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Thermodynamic properties of poly(ethyl methacrylate) in binary mixtures

2. Ethyl acetate/ethanol

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SUMMARY

Behaviour of poly(ethyl methacrylate) (PEMA) in ethyl acetate/ethanol system has been studied. Preferential sorption of ethyl acetate in the composition range studied has been observed. This is justified for the self-association of alcohol and the formation of 1:1 complex between this one and ethyl acetate.

INTRODUCTION

The ternary systems have been object of a great deal of theoretical and experimental works (Katime et al. 1979; Katime et al. 1977; Abdel-Azim, Huglin 1982) due to the advantages arising with regard the binary systems. One of such advantages is that, starting from the characteristics of each one of the pure liquids of the solvent mixture, it is possible to obtain a continuos gradation of the solvent medium properties as a function of composition, such as in the case of the polymer/solvent/precipitant systems, of general use on the fractionations by solubility.

Among the characteristics of this type of systems is the preferential solvation (Katime et al. 1985; Cesteros et al. 1986), which is due to differences of thermodynamic quality and liquid molecules size of solvent binary mixture.

In this paper we report the thermodynamic behaviour of poly(ethyl methacrylate)(PEMA) in ethyl acetate/ethanol mixture by laser light scattering, differential refractometry and viscometry.

EXPERIMENTAL

Polymer. Polymer was obtained by radical polymerization from ethyl methacrylate (Fluka) at 333 K, using 1,2 azobis

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*To whom correspondence should be addressed (isobutyronitrile) (AIBN) (Fluka puriss) as initiator. The polymer was fractionated by solubility in acetone/acetone + water system. The molecular weight of each fraction was determined by gel permeation chromatography (GPC), laser light scattering and membrane osmometry. Polydispersities lower than 1.27 was obtained.

Liquids. Ethyl acetate (Merck p.a.) and ethanol (Merck p.a.) were purified and bidistilled before use. The binary mixtures were made up by volume, belonging their composition to fraction in volume of ethanol before mixture.

Laser light scattering. Light scattering measurements have been made in a photogoniodiffusometer model FICA 42000 equiped with a He-Ne laser (Spectra Physics) that emit to wavelength 633 nm. The pure liquids and the solutions have been clarified by centrifugation for 90 min. at 14000 rpm. The Zimm plot (Zimm 1948) has been used to determine different parameters.

Refractive index increments. Differential refractive index increments of the PEMA solutions were measured at 303 K with a Brice-Phoenix differential refractometer, BP 2000 model, equipped with a He-Ne laser of wavelength 633 nm. The refractive index of pure liquids and their mixtures was determined with an Abbé refractometer at 303 K.

Viscometry. The viscosities were measured at 303 and 313 K with a modified Ubbelhode viscometer, the temperature of water bath was regulated at ±0.01 K. The intrinsic viscosity, [n], was determined extrapolating to zero concentration from Huggins (Huggins 1942) and Kraemer (Kraemer 1938) equations. The unperturbed dimensions parameter of polymer, K_θ, and the polymer-solvent parameter, B, have been calculated using the Stockmayer-Fixman equation (Stockmayer, Fixman 1963).

Preferential adsorption coefficient. The preferential adsorption coefficient, λ, for the fraction of molecular weight $\bar{M}_w$ = 719000 was determined by laser light scattering and differential refractometry using the equation:

$$\lambda = \left[\left(\frac{M_w^*}{M_w}\right)^{1/2} - 1\right] \frac{(dn/dc)_{u_2}}{dn/dU_2}$$

were M_w and M_w^* are, respectively, the true and the apparent molecular weight of the polymer, $(dn/dc)_{u_2}$ is the variation of the refractive index with concentration at constant solvent composition, and dn/dU_2 is the variation of the refractive index of the binary solvent mixture with the composition.

