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Viscometric Behaviour of PMMA(3)/THF(1)Water(2) System

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SUMMARY

We have studied the PMMA viscometric behaviour in the polar binary mixture THF(1)/water(2). The results obtained point out that this mixture presents a synergistic effect in the composition interval $0 < u_2 < 12\%$ (w/w) water. We have found also a sharp variation of the PMMA unperturbed dimensions, K_θ, which can be due to a conformational change. Starting from the evaluation of the intermolecular interaction parameter, B, and the Mark-Houwink-Sakurada exponent, the theta composition of the system has been determined.

INTRODUCTION

In the last year it has been a growing interest in the study of polar polymers solved in polar binary mixtures (KATIME-VALENCIANO, 1979, 1980), where interesting phenomena such as cosolvency (GARGALLO et al., 1980, 1981), non-cosolvency (HORTA, 1981), preferential solvation (KATIME-STRAZIELLE, 1977), conformational transitions (DONDOS 1972) and variations in the polymer unperturbed dimensions (SPYCHAJ et al. 1979) has been observed.

In this work we have continued the viscometric study of the atactic PMMA behaviour in polar binary mixtures: solvent(1)/water(2).

The system acetone(1)/water(2) has been studied in a previous work (KATIME-CESTEROS) and in this one we have remplaced the first component of the binary mixture by THF.

In this work we aim to verify that the Dondos and Patterson predictions relating the excess Gibbs free energy, G^E, to the intrinsic viscosity variations in very polar systems, are true.

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EXPERIMENTAL

This study was carried on with five fractions of atactic PMMA prepared by free radical polymerization at 343 K in benzene using 1,2 azobisisobutyronitrile. The weight-average molecular weights, M_w, were determined by light scattering in benzene at 298 K as described previously (KATIME et al. 1979a). The weight-average molecular weights of the fractions used were: $1.075 \cdot 10^6$, $5.50 \cdot 10^5$, $4.84 \cdot 10^5$, $2.30 \cdot 10^5$ and $2.10 \cdot 10^5$.

Viscosities of the binary solvents and of solutions in the concentration range 0.25-1.0 g/dl, at 298 K, were measured in capilary viscometer of such dimensions that shear effects were negligible. Kinetic energy corrections were made where applicable. Intrinsic viscosities were obtained by extrapolation of linear plots of η_{sp}/c and $\ln \eta_r/c$ against c by the method of least squares.

To purify the solvents, they were preliminary treated and fractionally distilled before their use according to a standard method. The solvent was used inmediately after purification.

Solvent mixture of THF/water were made up by weight. The refractive index of the solvents and the binary solvent mixtures was measured with a Abbé refractometer at 298 K.

RESULTS AND DISCUSSION

In the Table 1 we present the intrinsic viscosity, $\{\eta\}$, values for five PMMA fractions as a function of the binary mixture composition u_2. As it can be seen, the viscometer behaviour of this system presents a pronunced synergistic effect, particulary important in the fractions of higher molecular weights, in which the addition of water highly affect its viscosity. This fact is in agreement with the Dondos and Patterson (1979) predictions, that related the viscosity with the Gibbs free energy, G^E, of the binary mixture used as solvent.

The THF(1)/water(2) mixture is a system that strongly deviates from the ideal behaviour, because it presents a negative excess volume, an in spite of this, its excess free energy, G^E, is positive in the whole composition range (SIGNER et al. 1969). The last fact is responsible for the observed viscosity increment, which presents a maximun for the THF(1)/water(2) mixture composition,

TABLE 1. Intrinsic viscosity of the system PMMA(3)/ THF(1)/water(2) as function of binary solvent mixture, u_2, at 298K.

	$\{\eta\}$ dl/g							
$M.10^{-5}$	0%	3%	6%	9%	12%	15%	18%	21%
10.75	1.85	1.91	2.04	1.98	1.88	1.68	1.47	1.15
5.50	1.13	1.16	1.18	1.18	1.14	1.03	0.90	0.78
4.84	1.06	1.13	1.09	1.10	1.09	0.99	0.90	0.74
2.30	0.59	0.61	0.62	0.61	0.61	0.60	0.56	0.50
2.10	0.57	0.58	0.58	0.57	0.56	0.55	0.51	0.45

6% (w/w) water.

For higher compositions, a viscosity decrease can be observed, this is caused by the high proportion in water, which is a precipitant for PMMA. The solubility test accomplished for this system, indicate us that the PMMA is soluble in the THF(1)/water(2) mixtures up to compositions close to 25% (w/w) water.

The values of the unperturbed dimensions, K_θ, and the long range interactions parameter, B, where determined by the Stockmayer-Fixman equation:

$$\{\eta\}M^{-1/2} = K_\theta + 0.51\Phi_o BM^{1/2}$$

In figure 1 and 2 the values of these parameters can be observed as a function of the solvent binary mixture composition.

It is to be remarked the existence of an important lack of continuity in the K_θ values, which can be attributed to the existence of a conformational change in the macromolecular coil. This phenomenon has been already observed for the PMMA solved in polar binary mixtures (DONDOS 1972; KATIME et al. 1980), and its magnitude for our system is about 12 per cent. It is also important to emphasize that in the composition range where the new conformation becomes stabilize, important lack of continuities are not appreciate and that it coincides exactly with the viscosity maximum.

In this interval the values of the long range interaction parameter B are also maximum, all this lead us to think that the coil expansion by the solvent masks the decrease of its unperturbed dimensions.

