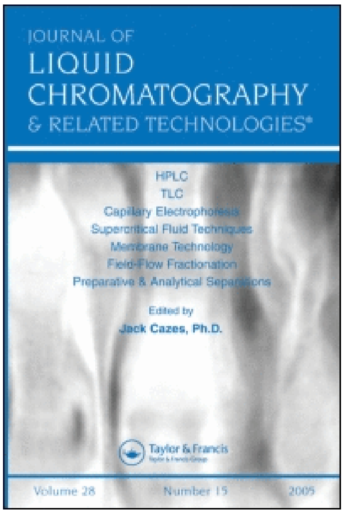

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PREFERENTIAL SOLVATION STUDY OF POLYVINYLPYRROLIDONE IN ORGANIC OR AQUEOUS MIXED SOLVENTS BY GPC.

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ABSTRACT

This paper deals with the use of gel permeation chromatography for the determination of the preferential solvation of polyvinylpyrrolidone in binary solvent mixtures. It is the first time that this technique is applied to preferential solvation in both organic and aqueous systems. With this rapid and accurate method, we determined values of the preferential solvation coefficient λ_1, which are compared with those obtained by light scattering or dialysis equilibrium.

INTRODUCTION

The preferential solvation phenomenon, which occurs when a polymer species is dissolved in a binary solvent mixture, is classically studied by light scattering ([1]) and dialysis equilibrium ([2]).

More recently, gel permeation chromatography (GPC) was suggested by Berek, Bleha and Pevna ([3]) for this purpose. Such a preferential solvation of a polymer by one of the solvents renders the solvent composition close to the molecular chains different from that which exists at a longer distance. A GPC analysis of a ternary mixture, using the same binary solvent as mobile phase, allows separation of the solvated polymer from the injected solvent which remains. As a result, a chromatographic peak corresponding to the solvent in excess relative to the initial composition is observed, in addition to the classical polymer peak.

The first GPC quantitative study of preferential solvation was carried out on polystyrene, but it was for a single composition of the solvent mixture : benzene (77.8 %)/methanol (22.2 % v/v) ([3]). Simultaneously with our work ([4]), another GPC study was published on polymethylmethacrylate and polydimethylsiloxane preferential solvation, for a wide range of benzene/methanol compositions ([5]).

We previously described the preferential solvation of polyvinylpyrrolidone (PVP) in organic mixed solvents by light scattering ([6]), infrared spectroscopy ([7]) and ^{13}C NMR solvent relaxation time ([8]) and we present here a quantitative study by GPC.

Fortunately, PVP is soluble both in organic and aqueous solvents ; thus, we carried out GPC experiments with 1,2-dichloroethane (DCE)/ ethanol and water /dioxan mixtures. In the former binary solvent mixture, PVP exhibits an inversion of preferential solvation (DCE in concentrated ethanol mixtures and conversely) and we wanted to confirm this by GPC. In water/dioxan mixtures, PVP leads to a phase separation with dioxan compositions greater than 73.5 % v/v. However, we succeeded in evaluating the preferential solvation in coacervates through GPC measurements of the solvent compositions of the corresponding supernatants.

MATERIALS AND METHOD

Chemicals

PVP (viscometric molecular weight : 700,000) from U.C.B., Brussels, was lyophilized and stored under vacuum. Anhydrous absolute ethanol was kept under nitrogen and DCE distilled over P_2O_5. Dioxan "UCB" and demineralised water were, respectively, filtered on FH and GA Millipore membranes before their mixing.

Apparatus

The GPC instrument used was a Waters Associates ALC 201 equipped with an M-6000 solvent delivery system, a U6K universal injector and an R-401 differential refractometer.

Materials

For organic mixtures (DCE/ethanol), the stationary phase was Styragel, 10^3 Å (particle size : 15-25µ). This porous material excludes molecular weights higher than 40,000 and its swelling does not vary with the binary solvent compositions used in the present work . The column (60 cm length, 7 mm I.D.) was packed in the Laboratory with the gel previously swollen in a DCE/ethanol (48.6 % v/v) mixture. The efficiency is about 1,200 plates per foot at a flow rate of 2 ml/min. Injection volumes (90µl) were picked up from PVP solutions (4-10 mg/ml).

