

Predicting Solubilities of Vinyl Polymers

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Synopsis

Accurate solubility limits of polymers are best expressed by molecular weight fractionation curves. Individual curves may be obtained for each polymer-solvent (-non-solvent) system. A method for predicting solubility behavior, based on solubility parameter δ and hydrogen bonding index γ , is proposed here. The correlation is of the form

$$[\eta] = k \frac{T^{(cQ)}}{(v.f.)^{(ab+R)}}$$

where $[\eta]$ = intrinsic viscosity of precipitated polymer; T = absolute temperature; $(v.f.)$ = volume fraction of solvent; $R = (\delta_s - \delta_n) - 0.3(\gamma_s - \gamma_n)$; $Q = (\gamma_p - \gamma_e)^{2.2} / (\delta_p - \delta_e)$; p refers to polymer; s refers to solvent; n refers to nonsolvent; e refers to solvent system at theta temperature; and a, b, c , and k are fitted constants. The correlation was derived from data for poly(vinylpyrrolidone) and polyacrylamide. It probably is limited to systems in which the precipitate occurs as a liquid.

INTRODUCTION

The prediction of polymer solubilities is seldom considered as a facet of molecular weight fractionation, however, the two studies are one and the same. Prediction of the point of precipitation entails a complete knowledge of the solubility limit of a given molecular weight polymer in a given solvent system. To predict this from intrinsic properties of the polymer and solvent requires a complete characterization of the factors affecting the mechanism of solution. Although attempts have been made at correlating solubilities with intrinsic properties, the results have been generally unsatisfactory and incomplete. Presented within this paper is a new technique of predicting limiting solubility of a polymer in any combination of solvents. To characterize the components, only the solubility parameter and hydrogen bonding index were found necessary.

THEORETICAL CONSIDERATIONS

As a basis for the proposed correlation, the characteristic features of phase equilibria theory must be presented. The equilibrium between a

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single solvent and single polymer homolog will be considered understood. The discussion, also, will be limited to systems in which both phases are amorphous and liquid. In systems of reasonable molecular weight (greater than 10,000), it was substantiated by Flory that phase separation occurs near the theta temperature and is unaffected by polymer concentration in the dilute range.¹

The conditions for equilibrium between two phases consisting of a single solvent and a polymer with a distribution of molecular weights may be described by chemical potential expressions

$$\mu_0 = \mu_0' \text{ (for the solvent)}$$

$$\mu_x = \mu_x' \text{ (for each polymer species } x\text{).}$$

The primed symbols will refer to the precipitated phase. It is theoretically possible to derive exact conditions of equilibrium for any given value of the polymer-solvent interaction parameter, χ , and specified molecular weight distribution. This yields theoretical values which may be treated as maxima, since the calculations ignore polymer-polymer interactions, chain entanglements, and agglomerations. Since a general treatment based on thermodynamic relations is necessarily very involved mathematically, the relatively simple equations and concepts of the Flory-Huggins theory will be used here following the technique of Huggins and Okamoto.²

The chemical potentials of polymer species x in the two phases are equated and combined with the partial molal Gibbs free energy of mixing, $\Delta\bar{G}_x$, neglecting higher order terms,

$$\mu_x = \mu_x'.$$

The free energies of mixing as given by the chemical potentials of polymer species of molecular weight x in the dilute and precipitated phases are

$$\Delta\bar{G}_x = \mu_x - \mu_x^0 = R'T \left[\ln(1 - v_x) + \left(1 - \frac{1}{x_n}\right) v_x + \chi v_x^2 \right]$$

$$\Delta\bar{G}_x' = \mu_x' - \mu_x^0 = R'T \left[\ln(1 - v_x) + \left(1 - \frac{1}{x_n}\right) v_x' + \chi v_x'^2 \right]$$

where R' = molal gas constant; T = absolute temperature; μ_x^0 = chemical potential of polymer at standard conditions; v_x = volume fraction of polymer in solution; χ = polymer-solvent interaction parameter; and $x_n = \bar{V}_{n,x}/V_1$, the ratio of the (number average) molal volume of the polymer to that of the solvent.

