The Effect of Solvent on Association in Polyacrylonitrile Solutions

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Kinetic viscometric measurements have been used to investigate the effect of change of solvent on association in polyacrylonitrile solutions. For solutions of the polymer in N,N′-dimethylformamide, N,N′-dimethylacetamide and γ-butyrolactone with benzene and carbon tetrachloride as added non-solvents, the dependence of the association on the solubility parameter, calculated for the mixed liquids, is shown to be most pronounced for solutions in dimethylformamide. The temperature dependence of the rate constant has been determined for each solvent/non-solvent system and the activation energy was found to be 7·3±2·6 kcal mole^{-1}, assuming that two intermolecular bonds are required to form the micro-gel particle.

THE kinetic features of the association occurring in solutions of polyacrylonitrile in dimethylformamide have already been reported in some detail[1]. It has been shown that the rate of association determined viscometrically, depends on the non-solvent concentration and to a variable degree, on the polymer concentration. Measurements have been confined to polymer concentrations of less than 1 g dl^{-1} to avoid macro-gel formation. The primary effect of a change in non-solvent is a shift in the volume composition of the solvent/non-solvent mixture at which association occurs. This has been shown to be in inverse proportion to the solubility parameter of the non-solvent.[2]

Kinetic viscometric measurements made over a range of temperatures for polymer solutions in dimethylformamide with benzene as non-solvent have shown that an activation energy of 8·5±1·0 kcal mole^{-1} is involved in the process of association[3]. In arriving at this figure it has been assumed that two inter-molecular bonds form per molecule to produce the micro-gel particle. This value for the activation energy correlates closely with calculations made on CN dipolar pair bond formation in low molecular weight nitriles and di-nitriles which also show enhanced colligative properties. Association in polyacrylonitrile solutions also seems to occur through dipolar forces between CN groups in neighbouring polymer molecules. The evidence, as yet, remains circumstantial and spectroscopic evidence is being sought which will give direct information concerning the role played by the CN groups during association. The most cogent experimental data have been obtained by Climie and White[4] who showed unambiguously that the process of association in polyacrylonitrile solutions is controlled by the distribution of acrylonitrile residues along the chain.

It should then follow that just as the non-solvent has been shown to control, but not be the prime cause of association in polyacrylonitrile solutions, so too should the solvent, once solution has been effected, also be of secondary importance. The experiments to be described were carried out to test this hypothesis. It is however of greater interest to examine the nature of the temperature dependence of the rate constant for associatio of the polymer in various solvents. If, as suggested by the previous eviden association occurs through CN dipolar interaction then the activation en for this process should be substantially independent of both solven non-solvent.

In order to investigate this, viscometric measurements have been continued as described previously[1] using solutions of the polymer in, N,N′-dimethylformamide, γ-butyrolactone and N,N′-dimethylacetamide. Benzene and carbon tetrachloride were chosen as non-solvents to give continuity with the previous work and also because they are unlikely to participate in dipolar bond interactions. Greater attention has been paid than previously to the elimination of water from the various liquids in order to minimise interference with the process of association.

EXPERIMENTAL

Materials

Polymer—Measurements were made with a new preparation of polyacrylonitrile (W17) using redox polymerization conditions. The limiting viscosity number was slightly higher than previously[5] with a value of 2·16 ± 0·04 g dl^{-1} when determined in dimethylformamide at 25·00 ± 0·01 °C.

Non-solvents—Benzene and carbon tetrachloride (B.D.H. Ltd, Analar grade) were used as received without further distillation. The liquids were kept under dry, oxygen-free nitrogen using vaccine caps to replace the bottle seals.