For aqueous mixtures, we used a series of two micro-Bondagel columns (Waters Assoc.) consisting of one type E-300 and one type E-500 (MW exclusion limits of 100,000 and 500,000, respectively). The efficiency of this rigid material is about 5,000 plates per foot at a flow rate of 0.5 ml/min. The small dimensions of these columns lead to a small void volume ≃ 3.2 ml and total solvent volume ≈ 5.6 ml. Injection volumes were 25µl for PVP solutions (2 to 10 mg/ml).

Method

As an example, Figure 1 shows the chromatogram recorded with a PVP/dioxan/water mixture (volume fraction = 0.3 in Dioxan). The polymer peak, located at the void volume $V_o = 3.2$ ml, is followed by a positive peak ($V_e = 5.7$ ml) of the excess solvent (dioxan). For PVP/DCE/ethanol systems, the solvent peak is either positive or negative according to the mobile phase composition. For 75 % in ethanol, the solvent peak is negative (ethanol in excess) as shown in Figure 2a.

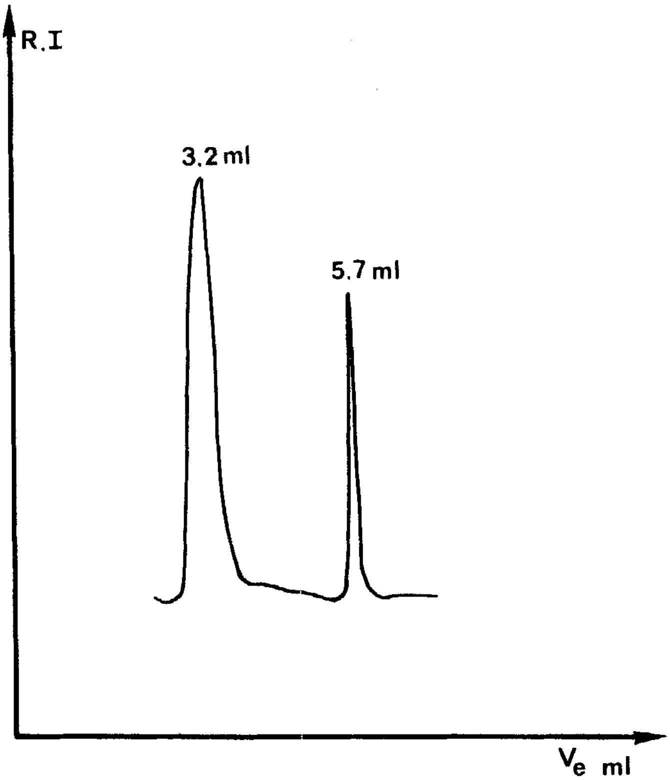

Figure 1 : Typical chromatogram with PVP/dioxan/water system (solvent volume fraction 0.3 in dioxan). Microbondagel E 300 and E 500. Flow rate : .5 ml/min. Injection volume : 25µl. PVP concentration :7.18mg/ml. Detector sensibility : 4x.

In addition, traces of water in injected mixtures disturb the phenomenon and produce a negative peak located slightly before the solvent peak (see Figure 2a). By injecting binary mixtures containing water traces (Figure 2b), we have then observed that the water peak (V_e = 20.9ml) was associated with a DCE peak (V_e = 25ml), in relation with the preferential solvation of water by ethanol. For each composition of solvent mixture, the ratio of DCE/water peak heights is constant. Such an induced DCE peak over-

