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Thermodynamic properties of poly(ethyl methacrylate) in binary mixtures

III. Ethyl acetate/n-propanol

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SUMMARY

The behaviour of poly(ethyl methacrylate) (PEMA) in the solvent(1)/precipitant(2) ethyl acetate(1)/n-propanol(2) binary mixture is studied by laser light scattering, differential refractometry and viscometry. A preferential adsorption of n-propanol is observed in all range of compositions studied, as well as an inversion in the thermodinamic quality of the solvent mixture with the temperature.

INTRODUCTION

The systems of solvent-precipitant type have been object of many studies (1-6), being the fractionationes by solubility one of their more generalized uses.

In general, the ternary systems are characterized by a preferential adsorption phenomenon (7-9), due to the differences in the thermodinamic quality and in the size of solvents molecules.

In this work, we have studied the behaviour of the poly(ethyl methacrylate) in solvent(1)-precipitant(2) ethyl acetate(1)/n-propanol(2) binary mixture by laser light scattering, differential refractometry and viscometry.

EXPERIMENTAL

Polymer

The polymer was obtained by radical polymerization from the commercial monomer (Fulka) at 333 K, using 2,2-azobisisobutyronitrile (AIBN) (Fulka puriss) as initiator. Fractionation by solubility in acetone/acetone + water system was realized. The molecular weight of every fraction was determined by laser light scattering, membrane osmometry and gel permeation chromatography (GPC), $\bar{M}_w(I) = 910000$, $\bar{M}_w(II) = 719000$, $\bar{M}_w(III) = 400000$, $\bar{M}_w(IV) = 280000$ and $\bar{M}_w(V) = 190000$, being 1.27 the highest polidispersity obtained.

Liquids

Ethyl acetate (Merck p.a.) and n-propanol (Merck p.a.) were both purified and bidistilled before their use. The solvent binary mixtures were made up by volumetry, belonging to the fraction in volume of n-propanol before mixture, their composition.

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Laser light scattering

The laser light scattering measurements were determined in a photogoniodiffusometer model FICA 42000 at 303 K, equiped with Spectra Physics He-Ne laser that emits to 633 nm. The pure liquids and the solutions were clarified by centrifugation for at 14000 rpm for 1.5 h. The Zimm plot (10) was used to determine different parameters.

Refractive index increment

The specific refractive index increments of PEMA with concentraction (dn/dc) were measured in a Brice-Phoenix differential refractometer, BP-2000 model, equipped with a He-Ne laser of 633 nm at 303 K. The refractive index of pure liquids and their mixtures was determined with Abbé refractometer (Warsawa) at 303 K.

Viscometry

The viscosity measurements were carried out in modified Ubbelhode viscometer of hanging level, immersed in a thermostatized bath at 303 or 313 K, with temperature control of ±0.01 K. The intrinsic viscosity, $[\eta]$, was determined by extrapolating to zero concentration from Huggins (11) and Kraemer (12) equations. The parameter of the unperturbed dimensions of the polymer, K_Θ, and the polymer-solvent interaction parameter, B, were determined through Stockmayer and Fixman equation (13). Likewise, the parameter a for every n-propanol composition was obtained using Mark-Houwink-Sakurada equation (14).

Preferential adsorption coefficient

The preferential adsorption coefficient, λ, (1,15) for the fraction II was determined by laser light scattering and differential refractometry using the equation:

$$\lambda = \left[\left(\frac{\bar{M}_w^*}{\bar{M}_w}\right)^{1/2} - 1\right]\frac{(dn/dc)_{u2}}{dn/dU_2}$$

where $\bar{M}_w$ and $\bar{M}_w^*$ are, respectively, the true and the apparent molecular weight of the polymer, $(dn/dc)_{u2}$ is the refractive index variation with the concentration at constant solvent composition, and dn/dU_2 is the variation of the refractive index of the binary mixture with the composition.

