

The Solubility of Poly(vinylidene Chloride) in Solvent Mixtures

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

Synopsis

Effective solvents for poly(vinylidene chloride) (PVDC) were obtained by mixing a polar aprotic solvent with a less polar solvent of cyclic structure. The polar components included sulfoxides, N,N-dialkylamides, and N-alkyl lactams. The cyclic cosolvents included aliphatic and aromatic hydrocarbons, ketones, ethers, and thioethers. The problem of solubility of a crystalline polymer in a mixed solvent was analyzed by extending the Flory theory of melting point depression to three component mixtures. The results predict that favorable mixtures arise when at least one of the components interacts strongly with the polymer but is nearly incompatible with the cosolvent. This is in qualitative agreement with the observed behavior of PVDC.

INTRODUCTION

An experimental study of the melting point depression of poly(vinylidene chloride) (PVDC) in solvent mixtures has been carried out. This polymer shows enhanced solubility in certain solvent pairs. It is the purpose of this study to show that such enhanced solubility can be predicted by extending the Flory theory of melting point depression¹ to three component mixtures.

Highly crystalline polymers such as polyethylene are normally insoluble, except at temperatures near or above their melting points. This can be easily deduced from Flory's equation for all cases in which χ_1 is positive:

$$\frac{1}{T_M} - \frac{1}{T_M^0} = \frac{RV_u}{\Delta H_u V_1} (\varphi_1 - \chi_1 \varphi_1^2). \quad (1)$$

Polar crystalline polymers, on the other hand, can be dissolved in certain specific solvents at temperatures far below T_M^0 . A common characteristic of such systems is a negative value for χ_1 . As a consequence, the intrinsic viscosity of polar polymers in specific solvents has a negative temperature dependence. In extreme cases, phase separation can be induced by heating; i.e., this type of polymer may exhibit inverse solubility also.²

Polar polymers also dissolve more readily in specific solvent mixtures. The cellulose derivatives are classic examples.³ This analysis will show that active solvent mixtures can be characterized by a negative value for one of the pair interaction parameters, χ_{ij} . This result follows from an

extension of the Flory theory to a system involving two liquid components and one polymeric crystalline component. A relationship is derived to show how the melting point of the polymer in a mixture changes with solvent composition. This relationship is used to evaluate the experimental results.

THEORETICAL

The chemical potential per mole of segments is given¹ by

$$\frac{\mu_u - \mu_u^0}{RT} = -\phi_s \frac{V_u}{V_1} \left[v_1 + \frac{v_2}{x_2} - (\chi_{31}v_1 + \chi_{32}v_2 - \chi_{12}v_1v_2)\phi_s \right] \quad (2)$$

where ϕ_s is the total volume fraction of solvents in the mixture; v_1, v_2 are the volume fractions of each component in the solvent mixture; x_2 is the ratio of molar volumes of the two solvents; χ_{ij} are the pair interaction parameters per segment; and the polymer is component 3. (The approximation has been introduced that the molecular weight of the polymer is large; therefore, terms involving $1/x^3$ have been dropped.)

The derivation of the melting point depression equation can be obtained by following Flory's procedure. This yields the equation

$$\frac{1}{T_M} - \frac{1}{T_M^0} = \frac{RV_u\phi_s}{\Delta H_u V_1} \left[v_1 + \frac{v_2}{x_2} - (\chi_{31}v_1 + \chi_{32}v_2 - \chi_{12}v_1v_2)\phi_s \right]. \quad (3)$$

Equation (3), as written, is not convenient for examining the effect of solvent composition on T_M at fixed ϕ_s . Therefore, eq. (3) must be rearranged introducing at the same time an expression for the temperature dependence of the χ_{ij} . (Composition dependence is ignored for the sake of simplicity.) Substituting with the equation

$$\chi_{ij} = \alpha_{ij} + \frac{\beta_{ij}}{T} \quad (4)$$

and rearranging gives the desired function, $T_M(v_1)$:

$$T_M = \frac{1 + \frac{RV_u\phi_s^2(\beta)}{\Delta H_u V_1}}{\frac{1}{T_M^0} + \frac{RV_u\phi_s}{\Delta H_u V_1} \left[v_1 + \frac{v_2}{x_2} - (\alpha)\phi_s \right]} \quad (5)$$

where $(\alpha) = \alpha_{32} + (\alpha_{31} - \alpha_{32} - \alpha_{12})v_1 + \alpha_{12}v_1^2$; $(\beta) = \beta_{32} + (\beta_{31} - \beta_{32} - \beta_{12})v_1 + \beta_{12}v_1^2$.

Equation (5) contains no further approximations beyond those in the original Flory treatment. It reduces to the Flory theory at the limits $v_1 = 0$, $v_1 = 1$. Therefore, the behavior of the three-component mixture can in principle be deduced from a knowledge of the various two-component mixtures. The parameters χ_{31} and χ_{32} are obtained at $v_1 = 1$, $v_1 =$

0, respectively. The third interaction parameter can be estimated from the Hildebrand equation:⁴

$$\chi_{12} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (6)$$

where δ_1 is the square root of the cohesive energy density.