Solvents—The solvents, N,N′-dimethylformamide (DMF, B.D.H. Ltd), γ-butyrolactone (γ-But, Kodak Ltd) and N,N′-dimethylacetamide (DMA, Kodak Ltd) were all treated in the same manner based on methods I and II of the purification procedure for DMF described by Thomas and Rochow[6]. Briefly the method was as follows. The solvent was shaken for a day with 10% by volume of benzene which had been passed through a silica gel column. This was followed by distillation at NTP to remove the benzene and benzene/water azeotrope. The progress of the distillation was followed using a refractometer and the distillation stopped when the refractive index of the residue became constant and close to the tabular value for the solvent. Infra-red examination of the liquids showed no detectable benzene in the residue. The benzene/dry solvent mixture was then shaken for a day with barium oxide (3g/100 ml; B.D.H. Ltd, anhydrous technical grade) which had been previously dried for 12 h in an air oven at 250 °C and subsequently stored over silica gel. The solvent was then decanted off and distilled at 15 mmHg through a 30 cm column of glass beads (DMF, 40 °C; γ-But, 87 °C; DMA, 40 °C) and the middle fraction retained. Solvent fractions were subsequently stored under dry oxygen-free nitrogen in flasks with vaccine seals and the batches of flasks were stored in a desiccator over silica gel. Values for the refractive index (± 0·0003) and density (± 0·002 g ml^{-1}) were in satisfactory agreement with available data[7] and the values of n_D^{25} and ρ_4^{25} respectively were as follows: DMF, 1·4286, 0·950 g ml^{-1}; γ-But, 1·4348, 1·124 g ml^{-1}; DMA, 1·4361, 0·940 g ml^{-1}.

The absence of diethylamine during the distillation of DMF was verified colorimetrically, use being made of the formation of a complex between diethylamine and 1-fluoro-2,4-dinitrobenzene (FNB) which absorbs strongly at 381 nm. This was established from quantitative measurements made of the absorption by the complex in solutions (0·07% w/w) of FNB in acetone using a Hilger H 700 UV spectrophotometer.

Measurements of the water content of the various liquids have been made using the method of Fischer[8] and carried out routinely on all liquid samples removed from the viscometers at the end of an experiment.

Preparation of the solutions

It has been shown previously that in the region of micro-gel formation ($c_0 < 1{\cdot}0$ g ml^{-1} for polymer solutions in DMF) the kinetic constants depend on polymer concentration[1]. To simplify the experimental procedure the polymer concentration in each solvent system was kept constant. To maintain a reasonable flow time in the viscometers and so that the kinetic energy correction could be neglected the polymer concentration was kept at about 0·5 g dl^{-1} except for γ-butyrolactone. Stock solutions ($\pm 0{\cdot}002$ g dl^{-1}) were prepared with, DMF, $c_0 = 0{\cdot}504$ g dl^{-1}; γ-But, $c_0 = 0{\cdot}301$ g dl^{-1} and DMA, $c_0 = 0{\cdot}503$ g dl^{-1} and were filtered through no. 3 sinters before storage under dry oxygen-free nitrogen in flasks sealed with vaccine caps. All dispensing of solutions was carried out using 10 ml syringes fitted with long stainless steel needles (Polymer Consultants Ltd) with dry oxygen-free nitrogen flushing. Solutions were dispensed into the viscometers from $10 \times 0{\cdot}01$ ml burettes fitted with long tips and sealed with vaccine caps. A standing supply of solution was maintained in the burettes throughout the course of the experimental work to minimise handling and economize on liquids.

Viscometry

Details of the viscometric procedure have been given earlier[1]. The viscosity number of the solution was determined at suitable time intervals after the addition of the non-solvent, this being calculated from the polymer concentration c_1 after correction for dilution by the non-solvent. Values of t_0 were determined for each viscometer (Polymer Consultants Ltd, suspended level dilution viscometers fitted with sintered filters) and at each temperature to be later employed, in a series of preliminary experiments. This enabled the self consistency of the data to be examined and helped to conserve liquids. At temperatures below 15°C similar viscometers fitted with larger capillaries were used.

Determination of suitable non-solvent concentrations

The experiment is concerned primarily with the temperature dependence of the rate constants for association in the various solvent/non-solvent systems. It is however necessary to adjust the non-solvent concentration so that (1) only slight curvature of the rate plots occurs, and (2) reasonable values of the rate constants can be obtained at all temperatures to be employed.

Preliminary experimental work along the lines described previously[1] for the various systems had established that the nature of the viscometric changes was qualitatively similar. This is demonstrated in *Figure 1* which shows the dependence of the rate constant on volume composition of the liquid mixture for the five systems investigated. Earlier results obtained with dimethylformamide and benzene are indicated by the broken line. Data given in *Figure 1* were obtained at 25°C so that values of the rate constant are near to their maximum values. In order to meet both the above conditions it was decided to keep the rate constant close to a value of 10^{-5} sec^{-1} at 25°C. The appropriate non-solvent concentrations can then be obtained from *Figure 1*. These concentrations have however been varied slightly in order to make the dispensing of the liquids simpler and the non-solvent volume concentrations ($\pm 0{\cdot}2\%$) finally adopted are given in *Table 1*.

