

## Note

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### Interaction complexes between polymers and surfactants

#### I. Interactions of polyethylene oxide with surfactants studied by gel permeation chromatography

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In the course of technological processes and biological systems<sup>1</sup>, many polymers interact with surfactants. Some types of interaction may be characterized by sorption measurements. However, there are other molecular and or micellar types of interactions between surfactants and polymer when both are dispersed in a solvent. The study of these phenomena is important from a theoretical as well as a practical point of view.

Owing to interactions of surfactants with polymers, flocculation can take place. Thus, water contaminated with some polymers can be treated by addition of suitable surfactants.

The properties of systems containing surfactants and water-soluble polymers have been characterized by surface tension, electrical conductance, viscosity and other measurements<sup>2</sup>, but such methods often give only a qualitative measure of the complexing properties of the system.

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 result secondary separation mechanisms take place. These secondary mechanisms or side phenomena enable the range of individual polymer-surfactant to be estimated. GPC has been used<sup>3-6</sup> to study these phenomena.

The aim of this work is to study some side effects of GPC measurements in the system consisting of polyethylene oxide (PEO) and some surfactants dissolved in water in order to determine the above interactions.

#### EXPERIMENTAL

##### *Apparatus*

A Knauer (F.R.G.) liquid chromatograph of with HPLC pump Model FR-30

was used. The detector was a differential refractometer Model 2025-50 KN, the signal of which was obtained on a recorder Type 185 (Kutesz, Hungary). For statistical calculations, a computer Model 270 (Tesla, Czechoslovakia) was used. Separate measurements of the refractive indices of the mobile phases were carried out with an Abbe refractometer (Zeiss, G.D.R.). Two columns filled with Sepharon P-1000, 25–40  $\mu\text{m}$  (Laboratory Instruments, Prague, Czechoslovakia) were connected in series.

### Chemicals

Polyethyl oxide (PEO), mol.wt 1200 (G.D.R.) was used as model polymer with two types of surfactants: anionic, sodium dodecyl sulphate (SDS) (Sigma, St. Louis, MO, U.S.A.) and non-ionic, nonylphenol polyglycol ether, Slovafo 909 (CHZWP, Nováky, Czechoslovakia). Redistilled water and aqueous solutions of SDS (0.5%, w/v) and Slovafo 909 (0.5%, w/v) were used as eluent and solvent for PEO. The eluent flow-rate was 1.37 ml/min at 22°C and an inlet pressure of 4 MPa was applied. The estimated concentration of PEO was in the range of 0.1–2 g per 100 ml in all three eluents used.

### RESULTS AND DISCUSSION

The presence of a surfactant in the mobile phase had two effects: lower PEO elution volumes,  $V_e$ , and the occurrence of negative vacant peaks when compared with the chromatograms obtained with water as a mobile phase (Fig. 1). The shift in  $V_e$  values of PEO can be explained by the strong interactions between molecules of PEO and the surfactants. Lower elution volumes may be regarded as a result of the formation of a stable polymer–surfactant “interaction complex”<sup>7–13</sup>.

The interaction between PEO and both surfactants (SDS and Slovafo 909) is also confirmed by the occurrence of vacant peaks<sup>14</sup>. Their negative values correspond to the excess of that component, *i.e.*, water of the mixed solvent which has the lower refractive index. The position of these peaks is in agreement with those of the surfactants eluted with water. Thus, these vacant peaks correspond to the “deficit” of surfactant in the elution zone of the polymer. This means that the surfactant has interacted preferentially with polymer. The intensity of the vacant peaks is proportional to the PEO concentration (Fig. 2).

This result was used for the estimation of the interaction of PEO with both surfactants on the basis of the calculation of the so-called coefficients of preferential solvation,  $\lambda$ <sup>15–17</sup>

$$\lambda = \frac{\Delta W}{U} \cdot \frac{V}{M_M} \quad (1)$$

where  $\Delta W$  = the number of preferentially sorbed molecules of one eluent component expressed per gram of polymer,  $U$  = the number of monomer units per gram of polymer,  $V$  = the molar volume of the solvated compound and  $M_M$  = the molecular weight of one monomer unit. For calculating the  $\Delta W$  values, the peak heights corresponding to the surfactants were used. These peaks were obtained by using different concentrations of surfactant measured to the eluent containing 0.5% of the pertinent surfactant. The values obtained were used for constructing a calibration plot of peak

