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Evaluation of preferential solvation by gel permeation chromatography*

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Preferential solvation parameters for the ternary system poly(dimethylsiloxane)–benzene–methanol have been determined by comparing the areas of the solvated and non-solvated polymer g.p.c. peaks. Good agreement is found between the present results and those from other methods. The present method has the advantages of simplicity, speed and accuracy.

(Keywords: preferential solvation; g.p.c.; poly(dimethylsiloxane))

INTRODUCTION

When a polymer is dissolved in a mixture of solvents preferential solvation by one of the components usually occurs, i.e. there is an increase in the concentration of one of the solvent components in the vicinity of the polymer chain and a corresponding decrease of the concentration of this component in the rest of the solvent. If the solvated polymer and the rest of the mixed solvent injected with it can be separated by means of a suitable liquid-chromatographic method, i.e. g.p.c., the chromatograms can be used to quantitatively assess the degree of solvation from either the solvent peak or the solvated polymer peak. The method has the advantage of speed and simplicity compared with the classical methods, such as dialysis equilibrium[1] and light scattering[2]. Berek *et al.*[3] and Campos *et al.*[4] have shown the reliability of the method by measuring the areas of the solvent peaks, i.e. the so-called vacant peaks. However, in our experience two factors which are difficult to eliminate, may affect the area of the solvent peak. These are: (1) selective evaporation of one component of the mixed solvent from the sample solution before injection; (2) selective adsorption of one component of the mixed solvent on the membrane during filtration. The area of the solvated polymer peak is less affected by these two factors. This is because the area of the vacant peak is very sensitive to small changes in solvent composition, whereas the area of the solvated polymer peak is not. In this paper we report g.p.c. results obtained from the poly(dimethylsiloxane) (PDMS)–benzene–methanol ternary system by analysis of the solvated polymer peak.

As is well known, benzene preferentially solvates PDMS chains dispersed in a mixture of benzene and methanol. When the same benzene–methanol mixed solvent is used both to dissolve the PDMS and as the eluent in chromatography, there are two possibilities:

1. If the chromatographic column can separate the polymer from the rest of the injected sample solution completely, the area of the solvated-polymer peak (A_p^s) can be regarded as the sum of contributions from the polymer (A_p) and from the extra solvating benzene (A_b), i.e.

$$A_p^s = A_p + A_b \tag{1}$$

   and the area of the vacant peak (A_v) which is attributable to excess methanol is equal to A_b in magnitude but opposite in sign.
2. If a non-separating column is used or if there is no column at all, the solvated-polymer peak and the vacant peak will merge into a single peak. The area of this peak is equal to A_p, since the contribution of A_b is balanced in the measured peak area (A) on this occasion.

When a differential refractometer is employed as detector, its area response constant K for a given solute–solvent combination can be written as

$$K = k\left(\frac{dn}{dc}\right) \tag{2a}$$

where k is the instrumental response constant and (dn/dc) is the refractive index increment. As long as the concentration of the solute is low, K can be determined directly from the weight of the sample in the injected solution (W) and A:

$$K = \frac{A}{W} \tag{2b}$$

By combining equations (1) and (2b), the volume of benzene V_b which produces a peak area A_b can be

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calculated from

$$V_b = \frac{A_p^s - A_p}{K_b} v_b = \frac{K_p^s - K_p}{K_b} W_p v_b \qquad (3)$$

where v_b is the specific volume of benzene and, in the present work, W_p is the weight of PDMS in the injected solution and K_p^s, K_p and K_b are the area response constants of solvated PDMS, non-solvated PDMS and benzene, respectively. Defining a preferential solvation parameter λ_b, i.e. the excess volume of benzene absorbed per unit mass of the polymer, we obtain

$$\lambda_b = \frac{V_b - V_b\phi_b}{W_p} = \frac{K_p^s - K_p}{K_b}(1 - \phi_b)v_b \qquad (4)$$

where ϕ_b is the volume fraction of benzene in the eluent.