By equating the chemical potentials and rearranging, the following equation may be obtained relating the concentration of mer x in the precipitated phase to that of the dilute phase:

$$\ln(v_x'/v_x) = \sigma x \quad (1)$$

where

$$\sigma = v_x \left(1 - \frac{1}{x_n}\right) - v_x' \left(1 - \frac{1}{x_n}\right) + \chi[(1 - v_x)^2 - (1 - v_x')^2]. \quad (2)$$

Equation (1) is one of the bases for fractionation theory. Because σ is not a function of the molecular weight x , the differences of the polymer concentrations between the two phases increase with molecular weight. The polymer species of higher weight (x) are selectively transferred to the concentrated phase.

However, it suffices that there exists a partitioning coefficient σ , such that $\ln(v_x'/v_x) = \sigma x$. A far more detailed mathematical treatment is presented by Huggins and Okamoto in Cantow's book *Polymer Fractionation*. It covers the many diverse combinations of polymers, solvents, and nonsolvents, as well as polymer-polymer, solvent-nonsolvent, and higher-order interaction terms. All analyses have the salient features noted above; and a partitioning coefficient σ exists, which is a function of one (or more) interaction parameters. It is further noted that σ increases with χ which can be estimated by Hildebrand's solubility parameters. The interaction parameter between two components is defined as³

$$\chi_{12} = \beta + (\bar{V}_1/R'T)(\delta_1 - \delta_2). \quad (3)$$

This illustrates the dependence of the partitioning coefficient upon solubility parameters, and this will be explored in depth later.

If V and V' represent the equilibrium solution volumes, the fraction f_x (of x in the dilute phase) is given by

$$f_x = Vv_x/(Vv_x + V'v_x') = 1/(1 + \rho v_x'/v_x)$$

where $\rho = V'/V$. Then, by substitution,

$$f_x = 1/(1 + \rho e^{\sigma x}). \quad (4)$$

Thus, the fraction in the precipitated phase is

$$f_x' = \rho e^{\sigma x}/(1 + \rho e^{\sigma x}). \quad (5)$$

The preceding referred directly to cooling a single solvent system. The more common technique of nonsolvent addition has similar relations, but a three-component system (polymer-solvent-nonsolvent) now exists rather than the simple binary system. The major difference is that the solvent-nonsolvent ratio may be larger in the precipitate than in the dilute phase, and this would be reflected in the value of σ . This concentration difference between the two phases could actually increase the fractionating efficiency, and the ρ values for equivalent partitioning would be lower.

In the two techniques of polymer fractionation considered, σ is increased (either by cooling below the theta temperature or by nonsolvent addition) until phase separation occurs. It is clear from eq. (4) that as σ is increased, the partitioning of any given molecular weight between the two phases

will increase (i.e., the fraction in the dilute phase will approach zero) and that successively lower molecular weights will be caused to precipitate. At a constant ratio of volume fraction polymer in the precipitate to that in the dilute phase ($v_x'/v_x = \text{constant}$), the partitioning coefficient is seen to be inversely proportional to the molecular size:

$\sigma x = \text{constant}$, therefore

$$\sigma \propto \frac{1}{(M)}$$

Then substituting the Mark-Houwink relationship,

$$[\eta] = K'(M)^a$$

$$\sigma \propto [\eta]^{1/a}$$
(6)

and then substituting χ for σ from eq. (2),

$$[\eta]^{1/a} \propto \chi + \text{constant}$$

which becomes

$$[\eta]^{1/a} \propto (\delta_1 - \delta_2)^2 + \text{constant.}$$
(7)

If the differentials are now taken with respect to the variables influencing precipitation (volume fraction nonsolvent and temperature), the following relations are obtained:

$$\frac{\partial([\eta]^{1/a})}{\partial(v.f.)} \propto \frac{\partial(\delta_p - \delta_e)^2}{\partial(v.f.)}$$
(8)

$$\frac{\partial([\eta]^{1/a})}{\partial(T)} \propto \frac{\partial(\delta_p - \delta_e)^2}{\partial(T)}$$
(9)