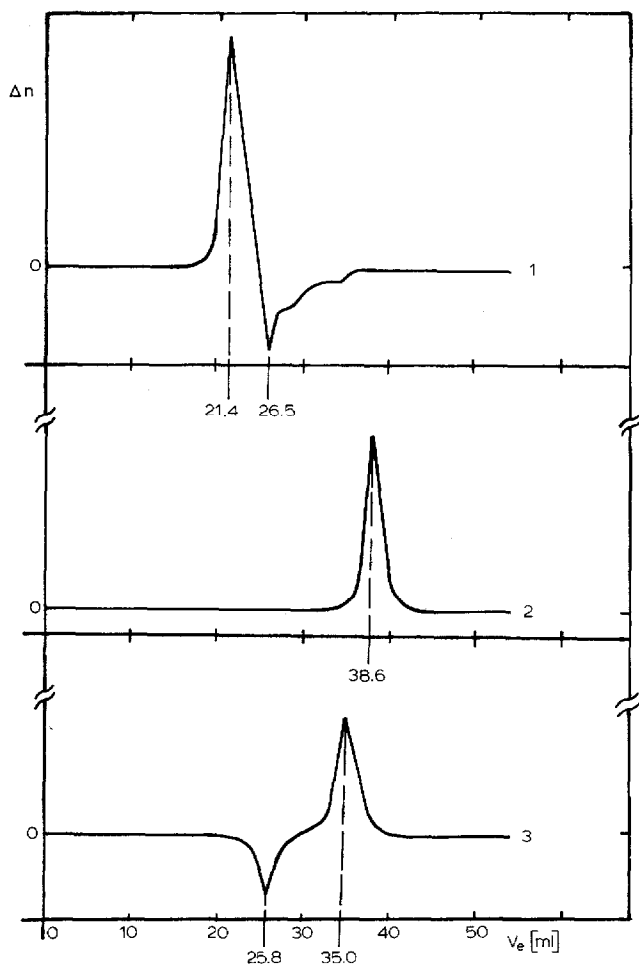


Fig. 1. Chromatograms of PEO 1000 in different eluents: 1, 0.5% (w/v) SDS; 2, water; 3, 0.5% (w/v) Slovafof 909.

heights vs. concentration of surfactant. Using both types of these plots (Fig. 2, and calibration plot for surfactant), it was possible to obtain a relationship between the polymer concentration and the corresponding surfactant concentration. For instance, Fig. 3 shows this dependence for SDS surfactant and PEO polymer.

The coefficients of preferential solvation were calculated according to

$$\lambda = \frac{m_{\text{sur}}}{\rho_{\text{sur}}} \cdot \left( 1 - \frac{x_2}{x_1} \right) \quad (2)$$

which was derived from eqn. 1<sup>18</sup>. here  $m_{\text{sur}}$  = the mass of surfactant in 100 ml of mixed solvent,  $\rho_{\text{sur}}$  = the density of the surfactant,  $x_2$  = the molar concentration of surfactant at zero concentration of polymer and  $x_1$  = the molar concentration of surfactant at a polymer concentration of 1 g/100 ml. The densities of the surfactants

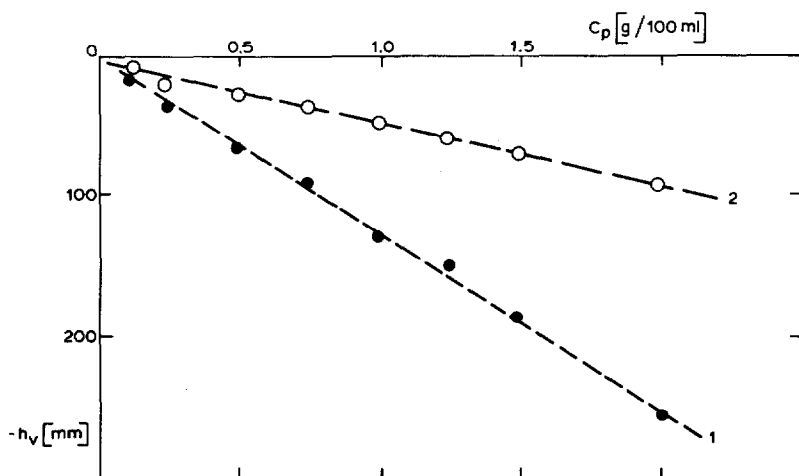


Fig. 2. Vacant peak height vs. concentration of PEO 1000: 1, in 0.5% (w/v) SDS; 2, in 0.5% (w/v) Slovafof 909.