A more direct approach would be to evaluate χ_{12} from the derivatives of eq. (5). However, tractable expressions for the latter can only be obtained by introducing additional approximations. Assume first that the solvents have roughly equal molar volumes,

$$v_1 + \frac{v_2}{x_2} \simeq 1. \quad (7)$$

Assume further that

$$\chi_{ij} = \frac{V_i B_{ij}}{T} + \chi_s \quad (8)$$

where B_{ij} is the pair interaction energy density as defined by Flory.

The factor χ_s is usually required to correlate χ_{ij} with cohesive energy densities. For most nonpolar polymers it has a value⁵ of ~ 0.34 . The approximation, eqs. (6) and (8), make (α) a constant, and eq. (5) reduces to

$$T_M = \frac{1 + \frac{V_u \phi_s^2}{\Delta H_u} [B_{32} + (B_{31} - B_{32} - B_{12})v_1 + B_{12}v_1^2]}{\frac{1}{T_M^0} + \frac{RV_u \phi_s}{\Delta H_u V_1} [1 - 0.34\phi_s]} \quad (9)$$

The qualitative influence of composition on solution temperature can now be mapped out by examining the derivatives of eq. (9). Assuming the B_{ij} are independent of solvent composition, then

$$\frac{dT_M}{dv_1} = \frac{\frac{V_u \phi_s^2}{\Delta H_u} [(B_{31} - B_{32} - B_{12}) + 2B_{12}v_1]}{\frac{1}{T_M^0} + \frac{RV_u \phi_s}{\Delta H_u V_1} [1 - 0.34\phi_s]} \quad (10)$$

and

$$\frac{d^2 T_M}{dv_1^2} = \frac{\frac{2V_u \phi_s^2 B_{12}}{\Delta H_u}}{\frac{1}{T_M^0} + \frac{RV_u \phi_s}{\Delta H_u V_1} [1 - 0.34\phi_s]} \quad (11)$$

The simplified theory predicts that a plot of dT_M/dv_1 against v_1 will be linear. The slope of such a plot can be used to calculate B_{12} since the other parameters can be evaluated independently from the limiting conditions.

The case in which $B_{12} = 0$ is defined as an ideal mixture; i.e., one with no interaction between the solvent components. The solution temperature in an ideal mixture is a linear function of composition.

There are several kinds of nonideal mixtures to consider, depending on the signs of the B_{ij} . If all are positive, the mixtures can be described in terms of solubility parameters or regular solution theory,⁵ where

$$B_{ij} = (\delta_i - \delta_j)^2 \quad (12)$$

Solubility will depend on the relative values of δ_1 and δ_2 with respect to δ_3 , the solubility parameter of the polymer; for example, if $\delta_1 < \delta_2$; $\delta_1 > \delta_3$; then the melting point of the mixture will fall as v_1 increases.

The only possibility for enhanced solubility in a regular mixture is where $\delta_1 > \delta_3 > \delta_2$ (or vice versa). This was first pointed out by Gee for solutions involving amorphous polymers.⁶ In this case, the melting point of the mixture falls to a minimum at the point where the average solubility parameter of the mixture matches that of the solvent.

If one of the polymer interaction parameters is negative, two other types of nonideal mixtures, depending on the sign of B_{12} , are possible:

1. Favorable mixtures

$$B_{12} > 0; \frac{d^2T_M}{dv_1^2} > 0 \quad (13)$$

2. Unfavorable mixtures

$$B_{12} < 0; \frac{d^2T_M}{dv_1^2} < 0 \quad (14)$$

Mixtures of the first type are again more effective than an ideal mixture. Those of the second type, however, are poorer. T_M -versus- v_1 curves having either a maximum or a minimum are possible. The critical condition for this to occur is obtained by setting eq. (10) equal to zero:

$$v_1 \text{ (critical)} = \frac{B_{32} - B_{31} + B_{12}}{2B_{12}} \quad (15)$$

with the obvious limitation that $0 \leq v_1 \leq 1$. Therefore, it follows that

$$0 \leq B_{32} - B_{31} \leq B_{12} \quad (16)$$

in order to observe a critical point. The critical composition is $v_1 = 0.5$ when $B_{31} = B_{32}$, and it approaches 1 as the difference $(B_{32} - B_{31})$ approaches B_{12} .

One other theoretically possible mixture is that in which all the interaction parameters are negative. According to eq. (11), the second derivative is always negative for this case. Consequently, if all interactions are favorable, the mixture will be better than ideal. This case also predicts a minimum in a T_M -versus- v_1 plot if $B_{31} < (B_{12} + B_{32})$.

