Polymer Bulletin 6, 429–436 (1982)

Polymer Bulletin

Polymer Cosolvent Systems
3. PMMA(3)/CCl_4 (1)/n-Butyl Chloride(2)

I. Katime, J.R. Ochoa, L.C. Cesteros and J. Peñafiel

Departamento de Química Física, Grupo de Propiedades Termodinámicas de Macromoléculas en Disolución, Universidad del País Vasco, Apartado 644, Bilbao, España

SUMMARY

In this paper we have studied the behaviour of PMMA in the binary mixture CCl_4/n-butyl chloride by viscometry, light scattering and dyalisis. We have found that the CCl_4/n-butyl chloride mixture behaves as cosolvent in the range $10 < u_2 < 90\%$ n-butyl chloride. The n-butyl chloride is preferentially adsorbed in the whole composition range. The obtained results are discussed attending to G^E and the liquid order.

INTRODUCTION

The study of cosolvent systems has acquired a great interest in the last years due to the potential application they have in the industry. The Group of Properties of Macromolecules in Solution of Universidad del País Vasco has been studied this subject for several years in order to obtain a simple relation between the excess Gibbs free energy, G^E, liquid order, preferential solvation and cosolvency phenomenon.

In this work we have studied the above parameters for PMMA(3)/ CCl_4(1)/n-butyl chloride(2) system at 298 K.

EXPERIMENTAL PROCEDURES

Solvents used in this study were carbon tetrachloride (Merck p.a) and n-butyl chloride (Merck p.a). Solvent mixtures were made up by volume. The refractive indices of the solvents and binary solvent mixtures were measured with an Abbé refractometer at 298 K. The PMMA samples was prepared by free radical polymerization in a benzene solution initiated with 1,2-azobisisobutyronitrile. It was divided into 12 fractions by fractional precipitation from

0170-0839/82/0006/0429/$01.60

benzene with methanol. The molecular weight of the fractions were determined by light scattering and membrane osmometry in ethyl acetate at 298 K.

The viscosities were measured in a Ubbelhode suspended level viscometer, adapted for dilution in situ. The intrinsic viscosity was obtained by the usual extrapolation.

Weight-average molecular, M_w, were measured by light scattering in a FICA PGD model 4200 using green light (546 nm). The photogoniodifusometer was previously calibrated with benzene using natural polarization and taking the Rayleigh ratio as $16.3 \cdot 10^{-6}$ cm^{-1} (CARR ZIMM, 1950). The refractive index increment, dn/dc, was measured in a Brice-Phoenix differential refractometer previously calibrated with solutions of highly purified KCl.

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 λ parameter was calculated by dyalisis using the equation

$$\lambda = \frac{(dn/dc)_{\mu} - (dn/dc)_{k}}{(dn/du)}$$

where $(dn/dc)_{\mu}$ and $(dn/dc)_{k}$ are the refractive index increment at constant chemical potential and chemical composition, respectively.

RESULTS AND DISCUSSION

As it can be seen in Table 1, the composition range in which the binary mixture behaves as cosolvent is $10 < u_2 < 90\%$ n-butyl chloride. In figure 1, it can also be seen for a sample $5.5 \cdot 10^5$ of molecular weight, that approximately at a 40% n-butyl chloride a minimum in the precipitation temperature, T_p, appears, confirming the cosolvent behaviour of the mixture.

The viscometric measurements indicate that between 20 and 40%n-bu-

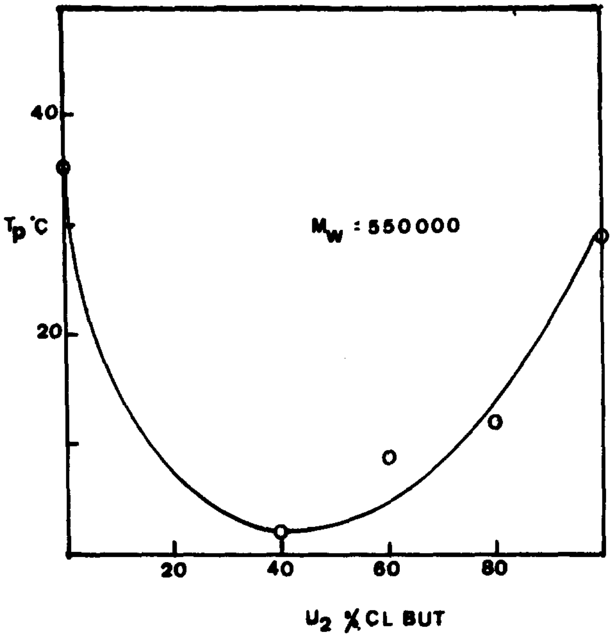

Figure 1. Precipitation temperature, T_p, as a function of binary mixture composition, u_2, for a PMMA sample of molecular weight $5.5 \cdot 10^5$