Simplification of eq. (8) is a difficult matter, but several features should be noted. It may be assumed that the solubility parameter of the polymer, δ_p , does not change significantly with molecular weight, thus eliminating one variable. Further, the solubility parameter of the solution (at the theta point), δ_e , is a composite term of that of the solvent plus that of the nonsolvent. This reduces $\partial(\delta_e)/\partial(v.f.)$ to $(\delta_s - \delta_n)$. The final form of the relation is found empirically but does follow the dependence upon the solubility parameters.

Further reduction of eq. (9) is also difficult, since both δ_p and δ_e change significantly with temperature. It can be further seen that since $\delta_e \propto T^{1/2}$ for all solvents and $\partial(\delta_p)/\partial(T)$ must be constant for a single polymer, any simple relation based only on $(\delta_p - \delta_e)$ will not be sufficient even to approximate the behavior.

Recalling that eq. (3) is only an approximation, it is evident that the interaction parameter is a function of more than the solubility parameters. The success of plotting solubility contours on a solubility parameter/hydrogen bonding index grid suggests that deviations may be corrected by taking into account the hydrogen bonding. It will be shown in the

results that by empirically deriving relations involving both solubility parameters and hydrogen bonding indexes, the data can be correlated better than by the simplified theory. However, the results will be fully within the framework of the theory.

EXPERIMENTAL

Poly(vinylpyrrolidone) was the polymer which was of major interest in the work presented here. This polymer was chosen because the majority of the applications of PVP are dependent upon the molecular weight. In fact, for some potential applications the commercial polymer must be carefully fractionated. Moreover, it is a water-soluble polymer with an extremely wide solubility and compatibility range. The second polymer to be investigated was polyacrylamide. It was chosen because its physical similarity was felt to have the greatest probability of fitting the same solubility model. The average molecular weights of the unfractionated PVP and PAM were 360,000 and 400,000, respectively.

The experimental procedures used were the classical techniques of non-solvent addition and cooling below the theta temperature. In fractionating the samples by nonsolvent addition, the polymer was dissolved in the solvent and precipitated by the slow addition of nonsolvent at 30°C. Precipitation was always preceded by turbidity, indicating a tendency to supersaturate. All solutions were allowed to stand 24 hr after turbidity disappeared. Fractions were normally limited to 1% of the volume of the solution. Solutions were limited to 3 g/dl concentration to assure that the precipitate would not occlude any lower molecular weights.

Precipitation from a theta solvent by cooling involved dissolving the polymer in a heated theta solvent and then cooling. Since there is a limited number of theta solvents, solvent-nonsolvent pairs were often used. In using a solvent pair, the polymer was first dissolved in hot solvent; then hot nonsolvent was added until the first precipitation occurred; and finally, the solution was heated further to redissolve the precipitate, and fractions were obtained by cooling. Fraction volumes and concentrations were limited in the same manner as the nonsolvent addition.

The polymers investigated introduced an additional complication. The polymers have such a high complexing ability that they retain a certain amount of solvent under any common drying procedures. It, therefore, became necessary to remove residual water from the polymers when using nonaqueous systems. This was accomplished by boiling the polymer in the immiscible nonsolvent (or solvent) and separating the immiscible water in a reflux condenser.

ANALYSIS

The sample preparation for analysis was also very important, as it was shown that absorbed solvent affected the properties of the polymers.

The precipitates were dried 24 hr at 60°C, then redissolved in water a second time and dried for 48 hr. The samples were then weighed and redissolved in distilled water. Viscosities were measured using an Ubbelohde viscometer at 30°C. Huggins' equation was used to obtain $[\eta]^4$.