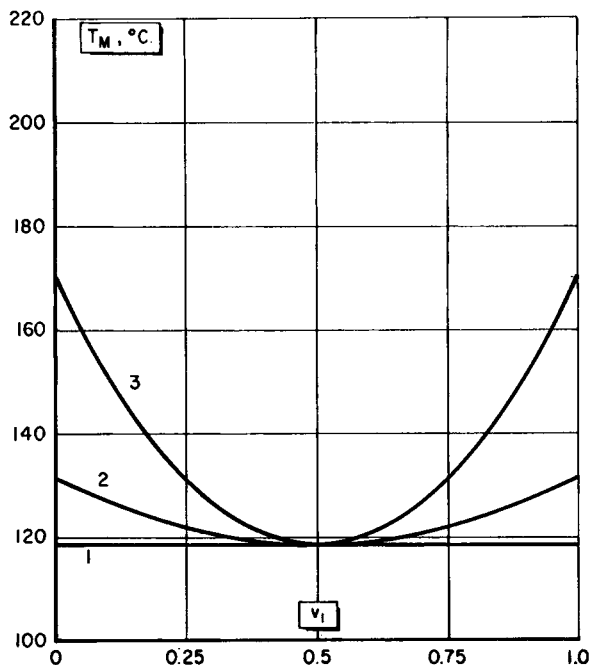


Fig. 1. Solution temperature in nonpolar mixtures: (1) ideal solution; ideal mixture $\delta_1 = \delta_2 = \delta_3 = 10$; (2) $\delta_1 = 9$; $\delta_2 = 11$; $\delta_3 = 10$; (3) $\delta_1 = 8$; $\delta_2 = 12$; $\delta_3 = 10$.

Theoretical curves according to eq. (9) are plotted in Figure 1. Solubility parameters were used to calculate the B_{ij} . The material constants for all the calculations are: $T_M^0 = 473^\circ\text{K}$; $\Delta H_u = 1500$ cal/mole; $V_u = 50$ cc/mole; $V_1 = 100$ cc/mole; $V_2 = 100$ cc/mole.

The maximum T_M depression is observed when the solvent pair are on the threshold of incompatibility; $\delta_1 - \delta_2 = 4$. But as expected, the optimum mixture is no better than an ideal mixture in which $\delta_1 = \delta_2 = \delta_3$.

In systems involving polar solvents, χ_s is usually close to zero. This approximation changes eq. (9) to

$$T_M = \frac{1 + \frac{V_u \phi_s^2}{\Delta H_u} [B_{32} + (B_{31} - B_{12})v_1 + B_{12}v_1^2]}{\frac{1}{T_M^0} + \frac{RV_u \phi_s}{\Delta H_u V_1} [1 - 0.34(1 - v_1)\phi_s]} \quad (17)$$

Plots of this function are shown in Figures 2 and 3. (Values of B_{ij} were chosen arbitrarily.) In the first case, where component 1 interacts favorably ($B_{31} < 0$) and component 2 forms an athermal mixture ($B_{32} = 0$), the observed behavior depends on B_{12} . If $B_{12} = 0$, (solvents mix ideally), T_M increases almost linearly as the proportion of the poorer solvent is increased. This can again be defined as an ideal type of mixture. If $B_{12} >$

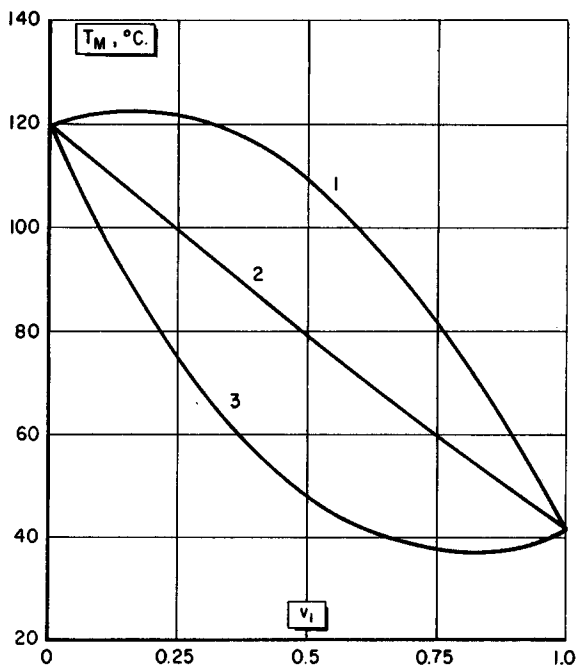


Fig. 2. Effect of solvent 1-solvent 2 interaction on solution temperature in polar mixtures: (1) unfavorable mixture, $B_{31} = -200$; $B_{32} = 0$; $B_{12} = -500$; (2) ideal mixture, $B_{31} = -200$; $B_{32} = 0$; $B_{12} = 0$; (3) favorable mixture, $B_{31} = -200$; $B_{32} = 0$; $B_{12} = +500$.

