Dependence of Association in Polyacrylonitrile Solutions on the Molecular Volume of the Nonsolvent

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Synopsis

An examination of data obtained from viscometric measurements of the association occurring in solutions of polyacrylonitrile in dimethylformamide, γ-butyrolactone, and dimethylacetamide has shown that the solubility parameter of the solvent–nonsolvent liquid mixture at the aggregation point is closely related to the molecular volume of the nonsolvent used to bring about association.

The kinetic features of the association occurring in solutions of polyacrylonitrile in N,N'-dimethylformamide (DMF) have been examined in some detail.[1] Viscometric measurements made over a range of temperatures[2] and with a variety of nonsolvents[3] have established that association occurs through dipolar interaction between CN groups along the polymer molecule. It has been shown[1] that large changes occur in the viscosity number of the solution over a narrow range of nonsolvent composition. It has been found convenient to characterize the association by determining the vol-% nonsolvent P at which the association rate constant has a value of 1×10^{-6} sec^{-1}.

Although qualitatively the association of the various solvent–nonsolvent systems so far examined is similar, the primary effect of the nonsolvent is to determine the volume concentration at which association occurs. It has been shown[3] that a relationship exists between the solubility parameter δ_{NS} of the nonsolvent and P as follows:

$$100/P = A\delta_{NS} - B \tag{1}$$

where A and B are constants. Calculations carried out subsequently as a result of an examination of the effect of variation of the solvent on the association in polyacrylonitrile solutions has shown that the solubility parameter of the liquid mixture δ_a at a composition corresponding to P showed much less variation than the values of δ_{NS}. Initially it was considered that δ_a had a constant value for a particular solvent or nonsolvent system, but since association can be observed in systems for which $\delta_S \gtrless \delta_{NS}$, then clearly this supposition was unrealistic. Subscripts S and NS are here taken to denote the solvent and nonsolvent components, respectively. A misplaced parameter led to calculations being made of the molecular volumes of the nonsolvents used, and it was found that variation in δ_a, although subjected

to a significant error, was closely related to changes in molecular volume of the nonsolvent.   This was an observation of some interest and gave a basis for remarks previously made[1] that the nonsolvent acted principally as a diluent.

If the volumes of solvent and nonsolvent required to cause association with a rate constant of 10^{-6} sec^{-1} are v_S and v_{NS}, then

$$P = 100v_{NS}/(v_S + v_{NS}) \qquad (2)$$

and it can be shown that the corresponding wt-% nonsolvent w_{NS} and mole fraction x_{NS} are given by

$$w_{NS} = 100/(1 + \alpha P') \qquad (3)$$

$$x_{NS} = 1/(1 + \alpha\beta P') \qquad (4)$$

For convenience, the ratio of the densities $\rho_S/\rho_{NS} = \alpha$, the ratio of the molecular weights $M_{NS}/M_S = \beta$, and $P' = 100/P - 1$.   Since $x_S + x_{NS} = 1$, it follows that

$$x_S/x_{NS} = \alpha\beta P'. \qquad (5)$$

If it is assumed that the solubility parameter for the liquid mixture is given[4] by

$$\delta_a = (x_{NS}V_{NS}\delta_{NS} + x_S V_S \delta_S)/(x_{NS}V_{NS} + x_S V_S) \qquad (6)$$

where V_S and V_{NS} are the molecular volumes of the two liquids then substitution from eq. (5); and since

$$V_{NS}/V_S = \alpha\beta, \qquad (7)$$

it follows that eq. (6) may be written as

$$\delta_a = (\delta_{NS} + P'\delta_S)/(1 + P') \qquad (8)$$

or

$$P' = (\delta_{NS} - \delta_a)/(\delta_a - \delta_S). \qquad (9)$$

Since δ_a will always lie between δ_{NS} and δ_S, then P' will always be positive. Calculation of δ_S for DMF has been made using boiling point data[3] to give $\delta_S = 11.60 \pm 0.03$ (cal/cm^3)$^{1/2}$, and this now permits δ_a to be calculated from eq. (9) as shown in Table I.   It is clear that δ_a is not constant.   Corresponding values of the molecular volumes calculated at 25°C using the density values given by Timmermans[5] are given in the last column and show that δ_a gradually decreases with increase in V_{NS}.   With the exception of results for acetone and benzyl alcohol, a very close correlation exists between the two parameters, as follows:

$$\delta_a = C - DV_{NS} \qquad (10)$$

the constants C and D having values 12.4 ± 0.1 and 0.014 ± 0.004, respectively, for results obtained in DMF.