TABLE 1. Intrinsic viscosities as a function of binary mixture composition, u_2, for several PMMA samples at 298 K.

	{η} dl/g				
$M.10^{-4}$	30%	40%	60%	80%	100%
4.6	0.123	0.124	0.121	0.111	0.100[a]
11.0	0.222	0.221	0.211	0.176	-
21.5	0.333	0.336	0.322	0.262	-
46.0	0.560	0.562	0.516	0.413	-

a) KIRSTE,R., Phys. Chem. N.F., 30, 171(1971)

tyl chloride the solvating power of the mixture is maximum and there after remains practically constant. For higher compositions decrease of the mixture goodness is observed. This fact is confirmed when calculating the exponent of the Mark-Houwink-Sakurada equation. Figure 2 shows that the Mark-Houwink-Sakurada's a values obtained in the 30-60% interval are comparable to those obtained in good solvents(KURATA et al. 1975).

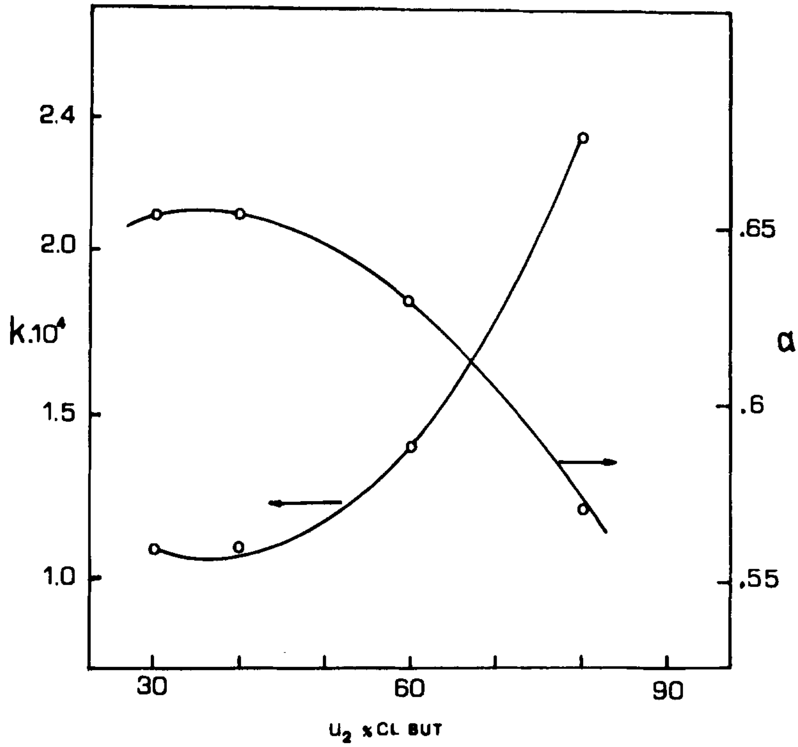

Figure 2. Plot of k and a as a function of binary mixture composition, u_2

For this reason, the influence of the cosolvency in the polymer unperturbed dimensions, evaluated using the Stockmayer-Fixman equation, has been determined. The obtained results (Figure 3) indicates that K_θ barely changes with the composition of the binary mixture which is in good agreement with the results obtained in other cosolvent systems (DEB et al. 1977; GARGALLO et al. 1981). In spite of it, the interaction parameter, B, presents a strong diminution as the composition increases. This result confirms what we have previously stated about of the thermodynamic quality of the binary mixture.