0 (the solvents mix unfavorably), the ability of the mixture to dissolve the polymer is enhanced. The plot, in fact, shows a minimum indicating that mixtures in this range are better solvents than the better component by itself.

If, however, $B_{12} < 0$ (the solvents interact favorably), then the cosolvent is competing with the polymer to form interaction pairs with the active solvent. If it interacts more favorably, as in the case shown, solubility in the mixture can be reduced; hence a maximum in T_M is observed.

The plot in Figure 3 shows an example where the cosolvent interacts unfavorably with the polymer ($B_{32} > 0$). Even so, favorable mixtures can be formed if the interaction between the solvents is sufficiently poor. When B_{12} becomes very positive, a minimum again appears, indicating enhanced solubility in the mixture over either of the pure components.

EXPERIMENTAL

The solvents, polymer samples, and technique used to obtain solution temperatures have been described earlier.⁷ Solvent mixtures were made up by volume. The mixtures contained 0.25 g polymer in 15 cc total solvent. (This is approximately 1% by volume.) The usual procedure was

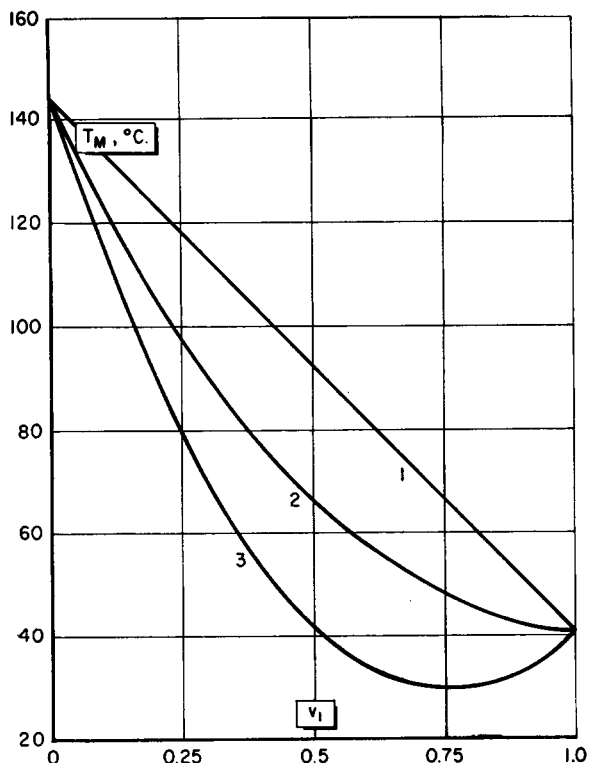


Fig. 3. Effect of solvent interaction on solution temperature in a good solvent/poor solvent mixture: $B_{31} = -200$; $B_{32} = 100$; (1) $B_{12} = 0$; (2) 400; (3) 800.

to disperse the powdered polymer in the poorer solvent component, add the second component, and start heating immediately. Variation in the visually observed endpoint was less than $\pm 2^\circ\text{C}$, provided the mixtures were prepared at 0°C or lower. The solvents, obtained from a variety of sources, were practical grade or better and were used as received.

RESULTS

The theoretical analysis predicts the existence of ideal mixtures (T_M -versus- v_1 plots are linear), favorable mixtures that are better than ideal, $d^2T_M/dv_1^2 > 0$, and mixtures that are poorer than ideal, $d^2T_M/dv_1^2 < 0$. It also predicts that certain solvents should show a maximum or minimum in the T_M -versus- v_1 plot. Examples that appear to fit all of these categories have been observed experimentally.

Some linear T_M -versus- v_1 plots are shown in Figure 4. Assuming these are normal mixtures, the linearity requires that $\delta_1 = \delta_2$. This does not appear to be the case. Other examples of normal mixtures showing slightly curved plots are shown in Figure 5. All mixtures are better than

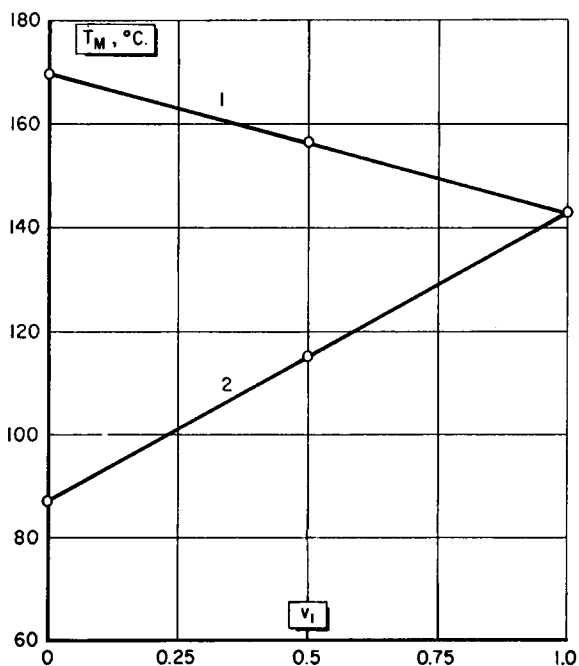


Fig. 4. Solution temperatures for PVDC in ideal mixtures (1% polymer): (1) decahydronaphthalene in tetrahydronaphthalene, $\delta_1 = 8.3$; $\delta_2 = 9.5$; (2) tetrahydrothiophene in tetrahydronaphthalene, $\delta_1 = 9.0$; $\delta_2 = 9.5$.