EXPERIMENTAL

Measurements were carried out at room temperature (~25°C) by means of a Waters Associates model 244DS liquid chromatograph, equipped with a model R401 differential refractometer (attenuator set at 1/16) and a model 730 microcomputer. A single column packed with μ-Styragel (nominal porosity 500 Å, length 30 cm) separated PDMS species with molecular weights up to 10000. The PDMS sample used had a number-average molecular weight $\bar{M}_n = 5.31 \times 10^4$ and a polydispersity ratio $\bar{M}_w/\bar{M}_n = 1.75$, both from g.p.c.

Solvents (analytical grade purity) were purified before use. Methanol was fractionally distilled and the middle cut used. Benzene was purified by repeatedly shaking with concentrated sulphuric acid (15 vol% benzene) in a separating funnel until the acid phase remained colourless. The benzene phase was then washed with water, aqueous sodium hydroxide (10 wt%), again with water, dried with anhydrous calcium chloride, and finally distilled.

The eluents were methanol–benzene mixtures of various compositions at a flow rate of 0.4 cm^3 min^{-1}. The mixtures were made by volume and equilibrated in the sample reservoir of the g.p.c. system. Sample solutions (0.5–10 mg ml^{-1}) were prepared using solvent mixtures from the solvent reservoir and were injected (50–200 μl) into the g.p.c. system: (1) after filtration and with the column attached; (2) without filtration and without the column. In each case A_p^s was measured.

RESULTS AND DISCUSSION

A schematic g.p.c. curve for PDMS–benzene–methanol obtained with the column in place is shown in *Figure 1*. The two negative peaks correspond (as indicated) to solvated polymer and excess methanol (vacant peak). Plots of solvated polymer peak area *versus* weight of PDMS injected into the g.p.c. system with and without the column are shown in *Figure 2*. The slopes of the straight lines through the data points obtained with the column are always larger (less negative) than those of the corresponding lines through the points obtained without the column, which reflects the preferential solvation of PDMS by benzene, as the detector response for benzene is positive: see the plots of peak area *versus* excess weight of benzene injected shown in *Figure 3*. The difference in slope between the lines through the data points for solvent of the same composition obtained with

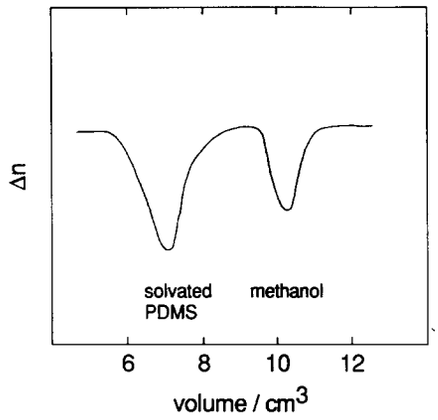

Figure 1 Schematic g.p.c. curve for PDMS in a benzene–methanol mixture (90:10 v/v). The solvated polymer peak and the excess methanol (vacant) peak are indicated

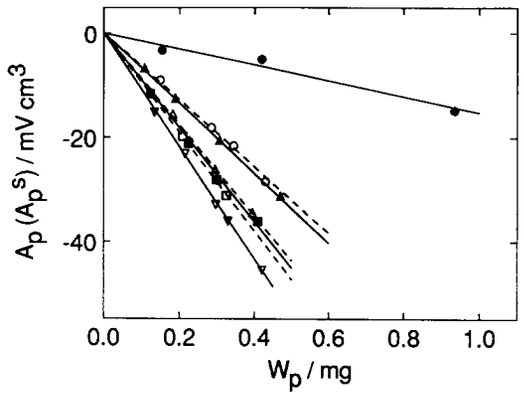

Figure 2 PDMS peak area (A_p^s, A_p) *versus* weight of PDMS (W_p) in the injected solution. Solid symbols refer to results obtained with the column in place, and open symbols to results obtained without the column. Solvent compositions (ϕ_b, volume fraction benzene) were: (●, ○) 0.80; (▲, △) 0.90; (■, □) 0.95; (▼, ▽) 1.00

