Preferential solvation of solvent 1/polymer 2/polymer 3 ternary systems by gel permeation chromatography

Introduction

The preferential solvation of polymers in binary solvent mixtures is a well established phenomenon. It has been studied by different physicochemical[1–4] and spectroscopic techniques[5–8]. Gel permeation chromatography (g.p.c.) is a new tool to add to those techniques[9,10].

To our knowledge, there are no references about preferential solvation in ternary systems such as solvent 1/polymer 2/polymer 3. We wish to report here results on the determination by g.p.c. of preferential solvation parameters for the benzene/poly(dimethyl siloxane)/polystyrene system.

The experimental method followed is similar to that one of differential gel permeation chromatography used by J. F. Johnson and coworkers to determine polymer hydrodynamic dimensions[11,12]. The method involves dissolving polymer 3 in a solvent 1/polymer 2 mixture of known composition. The g.p.c. measurements are then made in the usual way.

Classical dialysis equilibrium measurements[4], with the appropriate pore size membranes in order to allow solvent 1/polymer 2 mixture to pass through them, have also been undertaken in order to test the reliability of the λ values obtained by g.p.c.

Results and discussion

When solvent 1 is preferentially adsorbed in a solvent 1/solvent 2/polymer 3 ternary system, the chromatograms of polymer 3 in a given solvent 1/solvent 2 eluent mixture show two peaks[9] corresponding to solvated polymer and to non-solvated solvent 2, h_2 being the height of the latter. When the eluent with an excess of component 2 is injected before any other polymer, the size, h_1, of the resulting solvent 2 peak happens to be related[9,10] to the solvent 1 excess volume fraction $\Delta\nu_1^0$. The λ preferential solvation parameter can be related to the sizes of solvent 2 peaks[10], h_1 and h_2, by:

$$\lambda = \frac{\Delta\nu_1^0 h_2}{c_3 h_1}$$

Low molecular weight poly(dimethyl siloxane) samples (PDMS) have been used instead of solvent as component 2. The results of the chromatograms obtained for different benzene/PDMS/polystyrene systems are indicated in *Table 1*. M_2 and M_3 are the PDMS and polystyrene molecular weights respectively; ν_1 is the benzene volume fraction, c_2 is the injected PDMS concentration yielding a peak, h_1 is the height, corresponding to an $\Delta\nu_1^0$ in benzene; c_3 represents the polystyrene concentration giving rise to an additional PDMS peak of height h_2. The preferential solvation parameters have been obtained by the above formula and they are indicated in *Table 1* as $\lambda_{g.p.c.}$. λ values obtained by dialysis equilibrium measurements (λ_{dia}) have also been collected in the Table.

No experimental complexities arise in the g.p.c. chromatograms with the use of a polymer as component 2. The PDMS elution volumes from chromatograms of PDMS in excess in the different mixtures were in accordance with the elution volumes of the additional peaks. The differences between $\lambda_{g.p.c.}$ and λ_{dia} are less than 8–10% and the agreement between λ's obtained from cumbersome classic techniques and from g.p.c. is then remarkable.

We have not found other data in the literature for comparison. However the λ values seem to be reasonable and they are of the same order of magnitude as those of a good solvent/poor solvent/polymer system, PDMS playing the role of a poor solvent. When molecular weight increases, incompatibility must also increase and a similar trend should be expected for preferential solvation as indeed happens to be the case. Moreover, λ values increase when polystyrene molecular weight decreases as occurs in binary solvent mixtures.

Further measurements are in progress and will be reported in the near future.

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Table 1 Determination of preferential solvation parameter for benzene/PDMS/polystyrene systems, from g.p.c. and dialysis equilibrium measurements

M_3	M_2	ν_1	$c_2 \times 10^2$ (ml/ml)	$\Delta\nu^0{}_1 \times 10^2$	h_1 (mm)	$c_3 \times 10^2$ (g/ml)	h_2 (mm)	$\lambda_{g.p.c.}$ (ml/g)	λ_{dia} (ml/g)
270 000	8700	0.940	0.203	0.191	52	0.190	19	0.36_6	0.33_7
						0.391	38	0.35_8	
						0.580	58	0.36_7	
135 000	1850	0.900	0.222	0.199	53	0.350	39	0.41_8	0.43_7
						0.520	59	0.42_6	
135 000	1100	0.890	0.213	0.189	52	0.200	20	0.36_3	0.32_6
						0.390	37	0.34_5	
						0.620	60	0.35_1	