

Preferential Solvation in Polymer Cosolvent Systems: Polystyrene + Cyclohexane + Ethanol and Poly(vinyl-2-pyridine) + Nitromethane + Carbon Tetrachloride

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Synopsis

Two cosolvent systems are studied by light scattering and viscosity measurements. The cosolvency mechanism is discussed in relation to the preferential adsorption, solubility parameter, and excess free energy of mixing of the two liquid components. The cosolvency effects are attributed to a "true" and an "apparent" cosolvency.

INTRODUCTION

Cosolvent systems comprise one of the most important classes of ternary systems in that the polymer is dissolved in a certain region of the binary mixture, whereas each of the mixture liquids is either a very weak solvent or a nonsolvent for the particular polymer.¹⁻⁴ A number of cosolvent systems have already studied, but the mechanism is as yet very little understood. It has been shown that for the majority of these systems the solvent composition at which both the intrinsic viscosity $[\eta]$ and the second virial coefficient A_2 reach their maximum nearly coincides with the composition at which the preferential adsorption coefficient λ' undergoes a change of sign.⁵⁻⁷ At such a composition the binary solvent mixture is thermodynamically at its best. Cosolvency is also possible in systems where inversion of λ' is not observed.⁸⁻¹⁰

The magnitude and sign of the binary interaction parameter g_{12} must be considered as a guide to a possible case of cosolvency.¹¹⁻¹³ Thus when g_{12} is relatively large and positive for a mixture of two nonsolvents, the solvent(1)-polymer(3)-solvent(2) contacts are more favorable than the solvent(1)-solvent(2) contacts.

In this work two cosolvent systems are studied: polystyrene + cyclohexane + ethanol and poly(vinyl-2-pyridine) + nitromethane + carbon tetrachloride. The effect of the composition of the binary solvent system on the intrinsic viscosity $[\eta]$ and the coefficient of preferential adsorption λ' at constant temperature is also studied.

EXPERIMENTAL

The polystyrene and poly(vinyl-2-pyridine) samples are fractions of the polymer prepared by anionic polymerization at low temperature (-75°C)

within THF. The polydispersity of polystyrene was determined by GPC and was found not to exceed 1.2. The polydispersity of poly(vinyl-2-pyridine) was also low: $(M_w/M_n) < 1.2$ as determined by the method of Mussa.¹⁴

The molecular weight (M_w) of each polymer was determined by light scattering using a Fica model 42000, P.G.D. instrument operating at the 546 nm unpolarized green line of mercury. Intrinsic viscosity values $[\eta]$ (in ml/g) were obtained by measurements of the specific viscosity of the polymer solution η_{sp} using a modified Ubbelohde viscometer under constant pressure. The viscometer was positioned in a constant temperature bath.

The intrinsic viscosity at each composition was calculated using the relation¹⁵

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (1)$$

where k' is a constant.

The preferential solvation of each sample was calculated from light scattering data according to the method proposed by Strazielle and Benoit¹⁶ from the equation

$$M^* = M \left[1 + \lambda' \left(\frac{dn}{d\phi_1} / \frac{dn}{dc} \right) \right]^2 \quad (2)$$

where M^* is the apparent molecular weight as determined by light scattering, M is the true molecular weight, dn/dc is the refractive index increment at a certain composition of the binary solvent mixture, and $dn/d\phi_1$ is the variation of the refractive index of the solvent mixture n with its composition expressed as the volume fraction ϕ_1 of the solvent 1. The coefficient of preferential solvation λ' is defined by

$$\lambda' = \frac{\gamma_1}{M} V_1 \quad (3)$$

where γ_1 is the excess number of molecules of solvent 1 of partial molar volume V_1 preferentially adsorbed in the vicinity of the macromolecular chain. In all cases the solvent mixture was prepared before addition of the polymer. The solvent composition is expressed in volume fractions ϕ . All measurements have been obtained at 25°C.