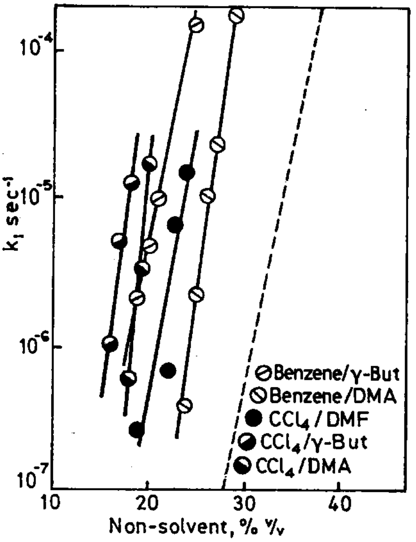

Figure 1—Dependence of the rate constant for association in polyacrylonitrile solutions at 25°C on the volume per cent non-solvent. Earlier results for the dimethylformamide/benzene system are indicated by the broken line

Table 1. Volume concentrations of non-solvent used in the viscometric measurements

Solvent	*Non-solvent*	
	Benzene	CCl_4
DMF		23·9
γ-But	21·4	17·7
DMA	25·5	19·5

Analysis of the data

Since the curvature of the plots of $\ln(\eta_{sp}/c_1)$ against time has been kept small, the rate constant will be given by[3],

$$\ln(\phi/\phi_0) = -k_1 t \qquad (1)$$

where $\phi = \eta_{sp}/c_1$ and $\phi = \phi_0$ when $t = 0$. Viscometric measurements have been carried out at short intervals of time up to about 3×10^4 sec and k_1 determined from the slope of the plots. The temperature dependence of k_1 has subsequently been examined assuming an Arrhenius expression,

$$k_1 = A \exp(-E/RT)$$

where A is a constant, R the gas constant and E is taken to be the activation energy for the association process.

RESULTS AND DISCUSSION

Association in the various solvent/non-solvent systems at 25°C

The rate constants for association determined over a narrow range of non-solvent volume concentration are given in *Figure 1*. As already described, these measurements were carried out as part of the preliminary experimental work but may now be considered in more detail.

Variation of non-solvent concentration—The logarithmic values of the rate constants change rapidly and in a linear manner over a range of a few per cent variation in non-solvent concentration for each system. These changes occur in the region 10 to 40% v/v non-solvent as previously observed for solutions in DMF with a variety of non-solvents[2]. It was then observed that the rate constant plots were convergent with an intercept at 0% v/v non-solvent, the rate constant having a value of roughly 10^{-13} sec^{-1}. The results of a least-squares analysis of the data are given in *Table 2* where, following the previous procedure, P is the volume per cent non-solvent for which $k_1 = 1 \times 10^{-6}$ sec^{-1} and a is the slope of the line [as before, $a = d(\ln 10^6 k_1)/dx$ where x is the volume per cent non-solvent]. For each solvent system the slopes and respective values of P indicate that the plots are convergent as before. Although only an indication of the rate constant for association in the initial polymer solutions can be made, it is clear that whereas it lies between 10^{-12} and 10^{-15} sec^{-1} for solutions of polyacrylonitrile in DMF and γ-butyronitrile, the value is significantly lower for solutions in DMA and lies between 10^{-18} and 10^{-20} sec^{-1}.

Table 2. Derived parameters for association in various solvent/non-solvent systems at 25°C

	Benzene		CCl_4	
Solvent	*a*	*P* %	*a*	*P* %
DMF	0·34*	30·9*	0·36	21·1
γ-But	0·35	18·1	0·55	15·9
DMA	0·52	23·9	0·77	18·3

*Taken from ref. 2.