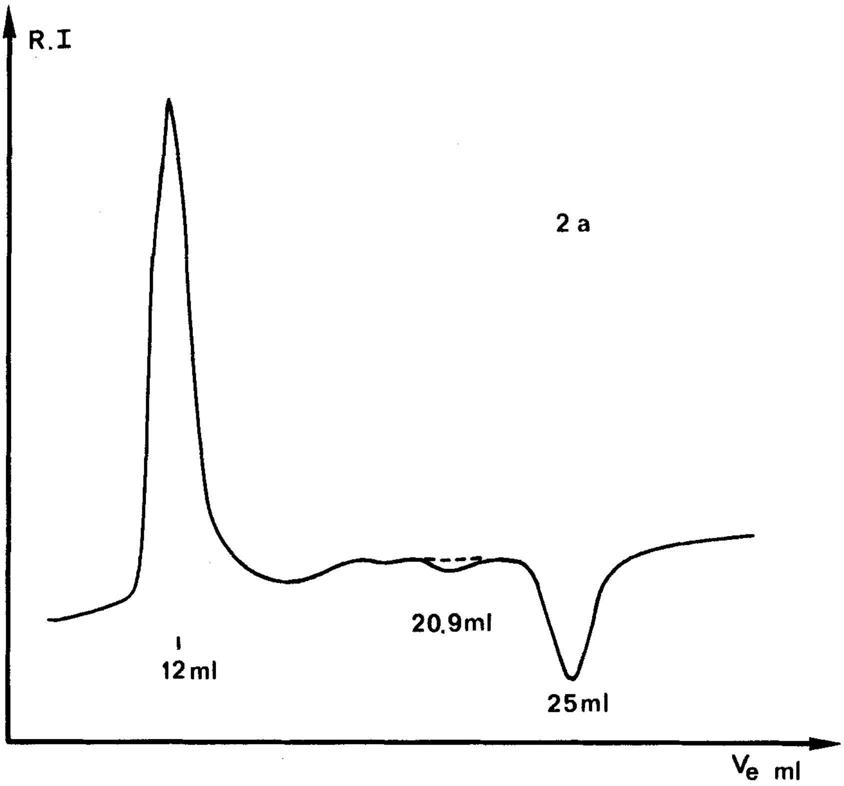

Figure 2a : Typical chromatogram with PVP/DCE/ethanol system (ethanol volume fraction ϕ_I : 0.75). Styragel 10^3Å. Flow rate : 2 ml/min. Injection volume: 90µl. PVP concentration : 4.68 mg/ml. Detector sensibility : 8x.

laps the peak resulting from the polymer preferential solvation (see Figure 2c). The corrected height of the solvent peak is, consequently, the algebraic summation of the experimental and water solvation peak heights. In this example, we can consider that correction is weak (< 10%), assuming that water, introduced in the ternary system, does not disturb the solvation in the vicinity of the polymer. We have noticed that polymer solutions containing water traces lead, after correction, to a preferential

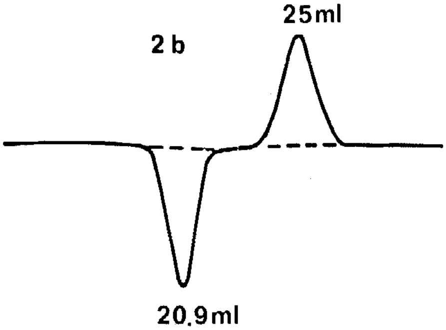

Figure 2b : Preferential solvation induced by water traces in a DCE/ethanol binary mixture.

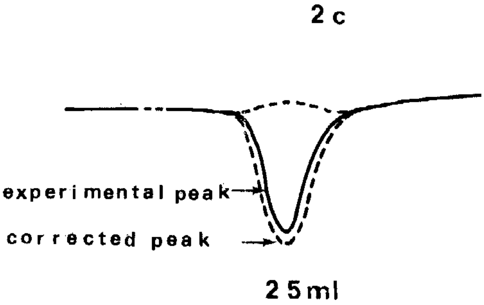

Figure 2c : Correction of the solvent peak on account of water traces.

solvation coefficient very close to that obtained with anhydrous ternary solutions. The use of very high resolution columns makes the water trace detection and correction of the solvent peaks easier. The same precautions have to be taken in the study of aqueous systems, where the water peak is easily detectable by injections of binary solvents enriched in water.

