

Interpretation of the Enhanced Solubility of Poly(vinylidene Chloride) in Certain Solvent Mixtures

R. A. WESSLING, *Polymer Science Group, Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640*

Synopsis

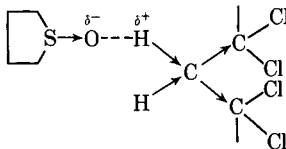
The 3-component mixture poly(vinylidene chloride)-tetramethylene sulfoxide-tetrahydrophalene has been investigated by viscometric methods. This solvent pair shows an unusual affinity for the polymer. This can be attributed to the strong polar interaction between the acidic polymer and the basic sulfoxide which is enhanced by the presence of the nonpolar diluent.

INTRODUCTION

The unusual ability of certain solvent mixtures to dissolve poly(vinylidene chloride) (PVDC) has been recently described.¹ The best combinations involved a polar aprotic solvent such as tetramethylene sulfoxide (TMSO), which was in itself a fairly good solvent for the polymer. The best cosolvents were found to be relatively nonpolar solvents with a cyclic structure such as tetrahydronaphthalene (THN).

The behavior of these systems was in qualitative agreement with the Flory theory of melting point depression extended to three-component mixtures. But the analysis did not provide information about the nature of the interactions between the various components.

It was postulated that polar aprotic solvents form a strong dipole bond with PVDC.^{1,2} This is illustrated schematically below:



This can be viewed as a Lewis acid-base interaction where PVDC functions as the acid.

The above-described system involves a highly crystalline polymer, PVDC. Enhanced solubility in mixed solvents is much more commonplace with amorphous polymers. The mixtures usually include one component with a higher cohesive energy than the polymer and another component with a lower cohesion energy. The optimum mixture is one that has matching cohesive energy. Gee³ has analyzed the thermodynamics of this case.

In mixtures involving polar polymers, however, the enhanced solubility is often attributed to the formation of specific interactions like that described for PVDC. One component is postulated to form a complex with the polymer; the complexed polymer is then solvated by the other component.⁴

The system cellulose nitrate-ether-alcohol is the classic example.⁵ Both components are nonsolvents, but mixtures readily dissolve the polymer. Spurlin⁶ has examined this system and concluded that the matching of cohesive energies is probably most significant. This follows from the observation that many nonpolar solvents will dissolve cellulose nitrate when mixed with alcohols.

Spurlin also points out that these mixtures do not dissolve cellulose trinitrate, which is a highly crystalline polymer. They function only for polymers of intermediate degree of nitration which show little crystallinity.

The present study was intended to show how interactions such as that described above contribute to increased solvating power in mixtures involving a crystalline polymer. The system PVDC-TMSO-THN was investigated by viscometric methods.

EXPERIMENTAL

The polymer samples used in this study were described previously.² Specific volumes of the solvent mixtures were measured in calibrated volumetric flasks at $60^\circ \pm 0.02^\circ\text{C}$.

Viscosities were measured in a Cannon-Ubbelohde viscometer. Flow times were converted to absolute viscosity using the calibration factor supplied by the manufacturer. Intrinsic viscosities were measured by a double extrapolation of relative viscosities determined at three concentrations.

RESULTS AND DISCUSSION

The solution temperatures for 1% PVDC in various solvent mixtures are shown in Figure 1. The minimum in T_m occurs at TMSO volume fraction of ~ 0.7 . The change in specific volume of the solvent mixtures as a function of composition is shown in Figure 2. The plot shows a slight positive deviation from ideality, indicating that the interaction parameter $\chi_{12} > 0$, but there is no evidence for any abnormal behavior in the range where the T_m minimum occurs. A value of χ_{12} for this system estimated from solubility parameters is² ~ 1.6 . This could be checked directly by vapor pressure measurements, but the main point to be made is that the interaction between the two components is unfavorable. This is to be expected for a mixture of a very polar solvent like TMSO with a nonpolar solvent like THN.