CORRELATION OF EXPERIMENTAL DATA

Early experiments were directed toward reducing the number of variables. The interfering effect of added amounts of polymer raised the question as to whether the polymer concentration affected the precipitation. Experimentation proved that for a range concentrations of a given polymer sample (i.e., same molecular weight and distribution), equal percentages were recovered at approximately the same volume fraction of nonsolvent in solutions of less than 3% by weight at point of precipitation. This concentration is higher than previously believed feasible without gross reduction in efficiency. In analyzing the data, the logarithm of the intrinsic viscosity of the precipitated polymer was plotted against the volume fraction of nonsolvent. To determine if the concentration dependence could be completely isolated from the effects of temperature, runs were made at several temperatures. The resultant plots were parallel, indicating no interdependence between temperature and nonsolvent effects.

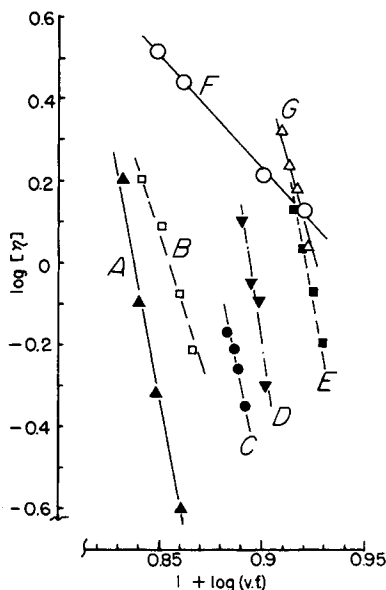


Fig. 1. Dependence of intrinsic viscosity of precipitated PVP (in dl/g) on volume fraction (*v.f.*) of nonsolvent at 30°C. Solvent/nonsolvent systems are: (A) ethanol/isooctane; (B) formamide/methyl ethyl ketone; (C) methanol/diethyl ether; (D) *n*-propanol/*n*-nonane; (E) *n*-propanol/isooctane; (F) water/acetone. Intrinsic viscosities were measured in water at 30°C.

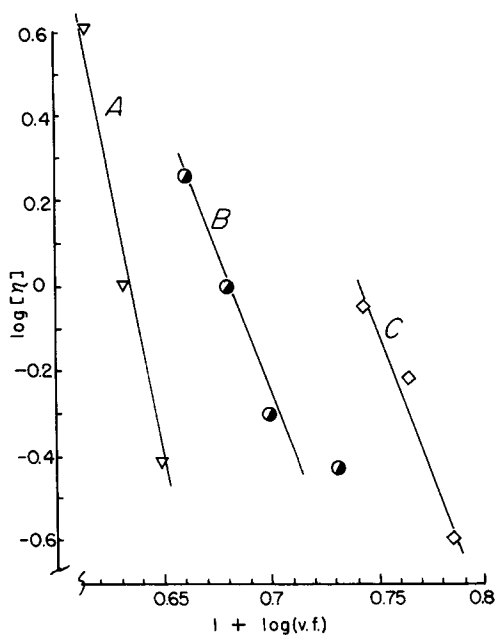


Fig. 2. Same polymer as in Fig. 1. Solvent/nonsolvent systems are: (A) chloroform/isooctane; (B) nitromethane/diethyl ether; (C) nitroethane/diethyl ether.