Berek et al. ($^{9-11}$) recently carried out a systematic study of the different parameters involved in polymer elution by GPC and also emphasized the importance of the anhydrous character of eluants (^{9}).

Determination of preferential solvation by GPC

For every solvent (1)/solvent (2)/polymer (3) system studied, solvent (1) always indicates the proton donor one (ethanol or water). Basically, in such ternary systems, preferential solvation is quantitatively characterized by the preferential adsorption coefficient λ_1 ([12]) which represents the volume $\Delta v'_1$ of the solvent (1) in excess in the vicinity of the chains, per polymer gram. In GPC experiments ([3-5]), this volume can be related to the solvent peak height h, through a calibration obtained by injecting solvent binary mixtures with compositions ϕ'_1 very close to the composition ϕ_1 of the mobile phase, which leads to :

$$h = k.\Delta v'_1 \simeq k(\phi_1 - \phi'_1).v_s$$

where v_s is the injection volume.

The calibration curve $h = f(\Delta v'_1)$ we obtained is a straight line which allows us to readily determine $\Delta v'_1$ from h. For a dilute polymer solution (concentration c_3) in a given binary solvent, the injection of a volume v_p (polymer amount : $q = c_3.v_p$) gives :

$$\lambda_1 = \frac{\Delta v'_1}{q} \qquad (1)$$

RESULTS AND DISCUSSION

PVP/DCE/ethanol system

In order to determine the preferential solvation of PVP in every solvent binary mixture, we injected successively, three times at least, 90µl of polymer solutions at three different concentrations. Calibration binary mixtures ϕ'_1 were made by adding a very small volume of one of the solvents to mixtures of composition ϕ_1. Experimental results corresponding to $\phi_1 = 0.75$ (chromatogram of Figure 2a) are given in Table 1, after correction for traces of water and recalculation for an injection volume of 100µl. Preferential solvation coefficients, λ_1, are directly calculated through relation (1) by using suitable calibration.

TABLE 1

Polymer solutions c_3 (mg/ml)	Corrected h	h for 100µl	$\Delta v'_1$ x 10^3 ml	λ_1
3.84	- 1.8	- 2	- 0.13	- 0.34
4.68	- 2.02	- 2.25	- 0.145	- 0.32
5.10	- 2.07	- 2.30	- 0.15	- 0.30

λ_1 negative values represent preferential solvation of the PVP chains by DCE in this solvent mixture.

We present, in Table 2, the results obtained in the entire range of solvent compositions. For every volume composition ϕ_1, only one experimental value which is the nearest of the mean value is tabulated.

TABLE 2

ϕ_1	c_3 (mg/ml)	h_{100} (cm)*	$\Delta v'_1$ x 10^3 (ml)	λ_1 ml.g^{-1}
0.10	5.58	3.95	0.22	0.40 ± 0.03
0.17	9.1	7.20	0.35	0.38 ± 0.04
0.25	8.46	3.55	0.285	0.34 ± 0.03
0.35	5.02	1.00	0.07	0.13 ± 0.02
0.42	9.45	- 0.85	- 0.07	- 0.08 ± 0.03
0.486	6.75	- 1.45	- 0.11	- 0.16 ± 0.04
0.55	7.40	- 2.90	- 0.175	- 0.23 ± 0.03
0.65	4.92	- 2.60	- 0.16	- 0.33 ± 0.02
0.75	4.68	- 2.25	- 0.145	- 0.32 ± 0.03
0.85	7.40	- 1.95	- 0.13	- 0.17 ± 0.03

*Detector response sensibility : 8x.