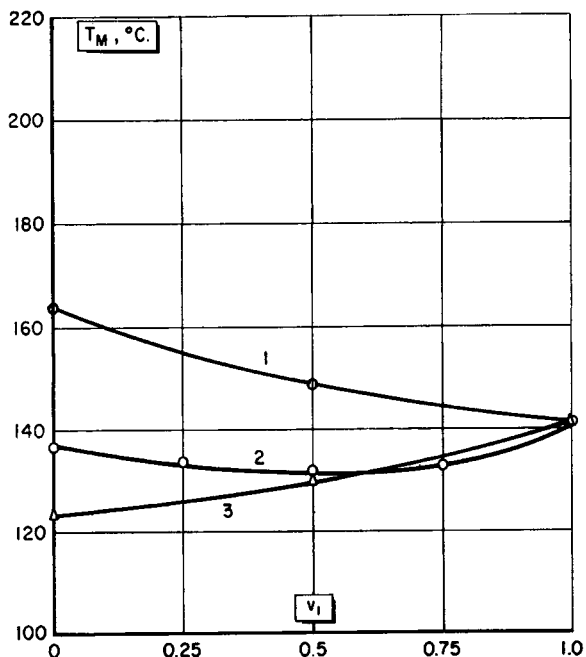


Fig. 5. Solution temperatures for PVDC in ideal mixtures (1% polymer): (1) *o*-ethyltoluene in tetrahydronaphthalene, $\delta_1 = 8.9$; $\delta_2 = 9.5$; (2) benzonitrile in tetrahydronaphthalene, $\delta_1 = 11.2$; $\delta_2 = 9.5$; (3) bromoform in tetrahydronaphthalene, $\delta_1 = 10.5$; $\delta_2 = 9.5$.

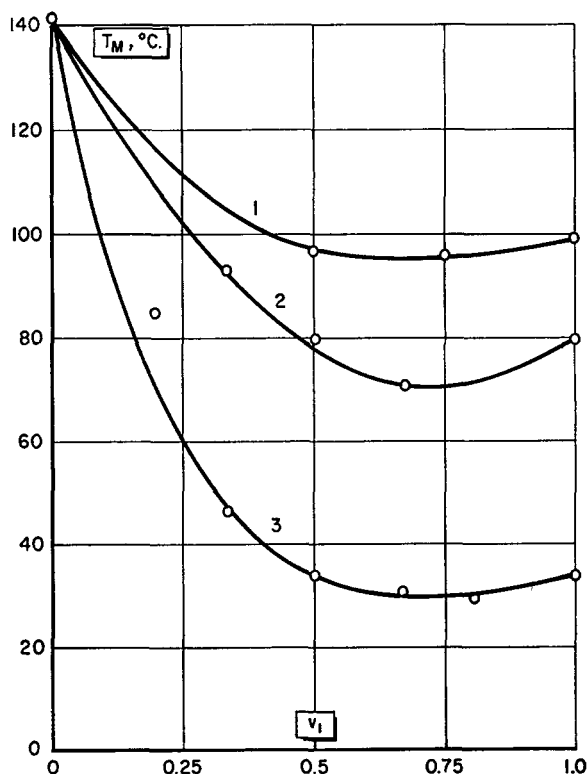


Fig. 6. Solution temperatures for PVDC in ideal mixtures (1% polymer): (1) tetrahydronaphthalene-*n*-butyl sulfoxide; (2) tetrahydronaphthalene-isopropyl sulfoxide; (3) tetrahydronaphthalene-tetramethylene sulfoxide.

ideal, but solubility is enhanced only where $\delta_1 < \delta_p < \delta_2$. As predicted, neither mixtures nor pure components are able to depress T_M very much.

Significantly different behavior is encountered when one or both of the components is a solvent known to interact strongly with PVDC. These include sulfoxides, dialkylamides, and alkyl lactams. Mixtures showing unusual effects were observed only when one of these solvents was present. This encompasses both favorable and unfavorable mixtures. A "favorable" mixture is arbitrarily defined as one in which addition of a cosolvent to the base solvent either lowers solution temperatures or does not significantly increase it. The base solvent is always taken as the better of the pair. T_M -versus- v_1 plots of "favorable" mixtures involving one active component are shown in Figures 6-9. In most of the cases studied, the cosolvent that formed active mixtures were less polar and contained a ring structure. Tetrahydrothiophene, tetrahydrofuran, tetrahydronaphthalene, and cycloheptanone were particularly effective as cosolvents.