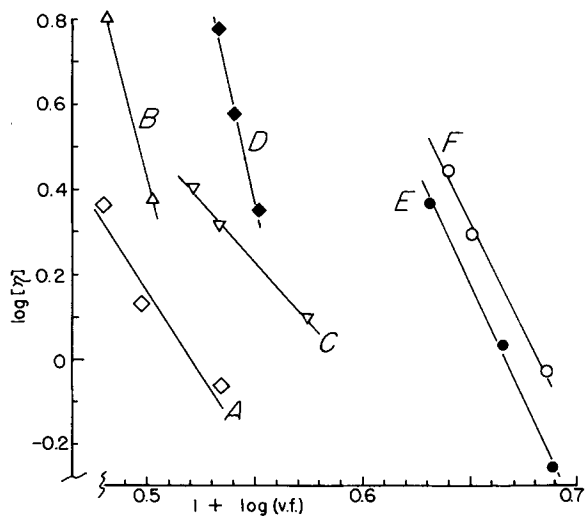
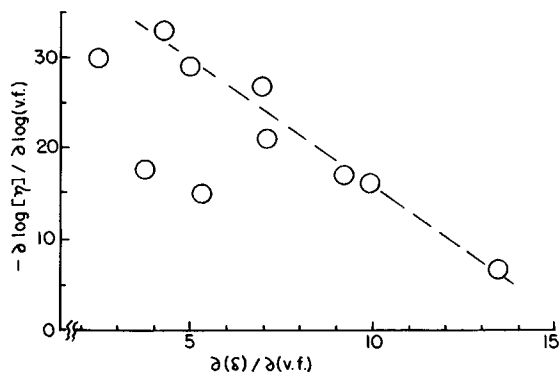


Fig. 3. Same variables as in Figs. 1 and 2 where polymer is polyacrylamide. Solvent/nonsolvent systems are: (A) water/*n*-propanol; (B) formamide/ethanol; (C) water/acetone; (D) formamide/methanol; (E) water/methanol; (F) water/ethanol.

The fact that the precipitation range and behavior is different for each solvent system is common knowledge. Therefore, various systems were examined to cover the largest possible area. The results of these are all similar in behavior and are plotted in Figures 1 to 3.

TABLE I
 Solvent Characteristics

Solvent	Solubility parameter	Hydrogen bonding index
Acetone	10.0	3.9
Benzene	9.2	2.6
Chloroform	9.3	0.6
Diethyl ether	7.4	5.2
Ethanol	12.7	7.5
Formamide	19.2	11.0
Methanol	14.5	7.5
Methyl ethyl ketone	9.3	3.1
Nitroethane	11.1	1.0
Nitromethane	12.7	1.0
<i>n</i> -Nonane	6.9	0
Isooctene	7.7	0
<i>n</i> -Propanol	11.9	7.5
Toluene	8.9	3.3
Water	23.4	15.6


 Fig. 4. PVP precipitation data correlated with rate of change of solubility parameter δ of solvent system.

To reduce the results to basic dependences, the solvents had to be characterized by intrinsic parameters. Following the simplified theoretical derivation, the rate of change of the intrinsic viscosity of the precipitate should be a function of the rate of change of the solubility parameter (in the case of nonsolvent addition). Solubility parameters of several solvents are presented in Table I. Although this procedure (Fig. 4) does show a trend, there exist extensive deviations and considerable scatter. Examination of individual points (Table II) reveals that deviations generally fall into groupings of similar solvent systems. The work of Beerbower, Kaye, and Pattison⁵ and others⁶ in characterizing the swelling of rubber and solubility of plastics on a solubility parameter/hydrogen bonding index grid-work suggested hydrogen bonding index as a second parameter.

TABLE II
Precipitation Data for Nonsolvent Addition at 30°C

System	$-\log([\eta])$ $\log(v.f.)$	$\frac{\partial(\delta)}{\partial(v.f.)}$	$\frac{\partial(\delta - 0.3\gamma)}{\partial(v.f.)}$
PVP/water/acetone	6.85	13.4	9.9
PVP/nitromethane/ether	15.0	5.3	7.6
PVP/formamide/MEK	16.1	9.9	7.5
PVP/formamide/acetone	17.0	9.2	7.1
PVP/nitroethane/ether	17.5	3.7	6.6
PVP/methanol/ether	21.1	7.1	6.4
PVP/ethanol/isooctane	26.8	6.9	4.7
PVP/n-propanol/isooctane	29.2	5.0	2.8
PVP/chloroform/isooctane	30.0	2.4	2.2
PVP/n-propanol/n-nonane	33.0	4.2	2.0
PAM/water/acetone	5.6		9.9
PAM/water/n-propanol	8.5		8.3
PAM/water/ethanol	10.0		7.3
PAM/water/methanol	11.0		5.5
PAM/formamide/ethanol	18.8		4.3
PAM/formamide/ethanol	23.0		2.8