The variations of preferential solvation coefficient λ_1 obtained by GPC and previously by light scattering (6) are plotted in Figure 3 as a function of ϕ_1. We have here recalculated

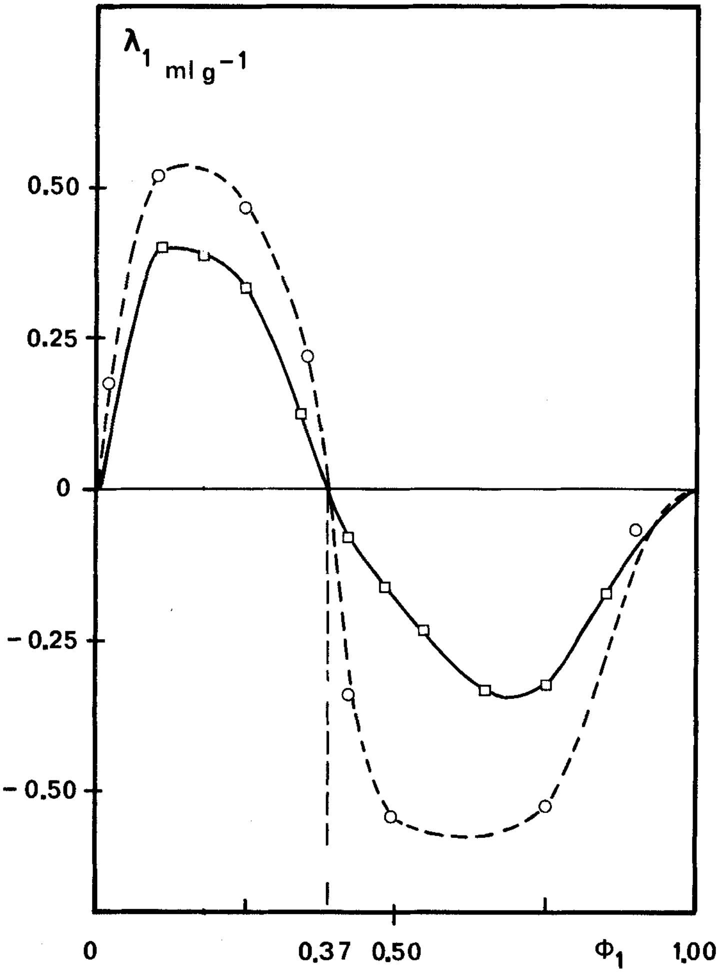

Figure 3 : Preferential solvation coefficient λ_1 vs volume fraction of ethanol (ϕ_1) for PVP/DCE/ethanol system. (□) : GPC results ; (○) : light scattering results (6).

the coefficients λ_1 from light scattering ([4,6]) by using a right value of the constant $dn_{12}/d\phi_1$ term. The same inversion of preferential solvation is observed with the two methods, for approximately the same value of ϕ_1. However, the exact determination, by GPC, of this inversion is difficult because the hygroscopic character of the solvents leads to the disturbing phenomenon caused by water traces whose magnitude, in this composition range, is of the same order of magnitude as the polymer preferential solvation. In fact, the accuracy of λ_1 values depends on accuracy of peak height measurements, calibration, polymer concentration and corrections for water traces. Results are reproducible when every measurement is performed within a short period of time (5-6 hours).

Recently, Dondos ([13]) pointed out variations of preferential solvation with the polymer molecular weight for the poly2-vinylpyridine/ethanol/cyclohexane system. He showed that preferential solvation by the inert solvent increases when molecular weight decreases. We checked this molecular weight effect on our system for $\phi_1 = 0.65$, with PVP samples in the range of 40,000 - 360,000 molecular weight, but we did not find any significant variation.

PVP/dioxan/water system

At room temperature, PVP (3)/dioxan (2)/water (1) mixtures, dilute in polymer, are homogeneous up to a volume composition of 0.735 in dioxan. Above this limit, polymer precipitation occurs, leading to a phase separation. We carried out experiments on preferential solvation in both homogeneous and heterogeneous ranges.

For homogeneous systems, the chromatograms obtained have the same shape as chromatogram represented in Figure 1. For the whole range of homogeneous compositions ($0 < \phi_2 < 0.735$), the polymer peak, located at the dead volume, is followed by a solvent positive peak corresponding to excess dioxan and resulting from a preferential solvation of polymer chains by water. All the general observations made for the previous organic system are the same except for injection volumes that are smaller here (< 25μl), because of the characteristics of μ-Bondagel columns. Experimental results, expressed as a function of volume composition of the solvent (2) (dioxan), are given in Table 3.