RESULTS AND DISCUSSION

The preferential adsorption coefficient (figure 1) in all composition range shows that only n-propanol adsorption on the macromolecular coil is produced, appearing a minimum about $U_2 = 6\%$ alcohol. This variation of preferential adsorption coefficient with the composition might be interpreted as being associated with an adsorption on the macromolecule at low alcohol composition increasing until $U_2 = 6\%$ alcohol. The value decreases from this composition suggesting that the self-association alcohol beings to be important. The observation of the average radius of gyration variation with the composition (figure 2) corroborates this fact, seeing a de-

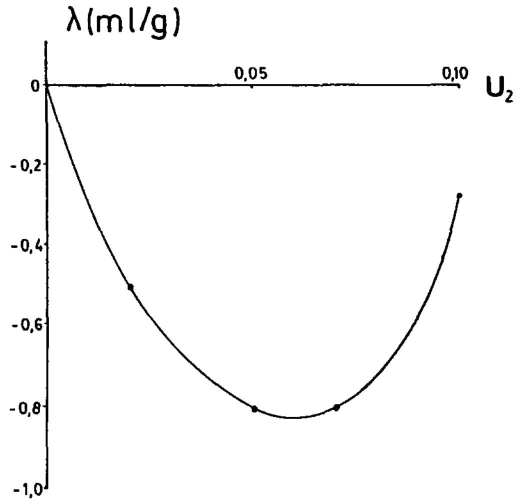

Figure 1. Experimental values of the preferential coefficient for PEMA/ethyl acetate/n-propanol system.

crease of the polymer dimensions with the composition; when the solvation phenomenon begins to reverse, the dimensions show an increase in R_G. This is due to the fact that ethyl acetate is a good solvent of PEMA whereas n-propanol is a precipitant of the same.

The intrinsic viscosity variation of the different fractions of PEMA with the composition at 303 K (figure 3a) shows negative sinergic effect, fact that occurs at 313 K too (figure 3b). These results are concordant with the these seen above, since a decrease of the average radius of gyration of PEMA must be traslated in a decrease of the intrinsic viscosity, fact that happens really. On the other hand, if the viscometry behaviour of fraction I at both temperatures is studied, it will be seen an increase of the intrinsic viscosity from the composition U_2 = 6% where a minimum in preferencial adsorption is observed.

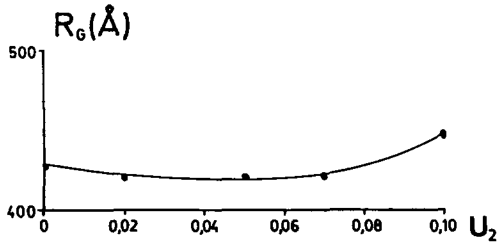

Figure 2. Values of average radius of gyration for PEMA in binary mixture ethyl acetate/n-propanol.

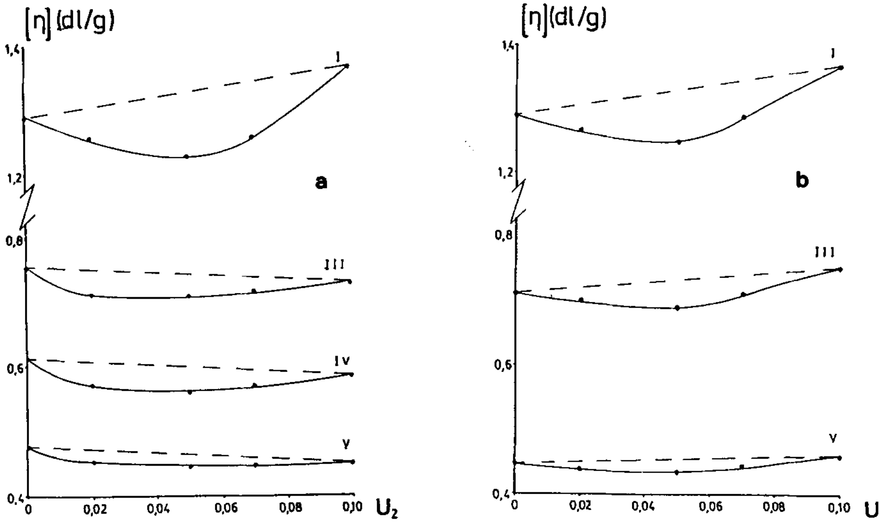

Figure 3. Intrinsic viscosity of diferent fractions of PEMA in the binary mixture ethyl acetate/n-propanol at a) 303 K and b) 313 K.

