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POLYMER COSOLVENT SYSTEMS—IV

PMMA–CCl_4–CHLOROALKANE VISCOMETRIC STUDY

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Abstract—We have studied the variation of the cosolvent power for PMMA–CCl_4–chloroalkane (butyl chloride, sec.butyl chloride and tert.butyl chloride) systems. The results indicate that, when the polarity and branching of the chloroalkane increase, the cosolvent power of the binary solvent mixture decreases.

INTRODUCTION

In recent years many symmetrical and non-symmetrical cosolvent binary mixtures for PMMA have been studied [1–5]. In this type of binary mixture, an inversion in solvation is produced. In an earlier paper [6] we reported a non-symmetrical cosolvent binary mixture for atactic PMMA (CCl_4-butyl chloride) in which anomalous behaviour with respect to the cosolvent mixtures previously studied was observed: no solvation inversion was found. The polar component of the binary solvent mixture was always adsorbed on the macromolecular coil.

In this work the viscometric study has been extended to CCl_4–sec.butyl chloride and CCl_4–tert.butyl chloride mixtures. First, we determined the composition interval over which these systems behave as cosolvents for atactic PMMA, ranging from 10 to 70% of sec.butyl chloride for CCl_4–sec.butyl chloride mixture, and from 10 to 50% of tert.butyl chloride for CCl_4–tert-butyl chloride mixture, at 298 K. Finally, a comparative study was made of the cosolvent behaviour for PMMA of the binary solvent mixtures studied here and previously [6].

EXPERIMENTAL

Solvent mixtures were made up by volume. The poly(methyl methacrylate) sample was prepared by free radical polymerization in benzene solution, initiated with azobisisobutyronitrile. It was divided into 12 fractions by fractional precipitation from benzene solution with methanol. The samples were subsequently thoroughly freeze-dried from benzene. Molecular weights of the fractions were determined by both light scattering and osmometry in ethyl acetate at 298 K. Measurements were made on several fractions of weight-average molecular weight ranging from $4.6 \cdot 10^4$ to $55.0 \cdot 10^4$. Polydispersities of the fractions used in this work lay between 1.2 and 1.3 as obtained from GPC measurements. Viscometric measurements were carried out in a Ubbelhode suspended level viscometer, adapted for dilution *in situ*. All measurements were carried out at 298 K.

RESULTS AND DISCUSSION

Intrinsic viscosities, $[\eta]$, for several fractions of atacic PMMA in the systems studied in this work are given in Tables 1 and 2. Viscometric measurements indicate that the optimum composition is located at $u_2 = 30\%$ where $u_2 = \%$ by volume of chloroalkane, for both cosolvent mixtures. Likewise, from these measurements we have obtained that the Huggins constants, K_h, for PMMA in CCl_4–sec.butyl chloride and CCl_4–tert.butyl chloride mixtures ranged from 0.7 to 1.3 and from 0.9 to 1.45, respectively, depending on molecular weight and composition. This fact indicates [7] that, in both cosolvent mixtures, PMMA shows a tendency to form associates; the tendency increases when the molar volume and branching of the chloroalkane increase, in accordance with our previous results [8].

Table 1. PMMA–CCl_4–sec.butyl chloride system

	$u_2(\%)$					
$M \cdot 10^{-4}$	10	20	30	40	50	70
55.0	—	0.485	0.510	0.486	0.464	—
48.1	—	0.444	0.465	0.452	0.428	—
42.0	—	0.410	0.423	0.419	0.392	0.299
30.0	0.808	0.337	0.340	0.350	0.331	0.255
24.3	0.285	0.300	0.306	0.304	0.294	0.236
8.0	0.156	0.166	0.164	0.167	0.161	0.145

Intrinsic viscosities, $[\eta]$, as a function of the binary mixture composition, u_2, at 298 K.

In Memoriam to Elhuyar Brothers in the bicentennial jubilee of their discovery of Wolfram.