In Figure 4, variations of preferential solvation coefficient λ_1, determined by GPC and dialysis equilibrium ([14]), are plotted as a function of the volume composition ϕ_2. The GPC and dialysis results are in rather good agreement and show that preferential adsorption of water is weak when the solvent composition is lower than 50% in dioxan and that a rapid increase of PVP solvation by water occurs between 50% and 73.5%. In addition, an inversion of preferential solvation does not occur in this system and, consequently, there is no preferential adsorption of dioxan. Water/dioxan system is characterized by very different molar volumes of the two solvents, whereas these parameters are close in the previous organic binary solvent mixtures. Thus, λ_1 values, expressed in ml of solvent in excess per polymer gram, give under-estimated values of water

TABLE 3

ϕ_2	c_3 (mg/ml)	h_{100} (cm)*	$\Delta v_2' \times 10^3$ (ml)	λ_1 ml.g^{-1}
0.10	8.2	2.8	- 0.012	0.03 ± 0.01
0.20	5.5	4.7	- 0.032	0.06 ± 0.02
0.30	7.18	9.8	- 0.057	0.08 ± 0.01
0.40	7.44	6.0	- 0.0835	0.11 ± 0.01
0.50	5.42	12.5	- 0.084	0.16 ± 0.01
0.60	7.14	25.6	- 0.22	0.29 ± 0.02
0.70	4.64	18.2	- 0.183	0.40 ± 0.02
0.72	2.24	9.1	- 0.047	0.42 ± 0.01

*detector response sensibility : 8x

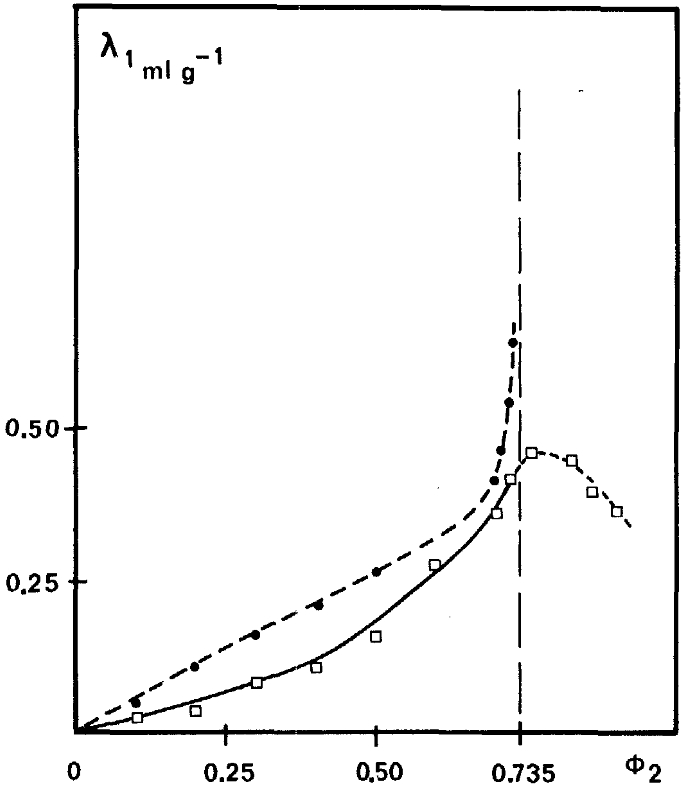

Figure 4 : Preferential solvation coefficient λ_1 vs volume fraction of dioxan (ϕ_2) for PVP/dioxan/water system. (□) : GPC results ; (●) : dialysis equilibrium results (^{14}).

concentrations in the vicinity of polymer chains, that should be practically more important.