RESULTS AND DISCUSSION

The variation of the preferential sorption coefficient with the composition (see Figure 1) indicates that ethyl acetate is absorbed in the whole range of composition, approaching to zero in the $10 < U_2 < 12,5\%$ ethanol range composition. It is remarkable the fact that two ranges exist where ethyl acetate adsorption on the macromolecular coil is produced: $0 < U_2 < 10\%$ ethanol and $U_2 > 12.5\%$ ethanol. This behaviour is rather peculiar and has not been described until now in the bibliography. These facts permit to hazard the next hypothesis: when the alcohol composition increases the formation of ethyl acetate-ethanol complex is produced, it can be responsible for macromolecular solvation. This hypothesis is guaranteed by UV spectroscopy measurements effect by Benamou and Bellon (Benamou, Bellon 1984). This explains the preferential sorption parameter decrease in the range $5 < U_2 < 12.5\%$ ethanol. On the other hand, the B parameter (Figure 2) increases appreciably although we are adding ethanol to the system, being this liquid a precipitant of the polymer. At higher ethanol compositions, alcohol self-association phenomenon prevails, and macromolecular sorption on the part of the ethyl acetate is observed, as figure 1 shows.

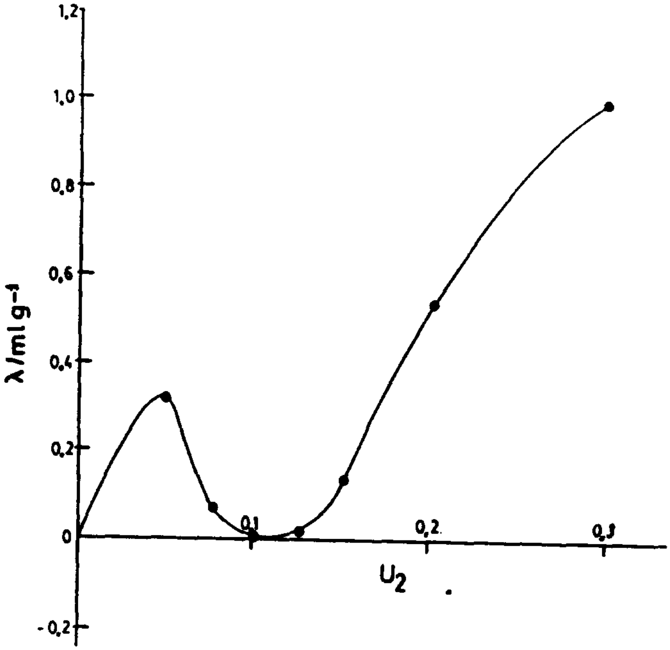

Figure 1. Experimental values of preferential adsorption coefficient for the PEMA/ethyl acetate/ethanol system.

The determination of the average radius of gyration, R_G, support this hypothesis too. As figure 3 shows, a little increase of PEMA molecular dimensions initialy and abrupt increase of these one later is produced, this could be indicative of the entrance in molecular coil of some compound of higher dimensions than ethyl acetate one. Presumably the ethyl acetate-ethanol complex.

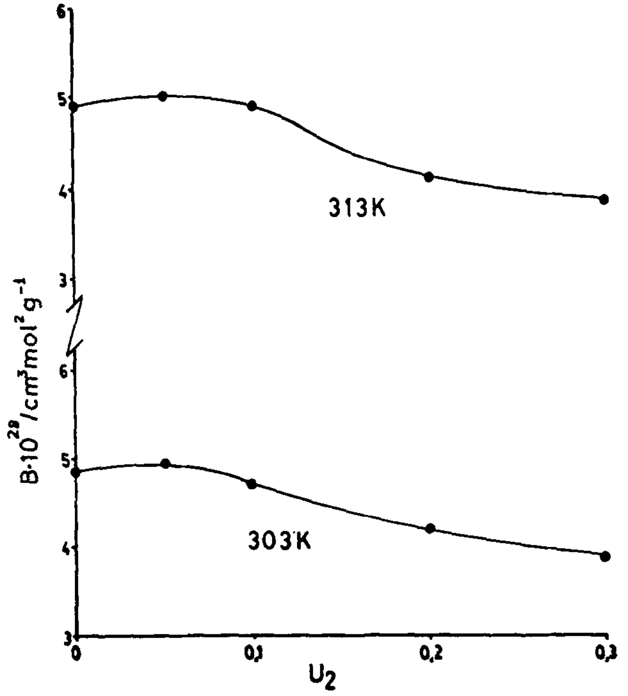

Figure 2. Variation of polymer-binary mixture interaction parameter, B, determined from Stockmayer-Fixman equation, for PEMA(3)/ethyl acetate(1)/ethanol(2) system at 303 K and 313 K.

In the figures 4 and 5, the viscometric behaviour of several PEMA fractions at 303 and 313 K is showed. As it is observed, a sinergic phenomenon in this mixture exists, since at the same time as the ethanol composition increases, the intrinsic viscosity of polymer decreases in relation to the arithmetic mean.