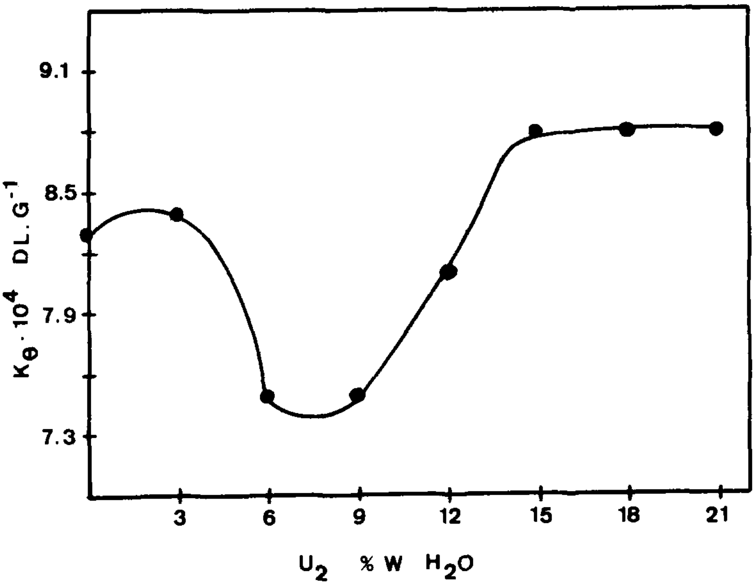

Figure 1. Variation of K_Θ parameter as a function of binary mixture composition, u_2

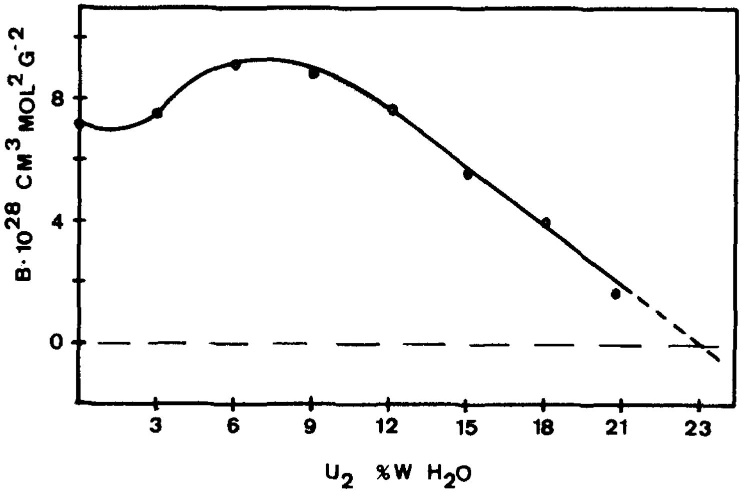

Figure 2. Variation of B parameter as a function of binary mixture composition, u_2

It still remains unexplained which is the process that induced the conformational transitions in the macromolecular coil. We think that this is provoked by a selective adsorption of water molecules, which would settle on the lateral groups of the PMMA chains, probably due to the hydrogen bond formation with the carboxilic groups of the PMMA. As the PMMA is an appreciable polar polymer, these >C=O groups must be the principal responsible for the short distance interactions, and therefore, for the unperturbed dimensions of the chain.

The THF would stabilize at different conformation, since the interactions of this solvent (moderately polar) with the carboxilic groups would be much smaller than those produced with the water molecules, which can easily establish hydrogen bonds with these groups and even interconnet different lateral groups, leading to an increment of flexibility in the coil with the resulting diminution of the unperturbed dimensions.

These hypothesis of water adsorption is supported by other results found for PMMA in solvent/precipitant mixtures in which the precipitant is adsorpted for alcohols (KATIME-STRAZIELLE 1977) as well as for water itself (KATIME-CESTEROS), in mixtures with low proportions of precipitant.

When the solvent increases its water content, we find the opposite phenomenon, on one hand it is logical that the macromolecular coil tends to surround itself with the good solvent (THF) and on the other it is feasible to think that the water enrichment of this mixture will make its molecules to have more tendency to interact and associate between them than with the macromolecular coil, establishing again a new conformation of similar characteristics than the original one, although having a higher value of K_Θ, which agrees with the Dondos and Benoit (1968) hypothesis about the influence of the G^E on the unperturbed dimensions in mixed solvents.

With respect to the long range interaction parameter, it begins to decrease in a practically linear way from a 12% in water, and therefore by extrapolation to $B = 0$ we can determine the Θ-composition of this mixture for the PMMA which approximately corresponds to a 23% of water as it can be seen in the figure 2.

The application to our system of the well-know Mark-Houwink-Sakurada viscometric equation $\{\eta\} = KM^a$, gives satisfactory results; in table 2, the values of K and a for the different compositions studied, can be seen. The variations of the B parameter and the a exponent are similar, which corroborate the synergistic effect, and besides, the extrapolation to Θ conditions (a = 0.50), leads to the same composition value as the one obtained by using the intermolecular interaction parameter, B.

TABLE 2. Values of the Mark-Houwink-Sakurada constants K and a for different binary solvent mixtures, u_2, at 298 K, of the system PMMA(3)/THF(1)/water(2)

u_2 % water	$K.10^5$ dl/g	a
0	8.68	0.72
3.0	8.27	0.72
6.0	5.89	0.75
9.0	6.01	0.75
12.0	8.11	0.72
15.0	17.42	0.70
18.0	27.8	0.62
21.0	57.8	0.55

Likewise, we have confirmed for this system the linearity of the log K versus 1/a plot, which corresponds to the equation

$$\ln K = C - \frac{D}{a}$$

where C = -10.3 and D = -4.80. This type of linearity has already been observed by other authors in similar systems (SPYCHAJ et al. 1979: AHARONI, 1977).

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