Table 2. PMMA–CCl_4–tert.butyl chloride system

$M \cdot 10^{-4}$	u_2(%) 10	20	30	40	50
4.6	0.114	0.117	0.118	0.115	0.104
8.0	0.155	0.158	0.158	0.154	0.136
10.6	0.170	0.179	0.184	0.176	—
24.3	0.261	0.271	0.289	0.261	—

Intrinsic viscosities, $[\eta]$, as a function of the binary mixture composition, u_2, at 298 K.

From viscometric measurements we have also calculated the K_θ parameter and the polymer–binary solvent mixture interaction parameter B for PMMA in these mixtures using the Stockmayer–Fixman equation [9]. Both parameters are plotted in Figs 1 and 2. The K_θ parameter, which characterizes the unperturbed dimension of PMMA, is practically the same and independent of composition in both cosolvent mixtures in agreement with results for other systems [6, 10]. However, intermolecular interaction parameters, B, are higher for CCl_4–sec.butyl chloride mixtures than for CCl_4–tert.butyl chloride mixtures, indicating that the first is a better cosolvent mixture for PMMA.

Figures 3 and 4 show plots of K_θ parameters and Mark–Houwink–Sakurada (MHS) constants, a, at several compositions, for the binary mixtures studied here and previously [6]. Unperturbed dimensions, characterized by K_θ, undergo a sharp increase when the side-group of the chloroalkane is branched. This fact can be explained by noting that, according to our previous results [6, 11], the chloroalkane is always the component preferentially adsorbed on PMMA; therefore, the rigidity of the polymer chain in the cosolvent mixture will increase (K_θ increases) when the branching of the chloroalkane increases. On the other hand, it is also possible to explain this fact noting that PMMA association in these mixtures, as K_h values have already shown above, increases when the branching of the chloroalkane increases and, since values of K_θ are obtained from the Stockmayer–Fixman equation by means of extrapolation to zero molecular weight, their values will be larger when the branching of the chloroalkane of the

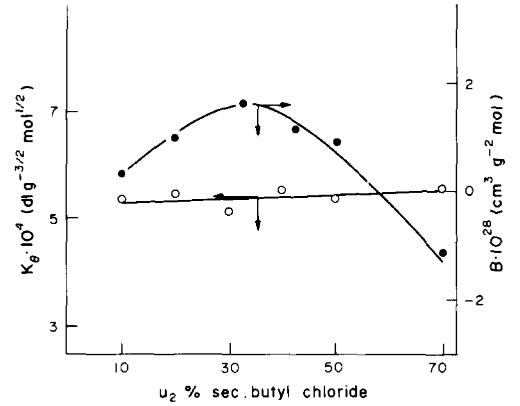

Fig. 1. Plot of K_θ and B parameters vs sec.butyl chloride composition, u_2, at 298 K.

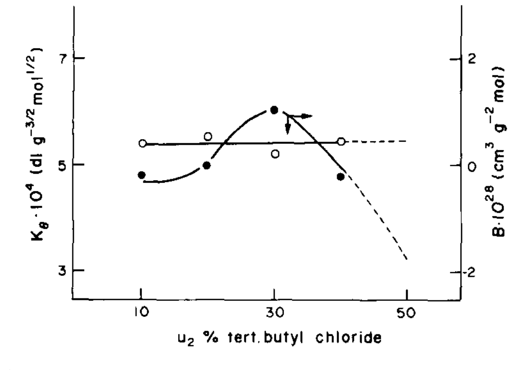

Fig. 2. Plot of K_θ and B parameters vs tert.butyl chloride composition, u_2, at 298 K.

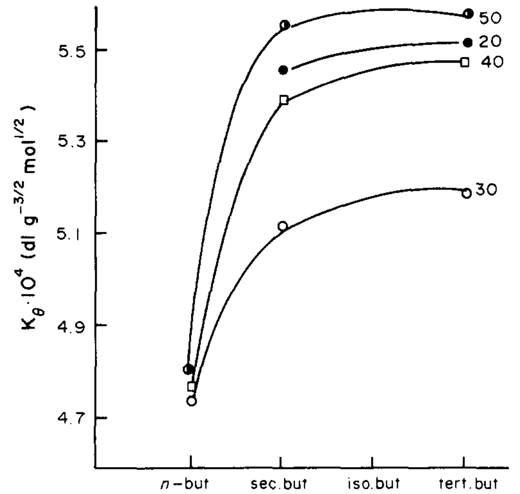

Fig. 3. K_θ variation for the three cosolvents systems studied, at several compositions, u_2.