at 22°C were  $\rho_{\text{SDS}} = 1.0124 \text{ g/cm}^3$  and  $\rho_{\text{Slov.}} = 1.0594 \text{ g/cm}^3$ . Using the  $\lambda$  values it is possible to determine the "binding ratio", BR (millimoles of surfactant bound to 1 g of PEO):  $\lambda_{\text{SDS}} = 1.84 \text{ ml/g}$ ,  $\text{BR}_{\text{SDS}} = 6.5 \text{ mmol/g}$ ;  $\lambda_{\text{Slov.}} = 1.55 \text{ ml/g}$ ,  $\text{BR}_{\text{Slov.}} = 2.7 \text{ mmol/g}$ . According to the  $\lambda$  and "binding ratio" values, PEO 1000 interacts more intensively with SDS.

The decrease in dimensions of macromolecules with increasing concentration is due to polymer-surfactant interactions. According to GPC measurements, greater retention values,  $V_e$ , of polymers were found at higher concentrations of the injected sample<sup>19-27</sup>. The dependence of  $V_e$  on concentration is linear in many cases. The slope of this plot increases with the molecular weight of the polymer and with the

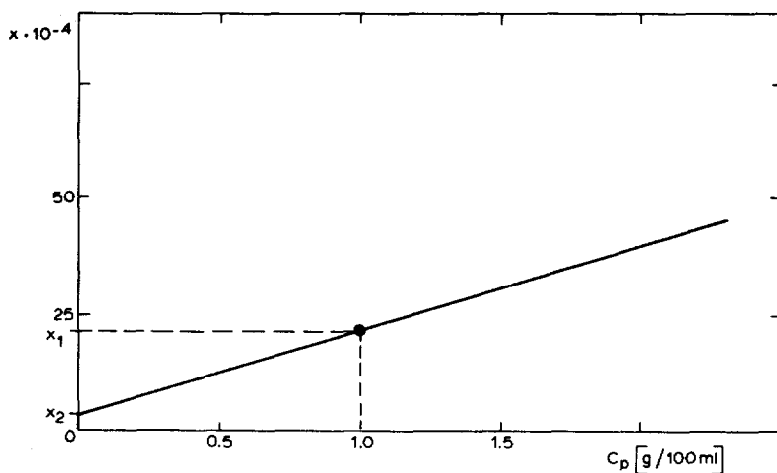


Fig. 3. The dependence of the molar concentration of SDS vs. concentration of PEO 1000.

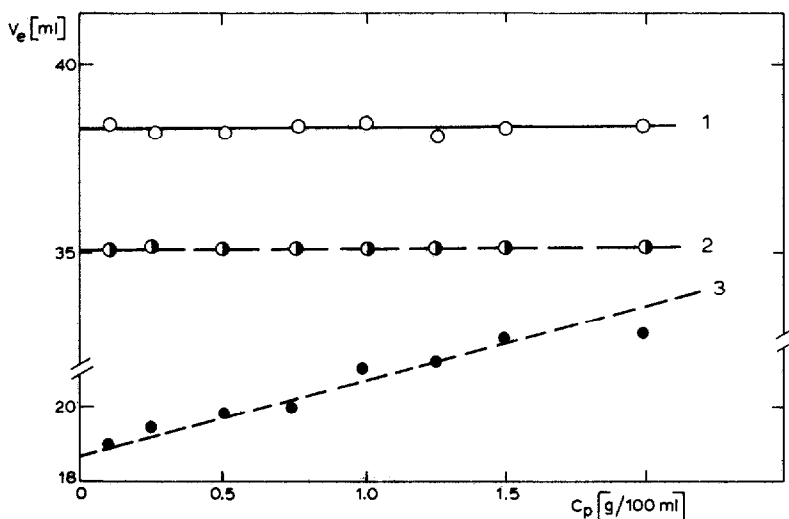


Fig. 4. The dependence of elution volumes of PEO vs. concentration of PEO 1000: 1, in water; 2, in 0.5% (w/v) Slovafo1 909; 3, in 0.5% (w/v) SDS.

eluent quality for a given polymer, defined thermodynamically. These phenomena can be used as a measure of the changes in interaction between a polymer and a solvent due to the presence of a surfactant. The changes of the slopes of the plots of polymer (PEO 1000) elution volumes against concentration after adding surfactants indicated strong interactions between PEO and the ionogenic surfactant SDS (Fig. 4).

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