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Co-Nonsolvency of PMMA

Inés Fernández-Piérola[1] and Arturo Horta[2,+]

[1] Departamento de Química Física, Facultad de Química, Universidad Complutense, Madrid 3, Spain
[2] Departamento de Química Física, Facultad de Ciencias, Universidad a Distancia (U.N.E.D), Madrid 3, Spain

Summary

Phase separation temperatures have been determined in the system PMMA/chlorobutane + amyl acetate. This liquid mixture is a co-nonsolvent (co-precipitant) of the polymer. The molecular origin of such co-nonsolvency is discussed in terms of the interactions pressumably present in the system.

The phenomenon of cosolvency presents numerous examples in the field of synthetic polymers. With regard to poly(methyl methacrylate)(PMMA), several cosolvents at room temperature and a true cosolvent mixture have been reported (DEB and PALIT 1973, WOLF and BLAUM 1975, FERNANDEZ-PIEROLA and HORTA 1980). A summary of them is contained in Table I. The liquids appearing in Table I are ordered according to their solubility parameter value (δ). The cosolvent mixtures are classified as: (1) symmetrical (S in Table I), when δ of PMMA is inbetween the δ's of the two single liquids; (2) nonsymmetrical (NS in Table I), when the δ's of the two liquids are both higher or both lower than δ of PMMA. In this way, Table I is divided into four different regions, designated as A, B, C, and D. Regions B and C correspond to symmetrical cosolvents and regions A and D to nonsymmetrical ones.

The liquids appearing in Table I are all poor solvents of PMMA, but their molecular characteristics vary widely. Some liquids, like CCl_4 and ClBu, are of low (or none) polarity. It has been reported that PMMA tends to associate in their solutions (SPĚVÁČEK and SCHNEIDER 1975, SUZUKI et al. 1977). Other liquids, are structurally (somewhat) ordered fluids. For example, the highly polar AcN whose molecules are orientation-

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(+) Correspondence to this author

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TABLE I

Cosolvents of PMMA classified as symmetric (S) or nonsymmetric (NS), according to their solubility parameter values. δ's in $(J/cm^3)^{1/2}$, at 25°C, from FERNANDEZ-PIEROLA and HORTA 1980.

	δ =	ClBu 17.3	CCl_4 17.7	AcN 24.3	FA 36.6
Hna				S	
iAmAc	17.0			S	
AmAc	17.4	A		S	B
ClBu	17.3			S	
CCl_4	17.7			S	
iAmOH		S		NS	
AmOH	21.6	S		NS	
sBuOH	22.2	S	C		D
BuOH	23.1	S	S	NS	
iPrOH	23.6	S		NS	
PrOH	24.4		S		
EtOH	26.4		S		NS
MeOH	29.2		S		

PMMA

PMMA

Hna=4-heptanone; (i)AmAc=(iso)amyl acetate; ClBu=1-chloro-n-butane; (i)AmOH=(iso)amyl alcohol; AcN=acetonitrile; FA=formamide; (s)BuOH=(sec)butanol; (i)PrOH=(iso)propanol; EtOH=ethanol; MeOH=methanol.

ally correlated (MICHEL and LIPPERT 1978), or the alcohols (and FA) which have a hydrogen bonded autoassociated structure. The role of such liquid order and of polymer association in determining cosolvency has been discussed before (FERNANDEZ-PIEROLA and HORTA 1980).

In the present work we focus our attention on region A, for which no cosolvent effect has been reported thus far. In this region A, the mixtures are nonsymmetrical, with both liquids having δ's lower than the of PMMA. In these mixtures one of the components is a reported promoter of polymer association (ClBu, CCl_4).

In region A we have found the existence of the effect opposite to cosolvency, namely: co-nonsolvency. This means that, at a given temperature, the polymer disolves completely in the two single solvents but not in

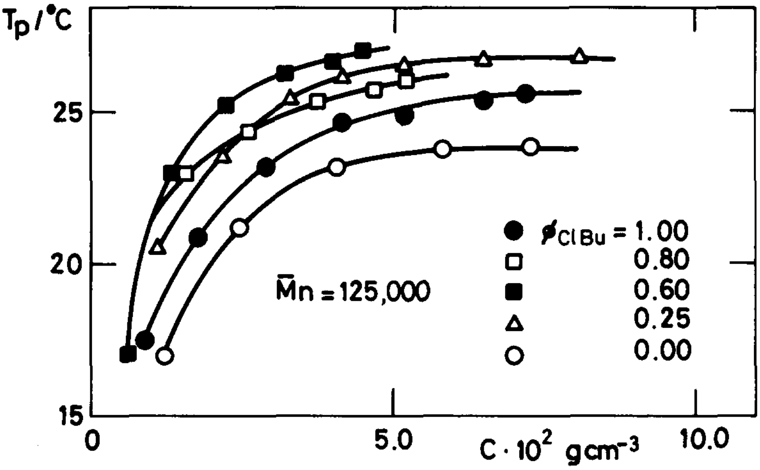


Fig. 1.- Phase separation temperatures (T_p) of the system PMMA/ClBu + AmAc

their mixtures of intermediate composition (WOLF and MILLMS 1978). The mixing of the two liquids, which are solvents of the polymer, produces, thus, precipitation at the constant temperature of reference. The system is a coprecipitant.

We report here results obtained with the coprecipitant system formed by PMMA/ClBu + AmAc. To our knowledge, this is the first case of co-nonsolvency described for PMMA.