The relationship between P and the solubility parameter—In solutions of the polymer in dimethylformamide where association has been brought about by addition of various non-solvents it has been shown[2] that P depends inversely on the solubility parameter of the non-solvent. It is therefore reasonable to consider that the formation of the inter-molecular bonds holding the micro-gel particle together will involve the polymer–liquid interaction parameter χ, which is related to the solubility parameters δ_a and δ_b of the liquid and polymer respectively by the approximate expression[9],

$$\chi = \beta + (V_a/RT)(\delta_a - \delta_b)^2 \tag{3}$$

where

$$\beta = (1/z)(1 - 1/m) \tag{4}$$

z being the lattice coordination number, m the chain length of the polymer and V_a the molar volume of the liquid. The data of *Table 2* have been analysed taking $\delta_b = 13{\cdot}8$ (cal/cm^3)$^{\frac{1}{2}}$ for the solubility parameter of the polymer[10], and by considering δ_a to be given by[11],

$$\delta_a = (x_{NS}V_{NS}\delta_{NS} + x_s V_s \delta_s)/(x_{NS}V_{NS} + x_s V_s) \tag{5}$$

where the subscripts NS and S refer to the non-solvent and solvent, x_{NS} and x_S ($x_{NS} + x_S = 1$) being the mole fractions of the two liquids determined at the volume composition corresponding to P. In addition, the molar volumes of the two liquids have been considered to be additive so that,

$$V_a = x_{NS}V_{NS} + x_s V_s \tag{6}$$

The solubility parameters of the various liquids have been calculated from[9],

$$\delta^2 = (\Delta H_{25} - RT)/V_a \tag{7}$$

where the heat of vaporization ΔH_{25} has been evaluated from the Hildebrand equation[11],

$$\Delta H_{25} = 23{\cdot}7\, T_b + 0{\cdot}020\, T_b^2 - 2\,950 \tag{8}$$

The various boiling points, T_b have been obtained from tables[7,12]. Values of the solubility parameters which have been calculated at 25°C using equations (7) and (8) and also the molar volumes of the liquids used are given in *Table 3*. The results of calculations of δ_a and the quantity $(V_a/RT)(\delta_a - \delta_b)^2$ evaluated from this data are now given in *Table 4*. The last column shows an unexpected feature, the value of δ_a being almost constant for a given solvent system; a point meriting further experimental investigation.

Table 3. Calculated values of the solubility parameters and molar volumes for the solvents and non-solvents used

	δ *(cal/cm^3)$^{\frac{1}{2}}$*	V *cm^3 mole^{-1}*
DMF	11·50	77·0
γ-But	12·72	76·6
DMA	10·73	92·7
Benzene	9·05	88·9
CCl_4	8·63	96·5
	±0·03	±0·2

The relationship between P and the solubility parameter is now shown in *Figure 2* and closely resembles curves indicating the swelling behaviour of a polymer in liquids of varying solubility parameter. The maximum of the curve corresponds to measurements in dimethylformamide which is well known as being a most satisfactory solvent for polyacrylonitrile[10]. *Figure 2* also shows the distinctive effects of both solvent and non-solvent on association in these solutions. The effect of variation of non-solvent previously reported[2] is clearly most marked in dimethylformamide solutions.

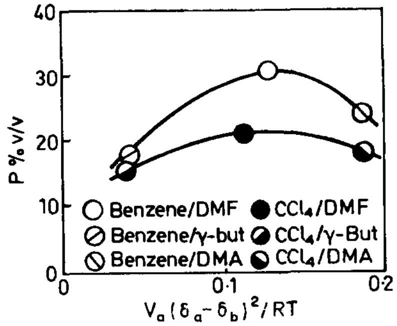

Figure 2—The dependence of P on the solubility parameter of the solvent/non-solvent mixture

Table 4. Calculated values for the mole fraction of non-solvent corresponding to the aggregation point P, and of the solubility parameters for the solvent/non-solvent mixtures at P

Solvent	*Non-solvent*	x_{NS}	δ_a $(cal/cm^3)^{\frac{1}{2}}$	$V_a(\delta_a-\delta_b)^2/RT$
DMF	Benzene	0·279	10·7	1·27
	CCl_4	0·176	10·9	1·14
γ-But	Benzene	0·160	12·1	0·40
	CCl_4	0·131	12·1	0·40
DMA	Benzene	0·247	10·3	1·87
	CCl_4	0·178	10·4	1·88

The temperature dependence of the association rate constants

Typical values of the rate constant k_1 determined at various temperatures and in polymer solutions having constant volume concentrations of non-solvent, as detailed in *Table 1*, are given in *Table 5*. Accuracy of the measurements is comparable to the previous data[3] being $\pm 0{\cdot}15 \times 10^{-5}$ sec^{-1}.