In all the above described "favorable" mixtures, one of the components is by itself a very good solvent. However, there are also a number of cases

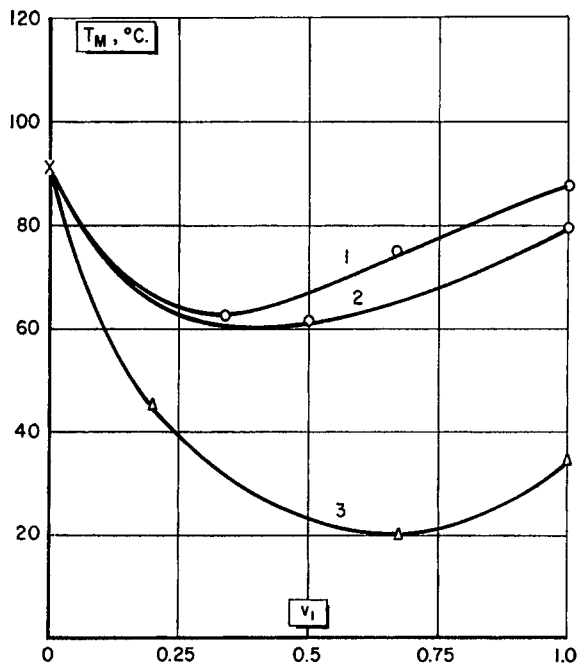


Fig. 7. Solution temperatures for PVDC in ideal mixtures (1% polymer): (1) di-methylacetamide; (2) isopropyl sulfoxide; (3) tetramethylene sulfoxide.

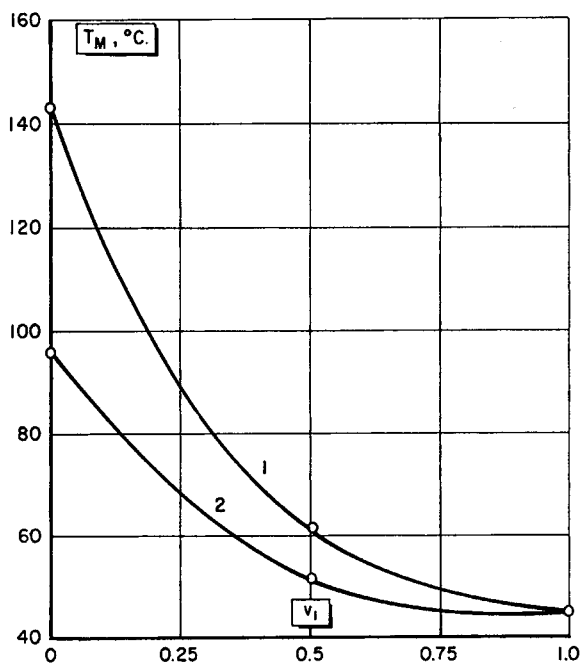


Fig. 8. Solution temperatures for for PVDC in ideal mixtures (1% polymer): (1) with tetrahydronaphthalene; (2) with cycloheptanone.

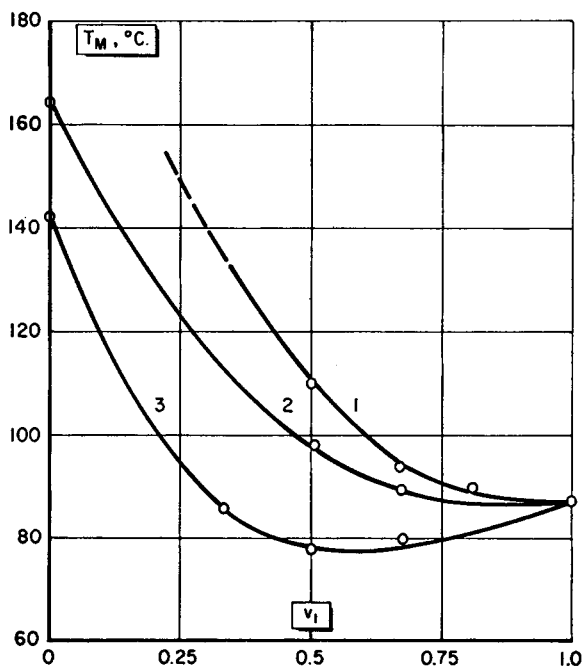


Fig. 9. Solution temperatures for PVDC in ideal mixtures (1% polymer): (1) ethyl-*t*-butylbenzene; (2) *o*-ethyltoluene; (3) tetrahydronaphthalene.