RESULTS AND DISCUSSION

Polystyrene + Cyclohexane + Ethanol Cosolvent System

Ethanol is a precipitant for polystyrene at all temperatures. On the other hand, cyclohexane is a Θ solvent at 34°C. Therefore at 25°C both liquids are precipitants for polystyrene. Dondos and Patterson¹¹ have studied this ternary system by viscosimetry and noticed a narrow cosolvency region. In this paper we extend the study of the system with light-scattering data, and thus we obtain the coefficient of preferential adsorption. We can then correct the

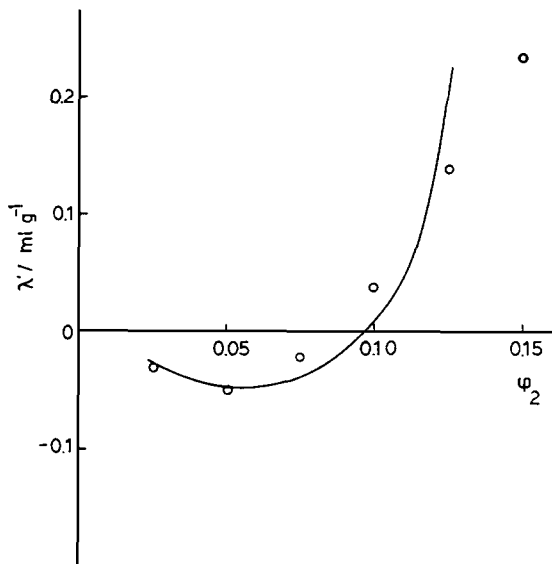


Fig. 1. Preferential adsorption coefficient λ' for the system PS + cyclohexane + ethanol. (○) Experimental points; (—) recalculated λ' values from Pouchly's assumption. Molecular weight of PS: 60,000.

intrinsic viscosity values to those corresponding to the actual solvent composition in the vicinity of the macromolecular chain.

In Figure 1 the coefficient of preferential adsorption λ' is plotted against the volume fraction ϕ_2 of ethanol. The coefficient is negative for compositions poor in ethanol. The inversion point is near $\phi_2 \approx 0.08$. It is therefore concluded that for ϕ_2 below 0.08, ethanol is preferentially adsorbed by the polymer, whereas cyclohexane is adsorbed above 0.08.

We would expect that ϕ_2 at the inversion point coincides with that composition where the maximum value of intrinsic viscosity $[\eta]$ occurs (Fig. 2). In practice this cannot be so. According to Živny et al.¹⁷ the difference in molar

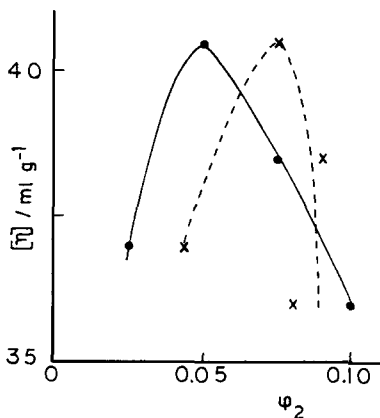


Fig. 2. Dependence of intrinsic viscosity $[\eta]$ on composition of ethanol, for the system: (●) experimental points; (x) corrected values of ($Z = 2$). M_w of PS: 310,000.

TABLE I
Corrected Composition ϕ_2 Values for the System Polystyrene + Cyclohexane + Ethanol, $Z = 2$

ϕ_2	x_1	λ' (ml g ⁻¹)	x'_1	ϕ'_2
0.025	0.955	-0.040	0.921	0.043
0.050	0.905	-0.050	0.863	0.077
0.075	0.860	-0.025	0.840	0.090
0.100	0.825	0.040	0.858	0.080

volumes of the liquid components is responsible for this disagreement. In our particular system the molar volume ratio is 1.85.

Taking into account the preferential adsorption effect, the curve $[\eta]$ versus ϕ_2 can be corrected to the actual composition existing in the vicinity of the polymer chain from the equation¹⁸

$$x'_1 = [Zx_1 + \lambda'(m/V_1)] / \{Z + \lambda'[(m/V_1) - (m/V_2)]\} \quad (4)$$

where x'_1 is the actual local mole fraction of liquid 1, x_1 is the uncorrected mole fraction, Z is the number of nearest-neighbor solvent molecules per monomer unit, m is the molar mass of the monomeric unit, and V_1 and V_2 are the molar volumes. The corrected values x'_1 are given in Table I. We have calculated x'_1 for values of Z equal to 2, 2.5, and 3.^{18,19} We have obtained the best correction of $[\eta]$ for $Z = 2$ (Fig. 2).