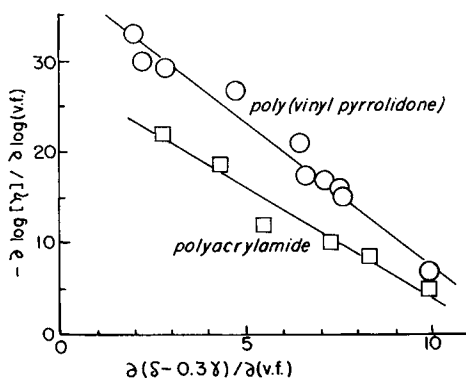


Fig. 5. Precipitation data for two polymers with common adjustment for hydrogen bonding index of solvent system.

It must be noted here that there is poor agreement in the literature on values of hydrogen bonding indexes. The table values are given in $\text{cm}^{-1}/10$, using IR spectra shift, and are corrected for media effects by $\gamma = \gamma_{\text{measured}}/\gamma_{\text{medium}}$.⁷ Complete and consistent tables are difficult to assemble. It is far more common simply to classify materials as being poor ($\gamma = 2.5$), moderate ($\gamma = 5.5$), or strong ($\gamma = 8.5$) with regard to hydrogen bonding.^{6,8} The data for both polymers were fitted by combining the solubility parameters and hydrogen bonding indexes. Figure 5 shows $\partial \log[\eta]/\partial \log(v.f.)$ plotted against $\partial(\delta - 0.3\gamma)/\partial(v.f.)$. The best average coefficient for the hydrogen bonding index was found to be 0.3 for the two polymers.

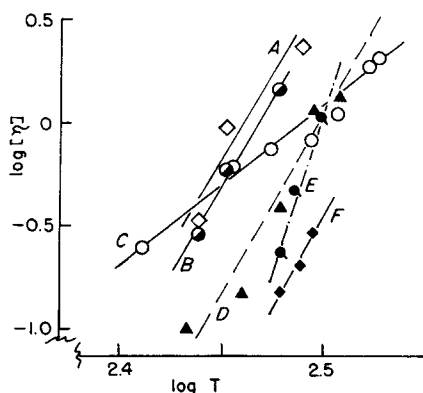


Fig. 6. Dependence of intrinsic viscosity of precipitated PVP (in dl/g) on temperature T ($^{\circ}\text{K}$). Solvent systems are: (A) nitroethane/diethyl ether; (B) nitromethane/diethyl ether; (C) water/acetone; (D) ethanol/isooctane; (E) benzene alone; (F) toluene alone.

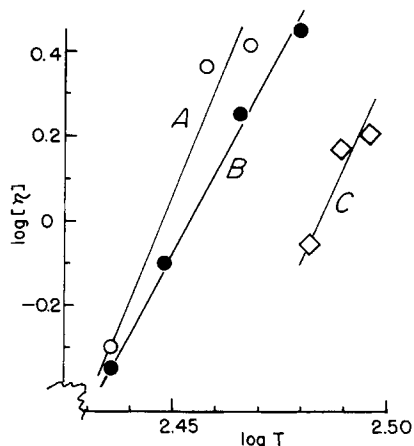


Fig. 7. Dependence of intrinsic viscosity of precipitated PAM (in dl/g) on temperature T ($^{\circ}\text{K}$). Solvent systems are: (A) water/ethanol; (B) water/methanol; (C) water/*n*-propanol.

The dependency of the limiting intrinsic viscosity of the precipitate can be expressed as

$$[\eta]_{\text{ppt}} = k(v.f.)^{-(36-2.88R)} \text{ for PVP}$$

$$[\eta]_{\text{ppt}} = k'(v.f.)^{-(28-2.44R)} \text{ for PAM}$$

where $R = (\delta_s - \delta_n) - 0.3(\gamma_s - \gamma_n)$; δ_s = solubility parameter of solvent; δ_n = solubility parameter of nonsolvent; γ_s = hydrogen bonding index of solvent; and γ_n = hydrogen bonding index of nonsolvent.