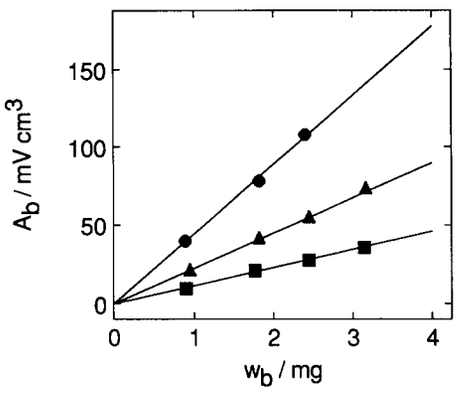

Figure 3 Benzene peak area (A_b) *versus* excess weight of benzene (w_b) in the injected solution (without column). Solvent compositions (ϕ_b, volume fraction benzene) were: (●) 0.80; (▲) 0.90; (■) 0.95

and without the column decreases as the benzene content of the solvent is increased (see *Figure 2*). As expected, when pure benzene ($\phi_b = 1$) was used as solvent the data obtained with and without the column lie on the same line.

According to equation (2b), the values of the slopes of the straight lines in *Figures 2* and *3* correspond to the area response constants for the polymer (K_p, *Figure 2*, without column), the solvated polymer (K_p^s, *Figure 2*,

Table 1 Preferential solvation parameters for the system PDMS–benzene–methanol at ~25°C

ϕ_b	$10^{-4}K_p^s$	$10^{-4}K_p$	$10^{-4}K_b$	λ_b
0.80	−1.56	−6.54	4.31	0.27
0.90	−6.88	−8.98	2.24	0.11
0.95	−9.48	−9.63	1.01	0.01
1.00	−10.95	−10.80	-	-

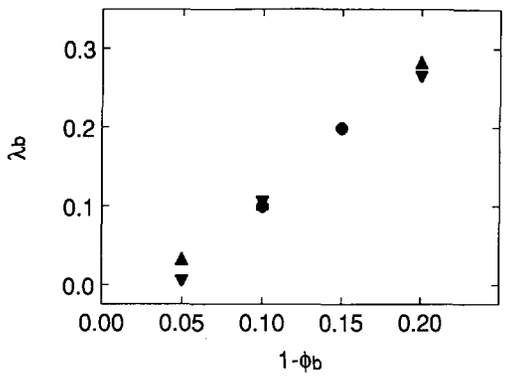

Figure 4 Dependence of the preferential solvation parameter for benzene (λ_b) on the composition of the mixture (volume fraction methanol, $1-\phi_b$) for the system PDMS–benzene–methanol: (▼) present work; (▲) from reference 4, g.p.c. by analysis of the area of the vacant peak; (●) from reference 1, dialysis equilibrium

with column) and benzene (K_b, *Figure 3*). These quantities are listed in *Table 1*, together with the preferential solvation parameters for benzene, λ_b, calculated according to equation (4). The values of λ_b are plotted against $(1-\phi_b)$, in *Figure 4*, together with the results for the same system reported by Campos *et al.*[4] from g.p.c. by analysing the area of the vacant peaks and by Hert and Strazielle[1] from measurements of dialysis equilibrium. The agreement of the present results with those from previous work shows that the proposed method is valid.

In common with previous work[3,4], the present method is simple and fast. However, in g.p.c. operations the sample solution is rigorously filtered before injection to avoid blocking the column with solid impurities. During filtration minor changes in solvent composition occur because of differences in the absorption on the filter and the evaporation of the two components. These unavoidable changes give rise to solvent signals unconnected with solvation of the dissolved polymer which have a deleterious effect on the accuracy and reproducibility of results based on measurements of the area of the solvent peak[3,4]. In the present work, preferential solvation parameters were obtained by comparing the areas of the solvated and non-solvated polymer peaks. The former area, measured with the column in place, was in direct proportion to the weight of polymer in the injected solution and a minor change in solvent composition had a negligible effect. The latter area, measured without the column in place, was the sum of the areas of the solvated polymer peak and solvent peak. Because no column was used unfiltered solutions could be injected directly into the system. Experimental precision was further improved by preparing sample solutions immediately before injection. As a consequence, the overall stability of the present method was very satisfactory without the need for special precautions.

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