Alternatively, we could look at the cosolvency effect by using the solubility parameter δ . The solubility parameter of cyclohexane is $\delta_1 = 8.2$ (cal cm⁻³)^{1/2} and that of ethanol is $\delta_2 = 12.7$ (cal cm⁻³)^{1/2}.²⁰ The solubility parameter of the mixture at $\phi_2 = 0.05$ is $\delta_m = 8.4$ (cal cm⁻³)^{1/2} calculated with the Scatchard equation.²¹ If we introduce the correction due to preferential adsorption, the new value of δ_m is 8.8 (cal cm⁻³)^{1/2}, a more reasonable value since it is now closer to the solubility parameter of the polymer: $\delta_p = 9.1$ (cal cm⁻³)^{1/2}.^{20,21}

There are several approaches in trying to relate the coefficient of preferential adsorption to thermodynamic parameters. Pouchly et al.²² express λ' in terms of the solvent mixture composition, the binary interaction parameters g_{ij} , and the ternary interaction parameter g_T . The preferential adsorption coefficient can be expressed as

$$A_1 = \lim_{\langle \phi_3 \rangle \rightarrow 0} \lambda' / v_3 \quad (5)$$

where $A_1 = -M_{13}/M_{11}$, M_{ij} are the second derivatives of the Gibbs energy of mixing with respect to the i and j volume fractions at $\phi_3 \rightarrow 0$; v_3 is the partial specific volume of the polymer.

If the ternary interaction parameter g_T is assumed to be a correction to the binary interaction parameter g_{12} according to

$$g_T = \alpha_g g_{12} \quad (6)$$

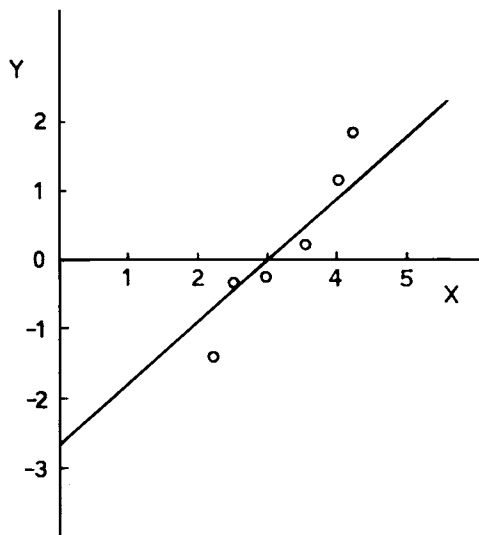


Fig. 3. Linearized plot Y versus X [cf. eq. (17), Ref. 22] for the system PS + cyclohexane + ethanol.

the ternary system can be treated by using eq. (17) in Ref. 22. The plot of Y versus X (see Fig. 3) is reasonably linear.

The intercept $(l - 1 + g_{13} - lg_{23})$ and slope $(1 - \alpha_g)$ obtained through linear regression yielded the binary interaction parameter difference, $g_{13} - lg_{23} = -3.54$ and $1 - \alpha_g = 0.962$, where $l = V_1/V_2$.

The binary interaction parameter is calculated from the equation²²

$$g_{12} = (x_1\phi_2)^{-1} \left\{ x_1 \ln \left(\frac{x_1}{\phi_1} \right) + x_2 \ln \left(\frac{x_2}{\phi_2} \right) \right\} + (x_1\phi_2)^{-1} \Delta G^E / RT \quad (7)$$

where x_i is the mole fraction of component i , and ΔG^E is the excess Gibbs

TABLE II
Binary Interaction Parameter g_{12} for Systems: (1) PS + Cyclohexane + Ethanol;
(2) PV2P + Nitromethane + Carbon Tetrachloride