The viscosity of these mixtures was measured as a function of composition as a further check for ordering or association in the liquid. As Alfrey pointed out,⁷ a direct plot of viscosity versus composition is not easily

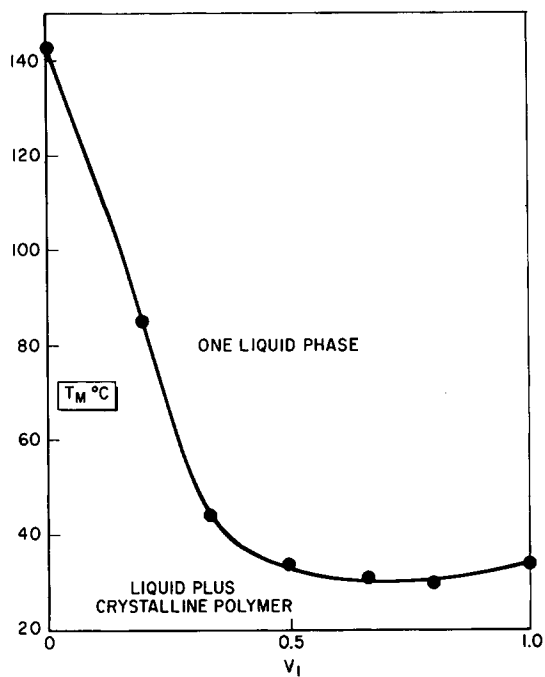


Fig. 1. Solution temperatures for 1% PVDC in TMSO-THN mixtures.¹

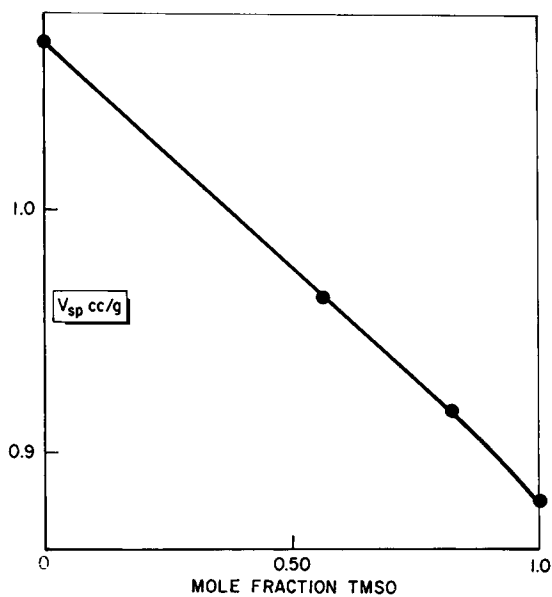


Fig. 2. Specific volume of TMSO-THN mixtures at 60°C.

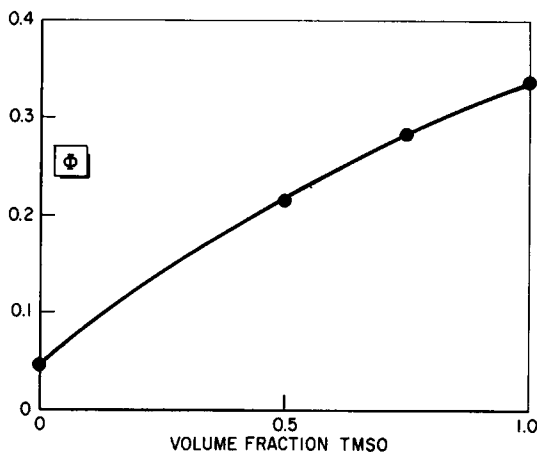


Fig. 3. Irany plot of viscosities of TMSO-THN mixtures.

interpreted. Irany⁸⁻¹⁰ has investigated this problem and devised a way to check for abnormal behavior in liquid mixtures. He developed an empirical viscosity function, Φ , which has the property of being a linear function of composition (expressed as volume fraction) for ideal mixtures. The breakup or formation of complexes or other ordered structures is evidenced by critical points on a Φ plot.