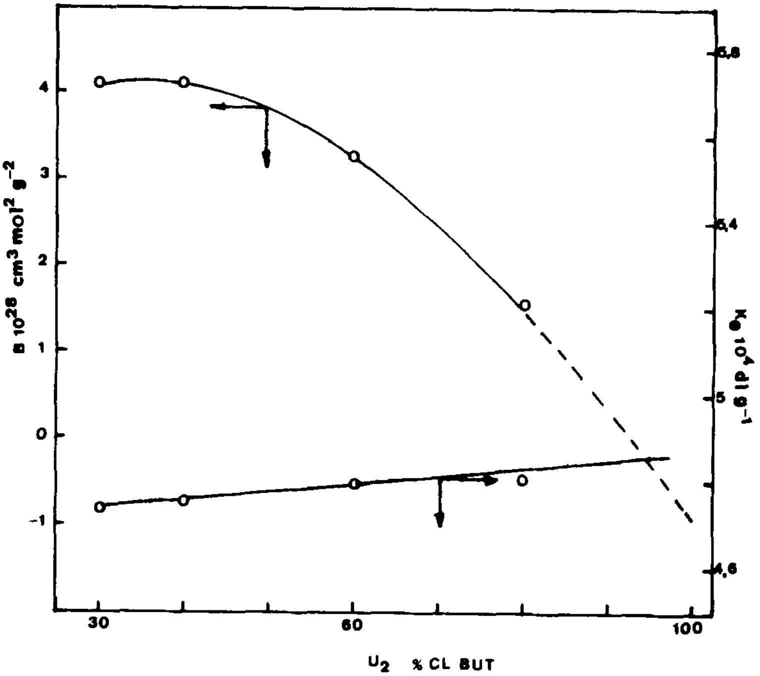

Figure 3. Plot of K_θ and B parameters versus n-butyl chloride composition, u_2, at 298 K

Preferential solvation determinations have also been made in this system by light scattering and dyalisis equilibrium which indicates that n-butyl chloride is preferentially adsorbed in the whole interval. This behaviour differs from the usual one found in cosolvent systems. However, the solvation until u_2 = 40% n-butyl chloride is very low, according to the viscometric results. There is a dependence on molecular weight,as it is shown in Figure 4. Why is not observed a solvation inversion in this system?. The solvation inversion is favoured by the following factors: i) low absolute values of $|L - 1|$, where L is the relation between the molar volumes of both solvents in the binary mixture, ii) low $|\chi_{13} - L\chi_{23}|$ values and iii) high χ_{12} values. In our system the factors i) and ii) favour the inversion ($|L - 1| = 0.074$). On the contrary, χ_{12} parameter is presumably low as deduced from viscosity measurements and bearing in mind the following expressions (POUCHLY, PATTERSON 1976; UTRACKY 1972)