1		2	
ϕ_2	g_{12}	ϕ_2	g_{12}
0.150	4.52	0.100	1.55
0.125	4.69	0.200	1.57
0.100	5.10	0.250	1.53
0.075	5.65	0.300	1.57
0.050	6.34	0.375	1.61
0.025	6.35	0.435	1.64
		0.500	1.68
		0.530	0.72
		0.600	1.77
		0.700	1.88
		0.750	1.93
		0.786	1.98

energy of mixing, values of which are taken from Ref. 23. As we can see from Table II, g_{12} values are comparatively high. The combination of high values of the slope and parameters g_{12} are consistent with the occurrence of inversion of preferential adsorption.²²

In Figure 1 the recalculated λ' values are plotted and compared with the experimental values to test the applicability of Pouchly's assumption. The fit is fairly good. The inversion point of the recalculated curve is shifted by 0.01 from the experimental inversion point.

Poly(vinyl-2-pyridine) + Nitromethane + Carbon Tetrachloride Cosolvent System

Nitromethane and carbon tetrachloride are both precipitants for poly(vinyl-2-pyridine). The polymer is dissolved by the solvent mixture in the range $\phi_2 = 0.1 < \phi_2 < 0.9$. The maximum of $[\eta]$ is at $\phi_2 = 0.7$ (Fig. 4). The polymer molecular weight is 45,000; higher molecular weights could not be dissolved at room temperature in the mixture. Figure 5 shows the dependence of λ' on mixture composition. The parameter of preferential adsorption is positive within the cosolvency region (Table III). This implies that γ_1 in eq. (3) is positive, or in other words that nitromethane is being preferentially adsorbed. This system, unlike the previous one, does not exhibit inversion of λ' .

The system presents large differences of the calculated values (from Pouchly's approach) from the experimental ones. The plot Y versus X shows large deviation from linearity (see Fig. 6). Apparently, more adjustable parameters are needed to describe the dependence of g_T on composition. An attempt

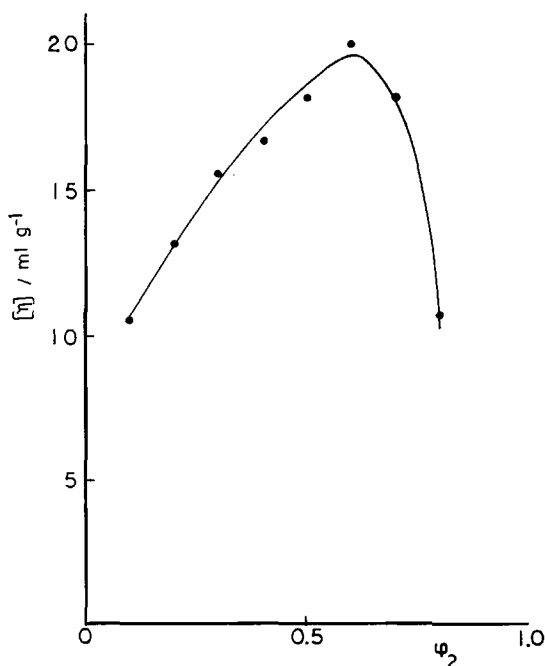


Fig. 4. Intrinsic viscosity $[\eta]$ of the system PV2P + nitromethane + carbon tetrachloride. Molecular weight of PV2P 45,000.

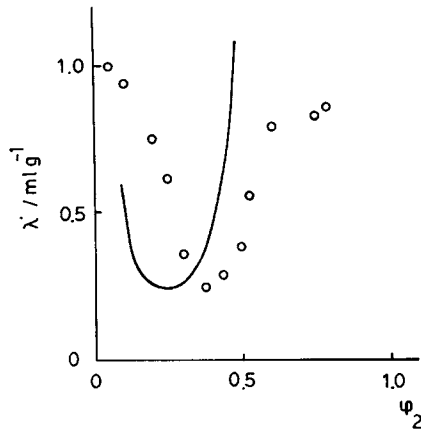


Fig. 5. Preferential adsorption coefficient λ' for the system PV2P + nitromethane + carbon tetrachloride. (O) Experimental points; (—) recalculated λ' values from Pouchly's assumption. Molecular weight of PV2P: 45,000.