The Mark-Houwink-Sakurada a parameter (see Figure 6), that measures the permeability of macromolecular coil for sol-

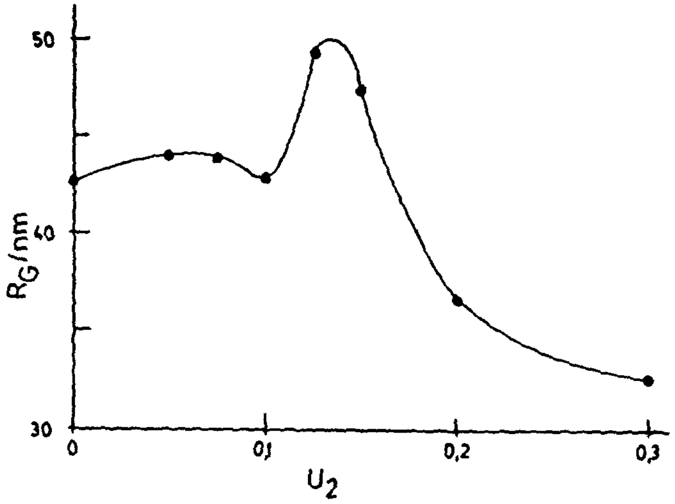

Figure 3. Values of average radius of gyration, R_G, for PEMA in binary mixture ethyl acetate(1)/ethanol(2).

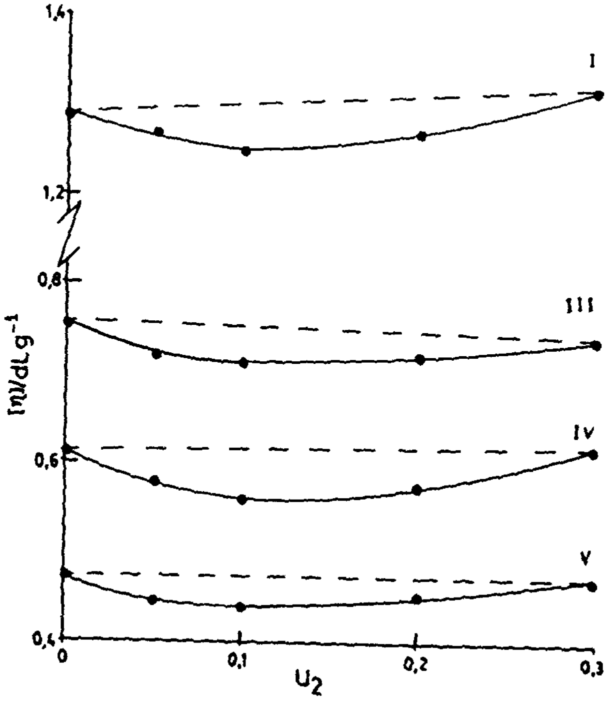

Figure 4. Intrinsic viscosities of fractions I, III, IV and V of PEMA in the binary mixture ethyl acetate(1)/ethanol(2), at 303 K.

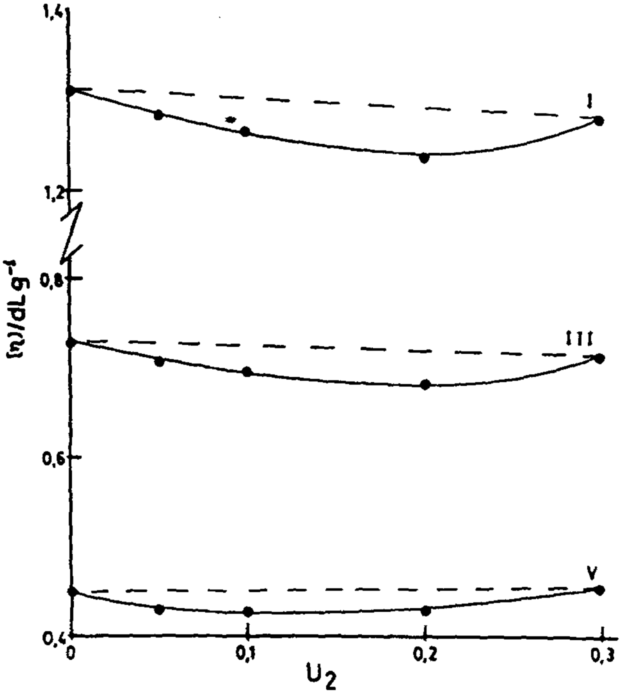

Figure 5. Intrinsic viscosities of fractions I, III and V of PEMA in the binary mixture ethyl acetate(1)/ethanol(2), at 313 K.