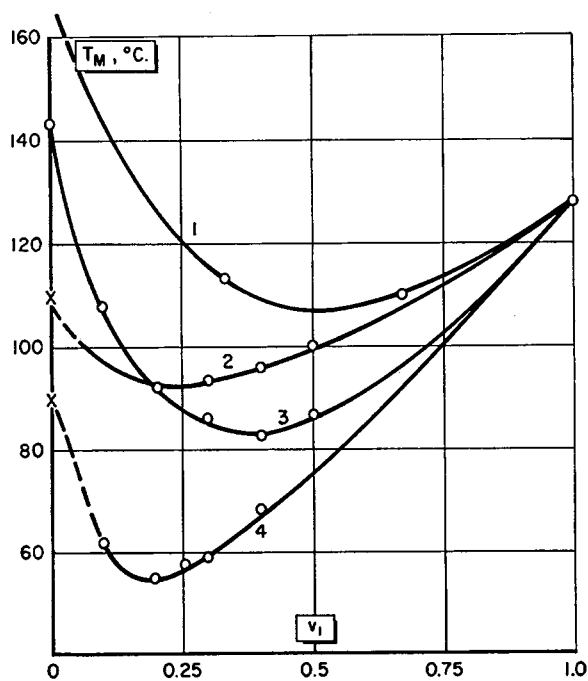


Fig. 10. Solution temperatures for PVDC in ideal mixtures (1% polymer): (1) diethylbenzene; (2) 1,4-dioxane; (3) tetrahydronaphthalene; (4) tetrahydrofuran.

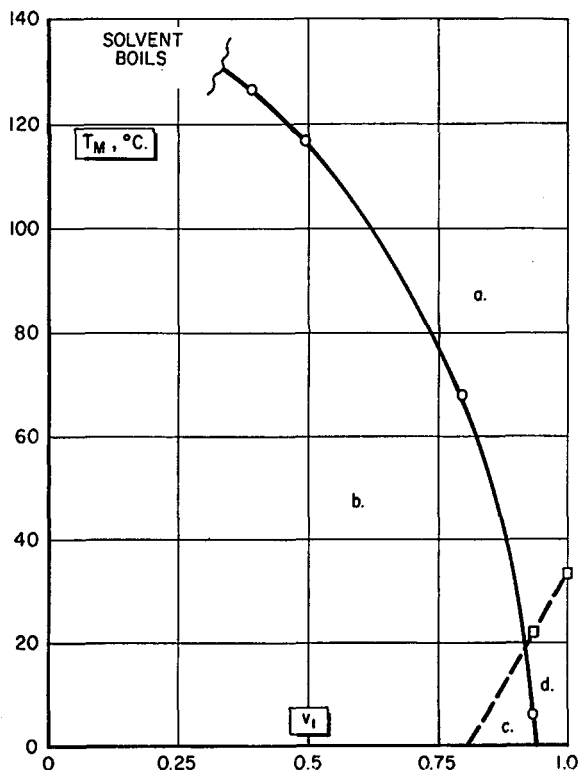


Fig. 11. Solution temperatures for PVDC in ideal mixtures (1% polymer): (a) one liquid phase region; (b) two liquid phases; (c) two liquid phases and one crystalline phase; (d) one liquid phase and one crystalline phase.

in which neither component is a good solvent, but together they form "favorable" mixtures. Each mixture contains at least one dipolar aprotic solvent from the groups listed above. The cosolvents are again usually cyclic solvents of lower polarity. Selected examples are plotted in Figure 10.

Another class of mixtures which were not thoroughly investigated are those involving immiscible components. The endpoints in these systems are not easy to detect with visual methods. Only one case, TMSO/1,2-dimethylcyclohexane, was studied sufficiently to define the behavior. Mixtures of the components form two phases at 25°C. When PVDC is added, it dissolves in the TMSO-rich phase. The mixture must then be heated to form a single phase. The results are shown in Figure 11. The upper curve defines the temperature at which the system becomes one phase. The lower curve shows the temperature at which the three-phase mixture melts into two liquid phases.

Only a limited number of "unfavorable" solvent mixtures were investigated. In these cases, the mixture is poorer than ideal. This behavior is usually observed in mixtures of dipolar aprotic solvents with H-bonding

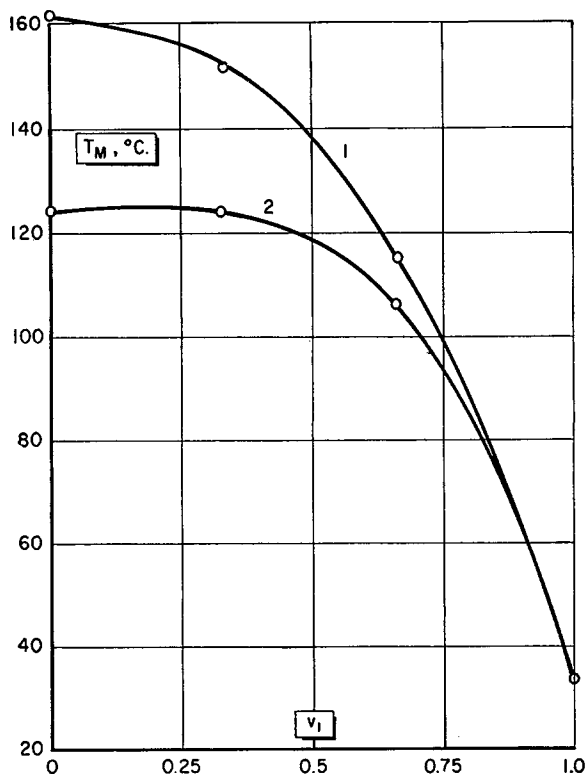


Fig. 12. Solution temperatures for PVDC in ideal mixtures (1% polymer): (1) benzyl alcohol-tetramethylene sulfoxide; (2) bromoform-tetramethylene sulfoxide.