The parallel behavior of the correlation suggests that if the intercept and slope could be determined by intrinsic properties of the polymer, the correlation could be reduced to one equation which would be valid for many

TABLE III
Precipitation Data for Cooling Below Theta Temperature^a

System	$c =$		δ_e	γ_e	$\frac{(\gamma_p - \gamma_e)^{2.2}}{(\delta_p - \delta_e)}$
	$\frac{\partial \log([\eta])}{\partial \log(T)}$	$\frac{\partial \log([\eta])}{\partial \log(T)}$			
PVP/water/acetone	0.5	13.72	6.61	0.0384	0.0384
PVP/ethanol/isooctane	15.91	8.48	4.14	1.185	1.185
PVP/benzene	46.3	9.2	2.6	3.34	3.34
PVP/toluene	29.39	8.9	3.3	2.195	2.195
PVP/nitroethane/ether	16.32	9.0	4.2	1.205	1.205
PVP/nitromethane/ether	20.0	9.92	4.07	1.5034	1.5034
PAM/water/methanol	18.6	19.33	8.5	0.504	0.504
PAM/water/ethanol	23.0	19.57	8.5	0.588	0.588
PAM/water/n-propanol	30.0	19.84	8.5	0.725	0.725

^a $\delta_{PVP} = 17$, $\gamma_{PVP} = 7$, $\delta_{PAM} = 21$, $\gamma_{PAM} = 9.5$.

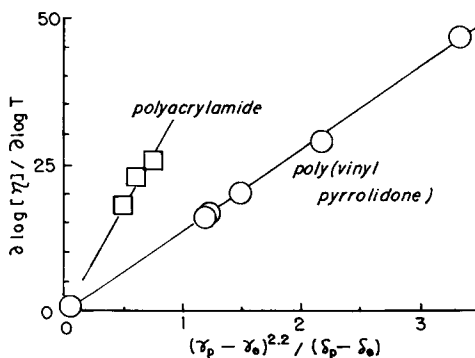


Fig. 8. Correlation of temperature dependence with solubility parameter δ and hydrogen bonding index γ . Subscript p refers to polymer and e refers to the solvent system at the theta temperature.

similar polymers. However, the lack of further data makes it unreasonable to predict even the form of such a correlation.

Having characterized fractionation by nonsolvent addition, the next logical step was to examine the effect of temperature, thereby covering the other major fractionation technique: cooling below the theta temperature. Typical results are shown in Figures 6 and 7.

The mathematical analysis proved more difficult. The simplified theoretical analysis did not yield any first-order dependences to use as starting points. For all solvents the solubility parameter is approximately proportional to temperature to the negative one-half power, and the hydrogen bonding index is proportional to the temperature to the negative 16 power.⁷ For a given polymer, solubility parameter and hydrogen bonding index behavior would be expected to remain the same.

The correlation was obtained by purely empirical means from the data in Table III. The following correlation is obtained (Fig. 8):

$$\log [\eta] = \log k'' + [c(\gamma_p - \gamma_e)^{2.2} / \delta_p - \delta_e] \log T.$$

The PVP data correlate well. However, the PAM data inspire less confidence.

SUMMARY

The preceding relations can be reduced to a single equation predicting the intrinsic viscosity (or molecular weight) of a precipitate:

$$[\eta] = \frac{kT^{(cQ)}}{(v.f.)^{(a+bR)}}$$

where $Q = (\gamma_p - \gamma_e)^{2.2}/(\delta_p - \delta_e)$; $R = (\delta_s - \delta_n) - 0.3(\gamma_s - \gamma_n)$; and a , b , c , and k are constants dependent upon the particular polymer, with subscripts defined as s = solvent, n = nonsolvent, p = polymer, and e = theta solvent or solution at theta point.

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