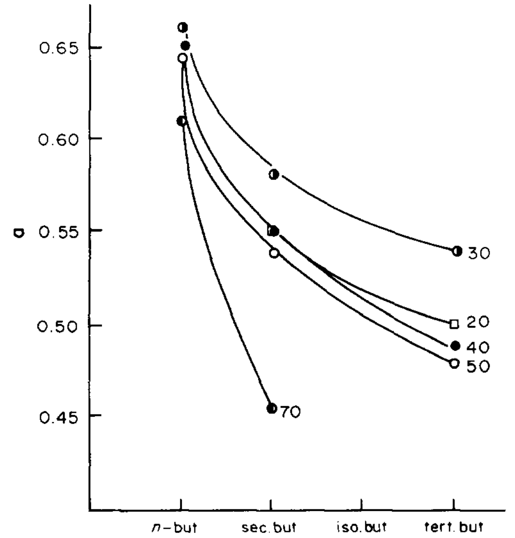

Fig. 4. Variation of Mark–Houwink–Sakurada constant, a, for the three binary mixtures studied, at several compositions, u_2.

binary mixture increases. Thus PMMA association in the cosolvent mixture increases.

Likewise, the variation of MHS parameters, a, (Fig. 4) indicates that the dissolving power of these cosolvent mixtures decreases from CCl_4–butyl chloride to CCl_4–tert.butyl chloride. In order to explain this fact, it is necessary to take into account the following points:

1. Excess Gibbs functions, G^E, for these cosolvent mixtures increase from CCl_4–tert.butyl chloride ($G^E = 145$ J/mol, $x_2 = 0.5$) to CCl_4–butyl chloride ($G^E = 605$ J/mol, $x_2 = 0.5$) [12], where x_2 denotes mole fraction of chloroalkane. Consequently, the incompatibility between their components, and therefore their cosolvent powers, increase in the same order since the incompatibility between the liquids of the binary mixture makes more favourable the polymer–binary solvent mixture contacts than the liquid–liquid contacts.
2. The shapes of these chloroalkanes change from linear (butyl chloride) to globular (tert.butyl chloride) in which the interaction with the polymer is more difficult because of steric hindrance.
3. PMMA association increases from butyl chloride to tert.butyl chloride [8].
4. Molar volumes of the chloroalkanes studied in this work increase from butyl chloride (105 cm^3/mol) to tert.butyl chloride (110 cm^3/mol) which makes the interaction with the macromolecular coil more difficult.
5. Dipole moments of the chloroalkane, μ, increase from butyl chloride ($\mu = 1.90$ D) to tert.butyl chloride ($\mu = 2.15$ D) which could explain the decrease in cosolvent power in the same order because, when the polarity of the chloroalkane increases, its tendency to interact with itself by means of dipole–dipole interactions should increase, so establishing a more ordered structure. Therefore, liquid–liquid contacts would increase so producing a decrease of polymer–binary solvent mixture contacts and consequently the cosolvent power of the binary mixture would decrease. Laser light scattering measurements [12] indicate that the tendency for self-association of these chloroalkanes is small and, therefore, point 5 cannot explain the different cosolvent powers from PMMA of these binary mixtures. On the other hand, the difference in molar volumes between the chloroalkanes (about 5%) is not enough to explain the decrease of the dissolving power as going from CCl_4–butyl chloride mixture to CCl_4–tert.butyl chloride mixture. Therefore, according to our experimental results [8, 12], we think that points 1, 2 and 3 are responsible for the different cosolvent behaviour for atactic PMMA of the CCl_4–chloroalkane binary solvent mixtures.

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