TABLE I
Calculated Values of Molecular Volumes of the Nonsolvents Used and of Solubility Parameters for the Solvent–Nonsolvent Mixtures Causing Association in Polyacrylonitrile Solutions at 25°C

Nonsolvent	$\delta_{NS},$ $(cal/cm^3)^{1/2}$	$P,$ $\%$	$\delta_a,$ $(cal/cm^3)^{1/2}$	$V_{NS},$ $cm^3/mole$
N,N′-Dimethylformamide[a]				
Water	21.2	7.1	12.2	18.1
Methanol	12.9	16.5	11.7	40.7
Ethylene glycol	14.7	13.1	11.9	55.9
Acetone	9.3	45.8	10.5	74.0
n-Propanol	10.3	14.7	11.3	75.1
Isopropanol	9.81	16.0	11.2	76.9
Benzene	9.05	31.1	10.7	89.4
n-Butanol	9.77	16.8	11.2	92.0
Carbon tetrachloride	8.64	21.1	10.9	96.5
Benzyl alcohol	10.9	19.4	11.4	103.8
Toluene	8.92	28.7	10.8	106.9
γ-Butyrolactone				
Benzene	9.05	18.1	12.1	89.4
Carbon tetrachloride	8.64	15.9	12.1	96.5
N,N′-Dimethylacetamide				
Benzene	9.05	23.9	10.3	89.4
Carbon tetrachloride	8.64	18.3	10.4	96.5

[a] Values of δ_{NS} and P are taken from Beevers.[3]

Values of δ_a have also been calculated for solutions of polyacrylonitrile in N,N′-dimethylacetamide and γ-butyrolactone, using benzene and carbon tetrachloride as nonsolvents. Calculated values of δ_S for the two solvents are 10.73 ± 0.03 $(cal/cm^3)^{1/2}$ and 12.72 ± 0.03 $(cal/cm^3)^{1/2}$, respectively, and lie on either side of the value for DMF. Plotting the results to show the dependence of $\delta_a - \delta_S$ on V_{NS}, as in Figure 1, shows that the solvent has little effect on the association in these solutions.

Substituting for δ_a in eq. (8) gives eq. (1) with

$$A = 1/(C - DV_{NS} - \delta_S)$$
$$B = \delta_S/(C - DV_{NS} - \delta_S)$$

(11)

so that

$$B/A = \delta_S.$$

(12)

Substitution of values previously found[3] for A and B, namely 0.80 ± 0.07 and 3.3 ± 1.5, respectively, gives about half the value cited above for δ_S. However the inclusion of V_{NS} in the denominator of eq. (10) must vitiate the use of an equation of the form of eq. (1) to describe the association in polyacrylonitrile solutions. It is clearly preferable, as shown in Figure 1, to calculate δ_a from the experimentally determined value of P and relate
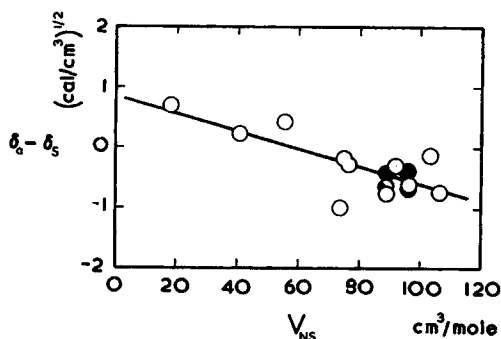
Fig. 1. Dependence of $\delta_a - \delta_S$ on the molecular volume of the nonsolvent V_{NS} for association in polyacrylonitrile solutions at 25°C: (O) dimethylformamide; (●) dimethylacetamide; (◔) γ-butyrolactone.

this to the molar volume of the nonsolvent used.   More careful examination of the results in Table I confirms this view.   Previously the scatter of points about the line represented by eq. (1) had been considered to be indicative of the experimental error, especially in view of the diverse nature of the nonsolvents used.   Since δ_a will depend on the choice of nonsolvent, it is necessary to compare nonsolvents which have similar values for δ_{NS}.   Carbon tetrachloride and toluene are similar in this respect; yet a relatively large difference exists between their values of P and which is not in accordance with eq. (1).   The data for the two nonsolvents, however, fit correctly when plotted according to eq. (10).   Association data for the isomers n-propanol and isopropanol also fit in correctly with the dependence of δ_a on molar volume.

For solvent–nonsolvent systems in which $|\delta_S - \delta_{NS}|$ is comparable, the amount of nonsolvent required to cause association will decrease with decrease in the molecular volume of the nonsolvent.   The specific chemical nature of the nonsolvent is not in evidence in Figure 1, so that, as previously, the nonsolvent may be considered to act by blocking the interactions which occur between the polymer and solvent.   Molecular size is not necessarily directly involved at the site of an interaction; but clearly when considering the nonequilibrium statistics of the distribution of nonsolvent molecules, molecular size will become of importance through its effect on molecular mobility.

References

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