 20mM NaDDBS (fig.6b) produces a different and more complex result. The origin of the result in fig.6b can be understood by the chromatogram in fig.7. In fig.7 the eluent is 10mM NaDDBS (no salt) and the injected sample is 0.7mM NaCl dissolved in the eluent. As can be seen a strong negative peak is produced, at about the retention time for the micelles, together with the positive NaCl peak. The negative peak must be the effect of salt concentration on the micellar size. Addition of salt causes a growth in micellar size which will form micelles having a smaller retention time. As the larger micelles are chromatographically separated from the salt, they will start to shrink again and are probably spread out over the column leaving a negative peak behind. In fig. 6b variations in the salt concentration are generated by osmotic redistribution effects due to the higher surfactant concentration in the injected sample. The result can be quite complex as salt and surfactant are continuously redistributed as the different peaks propagate through the column. However, not all surfactants give these complex results since a requirement is that the micellar size is salt sensitive. For instance some ethoxylated sulfonates have been found to give

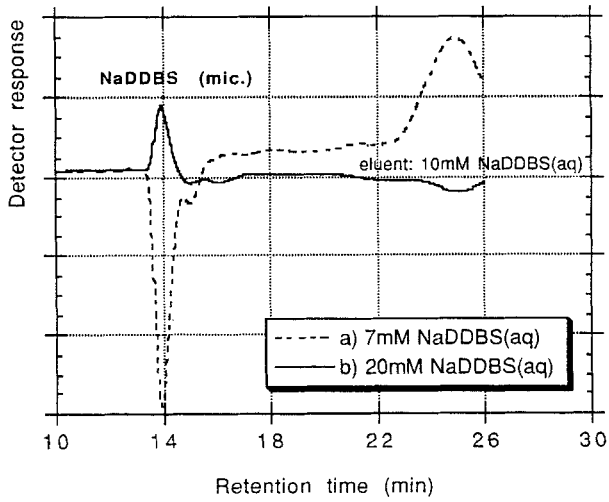

FIGURE 5. GPC-chromatograms where the eluent is 10mM NaDDBS(aq), in a) 7mM NaDDBS(aq) and in b) 20mM NaDDBS are injected. The flow rate is 0.5 ml/min and an RI-detector is used.

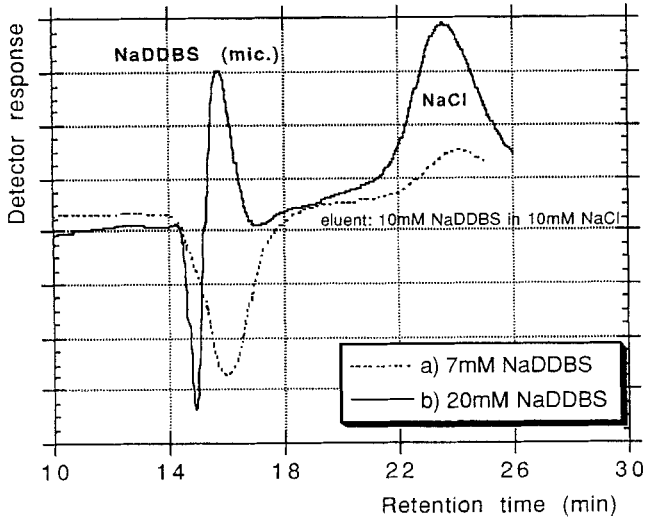

FIGURE 6. GPC-chromatograms where the eluent is 10mM NaDDBS in 10mM NaCl, in a) 7mM NaDDBS and in b) 20mM NaDDBS both in 10mM NaCl, are injected. The flow rate is 0.5 ml/min and an RI-detector is used.

