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Selective Adsorption of PMMA in Polar Binary Mixtures
3. Chloroform(1)/Acetic Acid(2)

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SUMMARY

In this paper, we study the behaviour of PMMA(3) in the polar binary mixture chloroform(1)/acetic acid(2). In this system chloroform is preferentially adsorbed by PMMA in the range $0 < u_2 < 89\%$ acetic acid. From this composition a weak adsorption of acetic acid has been detected; this can be explained suppossing an specific interaction between the polymer and the acetic acid, which might be of dipole-dipole type or by hydrogen bond.

INTRODUCTION

Systematic work on thermodynamic properties of polymers in binary solvent mixtures has been done quire recently. However, a considerable amount of papers about this subject have been reported by now (KATIME et al. 1975; DONDOS, BENOIT 1968; HERT et al. 1973). When solvent mixtures are used, a serie of peculiarities which are not observed in single solvents appear. In fact, if both solvents interact in a different way with the polymer, a selective adsorption of one of the components in the binary mixture by the polymer will occur, due to this, the local composition of the binary solvent mixture in the enviroment of the macromolecule will be different than in the enviroment of the solution. This fact sometimes produce paradoxical behaviours (DONDOS, BENOIT

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1970; HERT, STRAZIELLE 1973).

In general, most works have been done with no-polar binary mixtures. However, when polar binary mixtures are used other phenomena occur as a consequence of the existence of specific interactions between the different dipoles existing in the solution (LETY-SISTEL et al.1973; CHAUFER et al. 1975).

In this paper, the obtained results for the PMMA(3)/Chloroform(1)/Acetic acid(2) system will be presented to continue the study, which has been already started, about this kind of mixtures (KATIME, VALENCIANO 1979a; KATIME et al. 1979b).

EXPERIMENTAL PROCEDURES AND RESULTS

A PMMA sample was obtained by radical polymerization of methyl methacrylate (Fluka purum) at 323 K using 1,2-azobisisobutyronitrile (Fluka puriss)as initiator. These sample was fractionated by solubility in the benzene/methanol system and·one fraction was used. The weight average molecular weight was determined by light scattering in p-dioxane, ethyl acetate, chloroform and acetic acid, and found to be $2.80.10^5$. Molecular weight distribution on this fraction showed that $\bar{M}_w/\bar{M}_n < 1.3$.

Solvent mixtures were characterized by its volume fraction u_2 in acetic acid. The refractive indices of the solvent and of the binary solvent mixtures were measured with a Abbé refractometer at 298 K.

The preferential adsorption coefficient has been calculated by light scattering using the equation (STRAZIELLE BENOIT 1961)

$$\lambda = \{(\frac{M^*}{M})^{1/2} - 1\}\frac{(dn/dc)}{(dn/du)}$$

where M and M* are the weight average molecular weights of the polymer in pure and mixed solvents, respectively. The refractive index increments, dn/dc, for green light were measured in a Brice-Phoenix differential refractometer and employing a sealed-type differential cell with ground-glass stoppers to prevent loss of the solvent. The viscosities were measured by means of an Ubbelhode suspended level viscometer prepared for dilution in situ at 298 K: kinetic energy correction was made.

DISCUSSION

In this system both components in the binary mixture behave as good solvents for the polymer, so it can be expected the PMMA to adsorb preferentially one of them which is usually the better solvent and in this case it is the chloroform. All of this is fulfilled in this system although several interesting facts are observed which differ from the theoretically expected behaviour. As shown in figure 1, chloroform is greatly adsorbed in the range 89> u_2 < 0 range. When u_2 = 89 per cent in acetic acid, an inversion in the solvation appears and,