For heterogeneous systems, the preferential solvation of PVP in coacervates can be studied by GPC, by injecting samples of supernatants. Thus, the volume of one of the solvents in excess in every supernatant can be determined and, consequently, leads to the evaluation of the volume of the other solvent in excess in the corresponding coacervate. Strictly speaking, the excess solvent volume in a coacervate cannot be directly related to the preferential solvation coefficient since such a phase may contain both "free" and preferentially adsorbed solvent. However, as the amount of solvent in the coacervates we studied is very weak, we assumed that solvent volumes in excess in that phase, correspond as a whole to the preferential solvation of the coacervated chains. Results are given in Table 4 for volume compositions between 0.77 and 0.90. Above $\phi_2 = 0.90$, it is not possible to dissolve PVP at high temperature, so as to get a phase separation at room temperature and, therefore, GPC experiments cannot be carried out.

λ_1 values are plotted in Figure 4 ; they show that preferential solvation by water varies without discontinuity when we cross through the demixing limit. This continuity seems to prove that the whole solvent in the coacervate is quite preferentially adsorbed.

INTERPRETATION

The GPC method allowed us to confirm the preferential solvation of PVP in mixtures of either DCE/ethanol (Fig. 3) or dioxan/water (Fig. 4). For the former system, variations of preferential solvation, obtained by GPC and light scattering, have the same shape and the solvation inversion detected by these methods occurs for approximately the same solvent composition.

TABLE 4

ϕ_2	c_3 (mg/ml)	h_{100}(cm)[x]	$\Delta v_2' \times 10^3$ (ml)	λ_1 $ml.g^{-1}$
0.77	6.42	26.0	0.305	0.46 ± 0.02
0.82	4.30	15.2	0.194	0.45 ± 0.02
0.858	10.80	17.8	0.435	0.40 ± 0.02
0.90	3.40	4.8	0.125	0.37 ± 0.02

[x] detector response sensibility : 8x

However, preferential adsorption coefficient values λ_1 given by GPC are systematically smaller than those deduced from light scattering. For homogeneous PVP/dioxan/water mixtures, GPC results are also smaller than the ones determined by dialysis equilibrium.

On the contrary, Berek et al. (^{3}) obtained the same values by GPC and light scattering, for a polystyrene/benzene/methanol mixture. Campos et al. (^{5}) came to the same conclusion with polydimethylsiloxane/benzene/methanol system but observed that GPC values are greater than dialysis ones when polymethylmethacrylate is preferentially solvated by methanol and attributed that difference to an adsorption phenomenon onto the packing. We checked that λ_1 values we determined did not depend upon the packing nature by testing some PVP/DCE/ethanol mixtures on both Styragel and μ-Bondagel.

As λ_1 represents the solvent (1) volume in excess per polymer gram, we must admit that GPC defines a solvent volume near every polymer chain which is smaller than the one involved in the other methods (light scattering or dialysis). In other words, solvent molecules, dynamically eluted with polymer chains at the column dead volume, do not correspond to the solvent molecules statically perturbed by the chains, in the light scattering and dialysis methods. This remark points out the ambiguity for defining the solvent volume which preferentially solvates the polymer chains, for it depends upon the method used.

CONCLUSION

We systematically studied by GPC preferential solvation of PVP in binary mixed solvents DCE/ethanol and dioxan/water, in the whole range of polymer solubility. In addition, by determining water/dioxan compositions surrounding the polymer chains in coacervates, we could evaluate the preferential solvation coefficient beyond phase separation which is not experimentally accessible by the other classical methods.

GPC is a very suitable technique for the study of preferential solvation of polymer in organic or aqueous mixed solvents. It involves weak amounts of polymer and measurements are relatively rapid. The main condition concerns the choice of packing which must be rigid enough to avoid swelling variations with changes of solvent composition, and highly efficient to permit the detection of water traces that disturb the accurate determination of polymer preferential solvation.

In the present work, we did not analyze elution volumes of solvated polymer peaks which could provide interesting information about polymer behaviour in these systems. This more sophisticated study will be soon carried out by using a more suitable column set and viscometric detection (^{15}) which is needed to observe variations of polymer hydrodynamic volumes.

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