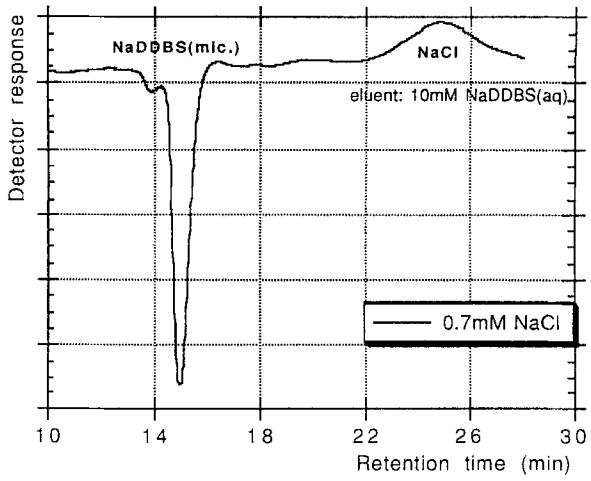

FIGURE 7. GPC-chromatogram where 10mM NaDDBS is the eluent. The injected sample is 0.7mM NaCl. The flow rate is 0.5 ml/min and an RI-detector is used.

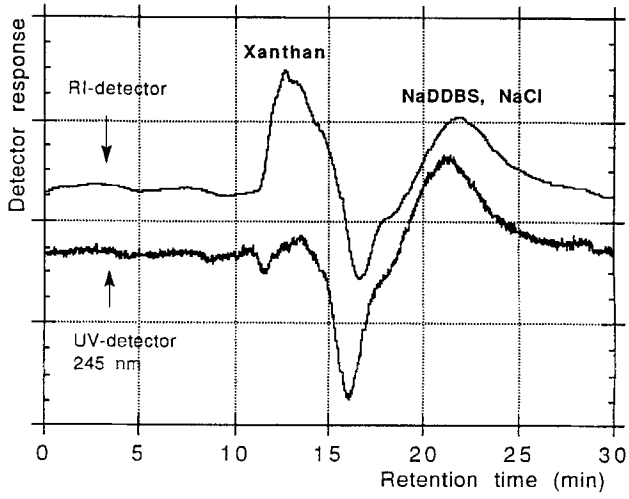

FIGURE 8. GPC-chromatograms where 10mM NaDDBS in 10mM NaCl is the eluent. 0.35% xanthan is dissolved in the eluent and injected. The flow rate is 0.5 ml/min and both an UV(245nm)- and an RI-detector are used.

"normal" chromatogram (data not shown) also with salt present in the eluent as higher or lower concentrations of surfactant are injected.

An example of polymer-surfactant chromatograms where the secondary separation mechanisms are large is shown in fig.8. The anionic biopolymer xanthan is dissolved in the eluent consisting of 10mM NaDDBS and 10mM NaCl. NaDDBS is an anionic surfactant, so there are repulsive interactions between the polymer and the surfactant micelles. Fig.8 shows chromatograms detected both with RI and UV(245nm). The xanthan peak is not detected by the UV-detector, but a redistribution of the NaDDBS micelles is clearly seen. Based on the results from figs.5-7, all effects; osmosis, Donnan effects and the salt effect on micellar size take part in these separations. Since secondary separation mechanisms are present also in nonionic systems electrostatic repulsions will not contribute to the total separation.

CONCLUSIONS

Using multicomponent solvents or eluents in a gel permeation chromatography column secondary separation mechanisms must be carefully considered. Osmotic pressure differences between the injected sample and the eluent will lead to separation of components even though the column is equilibrated with one of the components. The smallest components dominate the separation due to the highest diffusion rate. Charged macromolecules will give a lager osmotic effects due to the mobile counterions. Salt will redistribute due to Donnan equilibrium when polyelectrolytes are present. For surfactant solutions the salt redistribution may have large consequences, especially when the micellar size is very salt sensitive. The secondary separation mechanisms must be known to be able to understand the complex chromatograms obtained for polymer-surfactant systems having mutual repulsive interactions.

ACKNOWLEDGEMENTS

K. Veggeland is indebted to The Norwegian Research Council, NFR, for financial support. The work is partly funded by the state supported programme on Reservoir Utilisation through advanced Technological Help (RUTH).

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Received: March 24, 1995
Accepted: April 2, 1995