Its coprecipitant nature has been ascertained by determining incipient phase separation temperatures (T_p), as a function of liquid mixture composition, at several polymer concentrations. The experimental procedure followed to determine T_p is the same as that described previously (FERNANDEZ-PIEROLA and HORTA 1980). Capillary tubes filled with polymer solutions are placed in a water bath and the temperature cooled down slowly. T_p is determined visually when a copper wire, placed behind the tubes, blurrs. The samples of PMMA studied are Monopol monodisperse standards supplied by Dr. T. G. Croucher (Polymer laboratories Ltd., Shrewsbury, England). Their molecular weights are: M_n (M_w/M_n) = 125,000 (≤ 1.1) and 65,000 (≤ 1.17), as specified by the supplier.

The results obtained for T_p are shown in Figures 1 and 2, where c means polymer concentration in the solution, and ϕ_{ClBu} volume fraction of ClBu in the solvent mix-

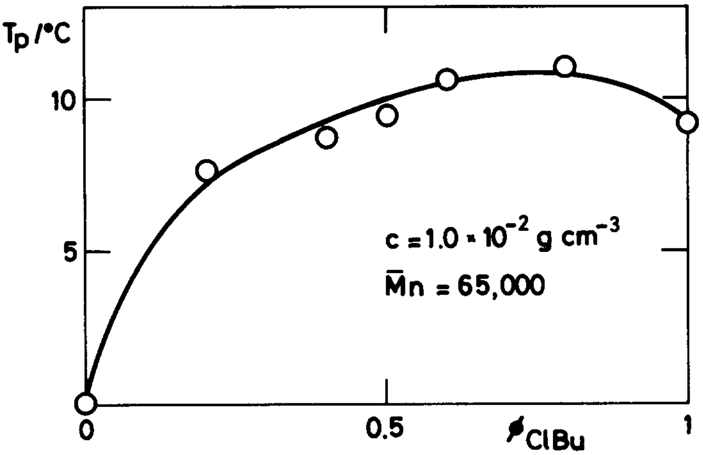


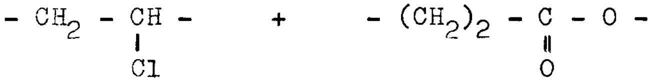
Fig. 2.- Phase separation temperatures (T_p) of the system PMMA/ClBu + AmAc

ture. The solutions whose T_p's are represented in Figures 1 and 2 have been prepared in two slightly different ways. One was to prepare two separate single solvent solutions having the same c and, by proper mixing, to obtain solutions of intermediate ϕ_{ClBu} and constant c. In this way we obtained the T_p's represented in Figure 2. The other way consisted on preparing a solution of given c using as solvent a ClBu + AmAc mixture having known ϕ_{ClBu}. This polymer solution was then diluted progressively with more solvent mixture of the same ϕ_{ClBu} to obtain solutions of constant ϕ_{ClBu} and decreasing c. This was the way followed to obtain the T_p's represented in Figure 1.

We can see that, in both cases, the system shows a co-nonsolvent effect. This effect is not large, however.

Co-nonsolvency is much more difficult to find than cosolvency because endothermic effects between simple liquids tend to favour polymer solubility. Only mixtures in which the components interact through strong specific forces, such as acid-base complex formation (GEE 1944, CHEN and LAI 1979), or in which the liquids are incompletely miscible (WOLF and MILLMS 1978), have been reported. In the case of our coprecipitant mixture, no such phenomena are present.

ClBu and AmAc have δ's which are practically identical (see Table I), so that endothermic effects in their mixture are expected to be very small, if at all present. In the abscence of endothermic interactions, the excess entropy is positive if the liquid components differ in molecular size, as happens with the ClBu + AmAc pair. Thus, a small $S^E>0$ would be enough to yield a negative excess Gibbs function and contribute to co-nonsolvency. However, it is possible that the mixture of these two liquids be even exothermic. No data could be found in the literature to confirm this point, but one is led to think on the possible formation of an exothermic interaction between the chloroalkane and ester groups of ClBu and AmAc, in much the same way that the compatibility of the chemically related pair poly(vinyl chloride) + poly(ε-caprolactone)



$$- CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} - \qquad + \qquad - (CH_2)_2 - \underset{\displaystyle O}{\underset{\|}{C}} - O -$$

is attributed to the formation of a charge transfer complex (CRUZ et al. 1979). Such favourable interactions between the two liquids would lead to an enhanced tendency of the mixed solvent to segregate the polymer by cutting solvent-polymer contacts and forming solvent 1 - solvent 2 and polymer-polymer ones.

Several liquid mixtures are known which have exothermic interactions giving a negative value of G^E, at room temperature. For example, chloroform + dioxane. However, the Θ temperatures of PMMA in these single solvents are very low, and no coprecipitant effect is observed at normal temperatures. In other words, the appearence of the phenomenon of co-nonsolvency (and of cosolvency as well) does not only depend on the G^E of the liquid mixture, but also on the thermodynamic interactions between the polymer and each one of the liquids. In this sense, the system ClBu + AmAc is an interesting one, because both Θ temperatures are close to ambient and the coprecipitant effect is easily accesible to experimental determination.

ClBu and also AmAc participate in forming both cosolvents and co-nonsolvents of PMMA. For example, the mixtures ClBu + AcN, AmAc + AcN, and ClBu + alcohol are all cosolvents of PMMA (regions B and C of Table I). In these systems, endothermic effects between liquids are prevalent and the solvent 1 - solvent 2 contacts are avoided by forming polymer-solvent 1 and polymer-solvent 2 contacts, thus yielding increased solvation of the macromolecular coils (cosolvency). On the other hand, when ClBu and AmAc mix together (region A of Table I) the possibly favourable interactions between the two liquids seem to enhance the contacts between polymer segments and yield premature phase separation (co-nonsolvency).

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