$$\Delta\{\eta\} = \frac{1.02 M v_3^2 \Phi_o G^E}{N_o R T V_m}$$

$$\frac{G^E}{V_m \Phi_1 \Phi_2} = \sum (\delta_{1i} - \delta_{2i})^2$$

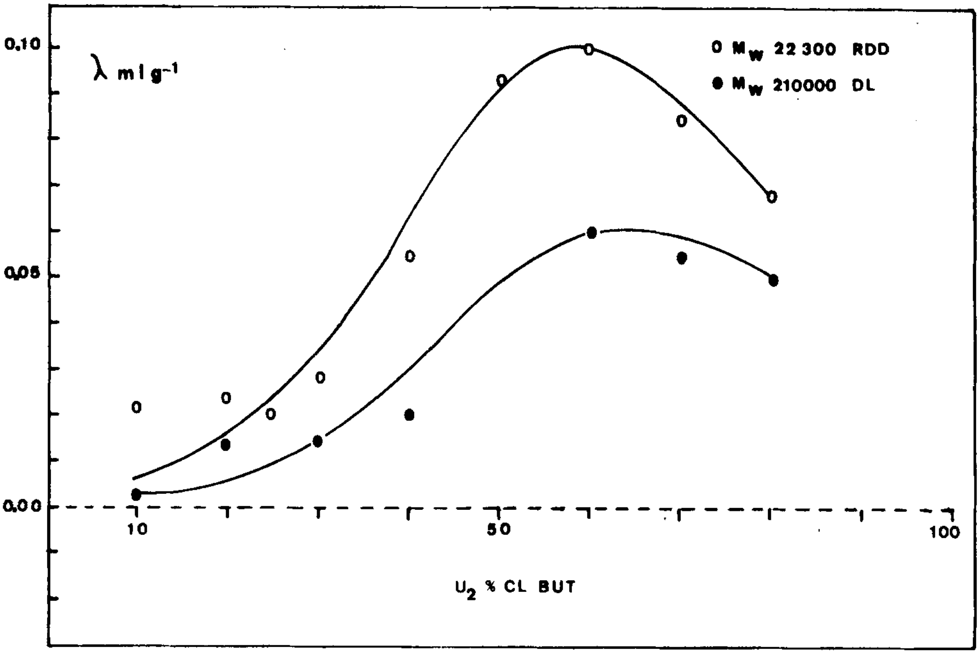

Figure 4. Plot of λ as a function of binary mixture composition, u_2

Usually in the cosolvent mixtures studied up to now, a solvation inversion occurs, the component of lower proportion being initially adsorbed (PIEROLA, HORTA 1981). As G^E is high in these mixture (and therefore is high χ_{12}) the adsorption of the component of lower proportion favours the decrease of the unfavourable interactions between both solvents. In our case, as we have already seen, G^E is small and therefore is the same for the polymer interact with any of the two components of the binary mixture; this is the reason for such a low adsorption, and the n-butyl chloride is adsorbed because, it is slightly polar, and it can interact with the polymer. An association of the PMMA has been detected in CCl_4 (SPEVACEK, SCHNEIDER 1974, 1975) and therefore CCl_4 is

not solvent for PMMA. The addition of n-butyl chloride breaks this association, producing the dissolution of the polymer and the mixture behaves as cosolvent. When n-butyl chloride composition increases, this one interacts with PMMA, consequently there is an increment of the preferential adsorption coefficient, as it can be seen in figure 4. In spite of that there is not a great tendency for the polymer to interact with one of the solvents exclusively, as we have been before. Finally, when the n-butyl chloride composition increases (μ = 1.90 D), its molecules tend to a state of order due to little electrostatic interactions (because it is weakly polar) which leads to a decrease of the solvating power (the n-butyl chloride is a theta solvent at 298 K) and to an increment of the polymer association (SUZUKI et al. 1977).
We think that CCl_4 interact with n-butyl chloride (and on the other compounds such as alcohols) (KATIME et al. 1979) producing a screen between adjacent molecules that breaks the order of the polar liquids, and allows it to interact with the polymer, showing the cosolvency phenomenon.

Acknowledgments. L.C.C. and J.R.O. acknowledges the award of a Fellowship by the Gobierno Vasco and the Ministerio de Eduación y Ciencia, respectively.

REFERENCES

CARR, C.I. and ZIMM, B.H., J. Chem. Phys., 18, 1616(1950)
DEB, P.C., PRASAD, J. and CHATTERJE, S.R., Makromol. Chem., 178, 1455(1977)
GARGALLO, L., RADIC, D. and KATIME, I., European Polymer J., 16, 383(1981)
KATIME, I., TAMARIT, J. and TEIJON, J.M., Anal. Química (Madrid), 75, 7(1979)
KIRSTE, R., Phys. Chem. N.F., 30, 171(1971)
KURATA, M., TSUNASHIMA, Y., IWAMA, M. and KAMADA, K., Polymer Handbook, Brandrup, J. and Immergut, E.H., Editors, John Wiley, 1975
FERNANDEZ PIEROLA, I. and HORTA, A., Macromolecules (in press)
POUCHLY, J. and PATTERSON, D., Macromolecules, 9, 574(1976)

SPEVACEK, J. and SCHNEIDER, B., Makromol. Chem., 175, 2939(1974)
SPEVACEK, J. and SCHNEIDER, B., Makromol. Chem., 176, 3409(1975)
STRAZIELLE, C. and BENOIT, H., J. chim. Phys., 59, 675(1961)
SUZUKI, H., HIYOSHI, T. and INAGAKI, H., J. Polymer Sci.: Polymer Symp. 61, 291(1977)
UTRACKY, L.A., J. Appl. Polymer Sci., 16, 1167(1972)

Received January 2, accepted January 18, 1982