solvents, alkyl halides, or any other solvent containing an acidic H. In all cases, the cosolvent competes with the polymer to form contacts with the active solvent. Two examples of unfavorable mixtures are shown in Figure 12. No maximum is observed in the TMSO/benzyl alcohol system, but a definite maximum at low TMSO content is observed in mixtures with bromoform.

DISCUSSION

These results are consistent with the view that PVDC acts as a weak Lewis acid when dissolved in polar aprotic solvents.⁷ Mixtures involving a strong Lewis base and a nonpolar or weakly basic cosolvent were found to be favorable; mixtures with hydrogen-bonding or Lewis acid cosolvents were found to be unfavorable.

The behavior is not general, however; only specific classes of solvents were effective. The polar component in all the cases observed contained either the sulfoxide or amide functionality (the latter included dialkylamides; *N,N*-cyclic amides and alkyl lactams). The good cosolvents were ring compounds including cyclic aliphatic hydrocarbons, aromatic

hydrocarbons, cyclic ketones, cyclic sulfides, and cyclic ethers. None of the halocarbons (whether cyclic or otherwise) were effective cosolvents in spite of their low polarity.

The specificity of solvent pairs suggests that nonideal entropies of mixing may be the rule in these systems. If so, the approximation that the χ_{ij} are not functions of composition would certainly not be valid.

In comparing theoretical and experimental T_M -versus- v_1 plots, one is struck by the similarities. However, attempts to analyze the data using the simplified equations [eqs. (9-11)] were generally not successful. More often than not, plots of dT_M/dv_1 were not linear; and even in cases where they were, values of B_{12} derived from the slope did not agree with those calculated from solubility parameters. For example, the mixture of decahydronaphthalene ($\delta_1 = 8.3$) and tetrahydronaphthalene ($\delta_1 = 9.5$) should exhibit a curved T_M -versus- v_1 plot. However, it is observed to be linear indicating $\delta_1 = \delta_2$.

One possible explanation, advanced above, is that χ_{ij} are functions of composition due to nonideal entropy effects such as association and cooperative dipolar interactions. Or, more generally, the Flory-Huggins theory may not be adequate to predict behavior in mixtures that are not regular.⁸ Another obvious factor is that $V_1 \neq V_2$ in most of the cases studied. Significant deviations from the simplified theory occur when V_2/V_1 is large. At the limit where $v_1 = 0$, for example, the interaction parameter is $B_{32}V_1/RT$ in the simplified version, whereas it should be $B_{32}V_2/RT$.

Another factor, more difficult to evaluate, is that the measured T_M values were not obtained at thermodynamic equilibrium. Previous results have shown that the T_M values obtained with "as polymerized" PVDC can be significantly below the theoretical value obtained by extrapolation of a T_M -versus- T_c plot (where T_c is the temperature at which the polymer was crystallized from solution). One might expect that the T_M value in poor solvents would be closer to theoretical due to annealing during the heating. The net effect would be to distort the T_M -versus- v_1 plot. Studies are now underway to determine if this is the case.

Even though quantitative agreement with theory is lacking, the qualitative predictions seem to be sound. It appears that the solvent mixtures most effective in dissolving PVDC contain a strongly interacting component ($B_{31} < 0$) and a cosolvent that interacts unfavorably with it ($B_{12} \gg 0$). The value of the third parameter is less critical. Ideally, the best mixture would be $B_{31} \approx B_{32} \ll 0$ and $B_{12} \gg 0$; i.e., a pair of strong solvent that are nearly incompatible with each other.

This analysis should also apply to other systems. Preliminary results in this laboratory suggest that poly(vinylidene fluoride) acts very much like PVDC. The study of Adelman and Klein⁹ on the solubility of PVC in solvent mixtures suggests that it behaves similarly.

Theoretically, there is no reason why the analysis should not apply to systems of opposite polarity. One might predict that mixtures of Lewis

acids with nonpolar cosolvents should form favorable mixtures for a polyester; mixtures containing a Lewis base as cosolvent should be less effective.

The author enjoyed many stimulating discussions on this subject with Drs. T. Alfrey, Jr. and K. W. Suh of The Dow Chemical Company and Professor H. Morawetz. Mr. J. T. Woodard assisted with experimental portions of the work.

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