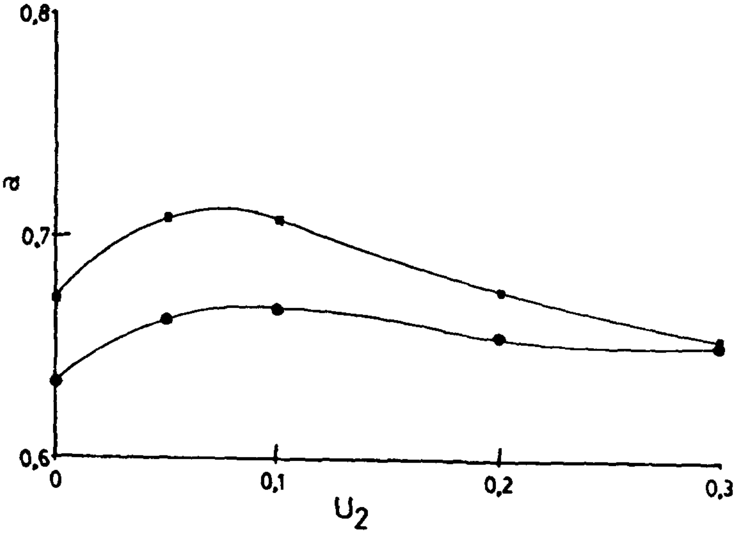

Figure 6. Dependence of Mark-Houwink-Sakurada a parameter on the volume fraction of ethanol for the PEMA(3)/ethyl acetate(1)/ethanol(2) system at 303 (A) and 313 K (B).

vent molecules and indicates the facility that these have to go into the coil and to make interaction with segments of its interior part, increases in the composition range aforementioned, that is to say its behaviour is very similar to B parameter one, which confirms the hypothesis above mentioned.

The variation of unperturbed dimensions of polymer, K_θ, (Figure 7) shows a initial decrease, which is in correspondence with the fact that the macromolecule is solvated by ethyl acetate(1)/ethanol(2) complex, and a later increase of this parameter when alcohol self-association begins and the ethyl acetate is preferentialy solvating.

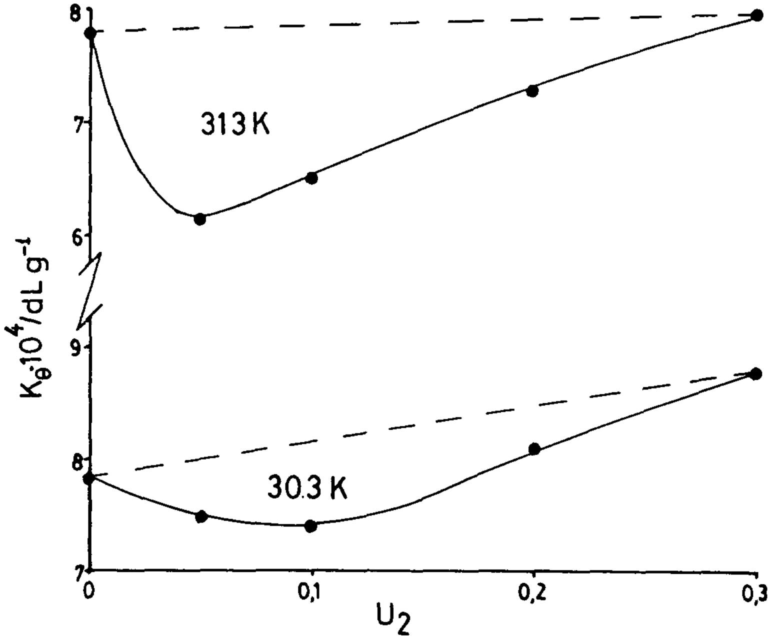

Figure 7. Values of unperturbed dimensions parameter, K_θ, determined from Stockmayer-Fixman equation for PEMA(3) in binary mixture ethyl acetate(1)/ethanol(2) at 303 and 313 K.

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