TABLE III
Light Scattering Results for the System Polyvinyl-2-pyridine + Nitromethane + Carbon Tetrachloride ($M_w = 45,000$, $dn/d\phi_2 = -0.0812$)

ϕ_2	dn/dc (ml g ⁻¹)	M_{ap}/M_w	λ' (ml g ⁻¹)
0.050	0.2020	0.355	1.004
0.100	0.1989	0.378	0.944
0.200	0.1918	0.467	0.749
0.250	0.1889	0.544	0.612
0.300	0.1847	0.711	0.357
0.375	0.1793	0.789	0.247
0.435	0.1740	0.755	0.287
0.500	0.1705	0.667	0.384
0.530	0.1684	0.555	0.560
0.600	0.1560	0.355	0.776
0.750	0.1525	0.311	0.827
0.786	0.1500	0.289	0.854

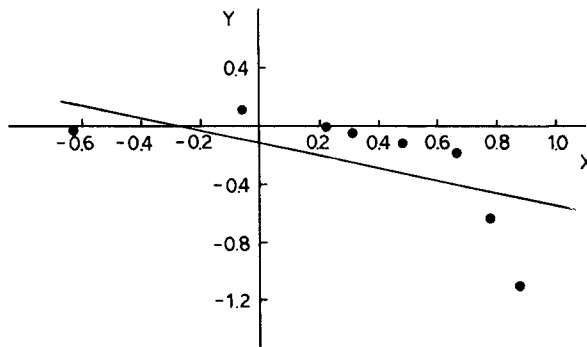


Fig. 6. Linearized plot Y versus X [cf. eq. (17), Ref. 22] for the system PV2P + nitromethane + carbon tetrachloride.

to linearize the Y versus X plot based on Pouchly's assumption for 9 experimental points, neglecting those near $\phi_2 = 0$, yields $1 - \alpha_g = -0.4$ and $g_{13} - Ig_{23} = 0.35$. In Figure 5 the resulting λ' curve shows a functional similarity to the experimental points.

Values of the binary parameter g_{12} are listed in Table II and are obtained through ΔG^E data from Ref. 24. We note that the low g_{12} values together with the relatively low absolute value of $1 - \alpha_g$ are consistent with the absence of inversion of the preferential adsorption coefficient.

Nitromethane and ethanol both have the same solubility parameter, 12.7 (cal cm^{-3})^{1/2}. Ethanol is an excellent solvent for poly(vinyl-2-pyridine)²⁵ and similar behavior is expected from nitromethane. The polar nitromethane shows a self association tendency by forming dimers of antiparallel configuration with two nearly linear weak H bonds.²⁶ This results in the precipitation of polybase poly(vinyl-2-pyridine), since contacts between the polymer and the solvent molecules are restricted. Even a small amount of carbon tetrachloride in the mixture will disrupt the nitromethane molecule self-association and allow the formation of H bonds between poly(vinyl-2-pyridine) and nitromethane; thus, the polymer is dissolved.

CONCLUSIONS

The two cosolvent systems studied in this work exhibit a distinct difference in terms of their preferential solvation parameters. For the system polystyrene + cyclohexane + ethanol, λ' undergoes inversion, unlike the system poly(vinyl-2-pyridine) + nitromethane + carbon tetrachloride, for which λ' remains positive within the cosolvency region ($\phi_2 = 0.1-0.9$). We have here a case (1) of "true" cosolvency and a case (2) of "apparent" cosolvency. In the latter case nitromethane is adsorbed over the entire range of mixture composition while the role of carbon tetrachloride is to prevent formation of nitromethane dimers. Values of the excess free energy of mixing ΔG^E are positive for both systems, as is to be expected for cosolvent systems.^{23,24} Furthermore, g_{12} is large for the first system, being lower for the second cosolvent system. The fact that (1) g_{12} values are low, (2) nitromethane is solely adsorbed by the polymer, and (3) the solubility parameter of nitromethane is equal to that of ethanol, which is a good solvent for poly(vinyl-2-pyridine), leads us to denote this type of cosolvency as an "apparent" cosolvency.

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