Table 5. Values of the rate constant, $10^6 k_1$ sec^{-1}, for association in polyacrylonitrile solutions at various temperatures

t	*Benzene*		CCl_4		
(°C)	*γ-But*	*DMA*	*DMF*	*γ-But*	*DMA*
11·00	5·9	2·6	16·0	6·7	2·8
15·10	11·3	4·2	20·9	7·7	3·8
17·50	16·6	6·0	19·9	9·4	6·8
22·55	18·2	14·5	28·4	13·8	18·8
25·00	17·3	12·5	30·6	12·0	15·0
29·02	28·9	15·4	53·2	14·2	26·6

The dependence of the data on temperature is most clearly shown by *Figures 3* and *4* where $\log(10^6 k_1)$ has been plotted against $1000/T$. Figures *3* and *4* have been drawn in order to make a comparison between the solvents. In each diagram the results obtained previously for solutions in dimethylformamide with benzene as non-solvent are indicated by the broken lines. The experimental results, which incorporate a few additional points, not included in *Table 5*, fit a linear relationship satisfactorily, the lines here being constructed from a least-squares analysis of the data. The slopes of the lines are in reasonable accord with the earlier results and this is particu-

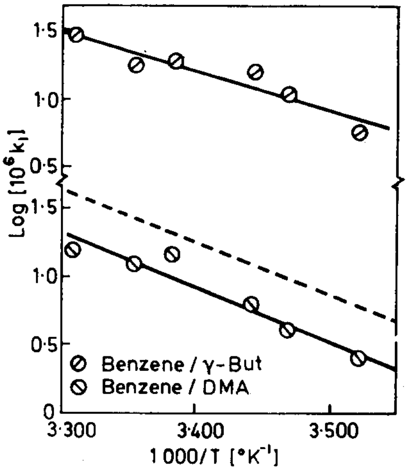

Figure 3—The effect of variation in temperature on the rate constant for association in polyacrylonitrile solutions with benzene as the non-solvent

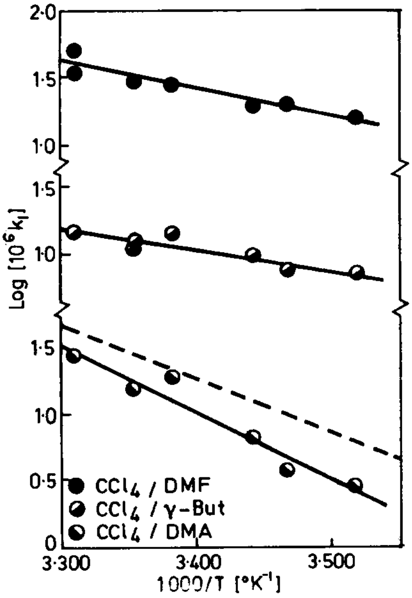

Figure 4—Temperature dependence of the rate constant for association in polyacrylonitrile solutions with carbon tetrachloride as the non-solvent

larly noticeable for results obtained with benzene. Values for 0·5 E calculated from the slopes, again assuming that two inter-molecular bonds per molecule participate in the formation of the micro-gel particle, are given in *Table 6*. Individual results are reliable to ±1·0 kcal mole^{-1} and show a slightly larger spread of values than at first anticipated from inspection of *Figures 3* and *4*. The benzene results have a mean value of 8·0±1·2 kcal mole^{-1} and taking the carbon tetrachloride results into account this falls to 7·3±2·6 kcal mole^{-1}.

Table 6. Values of 0·5 E in kcal mole^{-1} for association in polyacrylonitrile solutions

Solvent	*Non-solvent*	
	Benzene	CCl_4
DMF	8·5*	4·6
γ-But	6·4	3·7
DMA	9·1	11·3

*Taken from ref. 3.

Although interpretation of activation energy calculations requires considerable caution it would be reasonable to conclude from these results that the process of association in polyacrylonitrile solutions is largely independent of both the solvent and non-solvent. The evidence in favour of the formation of aggregates in these solutions through interaction of dipolar forces between the CN groups on the polymer molecule is further strengthened.

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