The Φ plot for the TMSO-THN system is shown in Figure 3. The smooth curve deviates slightly from linearity, but there is no evidence for abnormal structure at $v_1 = 0.7$.

The above results indicate that the solvent mixture behaves normally. Therefore, the abnormal features of this system must be associated with the polymer-solvent interaction. This aspect was explored by studying the effect of solvent composition on intrinsic viscosity.

A sensitive test for nonideal behavior can be made by comparing the temperature coefficient of intrinsic viscosity. The following rule is followed by many polymer-solvent systems:

$$\frac{d[\eta]}{dT} \text{ is zero or slightly negative in athermal solutions; } \chi_1 \approx 0$$

$$\frac{d[\eta]}{dT} > 0 \text{ in poor solvents; } \chi_1 > 0$$

$$\frac{d[\eta]}{dT} < 0 \text{ in active solvents; } \chi_1 < 0.$$

The active solvent, TMSO, was checked by this method. The results are listed in Table I.

This is a substantial decrease in $[\eta]$ for a relatively modest increase in temperature, indicating that $d[\eta]/dT < 0$ as required for a system with $\chi_1 < 0$. Although intrinsic viscosities in THN cannot be measured at these

TABLE I
Effect of Temperature on $[\eta]$ in TMSO

$[\eta]$, dl/g	T, °C
0.69	25
0.64	60

temperatures owing to polymer insolubility, it is possible to get data over a wide range of TMSO/THN ratios. These results are plotted in Figure 4.

The increase in solvent activity by the addition of a hydrocarbon to TMSO is demonstrated by the maximum in $[\eta]$ -versus- v_1 plots at both temperatures. Over the range studied, $[\eta]$ decreased when the temperature was raised to 60°C, as it did in the TMSO above. The greatest change occurred at the optimum composition, suggesting that the interaction is strongest in this mixture.

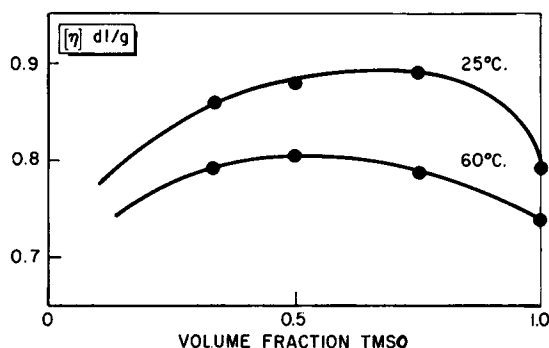


Fig. 4. Change in intrinsic viscosity with solvent composition in the system TMSO-THN.

A point of interest is that the curves must cross at some low TMSO concentration. This follows from the fact that $d[\eta]/dT > 0$ in THN. A value of $[\eta]$ at these temperatures cannot be obtained because of rapid crystallization of the polymer. However, $[\eta]$ must fall sharply as v_1 approaches 0. A value of $[\eta]_{\text{THN}} \approx 0.5$ would not be unreasonable at 60°C.

The compositions at which $[\eta]$ reaches a maximum are compared to the composition for the T_m minimum in Table II. The agreement suggests that the same factors that influence the melting point depression in these mixtures also increases the size of the polymer coil in solution.

TABLE II
Comparison of Optimum Compositions

Method	T, °C	Volume fraction TMSO
T_m	29	0.7
$[\eta]$	25	0.7
$[\eta]$	60	0.6

The results in Table II suggest that the enhanced solubility of PVDC in TMSO-THN system is not related to any abnormal feature of the solvent mixture. Its properties conform to what is expected for a mixture of polar and nonpolar molecules.

The primary effect of the mixed solvent is to expand the polymer coil in solution. This is characteristic of stronger interaction between polymer and solvent. The nature of the mixture suggests that the dipole bonding between TMSO and PVDC is favored in the presence of the hydrocarbon diluent, thus leading to a more negative value for their pair interaction parameter, χ_{31} . This should lead to a higher concentration of TMSO molecules in the vicinity of the polymer coil and, therefore, should be measurable by light scattering techniques.¹¹

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