As for the Mark-Houwink-Sakurada exponent (figure 4), an increase of this parameter is observed, showing a higher thermodinamic quality of the solvent from U_2 = 6% n-propanol at both temperatures; however, an inversion in the quality is observed at U_2 = 8% alcohol, being better at 303 K. It can due to the decrease of the self-association alcohol when the temperature increases, implicating a bigger quantity of free alcohol and so a less solvent power of the binary mixture. The polymer-solvent interaction parameter B (figure 5) shows the same behaviour at a minimum about U_2 = 6%.

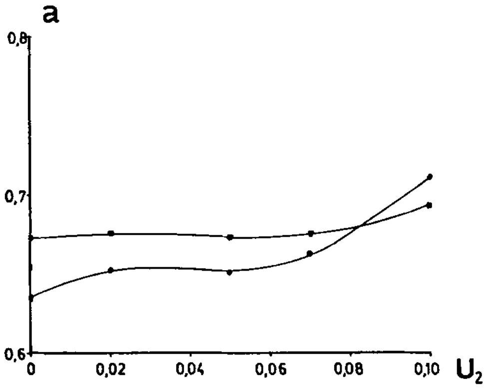

Figure 4. Dependence of parameter a on the volume fraction of n-propanol for the PEMA/ethyl acetate/n-propanol system at 303 (●) and 313 (■) K.

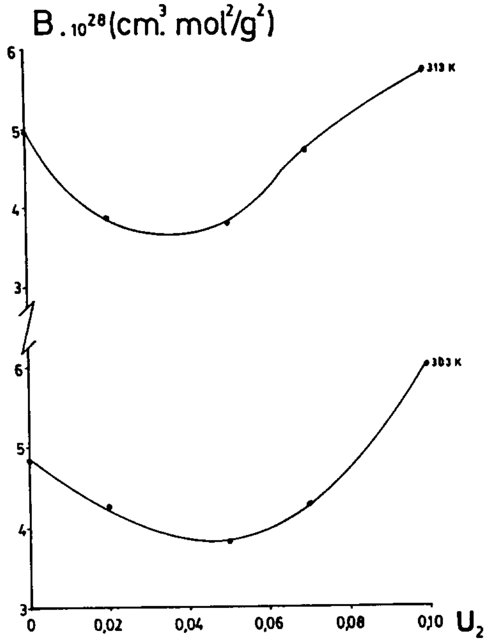

Figure 5. Variation of the polymer-binary mixture interaction, B, for PEMA/ethyl acetate/n-propanol system at 303 and 313 K.

The parameter of the unperturbed dimensions, K_θ (figure 6), has a maximum at U_2 = 6% n-propanol due to the fact the alcohol adsorption is the greatest at this composition because of the biggest quantity of the interactions of short range.

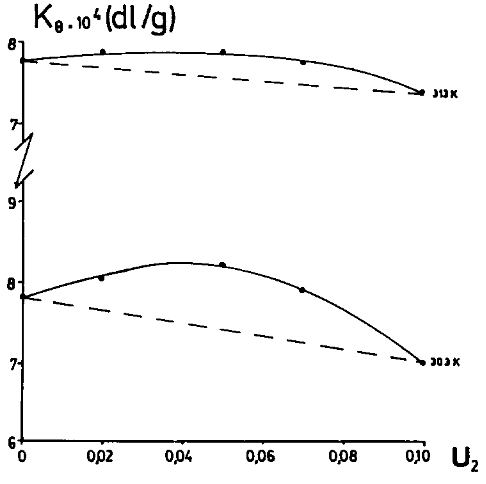

Figure 6. Values of the unperturbed dimensions parameter, K_θ, for PEMA in binary mixture ethyl acetate/n-propanol at 303 and 313 K.

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