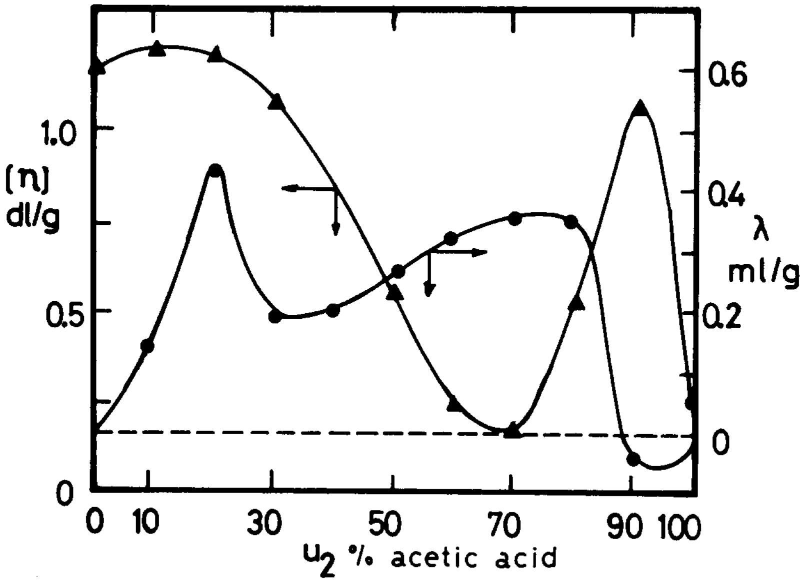

Figure 1. Plot of λ and {η} as a function of binary mixture composition.

acetic acid is preferentially adsorbed for higher compositions. This adsorption of acetic acid on PMMA can be explained supposing an specific interaction between the polymer and the solvent which might be of dipole-dipole type or by an hydrogen bond between the carboxilic group of the PMMA side-group and the hydrogen of the OH group of acetic acid. On the other hand, studying the range where the adsorption of the chloroform is produced, an increase of the phenomenon takes place between $0< u_2<30$ per cent acetic acid which indicates that the contacts chloroform-PMMA (1-3) increase referred to the (2-3) ones. A similar behaviour is observed in the variation of the intrinsic viscosity as a function of binary mixture composition (figure 1).

According to Zivny et al.(1967), the variation of the intrinsic viscosity with composition must decrease monotonously in those cases in which λ is positive for the whole composition range. However in this system, a maximum in $\{\eta\}$ is observed located at $u_2 \simeq 20$ per cent acetic acid. This anomalous fact, as we shall see later, is a consequence of the existence of a conformational change in PMMA due to the strong solvation of the polymer by chloroform. This conformational change leads to a decrease of molecular dimensions and therefore a decrease of intrinsic viscosity. The other maximum which appears at $u_2 \simeq 90$ per cent acetic acid is dued to the inversion of the preferential solvation ($\lambda = 0$ at $u_2 \simeq 89$ per cent acetic acid).

On the other hand, the decrease of the preferential adsorption coefficient, λ, at $u_2 = 20$ per cent acetic acid leads us to think that the PMMA suffers a conformational change at this composition (DONDOS 1972; KATIME, STRAZIELLE 1977a). To confirm this conformational change dn/dc measurements have been made as function of binary mixture composition, u_2. As can be seen in figure 2, the shape of the curve confirms the existence of a

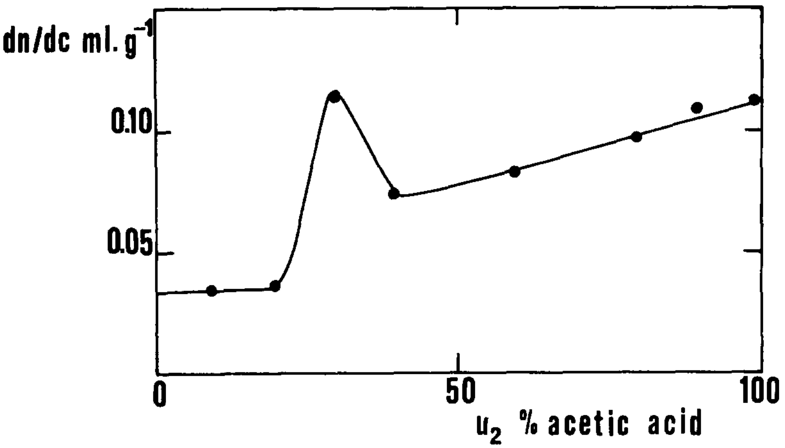

Figure 2. Plot of dn/dc as a function of binary mixture composition, u_2.

conformational transition in the polymer(KATIME et al. 1977b). To explain the existence of this phenomenon, it must be supposed that the strong adsorption of the chloroform by the PMMA is the one which gives enough energy to jump the potential barrier of the carbon atoms of the main chain, so that these ones can rotate with greater freedom around their valence cones. The inmediate consequence of this conformational change is a greater flexibility of the chain and so, a decrease of the molecular dimensions (KATIME et al. 1974) must be obtained.

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